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**Nanomateriais luminescentes de terras
raras utilizando complexos de
benzenotricarboxilatos como precursores**

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**Nanomateriais luminescentes de terras raras
utilizando complexos de benzenotricarboxilatos
como precursores**

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Universidade de São Paulo para obtenção do Título de
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RESUMO

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O material $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ vem sendo usado comercialmente como luminóforo vermelho desde da década de 1960, em uma grande variedade de aplicações devido ao seu elevado rendimento quântico (próximo de 100 %), elevada pureza de cor e boa estabilidade. Portanto, este trabalho propõe um novo método de síntese baseado nos complexos benzenotricarboxilatos (BTC) de terras raras trivalentes (RE^{3+}) dopados com íons Eu^{3+} . O objetivo principal é produzir materiais luminescente $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ a temperatura mais baixa (500 °C) e em escala nanométrica. Os complexos precursores $[\text{RE}(\text{BTC}):\text{Eu}^{3+}]$ e $[\text{RE}(\text{TLA})\cdot n(\text{H}_2\text{O}):\text{Eu}^{3+}]$, onde RE^{3+} : Y, Gd e Lu; BTC: ácido trimésico (TMA) e ácido trimelítico (TLA) foram calcinados em diferentes temperaturas de 500 a 1000 °C, a fim de obter os materiais luminescentes $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$. Os complexos foram caracterizados por análise elementar de carbono e hidrogênio, análise térmica (TG), espectroscopia de absorção no infravermelho (FTIR), difração de raios-X - método do pó (XPD) e microscopia eletrônica de varredura (SEM). Todos os complexos são cristalinos e termo estáveis até 460 °C. Dados de fosforescência dos complexos de Y, Gd e Lu mostram que o nível T_1 do anión BTC^{3-} tem energia acima do nível emissor $^5\text{D}_0$ do íon Eu^{3+} , indicando que os ligantes podem atuar como sensibilizadores de energia intramolecular. O estudo das propriedades fotoluminescentes dos complexos dopados foi baseado nos espectros de excitação e emissão e curvas de decaimento de luminescência. Ademais, foram determinados os parâmetros de intensidades experimentais (Ω_λ), tempos de vida (τ), taxas de decaimentos radiativo (A_{rad}) e não-radiativo (A_{nrad}). Os materiais luminescentes $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ foram sintetizados de forma bem sucedida por meio do método benzenotricarboxilatos calcinados a 500, 600, 700, 800, 900 e 1000 °C, apresentando alta homogeneidade química e controle de tamanho de cristalito. Os nanomateriais foram caracterizados pelas técnicas de FTIR, XPD,

SEM e TEM revelando a obtenção dos materiais C-RE₂O₃:Eu³⁺ mesmo a 500 °C. Os dados de XPD dos materiais confirmaram um aumento do tamanho dos cristalitos de 5 até 52 nm (equação de Scherrer) de em função da temperatura de calcinação de 500 a 1000 °C, respectivamente, corroborados pelas técnicas de SEM e TEM. Os espectros de emissão de RE₂O₃:Eu³⁺ mostram uma banda larga atribuída a transição interconfiguracional de transferência de carga ligante-metal (LMCT) em 260 nm, *i.e.* O²⁻(2p)→Eu³⁺(4f⁶). Além disso, foram observadas linhas finas de absorção devido as transições intraconfiguracionais 4f do íon európio (⁷F_{0,1}→⁵L_J; J: 0, 1, 2, 3 e 4), como esperado. As propriedades fotoluminescentes dos luminóforos foram baseadas nos espectros (excitação e emissão) e curvas de decaimento luminescente. Os parâmetros de intensidade experimental, tempos de vida, assim como as taxas de decaimentos radiativos e não radiativos foram calculados. As propriedades fotônicas dos nanomateriais são consistentes com o sítio de baixa simetria C₂ ocupado pelo íon Eu³⁺ no C-RE₂O₃:Eu³⁺, produzindo emissão vermelha dominada pela transição hipersensível ⁵D₀→⁷F₂ do íon Eu³⁺ no sítio C₂, ao invés do sítio centrossimétrico S₆. Além disso, os nanomateriais Y₂O₃:Eu³⁺ exibem características espectroscópicas semelhantes e elevados valores de eficiência quântica (η~91 %), compatível com os luminóforos comerciais disponíveis no mercado. Este novo método pode ser utilizado para o desenvolvimento de novos nanomateriais contendo íons terras raras, assim como outros íons metálicos.

Palavras chave: *Método benzenotricarboxilatos, complexos de terras raras, fotoluminescência, nanomateriais, európio e ítrio.*

ABSTRACT

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$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ has been used as luminophore since the early 1960s, despite the large variety of potential substitute materials tested so far, this luminophore still be used as commercial red-emission luminescent material in large range of applications due excellent quantum efficiency (close to 100 %), high color purity and good stability. Consequently, This work propose a new benzenetricarboxylate (BTC) method, which use Eu^{3+} ion doped in the trivalent rare earths (RE^{3+}) complexes to produce $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ luminescent materials at lower temperature (500 °C) and nanoscale. The $[\text{RE}(\text{BTC}):\text{Eu}^{3+}]$ and $[\text{RE}(\text{TLA})\cdot n(\text{H}_2\text{O}):\text{Eu}^{3+}]$ complexes where RE^{3+} : Y, Gd and Lu; BTC: trimesic acid (TMA) and trimellitic acid (TLA) and annealed materials (500, 600, 700, 800, 900 and 1000 °C) can be obtained without the need of intricate experimental setup. The complexes were characterized by carbon and hydrogen elemental analysis, thermal analyses (TG), infrared absorption spectroscopy (FTIR), X-ray powder diffraction (XPD) and scanning electron microscopy (SEM). The complexes are crystalline and thermostable up to 460°C. Phosphorescence data of the complexes with Y, Gd and Lu show that the T_1 state of the BTC^{3-} anion has energy higher than the $^5\text{D}_0$ emitting level of the Eu^{3+} ion, indicating that the ligands can act as an intramolecular energy sensitizer. The photoluminescence properties of the doped complexes were studied based on the excitation and emission spectra and luminescence decay curves. The experimental intensity parameters (Ω_λ), lifetimes (τ), radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates were determined and discussed. In addition, the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ nanomaterials were successfully synthesized with this unprecedented method using the benzenetricarboxylate precursor complexes annealed at 500, 600, 700, 800, 900 and 1000 °C, with controllable particle size and high chemical homogeneity, crystallite size from 6 to 52 nm

(Scherrer's equation), confirmed by SEM and TEM images. The nanomaterials characterized by the FTIR, XPD, SEM and TEM techniques revealed that the C-RE₂O₃:Eu³⁺ materials were obtained even at 500 °C. The RE₂O₃:Eu³⁺ excitation spectra show a broad absorption band assigned to interconfigurational ligand-to-metal charge-transfer (LMCT) band at 260 nm, *i.e.* O²⁻(2p)→Eu³⁺(4f⁶). Besides, it is observed the narrow absorption lines arising from the 4f intraconfigurational transitions of the Eu³⁺ ion (⁷F_{0,1}→⁵L_J; J : 0, 1, 2, 3 and 4), as expected. The characterization of the photoluminescence properties of the luminophores was also based on the analysis of the emission spectra and luminescence decay curves. The experimental intensity parameters (Ω_λ), lifetimes (τ), as well as radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates were calculated and discussed. The photonic properties of the luminophores are consistent with the low C₂ symmetry site occupied by the Eu³⁺ ion in the cubic C-type RE₂O₃:Eu³⁺, yielding the red emission color, which is dominated by the hypersensitive ⁵D₀→⁷F₂ transition of the Eu³⁺ ion in the C₂ instead of the centrosymmetric S₆ sites. Furthermore, the Y₂O₃:Eu³⁺ nanomaterials prepared by this new method exhibit similar emissions spectral features and high values of emission quantum efficiency ($\eta \sim 91\%$), compatible with the commercial phosphors currently available in the market. This novel synthetic method can be used to produce large range of rare earth nanophotonic materials, as well as other metal ions.

Keywords: *benzenetricarboxylate method, photoluminescence, rare earths complexes, nanomaterials, europium and yttrium.*

List of Symbols and Abbreviations

$A_{0 \rightarrow J}$	spontaneous emission rate
°	degree
Å	angstrom
A_{nrad}	non-radiative decay rate
A_{rad}	radiative decay rate
A_{total}	total decay rate
BTC	benzenetricarboxylate
c	speed of light
CIE	Commission Internationale de l'Eclairage
cm^{-1}	wavenumber
CNPEM	Centro Nacional de Pesquisa em Energia e Materiais
CQMA	Centro de Química e Meio Ambiente
D	average crystal size
DC	dynamic coupling
DMSO	dimethyl sulfoxide
DTG	differential thermogravimetry
e	electron charge
EMA	hemimelitic acid
FED	forced electric dipole
FEG	emission electron gun
FTIR	infrared absorption spectroscopy
FWHM	full width at half maximum
η	experimental emission quantum efficiency
h	hour
$\hbar$	reduced Planck constant
H_0	kinect energy hamiltonian
H_{CORR}	correction hamiltonian
H_{ER}	interelectronic repulsion hamiltonian
H_{FI}	free ion hamiltonian
H_{LF}	ligand field hamiltonian
H_{SO}	spin-orbit interaction hamiltonian
H_{tot}	total energy hamiltonian
IPEN	Instituto de Pesquisas Energéticas e Nucleares
IQ-USP	Instituto de Química – Universidade de São Paulo
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
LEB-f	Laboratório dos Elementos do Bloco f
LMCT	ligand-to-metal charge-transfer
Ln	lanthanides
LNNANO	laboratório Nacional de Nanotecnologia
mL	milliliter
MOF	metal-organic frameworks formation
n	refractive index
nm	nanometers
RE	rare earth

$\sigma_{0\rightarrow J}$	energy barycenter
$S_{0\rightarrow J}$	emission area
SEM	scanning electron microscopy
S_n	singlet state
τ	emission lifetime
TEM	transmission electron microscopy
TG	thermal analyses
TGA	thermogravimetric analysis
TLA	trimellitic acid
TMA	trimesic acid
T_n	triplet state
UV	ultraviolet
Ω_λ	experimental intensity parameter
XPD	X-ray powder diffraction
β	full width at half maximum
θ	Bragg angle
λ	wavelength
λ_{em}	emission wavelength
λ_{exc}	excitation wavelength
χ	Lorentz local field correction term
ω	angular velocity

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1. INTRODUCTION AND OBJECTIVES

1. INTRODUCTION

Rare earth (RE) containing materials show a versatility for application in the areas of science and technology specially in catalyses, permanent magnets, in hybrid cars batteries [1–3], electroluminescent materials, persistent luminophores, structural probes, luminescent markers, display panels and lasers *etc.* [4–9] Most of these applications are consequence of their intrinsic characteristics, sharp spectral lines, archiving high monochromatic emission colors over wide range from infrared to ultraviolet, [10] *e.g.* Nd^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} and Tm^{3+} ions, which emit in the infrared, red, ultraviolet, green and blue regions, respectively. In the last decades, complexes containing carboxylate ligands have been extensively used due to their great structural variety in producing materials with large range of chemical properties. Besides, the RE-complexes are applied as structural probes, luminescent markers, flouoroimmunoassay, lasers, electroluminescent materials, magnetic materials, gas storage, drug delivery, display panels, *etc.* [11–17].

The luminescent proprieties of the RE^{3+} ions are due to the unusual 4f energy level structure. The atomic like character of the 4f-4f transitions is due to the shielding from the chemical environment by the external filled 5s and 5p subshells [18]. The 4f intraconfigurational transitions are forbidden to first order by the *Laporte* rule, exhibiting low absorption and emission intensities. Therefore, to overcome the small absorption coefficients, luminescence sensitizers are used to absorb and transfer energy efficiently to the RE ions. This phenomenon is a key feature in design of luminescent materials [10,19].

It is noteworthy that the La^{3+} ($4f^0$), Y^{3+} ($4d^0$) and Lu^{3+} ($4f^{14}$) ions present no luminescence originated from the 4f–4f transitions because of no optically active electrons. Besides, the Gd^{3+} ($4f^7$) ion has a large energy gap ($\sim 32000 \text{ cm}^{-1}$) between the $^8\text{S}_{7/2}$ ground state and the first $^6\text{P}_{7/2}$ excited state. Therefore, these rare earth ions can be used as host matrices. For example, the $[\text{RE}(\text{BTC})\text{:Eu}^{3+}]$ (RE: La^{3+} , Gd^{3+} , Y^{3+} and Lu^{3+}) complexes (BTC: benzenetricarboxylate), the

energy level of the first triplet state (T_1) of the ligand is around 24000 cm^{-1} , which is above the emitting 5D_0 level of the Eu^{3+} ($\sim 17200\text{ cm}^{-1}$) [10,20] enabling the ligand-to-metal energy transfer.

Inorganic luminescent materials containing RE ions usually present very intense absorption bands in the ultraviolet region consistent with allowed interconfigurational transitions, $4f^N \rightarrow 4f^{N-1}5d$ [21,22]. For matrices such as vanadates, molybdates, tungstates and sesquioxides containing RE^{3+} ions are generally observed an efficient energy transfer from the ligand-to-metal charge-transfer (LMCT) band. In the special case, the Eu^{3+} ion shows a high absorption intensity arising from $\text{O}^{2-}(2p) \rightarrow \text{Eu}^{3+}(4f^6)$ LMCT transition, leading to strong luminescence intensity [23].

Usually, in solid state reaction is necessary high temperatures and long reaction time periods to prepare luminescent materials. This way to synthesize materials is also known as ceramic method, which promotes heterogeneous distribution of the activator ion within the matrix and generate materials with high crystallite and particle sizes. Alternative methods to obtain materials in milder reaction conditions are key to overcome the experimental limitation and improve their morphological properties [7].

In this work, we develop the benzenetricarboxylate method in order to prepare the $[\text{RE}(\text{TMA}):\text{Eu}^{3+}(x\text{ mol}\%)]$ and $[\text{RE}(\text{TLA}):\text{Eu}^{3+}(x\text{ mol}\%)]$ compounds (RE^{3+} : Y, Gd and Lu; x : 0.1, 0.5, 1.0, and 5.0) as well as $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ materials. These doped complexes were annealed at 500, 600, 700, 800, 900 and 1000 °C in static air atmosphere resulting in the respective $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ nanoluminophoros, which present high purity and equitable distribution of the luminescence activator in the matrices. The luminescent RE^{3+} complexes and materials were characterized by elemental analysis, infrared spectroscopy, thermogravimetry, X-ray powder diffraction, scanning electron microscopy and transmission electron microscopy. The experimental intensity parameters (Ω_2 and Ω_4), radiative and non-radiative rates (A_{rad} and A_{nrad}), for

the Eu^{3+} compounds have been calculated. The emission spectral features, the experimental emission quantum efficiency (η) and the emission lifetimes (τ) for nanomaterials have been also discussed.

1.1. Rare earths

According to the *International Union of Pure and Applied Chemistry* (IUPAC), the rare earth elements (RE) includes the lanthanide series (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) as well as Sc and Y elements. They are grouped together due to similar physical properties and the rare label resulting in difficult chemical separation processes. For example, for pure individual rare earth compounds, production processes require successive steps, especially in higher purities, with high costs and using harmful environment reactants, like concentrated acids, and generating large amount of unprocessed ores [1,24,25].

In the last decade, most commercially explored reserves are located in Asia, especially in China the largest producer and exporter of rare earths, controlling more than 90 % of worldwide supply. It is noteworthy that the large and mostly unexplored ore reserves can also be found in North America, Brazil and Australia [1,26,27]. The abundance of these elements in the earth's crust is considerably high, cerium being the most abundant with an approximate concentration of 60 ppm, and the less abundant of these elements is thulium (0.5 ppm), which is more abundant than silver (0.4 ppm) and iodine (0.1 ppm) [7,28].

The ionization energy of the lanthanide elements varies with increasing of their atomic numbers (Figure 1.1). However, the ionization energies of these elements show less variation in the loss of the first two electrons ($\text{Ln}^0 \rightarrow \text{Ln}^+$ and $\text{Ln}^+ \rightarrow \text{Ln}^{2+}$). On the other hand, the ionization processes of energy variation in $\text{Ln}^{2+} \rightarrow \text{Ln}^{3+}$ and $\text{Ln}^{3+} \rightarrow \text{Ln}^{4+}$ are more influenced by the atomic number. The ionization energies of the Ln ions can explain the stability of their different oxidation states. For example, the $\text{La}^{3+} \rightarrow \text{La}^{4+}$, $\text{Gd}^{3+} \rightarrow \text{Gd}^{4+}$ and $\text{Lu}^{3+} \rightarrow \text{Lu}^{4+}$ oxidation

process has higher energy due to the fact that these trivalent ions present electronic configuration $4f^0$, $4f^7$ and $4f^{14}$ (empty, half-filled and full 4f subshell), respectively, ensuring high stability. However the low energy of $Ce^{3+} \rightarrow Ce^{4+}$ is explained by generating empty 4f subshell ($4f^0$) (Figure 1.1) [7].

Figure 1.1. Ionization energies for successive ionization steps of lanthanide gaseous species [29].

All RE ions can be found mainly in the trivalent state, nevertheless some of these elements can also be found in the divalent (Sm^{2+} , Eu^{2+} , Tm^{2+} and Yb^{2+}) and tetravalent (Ce^{4+} , Pr^{4+} and Tb^{4+}) oxidation states. The most important feature of the RE^{3+} ions is the small radial extension of the 4f subshell that are only little affected by their chemical environments, due to the effective shielding of the 4f electrons from the external filled 5s and 5p subshells (Figure 1.2). In particular, the solid state spectra of RE^{3+} ions retain more or less their atomic character, which can act as local structural probes, presenting usually quite narrow absorption and emission bands, in contrast to the d-transition metal ions. Accordingly, the 4f-4f intraconfigurational

transitions undergo small influence of the ligand field of the chemical environment, facilitating the interpretation of the spectroscopic data from their absorption and emission spectra [30].

Figure 1.2. Radial charge density of the 4f, 5p and 6s subshells of Gd [31].

The trivalent rare earths (RE^{3+}) physical properties are very similar due to their comparable ionic radii, *e.g.* La^{3+} (1.16 Å) and Lu^{3+} (0.98 Å) with coordination number 8. The *lanthanide contraction* arises from the imperfect shielding of one for 4f electrons by another 4f electron [32].

1.2. Spectroscopic properties

The energy levels of the Ln ions can be explained in terms of the free-ion levels and the additional interaction with the ligand field. The Hamiltonian that describes the different interactions of the 4f-4f energy levels may be written as: (Equation 1.1) [33]:

$$\mathbf{H}_{\text{tot}} = \mathbf{H}_0 + \underbrace{\mathbf{H}_{\text{ER}} + \mathbf{H}_{\text{SO}} + \mathbf{H}_{\text{CORR}}}_{\mathbf{H}_{\text{FI}}} + \mathbf{H}_{\text{LF}} \quad (\text{Eq. 1.1})$$

Where $\mathbf{H}_{\text{tot}}$ represents the total energy of the system that contains the free ion ($\mathbf{H}_{\text{IF}}$) and ligand field ($\mathbf{H}_{\text{LF}}$) interactions. $\mathbf{H}_0$ represent the kinetic energy of the 4f electrons and their coulomb interaction with the nucleus effective charge, it does not remove any degeneracy of the 4f configuration. The $\mathbf{H}_{\text{ER}}$ represents the interelectronic repulsion and split the $4f^N$ configuration ($N>1$) into ^{2S+1}L spectroscopic terms, where S represents the total spin momentum and the L the orbital total angular momentum. The spin-orbit interaction is given by $\mathbf{H}_{\text{SO}}$ and remove the degeneracy of the ^{2S+1}L terms into J energy levels ($^{2S+1}L_J$), where J represents the total angular momentum [33–35].

The $\mathbf{H}_0 + \mathbf{H}_{\text{ER}} + \mathbf{H}_{\text{SO}}$ interactions provides the right order of magnitude of the parameters but it is not able to reproduce accurately all the experimental data and some discrepancies remain between theoretical and experimental data. In order to improve the fit was required the introduction of new interaction in the effective Hamiltonian, which is called as $\mathbf{H}_{\text{CORR}}$ and represents higher order corrections. For more information about the theoretical data see the reference Liu *et al.* [35].

Moreover, the interaction with the ligand field ($\mathbf{H}_{\text{LF}}$) removes a certain degree of degeneracy of the free-ion energy levels and considers the charge density of the surround chemical environment to calculate the potential energy of the 4f electrons. The 4f electrons interaction with the chemical environment is responsible for the splitting of $^{2S+1}L_J$ energy levels (*Stark* effect) in $^{2S+1}L_{J(\text{MJ})}$ sublevels, which depend on the site of symmetry around the RE^{3+} ion [34,35]. Furthermore, the magnitudes of these interactions follow the order: $\mathbf{H}_0$ (10^5 cm^{-1}) > $\mathbf{H}_{\text{ER}}$ (10^4 cm^{-1}) > $\mathbf{H}_{\text{SO}}$ (10^3 cm^{-1}) > $\mathbf{H}_{\text{LF}}$ (10^2 cm^{-1}) (Figure 1.3).

The 4f-4f transitions are forbidden by *Laporte* rule ($\Delta\ell = \pm 1$), nevertheless is slightly relaxed due to the mixing of opposite parity electronic configurations, produced by the odd components of the ligand field in a symmetry site with no inversion center [10,34]. On the other

hand, if the RE^{3+} ion occupies at a site with inversion center, the *Laporte* rule can not be relaxed, and the intraconfigurational transitions remain strictly forbidden [36,37].

Figure 1.3 shows that the $^{2S+1}L_J$ energy levels splitting caused by the ligand field is smaller than that caused by free ion interactions. The small effect of the ligand field interaction lead to the narrow absorption and emission bands, indicating that the RE^{3+} can be act as spectroscopic probes.

Figure 1.3. Partial energy level diagram of Eu^{3+} ion [38].

Carnall *at. al.* [39] made an exhaustive work on “A systematic analysis of the spectra of lanthanides doped into single crystal LaF_3 ”. This study used a C_{2v} site symmetry crystal field to approximate the C_2 site symmetry and were able to correlate extensive spectroscopy data for $\text{LaF}_3:\text{Ln}^{3+}$ with consistent set of free ion and crystal field parameters for the lanthanide series (Figure 1.4). The energy level diagrams of the $\text{LaF}_3:\text{Ln}^{3+}$ materials have supported works in the theoretical and application areas using rare earths ions.

Figure 1.4. Partial energy levels diagram of doped $\text{LaF}_3:\text{Ln}^{3+}$ system and main radiative transitions [39].

1.3. Luminescence behavior of RE³⁺ ions

The light provide different forms of interaction with the matter, allowing the use in different technological and scientific applications and helps in the study of the universe around us. The visible light range is only a small part of electromagnetic radiation (Figure 1.5) [1].

The luminescence process involves the spontaneous emission of radiation by a species in an excited state. The method of excitation determines how the process is called, like: *photoluminescence* (light), *electroluminescence* (electron stimulation), *triboluminescence* (friction, impact or breakage), *thermoluminescence* (heat), *chemiluminescence* (chemical reaction), *bioluminescence* (chemical reaction *in vivo*), *piezoluminescence* (pressure), etc [7,40].

Figure 1.5. Schematic representation of the wide range light spectrum with major applications in different wavelengths [1].

The photoluminescence can be divided in two phenomena, *fluorescence* and *phosphorescence*. The *fluorescence* is characterized by spin-allowed electronic transition ($\Delta S = 0$), its spontaneous emission is typically within 10^{-8} s after the exciting radiation is

extinguished. On the other hand, *phosphorescence* is characterized by an electronic transition with different spin multiplicity ($\Delta S \neq 0$), its emission may persist for long periods, even hours, but the lifetimes usually last milliseconds to seconds [10,41,42].

As was reported the luminescence of the Ln^{3+} ions is characterized by narrow emission lines due to the well defined energy levels and the position of excitation and emission bands change very little due to the small interaction with the ligand field.

The luminescence features of the $\text{RE}^{3+} 4f^N$ transitions can be divided as follows [10]:

- $\text{Sc}^{3+}(3d^0)$, $\text{Y}^{3+}(4d^0)$, $\text{La}^{3+}(4f^0)$ and $\text{Lu}^{3+}(4f^{14})$ where the 4f electrons are not optically active due to their completely empty or fully occupied subshells.
- $\text{Gd}^{3+}(4f^7)$ is a unique case due to its half-filled 4f layer, and therefore very stable. The energy difference between the lower emitting level ($^6P_{7/2}$) and the fundamental level ($^8S_{7/2}$) is approximately 32000 cm^{-1} , providing the opportunity for its application as inorganic matrices. Due to the chemical similarity with other RE^{3+} ions it is extensively used to study the emission of the ligands in coordination complexes.
- $\text{Sm}^{3+}(4f^5)$, $\text{Eu}^{3+}(4f^6)$, $\text{Tb}^{3+}(4f^8)$ and $\text{Dy}^{3+}(4f^9)$: in these ions the energy gap between the emitting and the lower levels are large enough to reduce the non-radiative decay process and accept energy from the ligands, interconfigurational transitions or charge transfer bands excited levels.
- $\text{Ce}^{3+}(4f^1)$, $\text{Pr}^{3+}(4f^2)$, $\text{Nd}^{3+}(4f^3)$, $\text{Ho}^{3+}(4f^{10})$, $\text{Er}^{3+}(4f^{11})$, $\text{Tm}^{3+}(4f^{12})$ and $\text{Yb}^{3+}(4f^{13})$: in these ions the energy gap between the emitting and lower levels are small, increasing the non-radiative decay process usually mediated by high energy vibrational modes in ligands. In this case, the luminescence process leads to a decreasing of the emission quantum efficiency.

The mostly used luminescent RE³⁺-containing materials are Eu³⁺ and Tb³⁺ ions ones that show high emissions intensities in the red and green regions, respectively. It is noteworthy that other RE³⁺ ions can emit in other spectral regions like: Gd³⁺ (ultraviolet), Sm³⁺ (orange), Dy³⁺ (yellow), Tm³⁺ (blue), Yb³⁺, Nd³⁺ and Er³⁺ (near infrared).

Indeed, the Eu³⁺ ion can act as an excellent activator in luminescent materials due to its exceptional spectroscopic properties. It exhibits strong red monochromatic emission color and it has also been considerably used as an efficient luminescent probe due to the following characteristics [43]:

- a) The first excited ⁵D₀ energy level is well separated ($\sim 12000\text{ cm}^{-1}$) from ⁷F₀₋₆ energy levels;
- b) The ⁵D₀ emitting level and the ground ⁷F₀ state are non-degenerated, thus the ⁵D₀→⁷F₀ transition displays a single peak when the Eu³⁺ ion occupies identical sites of symmetry of the type C_s, C_n or C_{nv}, which provides information on the eventual existence of more than one site of symmetry occupied by rare earth ion;
- c) Long luminescence decay lifetime for the emitting ⁵D₀ level (milliseconds);
- d) The radiative rate of the ⁵D₀→⁷F₁ transition is formally insensitive to the crystal field environment and consequently can be used as a reference transition that can be used to calculate the experimental intensity parameters (Ω_λ ; λ : 2, 4 and 6).
- e) The O²⁻(2p)→Eu³⁺(4f⁶) ligand-to-metal charge-transfer states (LMCT) is located at lower energy than the other trivalent rare earth ions.

The intraconfigurational 4f^N transitions of RE³⁺ ions are forbidden by *Laporte* rule, consequently, the energy absorption of RE³⁺ is limited. Therefore, to overcome the small absorption coefficients, luminescence sensitizers with strong absorption and efficient intramolecular energy transfer to the RE³⁺ ions are employed. This phenomenon is a key feature in design of highly luminescent materials.

The intramolecular energy transfer in the RE^{3+} complexes occurs as follows: 1) strong absorption from the ground singlet state (S_0) to the excited singlet state (S_1) of the ligand; 2) S_1 state decays non-radiatively to the triplet state (T_1) via intersystem crossing and 3) nonradiative energy transfer pathway from the T_1 state of the ligand to excited states of the Ln^{3+} ion. In some cases direct energy transfer from the S_1 singlet state to excited Ln^{3+} levels is also of importance [44].

In inorganic matrices such as vanadates, molybdates, tungstates and yttrium oxide generally it is observed an efficiently energy transfer derived from the ligand-to-metal charge-transfer (LMCT) $\rightarrow$ to RE^{3+} ions emitting levels efficiently. In addition, the Eu^{3+} also features the LMCT transition, which should be allowed, showing high absorption intensity, yielding high-intensity luminescence [23].

The cubic C-type rare earth sesquioxides $\text{C-RE}_2\text{O}_3$ can be readily doped with Eu^{3+} ions (Figure 1.6), which exhibit high luminescence efficiency. The Eu^{3+} ions occupy two sixfold-coordinated non-equivalent sites with C_2 and S_6 symmetries [45]. The induced electric dipole transitions in the S_6 site (centrosymmetric) cannot gain intensity by the mixing of opposite parity electronic configurations with the $4f^N$ one. However, the relatively weak magnetic dipole-induced transitions remain possible for ions in a site with inversion center. In contrast to the S_6 site, the C_2 site has no center of inversion that drastically affects the luminescence spectra of the RE^{3+} -doped materials. For example, the red emission color of the Eu^{3+} doped cubic $\text{C-RE}_2\text{O}_3$ is dominated by the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of the Eu^{3+} ion in the C_2 site [46].

Figure 1.6. A schematic illustration of the RE^{3+} ions occupying the two six-fold coordinated sites with C_2 and S_6 symmetries in cubic $\text{C-RE}_2\text{O}_3$ [45,47,48].

1.4. Benzenetricarboxylate method

Polycarboxylate ligands have wide variety of structures providing large range of chemical properties when combined with metal ions. It has been drawing attention in the different areas of science and technology. Among the most noticeable advantages of polycarboxylates are the high resistance to the environment and decomposition temperature (ordinarily above 350 °C, unusual in organic complexes). Most of these features is the result of metal-organic frameworks (MOF) formation.

The benzenetricarboxylate (BTC) group consists of three ligands: hemimellitic (EMA), trimellitic (TLA) and trimesic acids (TMA) (Figure 1.7). All RE^{3+} complexes of these group present high thermal stability, however the decomposition occurs in only one step at around 480–520 °C, enabling the synthesis of oxides at low temperature and nanoscale level [Appendix I-VI]. The remarkable ligand is the trimesic acid, greatly used due to its optical and thermal features and being symmetrical, very useful in MOFs systems.

Figure 1.7. Benzenetricarboxylic ligands (H_3EMA - left; H_3TLA - center; H_3TMA right).

The mostly used method for the preparation of luminescent materials are based on solid state reactions is the ceramic method. Typically, this method of preparation involves high temperatures and long reaction periods, promotes product sintering and heterogeneous distribution of the activator ion within matrices and materials with a high crystallite size. Therefore, it is necessary to develop new alternative methods for obtaining these materials in milder reaction conditions, which offer the possibility of improving the properties of the materials.

With the advent of nanoscience and nanotechnology, the photonic and morphological properties of $RE_2O_3:Eu^{3+}$ nanomaterials have been retaken and reinvestigated with new focuses [46,49]. These luminophores have been prepared by sol–gel [50,51], Pechini method [52,53], chemical vapor deposition [54,55], microemulsion [52,56], spray pyrolysis [57,58], co-precipitation [59,60], hydrothermal [61,62] and combustion methods [63,64].

Taking into account the large number of techniques developed for the synthesis of nanomaterials considering each of their advantages and disadvantages. This work proposed a new benzenetricarboxylates method of synthesis to prepare nanomaterials starting at (500 °C). For preparation of the rare earth complex precursors were used 1,3,5-benzenetricarboxylate

(TMA) and 1,2,4-benzenetricarboxylate (TLA) ligands, since such complexes have a low total decomposition temperature. Based on this thermal behavior was possible to prepare the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ commercial luminophores without side phases or impurities. On the other hand, the 1,2,3-benzenetricarboxylate (EMA) ligand was not used due to no present good thermal behavior to prepare nanomaterials (Figure 1.7).

This project involves the developing of a cost effective solid-state synthetic method at low temperature in a laboratorial scale. The ligands are easily found in chemistry laboratories, especially the TMA ligand, and the synthesis use available experimental apparatus, making easier its dissemination.

The goal of this work is to develop a new method of synthesis of nanostructured materials prepared at low temperature using the RE^{3+} benzenetricarboxylate complexes. These ligands present highly favorable thermal decomposition features. The photoluminescent study of the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (RE^{3+} : Y, Gd and Lu) nanomaterials produced by this method and compared with that reported in literature were discussed.

The synthesis, characterization and photoluminescent properties of $[\text{RE}(\text{TMA}):\text{Eu}^{3+} (\text{x mol}\%)]$ and $[\text{RE}(\text{TLA})\text{n}(\text{H}_2\text{O}):\text{Eu}^{3+} (\text{x mol}\%)]$ compounds (RE^{3+} : Y, Gd and Lu; x: 0.1, 0.5, 1.0, and 5.0 mol%) were prepared by a one-step synthesis in water are reported. These doped complexes were annealed at 500, 600, 700, 800, 900 and 1000 °C in static air atmosphere resulting in the respective nanostructured $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ luminophores with high purity and equitable distribution of the luminescence activator within the matrices.

2. EXPERIMENTAL PART

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2.1 Synthesis of precursor complexes and nanoluminophores

The rare earth chlorides $\text{RECl}_3 \cdot 6(\text{H}_2\text{O})$ (RE^{3+} : Y, Gd, Eu and Lu) were prepared from their respective oxides (CSTARM, 99.99 mol%) by digestion of their corresponding aqueous suspensions with the addition of concentrated hydrochloric acid (Vetec, high purity, 37 vol%) until pH reached *ca.* 6.0. The benzene-1,3,5-tricarboxylic acid (trimesic acid, Fluka, 97 mol%), $\text{H}_3(\text{TMA})$, and trimellitic acid (benzene-1,2,4-tricarboxylic acid – purchased as benzene-1,2,4-tricarboxylic acid 1,2-anhydride – Sigma-Aldrich, 97 mol%), $\text{H}_3(\text{TLA})$, were used without further purification. $\text{Na}_3(\text{BTC})$ aqueous solution was prepared by dropwise addition of 1 M sodium hydroxide solution (Vetec, 97 mol%) in $\text{H}_3(\text{BTC})$ aqueous suspension up to pH adjusted at *ca.* 6.0.

The doped $[\text{RE}(\text{TMA}):\text{Eu}^{3+}(\text{x mol}\%)]$ complexes (Eu^{3+} concentration of 0.1, 0.5, 1.0 and 5.0 mol%) were prepared by adding 50 mL of RECl_3 (~ 0.050 M) aqueous solution over 200 mL of previously prepared (BTC^{3-}) ligand aqueous solution (~ 0.0125 M), at temperature of 100 °C for 1 h. The resulting solid was filtered and washed with distilled water, the benzenetricarboxylate complexes are non-hygroscopic white crystalline powders, air-stable and insoluble in a large range of solvents (ethanol, acetone, acetophenone, benzene, chloroform and DMSO) (Figure 2.1).

In order to prepare the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ nanomaterials, the doped $[\text{RE}(\text{BTC}):\text{Eu}^{3+}(\text{x mol}\%)]$ (BTC: TMA and TLA; x: 0.1, 0.5, 1.0 and 5.0 mol%) complexes were used as precursors, which were added in porcelain capsules and annealed from room temperature up to the final annealing temperatures of 500, 600, 700, 800, 900 or 1000 °C, heating rate of 5 °C min^{-1} . After reaching the final temperature, the compounds were maintained for 1 h. After the ending of the annealing process the cooling was done naturally, compounds were milled and stored in vacuum desiccator.

Figure 2.1. Synthesis diagram of the $[\text{RE}(\text{BTC}):\text{Eu}^{3+}(\text{x mol}\%)]$ complexes and $\text{RE}_2\text{O}_3:\text{Eu}^{3+}(\text{x mol}\%)$ nanomaterials (RE^{3+} : Y, Gd and Lu; x: 0.1, 0.5, 1.0 and 5.0 %).

2.2 Instrumental techniques

2.2.1 Carbon and hydrogen elemental analysis

The elemental analyses of carbon and hydrogen of the $[\text{RE}(\text{BTC}):\text{Eu}^{3+}(\text{x mol}\%)]$ precursor complexes were carried out using a Perkin-Elmer 2400 CHN Elemental Analyzer of the Central Analítica do Instituto de Química – Universidade de São Paulo (IQ-USP).

2.2.2 Thermal analyses (TG)

The thermogravimetry analyses of the of [RE(BTC):Eu³⁺(x mol%)] precursor complexes were performed in a TA HI-RES TGA 2850 equipment from 30 to 900 °C (heating rate of 5 °C min⁻¹, in a dynamic synthetic air atmosphere, flux of 50 cm³ min⁻¹) present at the Central Analítica – Instituto de Química – Universidade de São Paulo (IQ-USP).

2.2.3 Infrared absorption spectroscopy (FTIR)

The infrared absorption spectra (FTIR) of [RE(BTC):Eu³⁺(x mol%)] precursor complexes and RE₂O₃:Eu³⁺(x mol%) nanomaterials were measured using KBr pellets at a Bomem MB100 FTIR from 400 to 4000 cm⁻¹. This equipment is present at the Central Analítica – Instituto de Química – Universidade de São Paulo (IQ-USP).

