**UNIVERSIDADE DE SÃO PAULO
INSTITUTO DE FÍSICA DE SÃO CARLOS**

Gaston Lozano Calderón

**White light emission under 980 nm and Judd-Ofelt
analysis of tellurite-zinc glasses doped with
 Er^{3+} - Yb^{3+} - Tm^{3+}**

São Carlos

2020

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analysis of tellurite-zinc glasses doped with
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Dissertation presented to the Graduate Program in Physics at the Instituto de Física de São Carlos, Universidade de São Paulo to obtain the degree of Master of Science.

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Advisor: Prof. Dr. Euclides Marega Junior

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To my Godfather, Adolfo Marín.

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“My father had taught me, looking at a bird, he says, “Do you know what that is? It’s a Brown-Throated Thrush. But in Portuguese, it’s a Hunto La Pero. In Italian, a Chutto La Pittida. In Chinese, it’s a Chung Wong Tah.” Etcetera. He says, “Now you’d know all the languages you want to know what the name of that bird is, and when you finish with all that” he says, “you’ll know absolutely nothing whatever about the bird”. He knew the difference between knowing the name of something and knowing something. ”

Richard Feynman

“Science cannot solve the ultimate mystery of nature. And that is because, in the last analysis, we ourselves are part of nature and therefore part of the mystery that we are trying to solve.”

Max Planck

“The good thing about science is that it’s true whether or not you believe in it.”

Neil deGrasse Tyson

“Would you tell me, please, which way I ought to go from here?”

“That depends a good deal on where you want to get to,” said the Cat.

“I don’t much care where—” said Alice.

“Then it doesn’t matter which way you go,” said the Cat.

“—so long as I get somewhere,” Alice added as an explanation.

“Oh, you’re sure to do that,” said the Cat, “if you only walk long enough.”

Lewis Carroll, Alice’s adventures in Wonderland

“One day your life will flash before your eyes. Make sure it’s worth watching.”

Gerard Way

Piensa en cosas felices, vive cosas felices, sé alguien feliz.

ABSTRACT

LOZANO, G. **White light emission under 980 nm and Judd-Ofelt analysis of tellurite-zinc glasses doped with Er^{3+} - Yb^{3+} - Tm^{3+}** . 2020. 82p. Dissertation (Master of Science) - Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2020.

In this dissertation, tellurite-zinc glasses doped with Tm^{3+} , Yb^{3+} and Er^{3+} were fabricated by conventional melt-quenching method and characterized by absorption spectroscopy, refractive index, lifetime measurements, excitation, luminescence and up-conversion spectroscopy. Tunable white to blue light emission based on the colour mixing of red, green and blue light was observed in the triply-doped samples via up-conversion under 980 nm and by adjusting the laser excitation intensity. The balancing of the relative intensity of each colour is provided by the energy transfer process between the rare-earth ions. Moreover, luminescence spectroscopy was performed with a 405 nm laser to further understand the energy transfer mechanism. According to the Judd-Ofelt theory, the intensity parameters (Ω_2 , Ω_4 and Ω_6) of Er^{3+} and Tm^{3+} for all samples present the trend $\Omega_2 < \Omega_4 < \Omega_6$. These parameters are related to the bonding and local structure in the vicinity of the rare-earth ions, which give information regarding to physical and chemical properties. The spectroscopic parameters were calculated with the Judd-Ofelt theory and the energy transfer micro-parameters (critical radius of interaction and energy transfer coefficient) were determined by the Dexter model. Such results shall be used to give a comprehensive explanation for the energy transfer process between these rare earth ions.

Keywords: Up-conversion. Judd-Ofelt. White light. Energy transfer. Tellurite. Rare-earths. Micro-parameters.

RESUMO

LOZANO, G. **Emissão de luz branca sob 980 nm e análise de Judd-Ofelt de vidros de zinco-telurito dopados com Er^{3+} - Yb^{3+} - Tm^{3+} .** 2020. 82p. Dissertação (Mestrado em Ciências) - Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2020.

Nesta dissertação, vidros de telurito-zinco dopados com Tm^{3+} , Yb^{3+} e Er^{3+} foram fabricados pelo método convencional de fusão-resfriamento e caracterizados através da espectroscopia de absorção, índice de refração, medidas de tempos de vida, espectroscopia de excitação, de luminescência e de conversão ascendente. Luz branca até azul sintonizável baseada na mistura de cores vermelha, verde e azul, foi observada nas amostras triplemente dopadas via conversão ascendente sob 980 nm e ajustando a intensidade de excitação do laser. O equilíbrio da intensidade relativa de cada uma das cores é determinado pelos processos de transferência de energia entre os íons de terras raras. Ademais, a espectroscopia de luminescência foi realizada com um laser de 405 nm. De acordo com a teoria de Judd-Ofelt, os parâmetros de intensidade (Ω_2 , Ω_4 e Ω_6) do Er^{3+} e Tm^{3+} para todas as amostras apresentam a tendência $\Omega_2 < \Omega_4 < \Omega_6$. Esses parâmetros estão relacionados à ligação e a estrutura local nas proximidades dos íons de terras raras, os quais fornecem informações sobre propriedades físicas e químicas. Os parâmetros espectroscópicos foram calculados a través da teoria de Judd-Ofelt e os micro-parâmetros de transferência de energia (raio crítico de interação e coeficiente de transferência de energia) foram determinados pelo modelo de Dexter. Tais resultados são utilizados para fornecer uma explicação compreensiva do processo de transferência de energia entre os íons de terras raras.

Palavras-chave: Conversão ascendente. Judd-Ofelt. Luz branca. Transferência de energia. Telurito. Terras raras. Micro-parâmetros.

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LIST OF ABBREVIATIONS AND ACRONYMS

ESA	Excited-stated absorption
CCT	Correlated colour temperature
CF	Crystal field
ED	Electric-dipole
ET	Energy transfer
IR	Infrared
JO	Judd-Ofelt
LS	Spin-orbit coupling
MD	Magnetic-dipole
NBO	Non-bridging oxygen
NIR	Near-infrared
NR	Non-radiative
REI	Rare-earth ion(s)
RET	Resonance energy transfer
TPA	Two-photon absorption
UC	Up-conversion

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1 INTRODUCTION

In recent years, rare-earth ions doped glasses have been widely studied for their luminescence properties, such as the near-infrared (NIR) to visible light emission via up-conversion (UC), which occurs when two or more low-energy photons generate the emission of photon energies higher than the initial light due to its non-linear dependence on incident light intensity.¹ Particularly, glass oxides (e.g., TeO_2 , SiO_2 and B_2O_3) are optically transparent from UV to NIR spectral range and their capability to incorporate high concentrations of REI into glass host matrices² makes them candidates for a wide variety of applications such as the development of temperature sensors, non-linear optics, telecommunications and lasers.³⁻⁵ However, UC process in silicate or borate glasses is difficult to observe because of their high phonon-energy, which suppresses the transitions with small energy level difference.⁶ In contrast, tellurite glasses exhibit low phonon-energy, low melting temperature (between 600 and 800 °C), high refractive index⁷ and excellent transmission in the visible and IR wavelength regions.⁸

The addition of ZnO into the TeO_2 matrix increases its refractive index, the density and the absorption edge shift to high energies.^{9,10} Therefore, zinc-tellurite glass system is a suitable up-converting material and generation of visible light can be achieved. For example, there is evidence of NIR-to-visible light with Er^{3+} doped tellurite glasses,¹¹ where green and blue light was observed. Furthermore, doped glass with $\text{Yb}^{3+}-\text{Er}^{3+}$ is an efficient system for UC due to the energy transfer (ET) process under 980 nm diode laser as an excitation source,¹² where Yb^{3+} acts as a donor for the Er^{3+} , giving red, green and blue (RGB) emission, which can be used to obtain white light by controlling the RGB light emission intensity.¹³⁻¹⁵ On the other hand, $\text{Yb}^{3+}-\text{Tm}^{3+}$ generates red and blue light via ET and excited state absorption (ESA).¹⁶ Hence, the Yb^{3+} as sensitizer ion and $\text{Er}^{3+}-\text{Tm}^{3+}$ as activator ions can produce simultaneously RGB light to generate white light¹⁷⁻¹⁹ by adjusting the excitation power with a 980 nm laser diode and, in this fashion, control the relative intensities of each emission band.