2.2.4 X-ray powder diffraction (XPD)

The diffraction data of [RE(BTC):Eu³⁺(x mol%)] precursor complexes and RE₂O₃:Eu³⁺(x mol%) nanomaterials were recorded by a Rigaku Miniflex II diffractometer using CuK_{α1} radiation (λ : 1.5406 Å) in the 2 θ range of 10 to 60 degrees, using a glass sample holder. This XPD instrument is present in the Laboratório de Nanotecnologia Molecular e Marcadores Integrados – Centro de Química e Meio Ambiente (CQMA) – Instituto de Pesquisas Energéticas e Nucleares (IPEN).

2.2.5 Scanning electron microscopy (SEM)

The scanning electron microscopy images of [RE(BTC):Eu³⁺(x mol%)] precursor complexes and RE₂O₃:Eu³⁺(x mol%) nanomaterials were measured with a Jeol, JSM-7401F (FEG) SEM of the Central Analítica – Instituto de Química – Universidade de São Paulo (IQ-USP). The sample particles were dispersed in isopropanol and sonicated for 10 min. After, the

samples were prepared by drying the isopropanol-dispersed particles on a cylindrical carbon mounts, which were inserted in the SEM equipment.

2.2.6 Transmission electron microscopy (TEM)

The TEM imaging for the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ materials (from $[\text{RE}(\text{TMA})]$ complexes) were performed using a JEM 2100 ARP transmission electron microscope, using an acceleration voltage of 200 kV from a LaB_6 thermo-ionic filament, present at the Laboratório Nacional de Nanotecnologia (LNNANO), Centro Nacional de Pesquisa em Energia e Materiais (CNPEM), Campinas-SP.

In addition, the micrographs of $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ materials (from $[\text{RE}(\text{TLA})]$ complexes) were performed using a TEM JEOL 2100 JEM transmission electron microscope, using an acceleration voltage of 200 kV from a LaB_6 thermo-ionic filament of the Central Analítica – Instituto de Química – Universidade de São Paulo (IQ-USP). The samples were prepared by dispersing the powder in isopropanol. The suspension formed was submitted to ultrasound and was placed on a Cu grid covered with a porous carbon film.

2.2.7 Photoluminescence spectroscopy

The luminescence study of doped $[\text{RE}(\text{BTC}):\text{Eu}^{3+}(\text{x mol}\%)]$ precursor complexes and $\text{RE}_2\text{O}_3:\text{Eu}^{3+}(\text{x mol}\%)$ nanomaterials was based on the excitation and emission spectra recorded at room temperature (300 K) and liquid nitrogen (77 K). The spectra of the Eu^{3+} materials were recorded with a HORIBA Jobin Yvon Fluorolog-2 spectrofluorometer, using a 450 W Xenon lamp as an excitation source and two 0.22 m double-grating SPEX 1680 monochromators for dispersing the radiation and a photomultiplier.

Luminescence decay of the Eu^{3+} containing compounds were measured using the SPEX 1934D phosphorimeter accessory to the 150 W pulsed Xenon lamp attached to the Fluorolog-

2 spectrofluorometer. It was also used a SPEX FL212 Fluorolog-3 spectrofluorometer, with a 450 W Xenon lamp as an excitation source and equipped with a mono- (excitation) and double-grating (emission) monochromators, with a Synapse HORIBA Jobin Yvon E2V CCD30 (1024x256 pixels) as CCD detector. These apparatuses are present at the Laboratório dos Elementos do Bloco f (LEB-f), Instituto de Química da Universidade de São Paulo (IQ-USP).

3. RESULTS AND DISCUSSION

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3.1 Characterization

The RE^{3+} complexes containing polycarboxylate ligands usually present solid state forms with high thermal and chemical stability, well defined crystalline structure and high crystallinity [65–69]. Ligands with chromophore groups can absorb, in the UV region, and transfer energy to the luminescent center, improving the emission quantum efficiency. Therefore, the benzenetricarboxylate (BTC) group shows these characteristics and has a low total decomposition temperature ($\sim 500^\circ\text{C}$), allowing the production of RE_2O_3 at low temperature leading to nanomaterials [A.I–III].

The elemental analysis of carbon and hydrogen (Table 3.1) of the RE^{3+} BTC complexes can be used to estimate the ratio of RE:BTC ligand:metal and the number of water molecules that can be corroborated with the thermogravimetric data.

The chemical compositions of the $[\text{RE}(\text{BTC})]$ complexes indicate the 1:1 ratio between the BTC ligands and the RE ions (Table 3.1) (*i.e.* $\text{Lu}(\text{TMA})$: calcd: C, 28.29; H, 0.79. found: C, 28.34; H, 0.88 %). The non-doped $[\text{RE}(\text{TMA})]$ complexes (RE^{3+} : Y, Gd and Lu) present the absence of coordinated water molecules, indicating that this compounds are anhydrous. When the $[\text{RE}(\text{TMA})\text{:Eu}^{3+}]$ complexes are doped with Eu^{3+} ion (at 0.1, 0.5, 1.0 and 5.0 mol%), the anhydrous complexes are formed, except for the $[\text{Gd}(\text{TMA})\cdot 6(\text{H}_2\text{O})\text{:Eu}^{3+}]$ complex doped with 5.0 mol% of Eu^{3+} ion, which contain six coordinated water molecules in the first coordination sphere (Table 3.1) [A.I,II]. On the other hand, The $[\text{RE}(\text{TLA})\cdot n(\text{H}_2\text{O})\text{:Eu}^{3+}(\text{x mol}\%)]$ coordination compounds are all hydrated at different Eu^{3+} concentrations (x: 0.1, 0.5, 1.0 and 5.0 mol%), where n: 4, 4 and 3 for Y^{3+} , Gd^{3+} and Lu^{3+} ions, respectively [A.III].

Table 3.1: Elemental analyses results for the [RE(BTC)] and [RE(BTC):Eu³⁺(x mol%)] (RE³⁺: Y, Gd and Lu; x: 0.1, 0.5, 1.0 and 5.0 mol%) complexes.

[RE(BTC)] complexes	%C		%H	
	Calc.	Exp.	Calc.	Exp.
[Y(TMA)]	36.52	36.02	1.02	1.12
[Y(TMA):Eu ³⁺ (0.1 mol%)]	36.51	35.91	1.02	1.11
0.5	36.48	35.79	1.02	1.08
1.0	36.44	35.92	1.02	0.95
5.0	36.13	35.35	1.01	1.05
[Gd(TMA)]	29.67	28.32	0.83	1.25
[Gd(TMA):Eu ³⁺ (0.1 mol%)]	29.67	29.32	0.83	1.14
0.5	29.67	28.85	0.83	1.07
1.0	29.67	29.43	0.83	1.12
5.0	22.89	23.51	3.20	2.91
[Lu(TMA)]	28.29	27.84	0.79	0.88
[Lu(TMA):Eu ³⁺ (0.1 mol%)]	28.29	27.43	0.79	0.83
0.5	28.30	27.92	0.79	0.96
1.0	28.31	28.03	0.79	0.90
5.0	28.38	28.12	0.79	0.92
[Y(TLA)]	29.33	28.89	3.01	2.59
[Y(TLA):Eu ³⁺ (0.1 mol%)]	29.36	28.89	3.01	2.59
0.5	29.34	28.73	3.01	2.43
1.0	29.32	28.96	3.01	2.37
5.0	29.12	28.71	2.99	2.69
[Gd(TLA)]	25.12	24.93	2.54	2.26
[Gd(TLA):Eu ³⁺ (0.1 mol%)]	24.77	24.93	2.54	2.16
0.5	24.77	24.97	2.54	2.11
1.0	24.77	24.76	2.54	2.11
5.0	24.78	24.43	2.54	1.97
[Lu(TLA)]	24.84	24.67	2.08	2.21
[Lu(TLA):Eu ³⁺ (0.1 mol%)]	24.79	24.67	2.08	2.21
0.5	24.79	25.06	2.08	2.16
1.0	24.80	24.66	2.08	2.13
5.0	24.85	24.81	2.09	2.17

3.1.1 Thermogravimetric analyses

The thermogravimetric analysis (TG) of the RE^{3+} BTC complexes provides information about the number of water molecules in the complexes, the thermal stability range, the decomposition temperature and allow to infer the final product after the total decomposition of the compounds. These data are used to confirm that the benzenetricarboxylate method could be successfully used to produce nanomaterials at low temperature than the traditional solid state method [A.I–III].

RE^{3+} TMA-complexes – The TG-DTG curves of the non-doped and Eu^{3+} doped complexes were recorded in the temperature interval from 30 to 900 °C. The anhydrous $[\text{RE}(\text{TMA})]$ complexes present no mass-loss event in the temperature range from 30 to 460 °C and only one single-step decomposition between 450 and 570 °C (Figure 3.1) [A.I,II]. On the other hand, the $[\text{Gd}(\text{TMA}) \cdot 6(\text{H}_2\text{O}) : \text{Eu}^{3+} (5.0 \text{ mol}\%)]$ systems exhibit an additional event, attributed to the removal of six coordinated water molecules in the 70–150 °C temperature interval (Figure 3.1) [A.I,II]. The temperature of the inflexion point of the organic moiety decomposition event for the different non-doped $[\text{RE}(\text{TMA})]$ complexes are very similar such as: 550, 557, 558 °C for complexes with Gd^{3+} , Y^{3+} and Lu^{3+} ions, respectively [A.I–III].

The $[\text{RE}(\text{TMA})\text{Eu}^{3+}(\text{x mol}\%)]$ complexes (x: 0.1, 0.5, 1.0 and 5.0 mol%) have the final decomposition temperature event higher than 500 °C, nevertheless if the annealing temperature is maintained for 1 h, the respective RE_2O_3 sesquioxides are formed. This thermal behaviour indicated a kinetic dependence. For the $[\text{RE}(\text{TMA}) : \text{Eu}^{3+} (5.0 \text{ mol}\%)]$ complexes, the inflexion point of the organic moiety decomposition is reduced to all systems after the doping process such as: 500, 507, 517 °C for complexes with Gd^{3+} , Y^{3+} and Lu^{3+} ions, respectively.

It was observed the decreasing of the thermal decomposition temperature with the doping process due to the different crystal structures for anhydrous $[\text{RE}(\text{TMA})]$ and hydrated

[Eu(TMA)·6(H₂O)] complexes. It is noteworthy that this effect not occur when the doping process is performed for the same crystalline structure, as reported in reference [A.IV]. In addition, the lowest decomposition temperature occurs for the [Gd(TMA)·6(H₂O):Eu³⁺ (5.0 mol%)] complex, indicating the lower thermal stability of this complex hydrate due to the crystal waters [A.III].

Figure 3.1. Thermogravimetric analyses (TG/DTG) of a) [RE(TMA)] and b) [RE(TMA):Eu³⁺(x mol%)] (RE³⁺: Y, Gd and Lu; x: 0.1, 0.5, 1.0 and 5.0 mol%), registered from 30 to 900 °C in synthetic air atmosphere.

RE³⁺ TLA-complexes – When compared the TG analysis of the [RE(TLA)·n(H₂O):Eu³⁺] complexes (RE³⁺: Gd, Y and Lu; n: 4 for Gd, Y and 3 for Lu), it is noted a large similarities with those of the [RE(TMA)] compounds, except for the presence of water molecule loss events. The water molecules mass-loss event occurs in the temperature interval from 50 to 330 °C (Figure 3.2). Besides, the organic moiety decomposition of complexes show only one single-step decomposition between 450 and 570 °C [A.II].

Figure 3.2. Thermogravimetric analyses (TG/DTG) of a) [RE(TMA)] and b) [RE(TMA):Eu³⁺(x mol%)] (RE³⁺: Y, Gd and Lu; x: 0.1, 0.5, 1.0 and 5.0 mol%), registered from 30 to 900 °C in synthetic air atmosphere.

The temperature of the inflexion point of the organic moiety decomposition for the different matrix are similar (520 °C for $[\text{Gd}(\text{TLA})\cdot 4(\text{H}_2\text{O}):\text{Eu}^{3+}]$, 535 °C for $[\text{Y}(\text{TLA})\cdot 4(\text{H}_2\text{O}):\text{Eu}^{3+}]$ and 545 °C for $[\text{Lu}(\text{TLA})\cdot 3(\text{H}_2\text{O}):\text{Eu}^{3+}]$).

All the complexes present good thermal stability and corroborates with their elemental analysis data (number of water molecules and ligand:RE ratio) (Table 3.1). The thermal behavior indicates the formation of metal-organic framework between the RE^{3+} ions and the BTC ligands [A.II].

Finally, the complexes prepared by new benzenetricarboxylate method present a single-step thermal decomposition of the total organic moiety, yielding their respective non-doped RE_2O_3 and doped $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ sesquioxides [A.II]. The similarities in the thermal decomposition curves on both precursor complexes indicate the reproducibility of the method. It is important to mention that the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ luminophores prepared by TMA ligands present slightly better thermal proprieties, however, the TLA ligand is cheaper than the TMA ligand.

3.1.2 Infrared absorption spectroscopy (FTIR)

Infrared absorption spectroscopy technique is based on the vibrational modes in molecules. Usually the IR spectrum is obtained by passing infrared radiation through the sample and determining what fraction of radiation is absorbed or transmitted. The observed peak in the absorption spectrum corresponds to a bond vibration frequency of the sample [70].

In solid state, the infrared absorption spectroscopy provides valuable information about their vibrational modes. Usually, the spectral measurements are based on in the dispersion of the solid samples in KBr salt, which is transparent from 400 to 4000 cm^{-1} . In the RE^{3+} BTC precursor complexes were possible to evaluate the carboxylic groups connectivity with the RE^{3+} ions, which can indicate the effective formation of the coordination compounds. In addition, it can be used to distinguish different coordination modes of the complexes, including the

presence of coordinated water molecules. Besides, the infrared absorption data of the RE_2O_3 nanomaterials can give information on vibrational modes of the host matrix and if there are water molecules adsorbed in the surface.

RE^{3+} BTC-complexes – In this section, we report the FTIR spectra for the $[\text{RE}(\text{BTC})\text{:Eu}^{3+}(1.0 \text{ mol}\%)]$ complexes to facilitate the presentation of obtained data (Figure 3.3). The infrared absorption spectra of the RE^{3+} BTC complexes are very similar for different Gd^{3+} , Y^{3+} and Lu^{3+} ions, even with Eu^{3+} doping concentrations (x: 0.1, 0.5, 1.0 and 5.0 mol%).

Figure 3.3. FTIR absorption spectra of a) $[\text{RE}(\text{TMA})\text{:Eu}^{3+}]$ and b) $[\text{RE}(\text{TLA})\cdot n(\text{H}_2\text{O})\text{:Eu}^{3+}]$ (1.0 mol%) (RE^{3+} : Y, Gd and Lu) complexes.

The FTIR spectra of the europium doped RE^{3+} BTC complexes (Figure 3.3) shows the absorption bands around at 1300 to 1600 cm^{-1} assigned to the BTC ligand symmetric $\nu_s(\text{C}=\text{O})$ and asymmetric $\nu_{as}(\text{C}=\text{O})$ stretching modes. The $[\text{RE}(\text{TMA})\text{:Eu}^{3+}]$ complexes present values

for $\Delta\nu$ ($\nu_{as} - \nu_s$) $\sim 175\text{ cm}^{-1}$ and for $\text{Na}_3(\text{TMA}) \sim 195\text{ cm}^{-1}$, indicating bridge-type coordination. The $[\text{RE}(\text{TLA})_n \cdot (\text{H}_2\text{O}) : \text{Eu}^{3+}]$ complexes present values of $\Delta\nu$ ($\nu_{as} - \nu_s$) $\sim 195\text{ cm}^{-1}$ (for Y and Gd systems) and $\sim 200\text{ cm}^{-1}$ and for $\text{Na}_3(\text{TLA})$ is 190 cm^{-1} , also indicating bridge-type coordination [A.IV–VI] [71].

Moreover, the narrow absorption peak at around 3070 cm^{-1} is assigned to C–H bond stretching characteristic of the anhydrous compounds for $[\text{RE}(\text{TMA})]$ and $[\text{Lu}(\text{TLA}) \cdot 3(\text{H}_2\text{O}) : \text{Eu}^{3+}]$, which is absent in hydrated $[\text{Gd}(\text{TMA}) \cdot 6(\text{H}_2\text{O}) : \text{Eu}^{3+} (5.0\text{ mol}\%)]$ and $[\text{RE}(\text{TLA}) \cdot 4(\text{H}_2\text{O}) : \text{Eu}^{3+}]$ (RE^{3+} : Y and Gd) complexes [A.I–III].

$\text{RE}_2\text{O}_3 : \text{Eu}^{3+}$ nanomaterials – The FTIR spectra of the $\text{RE}_2\text{O}_3 : \text{Eu}^{3+} (1.0\text{ mol}\%)$ luminophores annealed at 500, 600, 700, 800, 900 and 1000 °C temperatures prepared by the benzenetricarboxylate method (Figure 3.4 and Figure 3.5) show absorption bands similar to the commercial Y_2O_3 material [72]. The characteristic bands of $\text{RE}^{3+}\text{--O}$ vibrational modes frequencies centered at around 460 and 560 cm^{-1} indicate the effective formation of sesquioxides matrices. These absorption bands increase with the annealing temperature up to 800 °C.

The broad C=O absorption bands at 1200–1750 cm^{-1} are assigned to stretching mode of oxycarbonate arising from the decomposition of the BTC ligands or air CO_2 absorption. The C=O absorption bands decreases with increasing annealing temperature, due to decomposition of the oxycarbonate (Figure 3.4 and Figure 3.5) [73], especially for the $\text{Gd}_2\text{O}_3 : \text{Eu}^{3+}$ and $\text{Lu}_2\text{O}_3 : \text{Eu}^{3+}$ nanomaterials. In addition, it is possible to observe the broad absorption band centered at around 3400 cm^{-1} assigned to the O–H stretching vibration mode of the surface hydroxyl groups formed by the interaction of $\text{RE}_2\text{O}_3 : \text{Eu}^{3+}$ materials with humidity of the air. The hydroxyl vibrational band decreases with increasing annealing temperature from 500 to 1000 °C [72,74], probably due to the increased particles size and consequently reduction of the surface/volume ratio.

Figure 3.4. FTIR absorption spectra of a) $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, b) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$, c) $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$, annealed at 500, 600, 700, 800, 900 and 1000 °C for 1h using TMA ligand, and $[\text{RE}(\text{TMA}):\text{Eu}^{3+}]$ (1.0 mol%) (RE^{3+} : Y, Gd and Lu).

Figure 3.5. FTIR absorption spectra of a) $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, b) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$, c) $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$, annealed at 500, 600, 700, 800, 900 and 1000 °C for 1h using TLA ligand, and $[\text{RE}(\text{TLA}) \cdot n(\text{H}_2\text{O}) : \text{Eu}^{3+}]$ (1.0 mol%) (RE^{3+} : Y, Gd and Lu).

The infrared absorption spectroscopy data of the Eu^{3+} ion doped in the Y_2O_3 , Gd_2O_3 and Lu_2O_3 matrices present similar spectral features independent of the TMA and TLA precursor ligands (Figure 3.4 and Figure 3.5). The main differences can be observed in the O–H and oxycarbonate bands that exhibit smaller intensities at lower temperatures, especially for the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ materials originated from the TLA ligand [A.I,II].

3.1.3 X-ray measurements (XPD)

X-ray crystallography can be used to determine the arrangement of atoms of crystalline solids, the technique uses the property that the spacing between atoms, usually is similar to the wavelength of the X-ray light (angstroms) [75–77]. Diffraction occurs when the X-ray radiations encounter an obstacle. The resulting diffraction pattern is the consequence of destructive and constructive interaction of the X-ray waves. Polycrystalline materials are composed of a collection of many small crystals and the X-ray can be used to obtain a phase average data of these materials.

The X-ray measurements provide information about the crystalline structure, interplanar distances and crystallinity of the compounds. These information were helpful in the characterization of the complexes and nanoluminophores corroborating the elemental analysis, thermal and infrared absorption techniques. The X-ray data also were used to calculate the average crystallite size of the nanomaterials, using the Scherrer's formula in the polycrystalline oxides, since it is smaller than 200 nm [75–77].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (\text{Eq. 3.1})$$

$$\beta^2 = \beta_s^2 - \beta_r^2 \quad (\text{Eq. 3.2})$$

RE³⁺ BTC-complexes – The powder X-ray powder diffraction (XPD) patterns (Figure 3.5) shown that there are no relevant difference in the entire TMA or TLA precursors complexes in the RE³⁺ host matrices and ligands, indicating the formation of isomorphous series, except for [Gd(TMA)·6(H₂O):Eu³⁺(5.0 mol%)].

The diffractograms in Figure 3.5 show that the structure of all RE(TMA) anhydrous complexes are similar to the data of the [RE(TMA)], [RE(TMA):Dy³⁺] compounds reported in the literature [78] [A.I-IV], presenting monoclinic structure (C2/m, no. 12) with centrosymmetric feature. The X-ray diffraction patterns of the [RE(TLA)·n(H₂O):Eu³⁺] complexes are similar to the reference PDF (Powder Diffraction Patterns) for [Gd(TLA)·4(H₂O):Eu³⁺] and [Y(TLA)·4(H₂O):Eu³⁺] (00-056-1733) as well as [Lu(TLA)·3(H₂O):Eu³⁺] (00-058-1915), whereas Y³⁺ and Gd³⁺ complexes are isomorphs [79].

Figure 3.5. XPD patterns of the RE³⁺ BTC complexes (RE³⁺: Y, Gd and Lu; BTC: TMA and TLA).

It is noteworthy that the small differences in X-ray diffraction patterns are present only in the intensity of the peaks and not in their positions, indicating that the complex were successfully and reproducibly prepared. The similarity in the XPD data suggest that the crystalline structure of the precursor complexes present small perturbation due to the doping process, indicating the formation of solid solution between the Eu^{3+} dopant and the RE^{3+} in the host matrices owing to the similarity of the RE^{3+} ionic radii. For the smallest trivalent rare earth ions the limit for good solid solubility (size difference $<15\%$) allowed by the *Vegard's law* [80] [A.I-III].

$\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ nanomaterials – The XPD patterns of the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ materials prepared by the benzenetricarboxylate method (TMA and TLA) (Figure 3.6 and Figure 3.7) show that the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ materials after annealed at 500, 600, 700, 800, 900 and 1000 °C temperatures are crystalline with the cubic phase of RE_2O_3 ($Ia\bar{3}$ space group) [73]. No differences were observed in the 2θ values of the XPD reflections among the luminescent materials heated at different temperatures, for the same RE^{3+} matrix (RE^{3+} : Gd, Y and Lu). The absence of impurity reflections indicates that the RE_2O_3 sesquioxides are formed with heating at 500 °C for 1 h (for both systems). This result confirmed a complete solid solubility between the Eu^{3+} dopant and the RE^{3+} cations in host lattices, due to the similarity between the radii of the RE^{3+} ions [80,81] [A.I-III].

The average crystallite size of the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) materials was estimated from the powder diffraction data by using the Scherrer's formula (Equations 3.1,3.2) [82] where D is the average crystal size (m), λ the X-ray wavelength (m), β the full width at half maximum (FWHM) of the selected reflection (rad) and θ (°) half of the Bragg angle (2θ). In the present work, the (222) reflection (2θ : 28.3 °) was used. The reflection broadening due to the diffractometer setup was eliminated from the β_s value (Equation 3.2) by using a microcrystalline sodium chloride reference (β_r) (200 reflection at 32.8 °).

Figure 3.6. XPD patterns of a) $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, b) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$, c) $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) materials, annealed at 500, 600, 700, 800, 900 and 1000 °C for 1 h, from $[\text{RE}(\text{TMA}):\text{Eu}^{3+}(1.0 \text{ mol}\%)]$ precursor complex.

Figure 3.7. XPD patterns of a) $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, b) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$, c) $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) materials, annealed at 500, 600, 700, 800, 900 and 1000 °C for 1 h, from $[\text{RE}(\text{TLA}) \cdot n(\text{H}_2\text{O}) : \text{Eu}^{3+} (1.0 \text{ mol\%})]$ precursor complex.

The XPD patterns of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) showed broadening of the reflections for the materials annealed at 500 and 600 °C (Figure 3.6 and Figure 3.7), indicating smaller crystallite size. The crystallite size increases thoroughly in a sequence from 6, 14, 23, 33, 40 and 52 nm for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) material obtained from TMA precursor complexes (Figure 3.8a) as well as 11, 17, 18, 37, 46 and 62 nm from TLA precursor complexes (Figure 3.8b) with increasing annealing temperature from 500, 600, 700, 800, 900 and 1000 °C, respectively (Table 3.2). Simultaneously with the enlargement of the crystallite sizes, an increase in crystallinity is also observed at high temperatures as indicated by the higher intensity of the X-ray diffraction reflections [A.I,II].

Table 3.2 Lattice parameters calculated for the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (RE^{3+} : Y, Gd, and Lu) systems, annealed at 500, 600, 700, 800, 900 and 1000 °C for 1 h, obtained from TMA and TLA complex precursors.

Annealing Temperature (°C)	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ 1.0%		$\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ 1.0%		$\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ 1.0%	
	Crystallite Size (nm)	Edge (Å)	Crystallite Size (nm)	Edge (Å)	Crystallite Size (nm)	Edge (Å)
TMA						
500	6	10.65	6	10.80	6	10.41
600	14	10.65	14	10.83	10	10.41
700	22	10.64	27	10.79	15	10.39
800	30	10.62	37	10.80	18	10.39
900	34	10.63	46	10.81	23	10.39
1000	40	10.63	52	10.80	27	10.37
TLA						
500	11	10.64	17	10.80	8	10.43
600	17	10.63	30	10.82	11	10.40
700	18	10.62	49	10.78	17	10.45
800	37	10.61	79	10.80	25	10.39
900	46	10.58	95	10.78	37	10.42
1000	62	10.59	236	10.80	41	10.37

The XPD data of the Y_2O_3 , Gd_2O_3 and Lu_2O_3 matrices doped with Eu^{3+} ion are very similar (Figure 3.6 and Figure 3.7). The maximum of the (222) reflection moves to higher 2θ values with the decrease of the ionic radius of the rare earth ions, in agreement with the Bragg's law [72] and with the decrease in the cubic lattice parameter a . The crystallite size (Figure 3.8) increases in the RE_2O_3 with the increasing of RE^{3+} radius, as well.

Figure 3.8. Correlation between $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) materials, annealed at 500, 600, 700, 800, 900 and 1000 °C for 1 h, from a)TMA and b)TLA complex precursors.

The sintering process is favored for the gadolinium matrix due to the dependence of the higher reactivity of the Gd_2O_3 , with lower melting point (2339 °C) compared with Y_2O_3 (2410) and Lu_2O_3 (2427), this behavior is more pronounced in the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ originated from TLA complexes [83]. The crystallite size growths can also be explained by the lower decomposition temperature of the Gd precursor (Figure 3.8), resulting in a longer sintering time.

3.1.4 Electron microscopy

The electron microscopy provides magnifications much higher than is achieved with the optical microscope due to a high-energy electron beam (small wavelength), based in the duality wave-particle to provide higher resolution images. The scanning electron microscopy (SEM) is more appropriated to provide information about the morphology and particle size of the compounds due to lower energy electrons with smaller penetration. On the other hand, the transmission electron microscopy (TEM) provides structural and crystallite size information, with electrons of higher energy and penetration and the resolution can reach to the atomic scale [84–86].

3.1.4.1 Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) images of anhydrous $[\text{Y}(\text{TMA}):\text{Eu}^{3+}(1.0 \text{ mol}\%)]$ complex show particles with 6 to 12 μm width and 1 μm thickness sheets-like structure (Figure 3.9a) [A.III]. The images indicate different morphologies compared with the rods shaped structures obtained for the hydrated $[\text{Eu}(\text{TMA})\cdot 6(\text{H}_2\text{O})]$ complexes, as reported in the reference [87]. The SEM images of the $[\text{RE}(\text{TLA}):\text{Eu}^{3+}(1.0 \text{ mol}\%)]$ precursors show rods morphology for the $[\text{RE}(\text{TLA})\cdot 4(\text{H}_2\text{O}):\text{Eu}^{3+}(1.0 \text{ mol}\%)]$ complexes (RE^{3+} : Y and Gd) (Figure 3.9b,c). In addition, the $[\text{Lu}(\text{TMA})\cdot 3(\text{H}_2\text{O}):\text{Eu}^{3+}(1.0 \text{ mol}\%)]$ complex present a flower-like morphology (stacking of micrometric sheets of the material) (Figure 3.9d) [A.II].

Figure 3.9. SEM images of a) [Y(TMA):Eu³⁺(1.0 mol%)] and [RE(TLA)·n(H₂O):Eu³⁺(1.0 mol%)] (RE³⁺: b) Y c) Gd and d) Lu) precursor complexes.

Based on SEM images of the RE₂O₃:Eu³⁺ materials illustrated in the [Figure 3.10 a, b, c and d](#), it was observed that the original morphology of the corresponding precursor complexes were maintained to certain extent. The decomposition of the organic moiety leads to fracture of micrometric particles allowing the formation of the desired nanosessquioxides, increasing the porosity and surface area. The particle shape after the annealing process is important for the

design of nanomaterials with controlled morphology. Since it is possible to modify the complex morphologies, the desired particle shapes can be obtained by choosing the suitable synthetic method and reaction conditions [88,89].

Figure 3.10. SEM images of a) $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) annealed at 1000 °C from $[\text{Y}(\text{TMA}):\text{Eu}^{3+}(1.0 \text{ mol}\%)]$ complex, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) annealed at b) 700 °C and c) 1000 °C from $[\text{Y}(\text{TLA})\cdot 4(\text{H}_2\text{O}):\text{Eu}^{3+}(1.0 \text{ mol}\%)]$ complex and d) $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) annealed at 1000 °C from $[\text{Lu}(\text{TLA})\cdot 3(\text{H}_2\text{O}):\text{Eu}^{3+}(1.0 \text{ mol}\%)]$ complex.

3.1.4.2 Transmission electron microscopy (TEM)

In this work, the transmission electron microscopy (TEM) images were obtained only for the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ materials, using the $[\text{Y}(\text{TMA}):\text{Eu}^{3+}(1.0 \text{ mol}\%)]$ (Figure 3.11 a, b, c and d) and $[\text{RE}(\text{TMA}):\text{Eu}^{3+}(1.0 \text{ mol}\%)]$ (RE^{3+} : Y and Lu) as precursor complexes (Figure 3.11 e, f, g and h). At lower magnification, it is possible to observe that the materials are agglomerates of individual crystallites at nanoscale (Figure 3.11 a, c, e and g).

Based on the TEM data of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}(1.0 \text{ mol}\%)$ nanomaterials (annealed using $[\text{Y}(\text{TMA}):\text{Eu}^{3+}(1.0 \text{ mol}\%)]$ as a precursor) were calculated the crystallite size with values of (5 ± 1) , (13 ± 3) , (30 ± 7) , (38 ± 7) , (45 ± 9) and (53 ± 11) nm (Table 3.3). These results are very similar compared to the crystallite size obtained by Scherrer data (6, 14, 23, 33, 40 and 52 nm), annealed at 500, 600, 700, 800, 900 and 1000 °C, respectively (Table 3.3).

Figure 3.11 b, d, f and h show that the TEM images of materials recorded at higher magnification present no defects for the nanocrystals (except for the edges), suggesting the formation of a solid solution between the Eu^{3+} ions and the RE_2O_3 host matrices. This behavior is due to the similar ionic radii of the Eu^{3+} , Gd^{3+} , Y^{3+} and Lu^{3+} ions.

Table 3.3 Crystallite size of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanomaterials, annealed at 500, 600, 700, 800, 900 and 1000 °C for 1 h, from TMA complex precursors, obtained by Scherrer's formula and TEM micrographs.

$\text{Y}_2\text{O}_3:\text{Eu}^{3+}(1.0 \text{ mol}\%)$	Crystallite size (nm)	
$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$	Scherrer's formula	TEM
500	6	5 ± 1
600	14	13 ± 3
700	23	30 ± 7
800	33	38 ± 7
900	40	45 ± 9
1000	52	53 ± 11

Figure 3.11. TEM images of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) annealed at a), b) 700 and c), d) 1000 °C from $[\text{Y}(\text{TMA}):\text{Eu}^{3+}$ (1.0 mol%)] complex, e), f) $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) annealed at 1000 °C from $[\text{Y}(\text{TLA})\cdot 4(\text{H}_2\text{O}):\text{Eu}^{3+}$ (1.0 mol%)] complex and g), h) $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) annealed at 1000 °C from $[\text{Lu}(\text{TLA})\cdot 3(\text{H}_2\text{O}):\text{Eu}^{3+}$ (1.0 mol%)] complex.

3.2. Eu^{3+} photoluminescence proprieties

Rare earth (RE) containing materials show a versatility for application in the areas of science and technology specially in catalyses, permanent magnets in hybrid cars batteries,[2,3] electroluminescent materials, persistent phosphors, structural probes, luminescent markers, display panels, *etc.*[4–9]

Among the metal centers, trivalent rare earth ions (RE^{3+}) are largely explored owing to the structural and photoluminescence properties. The research interest in the last decades on Eu^{3+} -containing compounds has been improved dramatically due to the high red color monochromaticity of this ion in the trivalent oxidation state. This property is mainly due to the 4f subshell is well shielded from its environment by the closed $5s^2$ and $5p^6$ outer subshells, conferring it an atomic emitting feature.

In last decade, persistent luminescence materials that can store energy and can release it over several hours without a continuous excitation source, have received exceptional attention. Their applications are versatile and extend from luminous paints and ceramics *e.g.* emergency signs to highly sophisticated uses in micro defect sensing, optoelectronics for image storage and high energy radiation detection as well as in pressure/temperature sensing. The divalent europium ion (Eu^{2+}) has been drawing attention especially in persistent luminescent materials [90,91]. The optical properties of Eu^{2+} ion depends directly on the host matrices used, presenting a broad emission band due to the $4f^6 5d \rightarrow 4f^7$ interconfigurational electronic transition that are parity-allowed and usually exhibits high intensity [92,93].

The Eu^{3+} ion shows strong red luminescence, which is also interesting due to the even number of electrons in the 4f subshell ($4f^6$ configuration), the crystal-field perturbation of the crystalline systems lifts partly or completely the degeneracies of the $^{2S+1}L_J$ levels [94]. The other special feature of the Eu^{3+} over other rare earths ions is that the ground (7F_0) and main emitting (5D_0) levels are non-degenerate ($J = 0$) facilitating the interpretation of both the absorption and

the luminescence spectra. In addition, the observed amount of lines for the ${}^7F_0 \rightarrow {}^{2S+1}L_J$ transitions in the absorption spectra or ${}^5D_0 \rightarrow {}^7F_J$ transitions in the emission spectra can suggest the site symmetry of the Eu^{3+} ion and sometimes information on the coordination polyhedron [94].

The Eu^{3+} ion acts as an excellent activator in luminescent compounds due to its unique spectroscopic properties. Usually, it exhibits strong red monochromatic emission color and is used as efficient luminescent probe due to the main emitting (5D_0) and ground (7F_0) levels are non-degenerated. Thus the ${}^5D_0 \rightarrow {}^7F_0$ transition displays a single peak when the Eu^{3+} ion occupies identical sites of symmetry of the type C_s , C_n or C_{nv} , which provides information on the eventual existence of more than one sites of symmetry occupied by rare earth ion [43].

In addition, the first excited 5D_0 energy level is well separated from ${}^7F_{0-6}$ energy levels, reducing the non-radiative decay, the emission present long luminescence decay time for the emitter 5D_0 level (milliseconds). The ${}^5D_0 \rightarrow {}^7F_1$ transition is formally insensitive to the crystal field environment and consequently can be used as a reference transition that can be used to calculate the experimental intensity parameters (Ω_λ ; $\lambda: 2, 4$ and 6). The presence of the very intense hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ transition indicates that the Eu^{3+} ion is in chemical environment with has non-centrosymmetric site [94–96].

Usually, the europium ion doped in inorganic matrices present the $\text{O}^{2-}(2p) \rightarrow \text{Eu}^{3+}(4f^6)$ ligand-to-metal charge-transfer (LMCT) band is located in the UV energy region and can be used to excite the europium ion [93].

From the emission spectra of the Eu^{3+} ion, it is possible to determine the experimental intensity parameters Ω_2 , Ω_4 and Ω_6 by using the ${}^5D_0 \rightarrow {}^7F_2$, ${}^5D_0 \rightarrow {}^7F_4$ and ${}^5D_0 \rightarrow {}^7F_6$ transitions, respectively. The coefficient of spontaneous emission ($A_{0 \rightarrow J}$) is given by Equation 3.3 [10,18]:

$$A_{0 \rightarrow J} = \left(\frac{\sigma_{0 \rightarrow J}}{S_{0 \rightarrow J}} \right) \left(\frac{S_{0 \rightarrow J}}{\sigma_{0 \rightarrow J}} \right) A_{0 \rightarrow J} \quad (\text{Eq. 3.3})$$

where $\sigma_{0 \rightarrow 1}$ and $\sigma_{0 \rightarrow J}$ correspond to the energy barycenter of the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_J$ transitions, respectively. The $S_{0 \rightarrow 1}$ and $S_{0 \rightarrow J}$ are the emission area of the spectrum corresponding to the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_J$ transitions, respectively [97]. Since the magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition is almost insensitive to changes in the chemical environment around the Eu^{3+} ion the $A_{0 \rightarrow 1}$ rate can be used as an internal standard to determine the $A_{0 \rightarrow J}$ coefficients for Eu^{3+} compounds [10].

The lifetime (τ) of the Eu^{3+} -doped compounds were obtained from the luminescence decay curves adjusted with an exponential decay function. The emission quantum efficiency (η) of the 5D_0 emitting level is determined according to the Equation 3.4:

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{nrad}}} \quad (\text{Eq. 3.4})$$

where the total decay rate, $A_{\text{tot}} = 1/\tau = A_{\text{rad}} + A_{\text{nrad}}$ and the $A_{\text{rad}} = \sum J A_{0 \rightarrow J}$. The A_{rad} and A_{nrad} are the radiative and non-radiative rates, respectively. The transitions $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_4$ can be used to estimate the experimental intensity parameters (Ω_λ , $\lambda = 2$ and 4). The Ω_6 intensity parameter is not included in this study since the $^5D_0 \rightarrow ^7F_6$ transition was not observed for these materials. The coefficient of spontaneous emission, $A_{0 \rightarrow J}$, is given by Equation 3.5:

$$A_{0 \rightarrow J} = \frac{4e^2 \omega^3}{3\hbar c^3} \chi \sum_{\lambda} \Omega_{\lambda} \left\langle ^7F_J \| U^{(\lambda)} \| ^5D_0 \right\rangle^2 \quad (\text{Eq. 3.5})$$

where, $\chi = n(n+2)^2/9$ is the Lorentz local field correction and n is the refraction index of the medium (1.5 for these materials). The square reduced matrix elements $\langle ^7F_J \| U^{(\lambda)} \| ^5D_0 \rangle^2$ are 0.0032 and 0.0023 calculated for $J = 2$ and 4, respectively [97,98].

The Ω_λ parameters depend mainly on the local geometry, bonding atoms and polarizabilities in the first coordination sphere of the RE^{3+} metal ion, and are governed by both the forced electric dipole (FED) and dynamic coupling (DC) mechanisms. Moura *et al* [99]

reported that the Ω_2 parameter values are very sensitive to small angular changes in the local coordination geometry (much more than the $\Omega_{4,6}$ parameters). This spectroscopic behavior is associated with the hypersensitivity of certain 4f-4f transitions, to changes in the chemical environment, which are usually governed by the Ω_2 intensity parameter. On the other hand, the Ω_4 and Ω_6 values are most sensitive the chemical bond distances to the ligating atoms around the lanthanide ion. Indeed, as reported in reference [99], covalency in the ion-ligand bonding becomes more important with the increasing rank of the Ω_λ , supporting the idea that the Ω_4 and Ω_6 parameters are better probes than Ω_2 to quantify covalency in these compounds [A.II].

3.2.1. RE³⁺ BTC complexes doped with Eu³⁺ ion

The synthesis, characterization and photoluminescent properties of [RE(TMA):Eu³⁺(x mol%)] and [RE(TLA):Eu³⁺(x mol%)] compounds (RE³⁺: Y, Gd and Lu; x: 0.1, 0.5, 1.0 and 5.0 mol%) prepared by a one-step synthesis in water are reported [A.I-VI]. The compounds are white insoluble powders with high crystallinity and thermal stability and low total decomposition temperature, ideal for the production of nanosquioxides at low temperature. It is noteworthy that the coordination compounds present excellent spectral proprieties, especially of the anhydrous [RE(TMA):Eu³⁺(x mol%)] complexes.

The excitation spectra of the anhydrous [RE(TMA):Eu³⁺(x mol%)] (RE³⁺: Y, Gd and Lu; x: 0.1, 0.5 1.0 and 5.0) and hydrated [Gd(TMA)·6(H₂O):Eu³⁺(x mol%)] compounds were monitored at the hypersensitive transition $^5D_0 \rightarrow ^7F_2$ (614 nm) at 300 (Figure not shown) and 77 K temperatures (Figure 3.11a). The energy levels of the Eu³⁺ complexes were assigned to the narrow absorption bands originated from the ground state 7F_0 to the excited levels such as (in cm⁻¹): 5D_0 (17280), 5D_1 (19025), 5D_2 , (21530), 5D_3 (24380), 5L_6 (25390), 5L_7 (26475) and 5D_4 (27670) [A.III].

In addition, the excitation spectra of the $[\text{RE}(\text{TLa}) \cdot 4(\text{H}_2\text{O}) : \text{Eu}^{3+}(\text{x mol}\%)]$ (RE^{3+} : Y and Gd; x: 0.1, 0.5 1.0 and 5.0) and $[\text{Lu}(\text{TLa}) \cdot 3(\text{H}_2\text{O}) : \text{Eu}^{3+}(\text{x mol}\%)]$ hydrated complexes were recorded at 616 nm in the same conditions, as mentioned above (Figure 3.11b). These complexes present similar absorption bands assigned to the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_J$ transitions (in cm^{-1}): ${}^5\text{D}_0$ (17280), ${}^5\text{D}_1$ (19020), ${}^5\text{D}_2$ (21530), ${}^5\text{D}_3$ (24365), ${}^5\text{L}_6$ (25390), ${}^5\text{L}_7$ (26360) and ${}^5\text{D}_4$ (27675) [A.II].

It is noteworthy that the relative intensities of the 4f intraconfigurational transitions of the Eu^{3+} ion in the $[\text{RE}(\text{TLa}) \cdot 4(\text{H}_2\text{O}) : \text{Eu}^{3+}(\text{x mol}\%)]$ are smaller than in the $[\text{RE}(\text{TMA}) : \text{Eu}^{3+}(\text{x mol}\%)]$ complexes comparing with the broad absorption bands of the ligands (Figure 3.11). The highest intensity of the BTC ligand absorption bands are localized at higher energy in the UV region (~ 300 nm) assigned to the $\text{S}_0 \rightarrow \text{S}_1$ transition. The energy levels of the Eu^{3+} -samples are very similar, even taking into account the different structures. For example, the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition (25390 cm^{-1}) for $[\text{RE}(\text{TMA}) : \text{Eu}^{3+}(5.0 \text{ mol}\%)]$ complex exhibits the highest intensity among the 4f-4f transitions.

The emission spectra of the $[\text{RE}(\text{TMA}) : \text{Eu}^{3+}(\text{x mol}\%)]$ complexes (RE^{3+} : Y, Gd and Lu; x: 0.1, 0.5 1.0 and 5.0), were recorded under excitation in the TMA ligand band (~ 300 nm) at 300 (Figure not shown) and 77 K temperatures (Figure 3.12). The emission energy levels of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions of the Eu^{3+} ion are attributed as (in cm^{-1}): ${}^7\text{F}_0$ (17195); ${}^7\text{F}_1$ (16875); ${}^7\text{F}_2$, (16190); ${}^7\text{F}_3$ (15040) and ${}^7\text{F}_4$ (14215) [A.III]. In the case of $[\text{RE}(\text{TLa}) \cdot n(\text{H}_2\text{O}) : \text{Eu}^{3+}(\text{x mol}\%)]$ complexes (RE^{3+} : Y, Gd and Lu; x: 0.1, 0.5 1.0 and 5.0), their spectra emissions were also recorded at similar experimental conditions (Figure 3.13). These complexes exhibit sharp emission bands assigned to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions of the Eu^{3+} ion (in cm^{-1}): ${}^7\text{F}_0$ (17270), ${}^7\text{F}_1$ (16890), ${}^7\text{F}_2$, (16235); ${}^7\text{F}_3$ (15190) and ${}^7\text{F}_4$ (14265) [A.III].

Figure 3.11. Excitation spectra of a) [RE(TMA):Eu³⁺(x mol%)] and b) [RE(TLA):Eu³⁺(5.0 mol%)] complexes (RE³⁺: Y, Gd and Lu) recorded at 77 K, monitored at 614 nm.

The $^5D_0 \rightarrow ^7F_0$ transition presents only one emission band suggesting that the Eu³⁺ ion occupies one symmetry site [100]. For the [RE(TMA):Eu³⁺(x mol%)] complexes the emission spectra indicate that the chemical environment of Eu³⁺ has a centrosymmetric character, corroborating the X-ray data, due to comparable intensities for the hypersensitive transition $^5D_0 \rightarrow ^7F_2$ (forbidden by electric dipole mechanism) compared with the $^5D_0 \rightarrow ^7F_1$ transition (allowed by magnetic dipole mechanism) [18,101].

Figure 3.12. Emission spectra of [RE(TMA):Eu³⁺(x mol%)] (RE³⁺: a) Y, b) Gd and c) Lu) complexes recorded at 77 K, with excitation at 300 nm.

The decrease in the phosphorescence intensities of the TMA ligand broad bands with the increase of the Eu^{3+} concentrations (0.1, 0.5 1.0 and 5.0 mol%), in the spectral range from 420 to 500 nm (Figure 3.13) indicate that the intramolecular energy transference process from the TMA ligand-to-europium ion becomes more efficient [102,103].

The efficient energy transfer of TMA ligand-to- Eu^{3+} ion is due to the absence of non-radiative decay mediated by water molecules due to the absence of O–H oscillators, except for the $[\text{Gd}(\text{TMA})\cdot 6(\text{H}_2\text{O})\text{:Eu}^{3+}(5.0 \text{ mol}\%)]$ compound (Figure 3.12). Besides, the emission spectra of the $[\text{RE}(\text{TMA})\text{:Eu}^{3+}(x \text{ mol}\%)]$ anhydrous compounds show similar profile suggesting that this system present equivalent chemical environment around RE^{3+} ions and optical behavior.

The emission spectra profiles for $[\text{RE}(\text{TLA})\cdot 4(\text{H}_2\text{O})\text{:Eu}^{3+}(x \text{ mol}\%)]$ (RE^{3+} : Y and Gd) and $[\text{Lu}(\text{TLA})\cdot 3(\text{H}_2\text{O})\text{:Eu}^{3+}(x \text{ mol}\%)]$ are different, in contrast with the X-ray diffraction data which show that the complexes $[\text{Y}(\text{TLA})\cdot 4(\text{H}_2\text{O})\text{:Eu}^{3+}(x \text{ mol}\%)]$ and $[\text{Gd}(\text{TLA})\cdot 4(\text{H}_2\text{O})\text{:Eu}^{3+}(x \text{ mol}\%)]$ complexes have the same structure. This discrepancy is probably due to the presence of more than one phase, at low quantity and not found in X-ray diffraction or minor differences in the first coordination sphere of the Eu^{3+} ion (Figure 3.12a), confirming spectroscopic probe of character Eu^{3+} ion. The efficient intramolecular energy transference from TLA ligand-to- Eu^{3+} ion is evidenced by the absence of ligand broad phosphorescence band in the emission spectra in the spectral range from the 400 to 580 nm for $[\text{Lu}(\text{TLA})\cdot 3(\text{H}_2\text{O})\text{:Eu}^{3+}(x \text{ mol}\%)]$ complexes, similar results were found to Y and Gd host ions complexes [A.II,IV] (Figure 3.13b).

The luminescence decay curves of Eu^{3+} doped BTC complexes were obtained by monitoring the emission at the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition ($\sim 615 \text{ nm}$) with excitation at the $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition (394 nm) (Figure not shown), at room temperature. The lifetime values (τ) of the emitting $^5\text{D}_0$ level of the Eu^{3+} ion were determined, the curves were adjusted or fitted with a first-order exponential decay function (Figure 3.14) [104].

Figure 3.14 shows that an increasing of Eu^{3+} -doping concentration from 0.1, 0.5, 1.0 to 5.0 mol% changes very little the lifetime values, indicating that the concentration quenching process is not operative for these complexes. Besides, the lifetime values of the emitting $^5\text{D}_0$ level are much more influenced by the RE^{3+} ions than the concentration of the Eu^{3+} ion. Moreover, this decay behaviour is also influenced by the large Eu^{3+} energy gap between the $^5\text{D}_0$ emitting and $^7\text{F}_J$ ground levels [A.III,IV]. The lifetime values of the $[\text{RE}(\text{TLA})\cdot n(\text{H}_2\text{O}):\text{Eu}^{3+} (x \text{ mol}\%)]$ hydrated complexes ($n = 3$ or 4) containing Gd^{3+} and Y^{3+} are higher compared to that with Lu^{3+} ion (Figure 3.14b).

Figure 3.13. Emission spectra of a) $[\text{RE}(\text{TLA})\cdot 4(\text{H}_2\text{O}):\text{Eu}^{3+}(1.0 \text{ mol}\%)]$ (RE^{3+} : Y, Gd) and $[\text{Lu}(\text{TLA})\cdot 3(\text{H}_2\text{O}):\text{Eu}^{3+}(5.0 \text{ mol}\%)]$ complexes and b) $[\text{Lu}(\text{TLA})\cdot 3(\text{H}_2\text{O}):\text{Eu}^{3+}(x \text{ mol}\%)]$ recorded at 77 K, with excitation monitored at 300 nm.

In general, the anhydrous $[\text{RE}(\text{TMA})]$ complexes present higher lifetime values than the respective hydrated compounds (Figure 3.14). The lifetime values ($\sim 2.90 \text{ ms}$) of the $[\text{RE}(\text{TMA}):\text{Eu}^{3+}(x \text{ mol}\%)]$ luminophores are longer than for the majority of the Eu^{3+} -

complexes reported in the literature [A.III][10]. Besides, they are one magnitude order higher than the $[\text{Eu}(\text{TMA})\cdot(\text{H}_2\text{O})_6]$ (0.23 ms) and three times higher than the $[\text{Gd}(\text{TMA})\cdot 6(\text{H}_2\text{O})\text{:Eu}^{3+}(5.0 \text{ mol}\%)]$ (0.73 ms), these lifetimes are smaller due to the presence of water molecules in the complexes. This optical property corroborates that the absence of water molecules in the first coordination sphere is very important in the intramolecular energy transfer process. This feature avoids the luminescence quenching by water molecules due the non-radiative decay pathways mediated by vibrational levels of the O–H oscillators (Figure 3.14).

Figure 3.14. Correlation between a) $[\text{RE}(\text{TMA})\text{:Eu}^{3+} (\text{x}\%)]$ and b) $[\text{RE}(\text{TLA})\cdot \text{n}(\text{H}_2\text{O})\text{:Eu}^{3+} (\text{x mol}\%)]$ (RE^{3+} : Y, Gd and Lu; x: 0.1, 0.5, 1.0 and 5.0) lifetimes and Eu^{3+} -doping concentrations.

It is noteworthy that the $[\text{RE}(\text{TMA}):\text{Eu}^{3+}(\text{x mol}\%)]$ lifetime values (Figure 3.14) are higher for Gd^{3+} and Y^{3+} containing complexes when compared to the Lu^{3+} ion complex. On the other hand, no change in the lifetime behavior was observed with increasing doping concentration from 0.1, 0.5, 1.0 to 5.0 mol%, with the same rare earth ion host (Figure 3.14).

The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions were used to estimate the experimental intensity parameters (Ω_λ , $\lambda = 2$ and 4). The Ω_6 intensity parameter is not included in this study since the $^5\text{D}_0 \rightarrow ^7\text{F}_6$ transition was not observed for these materials.

The Ω_λ ($\lambda = 2$ and 4) parameter values for the anhydrous $[\text{RE}(\text{TMA}):\text{Eu}^{3+}(\text{x mol}\%)]$ compounds (RE^{3+} : Y, Gd and Lu; x: 0.1, 0.5, 1.0 and 5.0 mol%) are presented in Table 3.3. The Ω_2 values of these complexes are much smaller ($\sim 2 \cdot 10^{-20} \text{ cm}^2$) than that of $[\text{Eu}(\text{TMA}) \cdot 6(\text{H}_2\text{O})]$ complex ($\sim 11 \cdot 10^{-20} \text{ cm}^2$) [A.III,VI], agreeing with the crystallography data [101], which state that the anhydrous complex tends to a point group with inversion center. Besides, the Ω_4 parameter of $[\text{RE}(\text{TMA}):\text{Eu}^{3+}(\text{x mol}\%)]$ compounds has a small values ($\sim 1 \cdot 10^{-20} \text{ cm}^2$), probably, due to the absence of coordinated water molecules, causing a smaller polarizability effect around the Eu^{3+} ion. [105].

The Ω_2 values ($\sim 6 \cdot 10^{-20} \text{ cm}^2$) for the $[\text{RE}(\text{TLA}) \cdot n(\text{H}_2\text{O}):\text{Eu}^{3+}(\text{x mol}\%)]$ compounds (x: 0.1, 0.5, 1.0 and 5.0 mol%) are systematically larger than for the $[\text{RE}(\text{TMA}):\text{Eu}^{3+}]$ anhydrous complexes ($\sim 2 \cdot 10^{-20} \text{ cm}^2$) values, reflecting the higher hypersensitive character of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition [105].

Table 3.3. Experimental intensity parameters ($\Omega_{2,4}$), radiative (A_{rad}), non-radiative (A_{nrad}) and total (A_{tot}) rates, lifetimes of the 5D_0 emitting level (τ) and quantum efficiencies (η) for the $[\text{RE}(\text{TMA}):\text{Eu}^{3+}(\text{x mol}\%)]$ (RE^{3+} : Y, Gd and Lu; x: 0.1, 0.5, 1.0 and 5.0) complexes.

$[\text{RE}(\text{TMA}):\text{Eu}^{3+}(\text{x mol}\%)]$	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	τ (ms)	η (%)
$[\text{Y}(\text{TMA}):\text{Eu}^{3+}(0.1)]$	2	1	154	202	356	2.812	43
(0.5)	2	1	152	188	339	2.954	45
(1.0)	2	1	155	185	340	2.948	46
(5.0)	2	1	157	204	362	2.763	43
$[\text{Gd}(\text{TMA}):\text{Eu}^{3+}(0.1)]$	2	2	160	190	348	2.876	46
(0.5)	2	1	155	187	341	2.931	45
(1.0)	2	2	135	249	384	2.602	35
$[\text{Gd}(\text{TMA})\cdot 6(\text{H}_2\text{O}):\text{Eu}^{3+}(5.0)]$	6	3	147	1935	2083	0.731	7
$[\text{Lu}(\text{TMA}):\text{Eu}^{3+}(0.1)]$	2	1	153	195	348	2.876	44
(0.5)	2	1	156	190	346	2.892	45
(1.0)	2	1	160	182	342	2.920	47
(5.0)	2	1	153	166	320	3.138	48
$[\text{Eu}(\text{TMA})\cdot 6(\text{H}_2\text{O})]$ [A.VI]	11	10	623	2015	2637	0.230	12

The emission quantum efficiency values of the anhydrous compounds ($\eta \sim 45\%$) are higher than for $[\text{Eu}(\text{TMA})\cdot 6(\text{H}_2\text{O})]$ ($\eta = 12\%$) and $[\text{Gd}(\text{TMA})\cdot 6(\text{H}_2\text{O}):\text{Eu}^{3+}(5.0 \text{ mol}\%)]$ ($\eta \sim 7\%$) complexes confirming that the water molecules are responsible by the luminescence quenching for hydrated compounds ([Table 3.3](#)). The emission quantum efficiency values of the $[\text{RE}(\text{TMA})\cdot n(\text{H}_2\text{O}):\text{Eu}^{3+}(\text{x mol}\%)]$ hydrated complexes are much lower ($\eta \sim 6\text{--}10\%$) compared with the $[\text{RE}(\text{TMA}):\text{Eu}^{3+}]$ anhydrous complexes ([Table 3.4](#)). It is also observed that increasing the Eu^{3+} concentration from 0.1 to 5.0 mol% produces no change in the emission quantum efficiency values, reinforcing that the luminescence quenching concentration effect is not operative for these systems. In summary, the anhydrous complexes present the best quantum

emission efficiency values due to the absence of non-radiative decay pathways mediated by water molecules, as expected.

Table 3.4. Experimental intensity parameters ($\Omega_{2,4}$), radiative (A_{rad}), non-radiative (A_{nrad}) and total (A_{tot}) rates, lifetimes of the 5D_0 emitting level (τ) and quantum efficiencies (η) for the $[\text{RE}(\text{TLA})\cdot\text{Eu}^{3+}(\text{x mol}\%)]$ (RE^{3+} : Y, Gd and Lu; x: 0.1, 0.5, 1.0 and 5.0) complexes.

$[\text{RE}(\text{TLA})\cdot\text{n}(\text{H}_2\text{O})\cdot\text{Eu}^{3+}(\text{x mol}\%)]$	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	τ (ms)	η (%)
$[\text{Y}(\text{TLA})\cdot 4(\text{H}_2\text{O})\cdot\text{Eu}^{3+}(0.1 \text{ mol}\%)]$	6	2	264	2492	2756	0.363	10
(0.5)	6	2	258	2642	2900	0.345	9
(1.0)	6	2	257	2475	2732	0.366	9
(5.0)	6	2	257	2948	3205	0.312	8
$[\text{Gd}(\text{TLA})\cdot 4(\text{H}_2\text{O})\cdot\text{Eu}^{3+}(0.1 \text{ mol}\%)]$	5	2	216	1936	2151	0.465	10
(0.5)	5	2	219	1862	2081	0.481	11
(1.0)	5	2	225	1928	2153	0.464	10
(5.0)	5	2	217	1870	2087	0.479	10
$[\text{Lu}(\text{TLA})\cdot 3(\text{H}_2\text{O})\cdot\text{Eu}^{3+}(0.1 \text{ mol}\%)]$	5	2	234	3587	3821	0.262	6
(0.5)	5	2	229	3693	3922	0.255	6
(1.0)	5	2	229	3641	3870	0.258	6
(5.0)	5	2	229	3792	4021	0.249	6

The color coordinates of the complexes in the CIE chromaticity diagram (*Commission Internationale de l'Eclairage*) are shown in [Figure 3.15](#). The $[\text{RE}(\text{TMA})\cdot\text{Eu}^{3+}(\text{x mol}\%)]$ complexes color purity increases with the raise of Eu^{3+} -doping concentration. In addition, the $[\text{RE}(\text{TLA})\cdot\text{n}(\text{H}_2\text{O})\cdot\text{Eu}^{3+}(\text{x mol}\%)]$ complexes are little influenced by the doping process presenting higher monochromaticity. The crystalline powder samples emits an intense red light, when irradiated with light in the ultraviolet region [\[106\]](#).

Figure 3.15. CIE Diagram and images and of a) [RE(TMA):Eu³⁺] and b) [RE(TLA)·n(H₂O):Eu³⁺] (RE³⁺: Y, Gd and Lu), under excitation at 254 nm. The inset figures are photographs of the complexes (1.0 mol%) nanomaterials taken with a digital camera displaying the red emission under UV irradiation at 254 nm.

3.2.2 RE₂O₃:Eu³⁺ luminescent materials prepared by benzenetricarboxylate method

Y₂O₃:Eu³⁺ has been used as luminophore since the early 1960s, despite the large variety of potential substituted materials tested so far, this luminophore still is a commercial red-emission luminescent material with excellent quantum efficiency (close to 100 %), high color purity and good stability. Nowadays it is still providing the red color for large range of fields of modern lighting and display, such as fluorescent lights, cathode ray tube, field mission display, lighting-emission diode, *etc.* With the ever-increasing modern lighting need of high luminosity and energy saving device, the requirements for Y₂O₃:Eu³⁺ materials with improved luminescence properties is essential [96,107].

The 4f-4f transitions of the Eu³⁺ ion cannot absorbed efficiently the UV light because it is forbidden by Laporte rule. In order to obtain an efficient luminophores, it is necessary to absorb the radiation through an allowed transition. The energy absorbed by the O²⁻(2p)→Eu³⁺(4f⁶) ligand-to-metal charge-transfer (LMCT) transition can be transferred to ⁵D_J levels and by radiative decay to ⁷F_J ground levels. The position of the LMCT band depends on the ligand nature, the size and the nature of the host cation and the crystalline structure.

Luminescent materials have been prepared by ceramic method due to the simplicity and large-scale production capability. Usually, this preparation method involves high temperatures and long reaction periods, promotes product sintering and heterogeneous distribution of the activator ion within the matrix and materials with a high crystallite size. Taking into account the large number of techniques developed for the synthesis of nanomaterials considering each of their advantages and disadvantages this work proposed the novel benzenetricarboxylate method to prepare nanomaterials at low temperature (500 °C). Based on [RE(BTC):Eu³⁺(x mol%)] (RE³⁺: Y, Gd and Lu; BTC: TMA and TLA) precursor complexes, it is possible to prepare the RE₂O₃:Eu³⁺ commercial luminophores without side phases or impurities at lower temperature (~500 °C).

3.2.2.1. Analysis of excitation spectra

The excitation spectra of the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}(\text{x mol}\%)$ materials (RE^{3+} : Y, Gd and Lu; x: 0.1, 0.5, 1.0 and 5.0) prepared at temperatures of 500, 600, 700 800, 900 and 1000 °C (Figures 3.16, 3.17 and 3.18) were recorded in the spectral range from 200 to 590 nm, at 300 and 77 K, with emission monitored at 613 nm.

Figures 3.16, 3.17 and 3.18 show that the spectra are dominated by the narrow absorption bands of the 4f intraconfigurational transitions from the Eu^{3+} ion in the range from 17000 to 34000 cm^{-1} . In addition, at higher energy a broad absorption band can be observed centered at around 38900 cm^{-1} was assigned to the $\text{O}^{2-}(2p) \rightarrow \text{Eu}^{3+}(4f^6)$ ligand-to-metal charge-transfer (LMCT) transition. All excitation spectra exhibit similar spectral features, except for the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}(\text{x mol}\%)$ (x: 0.1, 0.5, 1.0 and 5.0) materials, whereas the spectra also include sharp lines from the 4f-4f intraconfigurational transitions of the Gd^{3+} ion.

For example, the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}(1.0 \text{ mol}\%)$ annealed at 700 °C from the TMA precursor complex, the weak $^7\text{F}_0 \rightarrow ^5\text{D}_0$ and $^7\text{F}_1 \rightarrow ^5\text{D}_0$ transitions (hot bands from the lower $^7\text{F}_1$ levels at *ca.* 210 and 280 cm^{-1}) show only one strong line each at 17216 and 17010 cm^{-1} for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, respectively. The thermal population of the highest $^7\text{F}_1$ level at *ca.* 445 cm^{-1} (and the $^7\text{F}_2$ levels at *ca.* 1000 cm^{-1}) are quite low but the hot band absorption from these levels can be seen at 300 K as broad bands without enough resolution for exact assignment to be made for $^7\text{F}_2$. The transitions observed have similar intensities for all $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ materials annealed at 700 °C (Figures 3.16, 3.17 and 3.18).

Since the magnetic-dipole induced $^7\text{F}_{0,1} \rightarrow ^5\text{D}_1$ transitions of Eu^{3+} are allowed by parity for both the C_2 and S_6 symmetries, several narrow absorption lines (or groups of lines) can be observed below 19050 (C_2) and at 18990 and 19120 cm^{-1} (S_6 site), as well. Because of the high intensity of the $^7\text{F}_1 \rightarrow ^5\text{D}_1$ transitions, they dominate this spectral range, but even hot band excitation from the $^7\text{F}_2$ levels can be found – though very weak. The assignment of these

energies is in qualitative agreement with those reported in the literature for $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ [108,109]. Since the total splitting of the $^7\text{F}_1$ level is around 396 cm^{-1} , the expected splitting of the $^5\text{D}_1$ levels is some 20-30 % of the $^7\text{F}_1$ value, *i.e.* *ca.* $80\text{--}130\text{ cm}^{-1}$. This relation is quite universal among the Eu^{3+} energy levels in different hosts [110] and was observed here for both the C_2 and S_6 sites.

In comparison with other 4f-4f transitions, the prominent absorption bands, in the spectral region from 21400 to 21600 cm^{-1} , were assigned to the characteristic $^7\text{F}_0 \rightarrow ^5\text{D}_2$ transition of the Eu^{3+} doped RE_2O_3 host matrices (Figures 3.16, 3.17 and 3.18). In addition, the forbidden $^7\text{F}_0 \rightarrow ^5\text{D}_3$ electric-dipole transition can be also observed as three weak absorption lines at $24300\text{--}24533\text{ cm}^{-1}$ due to the J-mixing effects in the $^7\text{F}_J$ manifold. Besides, several narrow absorption bands originating from the $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition are also shown in the spectral range from 24600 to 25600 cm^{-1} (Figures 3.16, 3.17 and 3.18). Other characteristic Eu^{3+} lines, originating from the absorption from the $^7\text{F}_{0,1}$ levels to the following ones (energy in cm^{-1}): $^5\text{G}_{2-6}$ (25800), $^5\text{L}_{7,8}$ (26600), $^5\text{D}_4$ ($27250\text{--}27800$), $^5\text{H}_J$, $^5\text{F}_J$, $^5\text{I}_J$ and $^3\text{P}_0$ ($29600\text{--}35150$) are also observed.

The excitation spectra of the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ materials present similar profiles to those of Y^{3+} and Lu^{3+} ions hosts, except for the spectral range at higher energy between 31600 and 37000 cm^{-1} (Figure 3.16, 3.17 and 3.18). The characteristic $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{7/2}$ (*ca.* 31970 cm^{-1}), $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{5/2}$ (*ca.* 32530 cm^{-1}) and $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{3/2}$ (*ca.* 33100 cm^{-1}) transitions arising from the Gd^{3+} ion resulted in strong absorption lines, indicating energy transfer from the Gd^{3+} to Eu^{3+} ion [111]. The $^8\text{S}_{7/2} \rightarrow ^6\text{I}_{7/2}$ (*ca.* 35660 cm^{-1}) and $^8\text{S}_{7/2} \rightarrow ^6\text{I}_{9/2}$, $^6\text{I}_{17/2}$ ($36000\text{--}36500\text{ cm}^{-1}$) transitions are overlapped with the LMCT band [112].

Figure 3.16. Excitation spectra of $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) (RE^{3+} : a) Y, b) Gd and c) Lu) annealed at 500, 600, 700, 800, 900 and 1000 °C, formed by annealing of the TMA precursor complexes, recorded at 300 K with emission monitored at 613 nm.

Figure 3.17. Excitation spectra of $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) (RE^{3+} : a) Y, b) Gd and c) Lu) annealed at 500, 600, 700, 800, 900 and 1000 °C, formed by annealing of the TLA precursor complexes, recorded at 77 K with emission monitored at 613 nm.

The broad absorption bands are assigned to the $O^{2-}(2p) \rightarrow Eu^{3+}(4f^6)$ LMCT in the $RE_2O_3:Eu^{3+}$ luminophores (Figures 3.16, 3.17 and 3.18). For the $RE_2O_3:Eu^{3+}$ (1.0 mol%) annealed at 700 ° from the TMA precursor complex, the barycenter values of the LMCT states are 37930, 38600 and 38765 cm^{-1} for the Gd^{3+} , Y^{3+} and Lu^{3+} oxides, respectively. The $RE_2O_3:Eu^{3+}$ (1.0 mol%) using the TLA complex precursor show slightly different values of the LMCT bands, 37735 (Gd^{3+}) and 38315 (Y^{3+} and Lu^{3+}) cm^{-1} . The shifts to higher energy of LMCT bands suggest that the chemical environment of the Lu_2O_3 host lattice exert stronger influence on the Eu^{3+} ion than the Gd_2O_3 and Y_2O_3 hosts, due to the decreasing ionic radii [81], the ligand field around the Eu^{3+} ion should be the strongest from $Gd^{3+} < Y^{3+} < Lu^{3+}$. In addition, the LMCT band intensities of the $RE_2O_3:Eu^{3+}$ materials prepared from $[RE(TLA) \cdot n(H_2O):Eu^{3+}(x \text{ mol\%})]$ precursor complexes are higher compared with the material originated from the annealing of $[RE(TMA):Eu^{3+}(x \text{ mol\%})]$ compounds.

Figure 3.18. Excitation spectra of RE₂O₃:Eu³⁺(1.0 mol%) (RE³⁺: Y, Gd and Lu) annealed at 700 °C, formed by annealing the a) TMA (300 K) and b) TLA (77 K) precursor complexes, with emission monitored at 613 nm.

3.2.2.2. Analysis of emission spectra

The emission spectra of the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ materials prepared at 500, 600, 700, 800, 900 and 1000 °C were recorded in the spectral range from 400 to 750 nm at 300 and 77 K temperatures, under excitation in the LMCT band at 260 nm (Figures 3.19, 3.20 and 3.21). All the spectra exhibit narrow emission lines arising from the $^5\text{D}_J \rightarrow ^7\text{F}_{J'}$ transitions (J : 0–3 and J' : 0–6) with similar spectral features irrespective of the host; even the material heated at 500 °C shows similar photoluminescent characteristics. The analyses are based on the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) prepared by annealing the $[\text{Y}(\text{TMA}):\text{Eu}^{3+} (1.0 \text{ mol\%})]$ at 700°C [A.I,II].

For the materials heated at 700 °C (Figures 3.19, 3.20 and 3.21), only one emission peak at 17215 cm^{-1} is observed and assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition of the Eu^{3+} ion in the C_2 site of the cubic C-type $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. The $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition lines broaden with decreasing crystallite size and crystallinity as a result of inhomogeneous broadening. Since the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is allowed for both the C_2 and S_6 sites, thus there are emission lines (Figures 3.19, 3.20 and 3.21) at 16665 , 16845 and 17015 cm^{-1} as well as at 16770 and 17165 cm^{-1} originating from the C_2 and S_6 sites, respectively, in fair agreement with the works reported in references [108,109]. Taken into account the splitting of the $^5\text{D}_1$ level for the S_6 site, with the $^7\text{F}_1$ splitting at *ca.* 400 cm^{-1} , this should be of the order of 80 to 132 cm^{-1} [110] to which the experimental value (130 cm^{-1}) compares very well. The total $^7\text{F}_1$ splittings are 349 (C_2) and 396 (S_6) cm^{-1} , indicating clearly stronger crystal field effect in the S_6 site [A.I,II].

The refractive index (n) of the bulk $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ is considerably high (~ 1.9), and in this bulk material the $^5\text{D}_0$ lifetime (τ) is around 1.0 ms [113,114]. It is conceivable that in the nanoparticle scale, with average sizes around 20 nm, which are much smaller than the wavelength of the exciting radiation, the n and τ values in the RE_2O_3 host matrices are different ($\tau \sim 1.4\text{--}2.0 \text{ ms}$). Moreover, the differences between the Eu^{3+} ions on the surface and within the nanoparticles may play a role in the profile of the decay curves [A.I,II].

Figure 3.19. Emission spectra of $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) (RE^{3+} : a) Y, b) Gd and c) Lu) annealed at 500, 600, 700, 800, 900 and 1000 °C, formed by annealing of the TMA precursor complexes, recorded at 300 K with excitation at 260 nm.

Figure 3.20. Emission spectra of $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) (RE^{3+} : a) Y, b) Gd and c) Lu) annealed at 500, 600, 700, 800, 900 and 1000 °C, formed by annealing of the TLA precursor complexes, recorded at 300 K with excitation at 260 nm.

The radiative rate (A_{01}) of the $^5D_0 \rightarrow ^7F_1$ transition of Eu^{3+} ion (allowed by the magnetic dipole interaction) is formally insensitive to the ligand field environment. Therefore it can be used as a reference transition, and has been given values around 50 s^{-1} [18,106,115]. Based on this value, the refractive indices were determined and compared to the lifetime and crystallite size values reported in references [113–115]. Both the experimental intensity parameters and measured lifetimes (1.4–2.0 ms) were actually then reproduced using the effective refractive index values between 1.5 and 1.6.

Figure 3.21. Emission spectra of $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) (RE^{3+} : Y, Gd and Lu) annealed at 700°C , formed by annealing the a) TMA (300 K) and b) TLA (77 K) precursor complexes, with excitation at 613 nm.

The values of the experimental intensity parameters (Ω_λ) as well as the radiative (A_{rad}) and non-radiative (A_{nrad}) rates and emission quantum efficiencies (η) of the 5D_0 emitting level of the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ are presented in Table 3.5 and 3.6.

Table 3.5. Experimental values of intensity parameters (Ω_λ), radiative (A_{rad}) and non-radiative (A_{nrad}) rates as well as emission lifetimes and emission quantum efficiencies of the $^5\text{D}_0$ emitting level determined for the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) (RE^{3+} : Y, Gd and Lu) luminophores, annealed at 500, 600, 700, 800, 900 and 1000 °C, from the $[\text{RE}(\text{TMA})]$ complexes precursors, based on the emission spectra recorded at room temperature.

$\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) T (°C)	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	τ (ms)	η (%)
$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$							
500	13	2	458	104	562	1.778	81
600	13	2	465	90	554	1.804	84
700	13	2	454	81	536	1.867	85
800	12	1	479	52	531	1.880	90
900	13	1	513	50	563	1.774	91
1000	12	2	573	84	579	1.725	85
$\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$							
500	15	3	541	163	704	1.421	77
600	15	2	524	145	669	1.495	78
700	14	1	476	225	701	1.427	68
800	14	1	503	98	602	1.662	84
900	14	1	489	107	596	1.677	82
1000	13	1	465	246	711	1.406	65
$\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$							
500	13	2	449	222	672	1.489	67
600	13	2	468	200	669	1.495	70
700	13	2	461	236	697	1.434	66
800	13	2	419	149	568	1.762	74
900	12	2	389	120	509	1.963	76
1000	12	2	383	108	491	2.035	78

Table 3.6. Experimental values of intensity parameters (Ω_λ), radiative (A_{rad}) and non-radiative (A_{nrad}) rates as well as emission lifetimes and emission quantum efficiencies of the $^5\text{D}_0$ emitting level determined for the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) (RE^{3+} : Y, Gd and Lu) luminophores, annealed at 500, 600, 700, 800, 900 and 100 °C, from the [RE(TLA)] complexes precursors, based on the emission spectra recorded at room temperature.