In this dissertation, luminescence properties in $\text{Er}^{3+}-\text{Yb}^{3+}-\text{Tm}^{3+}$ doped zinc-tellurite glasses for white light emission were discussed. Such white light is generated by the mixture of RGB light provided by Er^{3+} and Tm^{3+} via ET and UC process using the Yb^{3+} as sensitizer, and also was characterized according to the CIE-1931 standards. In order to give a comprehensive explanation of the energy transfer process between Er^{3+} , Yb^{3+} and Tm^{3+} , absorption spectroscopy, decay curve, refractive index, up-conversion emission spectroscopy, together with the theoretical calculations given by the Judd-Ofelt theory, were performed. This theory allows us to calculate some spectroscopic parameters namely spontaneous radiative transition probabilities, radiative lifetimes, fluorescence branching

ratio, fluorescence quantum efficiency, absorption and emission cross sections, as well as the ET micro-parameters, which are the critical radius of interaction and the ET coefficient.

2 THEORETICAL BACKGROUND

2.1 Tellurite glasses

A glass is “an inorganic product of fusion which has been cooled to a rigid condition without crystallization”,²⁰ hence, glasses exhibit an amorphous structure in contrast with crystals. Glasses are used as host materials for rare-earth ions (REI*) because of its ability to incorporate high concentrations of dopants capable to change its optical properties.

Tellurite glasses based on tellurium dioxide (TeO_2) present superior properties if we compare with other sorts of glasses, specially optical properties. Some of these features are summarised in Table 1, where its low phonon energy and high refractive index become tellurite glasses in propitious materials for near infrared and up-conversion luminescence when are doped with REI.²¹ Moreover, these glasses exhibit non-linear properties which can be used in the manufacture of optical fibres, waveguides, ultrafast optical switching and luminescent devices.²²

Table 1 – Comparison of optical and physical properties of various sorts of glasses. Some values depend on the synthesis and glass composition.

Properties	TeO_2	GeO_2	Silica	Fluoride	Chalcogenide
Linear refractive index	1.9 – 2.3	1.7 – 1.8	1.46	1.4 – 1.6	2 – 3.3
Abbe number	10 – 20	25 – 40	80	60 – 100	
Phonon energy (cm^{-1})	780	880	1100	500 – 630	350
Band gap (eV)	3	3.5 – 4	10	9 – 11	1 – 3
Thermal expansion coefficient ($\times 10^{-7} \text{ }^\circ\text{C}^{-1}$)	120 – 170	100 – 130	5	150 – 200	140 – 210
Glass transition temperature T_g ($^\circ\text{C}$)	280 – 480	450	1000	270 – 300	300 – 420
Density (g cm^{-3})	5.5	6.4	2.2	5.0	4.5

Source: Adapted from JHA *et al.*²³

In general, tellurite glasses are prepared by melt-quenching method and can be improved by adding oxides. With addition of ZnO , the glass transition temperature and density are modified,²⁴ and also decreases the absorption in shorter wavelengths in the UV region,¹⁰ i.e., the tellurite glasses are more transparent in the visible region.

2.2 Rare-earth ions

Trivalent rare-earth ions present $4f^n 5s^2 5p^6$ electron configuration, where $n = 1, 2, \dots, 13$, in this way the $4f$ shield defines its optical and magnetic properties as a result

* In this dissertation, when rare-earth ions are mentioned, it refers to trivalent rare-earth ions.

of $4f \rightarrow 4f$ electron transitions, besides is shielded by the $5s^2$ and $5p^6$ orbitals. Hence, being doped in a host material, the host lattice influence is weak,²⁵ the spin-orbit (LS) interaction is predominant and the REI experiments an electrostatic field caused by the charge distribution within the host matrix environment. This electrostatic potential is named crystal field (CF) potential, which generates a small perturbation in the $^{2S+1}L_J$ states, splitting a maximum number of $2J + 1$ or $J + 1/2$ (odd J [†]) Stark levels.

Figure 1 – Energy level diagram for trivalent rare-earth ions in LaCl_3 .

Source: WITHNALL *et al.*²⁷

In Figure 1, the energy level diagram of some trivalent REI in lanthanum chloride (LaCl_3) is illustrated. This diagram is named *Dieke diagram* and is helpful to predict the emission/absorption spectra of the REI because the energy levels remain unchanged when

[†] The Kramers theorem says that all electronic levels that have an odd number of electrons, at least one of them is doubly degenerated.²⁶

another host material is used, however, the width, which indicates the magnitude of the CF splitting, of each state can change slightly.²⁶ The $^{2S+1}L_J \rightarrow ^{2S'+1}L'_{J'}$ transitions are governed by the Laporte selection rules between electric-dipole states²⁸

$$\Delta L = \pm 1; \Delta S = 0; \Delta J = \{0, \pm 1\} (0 \nleftrightarrow 0) \quad (2.1)$$

Therefore, the $4f \rightarrow 4f$ transition is forbidden. Nevertheless, when a REI is located on a non-symmetric lattice (because of a non-inversion symmetry CF), the parity selection rule is relaxed and emissions are observed.²⁷ Thus, these transitions become allowed by the forced electric-dipole²⁶ and can be explained by the Judd-Ofelt theory.

2.3 Judd-Ofelt theory

In 1962, Judd²⁹ and Ofelt³⁰ independently developed a theoretical model to describe the $4f$ electron transitions in REI. The REI, which is inside of a host matrix, interacts with the CF potential described in terms of spherical harmonics

$$V_{CF} = \sum_{t,p} A_{t,p} \sum_i r_i^t V_p^t(\theta_i, \phi_i) \quad (2.2)$$

Where $A_{t,p}$ is the field parameter, which depends on the crystal-symmetry group, r_i^t is the radial coordinate. $V_p^t(\theta_i, \phi_i)$ is the p -th component of the spherical harmonic of order t , and θ_i, ϕ_i are the angular coordinates of the i -th electron. Equation 2.2 can be separated into even and odd t term as follows

$$V_{CF} = \sum_{t,p}^{t=even} A_{t,p} \sum_i r_i^t V_p^t(\theta_i, \phi_i) + \sum_{t,p}^{t=odd} A_{t,p} \sum_i r_i^t V_p^t(\theta_i, \phi_i) \quad (2.3)$$

$$V_{CF} = V_{CF}^{even} + V_{CF}^{odd} \quad (2.4)$$

Hence, the perturbed Hamiltonian is

$$H = H_0 + V_{CF}^{even} + V_{CF}^{odd} \quad (2.5)$$

The odd term of the CF potential is responsible to the coupling between even and odd states. This allows the mixture of the $4f$ (same parity) and $5d$ (opposite parity) states.³¹ The non-perturbed Hamiltonian term H_0 only considers the electrostatic interaction and the LS coupling of a free ion (even parity). Restricting to interactions between the $4f^N$ electrons, the energy E_a of the a -th energy level is

$$H |\phi_a\rangle = (H_0 + V_{CF}^{even}) |\phi_a\rangle = E_a |\phi_a\rangle \quad (2.6)$$

Where $|\phi_a\rangle$ is expressed as a non-perturbed state in the LS coupling scheme

$$|\phi_a\rangle = \sum_k a_k |f^N \psi J J_z\rangle \quad (2.7)$$

ψ denotes the necessary quantum numbers to completely describe the level. In this Russell-Saunders coupling scheme, these quantum numbers are S and L . Similarly, with Equation 2.7, we may write an excited state $|\phi_b\rangle$

$$|\phi_b\rangle = \sum_k b_k |f^N \psi' J' J'_z\rangle \quad (2.8)$$

Condon and Shortly defined the electric and magnetic-dipole line strength between two levels a and b ³²

$$S_{ED}(a, b) = \sum_{a,b} |\langle \phi_a | \hat{p} | \phi_b \rangle|^2 \quad (2.9)$$

$$S_{MD}(a, b) = \sum_{a,b} |\langle \phi_a | \hat{M} | \phi_b \rangle|^2 \quad (2.10)$$

Note that $\hat{p}$ and $\hat{M}$ are the electric-dipole (ED) and magnetic-dipole (MD) operator, respectively, defined as

$$\hat{p} = -e \sum_k \hat{r}_k \quad (2.11)$$

$$\hat{M} = -\frac{eh}{2\pi m_e c} \sum_k (\hat{L}_k + 2\hat{S}_k) \quad (2.12)$$

Where e is the electron charge, h is the Planck constant, m_e is the electron mass and c is the speed of light. In general, the matrix elements of $\hat{p}$ between two states ϕ_i and ϕ_j may be non-zero only if i and j do not have the same parity[‡], while the magnetic-dipole operator is of even parity[§].

As mentioned earlier, the odd-parity terms of the CF potential must be considered for mixed-parity states. Let $|\phi_\beta\rangle$ be an excited state with opposite-parity at an energy E_β written as

$$|\phi_\beta\rangle = \sum_k \beta_k |f^N \psi'' J'' J''_z\rangle \quad (2.13)$$

[‡] This is because the operator $\hat{r}$ has odd parity, and the contribution of both $\hat{r}$ and $-\hat{r}$ terms are equal but opposite whether ϕ_i and ϕ_j have the same parity.

[§] Both operators $\hat{L}$ and $\hat{S}$ have even parity.

From the mixture of the $|\phi_a\rangle$, $|\phi_b\rangle$ and $|\phi_\beta\rangle$ states, the following mixed-parity states can be obtained

$$|\chi_a\rangle = |\phi_a\rangle + \sum_{\beta} \frac{\langle\phi_\beta| V_{CF}^{odd} |\phi_a\rangle}{E_a - E_\beta} |\phi_\beta\rangle \quad (2.14)$$

$$|\chi_b\rangle = |\phi_b\rangle + \sum_{\beta} \frac{\langle\phi_\beta| V_{CF}^{odd} |\phi_b\rangle}{E_b - E_\beta} |\phi_\beta\rangle \quad (2.15)$$

Therefore, the matrix elements of the electric-dipole transition from a mixed-parity state $|\chi_a\rangle$ to $|\chi_b\rangle$ is

$$\langle\chi_a|\hat{p}|\chi_b\rangle = \sum_{\beta} \left\{ \frac{\langle\phi_b|\hat{p}|\phi_\beta\rangle \langle\phi_\beta| V_{CF}^{odd} |\phi_a\rangle}{E_a - E_\beta} + \frac{\langle\phi_a|\hat{p}|\phi_\beta\rangle \langle\phi_\beta| V_{CF}^{odd} |\phi_b\rangle}{E_b - E_\beta} \right\} \quad (2.16)$$

Using appropriate approximations as detailed in reference,³³ we find the following expression

$$\begin{aligned} S_{ED}(J, J') &= |\langle\chi_a|\hat{p}|\chi_b\rangle|^2 \\ &= e^2 \sum_{\lambda} \Omega_{\lambda} |\langle f^N \psi J | U^{\lambda} | f^N \psi' J' \rangle|^2 \end{aligned} \quad (2.17)$$

Where Ω_{λ} ($\lambda = 2, 4, 6$) are the Judd-Ofelt intensity parameters and U^{λ} is a unit tensor which connects the states $|\chi_a\rangle$ and $|\chi_b\rangle$, being $|\langle f^N \psi J | U^{\lambda} | f^N \psi' J' \rangle|^2$ independent elements of the host matrix where the REI are inside, which were determined by Carnall, et al.³⁴ Those parameters are important for the investigation of bonding and local structure in the vicinity of REI. Ω_2 is related to the structural change, covalency and symmetry, whereas Ω_4 and Ω_6 characterize the rigidity, viscosity and dielectric properties.³⁵ It should be noted that the allowed selection rules for ED transitions derived from the JO theory are $\Delta S = 0$, $\Delta L = \Delta J \leq \pm 6$.³⁶

In glasses, the MD contribution is relatively weak if is compared with ED transitions because the REI is located at a low symmetry in a vitreous medium.³⁶ Nevertheless, it will be considered for emission probabilities between intermediate states. The selection rules for MD transitions are $\Delta S = \Delta L = 0$, $\Delta J \leq \pm 1$ ($0 \leftrightarrow 0$), and the line strength for MD transitions expressed with the $|f^N \psi J\rangle$ and $|f^N \psi' J'\rangle$ states is³⁶

$$S_{MD}(J, J') = \left(\frac{eh}{2\pi m_e c} \right)^2 |\langle f^N \psi J | \hat{L} + 2\hat{S} | f^N \psi' J' \rangle|^2 \quad (2.18)$$

The matrix elements of the MD operator for all cases permitted by $\Delta J = \{0, \pm 1\}$ selection rule are³⁷

a) $J = J'$

$$\langle f^N \psi J | \hat{L} + 2\hat{S} | f^N \psi J \rangle = \left[1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \right] [J(J+1)(2J+1)]^{1/2} \quad (2.19)$$

b) $J' = J - 1$

$$\langle f^N \psi J | \hat{L} + 2\hat{S} | f^N \psi J - 1 \rangle = \left[\frac{(S+L+J+1)(S+L-J+1)(S+J-L)(L+J-S)}{4J} \right]^{1/2} \quad (2.20)$$

c) $J' = J + 1$

$$\langle f^N \psi J | \hat{L} + 2\hat{S} | f^N \psi J + 1 \rangle = \left[\frac{(S+L+J+2)(S-L+J+1)(L-S+J+1)(L+S-J)}{4(J+1)} \right]^{1/2} \quad (2.21)$$

The theoretical or calculated oscillator strength (f_{cal}) of the ED transition from the ground state is³⁸

$$f_{cal} = \frac{8\pi^2 m_e c}{3he^2 \lambda (2J+1)} \frac{(n^2 + 2)^2}{9n} S_{ED}(J, J') \quad (2.22)$$

In this case, λ is the wavelength of the electronic transition, J is the angular momentum of initial (ground) state and n is the wavelength-dependent refractive index of the medium. The experimental oscillator strength (f_{exp}) is proportional to the area under the absorption curve and is defined as³⁸

$$f_{exp} = \frac{m_e c}{\pi e^2 N} \int \alpha(\nu) d\nu \quad (2.23)$$

In Equation 2.23, N is the number of ions per unit volume, $\alpha(\nu)$ is the absorption coefficient in function of the frequency ν , which can be written in terms of the absorption cross-section (σ_{abs}) as²⁶

$$\alpha(\nu) = \sigma_{abs}(\nu) N \quad (2.24)$$

The spontaneous emission probability for electric and magnetic-dipole contributions between two states ($J \rightarrow J'$) is³⁹

$$A(J, J') = \frac{64\pi^4}{3h\lambda^3(2J+1)} \left[\frac{n(n^2 + 2)^2}{9} S_{ED} + n^3 S_{MD} \right] \quad (2.25)$$

This emission probability gives the radiative lifetime of an excited state

$$\tau_{cal} = \frac{1}{\sum_{J'} A(J, J')} \quad (2.26)$$

Where the sum is over all transition probabilities for the levels above the specific emission state. Furthermore, the emission quantum efficiency (η) is determined with calculated and experimental (τ_{exp}) radiative lifetime as follows

$$\eta = \frac{\tau_{exp}}{\tau_{cal}} \quad (2.27)$$

Other parameter that can be calculated with τ_{cal} is the luminescence branching ratio, which characterizes the possibility of exciting stimulated emission in a given channel³⁹

$$\beta = A(J, J')\tau_{cal} \quad (2.28)$$

In other words, β represents the percentage of emitted radiation in a level J with respect to all other transitions from this state.