$\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) T (°C)	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	τ (ms)	η (%)
$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$							
500	13	3	470	264	734	1.362	64
600	13	2	461	207	668	1.496	69
700	13	2	462	181	643	1.555	72
800	13	2	459	113	571	1.751	80
900	12	2	446	107	553	1.808	81
1000	12	2	435	111	546	1.830	80
$\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$							
500	13	2	458	788	1246	0.803	37
600	13	2	447	632	1079	0.927	41
700	12	2	438	428	866	1.155	51
800	12	2	438	265	702	1.424	62
900	12	2	430	195	625	1.600	69
1000	11	2	419	166	585	1.709	72
$\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$							
500	12	3	434	284	719	1.391	60
600	12	3	435	253	688	1.454	63
700	11	3	431	155	588	1.701	73
800	11	3	433	107	541	1.850	80
900	12	3	434	95	529	1.890	82
1000	11	3	422	104	526	1.900	80

The Ω_2 values are very similar for the same matrix annealed at different temperatures indicating that for each matrix there is no change in the hypersensitive character of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of the Eu^{3+} ion. Therefore, the same chemical environment around Eu^{3+} ion is expected for these materials.

In addition, the emission spectra (Figure 3.19, 3.20 and 3.21) of $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ nanomaterials exhibit similar spectral features, corroborating with the similarity of the Ω_2 and Ω_4 values for all rare earth sesquioxides matrices. The considerably high values of the Ω_2 parameters are consistent with a very low point symmetry of the C_2 site occupied by the Eu^{3+} ion.

For the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) (RE^{3+} : Y, Gd and Lu) nanomaterials annealed at 500 – 1000 °C, using the $[\text{RE}(\text{TMA}):\text{Eu}^{3+}$ (1.0 mol%)] precursor complex, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ showed higher average values of emission quantum efficiency ($\eta_{\text{aver}} \sim 86\%$) than $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ (76 and 72 %, respectively). The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ material annealed at 900 °C also gave the highest value of $\eta \sim 91\%$ while the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ at 1000 °C showed the lowest value ($\eta \sim 65\%$), due to its high value of the non-radiative rate ($A_{\text{nrad}} = 246 \text{ s}^{-1}$).

In the case of the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) (RE^{3+} : Y, Gd and Lu) system obtained from those of TLA complex showed lower emission quantum efficiencies. For these materials, the Eu^{3+} doped Y_2O_3 also showed the higher values of emission quantum efficiency ($\eta_{\text{aver}} \sim 75\%$) than $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ (55 and 72 %, respectively). The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ material annealed at 900 °C also gave the highest value of $\eta = 81\%$ while the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ at 500 °C showed the lowest value ($\eta \sim 37\%$), due to its high value of the non-radiative rate ($A_{\text{nrad}} = 458 \text{ s}^{-1}$).

In general, it was observed that the luminescent nanomaterials presented an increasing of emission quantum efficiency (η) with augment from 500 to 800 °C annealing temperature. On the other hand, when the annealing temperature is higher than 800 °C the η values decrease probably due to increasing of the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ crystallite size, especially for gadolinium matrix that has the largest crystallite size. Accordingly, the η values of luminophores formed by TMA complexes are higher for all systems, compared to the originated from TLA compounds, especially for the of Y^{3+} matrix.

CIE Diagram

The CIE (*Commission Internationale de l'Eclairage*) chromaticity coordinates generated from the emission spectra of Eu^{3+} doped RE_2O_3 (Figure 3.22) are x : 0.656 and y : 0.332 [106]. The color coordinates are practically the same irrespective of the sesquioxide host or the annealing temperature.

The luminophores containing Gd^{3+} , Y^{3+} , Lu^{3+} ions exhibit the same characteristic nearly monochromatic emission. The images of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) nanomaterials under UV irradiation (inset of Figure 3.22) show nearly identical strong red emission for all the luminophores annealed at temperatures from 500 to 1000 °C.

Figure 3.22. CIE chromaticity diagram showing the x , y emission color coordinates for the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (x mol%) (RE^{3+} : Y, Gd and Lu; x : 0.1, 0.5, 1.0 and 5.0) nanophosphors annealed at 600, 700, 800, 900 and 1000 °C. The inset figures are photographs of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) nanomaterials annealed from a) $[\text{Y}(\text{TMA}):\text{Eu}^{3+}(1.0 \text{ mol}\%)]$ (left) and b) $[\text{Y}(\text{TLA})\cdot 4(\text{H}_2\text{O}):\text{Eu}^{3+}(1.0 \text{ mol}\%)]$ (right) taken with a digital camera displaying the red emission under UV irradiation at 254 nm.

4. CONCLUSION

4. CONCLUSION

[RE(BTC):Eu³⁺(x mol%)] complexes

These complexes were prepared by a one-step synthesis in aqueous solution, they are non-hygroscopic white crystalline powders, air-stable and insoluble in a large range of solvents. The elemental analyses were used to determine the chemical compositions of the [RE(BTC):Eu³⁺] complexes indicating 1:1 ratio between the BTC ligands and the RE³⁺ ions. The anhydrous [RE(TMA):Eu³⁺] complexes present no mass-loss event in the temperature range from 30 to 460 °C. On the other hand, the [Gd(TMA)·6H₂O:Eu³⁺(5.0 mol% of Eu³⁺)] and [RE(TLA)·nH₂O:Eu³⁺(x mol%)] exhibit additional event, attributed to the removal of water molecules in the 70–150 °C temperature interval. All the complexes present one event between 450 and 570 °C assigned to the total decomposition of the organic moiety, yielding their respective doped RE₂O₃:Eu³⁺ sesquioxides.

The FTIR spectra analysis of the europium doped RE³⁺ BTC complexes using the symmetric $\nu_s(\text{C}=\text{O})$ and asymmetric $\nu_{as}(\text{C}=\text{O})$ stretching bands modes indicate bridge-type coordination. The powder XPD patterns showed that there are no relevant difference in the entire TMA or TLA precursors complexes for the same RE³⁺ ion, indicating the formation of isomorphous series, except for [Gd(TMA)·6(H₂O):Eu³⁺(5.0 mol%)]. The SEM images of anhydrous [Y(TMA):Eu³⁺(1.0 mol%)] complex show particles with 6 to 12 μm width and 1 μm thickness sheets-like structure. The [RE(TLA):Eu³⁺(1.0 mol%)] precursors exhibit rods morphology for the [RE(TLA)·4(H₂O):Eu³⁺(1.0 mol%)] complexes (RE³⁺: Y and Gd) and a flower-like morphology for [Lu(TMA)·3(H₂O):Eu³⁺(1.0 mol%)] complex.

[RE(TMA):Eu³⁺] anhydrous compounds present monochromatic red emission and quantum efficiency at around 45%. The small values of the Ω_2 and Ω_4 parameters for the anhydrous compounds corroborates with a local point symmetry, obtained by the XPD, data and also a rather low polarizability around the Eu³⁺ ion, respectively. The lifetime values (~ 2.90

ms) presented by the $[\text{RE}(\text{TMA}):\text{Eu}^{3+}(\text{x mol}\%)]$ phosphors are longer than for the majority of the Eu^{3+} -complexes reported, one magnitude order higher than the $[\text{Eu}(\text{TMA})\cdot 6(\text{H}_2\text{O})]$ (0.230 ms) and three times higher than the $[\text{Gd}(\text{TMA})\cdot 6(\text{H}_2\text{O}):\text{Eu}^{3+}(5.0 \text{ mol}\%)]$ (0.731 ms). When the Eu^{3+} -doping concentration increases, the lifetimes show that the concentration quenching is not operative resulting in small differences in the lifetime values. Photoluminescence data show that these materials can act as an efficient red light conversion molecular devices (LCMDs) and the lowest Eu^{3+} -concentration doped compounds can be used as efficient and more economically viable optical markers.

$\text{RE}_2\text{O}_3:\text{Eu}^{3+}(\text{x mol}\%)$ nanomaterials

These nanomaterials were successfully synthesized with an unprecedented method using benzenetricarboxylate precursor complexes annealed at different temperatures (500, 600, 700, 800, 900 and 1000 °C), with controllable particle size and high chemical homogeneity. Another advantage of this new synthesis is the significantly lower temperature regime (500 °C) than the usual solid-state method. The FTIR spectra of the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}(1.0 \text{ mol}\%)$ luminophores show the characteristic bands of $\text{RE}^{3+}\text{--O}$ vibrational modes frequencies centered around 460 and 560 cm^{-1} indicate the effective formation of sesquioxides matrices.

XPD patterns show that the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ materials are crystalline with the cubic phase of RE_2O_3 ($Ia \bar{3}$ space group) where the Eu^{3+} ions can occupy two sixfold-coordinated non-equivalent sites with C_2 and S_6 symmetries. The crystallite size calculated using the Scherrer's formula indicate nanosized $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ sesquioxides. $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ SEM images show that the original morphology of the corresponding precursor complexes were maintained. The decomposition of the organic moiety leads to fracture of micrometric particles allowing the formation of the desired nanosesequioxides, increasing the porosity and surface area. The TEM data of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}(1.0 \text{ mol}\%)$ nanomaterials (annealed using $[\text{Y}(\text{TMA}):\text{Eu}^{3+}(1.0 \text{ mol}\%)])$ were

used to calculate the crystallite size with values of (5 ± 1) , (13 ± 3) , (30 ± 7) , (38 ± 7) , (45 ± 9) and (53 ± 11) nm. These results are very similar when compared to the crystallite size obtained by Scherrer data (6, 14, 23, 33, 40 and 52 nm), annealed at 500, 600, 700, 800, 900 and 1000 °C, respectively. Higher magnification TEM images of $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ nanomaterials recorded present no defects for the nanocrystals (except for the edges), suggesting the formation of a solid solution between the Eu^{3+} ions and the RE_2O_3 host matrices.

The $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ spectroscopic properties are consistent with the low symmetry of the C_2 site occupied by the Eu^{3+} ion in the cubic C-type $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$, which is essential for optical applications. It was observed that the increase of the annealing temperature improved the emission quantum efficiency up to 800 °C. Furthermore, the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanomaterials from the TMA ligand showed higher values of emission quantum efficiency ($\eta_{\text{aver}} = 86\%$) than $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ (76%) and $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ (72 %). The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ material annealed at 900 °C also gave the highest value of $\eta = 91\%$, compatible with the commercial phosphors currently available in the market, proving the success of the benzenetricarboxylate method. The $[\text{RE}(\text{TMA}):\text{Eu}^{3+}]$ complexes proved to be better precursor for the preparation of $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ sesquioxides than the $[\text{RE}(\text{TLA}) \cdot n\text{H}_2\text{O}:\text{Eu}^{3+}(\text{x mol}\%)]$ complexes, however, it is noteworthy that the TLA ligand is cheaper and can be used as a more economic viable source for the nanomaterials.

As a result, this novel synthetic method can be extended to produce rare earth nanomaterials, as well as other metal ions materials, for application in areas of photonic, magnetism, superconductivity, catalysis, *etc.*

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APPENDIX

I

Low temperature synthesis and optical properties of the $R_2O_3:Eu^{3+}$ nanophosphors (R^{3+} : Y, Gd and Lu) using TMA complexes as precursors

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ABSTRACT

The $R_2O_3:Eu^{3+}$ (R^{3+} : Y, Gd and Lu) nanophosphors were synthesized with a low temperature thermolysis method using rare earth 1,3,5-benzenetricarboxylate (TMA) complexes as precursors. The $R(TMA):Eu^{3+}$ (1 mole %) complexes were synthesized using the co-precipitation method which complexes were then annealed at temperatures from 500 to 1000 °C for 1 h, yielding the cubic C-type $R_2O_3:Eu^{3+}$ materials. The XPD patterns revealed no impurities in C- R_2O_3 obtained at any temperature. The Scherrer's equation based on powder diffraction data confirmed an increase in crystallite size from 6 to 52 nm with increasing annealing temperature from 500 to 1000 °C for Y_2O_3 , respectively, agreeing with the SEM and TEM data. Similar results were obtained for the other $R_2O_3:Eu^{3+}$. The excitation spectra show a broad oxide to europium charge transfer absorption band at 260 nm, i.e. $O^{2-}(2p) \rightarrow Eu^{3+}(4f^6)$ LMCT, as well as the narrow lines assigned to the $4f-4f$ transitions of the Eu^{3+} ion. The characterization of the photoluminescence properties of the phosphors was also based on the analysis of the emission spectra and luminescence decay curves. The experimental intensity parameters (Ω_2), lifetimes (τ), as well as radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates were calculated and discussed.

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1. Introduction

During the last five decades, luminescent rare earth (R^{3+}) materials have attracted much interest due to their special spectroscopic properties and commercial applications in different areas such as: displays, lighting, lasers, luminescent security inks [1–6]. The $Y_2O_3:Eu^{3+}$ phosphor shows almost monochromatic red emission colour, high emission quantum yield and good thermal stability.

The cubic C-type rare earth sesquioxides C- R_2O_3 can be readily doped with Eu^{3+} ions, which usually exhibit high luminescence efficiency. The Eu^{3+} ions occupy two six-fold coordinated non-equivalent sites with C_2 and S_6 symmetries (Fig. 1) [7]. The induced electric dipole transitions in the S_6 site cannot gain intensity by the mixing of opposite parity electronic configurations with the $4f^N$ one. However, the relatively weak magnetic dipole-induced transitions remain possible for ions in a site with inversion centre. In

contrast to the S_6 site, the C_2 site has no centre of inversion that drastically affects the luminescence spectra of the Eu^{3+} -doped materials. For example, the red emission colour of the Eu^{3+} doped cubic C- R_2O_3 is dominated by the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition of the Eu^{3+} ion in the C_2 site.

In the R_2O_3 lattices, the Eu^{3+} dopant ion can substitute the other R^{3+} ions without introducing major distortions in the crystal structure, owing to the similarity of the ionic radii (in Å) of Eu^{3+} (0.947), Gd^{3+} (0.938), Y^{3+} (0.900) and Lu^{3+} (0.861) [8], following the Vegard's rule [9]. Besides, the Eu^{3+} doped R_2O_3 materials usually show an intense absorption band in the ultraviolet region, consistent with the allowed transition: $O^{2-}(2p) \rightarrow Eu^{3+}(4f^6)$ ligand-to-metal charge-transfer states (LMCT), which can improve its luminescence efficiency [10].

With the advent of nanoscience and nanotechnology, the photonic and morphological properties of $R_2O_3:Eu^{3+}$ nanomaterials have been retaken and reinvestigated with new focuses [11,12]. These phosphors have been prepared by sol–gel [12], chemical vapour deposition [13], microemulsion [14,15], spray pyrolysis

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[16,17], co-precipitation [18,19], hydrothermal [20] and combustion methods [21].

In this work, $R_2O_3:Eu^{3+}$ nanophosphors (R^{3+} : Y, Gd and Lu) were prepared for the first time with a thermolysis method using $R(TMA):Eu^{3+}$ complexes as precursors. This synthesis method produces highly luminescent nanomaterials by one-step ligand decomposition which occurs at lower temperature than for the solid state method, producing the sesquioxides at around 500 °C [22]. The structure and surface morphology were characterized by thermogravimetric analyses (TG–DTG), infrared absorption spectroscopy (FTIR), X-ray powder diffraction (XPD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The photoluminescence properties were evaluated based on the excitation and emission spectra, as well as luminescence decay lifetimes of the emitting 5D_0 level of Eu^{3+} . The experimental intensity parameters, emission efficiency, radiative and non-radiative probabilities and CIE colour coordinates (x, y) were also determined.

2. Experimental

The rare earth chlorides $RCl_3 \cdot 6H_2O$ (R : Y, Gd, Eu and Lu) were prepared from their respective oxides (CSTARM, 99.99%) by digestion of the corresponding aqueous suspensions with the addition of concentrated hydrochloric acid until pH reached ca. 6.0. The benzene-1,3,5-tricarboxylic acid (trimesic acid, Fluka, 97%), $H_3(TMA)$, was used without further purification. Aqueous $Na_3(TMA)$ solution was prepared by the drop-wise addition of 1 M sodium hydroxide solution in the aqueous $H_3(TMA)$ suspension up to pH of ca. 6.0.

For the preparation of the $R(TMA):Eu^{3+}$ complexes, 50 cm³ of aqueous RCl_3 solution (0.05 M) was added slowly (ca. 1 drop per second) into 200 cm³ of the previously prepared $Na_3(TMA)$ solution (0.0125 M) with a 1:1 molar ratio at ca. 100 °C. The reaction mixture was refluxed for 4 h and the precipitate was filtered and washed four times with distilled water, dried and stored at reduced pressure. The $R(TMA):Eu^{3+}$ complexes obtained are non-hygroscopic, white crystalline powders, stable in air and insoluble in solvents such as acetone, ethylalcohol, dimethyl sulfoxide, acetonitrile, chloroform and water. Afterwards, the $R_2O_3:Eu^{3+}$ nanomaterials were obtained by annealing the $R(TMA):Eu^{3+}$ complexes at 500, 600, 700, 800, 900 and 1000 °C temperatures in static air.

Fig. 1. A schematic illustration of the R^{3+} ions occupying the two six-fold coordinated sites with C_2 and S_6 symmetries in cubic $C-R_2O_3$ [7].

The elemental analysis of the hydrogen and carbon contents was performed with a Perkin-Elmer CHN 2400 elemental analyser. The infrared absorption spectra were recorded using the KBr pellet technique with a Bomem MB100 FTIR spectrometer in the spectral range from 400 to 4000 cm⁻¹. The XPD patterns were recorded by a Rigaku Miniflex II ($CuK_{\alpha 1}$, 1.5406 Å) from 4 to 70° (in 2θ). The TG–DTG analyses were obtained with a TA Instruments HI-RES TGA 2850 equipment in the temperature interval from 30 to 900 °C with constant heating rate of 5 °C min⁻¹, in dynamic synthetic air with a flow rate of 50 cm³ min⁻¹.

The average crystal size of the materials was estimated from the powder diffraction data by using the Scherrer formula (Eq. (1)) [23] where D is the average crystal size (nm), λ the X-ray wavelength (m), β the full width at half maximum (FWHM) of the selected reflection (rad) and θ (°) half of the Bragg angle (2θ). In the present work, the (222) reflection (2θ : 28.3 °) was used. The reflection broadening due to the diffractometer setup was eliminated from the β_s value (Eq. (2)) by using a microcrystalline sodium chloride reference (β_r) (200 reflection at 32.8°).

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

$$\beta^2 = \beta_s^2 - \beta_r^2 \quad (2)$$

The SEM images were obtained with a JEOL JSM 7401F Scanning Emission Electron Field Microscope. The solid samples were deposited on a double-sided copper tape, attached to the sample holder. The TEM imaging was performed using a JEM 2100 ARP transmission electron microscope, using an acceleration voltage of 200 kV from a LaB6 thermo-ionic filament yielding 2.4 Å resolution. The images were processed with a Gatan ES500W 35 mm camera (low magnification and SADP images) and Gatan MSC 794 digital camera. Samples were prepared by dispersing the powder in isopropanol. The suspension formed was submitted to ultrasound and was placed on a Cu grid covered with a porous carbon film.

The photoluminescence study was based on the excitation and emission spectra recorded at room temperature (300 K) using front face data collection mode (22.5°), with a 450 W Xenon lamp as the excitation source coupled to a SPEX-Fluorolog 2 spectrometer with 0.22 m double monochromators. The luminescence decay of the phosphors was investigated using the SPEX 1934D phosphorimeter accessory attached with a 150 W pulsed Xenon lamp.

3. Results and discussion

Elemental analysis (H and C) of the chemical compositions of the $R(TMA)$ complexes indicates the 1:1 ratio between the TMA ligand and the R ions (i.e. $Lu(TMA)$: calcd: C, 28.29; H, 0.79. found: C, 28.34; H, 0.88%) and the absence of coordinated water molecules in the non-doped $R(TMA)$ complexes (R : Y, Gd and Lu). When the complexes were doped with Eu^{3+} (at 0.1, 0.5, 1 and 5 mole %), the anhydrous complexes were formed, except for the Gd(TMA) doped with 1.0 and 5.0 mole % of Eu^{3+} which contain six coordinated water molecules (Table S1). This result is in agreement with the TG analyses (Fig. 2).

The TG–DTG curves of the non-doped and Eu^{3+} doped complexes were recorded in the temperature interval from 30 to 900 °C. The anhydrous $R(TMA)$ complexes show only one single-step decomposition between 450 and 570 °C (Fig. 2a). On the other hand, the $Gd(TMA) \cdot 6H_2O:Eu^{3+}$ (1 and 5 mole % of Eu) systems exhibited an additional event, attributed to the removal of six coordinated water molecules (70–150 °C) (Fig. 2b). All the R^{3+} complexes have the final decomposition temperature event higher than 500 °C, but if annealed for 1 h, the respective R_2O_3 sesquioxides are formed (Fig. 2), indicating a kinetic dependence. The decomposition temperature of the $R(TMA)$ complexes varies with

Fig. 2. The TG and DTG curves of (a) R(TMA) and (b) R(TMA):Eu³⁺ (5 mole %) (R: Y, Gd and Lu).

the host cation, decreasing from Y³⁺ to Lu³⁺. However, the lowest decomposition temperature occurs for the Gd(TMA)·6H₂O:Eu³⁺ (5 mole %) indicating the lower thermal stability of this complex hydrate due to the crystal waters.

The FTIR spectra of the R₂O₃:Eu³⁺ (1 mole %) phosphors annealed at different temperatures (Fig. S1) show a broad absorption band centred at around 3400 cm⁻¹ assigned to the O–H stretching vibration mode of the surface hydroxyl groups.

The strength of the OH absorption bands decreases with increasing annealing temperature from 500 to 1000 °C [24,25]. The absorption bands from 1200 to 1750 cm⁻¹ are assigned to stretching mode of oxycarbonate arising from the decomposition of the TMA ligand. The C=O absorption decreases with increasing annealing temperature (Fig. S1), due to decomposition of the oxycarbonate [26]. In addition, the absorption bands characteristic of the R³⁺–O stretching frequencies are centred at 460 and 560 cm⁻¹ in the spectra of the annealed samples. The infrared data of the Eu³⁺ doped Y₂O₃, Gd₂O₃ and Lu₂O₃ have similar spectral profiles (Fig. S1).

The XPD patterns (Fig. 3a) show that the R₂O₃:Eu³⁺ materials annealed at 500–1000 °C crystallize in the cubic phase of R₂O₃ with the *Ia* $\bar{3}$ (*a*: 10.65 Å, *Z*: 16) space group [26]. No differences were observed in the 2θ values of the XPD reflections between the materials heated at different temperatures. The absence of impurity reflections indicates that the rare earth sesquioxides are formed with heating at 500 °C for 1 h and that Eu³⁺ substitutes R³⁺ forming a solid solution. The XPD data revealed a complete solid solubility between the Eu³⁺ dopant and the R³⁺ cations in host lattices, due to the similarity between the radius of the Eu³⁺ and other R³⁺ ions [8,9].

The XPD patterns of Y₂O₃:Eu³⁺ (1 mole %) showed broadening of the reflections for the materials annealed at 500 and 600 °C

Fig. 3. XPD patterns of Y₂O₃:Eu³⁺ (1 mole %) materials sintered at different temperatures for 1 h (a); PDF: 88-1040 [28] and the correlation between the sesquioxide crystallite size and the annealing temperature for the R₂O₃:Eu³⁺ (1 mole %) materials (b).

(Fig. 3a), indicating smaller crystallite size. The crystallite size increases from 6, 14, 23, 33, 40 and 52 nm with increasing annealing temperature from 500, 600, 700, 800, 900 and 1000 °C, respectively (Fig. 3b), due to sintering of the nanocrystallites favoured at high temperatures. Simultaneously with the enlargement of the crystallite sizes, an increase in crystallinity is also observed at high temperatures as indicated by the higher intensity of the X-ray diffraction reflections.

The XPD data of the Y₂O₃ (Fig. 3a), Gd₂O₃ and Lu₂O₃ (Fig. S2) matrices doped with Eu³⁺ (1 mole %) are very similar. The maximum of the (222) reflection moves to higher 2θ values with the decrease of the ionic radius of the rare earth, in agreement with the Bragg's law [25] and with the decrease in the cubic lattice parameter *a*. The crystallite size (Fig. 3b) increases in the R₂O₃ with the increasing of R³⁺ radius, as well. The increase can be attributed to the higher reactivity of the Gd₂O₃, with lower melting point (2339 °C) compared with Y₂O₃ (2410) and Lu₂O₃ (2427) [27]. Therefore, the sintering process is favoured for the gadolinium matrix due to the dependence of the partial melting of the nanocrystals. The crystallite size growths can also be explained by the lower decomposition temperature of the Gd precursor (Fig. 2), resulting in a longer sintering time.

The SEM image of the $\text{Y}(\text{TMA})\text{:Eu}^{3+}$ (1 mole %) precursor complex (Fig. 4a) shows that the sheet-like morphology of the complex is similar to the $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ material after the heat treatment (Fig. 4b), even after annealing at 1000 °C. The oxides exhibited higher porosity due to the decomposition of the organic moiety. This shape property is important to the design of nanomaterials with controlled structure, since it is possible to modify the complex morphology with different synthetic methods and reaction conditions, which would result in the formation of the desired oxide particle shapes. The particle sizes observed in the SEM image of the materials annealed at 1000 °C (Fig. S3) range from 50 to 90 nm.

The TEM images (Fig. 5) confirm the increase in the crystallite size with increasing annealing temperature (Fig. 5a and c). The average particle size estimated from TEM images for $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ (1 mole %) prepared at temperatures from 500 to 1000 °C ranged from 5 to 52 nm, corroborating well with the Scherrer data. These images also show the cubic shape of the crystals and their narrow size distribution. The particles are agglomerated due to the sheet format of the precursor complexes, however.

At higher magnification (Fig. 5b and d), no defects are observed in the crystals (except for the edges), suggesting the formation of a solid solution between the Eu^{3+} ions and the host matrices. This behaviour is due to the compatibility between the identical trivalent charges and similar ionic radii of the Eu^{3+} dopant ion and the Gd, Y and Lu trivalent host ions of the matrices.

3.1. Analysis of excitation spectra

The excitation spectra of the $\text{R}_2\text{O}_3\text{:Eu}^{3+}$ phosphors (R^{3+} : Y, Gd and Lu) annealed at temperatures from 500 to 1000 °C (Figs. 6 and S4) were recorded in the spectral range from 200 to 590 nm, at room temperature (300 K), with emission monitored at 613 nm. In general, the spectra show the narrow absorption bands of the 4f–4f intraconfigurational transitions originating from the Eu^{3+} ion in the range from 17,000 to 34,000 cm^{-1} . In addition, at higher energy, a broad absorption band can be observed centred at ca. 38,900 cm^{-1} , assigned to the $\text{O}^{2-}(2p) \rightarrow \text{Eu}^{3+}(4f^6)$ ligand to metal charge transfer (LMCT) transition. All excitation spectra exhibit similar spectral features, except for the $\text{Gd}_2\text{O}_3\text{:Eu}^{3+}$ materials the spectra of which also include sharp lines from the 4f–4f intraconfigurational transitions of the Gd^{3+} ion (Figs. 6b and S4b).

The weak $^7\text{F}_0 \rightarrow ^5\text{D}_0$ and $^7\text{F}_1 \rightarrow ^5\text{D}_0$ (hot bands from the lower $^7\text{F}_1$ levels at ca. 210 and 280 cm^{-1}) transitions, show only one strong line each at 17,216 and 17,010 cm^{-1} for $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$, respectively. For more detailed $^7\text{F}_1$ energy level schemes, see the analysis of the Eu^{3+} emission spectra in the next section. The thermal population of the highest $^7\text{F}_1$ level at ca. 445 cm^{-1} (and the $^7\text{F}_2$ levels at

ca. 1000 cm^{-1}) are quite low but the hot band absorption from these levels can be seen at 300 K as broad bands without enough resolution for exact assignment to be made for $^7\text{F}_2$. The transitions observed have similar intensities for all $\text{R}_2\text{O}_3\text{:Eu}^{3+}$ materials annealed at 700 °C (Fig. 6b).

Since the magnetic-dipole induced $^7\text{F}_{0,1} \rightarrow ^5\text{D}_1$ transitions of Eu^{3+} are allowed by parity for both the C_2 and S_6 symmetries, several narrow absorption lines (or groups of lines) can be observed below 19,050 (C_2) and at 18,990 and 19,120 cm^{-1} (S_6 site), as well. Because of the high intensity of the $^7\text{F}_1 \rightarrow ^5\text{D}_1$ transitions they dominate this spectral range, but even hot band excitation from the $^7\text{F}_2$ levels can be found – though very weak. The assignment of these energies is in qualitative agreement with those reported in the literature for $\text{Lu}_2\text{O}_3\text{:Eu}^{3+}$ [29,30]. Since the total splitting of the $^7\text{F}_1$ level is some 396 cm^{-1} (cf. next section), the expected splitting of the $^5\text{D}_1$ levels is some 20–30% of the $^7\text{F}_1$ value, i.e. ca. 80–130 cm^{-1} . This relation is quite universal among the Eu^{3+} energy levels in different hosts [31] and was observed here for both the C_2 and S_6 sites.

In comparison with other 4f transitions, the absorption bands observed in the spectral region from 21,400 to 21,600 cm^{-1} are prominent and are assigned to the $^7\text{F}_0 \rightarrow ^5\text{D}_2$ transition of Eu^{3+} , which is characteristic of the Eu^{3+} doped R_2O_3 excitation spectra (Figs. 6 and S4). In addition, the forbidden $^7\text{F}_0 \rightarrow ^5\text{D}_3$ electric-dipole transition can be also observed as three weak absorption lines at 24,300, 24,426 and 24,533 cm^{-1} due to the J-mixing effects in the $^7\text{F}_1$ manifold. Besides, eight narrow bands originating from the $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition are also shown in the spectral range from 24,600 to 25,600 cm^{-1} (Figs. 6 and S4). Other characteristic Eu^{3+} lines, originating from the absorption from the $^7\text{F}_{0,1}$ levels to the following ones (energy in cm^{-1}): $^5\text{G}_{2-6}$ (25,800), $^5\text{L}_{7,8}$ (26,600), $^5\text{D}_4$ (27,250–27,800), $^5\text{H}_7$, $^5\text{F}_7$, $^5\text{I}_7$ and $^3\text{P}_0$ (29,600–35,150) are also observed.

The excitation spectra of the $\text{Gd}_2\text{O}_3\text{:Eu}^{3+}$ materials are similar to those of Y^{3+} and Lu^{3+} hosts, except for the spectral range at higher energy between 31,600 and 37,000 cm^{-1} (Figs. 6b and S4b). The characteristic $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{7/2}$ (ca. 31,970 cm^{-1}), $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{5/2}$ (ca. 32,530 cm^{-1}) and $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{3/2}$ (ca. 33,100 cm^{-1}) transitions arising from the Gd^{3+} ion resulted in strong absorption lines, indicating energy transfer from the Gd^{3+} to Eu^{3+} ion [32]. The $^8\text{S}_{7/2} \rightarrow ^6\text{I}_{7/2}$ (ca. 35660 cm^{-1}) and $^8\text{S}_{7/2} \rightarrow ^6\text{I}_{9/2}$, $^6\text{I}_{17/2}$ (36,000–36,500 cm^{-1}) transitions overlap with the LMCT band [33].

The broad absorption bands are assigned to the $\text{O}^{2-}(2p) \rightarrow \text{Eu}^{3+}(4f^6)$ LMCT in the $\text{R}_2\text{O}_3\text{:Eu}^{3+}$ phosphors (Figs. 6 and S4). The barycentre values of the LMCT states are 37,930, 38,600 and 38,765 cm^{-1} for the Gd^{3+} , Y^{3+} and Lu^{3+} oxides, respectively. The shifts to higher energy of LMCT bands suggest that the chemical environment of the Lu_2O_3 host lattice exert stronger influence on

Fig. 4. SEM images of the $\text{Y}(\text{TMA})\text{:Eu}^{3+}$ (1 mole %) complex precursor (a) and $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ (1 mole %) phosphor sintered for 1 h at 1000 °C (b).

Fig. 5. TEM images of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1 mole %) phosphor annealed for 1 h at 700 (a and b) and 1000 °C (c and d).

Fig. 6. Excitation spectra recorded at 300 K monitoring the emission at 613 nm of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1 mole %) annealed at different temperatures (a) and of the $\text{R}_2\text{O}_3:\text{Eu}^{3+}$ (R: Y, Gd and Lu; 1 mole %) oxides annealed at 700 °C (b).

the Eu^{3+} ion than the Gd_2O_3 and Y_2O_3 hosts, due to the decreasing ionic radii [8], the ligand field around the Eu^{3+} ion should be the strongest for the Lu_2O_3 host.

3.2. Analysis of emission spectra

The emission spectra of the $\text{R}_2\text{O}_3:\text{Eu}^{3+}$ phosphors annealed at temperatures from 500 to 1000 °C were recorded in the spectral range from 400 to 850 nm at 300 K, under excitation in the LMCT band at 260 nm (Figs. 7 and S5). All the spectra exhibit narrow emission lines arising from the $^5\text{D}_J \rightarrow ^7\text{F}_J$ transitions (J: 0–3 and J': 0–6) with similar spectral features irrespective of the host; even

the material heated at 500 °C shows similar photoluminescent characteristics.

For the materials heated at 700 °C (Fig. 7b), only one emission line at $17,215\text{ cm}^{-1}$ is observed and assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition of the Eu^{3+} ion in the C_2 site of the cubic C-type $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. The $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition lines broaden with decreasing crystallite size and crystallinity as a result of inhomogeneous broadening. Since the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is allowed for both the C_2 and S_6 sites there are emission lines (Fig. 7b) at $16,666$, $16,846$ and $17,015\text{ cm}^{-1}$ as well as at $16,770$ and $17,165\text{ cm}^{-1}$ originating from the C_2 and S_6 sites, respectively, in fair agreement with [29,30]. Taken into account the splitting of the $^5\text{D}_1$ level for

Fig. 7. Emission spectra recorded at 300 K with excitation at 260 nm of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1 mole %) annealed at different temperatures (a) and of the $\text{R}_2\text{O}_3:\text{Eu}^{3+}$ (R: Y, Gd and Lu; 1 mole %) oxides annealed at 700 °C (b).

the S_6 site, with the 7F_1 splitting at ca. 400 cm^{-1} , this should be of the order of $80\text{--}132\text{ cm}^{-1}$ [31] to which the experimental value (130 cm^{-1}) compares very well. The total 7F_1 splittings are 349 and 396 cm^{-1} for the C_2 and S_6 sites, respectively, indicating clearly stronger crystal field effect in the S_6 site. However, the debate over the 7F_1 energy level scheme of Eu^{3+} in $\text{C-Y}_2\text{O}_3$ is far from over since the 7F_1 barycentre for the S_6 site (330 cm^{-1}) is far too low for such a strong crystal field.

The experimental intensity parameters (Ω_λ) were calculated from the coefficients of spontaneous emission, $A_{0\lambda}$, given by the Eq. (3) [34]:

$$A_{0\lambda} = \frac{4e^2\omega^3}{3hc^3} \chi \sum_y \Omega_\lambda \langle {}^7F_j \| U^{(\lambda)} \| {}^5D_0 \rangle^2 \quad (3)$$

where χ is the Lorentz local field correction term, given by $\chi = [n(n^2 + 2)^2]/9$, ω the energy of the ${}^5D_0 \rightarrow {}^7F_j$ transitions and $\langle {}^7F_j \| U^{(\lambda)} \| {}^5D_0 \rangle^2$ the squared reduced matrix elements whose values are 0.0032 and 0.0023 for the ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_4$ transitions, respectively [35].

The refractive index (n) of the bulk $\text{R}_2\text{O}_3:\text{Eu}^{3+}$ is considerably high (~ 1.9), and in this bulk material the 5D_0 lifetime (τ) is around 1.0 ms [36,37]. It is conceivable that in the nanoparticle scale, with average sizes around 20 nm, which are much smaller than the wavelength of the exciting radiation, the n and τ values in the R_2O_3 hosts are different. Moreover, the differences between the Eu^{3+} ions on the surface and within the nanoparticles may play a role in the profile of the decay curves.

The radiative rate (A_{01}) of the ${}^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} ion (allowed by the magnetic dipole interaction) is formally insensitive to the ligand field environment. Therefore it can be used as a reference transition, and has been given values around 50 s^{-1} [38]. Based on this value, the refractive indices were determined and compared to the lifetime and crystallite size values reported in references [36–38]. Both the experimental intensity parameters and measured lifetimes (1.4–2.0 ms) were actually then reproduced using the effective refractive index values between 1.5 and 1.6.

The $A_{0\lambda}$ transition rate values were thus taken as the reference, once it is magnetic dipole allowed and it is also practically independent of the ligand field. The following expression (Eq. (4)) was used [39]:

$$A_{0\lambda} = A_{01} \left(\frac{S_{0\lambda}}{S_{01}} \right) \left(\frac{\omega_{01}}{\omega_{0\lambda}} \right) \quad (4)$$

where S_{01} and $S_{0\lambda}$ are the integrated areas of the ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_\lambda$ transitions, with ω_{01} and $\omega_{0\lambda}$ being their energy barycentres, respectively [37]. Furthermore, the emission quantum efficiency (η) of the 5D_0 emitting level of the Eu^{3+} ion was determined according to Eq. (5):

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{nr}}} \quad (5)$$

The total decay rate, $A_{\text{tot}} = 1/\tau = A_{\text{rad}} + A_{\text{nr}}$, where A_{rad} ($= \sum A_{0 \rightarrow j}$) and A_{nr} are the radiative and non-radiative rates of the 5D_0 level, respectively.