2.4 Up-conversion

Up-conversion (UC) is the non-linear process where a material absorbs photons with a given frequency and stimulates the emission of a photon with a frequency greater than the exciting one. Two or more absorbed photons are required for UC emission, and the absorption of these photons must be sequential and not simultaneous,⁴⁰ in contradistinction to second (third, fourth, etc.) harmonic generation and two-photon absorption (TPA). The main difference between these two process and UC luminescence is that in an up-converting system real intermediate states are involved, and for harmonics generation and TPA need virtual intermediate states.⁴¹ There are two principal UC mechanisms: Excited-state absorption (ESA) and energy transfer (ET). Both process will be discussed in the following.

2.4.1 Excited state absorption

The excited-state absorption is the process where an excited level is reached due to successive absorption of photons by a single ion. To achieve highly efficient ESA, a ladder-like arrangement of the energy states of REI is required and some of them such as Er^{3+} , Tm^{3+} , Ho^{3+} and Nd^{3+} have such energy level structures, which also find an optimal excitation wavelength match with the output of diode lasers (at ~ 980 or 800 nm).⁴²

To give an explanation of the ESA process, Figure 2 illustrates an energy level diagram of Tm^{3+} doped in silica only for blue emission. Tm^{3+} absorbs an IR photon and is excited to the $^3\text{H}_5$ level and decays to $^3\text{H}_4$ via non-radiative (NR) process. In this level, the Tm^{3+} could be excited by another IR photon until the $^3\text{F}_3$ level (ESA_1) and subsequently decays non-radiatively to $^3\text{H}_4$ state. Finally, via ESA_2 , the Tm^{3+} is excited to $^1\text{G}_4$ level and emits a photon with a wavelength of 475 nm ($^1\text{G}_4 \rightarrow ^3\text{H}_6$ transition).

Figure 2 – Energy level diagram of Tm^{3+} doped in silica via ESA for blue emission.

Source: Adapted from BONAR *et al.*⁴³

2.4.2 Energy transfer

Energy transfer process is an exchange of energy from an excited ion (donor D) to other ion (acceptor A), which could be in the ground or an excited state. If the energy of the donor is greater than the gained energy of the acceptor, the energy difference is attributed to the phonon-assisted ET and when this difference is almost zero, we are dealing with a resonance ET process (RET). The probability of RET between the donor and acceptor, based on the Dexter's model, separated a distance R_{DA} considering dipole-dipole interaction is^{44,45}

$$P_{DA} = \frac{C_{DA}}{R_{DA}^6} = \frac{R_C^6}{R_{DA}^6 \tau_D} \quad (2.29)$$

with

$$C_{DA} = \frac{3c}{8\pi^4 n^2} \frac{g_{lower}^D}{g_{upper}^D} \int \sigma_{em}^D(\lambda) \sigma_{abs}^A(\lambda) d\lambda \quad (2.30)$$

where R_C is the critical radius of the interaction, τ_D is the lifetime of donor ions at the excited level, C_{DA} is the derived microscopic energy transfer coefficient, g_{upper}^D and g_{lower}^D are the degeneracies of the upper and lower state of the donor, respectively, $\sigma_{em}^D(\lambda)$

and $\sigma_{abs}^A(\lambda)$ are the emission and absorption cross-sections. σ_{abs} is given by Equation 2.24 and σ_{em} may be determined using the Fchtbauer–Ladenburg equation⁴⁶

$$\sigma_{em}(\lambda) = \frac{\lambda^4 A(J, J')}{8\pi c n^2} \frac{I(\lambda)}{\int I(\lambda) d\lambda} \quad (2.31)$$

In this case, $I(\lambda)$ is the normalized line-shape of emission spectrum. The probability of RET is proportional to the overlapping between $\sigma_{em}^D(\lambda)$ and $\sigma_{abs}^A(\lambda)$ as shown in Equation 2.30, and a typical example is illustrated in Figure 3. Additionally, Equation 2.30 describes a non-radiative ET, where the lifetime of the donor decreases in presence of the acceptor,⁴⁷ whereas the radiative energy transfer their lifetimes are not affected⁴⁸ and no significant interaction between the donor and acceptor is required.⁴⁹

Figure 3 – Schematic representation of the overlap between the emission and absorption cross-sections spectra of the donor and acceptor, respectively.

Source: By the author.

Non-resonant energy transfer occurs when there is a lack of overlap due to the energy difference between the donor and acceptor energy levels, which is attributed to the creation and annihilation of phonons (Stokes and anti-Stokes process). As an example of resonant and non-resonant ET between two REI, Figure 4 is illustrated, where the Er^{3+} is pumped with 976 nm and via ESA is excited until the $\text{Er}^{3+} : ^4\text{F}_{7/2}$ electronic level and decrease in green emission as a result of NR transitions and from this level, transfers its energy to Tm^{3+} in a non-resonant manner to the $\text{Tm}^{3+} : ^3\text{F}_2$ level because the energy difference is $\sim 3600 \text{ cm}^{-1}$. When the Er^{3+} is in the $\text{Er}^{3+} : ^4\text{F}_{9/2}$, RET is observed between $\text{Er}^{3+} : ^4\text{F}_{9/2}$ and $\text{Tm}^{3+} : ^3\text{F}_{2,3}$ energy levels (both levels have almost the same energy $\sim 1500 \text{ cm}^{-1}$).

Figure 4 – Energy level diagram of Er^{3+} and Tm^{3+} doped in germanium-tellurite glasses showing the UC process and ET mechanism.

Source: Adapted from RIVERA *et al.*⁵⁰

Based on the example detailed above, to summarize the ET process the following notation will be used:

For the non-resonant ET:

and for the RET:

In this dissertation, with the ESA and ET process, Yb^{3+} will be used to transfer energy when excited with an IR laser, allowing the emission of blue and red light generated by Tm^{3+} , red and green light generated by Er^{3+} . In this manner, doping the tellurite-zinc glasses with Er^{3+} , Yb^{3+} and Tm^{3+} , RGB light will be obtained to generated white light.

3 METHODOLOGY

3.1 Fabrication of the glasses

3.1.1 Materials

The nominal composition of the zinc-tellurite glasses were $(67-x-y)\text{TeO}_2$ - 30ZnO - $3\text{Yb}_2\text{O}_3$ - $x\text{Tm}_2\text{O}_3$ - $y\text{Er}_2\text{O}_3$. The compounds present a high purity ($\geq 99.9\%$) and were supplied by Sigma-Aldrich as powders. Each powder mixture has a mass of 8 g and was dried in a platinum crucible at 300°C for 30 minutes in order to avoid the presence of water molecules inside the precursor powders. This temperature is underneath its glass transition temperature, which depends on the concentration of TeO_2 and ZnO from 303 to 363°C .²⁴

Each sample was labelled according to its composition as TZYb-100* x -100* y , where the values of x and y are 0.00, 0.10, 0.2 and 0.00, 0.03, respectively, having six samples: TZYb-00-00, TZYb-00-03, TZYb-10-00, TZYb-10-03, TZYb-20-00 and TZYb-20-03. The composition of all compounds is shown in Table 2.

Table 2 – Concentrations in mol% of the TZYb-100* x -100* y glasses.