The values of the experimental intensity parameters (Ω_λ) as well as the radiative (A_{rad}) and non-radiative (A_{nr}) rates and emission quantum efficiencies (η) of the 5D_0 emitting level of the $\text{R}_2\text{O}_3:\text{Eu}^{3+}$ are presented in Table 1. The Ω_2 values are very similar for the same matrix annealed at different temperatures indicating that for each matrix there is no change in the hypersensitive character of the ${}^5D_0 \rightarrow {}^7F_2$ transition of the Eu^{3+} ion. Therefore, the same chemical environment around Eu^{3+} ion is expected for these materials.

In addition, the emission spectra (Fig. 7) exhibit similar spectral features, corroborating with the similarity of the Ω_2 and Ω_4 values for all matrices.

The considerably high values of the Ω_2 parameters are consistent with a very low point symmetry of the C_2 site occupied by the Eu^{3+} ion. The Eu^{3+} doped Y_2O_3 showed higher values of emission quantum efficiency ($\eta_{\text{aver}} = 86\%$) than $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ (76% and 72%, respectively). The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ material annealed at 900 °C also gave the highest value of $\eta = 91\%$ while the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ at 1000 °C showed the lowest value ($\eta = 65\%$), due to its high value of the non-radiative rate ($A_{\text{nr}} = 246\text{ s}^{-1}$).

The increase of the annealing temperature improved the quantum efficiency up to 800 °C in all systems. Beyond this temperature, the values stabilize or are lowered probably due to increase in the crystallite size of the $\text{R}_2\text{O}_3:\text{Eu}^{3+}$ materials, especially for $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ that has the largest crystallite size, decreasing the emission quantum efficiency.

Table 1

Experimental values of intensity parameters (Ω_2), radiative (A_{rad}) and non-radiative (A_{nrad}) rates as well as emission lifetimes and emission quantum efficiencies of the $^5\text{D}_0$ emitting level determined for the $\text{R}_2\text{O}_3:\text{Eu}^{3+}$ (1 mole%) (R: Y, Gd and Lu) phosphors based on the emission spectra recorded at room temperature.

$\text{R}_2\text{O}_3:\text{Eu}^{3+}$ (1 mole%)	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	τ (ms)	η (%)
$\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$							
500 °C	15.1	2.9	541	163	704	1.42	77
600 °C	15.0	1.8	524	145	669	1.49	78
700 °C	13.6	1.3	476	225	701	1.43	68
800 °C	14.4	1.5	503	98	602	1.66	84
900 °C	14.0	1.5	489	107	596	1.68	82
1000 °C	13.2	1.4	465	246	711	1.40	65
$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$							
500 °C	12.8	1.8	458	104	562	1.78	81
600 °C	13.1	1.6	465	90	554	1.80	84
700 °C	12.8	1.5	454	81	536	1.87	85
800 °C	12.0	1.0	479	52	531	1.88	90
900 °C	13.5	1.3	513	50	563	1.77	91
1000 °C	12.1	1.5	573	84	579	1.72	85
$\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$							
500 °C	12.5	1.7	449	222	672	1.49	67
600 °C	13.2	1.7	468	200	669	1.49	70
700 °C	12.9	1.6	461	236	697	1.43	66
800 °C	12.6	1.6	419	149	568	1.76	74
900 °C	11.6	1.5	389	120	509	1.96	76
1000 °C	11.5	1.4	383	108	491	2.03	78

Fig. 8. CIE chromaticity diagram showing the x, y emission colour coordinates for the $\text{R}_2\text{O}_3:\text{Eu}^{3+}$ (1 mole%) nanophosphors (R: Gd, Y and Lu) annealed at different temperatures. The inset figures are photographs of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1 mole%) nanomaterials taken with a digital camera displaying the red emission under UV irradiation at 254 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The CIE (*Commission Internationale de l'Eclairage*) chromaticity coordinates generated from the emission spectra of Eu^{3+} doped R_2O_3 (Fig. 8) are x : 0.656 and y : 0.332 [40]. The colour coordinates are practically the same irrespective of the sesquioxide host or the annealing temperature.

The phosphors containing Gd^{3+} , Y^{3+} , Lu^{3+} ions exhibit the same characteristic nearly monochromatic emission. The images of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1 mole %) nanomaterials under UV irradiation (inset of Fig. 8) show nearly identical strong red emission for all the phosphors annealed at temperatures from 500 to 1000 °C.

4. Conclusions

$\text{R}_2\text{O}_3:\text{Eu}^{3+}$ nanomaterials were successfully synthesized with an unprecedented method using benzenetricarboxylate precursor complexes annealed at different temperatures, with controllable particle size and high chemical homogeneity. Another advantage of this new synthesis is the significantly lower temperature regime than the usual solid-state method. The TEM and XPD data of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors confirmed the increasing crystallite size with temperature.

The photoluminescence results are consistent with the low symmetry of the C_2 site occupied by the Eu^{3+} ion in the cubic C -type $R_2O_3:Eu^{3+}$, which is essential for optical applications. Furthermore, the $Y_2O_3:Eu^{3+}$ nanophosphors exhibit high values of emission quantum efficiency, compatible with the commercial phosphors currently available in the market.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.optmat.2014.11.044>.

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II

Low Temperature Synthesis of Luminescent $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ Nanomaterials Using Trimellitic Acid Precursors

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Abstract

$[\text{RE}(\text{TLA})\cdot(\text{H}_2\text{O})_n:\text{Eu}^{3+}]$ (RE^{3+} : Y, Gd and Lu; TLA: trimellitic acid) precursor complexes were synthesized by an one step aqueous co-precipitation method. After annealing for 1h, $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors were formed through the benzenetricarboxylate low temperature thermolysis method (500–1000 °C). The compounds were characterized by using different techniques (CHN, FTIR, TG/DTG, XPD and SEM). The XPD data indicate that the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ materials have crystallite size range from 11 to 62 nm. The SEM and TEM images show that the annealed materials keeps morphological similarities with the precursor complexes. The photoluminescence properties were studied based on the excitation and emission spectra, and luminescence decay lifetimes of the $^5\text{D}_0$ emitting level of the Eu^{3+} ion. The experimental intensity parameters (Ω_λ), lifetimes (τ), as well as radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates were calculated and discussed. The $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ phosphors (RE: Y^{3+} and Lu^{3+}) annealed at 500 to 1000 °C have emission quantum efficiency (intrinsic quantum yield) values from 60 to 82 %, indicating that this material can be potentially used for optical markers applications.

Keywords: low temperature method, benzenetricarboxylate precursors, rare earth sesquioxides, photoluminescence materials

1. Introduction

Polycarboxylate ligands have wide variety of structure providing large range of chemical properties when combined with metal ions. It has been drawing the attention in the areas such as metal framework systems (*MOF*)^{1,2}, selective markers for medical applications³, magnetic materials⁴, gas storage⁵, drug delivery⁶, precursors for materials⁷ *etc.*

Rare earth (RE) containing materials show a versatility for application in the areas of science and technology specially in catalysis, permanent magnets in hybrid cars batteries,^{8,9} electroluminescent materials, persistent phosphors, structural probes, luminescent markers, display panels, *etc.*^{10–15} Most of those applications are consequence of their intrinsic characteristic: sharp intraconfigurational $4f^N$ transitions, archiving high monochromatic emission colors and a wide range of emissions, from infrared to ultraviolet,¹⁶ *e.g.* Nd^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} and Tm^{3+} ions which emit in the infrared, red, ultraviolet, green and blue regions, respectively.

One very important feature of the RE^{3+} is their $4f$ - $4f$ transitions, forbidden by the *Laporte's rule*. Associated to that, the shielding from the chemical environment by the filled $5s$ and $5p$ sub-shells¹⁷ over the $4f$ electrons lead to a characteristic sharp lines spectra with small absorptivity and emission intensities. Taking into account the RE^{3+} intraconfigurational transitions, these ions can be divided in four groups depending on their spectroscopic features: 1) $\text{Sc}^{3+}(4f^0)$, $\text{Y}^{3+}(4f^0)$, $\text{La}^{3+}(4f^0)$ and $\text{Lu}^{3+}(4f^{14})$ where the $4f$ electrons are non-optically active due to their completely empty or fully occupied subshells.¹⁶ 2) $\text{Gd}^{3+}(4f^7)$ is a singular case due to its half-filled $4f$ layer, and therefore very stable. The energy difference between the lower emitting level ($^6P_{7/2}$) and the fundamental level ($^8S_{7/2}$) is approximately 32000 cm^{-1} opening the opportunity for its application as inorganic matrices. Due to the chemical similarity with other RE^{3+} ions it is extensively used to study the emission of the ligands in coordination complexes. 3) $\text{Sm}^{3+}(4f^5)$, $\text{Eu}^{3+}(4f^6)$, $\text{Tb}^{3+}(4f^8)$ and $\text{Dy}^{3+}(4f^9)$: in these ions the energy gap between the emitting and the lower levels are large enough to reduce the non-radiative decay process and accept energy from the ligands, interconfigurational transitions or charge transfer bands excited levels (Figure 1). 4) $\text{Ce}^{3+}(4f^1)$, $\text{Pr}^{3+}(4f^2)$, $\text{Nd}^{3+}(4f^3)$, $\text{Ho}^{3+}(4f^{10})$, $\text{Er}^{3+}(4f^{11})$, $\text{Tm}^{3+}(4f^{12})$ and $\text{Yb}^{3+}(4f^{13})$: in these ions the energy gap between the emitting and lower levels are small, increasing the non-radiative decay process usually mediated by high energy vibrational modes in ligands (typically water molecules) or matrices (oxycarbonates, hydroxides *etc.*). In these cases the process accounts for a the decreasing in the final emission efficiency.

To overcome the small absorptivity coefficients, luminescence sensitizers can be used to absorb and transfer the energy efficiently to the RE ions, keeping their desirable atomic characteristics. This phenomenon is a key feature in design of luminescent materials.^{16,18,19}

Figure 1. Partial energy diagram of TLA ligand from $[\text{RE}(\text{TLA}) \cdot (\text{H}_2\text{O})_n]$ (RE^{3+} : Y, Gd and Lu) precursor (singlet and triplet states), Eu^{3+} ion and $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (LMCT) state.

In inorganic matrices such as vanadates, molybdates, tungstates and sesquioxides containing RE^{3+} ion, generally is observed an efficient energy transfer from the Ligand Metal Charge Transfer (LMCT) band to the metal ions. In the special case, the Eu^{3+} ion shows a high absorption intensity arising from the allowed LMCT transition, yielding a high intensity luminescence.²⁰

In solid state reactions, typically, is necessary high temperatures and long reaction time periods to prepare luminescent materials. This way to synthesize materials is known as ceramic method, which promotes heterogeneous distribution of the activator ion within the matrix and generate materials with high crystallite and particle sizes. Alternative methods to obtain materials in milder reaction conditions as: sol-gel, combustion or Pechini methods,^{21,22} are key to overcome the experimental limitation and improve their properties.

This report demonstrate the synthesis, characterization and optical properties of $[\text{RE}(\text{TLA}):\text{Eu}^{3+}(\text{x mol}\%)]$ complexes (RE^{3+} : Y, Gd and Lu; x: 0.1, 0.5, 1.0, and 5.0 mol%) and their low temperature annealing into the high luminescent $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ phosphors. All the precursor complexes and resulting nanophosphors were characterized by CHN, FTIR, TG/DTG, XPD and SEM. The photoluminescence properties of the doped materials were studied based on the excitation and emission spectra and luminescence decay curves of the Eu^{3+} ion $^5\text{D}_0$ excited level.

2. Experimental

High purity RE_2O_3 (RE^{3+} : Y, Eu, Gd and Lu; CSTARM, 99.99 %) were used to prepare the respective $\text{RECl}_3 \cdot (\text{H}_2\text{O})_6$ salts by reaction with concentrated HCl solution until total decomposition (~ 60 – 80 °C) of the solid and final pH ~ 6 . The trimellitic acid (in the form of 1,2,4-benzenetricarboxylic acid 1,2-anhydride or 1,3-dihydro-1,3-dioxo-5-isobenzofurancarboxylic acid; Aldrich, 97%) was solubilized in water by drop-wise addition of 1 mol L^{-1} sodium hydroxide up to pH ~ 6 .

For the preparation of the $[\text{RE}(\text{TLA})\text{:Eu}^{3+}]$ complexes, 50 mL of $\text{RECl}_{3(\text{aq})}$ (0.05 mol L^{-1}) was slowly added to a 200 mL solution of $\text{Na}_3(\text{TLA})_{(\text{aq})}$ ($0.0125 \text{ mol L}^{-1}$) at 1:1 molar ratio at *ca.* 100 °C. The reaction mixture was refluxed for 1 hour, the precipitate was filtered and washed four times with distilled water, dried and stored at reduced pressure.

The $[\text{RE}(\text{TLA})\text{:Eu}^{3+}]$ complexes obtained are non-hygroscopic, white crystalline powders, stable in air. The $\text{RE}_2\text{O}_3\text{:Eu}^{3+}$ nanophosphors were obtained by annealing the $[\text{RE}(\text{TLA})\text{:Eu}^{3+}]$ complexes at 500, 600, 700, 800, 900 and 1000 °C in a static air atmosphere, resulting in $\text{RE}_2\text{O}_3\text{:Eu}^{3+}$ nanophosphors.

Elemental analyses were performed with a Perkin-Elmer CHN 2400 analyzer. The FTIR were acquire from 400 to 4000 cm^{-1} in a KBr pallets form by using a Bomem MB100 FTIR. Thermogravimetry were performed from 30 to 900 °C (heating ramp of 5 °C min^{-1} , synthetic air dynamic atmosphere) in a TA HI-RES TGA 2850 equipment. The XPD patterns were obtained, from 5 to 50° (2θ), in a Miniflex Rigaku II equipament ($\text{CuK}\alpha_1$) from 5 to 50° (2θ). The SEM micrographs were recorded in a JEOL JSM 7401F Field Emission Scanning Electron Microscope. The TEM micrographs were recorded in a JEOL USA JEM-2100 LaB₆ Transmission Electron Microscope.

The luminescence study was based on the excitation and emission spectra recorded at room (300 K) and liquid nitrogen (77 K) temperatures. The measurements were performed in a SPEX-Fluorolog 3 instrument with double monochromators in front face mode (22.5°) using a 450 W Xenon lamp as excitation source. Luminescence decay curves were obtained by using a 150 W pulsed lamp and recorded in a SPEX 1934D phosphorimeter.

3. Results and Discussion

3.1. Characterization

A combination of elemental and thermogravimetric analysis (Table S1 and Figure 2) suggests an 1:1 molar ratio between the RE^{3+} ion and TLA ligand ($[\text{RE}(\text{TLA}) \cdot (\text{H}_2\text{O})_n\text{:Eu}^{3+}]$; n : 4, 4 and 3 for Y^{3+} , Gd^{3+} and Lu^{3+} , respectively).²³ The TG curves of coordination compounds show a water molecules mass-loss in the temperature interval between 50 and 330 °C. Although the organic moiety decomposition of the complexes present only one single-step between 450 and 570 °C. In this case, it was used annealing temperature of 500 °C during 1 hour, in order to eliminate all the organic part leading to formation of the $\text{RE}_2\text{O}_3\text{:Eu}^{3+}$ luminescent material.

Figure 2. TG and DTG curves a) $[\text{RE}(\text{TLA})]$ and b) $[\text{RE}(\text{TLA}):\text{Eu}^{3+} (5.0 \text{ mol}\%)]$ (RE^{3+} : Y, Gd and Lu).

The infrared absorption spectra (Figure S01) present similar spectral profile for the RE^{3+} complexes and Eu^{3+} -doped matrices. The absorption bands between 1300 and 1600 cm^{-1} in the FTIR spectra of $[\text{RE}(\text{TLA})\cdot(\text{H}_2\text{O})_n:\text{Eu}^{3+}]$ are assigned to the carboxylate symmetric $\nu_s(\text{C}=\text{O})$ and asymmetric $\nu_{as}(\text{C}=\text{O})$ stretching modes, respectively.^{19,24,25} The narrow absorption peak around 3070 cm^{-1} is assigned to the C–H bond stretching of the $[\text{RE}(\text{TLA}):\text{Eu}^{3+}]$ complexes and the broad band between 3100 – 3700 cm^{-1} correspond to the O–H stretching from the water molecules.²⁶

The sharp absorption bands around 510 and 580 cm^{-1} correspond to the characteristic RE^{3+} –O stretching vibration. It is worth mentioning that the broad bands from 1250 to 1600 cm^{-1} are assigned to stretching mode of oxycarbonate remainder from the decomposition of the organic moiety of TLA and decreases with increasing annealing temperature (Figure S01), due to oxycarbonate decomposition.²³ The broad absorption band located from 2800 to 3700 cm^{-1} is assigned to the superficial hydroxyl groups in the nanomaterials. Therefore, the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ materials originated from the $[\text{RE}(\text{TLA})]$ precursor complexes present similar chemical behavior compared to the sesquioxides prepared from the $[\text{RE}(\text{TMA})]$ complexes as reported in reference²³.

The X ray diffraction patterns of the $[\text{RE}(\text{TLA}):\text{Eu}^{3+}]$ complexes are similar of the PDF (Powder Diffraction Patterns) for $[\text{Gd}(\text{TLA})]:\text{Eu}^{3+}$ and $[\text{Y}(\text{TLA})]:\text{Eu}^{3+}$ (00-056-1733) and $[\text{Lu}(\text{TLA})]:\text{Eu}^{3+}$ (00-058-1915), Y^{3+} and Gd^{3+} complexes are isomorphs. Consequently, there is no change in position or formation of new diffraction peaks at different concentrations of the dopants. This result is consistent with the *Vegard's rule*^{27,28} which suggest a formation of a solid solution between the Eu^{3+} dopant and the RE^{3+} in the host matrices due to the high similarity in the radii of these RE^{3+} ions.²⁷

The XPD patterns of the annealed materials at 500, 600, 700, 800, 900 and 1000 °C (Figure 3) reveal a formation of $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ in a cubic phase crystallization with the $Ia\bar{3}$ space group.²⁹ The absence of 2θ shift and reflections of impurities in the patterns of the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ indicates the formation of pure RE^{3+} sesquioxides. The XPD data of the Y_2O_3 , Gd_2O_3 and Lu_2O_3 matrices (Figure 3) are very similar. Slight differences in the (222) reflection around 28°, moving to higher 2θ values with decreasing of the ionic radius of the RE^{3+} in the matrix, as predicted by Bragg's law³⁰.

Figure 3. XPD patterns of a) $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, b) $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ and c) $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) materials annealed for 1 h at different temperatures; reference pattern: PDF: 86-2477 and 86-2475, respectively.

The average crystal size of the doped materials was estimated from the powder diffraction data by using the Scherrer formula (Figure 4).^{23,31} The crystallite size of the RE_2O_3 materials increases as function of the RE^{3+} radius and annealing temperature. This behavior can be assigned to the higher reactivity of the Gd_2O_3 , with lower melting point (2339 °C) compared to Y_2O_3 (2410 °C) and Lu_2O_3 (2427 °C).³² Therefore, the sintering process is favored for the gadolinium matrix due to the dependence of the partial melting of the nanocrystals.²³

The narrowing of the diffraction peaks of $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) (RE^{3+} : Y, Gd and Lu) phosphors presented in the XPD patterns (Figure 3) as function of the annealing temperature,

indicat that the crystallite size increases from 11, 17, 18, 37, 46 and 62 nm as the annealing temperature increases from 500, 600, 700, 800, 900 and 1000 °C (Y_2O_3), respectively (Figure 4). This behavior is related to the sintering of the nanocrystallites favored at high temperatures. Although the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ annealed at 1000 °C was also included in this work, the Scherrer's formula is recommended only for crystallite sizes up to 200 nm (Figure 4).

Figure 4. Correlation between the sesquioxides crystallite size and annealing temperature for $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) materials.

The SEM images of the $[\text{RE}(\text{TLA}):\text{Eu}^{3+}$ (1.0 mol%)] precursors shows rods and a flower like morphologies (stacking of micrometric sheets of the material) for Y^{3+} / Gd^{3+} (Figure 5a,b) and Lu^{3+} complexes, respectively (Figure 5c). After annealing up to 1000 °C the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ materials retained the original morphology of the correspond precursor complex (Figure 5d,e,f). The nanos sesquioxides exhibit higher porosity due to the decomposition of the organic moiety. This property is important for the design of nanomaterials with controlled morphology. Since it is possible to modify the complex morphologies, the desired nanoparticle shapes can be obtained by choosing the suitable synthetic method and reaction conditions.^{33,34}

The TEM micrographs (Fig. 5g,h) show the cubic shape of the crystallites with high crystallinity. The particles retained the shape of the precursor agglomerates, show in the SEM microscopy. At higher magnification no defects were observed in the crystals (except for the edges and crystallite contact points), suggesting the formation of a solid solution between the Eu^{3+} ions and the host matrices, compatible with the similar RE^{3+} ionic radii and chemical behaviour of the Eu^{3+} and RE^{3+} matrices.

Figure 5. SEM images of $[\text{RE}(\text{TLA}):\text{Eu}^{3+} (1.0 \text{ mol}\%)]$ precursor complexes (a,b,c), $\text{RE}_2\text{O}_3:\text{Eu}^{3+} (1.0 \text{ mol}\%)$ phosphor annealed during 1 h (d,e,f) and TEM images of $\text{RE}_2\text{O}_3:\text{Eu}^{3+} (1.0 \text{ mol}\%)$ annealed during 1 h at 1000 °C (g,h).

3.2. Photophysical properties of materials

$[\text{RE}(\text{TLA}):\text{Eu}^{3+}]$ Precursor Complexes - The excitation spectra of $[\text{RE}(\text{TLA}):\text{Eu}^{3+} (x \text{ mol}\%)]$ (RE^{3+} : Y, Gd and Lu) compounds were obtained by monitoring the hypersensitive transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (619 nm) at 77 K (Figure 6). For all the complexes, the absorption bands are dominated by a high intensity broad TLA ligand band centered at 295 nm assigned to the $\text{S}_0 \rightarrow \text{S}_1$ transition, indicating an efficient energy

transfer $\text{TLA} \rightarrow \text{Eu}^{3+}$. The sharp peaks are assigned to the absorption of the Eu^{3+} ion originated from the ground state $^7\text{F}_0$ to the $^5\text{L}_6$ and $^5\text{D}_2$ excited levels. The excitation spectra of the $[\text{RE}(\text{TLA})\text{:Eu}^{3+} (x \text{ mol}\%)]$ (RE^{3+} : Y and Gd) compounds show similar profiles suggesting that this system present equivalent chemical environments around RE^{3+} ions and optical behaviors. On the other hand, $[\text{Lu}(\text{TLA})\text{:Eu}^{3+} (x \text{ mol}\%)]$ show slightly different spectral profile. For all $[\text{RE}(\text{TLA})\text{:Eu}^{3+}]$ systems the $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition (25445 cm^{-1} for $[\text{Y}(\text{TLA})\text{:Eu}^{3+} (5.0 \text{ mol}\%)]$) exhibits the highest intensity among the intraconfigurational transitions in the excitation spectra.

The emission spectra of the $[\text{RE}(\text{TLA})\text{:Eu}^{3+} (x \text{ mol}\%)]$ complexes (RE^{3+} : Y, Gd and Lu), were recorded under excitation in the TLA ligand band ($\sim 295 \text{ nm}$) at 77 K , to reduce the vibronic coupling compared to the room temperature case. The emission energy levels of $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions ($J = 0-4$) of the Eu^{3+} ion, can be attributed as the following (in cm^{-1}): $^7\text{F}_0$ (17270); $^7\text{F}_1$ (16920); $^7\text{F}_2$ (16210); $^7\text{F}_3$ (15337) and $^7\text{F}_4$ (14350), based at the $[\text{Y}(\text{TLA})\text{:Eu}^{3+} 5.0 \text{ mol}\%]$. The efficient energy transference $\text{TLA} \rightarrow \text{Eu}^{3+}$ ion is evidenced by the absence of ligand broad emission band in the emission spectra in the spectral range from the 400 to 700 nm.

Figure 6. The a) excitation spectra of $[\text{RE}(\text{TLA})\text{:Eu}^{3+} (5.0 \text{ mol}\%)]$ (RE^{3+} : Y, Gd and Lu), with emission monitored at 616 nm, b) emission spectra, with excitation at 295 nm, recorded at 77 K and c) correlation between $[\text{RE}(\text{TLA})\text{:Eu}^{3+} (x\%)]$ lifetimes and Eu^{3+} -doping concentrations (x : 0.1, 0.5, 1.0 and 5.0 mol%).

Using the optical data obtained from the emission spectra it is possible to calculate the radiative rates ($A_{0 \rightarrow J}$) from the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions using Eq. 1^{16,17}:

$$A_{0 \rightarrow J} = \left(\frac{\sigma_{0 \rightarrow 1}}{\sigma_{0 \rightarrow J}} \right) \left(\frac{S_{0 \rightarrow J}}{\sigma_{0 \rightarrow J}} \right) A_{0 \rightarrow 1} \quad (1)$$

where $\sigma_{0 \rightarrow 1}$ and $\sigma_{0 \rightarrow 2,4}$ correspond to the energy barycenter of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_{2,4}$ transitions, respectively. The $S_{0 \rightarrow 1}$ and $S_{0 \rightarrow J}$ are the areas calculated under the emission of the spectral curve corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions, respectively³⁵. Since the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is almost insensitive to changes with the chemical environment around the Eu^{3+} ion the $A_{0 \rightarrow 1}$ rate can be used as an internal standard to determine the $A_{0 \rightarrow J}$ coefficients for Eu^{3+} containing compounds.¹⁶

The lifetime (τ) of the luminescent compounds were obtained from the luminescence decay curve using a first order exponential decay, with excitation at the ${}^7F_0 \rightarrow {}^5L_6$ band. The emission quantum efficiency (η , or intrinsic quantum yield, Q_{Ln}^{Ln}), as it has been defined by Bünzli *et al*)³⁶ of the 5D_0 emitting level is determined according to the Eq. 2:

$$\eta = \frac{A_{rad}}{A_{rad} + A_{nrad}} \quad (2)$$

where the total decay rate, $A_{tot} = 1/\tau = A_{rad} + A_{nrad}$ and the $A_{rad} = \sum_J A_{0 \rightarrow J}$. The A_{rad} and A_{nrad} quantities are the radiative and non-radiative rates, respectively. Table 1 shows the experimental values of the radiative (A_{rad}), non-radiative (A_{nrad}) rates and 5D_0 emitting level emission quantum efficiency (η).

The [RE(TLA):Eu³⁺ (x mol%)] lifetime values (Table 1 and Figure 6) show higher values for Gd³⁺ and Y³⁺ containing complexes when compared to the Lu³⁺ ion case. On the other hand, there are no changes in the lifetime behavior doping with an increasing concentration from 0.1, 0.5, 1.0 and 5.0 mol%, within the same system.

The ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_4$ transitions can be used to estimate the experimental intensity parameters (Ω_λ , $\lambda = 2$ and 4). The Ω_6 intensity parameter is not included in this study since the ${}^5D_0 \rightarrow {}^7F_6$ transition was not observed for these systems. The coefficient of spontaneous emission, A, is given by Eq. 3:

$$A_{0 \rightarrow J} = \frac{4e^4 \omega^3}{3\hbar c^3} \chi \sum_\lambda \Omega_\lambda \left\langle {}^7F_J \left\| U^{(\lambda)} \right\| {}^5D_0 \right\rangle^2 \quad (3)$$

where, $\chi = n(n+2)^2/9$ is the Lorentz local field correction and n is the refractive index of the medium (refractive index used: 1.5 for all [RE(TLA):Eu³⁺] complexes and between 1.5 and 1.6 for RE₂O₃:Eu³⁺ materials). The squared reduced matrix elements $\langle {}^7F_J \| U^{(\lambda)} \| {}^5D_J \rangle^2$ are 0.0032 and 0.0023 calculated for J = 2 and 4, respectively.^{35,37}

The Ω_λ parameters depend mainly on the local geometry, bonding atoms and polarizabilities in the first coordination sphere of the RE³⁺ metal ion, and are governed by both the forced electric dipole (FED) and dynamic coupling (DC) mechanisms. Moura *et al*³⁸ reported that the Ω_2 parameter values are very sensitive to small angular changes in the local coordination geometry (much more than the $\Omega_{4,6}$ parameters). This spectroscopic behavior is associated with the hypersensitivity of certain 4f-4f transitions, to changes in the chemical environment, that are usually ruled by the Ω_2 intensity parameter. On the other hand, the Ω_4 and Ω_6 values are most sensitive the chemical bond distances to the ligating atoms around the lanthanide ion. Indeed, as concluded in Ref.³⁸, covalency in the ion-ligand bonding becomes more important with the increasing rank of the Ω_λ , supporting the idea that the Ω_4 and Ω_6 parameters are better probes than Ω_2 to quantify covalency in these compounds.

The Ω_λ ($\lambda = 2$ and 4) parameter values for the [RE(TLA):Eu³⁺ (x mol%)] compounds (x = 0.1, 0.5, 1.0 and 5.0 mole-%) are presented in Table 1. The Ω_2 values ($\sim 6 \cdot 10^{-20} \text{ cm}^{-2}$) found for these doped complexes are systematically larger than the [RE(TMA):Eu³⁺] (RE³⁺: Y and Lu) anhydrous complexes ($\sim 2 \cdot 10^{-20} \text{ cm}^{-2}$) values [RETMA] reported in reference,³⁹ reflecting the higher hypersensitive character of the ${}^5D_0 \rightarrow {}^7F_2$ transition.^{23,40,41}

The emission quantum efficiency values of the [RE(TLA):Eu³⁺ (x mol%)] are lower for the complexes containing Y³⁺ and Gd³⁺ ($\eta \sim 10\%$) and Lu³⁺ ($\eta \sim 6\%$) ions, which indicate a strong non-radiative decay pathway mediated by water molecules (Table 1). It is also observed that increasing the Eu³⁺ concentration from 0.1 to 5.0 mol% produces no change in the emission quantum efficiency values, suggesting that the luminescence quenching concentration effect is not operative for these systems.

Table 1. Experimental values of intensity parameters (Ω_k), radiative (A_{rad}) and non-radiative (A_{nrad}) rates, emission lifetimes and emission quantum efficiencies of the $^5\text{D}_0$ emitting level determined for the $[\text{RE}(\text{TLA})\text{:Eu}^{3+} (\text{x mol}\%)]$ (RE^{3+} : Y, Gd and Lu) phosphors based on the emission spectra recorded at 77 K.

$[\text{RE}(\text{TLA})\text{:Eu}^{3+} (\text{x mol}\%)]$	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	τ (ms)	η (%)
Y³⁺							
(0.1)	6.4	1.6	264	2492	2756	0.363	10
(0.5)	6.2	1.7	258	2642	2900	0.345	9
(1.0)	6.1	1.7	257	2475	2732	0.366	9
(5.0)	6.1	1.7	257	2948	3205	0.312	8
Gd³⁺							
(0.1)	4.7	1.7	216	1936	2151	0.465	10
(0.5)	4.8	1.8	219	1862	2081	0.481	11
(1.0)	5.1	1.7	225	1928	2153	0.464	10
(5.0)	4.7	1.8	217	1870	2087	0.479	10
Lu³⁺							
(0.1)	5.5	1.3	234	3587	3821	0.262	6
(0.5)	5.4	1.4	229	3693	3922	0.255	6
(1.0)	5.4	1.3	229	3641	3870	0.258	6
(5.0)	5.4	1.3	229	3792	4021	0.249	6

RE₂O₃:Eu³⁺ Materials - The excitation spectra of RE₂O₃:Eu³⁺ annealed phosphors (RE³⁺: Y, Gd and Lu) were recorded at 77 K in the spectral range from 200 to 590 nm, with the emission monitored at 613 nm (Figure 7 and Figure S03). They show the presence of a broad absorption band centered around ($\sim 39000 \text{ cm}^{-1}$) assigned to the $\text{O}^{2-}(2p) \rightarrow \text{Eu}^{3+}(4f^6)$ ligand-to-metal charge transfer (LMCT) transition. Besides, the narrow absorption bands arisen from 4f-4f transitions from the RE³⁺ ion (~ 17000 to 34000 cm^{-1}) are observed.

The excitation spectra recorded at 300 K (Figure S04) show the presence of the overlapped $^7\text{F}_0 \rightarrow ^5\text{D}_1$ and $^7\text{F}_1 \rightarrow ^5\text{D}_1$ transitions ($\sim 19000 \text{ cm}^{-1}$) allowed by magnetic-dipole mechanism ($\Delta J = 0, \pm 1$, but $0 \leftrightarrow 0$ is forbidden) for both the C₂ and S₆ symmetries. This optical results are due to the thermal population of the $^7\text{F}_1$ level that are in agreement with the results previously reported for RE₂O₃:Eu³⁺ ^{42,43}. The absorption bands assigned to the $^7\text{F}_0 \rightarrow ^5\text{D}_2$ transition allowed by induced electric dipole and dynamic coupling mechanisms were observed from 21500 to 21900 cm^{-1} . In addition, a weak absorption band around 24100 cm^{-1} is assigned to the forbidden $^7\text{F}_0 \rightarrow ^5\text{D}_3$ transition (by ΔJ selection rules) as a result of the relaxation of the selection rule due to the J-mixing effects in the $^7\text{F}_J$ manifolds. Moreover, the other absorption bands (Figure 7) originated from 4f-4f transitions of the Eu³⁺ ion were observed such as (in nm): the $^7\text{F}_0 \rightarrow ^5\text{L}_6$ (394), $^5\text{G}_{2-6}$ (387), $^5\text{L}_{7,8}$ (376), $^5\text{D}_4$ (363), $^5\text{H}_J$, $^5\text{F}_J$, $^5\text{I}_J$ and $^3\text{P}_0$ (between 286 and 335) are also observed.

It is worth mentioning that the excitation spectra of the Gd₂O₃:Eu³⁺ present the characteristic strong absorption (nm): $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{7/2}$ (313), $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{5/2}$ (307) and $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{3/2}$ (302) transitions, indicating efficient energy transfer from the Gd³⁺ to the Eu³⁺ ion upper levels.⁴⁴ The $^8\text{S}_{7/2} \rightarrow ^6\text{I}_J$ $J = 7/2, 9/2, 11/2$ (276) transitions overlap with the LMCT band. This high intensity absorption band indicates an efficient Gd³⁺

to Eu^{3+} energy transfer.⁴⁵

The luminescent materials prepared by the benzenetricarboxylate method present comparable excitation features, indicating the reproducibility of the method even when using different BTC ligands.²³

The emission spectra of the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (RE^{3+} : Y, Gd and Lu) annealed at temperatures from 500 to 1000 °C were recorded at 77 K from 400 to 750 nm, under excitation in the LMCT band at 260 nm (Figure 7). All the spectra exhibit only the sharp lines arising from the $^5\text{D}_{0,1,2,3} \rightarrow ^7\text{F}_{0-6}$ transitions of the Eu^{3+} ion. All materials show only one emission line assigned to $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition ($\sim 17270 \text{ cm}^{-1}$) of the C_2 site of the cubic C-type. The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is present in both sites in the region of 16666, 16846 and 17015 cm^{-1} as well at 16770 and 17165 cm^{-1} originating from the C_2 and S_6 sites.^{42,43}

As reported in references,^{46,47} the refractive index (n) of the bulk $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ is around 1.9 and the $^5\text{D}_0$ lifetime (τ) of europium ion is 1.0 ms. On the other hand, these values can be different in the case of the RE_2O_3 nanostructured materials, with average sizes around 20–30 nm (crystallite size inferior to the wavelength of exciting radiation). Moreover, the morphology and surface/volume ratio of the nanoparticles may play a role in the profile of the decay curves.

The radiative rate (A_{01}) of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition of Eu^{3+} ion (allowed by the magnetic dipole mechanism) is formally insensitive to the ligand field environment. Therefore it can be used as a reference transition which value is 50 s^{-1} assuming a refractive index equal to 1.6.^{17,48,49} Based on this value, the refractive indices were determined and compared to the lifetime and crystallite size values reported previously.^{46–48} The experimental intensity parameters ($\Omega_{2,4}$) and lifetimes (0.8–1.9 ms) values were obtained using the effective refractive index values between 1.5 and 1.6. The values of the experimental intensity parameters ($\Omega_{2,4}$) the radiative (A_{rad}) and non-radiative (A_{nrad}) rates and emission quantum efficiencies (η) of the $^5\text{D}_0$ emitting level of the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ are presented in Table 2.

Figure 7. The a) excitation spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%), with emission monitored at 613 nm, b) emission spectra, with excitation at 260 nm, recorded at 77 K.

The values for Ω_2 (~12) and Ω_4 (~2–3) are very similar in the same matrix (Table 2) for different annealing temperatures as shown the spectral profiles (Figure 7b).⁵⁰ These results are a reflection of the observed emission intensity variations of the $^5D_0 \rightarrow ^7F_2$ transition of the Eu^{3+} ion. This optical behavior demonstrate that the Eu^{3+} ion acts as efficient luminescence probe even for the samples annealed at different temperatures. In addition, Ω_2 and Ω_4 values are also comparable changing the RE^{3+} matrix, due to the similarity in the radii in the lanthanide series.