Sample	Concentration				
	TeO_2	ZnO	Yb_2O_3	Tm_2O_3	Er_2O_3
TZYb-00-00	67.00	30.00	3.00	0.00	0.00
TZYb-00-03	66.97	30.00	3.00	0.00	0.03
TZYb-10-00	66.90	30.00	3.00	0.10	0.00
TZYb-10-03	66.87	30.00	3.00	0.10	0.03
TZYb-20-00	66.80	30.00	3.00	0.20	0.00
TZYb-20-03	66.77	30.00	3.00	0.20	0.03

Source: By the author.

3.1.2 Thermal process

The TZYb glasses were prepared by conventional melt-quenching method and the synthesis is based on the developed by Rivera, et al.⁵¹ The powders were melted at 750 and 800°C (rates of $10^\circ\text{C}/\text{min}$) for 30 min for each temperature in a furnace under oxidizing conditions (oxygen flow of $0.5\text{ L}/\text{min}$), subsequently the melted glasses were poured in a pre-heated mould, annealed at 350°C for 300 min and slowly cooled down to room

temperature (rates of 1 °C/min). The studied samples were polished until ~ 1 mm in thickness for optical measurements.

3.2 Characterization of the glasses

3.2.1 Density

The TZYb glasses density were calculated using the Archimedes' method by the following expression

$$\rho = \frac{m}{m - m'} \rho_{H_2O} \quad (3.1)$$

Where m and m' is the mass of the glass measured in air and water, respectively, and ρ_{H_2O} the water density, which depends on the temperature. The values of ρ_{H_2O} in the function of temperature were found in Reference.⁵² Three measurements were performed for all samples using a Mettler Toledo AG285 analytical balance of accuracy 0.0001 g and deionized water at a temperature of 23.2 ± 0.3 °C.

3.2.2 Refractive index

A Metricon 2010 M-line was used to measure the refractive index of all samples at different wavelengths (532.0, 632.8 and 1538 nm). Its operation is based on prism coupling technique, which consists in brought into contact the sample with the base of a prism by a coupling head as illustrated in Figure 5a.

Figure 5 – a) Schematic representation of the prism coupler. b) The characteristic curve of the Metricon 2010.

Source: Adapted from METRICON CORPORATION.⁵³

A laser beam insides with a variable angle θ into the prism (refractive index n') and trough until the sample surface and is reflected onto the detector. The prism rotates

until the incident angle becomes less than the critical angle θ_c , which can be found when there is a sharp drop in the detector intensity as shown in Figure 5b.

The Sellmeier's equation is an empirical relation between refractive index and wavelength, described as follows

$$n(\lambda) = \sqrt{1 + \sum_i \frac{A_i}{1 - B_i \lambda^{-2}}} \quad (3.2)$$

Where A_i and B_i are the Sellmeier parameters, which can be deduced by the collected data. In this case, as we only have three points for the fitting curve, Equation 3.2 is expressed with the first term of the sum

$$n(\lambda) = \sqrt{1 + \frac{A}{1 - B \lambda^{-2}}} \quad (3.3)$$

3.2.3 Absorption spectroscopy

A light beam tends to attenuate after passing through a material medium, whose intensity I will depend on the intensity I_0 measured after traversing the medium and of the optical path length x *, written as²⁶

$$I = I_0 e^{-\alpha x} \quad (3.4)$$

Where α is the absorption coefficient. From Equation 3.4, the Beer-Lambert law can be obtained

$$A = \text{Log} \left(\frac{I}{I_0} \right) \quad (3.5)$$

Being A the absorbance and the fraction I/I_0 is the transmittance. Finally, using Equation 3.4 and 3.5 the absorption coefficient is

$$\alpha = \frac{A}{x \text{Log}(e)} \quad (3.6)$$

In a medium, the absorption of light generates transitions from the ground state to an excited state where, in the UV-VIS range, this light absorption causes electronic and vibrational excitations, and the absorption in the IR range generates rotational and vibrational transitions.⁵⁴ For absorption measurements, an UV-3600 Shimadzu spectrophotometer have been used.

* In the present study, the optical path length is the thickness of the glass.

3.2.4 Judd-Ofelt parameters

In order to find the JO parameters, it is necessary to compare both Equation 2.22 and 2.23 giving the following expression

$$\begin{aligned} S_{ED}^{exp}(J, J') &= \frac{3h\lambda(2J+1)}{8\pi^2 m_e c} \frac{9n}{(n^2+2)^2} f_{exp} \\ &= e^2 \sum_{\lambda} \Omega_{\lambda} |\langle f^N \psi J | U^{\lambda} | f^N \psi' J' \rangle|^2 \end{aligned} \quad (3.7)$$

Equation 3.7 can be written as its matrix representation for M transitions

$$S_{ED}^{exp} \doteq \begin{pmatrix} \|U_1^2\|^2 & \|U_1^4\|^2 & \|U_1^6\|^2 \\ \|U_2^2\|^2 & \|U_2^4\|^2 & \|U_2^6\|^2 \\ \vdots & \vdots & \vdots \\ \|U_M^2\|^2 & \|U_M^4\|^2 & \|U_M^6\|^2 \end{pmatrix} \begin{pmatrix} \Omega_2 \\ \Omega_4 \\ \Omega_6 \end{pmatrix} \quad (3.8)$$

Where S_{ED}^{exp} is a $M \times 1$ vector. Due to the number of equations is greater than the number of unknowns (overdetermined system), the standard least-squares method should be applied in order to minimize the absolute differences between the experimental and the calculated values.⁵⁵ In this case, it is convenient to write Equation 3.8 in its simplified matrix form

$$S = U\Omega \quad (3.9)$$

Being S the $M \times 1$ matrix for the S_{ED}^{exp} vector elements, U is the $M \times 3$ matrix for the square matrix elements of $|\langle f^N \psi J | U^{\lambda} | f^N \psi' J' \rangle|^2$ and Ω is the 3×1 matrix for the JO parameters. Therefore, the matrix Ω of the least-squares estimates of the JO parameters is⁵⁵

$$\Omega = (U^{\dagger}U)^{-1}U^{\dagger}S \quad (3.10)$$

The Ω_{λ} parameters were calculated by a program developed in *Wolfram Mathematica 11* (see Appendix A). Besides, to indicate the validity of JO theory, the root mean square (rms) deviation between experimental and calculated ED line strength for M absorption bands is³⁹

$$\delta_{rms} = \sqrt{\frac{\sum_{i=1}^M (S_{ED}^{exp} - S_{ED}^{cal})^2}{M-3}} \quad (3.11)$$

11 (see Appendix A) based on the procedure detailed in references.^{59,60} In the case of luminescence, a laser of 405 nm was employed using the same micro-spectrometer.

3.2.6 Lifetime measurements

Lifetime measurements for each UC emission band were performed with a Horiba FL3-22iHR spectrofluorimeter and calculated using the following equation⁶¹

$$\tau_{exp} = \frac{\int t I(t) dt}{\int I(t) dt} \quad (3.14)$$

where $I(t)$ is the luminescent intensity at time t . To set the appropriate excitation wavelength to collect the lifetime decay curve of each emission, the excitation spectroscopy was performed with the same spectrofluorimeter.

3.2.7 Energy transfer micro-parameters

With the collected absorption and emission spectra, the cross-sections were determined in order to estimate the ET micro-parameters[†], i.e., the critical radius and the microscopic energy transfer coefficient. The Yb^{3+} only posses one absorption band ($\text{Yb}^{3+}: {}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$), and is not possible to calculate its JO parameters. Therefore, to find the ET micro-parameters for Yb^{3+} , the spontaneous transition probability must be determined using the following equation⁶²

$$A(J, J') = \frac{8\pi c n^2 (2J' + 1)}{\lambda^4 N (2J + 1)} \int \alpha(\lambda) d\lambda \quad (3.15)$$

where J' and J are the total angular momentum for the upper and lower levels, respectively. The emission cross-section can be calculated by using the McCumber's theory (reciprocity equation)⁶²

$$\sigma_{em}(\lambda) = \sigma_{abs}(\lambda) \frac{Z_{lower}}{Z_{upper}} \exp\left(\frac{E_{ZL} - hc\lambda^{-1}}{k_B T}\right) \quad (3.16)$$

where Z_{lower} , Z_{upper} are the partition functions of the lower and upper states, respectively, E_{ZL} is the zero-line energy defined as the separation energy between the lowest crystal field levels of excited and ground states, k_B is the Boltzmann's constant and T is the temperature. The value of Z_{lower}/Z_{upper} will be considered equals to 4/3 for Yb^{3+} ^{63,64} and T will be room temperature.

[†] In this dissertation, it will be only considered the ressonant energy transfer cases, i.e., donor and emissor are ions of the same species in a specific emission/absorption band. Further, in view of the experimental error and theoretical approximations, these values have to be considered as referential.

4 RESULTS AND DISCUSSION

4.1 Fabrication of the glasses

The samples were fabricated under strict cleaning and precision conditions, ensuring that they present optimal transparency and the same thickness for the optical characterization. The glasses were cut into rectangular plates and then polished reaching a thickness of ~ 1 mm and show a desirable optical transparency as can be seen in Figure 7.

Figure 7 – Photograph of a polished tellurite-zinc glass showing a desirable optical transparency.

Source: By the author.

Initially, the samples had a thickness about ~ 2.5 mm and after the polished process, they were not broken, indicating that the thermal process avoided the possible residual stress induced by a rapid cooling and they are rigid enough for handling for the following measurements. This residual stress was removed when the glasses were slowly cooled down to room temperature during the thermal process.

It is important to highlight that though the addition of the oxygen flow, the studied glasses does not present a dark colour. This darkening is due to the reduction process from TeO_2 to TeO , which means the decrement of oxygen or the number of positives charges of an ion during the fusion process.⁶⁵ Additionally, the oxygen gas purifies the furnace chamber of possible impurities of the laboratory.

4.2 Characterization of the glasses

4.2.1 Refractive index and density

Refractive index and density of the TZYb samples are listed in Table 3, where the values of the density do not significantly differ for TZYb-00-00, TZYb-00-03 and TZYb-10-00, implying that the addition of E_2O_3 and Tm_2O_3 does not significantly influence the glass structure. On the other hand, density values decrease for TZYb-10-03, TZYb-20-00 and TZYb-20-03 glasses. Furthermore, the values of the refractive index decrease when increased the REI concentration, however, the sample TZYb-20-00 shows an increment when compared with sample TZYb-10-03, and then decreases in TZYb-20-03. This may be possible due to the concentration of REI greater than 3.13 %mol modify the glass matrix structure as a consequence of rearrangements of atoms and the presence of non-bridging oxygens (NBOs) that increases the refractive index of the material.⁶⁶ In Figure 8, refractive index of the TZYb-00-00, TZYb-10-03 and TZYb-20-00 samples in function of the wavelength is illustrated and were fitted according to the Sellmeier's equation.

Table 3 – Refractive index n in function of the wavelength λ (in nm) and density ρ (in g cm^{-3}) of the TZYb glasses

λ	TZYb-00-00	TZYb-00-03	TZYb-10-00	TZYb-10-03	TZYb-20-00	TZYb-20-03
	n					
532.0	2.0628 ± 0.0001	2.0563 ± 0.0000	2.0553 ± 0.0004	2.0546 ± 0.0003	2.0754 ± 0.0013	2.0606 ± 0.0014
632.8	2.0355 ± 0.0004	2.0298 ± 0.0001	2.0289 ± 0.0004	2.0285 ± 0.0000	2.0479 ± 0.0005	2.0337 ± 0.0002
1538	1.9855 ± 0.0001	1.9801 ± 0.0001	1.9792 ± 0.0003	1.9784 ± 0.0006	1.9963 ± 0.0002	1.9832 ± 0.0004
ρ	5.62 ± 0.04	5.61 ± 0.02	5.62 ± 0.05	5.58 ± 0.02	5.56 ± 0.06	5.56 ± 0.05

Source: By the author.

Figure 8 – Refractive index of TZYb glasses in function of the wavelength according to Sellmeier's model.

Source: By the author.

4.2.2 Absorption spectroscopy

Figure 9 shows the absorption spectra (with baseline correction) of the TZYb glasses in the VIS-NIR region (400 – 1600 nm), where the absorption bands are due to the electronic transitions from the ground state of Er^{3+} , Yb^{3+} and Tm^{3+} to their excited states. The spectra consist of twelve absorption bands: those that are peaked at 444, 452, 488, 521, 544 and 654 nm are attributed to the absorption transition from the ground state Er^{3+} : $^4\text{I}_{15/2}$ to the excited levels $^4\text{F}_{3/2}$, $^4\text{F}_{5/2}$, $^4\text{F}_{7/2}$, $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$, respectively, while the bands centred at 474, 663, 688, 794 and 1212 nm are attributed to the absorption transition from the ground state Tm^{3+} : $^4\text{H}_6$ to the excited levels $^1\text{G}_4$, $^3\text{F}_2$, $^3\text{F}_3$, $^3\text{H}_4$ and $^3\text{H}_5$, respectively, and the most representative transition is centred at 976 nm, which corresponds to the Yb^{3+} : $^4\text{F}_{7/2} \rightarrow ^4\text{F}_{5/2}$ and Er^{3+} : $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{11/2}$ electronic transition, therefore, all samples must be excited in ~ 980 nm to get an efficient up-conversion process. Nevertheless, because of the high concentration of Yb^{3+} , is not possible distinguish the 976 nm band from the Er^{3+} . Additionally, is also not possible distinguish the Er^{3+} : $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ absorption band (centred at ~ 1500 nm).

Figure 9 – Absorption spectra of the TZYb glasses showing the Er^{3+} , Yb^{3+} and Tm^{3+} absorption bands from their ground states. The spectra were vertically shifted for reading purposes. Inset: Absorption bands in the visible region (400–850 nm).

Source: By the author.

4.2.3 Judd-Ofelt parameters

The experimental and calculated oscillator strength for each absorption band are listed in Table 4 and the small rms values indicate a good agreement between f_{exp} and f_{cal} . It was not possible to find the f_{cal} for Yb^{3+} : $^4\text{F}_{7/2} \rightarrow ^4\text{F}_{5/2}$ band because of the Yb^{3+} presents one absorption band and the JO parameters cannot be calculable. Similarly, the f_{exp} for Er^{3+} in 976 nm was not calculated for the reason mentioned in the discussion of the absorption spectra. Results were displayed with four significant numbers due to the precision of the calculations.

Table 4 – Experimental and calculated oscillator strength ($\times 10^{-6}$) of the TZYb glasses. The values of δ_{rms} are given in units of $\times 10^{-6}$.