The experimental intensity parameter values for the phosphors using the TLA ligand as precursor are smaller for all the systems, as compared to those originated from the TMA ligand, especially for the of Gd^{3+} matrix.¹⁹

Table 2. Experimental values of intensity parameters (Ω_k), radiative (A_{rad}) and non-radiative (A_{nrad}) rates, emission lifetimes and emission quantum efficiencies of the 5D_0 emitting level determined for the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) (RE^{3+} : Y, Gd and Lu) phosphors, annealed for 1 hour, based on the emission spectra recorded at 77 K.

$\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%)	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	τ (ms)	η (%)
$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$							
500 °C	12.8	2.4	470	264	734	1.362	64
600 °C	12.6	2.3	461	207	668	1.496	69
700 °C	12.6	2.3	462	181	643	1.555	72
800 °C	12.5	2.2	459	113	571	1.751	80
900 °C	12.1	2.2	446	107	553	1.808	81
1000 °C	11.8	2.1	435	111	546	1.830	80
$\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$							
500 °C	12.6	1.9	458	788	1246	0.803	37
600 °C	12.3	1.9	447	632	1079	0.927	41
700 °C	12.0	1.8	438	428	866	1.155	51
800 °C	12.0	1.8	438	265	702	1.424	62
900 °C	11.7	1.8	430	195	625	1.600	69
1000 °C	11.4	1.7	419	166	585	1.709	72
$\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$							
500 °C	11.5	2.8	434	284	719	1.391	60
600 °C	11.5	2.7	435	253	688	1.454	63
700 °C	11.4	2.7	431	155	588	1.701	73
800 °C	11.5	2.6	433	107	541	1.850	80
900 °C	11.6	2.6	434	95	529	1.890	82
1000 °C	11.2	2.5	422	104	526	1.900	80

According to Table 2, the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ phosphors present an emission quantum efficiency values varying from 37 to 82 % with the annealing temperature (500 – 1000 °C). Among the materials the $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) with annealing at 900 °C present the highest emission quantum efficiency (η =

82 %). This phenomenon is probably associated to the removal of oxycarbonate from the matrices with increasing the annealing temperature. It is important to mention that the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ phosphors prepared by the benzenetricarboxylate method using the TLA ligand is cheaper than compared with the TMA ligand.

Figure 8: CIE Diagram (center) and images of $[\text{RE}(\text{TLA}):\text{Eu}^{3+}]$ (left) and $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ (right), excited at 254 nm.

The CIE (*Commission Internationale de l'Eclairage*) chromaticity coordinates generated from the emission spectra of Eu^{3+} doped RE_2O_3 (Figure 8) are x: 0.650 and y: 0.335.⁴⁹ The color coordinates show virtually no change for different sesquioxide matrices, concentration or annealing temperature. The phosphors containing Gd^{3+} , Y^{3+} , Lu^{3+} ions exhibit the same characteristic nearly monochromatic emission. The images of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (1.0 mol%) nanomaterials under UV irradiation show identical strong red emission for all the phosphors annealed at temperatures from 500 to 1000 °C.

Conclusions

$[\text{RE}(\text{TLA}):\text{Eu}^{3+}]$ complexes present low total decomposition of the organic moiety producing the high luminescent $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ materials at 500 °C. The benzenetricarboxylate method is reliable, efficient and reproducible for the synthesis of phosphors at low temperature. The red emission of the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ materials (RE^{3+} : Y^{3+} , Gd^{3+} and Lu^{3+}) arise mainly from the C_2 symmetry site. The large values of the Ω_2 experimental parameters corroborates with the high intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. Besides, these materials can act as efficient red light conversion devices in the studied Eu^{3+} -concentration range. Finally, the $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ phosphors prepared by the benzenetricarboxylate method using the $[\text{RE}(\text{TLA}):\text{Eu}^{3+}]$ present lower emission quantum efficiency ($\eta \sim 80\%$) than from the $[\text{RE}(\text{TMA}):\text{Eu}^{3+}]$ precursor complexes ($\eta \sim 90\%$). However they are cheaper, becoming an efficient and more economically viable system potentially usable as optical markers.

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Highly luminescent Eu^{3+} -doped benzenetricarboxylate based materials

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ABSTRACT

[RE(TMA)] anhydrous complexes (RE^{3+} : Y, Gd and Lu) present high red emission intensity with a quantum efficiency ($\sim 45\%$) for the $[\text{Y}(\text{TMA})\text{:Eu}^{3+}]$ complexes, due to the absence of non-radioactive decay pathways mediated by water molecules. The complexes were prepared in mild conditions. All the compounds are crystalline and thermostable up to 460°C . Phosphorescence data of the complexes with Y, Gd and Lu show that the T_1 state of the TMA^{3-} anion has energy higher than the $^5\text{D}_0$ emitting level of the Eu^{3+} ion, indicating that the ligand can act as an intramolecular energy sensitizer. The photoluminescence properties of the doped materials were studied based on the excitation and emission spectra and luminescence decay curves. The experimental intensity parameters (Ω_λ), lifetimes (τ), radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates were determined and discussed.

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1. Introduction

In the last decades, complexes containing carboxylate ligands have been extensively used due to their great structural variety in producing materials with large range of chemical properties and applications such as selective markers for medical applications, magnetic materials, gas storage, drug delivery, etc. [1–4].

Rare earth (RE) ions are used in applications like catalyzers and permanent magnets in hybrid cars batteries [5,6]. In photonic science these ions are very important due to their wide range of emissions, from infrared to ultraviolet [7], for e.g. Nd^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} and Tm^{3+} ions which emit in the infrared, red, ultraviolet, green and blue regions, respectively. Besides, RE ions are applied to electroluminescent materials, persistent phosphors, structural probes, luminescent markers, display panels, etc. [8–11].

The luminescent properties of RE^{3+} depend mostly on their unusual energy level structure. The atomic character of the 4f transitions is due to the shielding from the chemical environment by the filled 5s and 5p sub-shells [12]. The 4f intraconfigurational transitions are forbidden to first order by the Laporte rule. Therefore, to overcome the small absorptivity coefficients, luminescence

sensitizers are used to absorb and transfer energy efficiently to the RE ions. This phenomenon is a key feature in design of luminescent materials [13].

The Y^{3+} ($4d^0$) and Lu^{3+} ($4f^{14}$) ions exhibit no luminescence originated from the 4f–4f transitions, Gd^{3+} ($4f^7$) ion have a large energy gap ($\sim 32,000\text{ cm}^{-1}$) between the $^8\text{S}_{7/2}$ ground state and the first $^6\text{P}_{7/2}$ excited state. In the RE^{3+} –TMA (trimesic acid) complexes, the energy level of the first triplet state (T_1) of the ligand is around $24,000\text{ cm}^{-1}$, which is above the emitting $^5\text{D}_0$ level of the Eu^{3+} ion ($\sim 17,000\text{ cm}^{-1}$) [14], enabling the ligand-to-metal energy transfer, involving also the $^5\text{D}_2$ and $^5\text{D}_1$ levels.

The [RE(TMA)] complexes containing La^{3+} to Eu^{3+} ions have six water molecules and are anhydrous for compounds with Tb^{3+} to Lu^{3+} ions (including Y^{3+}). In addition, the Gd^{3+} –complexes can be obtained in both forms, this effect occurs due to the lanthanide contraction. Since the presence of water molecules causes luminescence quenching, the [RE(TMA)] (RE^{3+} : Y, Gd and Lu) complexes can be used as host matrices resulting in the [RE(TMA): Eu^{3+}] systems, showing higher luminescence efficiency compared to the hydrated complexes [14–17].

In this work the synthesis, characterization and optical properties of [RE(TMA): Eu^{3+} ($x\text{ mol}\%$)] compounds (RE^{3+} : Y, Gd and Lu; x : 0.1, 0.5, 1.0, and 5.0 mol%) are reported. These highly luminescent materials were prepared by a one-step synthesis in water. The materials were characterized by elemental analysis, infrared

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spectroscopy (FTIR), thermogravimetry (TG/DTG), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The photoluminescence properties were studied based on the excitation and emission spectra, and luminescence decay lifetimes of the emitting 5D_0 level of the Eu^{3+} ion. The experimental intensity parameters (Ω_λ), 5D_0 lifetime, emission efficiency (η), radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates and CIE color coordinates (x , y) were also determined.

2. Experimental section

The $\text{RECl}_3 \cdot (\text{H}_2\text{O})_6$ were obtained from their respective oxides RE_2O_3 (RE^{3+} : Y, Eu, Gd and Lu^{3+} – Cstarm, 99.99%) by reaction with concentrated HCl. The aqueous solution of trimesic acid (benzene-1,3,5-tricarboxylic acid – Sigma-Aldrich, 95%) was prepared adding NaOH solution until pH reached ~ 6.0 [18].

The doped $[\text{RE}(\text{TMA})\text{:Eu}^{3+}]$ complexes (Eu^{3+} concentration of 0.1, 0.5, 1.0 and 5.0 mol%) were prepared by adding 50 mL of RECl_3 (~ 0.050 M) aqueous solution over 200 mL of previously prepared (TMA^{3-}) ligand aqueous solution (~ 0.0125 M), at temperature of 100°C for 1 h. The resulting solid was filtered and washed with distilled water, the materials are non-hygroscopic white crystalline powders, air-stable and insoluble in a large range of solvents (ethanol, acetone, acetophenone, benzene, chloroform and DMSO) [14].

Elemental analysis was performed with a Perkin-Elmer CHN 2400 analyzer. The FTIR measurements were made in KBr pellets in a Bomem MB100 FTIR instrument from 400 to 4000 cm^{-1} . Thermogravimetry was performed in a TA HI-RES TGA 2850 equipment from 30 to 900°C (heating ramp of 5°C min^{-1} , synthetic air dynamic atmosphere). The XRD patterns were obtained in a Miniflex Rigaku equipment ($\text{CuK}\alpha$) from 5° to 50° (2θ). The SEM micrographs were recorded in a Field Emission Scanning Electron Microscope model JEOL JSM 7401F, the solid samples were placed on a double-sided copper tape.

The luminescence study was based on the excitation and emission spectra recorded at room (300 K) and liquid nitrogen temperature (77 K). The data was obtained in a SPEX-Fluorolog 2 instrument with double monochromators in front face mode (22.5°) with a 450 W xenon lamp as excitation source. Luminescence decay curves were recorded in a SPEX 1934D phosphorimeter accessory with a 150 W pulsed lamp.

3. Results and discussion

The elemental (Table S11) and TG analyses [19] of the coordination compounds confirm that the molar ratio between the RE^{3+} ion and TMA ligand is 1:1 with $[\text{RE}(\text{TMA})\text{:Eu}^{3+}]$ anhydrous general formula. On the other hand, the $[\text{Gd}(\text{TMA}) \cdot (\text{H}_2\text{O})_6\text{:Eu}^{3+}(5.0\text{ mol}\%)]$ system is the only one that is hydrated with 6 water molecules. The TG analysis of the $[\text{RE}(\text{TMA})\text{:Eu}^{3+}]$ anhydrous materials present no mass-loss event in the temperature range from 30 to 460°C , except for Gd^{3+} -system (5.0 mol%) that has water loss event from 50 to 150°C [19]. All the compounds present good thermal stability, corroborating with the elemental analysis data (Table S11). The thermal behavior indicates the formation of metal-organic framework between the RE^{3+} ions and the TMA ligand. The single-step decomposition event from 460 to 580°C correspond to the organic moiety decomposition, yielding their respective sesquioxides (RE_2O_3).

The FTIR spectra of the RE^{3+} -complexes (Fig. 1) shows the absorption bands at $1300\text{--}1600\text{ cm}^{-1}$ assigned to the TMA ligand symmetric $\nu_s(\text{C}=\text{O})$ and asymmetric $\nu_{\text{as}}(\text{C}=\text{O})$ stretching modes. The difference $\Delta\nu$ ($\nu_{\text{as}} - \nu_s$) for $\text{Na}_3(\text{TMA})$ is 195 cm^{-1} and the $\Delta\nu$

Fig. 1. Infrared spectra of the non-doped and doped $[\text{RE}(\text{TMA})\text{:Eu}^{3+}(x\text{ mol}\%)]$ systems.

Fig. 2. XRD patterns of the non-doped and doped $[\text{RE}(\text{TMA})\text{:Eu}^{3+}(x\text{ mol}\%)]$ systems.

values of $[\text{RE}(\text{TMA})\text{:Eu}^{3+}]$ materials are $\sim 175\text{ cm}^{-1}$, indicating bridge-type coordination [15,20]. Moreover, the narrow absorption peak around 3070 cm^{-1} is assigned to C–H bond stretching characteristic of the anhydrous compounds, which is absent in hydrated $[\text{Gd}(\text{TMA}) \cdot (\text{H}_2\text{O})_6\text{:Eu}^{3+}(5.0\text{ mol}\%)]$ complex [14]. The three sharp absorption bands between 690 and 780 cm^{-1} correspond to the out-of-plane C–H bending of the aromatic ring [21]. The infrared absorption spectra (Fig. 1) present similar spectral profile for the doped and undoped anhydrous complexes, except for Gd^{3+} -system (5.0 mol%) corroborated by TG analysis.

The powder XRD patterns (Fig. 2) show no relevant difference, in all the anhydrous samples, indicating that the $[\text{RE}(\text{TMA})\text{:Eu}^{3+}(x\text{ mol}\%)]$ can be grouped in one isomorphous series. The patterns are similar to the data for the $[\text{RE}(\text{TMA})]$, $[\text{RE}(\text{TMA})\text{:Dy}^{3+}]$ anhydrous complexes reported in the literature [15,22] presenting monoclinic structure (C2/m , no. 12) with centrosymmetric feature.

The similarity in the XRD data suggests that the crystalline structure of the $[\text{RE}(\text{TMA})]$ anhydrous complexes presents small perturbation by the doping process indicating the formation of solid solution between the Eu^{3+} dopant and the RE^{3+} in the host matrices due to the comparable radii of these RE^{3+} ions, Vegard's rule [23].

The SEM images show the $6\text{--}12\text{ }\mu\text{m}$ width and $1\text{ }\mu\text{m}$ thickness sheets-like structure of $[\text{Y}(\text{TMA})\text{:Eu}^{3+}(1.0\text{ mol}\%)]$ complex (Fig. 3). The images indicate different morphologies compared with the rods reported in Ref. [14] obtained for the hydrated $[\text{Eu}(\text{TMA}) \cdot (\text{H}_2\text{O})_6]$ complexes.

Fig. 3. SEM images of [Y(TMA):Eu³⁺ (1.0 mol%)].

Fig. 4. Excitation spectra of [RE(TMA):Eu³⁺ (x mol%)] system recorded at 77 K, monitored at 614 nm.

The excitation spectra of [RE(TMA):Eu³⁺ (x mol%)] (RE³⁺: Y, Gd and Lu) and hydrated Gd³⁺ compounds were monitored at the hypersensitive transition ⁵D₀ → ⁷F₂ (614 nm) at 77 K (Fig. 4). The energy levels of the Eu³⁺-samples were assigned to the absorption bands originated from the ground state ⁷F₀ to the excited levels such as (in cm⁻¹): ⁵D₀ (17,280); ⁵D₁ (19,025); ⁵D₂, (21,530); ⁵D₃ (24,380); ⁵L₆ (25,390); ⁵L₇ (26,475); ⁵D₄ (27,670) (based at the [Y(TMA):Eu³⁺ (5.0 mol%)] compound).

As it can be seen, the ⁷F₀ → ⁵L₆ transition (25,390 cm⁻¹) exhibits the highest intensity among the intraconfigurational transitions. The highest intensity of the TMA ligand absorption band is localized in higher energy in the UV region. The efficient energy transfer ligand-to-Eu³⁺ ion is due to the absence of non-radiative decay mediated by water molecules, except for the [Gd(TMA)·(H₂O)₆:Eu³⁺ (5.0 mol%)] compound. Besides, the excitation spectra of the [RE(TMA):Eu³⁺ (x mol%)] anhydrous compounds show similar profile suggesting that this system present equivalent chemical environment around RE³⁺ ions and optical behaviors.

The emission spectra of the [RE(TMA):Eu³⁺ (x mol%)] complexes (RE³⁺: Y, Gd and Lu) were recorded under excitation in the TMA ligand band (~300 nm) at 77 K, to reduce the vibronic coupling compared to the room temperature (Fig. 5). The emission energy levels of ⁵D₀ → ⁷F_J transitions (J=0–4) of the Eu³⁺ ion can be attributed as the following (in cm⁻¹): ⁵D₀ → ⁷F₀ (17,195); ⁷F₁ (16,875); ⁷F₂, (16,190); ⁷F₃ (15,040) and ⁷F₄ (14,215).

The ⁵D₀ → ⁷F₀ transition presents only one emission band indicating that the Eu³⁺ ion occupies one symmetry site [24]. The emission spectra show comparable intensities for the hypersensitive transition ⁵D₀ → ⁷F₂, allowed by the forced electric dipole and

dynamic coupling mechanisms for non-centrosymmetric point groups, and ⁵D₀ → ⁷F₁, allowed by magnetic dipole mechanism character [12,21]. The decrease in the phosphorescence intensities of the TMA ligand broad band in the region 420–500 nm with the increase of the Eu³⁺ concentrations indicates that the energy transfer process becomes more efficient [25,26].

Using the emission spectra it is possible to obtain the radiative rates ($A_{0 \rightarrow J}$) for the ⁵D₀ → ⁷F_J transitions by Eq. (1) [12,17]

$$A_{0 \rightarrow J} = \left(\frac{\sigma_{0 \rightarrow 1}}{\sigma_{0 \rightarrow 1}} \right) \left(\frac{S_{0 \rightarrow J}}{S_{0 \rightarrow 1}} \right) A_{0 \rightarrow 1} \quad (1)$$

where $\sigma_{0 \rightarrow 1}$ and $\sigma_{0 \rightarrow J}$ correspond to the energy barycenters of the ⁵D₀ → ⁷F₁, taken as the reference due to its magnetic dipole character, and ⁵D₀ → ⁷F_J transitions, respectively. The $S_{0 \rightarrow 1}$ and $S_{0 \rightarrow J}$ are the emission areas of the spectrum corresponding to the ⁵D₀ → ⁷F₁ and ⁵D₀ → ⁷F_J transitions, respectively [27]. Since the magnetic dipole ⁵D₀ → ⁷F₁ transition is almost insensitive to changes in the chemical environment around the Eu³⁺ ion the $A_{0 \rightarrow 1}$ rate can be used as an internal standard to determine the $A_{0 \rightarrow J}$ coefficients for Eu³⁺ compounds [17].

The lifetime (τ) of the [RE(TMA):Eu³⁺ (x mol%)] materials were obtained from the luminescence decay curve using a mono-exponential exponential decay. The emission quantum efficiency (η) of the ⁵D₀ emitting level is determined according to Eq. (2)

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{nr}}} \quad (2)$$

where the total decay rate, $A_{\text{tot}} = 1/\tau = A_{\text{rad}} + A_{\text{nr}}$ and the $A_{\text{rad}} = \sum_j A_{0 \rightarrow j}$. The A_{rad} and A_{nr} are the radiative and non-radiative rates, respectively. Table 1 shows the experimental values of the radiative (A_{rad}) and non-radiative (A_{nr}) rates, and emission quantum efficiency (η).

The transitions ⁵D₀ → ⁷F₂ and ⁵D₀ → ⁷F₄ can be used to estimate the experimental intensity parameters (Ω_λ , $\lambda=2$ and 4). The Ω_6 intensity parameter is not included in this study since the ⁵D₀ → ⁷F₆ transition was not observed in these materials. The coefficient of spontaneous emission, A, is given by Eq. (3)

$$A_{0 \rightarrow J} = \frac{4e^4 \omega^3}{3hc^3} \chi \sum_\lambda \Omega_\lambda \langle 7F_J || U^{(\lambda)} || 5D_0 \rangle^2 \quad (3)$$

where, $\chi = n(n+2)^2/9$ is the Lorentz local field correction and n is the refraction index of the medium (1.5 for these materials). The square reduced matrix elements $\langle 7F_J || U^{(\lambda)} || 5D_0 \rangle^2$ are 0.0032 and 0.0023 calculated for $J=2$ and 4, respectively [27,28].

The Ω_λ parameters depend on the local geometry, bonding atom and polarizabilities in the first coordination sphere of metal ion. The three parameters depend equally on the ligating atom

Fig. 5. Emission spectra of the doped [RE(TMA):Eu³⁺(x mol%)] systems recorded at 77 K, under excitation at 300 nm.

Table 1

Experimental intensity parameters ($\Omega_{2,4}$), radiative (A_{rad}), non-radiative (A_{nrad}) and total (A_{tot}) rates, lifetimes of the 5D_0 emitting level (τ) and quantum efficiencies (η) for the [RE(TMA):Eu³⁺(x mol%)] materials.

[RE(TMA):Eu ³⁺ (x mol%)]	Ω_2	Ω_4	A_{rad}	A_{nrad}	A_{tot}	τ	η
	(10 ⁻²⁰ cm ⁻²)	(10 ⁻²⁰ cm ⁻²)	(s ⁻¹)	(s ⁻¹)	(s ⁻¹)	(ms)	(%)
[Y(TMA):Eu ³⁺ (0.1)]	2	1	154	202	356	2.81	43
(0.5)	2	1	152	188	339	2.95	45
(1.0)	2	1	155	185	340	2.94	46
(5.0)	2	1	157	204	362	2.76	43
[Gd(TMA):Eu ³⁺ (0.1)]	2	2	160	190	348	2.87	46
(0.5)	2	1	155	187	341	2.93	45
(1.0)	2	2	135	249	384	2.60	35
[Gd(TMA)·(H ₂ O) ₆ :Eu ³⁺ (5.0)]	6	3	147	1935	2083	0.73	7
[Lu(TMA):Eu ³⁺ (0.1)]	2	1	153	195	348	2.87	44
(0.5)	2	1	156	190	346	2.89	45
(1.0)	2	1	160	182	342	2.92	47
(5.0)	2	1	153	166	320	3.13	48
[Eu(TMA)·(H ₂ O) ₆] ^a	11	10	623	2015	2637	0.23	12

^a Ref. [14].

polarizability. However, according to theory, the Ω_2 values are by far the most sensitive to small angular changes in the chemical environment around the Eu³⁺ ion, and it tends rapidly to decrease as the local symmetry tends to a higher one, possibly towards a one with center of inversion.

On the other hand Ω_4 and Ω_6 are by far the most sensitive to ligating atom–metal ion distances, and do not necessarily decrease rapidly as the local symmetry tend to a higher one, possibly towards a one with center of inversion. The Ω_λ ($\lambda=2$ and 4) values for the [RE(TMA):Eu³⁺(x mol%)] compounds ($x=0.1, 0.5, 1.0$ and 5.0 mol%) are presented in Table 1. The Ω_2 values of [RE(TMA)] are much smaller ($\sim 2 \cdot 10^{-20} \text{ cm}^{-2}$) than that of [Eu(TMA)·(H₂O)₆] complex ($\sim 11 \cdot 10^{-20} \text{ cm}^{-2}$) [14], agreeing with the crystallography data [21], which show that the anhydrous complex tends to a point group with inversion center [29,30]. Thus, these theoretical considerations might be used to rationalize the Ω_λ behaviors in Table 1.

The lifetime values (~ 2.90 ms) presented by the [RE(TMA):Eu³⁺(x mol%)] phosphors are longer than for the majority of the Eu³⁺-complexes reported in the literature [14,17] and one order of magnitude higher than the [Eu(TMA)·(H₂O)₆] (0.23 ms) and three

times higher than the [Gd(TMA)·(H₂O)₆:Eu³⁺(5.0 mol%)] (0.73 ms). This optical property corroborates that the absence of water molecules is very important, as indeed expected, to the photoluminescence efficiency, avoiding the luminescence quenching, due the non-radiative decay pathways mediated by vibrational levels of the O–H oscillators.

The emission quantum efficiency values of the anhydrous compounds ($\eta \sim 45\%$) are higher than for [Eu(TMA)·(H₂O)₆] ($\eta=12\%$) and [Gd(TMA)·(H₂O)₆:Eu³⁺(5.0 mol%)] ($\eta=7\%$) complexes confirming that the water molecules are responsible to the luminescence quenching for the hydrated compounds (Table 1) [14]. Moreover, the increase in the Eu³⁺ concentration from 0.1 to 5.0 mol% does not affect the emission quantum efficiency suggesting that the luminescence quenching concentration effect is not operative.

The color coordinates of the complexes in the CIE chromaticity diagram (Commission Internationale de l'Eclairage) are shown in Fig. 6 (left) [31]. The color purity increases with the raise of Eu³⁺-doping concentration (0.651, 0.337 for [Y(TMA):Eu³⁺(5.0 mol%)]). The [RE(TMA):Eu³⁺(x mol%)] crystalline powder samples emits an intense red light, when irradiated with light in the ultraviolet region Fig. 6 (right).

Fig. 6. CIE chromaticity diagram showing the x,y emission color coordinates for [Y(TMA):Eu³⁺ (x mol%)] (x: 0.1 (left), 0.5, 1.0 and 5.0 (right)) and picture of [RE(TMA):Eu³⁺ (1.0 mol%)] (RE³⁺: Y, Gd and Lu), irradiated at 254 nm. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

4. Conclusion

The highly efficient anhydrous red emitting [RE(TMA):Eu³⁺] materials were prepared by a one-step synthesis in aqueous solution. The TG curves show the absence of water molecules in the structure, thermostability up to 460 °C and single-step decomposition of the organic moiety. The XRD data indicate an isostructural series for the anhydrous complexes. The TMA ligand T₁ state has higher energy than the ⁵D₀ (Eu³⁺) emitting level, acting as intramolecular energy transfer donor to the Eu³⁺ ion. The [RE(TMA):Eu³⁺] anhydrous compounds present monochromatic red emission and quantum efficiency at around 45%. The small values of the Ω_2 and Ω_4 parameters for the anhydrous compounds corroborates with a local point symmetry and also a rather low polarizability around the Eu³⁺ ion, respectively. Photoluminescence data show that these materials can act as an efficient red light conversion molecular devices (LCMDs) and the lowest Eu³⁺-concentration doped compounds can be used as efficient and more economically viable optical markers.

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Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jlumin.2015.04.047>.

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IV

White emission phosphors based on Dy³⁺-doped into anhydrous rare-earth benzenetricarboxylate complexes

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ABSTRACT

White light emitting rare earth anhydrous complexes RE(TMA):Dy³⁺ (RE³⁺ = Y³⁺ and Lu³⁺) containing the trimesic acid ligands (TMA) were synthesized and characterized by elemental analysis, X-ray diffraction patterns, thermogravimetric analysis and infrared spectroscopy. The crystallinity and thermostability of these luminescent materials were determined. Since the first excited triplet state (T_1 : 24,000 cm⁻¹) of TMA ligand is located at higher energy than the main emitting ⁴F_{9/2} level (21,000 cm⁻¹) of the Dy³⁺ ion, TMA can act as efficient luminescent sensitizer in the intramolecular energy transfer of RE(TMA):Dy³⁺ material. The near-white emission colour originated from the intraconfigurational transitions of Dy³⁺ ion ⁴F_{9/2} → ⁶H_j is discussed.

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1. Introduction

The carboxylate complexes have been gaining ground in the area of coordination compounds in the past decades due to the variety of their molecular structures which enables different chemical applications in solid state as gas storage molecular devices [1], nanostructured magnetic materials [2]. These properties allow the construction of a wide range of coordination compounds and their widespread use in many areas of knowledge, such as synthesis precursor materials [3], biomarkers [4], and optical markers [5].

Rare earth ions (RE) have been widely used as emitting centres in luminescent applications, such as organic light emitting devices (OLEDs) [6], emergency signalling [7], luminescent markers [8] and display panels [9]. Some of the RE³⁺ ions exhibit visible emission, for example, the Eu³⁺, Tb³⁺ and Tm³⁺ ions emit in the red, green and blue region, respectively [10]. The RE³⁺ luminescence properties depend mainly on the electronic energy level structures that are little affected by their chemical environments owing to the effective shielding of the 4f electrons by the filled 5s and 5p external sub-shells [11]. Furthermore, to overcome the small molar absorptivity coefficients (<1 L mol⁻¹ cm⁻¹) of the RE³⁺ ions, the coordination ligands such as carboxylate and β-diketonate groups are widely used, mainly because of their high absorptivity coefficient and luminescence sensitising abilities. This phenomenon is often denoted as the *antenna effect*, largely used in the design and synthesis of luminescent complexes [12].

From the point of view of RE³⁺ optical characteristics, Dy³⁺ (4f⁹) ion has relatively large energy gap between their ⁴F_{9/2} emitting and ⁶H_j ground levels. The first triplet state (T_1) position of TMA ligand is around 24,000 cm⁻¹, which is above the emitting ⁴F_{9/2} level (~21,000 cm⁻¹) of the Dy³⁺ ion [13], permitting the ligand-to-metal energy transfer in the TMA complexes. On the other hand, Y³⁺ (4d⁰) and Lu³⁺ (4f¹⁴) ions exhibit no luminescence originated from the 4f intraconfigurational transitions. In addition, the Y(TMA) and Lu(TMA) complexes present no water molecules in the coordination sphere as a result of the smaller ionic radii of Y³⁺ and Lu³⁺ cations [14]. Therefore, trivalent dysprosium ion and RE(TMA) complexes were selected in the present study as the optical activator and host matrices, respectively.

It is reported the synthesis, characterization and optical properties of the non-doped RE(TMA) and doped RE(TMA):Dy³⁺(x%) materials (RE³⁺: Y and Lu; x: 0.1%, 0.5%, 1.0%, 5.0% and 10% mol) in this work. Photoluminescence data were obtained from the excitation and emission spectra and lifetimes measurements. The non-radiative energy transfer from the excited triplet state (T) of TMA ligand to the emitting ⁴F_{9/2} level of the Dy³⁺ ion as function of concentration (x% mol) were also investigated. The RE(TMA):Dy³⁺(x%) phosphors yield white-light emission.

2. Experimental section

2.1. Synthesis of the doped RE(TMA) system

The RE³⁺ chlorides were obtained from their respective oxides RE₂O₃ (Cstarm, 99.99%) by digestion of its aqueous suspension

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with the addition of concentrated hydrochloric acid until pH reaches 6. $\text{RECl}_3 \cdot (\text{H}_2\text{O})_6$ crystals were obtained and dried by water bath and afterwards stored under reduced pressure.

The trimesic acid (benzene-1,3,5-tricarboxylic acid – Fluka, 97%), $\text{H}_3(\text{TMA})$ (Fig. 1), was used without further purification. Considering the RE^{3+} ions as hard acids, the binding of these ions with carboxylates (hard base) is favoured because of their high negative charge density [15]. Since the pK_a 's of the $\text{H}_3(\text{TMA})$ are 3.12, 3.89 and 4.70 [16], its aqueous solution was prepared by the addition of 1 M sodium hydroxide solution until pH reached ~ 6.0 . At this condition, all carboxylate groups are deprotonated.

For the preparation of the doped $\text{RE}(\text{TMA})\text{:Dy}^{3+}(\text{x}\%)$ materials, 50 mL of RECl_3 (~ 0.050 M) aqueous solution of Y^{3+} or Lu^{3+} , with the required molar ratio of Dy^{3+} (0.1%, 0.5%, 1.0%, 5.0% and 10%) was dripped slowly (~ 1 drop per second) over 200 mL of previously prepared $(\text{TMA})^{3-}$ ligand aqueous solution (~ 0.0125 M) at boiling point at molar ratio 1:1. The reaction was refluxed for about 4 h and the resulting precipitate was filtered and washed with distilled water four times. The obtained complexes are air-stable and non-hygroscopic white crystalline powders. Besides, the complexes are insoluble in different solvents such as acetone, alcohol, DMSO, acetonitrile, chloroform, water or their mixtures [17].

2.2. Characterization techniques

Elemental analysis was performed in Perkin-Elmer CHN 2400. The infrared absorption spectra were performed using KBr pellets, with the equipment Bomem MB100 FTIR in the spectral region from 400 to 4000 cm^{-1} . The X-ray diffraction patterns were recorded by a Miniflex Rigaku (Cu $\text{K}\alpha 1$) from 4° to 60° (2θ). Thermogravimetry curves were obtained with the 2950 TGA HR V5.4A equipment from 30 to 900°C in a dynamic atmosphere of synthetic air with constant heating ramp of 5°C min^{-1} .

The photoluminescence study was conducted based on the excitation and emission spectra recorded at room temperature and 77 K, using the front-face data collection mode (22.5°), utilizing a 450 W Xenon lamp as excitation source coupled to the equipment SPEX-Fluorolog 2 with double monochromators. With a 150 W pulsed lamp attached to the phosphorimeter SPEX 1934D accessory, photoluminescence decay curves were recorded.

3. Results and discussion

The chemical composition of the RE^{3+} -TMA system determined by elemental analysis and calculated values are presented in Table S01. These results confirm the general 1:1 ratio between the TMA ligand and RE^{3+} ions and the absence of the coordinated water molecules in the $\text{RE}(\text{TMA})\text{:Dy}^{3+}(\text{x}\%)$ system.

The IR spectras were registered at room temperature and presented in Fig. S01. The symmetric $\nu_s(\text{C}=\text{O})$ and asymmetric $\nu_{as}(\text{C}=\text{O})$ stretching modes of the carboxylate group of the TMA

Fig. 1. Structural formula of the 1,3,5-benzenetricarboxylic acid – $\text{H}_3(\text{TMA})$.

ligand are observed in the spectral range from 1400 to 1600 cm^{-1} . The $\Delta\nu$ for $\text{Na}_3(\text{TMA})$ is 195 cm^{-1} ; the $\Delta\nu$ values of $\text{RE}(\text{TMA})\text{:Dy}^{3+}(\text{x}\%)$ materials are in the range of 150 to 160 cm^{-1} , indicating bridge-type coordination [18]. The sharp band observed in the infrared spectra of the $\text{Y}(\text{TMA})\text{:Dy}^{3+}(\text{x}\%)$ and $\text{Lu}(\text{TMA})\text{:Dy}^{3+}(\text{x}\%)$ samples around 3075 cm^{-1} is assigned to C–H bond stretching (Fig. S01). Besides, three sharp absorption bands were identified between 690 and 780 cm^{-1} which correspond to the out-of-plane C–H bending of the aromatic ring [19]. These IR spectral profiles are characteristics of anhydrous $\text{RE}(\text{TMA})$ materials.

The powder X-ray diffraction patterns of the doped and non-doped complexes are similar (Fig. 2). In addition, they present resemblances to the X-ray data for the $\text{Dy}(\text{TMA})$, $\text{Y}(\text{TMA})$ and $\text{Y}(\text{TMA})\text{:Eu}^{3+}$ anhydrous complexes reported by Serre et al. [20] and for the $\text{Y}(\text{TMA})\text{:H}_2\text{O}_6$ hydrated coordination compound reported by Daiguebonne et al. [21]. Whereas these X-ray diffraction patterns show small differences in the intensity and peak positions, except for the different intensity ratios between the diffraction peaks possibly due to the platelet-shaped of the samples and the presence of a peak around 26° . Furthermore, when the Dy^{3+} doping concentration changes, the diffraction peaks assigned to the $\text{Y}(\text{TMA})$ and $\text{Lu}(\text{TMA})$ host matrices show no displacement or formation of new diffraction patterns. These results also indicated the formation of a solid solution between the Dy^{3+} ion dopant and the RE^{3+} -matrices (RE^{3+} : Y and Lu) due to the similarity between the radii of rare earth ions (Fig. 2).

Fig. 3 shows the thermogravimetric curves of $\text{RE}(\text{TMA})\text{:Dy}^{3+}(\text{x}\%)$ system, which present no weight-loss event in the temperature range from 30 to 450°C , indicating good thermal stability of the samples. This can be explained by the formation of metal–organic framework between the RE^{3+} ions and the TMA ligand. The nonappearance of the weight-loss event corresponding to the release of water molecules in this temperature interval also confirms that the $\text{RE}(\text{TMA})\text{:Dy}^{3+}$ system are anhydrous, corroborating the elemental analysis. On the other hand, in the temperature interval of 450 to 600°C , the doped system presents only one single-step decomposition of the organic moiety, resulting in the formation of their respective sesquioxides (RE_2O_3).

4. Photoluminescent study

It is noteworthy to mention that the Dy^{3+} ion has an odd-electron configuration ($4f^9$). Therefore, it is labelled as a Kramer ion due to its electronic states that are at least doubly degenerate for any crystal-field perturbation. The maximum number of the Stark components for Kramer ions with $^{2S+1}L_J$ states is $J + 1/2$ for any symmetry lower than cubic [22].

The excitation spectra of the $\text{Y}(\text{TMA})\text{:Dy}^{3+}(\text{x}\%)$ system with emission monitored at 577 nm corresponding to the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transition of the Dy^{3+} ions are shown in Fig. 4 (left). The broad absorption band centered at 300 nm which is assigned to the TMA ligand is more intense than the narrow absorption peaks arising from $4f$ intraconfigurational transitions of the Dy^{3+} ion [17]. With the increased Dy^{3+} -doping, the $4f$ – $4f$ transitions become more pronounced. From the position of these absorption bands originated from the $^6\text{H}_{15/2}$ ground state of the Dy^{3+} ion, the excited energy levels can be attributed as the following (in cm^{-1}): $^4\text{F}_{9/2}$ (21,230); $^4\text{I}_{15/2}$ (22,269); $^4\text{G}_{11/2}$ (23,585); $^4\text{M}_{21/2}$ (25,316); $^4\text{K}_{17/2}$, $^4\text{F}_{7/2}$, $^4\text{I}_{13/2}$ (25,974); $^4\text{M}_{11/2}$ (26,523); $^6\text{P}_{5/2}$ (27,548); $^4\text{I}_{11/2}$ (28,011), $^4\text{M}_{11/2}$, $^6\text{P}_{7/2}$ (28,653); $^4\text{F}_{5/2}$, $^4\text{I}_{9/2}$ (29,673) and $^6\text{P}_{3/2}$ (30,864) (Fig. 4 right). As can be observed, the $^6\text{H}_{15/2} \rightarrow ^6\text{P}_{5/2}$ transition ($27,548\text{ cm}^{-1}$) exhibits the highest intensity among the $4f^9$ intraconfigurational transitions, indicating that in this case the direct excitation can be also used these transition from the dysprosium ion.