REI	Abs. band	λ_{abs}	TZYb-00-00		TZYb-00-03		TZYb-10-00		TZYb-10-03		TZYb-20-00		TZYb-20-03	
			f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}
Yb^{3+}	$^4\text{F}_{7/2} \rightarrow ^4\text{F}_{5/2}$	976	5.630		5.689		5.754		5.744		5.183		5.838	
	$^3\text{H}_6 \rightarrow ^3\text{H}_5$	1212					2.351	2.614	2.683	2.885	2.147	2.253	2.523	2.674
Tm^{3+}	$\rightarrow ^3\text{H}_4$	794					3.820	3.899	4.031	4.215	3.162	3.382	3.734	3.955
	$\rightarrow ^3\text{F}_3$	688					3.917	4.024	4.468	4.650	2.861	3.066	3.833	4.058
	$\rightarrow ^3\text{F}_2$	663					0.478	0.764	0.798	0.877	0.301	0.416	0.560	0.701
	$\rightarrow ^1\text{G}_4$	474					1.279	1.148	1.109	1.322	1.139	0.776	1.369	1.116
$\delta_{rms} :$							0.304		0.282		0.351		0.321	
Er^{3+}	$^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$	654			2.101	2.058			1.648	1.611			1.411	1.375
	$\rightarrow ^4\text{S}_{3/2}$	544			0.619	0.267			0.534	0.149			0.431	0.149
	$\rightarrow ^2\text{H}_{11/2}$	521			10.98	10.98			10.97	10.97			9.751	9.751
	$\rightarrow ^4\text{F}_{7/2}$	488			1.256	1.475			0.817	1.005			0.727	0.911
	$\rightarrow ^4\text{F}_{5/2}$	452			0.515	0.334			0.223	0.187			0.336	0.186
	$\rightarrow ^4\text{F}_{3/2}$	444			0.045	0.192			0.016	0.108			0.021	0.107
$\delta_{rms} :$							0.276		0.254				0.219	

Source: By the author.

Some $f \rightarrow f$ transitions of REI are a quite more sensitive to the environment which obey the selection rule $|\Delta J| \leq 2$, $|\Delta L| \leq 2$ and $\Delta S = 0$,⁶⁷ and are called hypersensitive transitions. For Er^{3+} , $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$ is a hypersensitive transition and exhibits the highest oscillator strength value for all samples, and its value decreases with the addition of Tm_2O_3 . This decrement is due to the decrease of covalency between Er^{3+} and the ligand anions,⁶⁸ i.e., is related to the Ω_2 parameters. In the case of Tm^{3+} , the $^3\text{H}_6 \rightarrow ^3\text{H}_5$ and $^3\text{H}_6 \rightarrow ^3\text{H}_4$ transitions are hypersensitive, and therefore present a large oscillator strength value, however, in those TZYb glasses, the f_{exp} value of the $^3\text{H}_6 \rightarrow ^3\text{H}_4$ transition

is comparable with the ${}^3\text{H}_6 \rightarrow {}^3\text{F}_3$ and both decrease with the increment of Tm_2O_3 (TZYb-10-00 compared with TZYb-20-00, and TZYb-10-03 compared with TZYb-20-03).

Table 5 – Judd-Ofelt parameters ($\times 10^{-20} \text{ cm}^2$) of the TZYb glasses. The values of δ_{rms} are given in units of $\times 10^{-20} \text{ cm}^2$.

REI	Sample	Ω_2	Ω_4	Ω_6	Ω_4/Ω_6	δ_{rms}
Er^{3+}	TZYb-00-03	4.58	1.44	0.46	3.13	0.09
	TZYb-10-03	4.75	1.22	0.26	4.71	0.09
	TZYb-20-03	4.24	1.00	0.26	3.92	0.08
Tm^{3+}	TZYb-10-00	3.90	2.06	1.07	1.93	0.11
	TZYb-10-03	3.96	2.41	1.23	1.96	0.05
	TZYb-20-00	4.02	2.15	0.57	3.77	0.07
	TZYb-20-03	4.09	2.33	0.97	2.39	0.06

Source: By the author.

Table 5 illustrates the JO parameters divided for Er^{3+} and Tm^{3+} . First, the parameters Ω_4 and Ω_6 of Er^{3+} decrease with the addition of Tm_2O_3 , which indicates the increment in the number of NBOs in the glass network and might explain the increment of refractive index when compared TZYb-00-03 with TZYb-20-03, also an increment in the Coulomb interaction⁶⁹ between Er^{3+} and the other REI in the host matrix, as well as the crystal environment. The smallest value of Ω_2 corresponds to the TZYb-20-03 sample, indicating the increment of symmetry around the Er^{3+} and a decrement of the covalent bonding between Er^{3+} and O^{2-} .

With regard to parameter Ω_2 of Tm^{3+} , this increases with the increment of Tm_2O_3 when compared TZYb-10-00 with TZYb-20-00 and TZYb-10-03 with TZYb-20-03, and increases with addition of Er_2O_3 when compared TZYb-10-00 with TZYb-10-03 and TZYb-20-00 with TZYb-20-03. Decrement of Ω_6 in samples TZYb-10-00 and TZYb-20-00 indicates the increment of NBOs and might explain why the refractive index increases from one sample to another, likewise TZYb-10-03 and TZYb-20-03 glasses. When compared TZYb-10-00 and TZYb-10-03, Ω_6 increases and therefore the refractive index decreases. Same behaviour in samples TZYb-20-00 and TZYb-20-03.

The ratio Ω_4/Ω_6 is called spectroscopic quality factor and is used to predict the magnitude of stimulated emission in a laser active medium.⁷⁰ The largest value of Ω_4/Ω_6 for Er^{3+} corresponds to the TZYb-10-03 sample (4.71), and for Tm^{3+} , its value increases with addition of Tm_2O_3 . Finally, the intensity parameters follow the trend $\Omega_2 > \Omega_4 > \Omega_6$ for all samples as reported in other tellurite glasses.^{12, 61, 66, 70, 71}

With the JO parameters, the spontaneous emission probabilities for electric (A_{ED}) and magnetic-dipole (A_{MD}) contributions, fluorescence branching ratios (β) and the radiative lifetimes (τ_{cal}) were calculated and are listed in Table 6 and 7 for Tm^{3+} and Er^{3+} , respectively. It can be seen that the radiative transition probabilities of Tm^{3+} : $^3\text{H}_4 \rightarrow ^3\text{H}_6$, Tm^{3+} : $^1\text{G}_4 \rightarrow ^3\text{H}_6$, Tm^{3+} : $^3\text{F}_3 \rightarrow ^3\text{H}_6$ and Er^{3+} : $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ are large, which the last three indicate a beneficial fluorescence emission in blue, red and green light, respectively.

Table 6 – Branching ratio β (in %), electric and magnetic-dipole transition probabilities $A_{ED/MD}$ (in s^{-1}) and calculated lifetimes τ_{cal} (in ms) for Tm^{3+} in TZYb glasses.

Em. band	TZYb-10-00			TZYb-10-03			TZYb-20-00			TZYb-20-03		
	A_{ED}	A_{MD}	β	A_{ED}	A_{MD}	β	A_{ED}	A_{MD}	β	A_{ED}	A_{MD}	β
$^1\text{G}_4 \rightarrow ^3\text{H}_6$	2466.64		38.0682	2464.76		38.0763	2562.32		38.165	2492.54		38.115
$\rightarrow ^3\text{F}_4$	2589.08		39.958	2586.31		39.954	2679.78		39.915	2611.71		39.937
$\rightarrow ^3\text{H}_5$	1246.88		19.243	1245.43		19.239	1289.06		19.200	1257.08		19.223
$\rightarrow ^3\text{H}_4$	50.025		0.772	49.961		0.772	51.642		0.769	50.399		0.771
$\rightarrow ^3\text{F}_3$	96.628		1.491	96.502		1.491	99.714		1.485	97.334		1.488
$\rightarrow ^3\text{F}_2$	30.281		0.467	30.241		0.467	31.244		0.465	30.501		0.466
$\tau_{cal} :$	0.154			0.154			0.149			0.153		
$^3\text{F}_2 \rightarrow ^3\text{H}_6$	1124.81		36.944	1123.58		36.949	1163.92		36.997	1134.50		36.969
$\rightarrow ^3\text{F}_4$	1449.57		47.611	1447.74		47.608	1496.79		47.578	1460.59		47.595
$\rightarrow ^3\text{H}_5$	447.878		14.7105	447.293		14.709	462.197		14.692	451.158		14.702
$\rightarrow ^3\text{H}_4$	22.229		0.730	22.199		0.730	22.927		0.729	22.386		0.729
$\rightarrow ^3\text{F}_3$	0.051	0.076	0.004	0.051	0.075	0.004	0.053	0.077	0.004	0.052	0.076	0.004
$\tau_{cal} :$	0.328			0.328			0.318			0.326		
$^3\text{F}_3 \rightarrow ^3\text{H}_6$	3911.65		72.808	3907.29		72.811	4046.42		72.863	3944.78		72.832
$\rightarrow ^3\text{F}_4$	707.644	136.714	15.716	706.742	136.571	15.715	730.573	140.332	15.682	712.967	137.557	15.703
$\rightarrow ^3\text{H}_5$	615.668		11.459	614.857		11.458	635.273		11.439	620.141		11.449
$\rightarrow ^3\text{H}_4$	0.854		0.016	0.853		0.016	0.881		0.016	0.860		0.016
$\tau_{cal} :$	0.186			0.186			0.180			0.185		
$^3\text{H}_4 \rightarrow ^3\text{H}_6$	4863.07		93.892	4857.35		93.892	5026.77		93.904	4902.48		93.897
$\rightarrow ^3\text{F}_4$	209.506		4.045	209.232		4.044	216.206		4.039	211.041		4.042
$\rightarrow ^3\text{H}_5$	84.921	21.948	2.063	84.808	21.924	87.602	22.516	2.057	85.527	1.633	22.076	2.061
$\tau_{cal} :$	0.193			0.193			0.187			0.192		
$^3\text{H}_5 \rightarrow ^3\text{H}_6$	428.24	110.34	97.951	427.69	110.231	97.951	442.047	113.25	97.954	431.43	111.022	97.952
$\rightarrow ^3\text{F}_4$	8.095	3.169	2.049	8.084	3.166	2.049	8.349	3.251	2.046	8.152	3.187	2.048
$\tau_{cal} :$	0.159			0.159			0.154			0.158		