Fig. 2. X-ray powder diffraction patterns of the non-doped complexes and doped RE(TMA):Dy³⁺(x%) system (RE: Y³⁺, Dy³⁺ and Lu³⁺; x: 5.0% and 10%).

These spectroscopic results suggest an efficient intramolecular energy transfer from the TMA ligand to the Dy³⁺ ion [23]. The excitation spectra of Lu(TMA):Dy³⁺ system, as well as the spectra registered at 300 K, display very similar profiles compared to the Y³⁺ based complexes and are shown in the Fig. S02.

One important fact is that the Dy(TMA) complex does not exhibit emission bands assigned to the Dy³⁺ ion in the spectral range of 400–800 nm. This optical behaviour is owing to the nature of small energy differences between the energy levels of dysprosium ion, resulting in luminescence predominantly in the infrared range. The luminescence is also greatly quenched by the cross relaxation mechanism, which is favoured by the short distance between the Dy³⁺ ions due to the bridge-type coordination of the TMA ligand.

However, the Y(TMA) and Lu(TMA) complexes exhibit no luminescence arisen from the RE³⁺ ions due to the vacant or completely filled 4f subshell of the Y³⁺ and Lu³⁺ ions, respectively [14]. By doping the Dy³⁺ into the RE(TMA) matrices with a relatively low concentration, the inter-system crossing is reduced as the Dy³⁺ ions are well dispersed and separated, providing an increased physical distance between the Dy³⁺ ions, subsequently reducing the non-radiative decay pathways [23]. Therefore, the desired luminescence can be fine-tuned and enhanced.

The emission spectra of the RE(TMA):Dy³⁺ system (RE = Y³⁺ and Lu³⁺) at liquid nitrogen temperature were recorded and shown in Fig. 5. The emission spectra are dominated by the ⁴F_{9/2}→⁶H_{15/2} (~20,620 cm⁻¹) and ⁴F_{9/2}→⁶H_{13/2} (~17,240 cm⁻¹) transitions originated from the Dy³⁺ ions in the visible region, yielding the near-white emission colour. Besides, the ⁴F_{9/2}→⁶H_{11/2} (~14,930 cm⁻¹) and ⁴F_{9/2}→⁶H_{9/2}, ⁶F_{11/2} (~13,240 cm⁻¹) transitions can be observed, however, with low emission intensities. It is observed that the emission spectra of Y(TMA):Dy³⁺ system (Fig. 5, left) are very similar with those recorded for the Lu³⁺ ion (Fig. 5, right), suggesting

Fig. 3. Thermogravimetric curves of solid samples Y(TMA):Dy³⁺(x%) (top) and Lu(TMA):Dy³⁺(x%) (down). All curves were recorded in dynamic synthetic air atmosphere.

that both rare earth ions can act as excellent luminescent matrices for this compounds. The emission spectra recorded at room temperature are shown in Fig. S03. They exhibit similar profiles with decreased peak-resolution due to increased vibronic contribution.

The absence of broadened phosphorescence band of the TMA ligand in the blue region (~450 nm) for the RE(TMA):Dy³⁺ system recorded at 77 K is more evident for compounds with doping concentration of Dy³⁺ ion from 0.5% to 10% (Fig. 5). When the spectra were recorded at room temperature (Fig. S03), the emission band from TMA ligand is not observed even at lower Dy³⁺-doping concentration (0.1%), suggesting that energy transfer from the lowest triplet state of the TMA ligand to the dysprosium ion is very efficient.

The lifetimes (τ) of the emitting ⁴F_{9/2} level of the Dy³⁺ ion were determined by first order exponential fitting of the photoluminescence decay curves registered at 300 K, monitoring the excitation and emission at 450 and 577 nm, respectively (Table 1). As the Dy³⁺-doping increases from 0.1% to 10%, the lifetime values decrease slightly, from 0.37 to 0.20 ms (Fig. 6). This results can be explained by the fact that the Dy³⁺ ions are well-dispersed in the RE(TMA) matrices, therefore the lifetimes of the emitting ⁴F_{9/2} level is relatively higher due to smaller cross relaxation. When the Dy³⁺-doping concentration increases, the lifetime is quenched by concentration due to increased degree of cross relaxation. Besides, the longer lifetime values of the emitting ⁴F_{9/2} level in the anhydrous RE(TMA):Dy³⁺ system are also associated with the absence of nonradiative decay channel induced by the vibronic coupling of the O–H oscillators of the water molecules [22]. Fig. 6.

Fig. 4. The excitation spectra of the Y(TMA):Dy³⁺(x%) system (left) and magnified peaks for the Dy³⁺(10%)-doped compound (right) recorded at 77 K, monitoring ⁴F_{9/2}→⁶H_{13/2} transition (577 nm).

Fig. 5. Emission spectra of the doped Y(TMA):Dy³⁺(x%) (left) and Lu(TMA):Dy³⁺(x%) (right) system recorded at 77 K, under excitation at 300 nm.

Table 1
Lifetimes (τ) of the excited $^4F_{13/2}$ state of RE(TMA):Dy $^{3+}$ system.

Doping concentration (%)	Lifetimes	
	Y(TMA):Dy $^{3+}$ (ms)	Lu(TMA):Dy $^{3+}$ (ms)
0.1	0.370	0.374
0.5	0.362	0.360
1.0	0.357	0.345
5.0	0.272	0.272
10	0.225	0.204

Fig. 6. Lu(TMA):Dy $^{3+}$ (x%) lifetimes versus dysprosium doping concentrations (x: 0.1%, 0.5%, 1.0%, 5.0% and 10%).

Fig. 7. CIE chromaticity diagram showing the x,y emission colour coordinates for: (a) Y(TMA):Dy $^{3+}$ (0.1%), (b) Lu(TMA):Dy $^{3+}$ (0.1%) and (c) RE(TMA):Dy $^{3+}$ (x%) (x: 0.5%, 1.0%, 5.0% and 10%; RE $^{3+}$: Y and Lu). The inset figure is of the Y(TMA):Dy $^{3+}$ (5.0%) powder taken with a digital camera displaying the near-white emission colour, under UV irradiated at 254 nm.

The emission colour chromaticity of these RE(TMA):Dy $^{3+}$ complexes was studied and the CIE (*Commission Internationale de l'Éclairage*) diagram is presented in Fig 7. It is important to mention

that the emission colour is independent to the Dy $^{3+}$ doping concentration and most phosphors present the same coordinates (0.373, 0.379) in the CIE diagram [24]. This result indicates that the RE(TMA):Dy $^{3+}$ rare earth phosphors exhibits near-white emitting colour.

5. Conclusion

Dy $^{3+}$ -doped anhydrous Y(TMA) and Lu(TMA) inorganic matrices were synthesized using an aqueous reaction. Under the UV excitation at the ligand absorption band, the resulting insoluble luminescent materials exhibit strong near-white emission arising from the $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$ intraconfigurational transitions of the Dy $^{3+}$ ions. Combined with their excellent thermal stability, these complexes can be considered as promising candidates for white-light emitting phosphors.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.optmat.2012.12.001>.

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V

Red (Eu^{3+}), Green (Tb^{3+}) and Ultraviolet (Gd^{3+}) Emitting Nitrilotriacetate Complexes Prepared by One-step Synthesis

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The $[\text{RE}(\text{NTA})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$ rare-earth complexes (RE^{3+} : Eu, Gd, Tb and NTA: nitrilotriacetate) were synthesized and characterized by elemental analysis, thermogravimetry, X-ray diffraction, and infrared spectroscopy. The complexes show high crystallinity and thermostability. The photoluminescence behavior was studied based on the excitation and emission spectra, and luminescence decay curves. The compounds exhibit red (Eu^{3+}), green (Tb^{3+}) and UV (Gd^{3+}) monochromatic emissions under UV excitation. The NTA ligand acts as luminescence sensitizer in the ligand-to- RE^{3+} intramolecular energy transfer process, owing to the fact that the first excited triplet state (T_1 : 29 000 cm^{-1}) is located above of the $^5\text{D}_0$ (Eu^{3+}) and $^5\text{D}_4$ (Tb^{3+}) emitting levels. The experimental intensity parameters Ω_λ (λ : 2 and 4) for the Eu^{3+} NTA complex were calculated, and the results are discussed. The Gd^{3+} -NTA complex exhibits a high-intensity emission band in the UV region (32 000 cm^{-1}) assigned to the $^6\text{P}_{7/2} \rightarrow ^8\text{S}_{7/2}$ intraconfigurational transition.

Key words: Rare-Earth Complexes, Tricarboxylates, Synthesis, Intramolecular Energy Transfer, Photoluminescence

Introduction

Complexes containing carboxylate ligands have been studied in many research areas due to the variety of their molecular structures which enables different chemical applications such as gas storage systems [1] or nanostructured magnetic materials [2]. These properties allow the construction of a wide range of materials and their widespread use in many areas, such as the synthesis of precursor materials [3], immunoassays [4] and optical markers [5]. The rare-earth complexes (RE) have been widely used as organic light-emitting devices (OLEDs) [6], emergency signage [7], luminescence markers [8], display panels [9], among others.

The spectroscopic properties of the RE elements are based on their peculiar electronic configuration of the filled $5s^2$ and $5p^6$ subshells which are beyond the $4f$ subshell, shielding it efficiently from the chemical environment and providing monochromatic emission [10]. Therefore, the RE^{3+} ions present narrow absorption and emission bands, maintaining their atomic character, which facilitates the interpretation of their energy level structures [11].

The RE^{3+} ions have low molar absorption coefficients because the $4f$ intraconfigurational transitions are forbidden by the Laporte rule, so the probability of these transitions is very low. In order to overcome this shortcoming, coordinating ligands such as carboxylate and β -diketonate groups are widely used, mainly be-

Fig. 1. Structural formula of nitrilotriacetic acid, $H_3(NTA)$.

cause of their high absorptivity coefficient in the UV region and the luminescence-sensitizing abilities [12]. This phenomenon is often denoted as the *antenna effect*, largely used in the design of luminescent RE^{3+} complexes [13].

Nitrilotriacetic acid $H_3(NTA)$, depicted in Fig. 1 is applied mostly in aqueous solution since the NTA ligand can be used as a biodegradable and biologically compatible substitute for EDTA as carrier of a large variety of metal ions [14, 15]. There are studies about the optical behavior of the RE^{3+} nitrilotriacetate complexes in solution [16, 17].

In this article, we report the one-step synthesis of complexes of the type $[RE(NTA)(H_2O)_2] \cdot (H_2O)$ and the study of their luminescence properties in the solid state. Photoluminescence data were obtained from the excitation, emission spectra and luminescence decay curves. The energy transfer processes from NTA excited states to the intraconfigurational states of the RE^{3+} ions were also investigated. The experimental intensity parameters (Ω_2 and Ω_4) were determined using the $^5D_0 \rightarrow ^7F_{2,4}$ transitions.

Experimental Section

Nitrilotriacetic acid (97%, Sigma-Aldrich) was used without further purification. The NTA^{3-} ligand solution was prepared by adding NaOH (1.0 M) to the aqueous ligand suspension until pH $\approx$ 6. The rare-earth chlorides $RECl_3 \cdot (H_2O)_6$ were obtained from their oxides (99.99%) Eu_2O_3 and Gd_2O_3 by dissolution in concentrated HCl. Tb_4O_7 was treated with addition of H_2O_2 . The obtained crystalline solids were dried on a water bath and stored under reduced pressure.

Syntheses

The RE^{3+} -NTA complexes were prepared by adding 50 mL of the $RECl_3(aq)$ solution (0.050 M) dropwise to 200 mL of the NTA^{3-} ligand solution (0.0125 M) and heating

the mixture at the boiling point for 4 h. The precipitates were filtered and washed three times with distilled water [18]. The rare-earth complexes are colorless crystalline powders, non-hygroscopic and insoluble in acetone, ethanol, DMSO, acetonitrile and chloroform.

$[Eu(NTA)(H_2O)_2] \cdot (H_2O)$: Elemental analysis (%) for $C_6H_{12}NO_9Eu$: calcd. C 18.28, H 3.07, N 3.5, Eu 38.56; found C 18.41, H 2.92, N 3.55, Eu 39.02. $[Gd(NTA)(H_2O)_2] \cdot (H_2O)$: Elemental analysis (%) for $C_6H_{12}NO_9Gd$: calcd. C 18.04, H 3.03, N 3.51, Gd 39.37; found C 18.14, H 2.92, N 3.41, Gd 39.74. $[Tb(NTA)(H_2O)_2] \cdot (H_2O)$: Elemental analysis (%) for $C_6H_{12}NO_9Tb$: calcd. C 17.97, H 3.02, N 3.49, Tb 39.62; found C 18.11, H 2.96, N 3.45, Tb 39.80.

Elemental analyses were performed with a Perkin-Elmer CHN 2400 analyzer. The complexometric titrations were performed using a microburette with the disodium ethylenediaminetetraacetic acid (EDTA) salt. The XRD patterns were recorded on a Miniflex Rigaku instrument (CuK_{α}) from 4 to 60° (2θ). The infrared absorption spectra (FTIR) were performed using KBr pellets with a Bomem MB100 FTIR instrument in the spectral region from 400 to 4000 cm^{-1} . Thermogravimetry curves were obtained with the TA Instruments HI-RES TGA 2850 equipment from 30 to 900°C in a dynamic atmosphere of synthetic air with a constant heating ramp of 5°C min^{-1} .

The luminescence study was based on the excitation and emission spectra recorded at room temperature (300 K) and in liquid nitrogen (77 K). The data were collected in front face mode (22.5°) with a 450 W xenon lamp as excitation source coupled to a SPEX-Fluorolog 2 instrument with double monochromators. Luminescence decay curves were recorded using a SPEX 1934D phosphorimeter accessory with a 150 W pulsed lamp.

Results and Discussion

Characterization

The elemental analyses and complexometric titrations confirmed the molar ratio of RE to NTA (1 : 1) and three water molecules, resulting in the general formula $[RE(NTA)(H_2O)_2] \cdot (H_2O)$ where RE^{3+} : Eu, Gd and Tb.

XRD patterns of the Eu^{3+} , Gd^{3+} and Tb^{3+} complexes and the calculated data based on the $[Sm(NTA)(H_2O)_2] \cdot (H_2O)$ structure obtained by Yu *et al.* [19] are presented in Fig. 2. The experimental and calculated XRD patterns are very similar, suggesting an isomorphic complex series. The coordination geometry of the RE^{3+} center can be described as a capped

Fig. 2 (color online). Powder X-ray diffraction patterns of $[RE(NTA)(H_2O)_2] \cdot (H_2O)$ complexes (RE^{3+} : Eu, Gd and Tb) recorded at room temperature, and calculated data.

square antiprism. The coordination occurs by the carboxylate oxygen atoms (monodentate and bridging), the nitrogen atom of the NTA ligand and two water molecules [19].

The FTIR absorption spectra of the RE^{3+} complexes show the characteristic symmetric (ν_s) and asymmetric (ν_{as}) stretching of the carboxylate group around 1690 and 1405 cm^{-1} , respectively. The difference between these values ($\Delta\nu$) is similar for all the complexes (285 cm^{-1}), and the $\Delta\nu$ of the sodium salt (Na_3NTA) is around 340 cm^{-1} (1730 and 1390 cm^{-1}), indicating monodentate and bridging coordination through the oxygen atoms [20]. Moreover, the spectra exhibit a broad band in the spectral range from 3000 to 3600 cm^{-1} assigned to the O–H stretching vibration of water molecules. The spectra also show a sharp peak around 3560 cm^{-1} which is assigned to free O–H stretching vibration of H_2O molecule coordinated to the RE^{3+} ions, indicating that these water molecules do not take part in hydrogen bonding [21].

The thermogravimetric analyses of the RE^{3+} -NTA complexes (Fig. 3) show three events assigned to the loss of water molecule in the temperature interval from 30 to 250 °C. The first and the second events occur from 30 to 140 °C and from 140 to 175 °C and correspond to the loss of 1 and 1.5 water molecule, respectively. The last event corresponds to the loss of

Fig. 3 (color online). Thermogravimetric curves of $[RE(NTA)(H_2O)_2] \cdot (H_2O)$ solid samples (RE^{3+} : Eu, Gd and Tb). All curves were recorded in dynamic synthetic air atmosphere.

0.5 water molecule between 175 °C and a final at 205 (Eu^{3+}), 215 (Gd^{3+}) and 225 °C (Tb^{3+}) (Fig. 3) possibly associated with the decrease of rare-earth ionic radii of 94.7, 93.8 and 92.3 pm, respectively. The TG data agree with the elemental analysis and IR data, which show vibrational stretching modes indicative of more than one type of water molecules in the RE^{3+} complexes. The thermal decomposition of the ligands in the complexes occurs between 320 and 600 °C. No events are observed after a calcination temperature at around 600 °C, suggesting the formation of Eu_2O_3 and Gd_2O_3 (colorless) or Tb_4O_7 (brown).

Photoluminescence study

The Gd^{3+} -NTA complex

Gadolinium complexes have been used to determine the first triplet state (T_1) of ligands [22], since there is a large energy gap ($\sim 32\,000\text{ cm}^{-1}$) between the $^8S_{7/2}$ ground state and the first $^6P_{7/2}$ excited state of the Gd^{3+} ion. Normally, this energy cannot be afforded from the lower-lying first excited T_1 state of the organic ligands *via* intramolecular energy transfer from ligand-to- Gd^{3+} ion. The ligand T_1 state energy is taken from the highest emission energy in the triplet state in the gadolinium complexes, which corresponds to the zero phonon transition [22].

The excitation spectrum at 77 K with emission monitored at 435 nm shows a broad band from 250 to

Fig. 4 (color online). The excitation spectrum of $[\text{Gd}(\text{NTA})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$ (a), with emission monitored at 435 nm, and the emission spectrum (b), with excitation at 270 nm, recorded at 77 K.

400 nm that is assigned to the $S_0 \rightarrow S_n$ singlet states of the NTA ligand (Fig. 4a).

The emission spectrum of the $[\text{Gd}(\text{NTA})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$ complex recorded at 77 K, under excitation at 270 nm (inset Fig. 4b), indicates that the T_1 state zero phonon transition of the ligand is around $29\,000\text{ cm}^{-1}$. The high energy of the triplet state in the NTA ligand can be explained by the absence of conjugation of π bonds [9, 23]. The T_1 state energy of the NTA ligand is higher than the 5D_0 ($\sim 17\,290\text{ cm}^{-1}$) and 5D_4 ($\sim 20\,400\text{ cm}^{-1}$) emitting levels of Eu^{3+} and Tb^{3+} ions, respectively. However, it is located below the $^6P_{7/2}$ ($\sim 32\,000\text{ cm}^{-1}$) emitting level of the Gd^{3+} ion. This spectroscopic behavior demonstrates that the NTA ligand can act as a luminescence sensitizer in the intramolecular energy transfer process for the Eu^{3+} and Tb^{3+} complexes.

It is noteworthy that the emission spectrum of the $[\text{Gd}(\text{NTA})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$ complex shows an exceptional narrow emission band arising from the $^6P_{7/2} \rightarrow ^8S_{7/2}$ transition of the gadolinium ion. This result suggests the impossibility of intramolecular energy transfer from the NTA ligand singlet states to the $^6P_{7/2}$ excited state of Gd^{3+} , located at lower energy than the S_1 excited state of the ligand. Therefore, this complex can be used as luminescence probe in

the UV region due to the presence of a high-intensity monochromatic emission at $31\,950\text{ cm}^{-1}$ (Fig. 4).

The Tb^{3+} -NTA complex

The green emission of Tb^{3+} -containing compounds around 546 nm under UV excitation is due to the high emission intensity of the $^5D_4 \rightarrow ^7F_5$ transition [24]. Intramolecular energy transfer can be interpreted in terms of energy transfer from the lowest triplet state of the NTA ligand (T_1) to the 5D_4 state or higher excited states composed mainly of the 5L_8 , 5G_3 , 5G_4 , and 5D_2 levels. The energy transfer occurs more efficiently when the energy gap is higher than 2000 cm^{-1} , avoiding the back energy transfer [25–28].

Fig. 5a shows the excitation spectrum of the $[\text{Tb}(\text{NTA})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$ complex with emission monitored at 545 nm and the emission spectrum with excitation at 300 nm at 77 K. The broad absorption bands of the NTA ligand are overlapping with the principal narrow bands originating from the 7F_6 ground state to the 5D_J , 5F_J , 5G_J , 5H_J , 5K_J , and 5L_J excited states of the Tb^{3+} ion.

The emission spectrum of the Tb^{3+} complex (Fig. 5b) presents sharp peaks assigned to the $^5D_4 \rightarrow ^7F_J$ transitions of the Tb^{3+} ion ($J: 6-0$): 7F_6

Fig. 5 (color online). The excitation spectrum of $[\text{Tb}(\text{NTA})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$ (a), with emission monitored at 545 nm, and the emission spectrum (b), with excitation at 350 nm, recorded at 77 K.

(20 283); ${}^7\text{F}_5$ (18 281); ${}^7\text{F}_4$, (17 094); ${}^7\text{F}_3$ (16 051); ${}^7\text{F}_2$ (15 360); ${}^7\text{F}_1$ (14 749) and ${}^7\text{F}_0$ (14 285 cm^{-1}). The efficient energy transfer from the NTA ligand to the Tb^{3+} ion is confirmed by the absence of any broad emission band.

The Eu^{3+} -NTA complex

The excitation spectrum of $[\text{Eu}(\text{NTA})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$ was recorded at 77 K and monitored at 613 nm (Fig. 6a). The absorption bands originate from the ${}^7\text{F}_0$ ground state to the excited levels ${}^5\text{L}_J$: ${}^5\text{D}_0$ (17 276); ${}^5\text{D}_1$ (19 065); ${}^5\text{D}_2$ (21 538); ${}^5\text{D}_3$ (24 454); ${}^5\text{L}_6$ (25 379); ${}^5\text{L}_7$ (26 737); ${}^5\text{D}_4$ (27 751); ${}^5\text{H}_3$ (31 538); ${}^5\text{F}_2$ (33 626); ${}^5\text{F}_4$ (35 144 cm^{-1}) (Fig. 6a). The ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition (25 379 cm^{-1}) exhibits the highest absorption intensity among the $4f^6$ intraconfigurational transitions, indicating that this transition is more efficient for the direct excitation of the Eu^{3+} ion. The absence of the NTA absorption bands in Fig. 6a is due to the large energy gap between the T_1 and ${}^5\text{D}_0$ states, suggesting that the energy transfer ligand- Eu^{3+} is not as efficient as in the Tb^{3+} compound.

Fig. 6b shows the narrow emission bands originating from the ${}^5\text{D}_0$ emitting level of Eu^{3+} : ${}^7\text{F}_0$ (17 276); ${}^7\text{F}_1$ (16 835); ${}^7\text{F}_2$, (16 181); ${}^7\text{F}_3$ (15 290); ${}^7\text{F}_4$ (14 367);

${}^7\text{F}_5$ (13 440 cm^{-1}) and from the ${}^5\text{D}_1$ emission level: ${}^7\text{F}_0$ (18 975); ${}^7\text{F}_1$ (18 587) and ${}^7\text{F}_2$ (17 953 cm^{-1}). According to the $(2J+1)$ -manifold, the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ splitting suggests that the Eu^{3+} ion has a low-symmetry environment. It is worth to mention that the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ shows only one peak which indicates that the metal ions have only one symmetry site.

The radiative rates ($A_{0 \rightarrow J}$) for ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ were calculated using Eq. 1 [29, 30],

$$A_{0 \rightarrow J} = \frac{\sigma_{0 \rightarrow 1} S_{0 \rightarrow J}}{S_{0 \rightarrow 1} \sigma_{0 \rightarrow J}} A_{0 \rightarrow 1} \quad (1)$$

where $\sigma_{0 \rightarrow 1}$ and $\sigma_{0 \rightarrow J}$ correspond to the energy barycenters of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions, respectively. $S_{0 \rightarrow 1}$ and $S_{0 \rightarrow J}$ are the areas of the emission curve corresponding to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions, respectively [31]. Since the magnetic dipole transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ is almost insensitive to changes in the chemical environment around the Eu^{3+} ion, the $A_{0 \rightarrow 1}$ rate can be used as an internal standard to determine the $A_{0 \rightarrow J}$ coefficients for Eu^{3+} complexes [30].

The lifetime (τ) of the Eu^{3+} -NTA complex was obtained from the luminescence decay curve using first order exponential decay (0.405 ms). The emission

Fig. 6 (color online). The excitation spectrum of $[\text{Eu}(\text{NTA})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$ (a), with emission monitored at 613 nm, and the emission spectrum (b), with excitation at 350 nm, recorded at 77 K.

quantum efficiency (η) of the $^5\text{D}_0$ emitting level is determined according to Eq. 2,

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{nrad}}} \quad (2)$$

where the total decay rate, $A_{\text{tot}} = \frac{1}{\tau} = A_{\text{rad}} + A_{\text{nrad}}$ and $A_{\text{rad}} = \sum_j A_{0 \rightarrow j}$. A_{rad} and A_{nrad} are the radiative and non-radiative rates, respectively.

The experimental intensity parameters (Ω_λ , λ : 2 and 4) are estimated from the $^5\text{D}_0 \rightarrow ^7\text{F}_{2,4}$ transitions in the emission spectrum of the Eu^{3+} complex. The Ω_6 intensity parameter is not included in this study since the $^5\text{D}_0 \rightarrow ^7\text{F}_6$ transition is not observed for this complex. The coefficient of spontaneous emission, A , is given by Eq. 3,

$$A = \frac{4e^2\omega^3}{3hc^3} \chi \sum_\lambda \Omega_\lambda \langle ^7F_J || U^{(\lambda)} || ^5D_0 \rangle^2 \quad (3)$$

where $\chi = \frac{n(n+2)^2}{9}$ is the Lorentz local field correction and n (1.5 for this complex) is the refraction index of the medium. The square reduced matrix elements $\langle ^7F_J || U^{(\lambda)} || ^5D_J \rangle^2$ are 0.0032 and 0.0023 calculated for $J = 2$ and 4, respectively [32, 33].

The values of the intensity parameters (Ω_λ) depend on the local geometry and the ligating atom polarizabilities in the first coordination sphere. The values of Ω_2 are most influenced by small angular changes in the chemical environment around the Eu^{3+} ion. The Ω_2 value of $[\text{Eu}(\text{NTA})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$ is much smaller than those of $[\text{Eu}(\text{TMA})(\text{H}_2\text{O})_2]$ or $[\text{Eu}(\text{BTC})(\text{H}_2\text{O})_n]$ (BTC: EMA, TLA and TMA) (Table 1), while the ratio

Table 1. Experimental intensity parameters ($\Omega_{2,4}$), radiative (A_{rad}), non-radiative (A_{nrad}) and total (A_{tot}) rates, lifetimes of the $^5\text{D}_0$ emitting level (τ) and quantum efficiencies (η) for $[\text{Eu}(\text{NTA})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$ and other representative complexes.

Eu^{3+} complexes	Ω_2 (10^{-20} cm^{-2})	Ω_4 (10^{-20} cm^{-2})	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	τ (ms)	η (%)
$[\text{Eu}(\text{NTA})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$	4	8	294	2174	2468	0.405	12
$[\text{Eu}(\text{EMA})(\text{H}_2\text{O})_2]^a$	14	10	623	2015	2638	0.379	24
$[\text{Eu}(\text{TLA})(\text{H}_2\text{O})_4]^a$	9	9	462	2116	2578	0.473	22
$[\text{Eu}(\text{TMA})(\text{H}_2\text{O})_6]^a$	11	10	522	4345	4867	0.230	12
$[\text{Eu}(\text{TTA})(\text{H}_2\text{O})_2]^b$	33	5	1110	2730	3840	0.260	29

^a Ref. [18]; ^b ref. [22].

Fig. 7 (color online). CIE chromaticity diagram showing the (x,y) emission color coordinates for $[RE(NTA)(H_2O)_2] \cdot (H_2O)$ complexes (RE^{3+} : Eu and Tb), irradiated at 350 nm [35]. The inset figures are photographs of nanomaterials taken with a digital camera displaying the red and green emissions, respectively, under UV irradiation at 254 nm.

between Ω_4 and Ω_2 is much higher in the present compound. This spectroscopic result suggests that the coordination polyhedron has a high point symmetry like the model described in reference [34].

Table 1 presents a small emission quantum efficiency value ($\eta \sim 12\%$) for $[Eu(NTA)(H_2O)_2] \cdot (H_2O)$ which can be explained owing to the presence of three water molecules in the complex.

The RE^{3+} -NTA complexes show (x,y) color coordinates in the red and green regions of the CIE chromaticity diagram (*Commission Internationale de l'Eclairage*) for Eu^{3+} (0.686, 0.309) and Tb^{3+} (0.338, 0.552) (Fig. 7). Therefore, these complexes act as light-conversion molecular devices (LCMDs) and can be applied in bicolor devices.

Conclusion

The emitting complexes $[RE(NTA)(H_2O)_2] \cdot (H_2O)$ were prepared in a one-step synthesis. The TG analyses show three water molecules in the structure and thermostability up to 300 °C. The XRD data indicate an isostructural series containing two coordinated and one crystal water molecules. The T_1 state of the NTA ligand has higher energy than the main 5D_0 (Eu^{3+}) and 5D_4 (Tb^{3+}) emitting levels and thus can act as intramolecular energy transfer donor to the metal ions, resulting in a red and green emission. The Tb^{3+} -NTA complex shows a more intense emission than the Eu^{3+} complex. Through excitation to higher energy states of the ligand, a monochromatic Gd^{3+} luminescence in the UV region can be obtained. The relative value of the experimental Ω_2 intensity parameter, in comparison with Ω_4 , for the Eu^{3+} -NTA complex suggests a high local symmetry. Photoluminescence data show that these complexes can act as light-conversion molecular devices (LCMDs) and can be used as red, green and UV emitting luminescent materials.

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Optical properties of red, green and blue emitting rare earth benzenetricarboxylate compounds

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ABSTRACT

Red, blue and green emitting rare earth compounds ($\text{RE}^{3+} = \text{Eu}^{3+}$, Gd^{3+} and Tb^{3+}) containing the benzenetricarboxylate ligands (BTC) [hemimellitic (EMA), trimellitic (TLA) and trimesic (TMA)] were synthesized and characterized by elemental analysis, complexometric titration, X-ray diffraction patterns, thermogravimetric analysis and infrared spectroscopy. The complexes presented the following formula: $[\text{RE}(\text{EMA})(\text{H}_2\text{O})_2]$, $[\text{RE}(\text{TLA})(\text{H}_2\text{O})_4]$ and $[\text{RE}(\text{TMA})(\text{H}_2\text{O})_6]$, except for Tb-TMA compound, which was obtained only as anhydrous. Phosphorescence data of Gd^{3+} -(BTC) complexes showed that the triplet states (T) of the BTC^{3−} anions have energy higher than the main emitting states of the Eu^{3+} ($^5\text{D}_0$) and Tb^{3+} ($^5\text{D}_4$), indicating that BTC ligands can act as intramolecular energy donors for these metal ions. The high values of experimental intensity parameters (Ω_2) of Eu^{3+} -(BTC) complexes indicate that the europium ion is in a highly polarizable chemical environment. Based on the luminescence spectra, the energy transfer from the T state of BTC ligands to the excited $^5\text{D}_0$ and $^5\text{D}_4$ levels of the Eu^{3+} and Tb^{3+} ions is discussed. The emission quantum efficiencies (η) of the $^5\text{D}_0$ emitting level of the Eu^{3+} ion have been also determined. In the case of the Tb^{3+} ion, the photoluminescence data show the high emission intensity of the characteristic transitions $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j=0-6$), indicating that the BTC ligands are good sensitizers. The RE^{3+} -(BTC) complexes act as efficient light conversion molecular devices (LCMDs) and can be used as tricolor luminescent materials.

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1. Introduction

Recently, metal carboxylate compounds have been widely recognized as one of the most promising and rapidly emerging research areas in the field of coordination chemistry. The great interest for these complexes is mainly owing to excellent properties, such as high luminescence intensity and porosity, contributing to an increase in the chemical and physical versatilities as compared to classical solid materials. The carboxylate complexes have already encountered several applications such as gas storage [1–3], molecular separation, catalyses [4], photoluminescence spectroscopy, magnetism, nonlinear optics, biomarkers, etc. An important feature of materials based on carboxylate ligands is the great facility in the synthesis of so-called metal-organic framework (MOF) materials [5,6]. The attractive structural properties of MOFs provide several industrial applications to these materials, which have been generally attributed to zeolite-related inorganic solids. However, as compared to zeolites, MOFs can present a huge kind of metal ions in their composition.

Although there is a great diversity of organic ligands that can be used as functionalized organic linkers, the particular attention given to carboxylate ligands is due to their coordination ability with transition metal and trivalent rare earth ions, coordinating to the metal centers by more than one bonding modes, such as unidentate, chelating, bridging or chelating/bridging bidentate. However, extensive efforts have been dedicated toward preparation of materials presenting three-dimensional structures using polycarboxylate ligands, especially tricarboxylate anion. Recent works [7–15] have been mainly focused on metal-organic compounds with 1,2,3-benzenetricarboxylic acid (hemimellitic acid), 1,2,4-benzenetricarboxylic acid (trimellitic acid) and 1,3,5-benzenetricarboxylic (trimesic acid) (Fig. 1). The majority of these works report the syntheses, structure and thermal properties of these systems.

Among the metal centers, trivalent rare earth ions (RE^{3+}) are largely explored owing to the structural and photoluminescence properties. The research on RE-carboxylate compounds has improved dramatically, and in this field, RE^{3+} ions generally act as network nodes bridged by spacer ligands. It is important to mention that the unusual structural features frequently obtained for RE-carboxylate are due to the combination of both high coordination numbers (from 8 to 10) of the RE^{3+} ions with low

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Fig. 1. Structural formulas of the tricarboxylate ligands: (a) 1,2,3-benzenetricarboxylate (EMA); (b) 1,2,4-benzenetricarboxylate (TLA) and (c) 1,3,5-benzenetricarboxylate (TMA).

stereochemical preference and the various coordination modes of the ligands [16].

A great number of luminescent RE³⁺-complexes investigated in the literature [17–21] present Eu³⁺ and Tb³⁺ ions as emitting center owing to the very intense red and green colors displayed by their compounds, respectively. Besides, the main emitting level (⁵D₀) of the Eu³⁺ ion is non-degenerate, which means that the emission bands assigned to the transitions ⁵D₀ → ⁷F_J (0 ≤ J ≤ 4) can provide information about the local symmetry by the split of the emission bands. Furthermore, a long lifetime of the emitting level, around milliseconds, is observed. Consequently, these coordination compounds play a crucial role in different fields, such as, biomedical analysis, organic light-emitting diodes (OLEDs) and sensors [22,23].

In contrast to the Eu³⁺ ion, detailed analyses of the energy-level structure and site of symmetry around the Tb³⁺ ion are complicated since the ⁵D₄ emitting level is nine-fold degenerate. In addition, this excited level is higher in energy than the ⁵D₀ emitting level of the Eu³⁺ ion. Thus, a donor energy ligand that can act as *antenna* for both Eu³⁺ and Tb³⁺ ions is expected to have its excited triplet state (T) with energy around 21,000 cm^{−1}. Some aromatic carboxylate ligands have shown donor T state with high energy, and these ligands can act as potential luminescence sensitizers for both Eu³⁺ and Tb³⁺ ions that exhibit red and green emission colors, respectively. Recently, RE³⁺-(1,3,5-tricarboxylate) compounds have been prepared by hydrothermal method in which a mixture of rare earth salt and H₃BTC ligand is heated in a sealed vial. The sieving and sensor function to small molecules and anions were investigated based on the luminescence intensity [6,24].

In this paper, we report the synthesis, characterization and photoluminescence properties of rare earth complexes with three different tricarboxylate ligands (EMA, TLA and TMA). Red, blue and green emission colors at room temperature are observed for the Eu³⁺, Gd³⁺ and Tb³⁺ ions, respectively. Furthermore, for Eu³⁺ ion, the experimental intensity parameters (*Q_s*), quantum emission efficiency (*η*), lifetimes of emitting ⁵D₀ levels, radiative (*A_{rad}*) and non-radiative (*A_{nrad}*) coefficients have also been reported. The CIE color coordinates (*x*, *y*) were determined from the emission spectra.

2. Experimental section

2.1. Preparation

The following commercially available chemicals were used without further purification. 1,2,3-benzenetricarboxylic acid (H₃EMA) was purchased from Fluka while 1,3,5-benzenetricar-

boxylic (H₃TMA) acid and 1,2,4-benzenetricarboxylic anhydride, precursor of 1,2,4-benzenetricarboxylic acid (H₃TLA) were purchased from Alfa Aesar. Solid [RECl₃·(H₂O)₆] compounds were synthesized as described in the literature [25].

2.1.1. Preparation of RE(EMA) complexes

1.5 g (~7.5 mmol) of 1,2,3-benzenetricarboxylic acid (hemicmelitic acid, H₃EMA) was dissolved in 200 mL of distilled water. To deprotonate the acid, NaOH 0.1 mol L^{−1} was added dropwise until pH ~6.0. To this mixture was added dropwise 50 mL of an equimolar aqueous solution of rare earth chloride (~7.5 mmol), under stirring. A few minutes after the beginning of the process, a starting white precipitate was observed. In order to increase the yield, the resulting reaction mixture was refluxed for 2 h. The solid product was filtered, washed with hot water several times and dried under vacuum for 12 h. All RE(EMA) complexes were stable in air, non-hygroscopic and insoluble in common organic solvents such as acetone, DMSO, acetonitrile, chloroform and ethanol.

[Eu(EMA)(H₂O)₂] Elemental analysis calcd for C₉H₇O₈Eu: C, 27.36%; H, 1.79%; Eu, 38.46%. Found: C, 27.44%; H, 2.07%; Eu, 37.93%. IR (KBr, cm^{−1}): 3634m, 3433b, 1533s, 1583m, 1489s, 1459m, 1363s, 1068w, 768m, 716m.

[Gd(EMA)(H₂O)₂] Elemental analysis calcd for C₉H₇O₈Gd: C, 27.00%; H, 1.76%; Gd, 39.27%. Found: C, 26.82%; H, 2.00%; Gd, 38.97%. IR (KBr, cm^{−1}): 3634m, 3434b, 1583m, 1533s, 1491s, 1462m, 1364s, 1068w, 768m, 715m.

[Tb(EMA)(H₂O)₂] Elemental analysis calcd for C₉H₇O₈Tb: C, 26.88%; H, 1.75%; Tb, 39.53%. Found: C, 26.93%; H, 2.12%; Tb, 39.19%. IR (KBr, cm^{−1}): 3431b, 1582m, 1537s, 1491s, 1459m, 1364s, 1068w, 766m, 717m, 3634m.

2.1.2. Preparation of the RE(TLA) complexes

1,2,4-benzenetricarboxylic acid (trimelic acid, H₃TLA) was obtained by the dissolution of 1.4 g (~7.5 mmol) of 1,2,4-benzenetricarboxylic anhydride in 200 mL of distilled water, and the pH was adjusted to 6.0 by adding dropwise NaOH 0.1 mol L^{−1}. To this mixture was added dropwise 50 mL of an aqueous solution of rare earth chloride (0.15 mol/L) under stirring. The white precipitate forms after addition of approximately 10 mL of the rare earth solution. The resulting reaction mixture was refluxed for 2 h, and then the solid product was filtered, washed with hot water several times and dried under vacuum. All complexes were stable in air, non-hygroscopic and insoluble in common organic solvents such as acetone, DMSO, acetonitrile, chloroform and ethanol.

[Eu(TLA)(H₂O)₄] Elemental analysis calcd for C₉H₇O₁₀Eu: C, 25.07%; H, 2.57%; Eu, 35.25%. Found: C, 25.37%; H, 2.75%; Eu, 35.29%. IR (KBr, cm^{−1}): 3448b, 3101w, 1586s, 1529s, 1496s, 1416s, 1079w, 844m, 789m.

[Gd(TLA)(H₂O)₄] Elemental analysis calcd for C₉H₁₁O₁₀Gd: C, 24.77%; H, 2.54%; Gd, 36.03%. Found: C, 24.79%; H, 2.57%; Gd, 36.24%. IR (KBr, cm⁻¹): 3446b, 3098w, 1586s, 1528s, 1496s, 1417s, 1079w, 845m, 790m.

[Tb(TLA)(H₂O)₄] Elemental analysis calcd for C₉H₁₁O₁₀Tb: C, 24.67%; H, 2.53%; Tb, 36.28%. Found: C, 24.60%; H, 2.49%; Tb, 36.69%. IR (KBr, cm⁻¹): 3443b, 3099w, 1586s, 1531s, 1496s, 1417s, 1079w, 846m, 790m.

2.1.3. Preparation of RE(TMA) complexes

1.5 g (~7.5 mmol) of 1,3,5-benzenetricarboxylic acid (trimesic acid, H₃TMA) was dissolved in 250 mL of distilled water and the pH was adjusted to 6.0 by adding dropwise NaOH 0.1 mol L⁻¹. To this mixture was added dropwise 50 mL of an aqueous solution of rare earth chloride under stirring. In this case, the white precipitate forms immediately with the addition of the rare earth solution. The resulting reaction mixture was refluxed for 2 h, and then the solid product was filtered, washed with hot water several times and dried under vacuum. All complexes were stable in air, non-hygroscopic and insoluble in common organic solvents such as acetone, DMSO, acetonitrile, chloroform and ethanol.

[Eu(TMA)(H₂O)₆] Elemental analysis calcd for C₉H₁₅O₁₂Eu: C, 23.14%; H, 3.24%; Eu, 32.53%. Found: C, 23.24%; H, 3.23%; Eu, 32.75%. IR (KBr, cm⁻¹): 3410b, 3263w, 3132w, 2926w, 1614s, 1561s, 1435s, 1375s, 1110w, 762m, 709m.

[Gd(TMA)(H₂O)₆] Elemental analysis calcd for C₉H₁₅O₁₂Gd: C, 22.88%; H, 3.20%; Gd, 33.28%. Found: C, 23.08%; H, 3.24%; Gd, 33.60%. IR (KBr, cm⁻¹): 3409b, 3265w, 3133w, 2925w, 1614s, 1562s, 1437s, 1376s, 1110s, 762m, 709m.

[Tb(TMA)] Elemental analysis calcd for C₉H₃O₆Tb: C, 29.53%; H, 0.83%; Tb, 43.42%. Found: C, 29.30%; H, 0.95%; Tb, 42.86%. IR (KBr, cm⁻¹): 1618s, 1549s, 1453s, 1389s, 1127m, 763s, 737s, 710s.

2.2. Characterization

Thermal analysis was performed on a thermobalance Schimadzu TGA-50. The samples were placed in platinum containers, and the TG curves were recorded in a dynamic synthetic air atmosphere of 50 cm³ min⁻¹ under a heating rate of 10 °C min⁻¹ in the temperature range from 25 up to 900 °C. Elemental analysis was carried out using a Perkin Elmer 240 microanalyzer. Infrared spectra were recorded in KBr pellets on a Bomen model MB-102 spectrophotometer in the range from 4000 up to 350 cm⁻¹. XRD patterns of the powders were recorded on a Rigaku Miniflex diffractometer using Cu K α radiation (30 kV and 15 mA) from 2° to 90° (2 h) and 1 s of pass time. Steady-state excitation and emission spectra of the complexes in solid state at room (298 K) and liquid nitrogen temperatures were recorded at an angle of 22.5° (front face) with a spectrofluorimeter (SPEX-Fluorolog 2) with double grating 0.22 m monochromator (SPEX 1680), and a 450 W Xenon lamp as excitation source. All spectra were recorded using a detector mode correction. The luminescence decay curves of the emitting levels were measured using a phosphorimeter SPEX 1934D accessory coupled to the spectrofluorometer.

3. Results and discussion

3.1. Characterization of RE³⁺-BTC complexes

The elemental analyses of CHN, after mineralization of the compounds and the complexometric titration with disodium ethylenediaminetetraacetic acid (EDTA) salt, confirm the general

formulas [RE(BTC)(H₂O)_n] for the complexes (where BTC=TMA, TLA and EMA; n=2, 4 and 6), except for the [Tb(TMA)] anhydrous complex.

XRD patterns of the [RE(BTC)(H₂O)_n] complexes in powder form present three isomorphous series when containing the same ligand and similar number of water molecules, except for the anhydrous [Tb(TMA)] complex (figure not shown).

The thermogravimetric curves of the [RE(BTC)(H₂O)_n] complexes were recorded in the temperature interval from 25 to 900 °C. As shown in Fig. 2a, the [Eu(EMA)(H₂O)₂] compound exhibits two mass loss events assigned to the loss of two water molecules at 245 °C and to the EMA ligand decomposition at 416 °C, producing europium oxide around 650 °C. This reveals that there are two water molecules coordinated to the Eu³⁺ ion, which corroborates with elemental analysis. In the [Eu(TLA)(H₂O)₄] complex (Fig. 2b), three thermal events for dehydration at 72, 148 and 250 °C correspond to the loss of one, two and one water molecules, respectively, were observed. In addition, there is another event at 508 °C assigned to TLA ligand decomposition. The same thermal behavior is observed for the gadolinium and terbium complexes. In the case of [Eu(TMA)(H₂O)₆] compound (Fig. 2c) there were only two dehydration events where four are lost at 112 °C and the remaining two water molecules at 131 °C. In this complex, TMA ligand decomposition occurs at 464 °C. The same thermal behavior is observed for the gadolinium and terbium coordination compounds, except for the [Tb(TMA)] complex, which presents no dehydration event, but only one at 464 °C assigned to the TMA ligand decomposition, indicating that this compound is anhydrous (Fig. 2d).

Infrared spectra of [RE(BTC)(H₂O)_n] complexes exhibit a broad band in the spectral range from 3500 to 3300 cm⁻¹ due the O–H stretching vibration of water molecule, indicating that these complexes are hydrated. Furthermore, IR data of the [RE(EMA)(H₂O)₂] display a sharp band around 3634 cm⁻¹, which is assigned to free O–H stretching vibration of H₂O molecule coordinated to the rare earth ions, indicating that the water molecules do not take part in hydrogen bonding. On the other hand, the absence of the broad band in the region 3000–3500 cm⁻¹ for the [Tb(TMA)] complexes indicates that this complex is anhydrous [26].

The coordination of the ligand to the rare earth ion was investigated comparing the infrared spectra of the complexes with those of the sodium-BTC salts as suggested by Deacon and Phillips [27]. The IR spectra of the BTC ligands in ionic form present strong bands at 1568 and 1382 cm⁻¹ for EMA, 1583 and 1392 cm⁻¹ for TLA and 1568 and 1373 cm⁻¹ for TMA, which are attributed to the $\nu_s(\text{C}=\text{O})$ and $\nu_{as}(\text{C}=\text{O})$ vibrational modes, respectively. For the RE³⁺-EMA complexes, $\Delta\nu$ values of around 170 and 126 cm⁻¹ are observed, suggesting that the carboxylate groups are coordinated to metal ions as bidentate bridge and chelate forms through oxygen atoms. On the other hand, the RE³⁺-TLA complexes exhibit values of $\Delta\nu$ around 112 cm⁻¹, which are significantly lesser than ionic values ($\Delta\nu=190$ cm⁻¹), suggesting coordination in chelating form. In the case of [RE(TMA)(H₂O)₆] (RE³⁺=Eu and Gd) the TMA ligand presents the bidentate bridge coordination form ($\Delta\nu=186$ cm⁻¹), and the anhydrous [Tb(TMA)] complex presents chelating.

The [Tb(TMA)] complex is anhydrous mainly because of the diminution of the ionic radius of the Tb³⁺ ion, which increases the steric repulsion when compared with those of Eu³⁺ and Gd³⁺ hexahydrated complexes. Therefore, the general formula [RE(TMA)] can also be expected for other heavy rare earth ions where RE³⁺=Dy–Lu. Therefore, the spatial conformation of the coordination TMA ligands change in a way that the water molecules are excluded from the first coordination shell of the complex structure of [Tb(TMA)]. The anhydrous behavior of these complexes is also supported by IR data.

Fig. 2. Thermogravimetric curves of the $[\text{Eu}(\text{BTC})(\text{H}_2\text{O})_n]$ complexes ($n=2, 4$ and 6) in solid state. All these curves were recorded at synthetic air dynamic atmosphere in the temperature interval from 20 to 900 °C.

3.2. Photoluminescence investigation

3.2.1. Phosphorescence of the Gadolinium complexes

The goal in the investigation of the photoluminescence of the Gd-BTC coordination compounds is to determine the energy of the excited states that belong to the BTC ligands. It is important to mention that the Gd^{3+} ion generally does not accept energy from organic ligands because the energy of the T states of these donor species is below the first excited ${}^6\text{P}_{7/2}$ state of the Gd^{3+} ion. Since there is a large energy gap ($\sim 32,000\text{ cm}^{-1}$) between the ${}^8\text{S}_{7/2}$ ground state and the first ${}^6\text{P}_{7/2}$ excited state of the Gd^{3+} ion [25,28,29], it cannot be widened by energy from the lower lying first excited T_1 state of the BTC ligands via intramolecular ligand-to-metal energy transfer.

Gd-BTC emission spectra exhibit only broad bands owing to the ligand centered transitions, giving information about triplet ligand donor state positions as compared with acceptor excited rare earth states. Fig. 3a–c shows the steady-state phosphorescence spectra of Gd^{3+} BTC-complexes recorded at liquid nitrogen temperature at 350–700 nm under excitation at around 290 nm. These spectra display two overlapped broad bands with maxima around 410 and 475 nm that are assigned to the vibronic contribution and phosphorescence due to the $\text{T} \rightarrow \text{S}_0$ (π, π^*) centered ligand transitions, respectively. This behavior has been observed for other rare earth carboxylate complexes reported in the literature [30]. The luminescence decay curves of the Gd-BTC compounds recorded with emission monitored at 475 nm showed long values of the emitting state lifetime at room temperature, 298 K (Table 1): for $[\text{Gd}(\text{EMA})(\text{H}_2\text{O})_2]$ ($\tau=7.113$ ms), $[\text{Gd}(\text{TMA})(\text{H}_2\text{O})_4]$ ($\tau=2.210$ ms) and $[\text{Gd}(\text{TMA})(\text{H}_2\text{O})_6]$ ($\tau=4.062$ ms) and increase when recorded at low temperature (77 K) $\tau=8.351, 12.025$ and 7.386 ms, respectively. These data confirm the triplet character of the emitting states that contribute to those bands around 475 nm.

In order to determine unequivocally the energy due to the triplet 0–0 phonon transition for each Gd^{3+} -BTC compound, time-resolved spectra (Fig. 3d–f) were recorded at liquid nitrogen temperature with excitation and emission monitored at 290 and 475 nm, respectively, using a delay of 1.0 ms. In this case, fluorescence bands decrease very fast as the flash delay is increased and only the phosphorescence from BTC ligands is displayed. The T states energy estimated from the shortest wavelength on the base of the emission bands 0–0 phonon transition is as follows: $25,694\text{ cm}^{-1}$ $[\text{Gd}(\text{EMA})(\text{H}_2\text{O})_2]$; $25,523\text{ cm}^{-1}$ $[\text{Gd}(\text{TMA})(\text{H}_2\text{O})_4]$ and $25,100\text{ cm}^{-1}$ $[\text{Gd}(\text{TMA})(\text{H}_2\text{O})_6]$. As can be observed, these triplet states have energy higher than the main emitting states of the Eu^{3+} (${}^5\text{D}_0$) and Tb^{3+} (${}^5\text{D}_4$), indicating that BTC ligands can act as intramolecular energy donors for these rare earth metal ions.

3.2.2. Luminescence of Eu^{3+} -BTC complexes

Excitation spectra of the $[\text{Eu}(\text{BTC})(\text{H}_2\text{O})_n]$ complexes ($n=2, 4$ and 6) in solid state were recorded at 77 K in the spectral range 240–600 nm under emission on the hypersensitive ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of the Eu^{3+} ion, at ~ 617 nm (Figs. 4a, b and c). These spectra present a strong broad band between 270 and 400 nm assigned to the photoexcitation process of the Eu^{3+} ion via the $\text{S}_0 \rightarrow \text{S}_1$ transition. Narrow bands can also be seen assigned to the following intraconfigurational transitions (in nm): ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ (578), ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$ (525), ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ (464), ${}^7\text{F}_0 \rightarrow {}^5\text{D}_3$ (409), ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ (494), ${}^7\text{F}_0 \rightarrow {}^5\text{L}_7$ (373), ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$ (360), ${}^7\text{F}_0 \rightarrow {}^5\text{H}_3$ (317) and ${}^7\text{F}_0 \rightarrow {}^5\text{F}_2$ (295). However, these bands are less intense than those bands corresponding to the $\text{S}_0 \rightarrow \text{S}_1$ transition. The excitation spectra of TMA and TLA complexes display higher luminescence intensity around 300 nm than from 4f–4f transitions; however, the broad band of EMA shows lower intensity than that of europium electronic transitions. This result gives evidence that europium

Fig. 3. Phosphorescence data of [Gd(EMA)(H₂O)₂], [Gd(TLA)(H₂O)₄] and [Gd(TMA)(H₂O)₆] complexes recorded at 77 K under excitation at 290 nm using the steady-state (a, b and c) and time-resolved (d, e and f) techniques.

Table 1

Lifetimes (τ) of the T state of BTC ligands and emitting 5D_J states of Eu^{3+} ($J=0$) and Tb^{3+} ($J=4$) ions for the [RE(BTC)(H₂O)_{*n*}] complexes ($n=2, 4$ and 6), at 298 K.

Complex	Emitting state	τ (298 K)	x	y
Eu(EMA)(H ₂ O) ₂	5D_0	0.379	0.67	0.31
[Eu(TLA)(H ₂ O) ₄]	5D_0	0.473	0.68	0.31
[Eu(TMA)(H ₂ O) ₆]	5D_0	0.230	0.68	0.31
[Gd(EMA)(H ₂ O) ₂]	T_1	7.113	0.16	0.24
[Gd(TLA)(H ₂ O) ₄]	T_1	2.210	0.15	0.16
[Gd(TMA)(H ₂ O) ₆]	T_1	4.062	0.17	0.19
[Tb(EMA)(H ₂ O) ₂]	5D_4	1.135	0.33	0.56
[Tb(TLA)(H ₂ O) ₄]	5D_4	0.782	0.34	0.25
[Tb(TMA)]	5D_4	1.572	0.37	0.54

Color coordinates (x , y) of the complexes are also presented.

luminescence sensitizerizations through intramolecular energy transfer from TLA and TMA ligands to Eu^{3+} ion are more efficient.

Emission spectra of the [Eu(BTC)(H₂O)_{*n*}] complexes ($n=2, 4$ and 6) in solid state recorded in the range from 370 to 800 nm, under excitation on BTC ligand bands at ~ 295 nm, at 77 K, show characteristic $^5D_0 \rightarrow ^7F_J$ ($J=0, 1, 2, 3$ and 4) transitions of the Eu^{3+} ion, with the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition (at 617 nm) being the most prominent (Figs. 4d, e and f). The presence of the $^5D_0 \rightarrow ^7F_2$ transition indicates that the Eu^{3+} ion is found in chemical environment without center of inversion, considering that Laporte's rule is slightly relaxed for 4f–4f transitions due to the mixing of opposite parity electronic configurations, produced by the odd components of a non-centrosymmetric ligand field. The emission spectra also present the f–f transitions: $^5D_1 \rightarrow ^7F_0$ (526 nm), $^5D_1 \rightarrow ^7F_1$ (536 nm), $^5D_1 \rightarrow ^7F_2$ (552 nm) and $^5D_1 \rightarrow ^7F_3$ (584 nm), but with very low intensities. The other feature optical data is that the emission spectra of all europium benzenetricarboxylate complexes do not exhibit the broad band of ligands (Fig. 4d, e and f), indicating an efficient intramolecular energy transfer from the BTC ligands to the Eu^{3+} ion, and these complexes act as light conversion molecular devices (LCMDs).

Fig. 4d shows the emission spectrum of the [Eu(TMA)(H₂O)₆] complex with $(2J+1)$ -components for the $^5D_0 \rightarrow ^7F_{0-4}$ transitions, suggesting the presence of only one site of symmetry around the

europium ion. The local-ligand field splitting is also evident for $^5D_0 \rightarrow ^7F_{0-4}$ transitions of the [Eu(TLA)(H₂O)₄] and [Eu(EMA)(H₂O)₂] complexes, however, presenting more than Stark $(2J+1)$ -components, indicating that the Eu^{3+} ion occupies more than one site of symmetry (Figs. 4e and f). It is observed that, in general, emission spectra of complexes with TLA and EMA ligands present different profiles, reflecting changes in the chemical environment around the Eu^{3+} ion having different chemical environments with site symmetries of the type C_s , C_n or C_{nv} , which is expected to form the coordination polymers.

In order to get further information on the chemical environment of the Eu^{3+} ions for the [Eu(BTC)(H₂O)_{*n*}] complexes, experimental intensity parameters Ω_λ ($\lambda=2$ and 4), radiative rates (A_0) for the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_4$ transitions and emission quantum efficiency (η) were determined (Table 2) according to Refs. [16,31].

$$A_{0 \rightarrow j} = \frac{\sigma_{0 \rightarrow 1} S_{0 \rightarrow j} A_{0 \rightarrow 1}}{S_{0 \rightarrow 1} \sigma_{0 \rightarrow j}} \quad (1)$$

where $\sigma_{0 \rightarrow 1}$ and $\sigma_{0 \rightarrow j}$ correspond to the energy barycenters of the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_j$ transitions (in cm^{-1}), respectively. In a similar way $S_{0 \rightarrow 1}$ and $S_{0 \rightarrow j}$ are the surface of the emission curve corresponding to the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_j$ transitions, respectively [32]. As it can be seen, for Eu^{3+} complexes the coefficients $A_{0 \rightarrow j}$ are determined by taking the magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition as an internal standard since $A_{0 \rightarrow 1}$ rate is almost insensitive to changes in the chemical environment around the europium ion with $A_{0 \rightarrow 1} \cong 50 \text{ s}^{-1}$. The radiative contribution is estimated based only on the relative intensities of the $^5D_0 \rightarrow ^7F_{0-4}$ transitions owing to the fact that the $^5D_0 \rightarrow ^7F_{5,6}$ transitions are not observed experimentally [16].

The lifetimes (τ) of the [RE(BTC)(H₂O)_{*n*}] complexes (Table 1) were obtained from the luminescence decay curves using the equation $I(t) = I(0) \exp(-t/\tau)$ and a curve-fitting program. In the same system, the τ values of Tb^{3+} ion are higher than those of Eu^{3+} ion owing to the larger energy gap of terbium ion ($14,800 \text{ cm}^{-1}$) compared with the europium gap ($12,300 \text{ cm}^{-1}$).

It is possible to determine the emission quantum efficiency (η) of the 5D_0 emitting level of the Eu^{3+} ion, according to the

Fig. 4. Photoluminescence spectral data of the $[\text{Eu}(\text{BTC})(\text{H}_2\text{O})_n]$ complexes ($n=2, 4$ and 6) in solid state recorded at 77 K . Excitation spectra obtained monitoring emission on the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of the Eu^{3+} ion, at $\sim 617\text{ nm}$ (a, b and c). Emission spectra recorded on BTC ligand bands at $\sim 295\text{ nm}$ (d, e and f).

Table 2

Photoluminescent data of the $[\text{Eu}(\text{BTC})(\text{H}_2\text{O})_n]$ complexes ($n=2, 4$ and 6) solid state.

Complex	$\Omega_2 \cdot 10^{-20} \text{ cm}^2$	$\Omega_4 \cdot 10^{-20} \text{ cm}^2$	$A_{\text{rad}} (\text{s}^{-1})$	$A_{\text{nrad}} (\text{s}^{-1})$	$A_{\text{tot}} (\text{s}^{-1})$	R_{02}	$\eta (\%)$
$[\text{Eu}(\text{EMA})(\text{H}_2\text{O})_2]$	14.3	10.1	623	2015	2637	0.1200	24
$[\text{Eu}(\text{TIA})(\text{H}_2\text{O})_4]$	9.5	8.7	462	1653	2116	0.0279	22
$[\text{Eu}(\text{TMA})(\text{H}_2\text{O})_6]$	10.8	10.4	522	3820	4345	0.0003	12

The experimental intensity parameters (Ω_i and R_{02}), radiative spontaneous emission coefficient A_{rad} , non-radiative spontaneous emission coefficient (A_{nrad}) and quantum efficiency (η) of the emitting $^5\text{D}_0$ level were obtained at room temperature (around 298°C).

equation

$$\eta = \tau A_{\text{rad}} \quad (2)$$

where the total decay rate,

$$A_{\text{tot}} = \frac{1}{\tau} = A_{\text{rad}} + A_{\text{nrad}},$$

where $A_{\text{rad}} (= \sum A_{0 \rightarrow j})$ and A_{nrad} are the radiative and non-radiative rates, respectively. Thus, based on the experimental lifetime (τ) of the $^5\text{D}_0$ emitting level and A_{rad} rate, it was possible to determine the non-radiative rates (A_{nrad}). The experimental values of the radiative (A_{rad}) and non-radiative (A_{nrad}) rates, and emission quantum efficiency (η) are presented in Table 2. The emission quantum efficiency data show that the higher values of η , 22% for $[\text{Eu}(\text{TIA})(\text{H}_2\text{O})_4]$ and 24% for $[\text{Eu}(\text{EMA})(\text{H}_2\text{O})_2]$ complexes, are due to the lower number of water molecules in the complexes, where this fact is reflected by the lower contribution of non-radiative (A_{nrad}) arising from the OH oscillator of water molecules. On the other hand, the six water molecules in the $[\text{Eu}(\text{TMA})(\text{H}_2\text{O})_6]$ complex contribute to the higher luminescence quenching and consequently lower value of η (12%).

From the emission spectra of Eu^{3+} complexes, the experimental intensity parameters (Ω_λ , $\lambda=2$ and 4) may be estimated using the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions, respectively, and expressing the emission intensity in terms of the area under the emission curve. The Ω_6 intensity parameter is not included in this study since the $^5\text{D}_0 \rightarrow ^7\text{F}_6$ transition is usually not observed for these complexes. The coefficient of spontaneous emission,

A , is given by equation

$$A = \frac{4e^2\omega^3}{3hc} \chi \sum_{\lambda} \Omega_{\lambda} \langle ^7\text{F}_j || U^{(\lambda)} || ^5\text{D}_0 \rangle^2 \quad (3)$$

where $\chi = n(n+2)^2/9$ is the Lorentz local field correction and n is the index of refraction of the medium. An average index of refraction equal to 1.5 has been used for these complexes. The quantities $\langle ^7\text{F}_j || U^{(\lambda)} || ^5\text{D}_j \rangle^2$ are the square reduced matrix elements and are equal to 0.0032 and 0.0023 for $j=2$ and 4 , respectively [33]. Since the intensity of the magnetic dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_1$ is relatively insensitive to the chemical environment of the Eu^{3+} ion, it may be used as the internal standard (reference transition) to avoid the difficulties in the experimental measurement of absolute emission intensities [34,35].

Analysis of the experimental intensity parameters (Ω_2 and Ω_4) gives a general trend concerning the link between the numbers H_2O and BTC ligands in the first coordination sphere of Eu^{3+} ion. As a matter of fact, the oxygen atoms that belong to EMA, TIA and TMA ligands differ from their polarizabilities.

Values of experimental intensity parameters Ω_λ ($\lambda=2$ and 4) for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions for Eu^{3+} -(BTC) complexes are presented in Table 2. The high values of the intensity Ω_2 parameter ($\geq 1 \times 10^{-20} \text{ cm}^2$) might be interpreted as a consequence of two concurrent factors. The first one is the very low symmetry around the Eu^{3+} ion, allowing the appearance of all odd-rank components in the sums-over-ligands. The second factor

is related to the hypersensitive behavior of the $^5D_0 \rightarrow ^7F_2$ transition [16], suggesting that the dynamic coupling mechanism is operative and that the chemical environment around the metal ion is highly polarizable, possibly due to the strong delocalization of the carboxylate oxygen charge.

The delocalization of the π -electrons of the chelate rings in EMA, TLA and TMA ligands increases the polarizability of the oxygen atoms in the $[\text{Eu}(\text{BTC})(\text{H}_2\text{O})_4]$ complexes with less number of H_2O molecules. Consequently, when four or six water molecules are coordinated to the metal ion, the chemical environment around the europium ion becomes less polarizable compared to those with only two H_2O molecules, which is reflected on the highest value of $\Omega_2 = 14.3 \times 10^{-20} \text{ cm}^2$ (Table 2).

Table 2 presents also the R_{02} intensity parameter, which is the ratio between the intensities of the $^5D_0 \rightarrow ^7F_0$ and $^5D_0 \rightarrow ^7F_2$ transitions. The R_{02} parameter may give information on the J -mixing effect associated with the $^5D_0 \rightarrow ^7F_0$ transition as described in detail in Ref. [36]. In this case, this effect is mainly due to the mixing between the 7F_2 manifold and the 7F_0 level though the rank-two components of the ligand field. By comparison between the three Eu^{3+} -(BTC) complexes the following order for the magnitude of the J -mixing effect is proposed: $\text{EMA} > \text{TLA} \gg \text{TMA}$.

3.2.3. Luminescence of Tb^{3+} -(BTC) complexes

The $[\text{Tb}(\text{BTC})_3(\text{H}_2\text{O})_n]$ complexes exhibit a highly intense green emission color under UV excitation. Fig. 5a–c shows the excitation spectra of the Tb^{3+} complexes recorded in the spectral range from 240 to 550 nm, at low temperature (77 K), with emission monitored on the $^5D_4 \rightarrow ^7F_5$ transition at 545 nm. The spectral data consist of broad bands of high absorption intensities in the spectral range from 240 to 370 nm, with maximum at 295 nm, which is attributed to the $S_0 \rightarrow S_1$ transitions of the EMA, TLA and TMA ligands. In addition to these bands, narrow bands arising from $4f-4f$ intraconfigurational transitions from the ground-state 7F_6 level to the 5L_8 (339 nm), 5L_9 (351 nm), 5G_5 (358 nm), $^5L_{10}$

(368 nm), 5G_6 (377 nm) and 5D_4 (486 nm) excited levels are also observed. However, the relative intensity of the broad band is higher than the $4f-4f$ transitions centered on the Tb^{3+} ion. It is also observed that the indirect excitation processes of the metal ion, via chromophore groups from the ligands, are more operative than in $^7F_6 \rightarrow ^5L_J$ transitions for the Tb^{3+} -(BTC) complexes.

The emission spectra of Tb^{3+} -(BTC) complexes, in the solid state, were registered in the range 320–700 nm under excitation at ligand transitions (300 nm) at liquid nitrogen temperature, as shown in Fig. 5d–f. The luminescence spectra of Tb^{3+} -complexes ($4f^8$ configuration) generally exhibit characteristic narrow emission bands arising from the $^5D_4 \rightarrow ^7F_J$ transitions ($J=0-6$) of trivalent terbium ion, which are assigned as follows: $^5D_4 \rightarrow ^7F_0$ (682 nm), $^5D_4 \rightarrow ^7F_1$ (669 nm), $^5D_4 \rightarrow ^7F_2$ (653 nm), $^5D_4 \rightarrow ^7F_3$ (621 nm), $^5D_4 \rightarrow ^7F_4$ (587 nm), $^5D_4 \rightarrow ^7F_5$ (545 nm) and $^5D_4 \rightarrow ^7F_6$ (490 nm) with the $^5D_4 \rightarrow ^7F_5$ transition as the most prominent band of the Tb^{3+} ion. The emission spectral data do not exhibit a broad band from the triplet state of the EMA, TLA and TMA ligands in the spectral range 370–550 nm, indicating an efficient energy transfer from the T state of the ligand to the emitting 5D_4 level of the terbium ion.

The large gaps between the emitting 5D_4 levels and final 7F_J levels of Tb^{3+} compounds are around $15,000 \text{ cm}^{-1}$. They usually exhibit a green color in the presence of UV radiation [37]. In contrast to the Eu^{3+} ion, detailed analyses of energy-level structure and symmetry site around the Tb^{3+} ion are not possible, since the 5D_4 emitting level and 7F_6 Stark level are nine-fold and thirteen-fold degenerated, respectively [38]. The $^5D_4 \rightarrow ^7F_5$ transition is the best luminescence probe for the terbium ion [39]. Otherwise, the sensitization pathway in luminescent Tb^{3+} complexes is similar to those of Eu^{3+} complexes. However, the triplet states of the β -diketonate (acetylacetonate-acac) [16] and carboxylate [39] ligands have to be located above or in resonance with the excited 5D_4 level ($\sim 20,400 \text{ cm}^{-1}$). The same behavior was observed for the Tb^{3+} -(BTC) complexes (BTC=TMA, TLA and EMA).

According to Reinholdt's empirical rule [40] the intersystem crossing process will be effective when the energy gap between S

Fig. 5. Photoluminescence spectral data of the $[\text{Tb}(\text{TMA})]$ and $[\text{Tb}(\text{BTC})(\text{H}_2\text{O})_n]$ complexes (BTC=TMA, TLA and EMA; $n=2, 4$ and 6) in solid state recorded at 77 K. Excitation spectra obtained monitoring emission on the $^5D_4 \rightarrow ^7F_5$ transition of the Tb^{3+} ion at $\sim 545 \text{ nm}$ (a, b and c). Emission spectra recorded on the BTC ligand bands at $\sim 295 \text{ nm}$ (d, e and f).

and T excited states of the ligands, $\Delta E[S(^1\pi\pi)-T(^3\pi\pi)]$, is around 5000 cm^{-1} . As the intersystem crossing process of the BTC ligands are efficient, it can be assumed that the singlet state present energy at $30,000\text{ cm}^{-1}$ for these carboxylate groups. In addition, Latva et al. [41] reported that the best intramolecular energy transfer from a T ligand to emitting 5D_4 level of Tb^{3+} ion occurs when the energy gap between the T state of the ligand and the first emitting 5D_4 level of the Tb^{3+} is higher than 2000 cm^{-1} . For these complexes, the energy gaps are in the range of $4600\text{--}5200\text{ cm}^{-1}$ that avoids the possibility of an energy back-transfer from the metal ion [42]. The photoluminescent data suggest that the BTC ligands act as efficient *antennas* sensitizing the luminescence of the Tb^{3+} ion for these complexes.

Fig. 6 shows the photographs of the $[\text{RE}(\text{TLA})(\text{H}_2\text{O})_4]$ complexes (where $\text{RE}^{3+}=\text{Eu}^{3+}$, Gd^{3+} and Tb^{3+}) taken at room temperature ($\sim 298\text{ K}$), which exhibit red, blue and green emissions colors. These primary colors arise mainly from the narrow bands of $^5D_0 \rightarrow ^7F_2$ and $^5D_4 \rightarrow ^7F_5$ transitions of the Eu^{3+} and Tb^{3+} ions, respectively. On the other hand, the blue emission color of the Gd^{3+} -complex is owing to the broad band of T $\rightarrow$ S transition from the BTC ligand phosphorescence band. Fig. 6 also shows the partial energy-level diagram of Eu^{3+} , Gd^{3+} and Tb^{3+} ions containing their excited and ground states.

The Eu^{3+} -BTC-complexes present similar (x,y) color coordinates (Table 1) in the red region of the CIE chromaticity diagram (Commission Internationale de l'Eclairage) from narrow 4f–4f transitions of rare earth ions (Fig. 7) [43]. The anhydrous $[\text{Tb}(\text{TMA})]$ complex displays the green yellow emission color when compared with $[\text{Tb}(\text{EMA})(\text{H}_2\text{O})_2]$ and $[\text{Tb}(\text{TLA})(\text{H}_2\text{O})_4]$ complexes that show green color. In case of Gd^{3+} -BTC-complexes

blue emission colors were observed, arising from the broad band ligand centered transitions of BTC^{3-} anion. As it can be seen, these complexes present emissions containing the three primary colors

Fig. 7. Chromaticity coordinates from emission spectra of the $[\text{RE}(\text{BTC})(\text{H}_2\text{O})_n]$ complexes ($\text{RE}^{3+}=\text{Eu}$, Gd and Tb ; $\text{BTC}=\text{EMA}$, TLA and TMA ; $n=2$, 4 and 6).

Fig. 6. Partial energy-level diagram of rare earth ions (Eu^{3+} , Gd^{3+} and Tb^{3+}). Triplet states of BTC ligands are shown on the left and arrows indicate emitting levels (photographs were obtained after UV irradiation).

(red, green and blue) that can be applied in tricolor devices. The Eu^{3+} and Tb^{3+} complexes act as light conversion molecular devices (LCMDs) and produce monochromatic emission colors.

4. Conclusion

In this work emitting Eu^{3+} , Gd^{3+} and Tb^{3+} complexes were prepared, containing the benzenetricarboxylate ligands (BTC) that exhibit red, blue and green emission colors, respectively. Phosphorescence data of Gd^{3+} -(BTC) complexes showed highly intensity blue emission at room temperature. The triplet states of the BTC^{3-} anions have energy higher than the main emitting states of Eu^{3+} ($^5\text{D}_0$) and Tb^{3+} ($^5\text{D}_4$), indicating that BTC ligands act as intramolecular energy donors for these metal ions. The high values of experimental intensity parameters (Ω_2) of Eu^{3+} -(BTC) complexes indicate that the europium ion is in a highly polarizable chemical environment. The emission quantum efficiency of the emitting $^5\text{D}_0$ level data shows that the highest value of η (24%) for the $[\text{Eu}(\text{EMA})(\text{H}_2\text{O})_2]$ complex is due to the lower number of coordinated water molecules arising from the lower contribution of non-radiative (A_{nrad}) from the OH oscillator. The Tb^{3+} -(BTC) complexes exhibit sharp green emission intensities assigned to the characteristic $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j=0-6$) transitions, indicating that the BTC ligands are good sensitizers. Photoluminescence data showed that the Eu^{3+} , Gd^{3+} and Tb^{3+} complexes act as efficient light conversion molecular devices (LCMDs) and can be used as red, green and blue emitter luminescent materials.

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