Source: By the author.

Table 7 – Branching ratio β (in %), electric and magnetic-dipole transition probabilities $A_{ED/MD}$ (in s^{-1}) and calculated lifetimes τ_{cal} (in ms) for Er^{3+} in TZYb glasses.

Em. band			TZYb-00-03			TZYb-10-03			TZYb-20-03		
			A_{ED}	A_{MD}	β	A_{ED}	A_{MD}	β	A_{ED}	A_{MD}	β
$^4F_{3/2}$	$\rightarrow$	$^4I_{15/2}$	1117.56		41.302	1114.64		41.309	1127.69		41.369
	$\rightarrow$	$^4I_{13/2}$	95.595		3.533	95.326		3.533	96.268		3.532
	$\rightarrow$	$^4I_{11/2}$	946.596		34.984	943.882		34.980	952.602		34.946
	$\rightarrow$	$^4I_{9/2}$	517.768		19.135	516.27		19.133	520.891		19.109
	$\rightarrow$	$^4F_{9/2}$	16.956		0.627	16.906		0.627	17.053		0.626
	$\rightarrow$	$^4S_{3/2}$	10.142		0.374	10.112		0.375	10.198		0.374
	$\rightarrow$	$^2H_{11/2}$	0.090		0.003	0.090		0.003	0.091		0.003
	$\rightarrow$	$^4F_{7/2}$	1.065		0.039	1.062		0.039	1.071		0.039
	$\rightarrow$	$^4F_{5/2}$	0.019	0.021	0.002	0.019	0.021	0.002	0.019	0.021	0.002
$\tau_{cal} :$			0.369			0.371			0.367		
$^4F_{5/2}$	$\rightarrow$	$^4I_{15/2}$	1237.41		37.1555	1234.17		37.160	1248.46		37.207
	$\rightarrow$	$^4I_{13/2}$	1548.45		46.495	1544.10		46.492	1559.25		46.469
	$\rightarrow$	$^4I_{11/2}$	229.533		6.892	228.873		6.891	230.976		6.884
	$\rightarrow$	$^4I_{9/2}$	155.238		4.661	154.788		4.661	156.167		4.654
	$\rightarrow$	$^4F_{9/2}$	150.559		4.521	150.119		4.520	151.415		4.512
	$\rightarrow$	$^4S_{3/2}$	1.859		0.056	1.854		0.056	1.869		0.056
	$\rightarrow$	$^2H_{11/2}$	3.388		0.102	3.377		0.102	3.406		0.102
	$\rightarrow$	$^4F_{7/2}$	1.932	1.989	0.118	1.926	1.984	0.118	1.942	1.998	0.117
$\tau_{cal} :$			0.300			0.301			0.298		
$^4F_{7/2}$	$\rightarrow$	$^4I_{15/2}$	3447.63		69.676	3438.38		69.679	3476.32		69.717
	$\rightarrow$	$^4I_{13/2}$	948.450		19.168	945.755		19.166	954.737		19.147
	$\rightarrow$	$^4I_{11/2}$	354.825		7.171	353.799		7.169	356.972		7.159
	$\rightarrow$	$^4I_{9/2}$	150.186		3.035	149.749		3.035	151.057		3.029
	$\rightarrow$	$^4F_{9/2}$	10.573	35.566	0.932	10.542	35.479	0.933	10.631	35.72	0.929
	$\rightarrow$	$^4S_{3/2}$	0.045		0.001	0.044		0.001	0.045		0.001
	$\rightarrow$	$^2H_{11/2}$	0.804		0.016	0.801		0.016	0.808		0.016
$\tau_{cal} :$			0.202			0.203			0.201		
$^2H_{11/2}$	$\rightarrow$	$^4I_{15/2}$	14749.8		96.221	14709.7		96.222	14867.1		96.228
	$\rightarrow$	$^4I_{13/2}$	215.534		1.406	214.917		1.406	216.918		1.404
	$\rightarrow$	$^4I_{11/2}$	133.114		0.868	132.728		0.868	133.901		0.867
	$\rightarrow$	$^4I_{9/2}$	180.598		1.178	180.070		1.178	181.626		1.176
	$\rightarrow$	$^4F_{9/2}$	49.989		0.326	49.842		0.326	50.264		0.325
	$\rightarrow$	$^4S_{3/2}$	0.068		0.000	0.068		0.000	0.068		0.000
$\tau_{cal} :$			0.065			0.065			0.065		
$^4S_{3/2}$	$\rightarrow$	$^4I_{15/2}$	999.538		67.081	996.797		67.084	1007.24		67.115
	$\rightarrow$	$^4I_{13/2}$	385.445		25.868	384.339		25.866	387.870		25.845
	$\rightarrow$	$^4I_{11/2}$	31.706		2.128	31.614		2.128	31.891		2.125
	$\rightarrow$	$^4I_{9/2}$	72.799		4.886	72.586		4.885	73.209		4.878
	$\rightarrow$	$^4F_{9/2}$	0.567		0.038	0.566		0.570	17.053		0.038
$\tau_{cal} :$			0.671			0.673			0.666		
$^4F_{9/2}$	$\rightarrow$	$^4I_{15/2}$	2069.79		91.823	2063.96		91.824	2084.08		91.832
	$\rightarrow$	$^4I_{13/2}$	109.802		4.871	109.482		4.871	110.445		4.867
	$\rightarrow$	$^4I_{11/2}$	66.348		2.943	66.153		2.943	66.717		2.939
	$\rightarrow$	$^4I_{9/2}$	8.162		0.362	8.138		0.362	8.206		0.362
$\tau_{cal} :$			0.443			0.445			0.441		

Source: By the author.

4.2.4 Up-conversion spectroscopy

4.2.4.1 Up-conversion

Figure 10a shows the UC spectra of the TZYb glasses excited under 980 nm with a I_{exc} of 637 W/cm². Six emission bands centred at 472, 651 and 692 nm, which correspond to Tm³⁺: $^1G_4 \rightarrow ^3H_6$, $^3F_2 \rightarrow ^3H_6$ and $^3F_2 \rightarrow ^3H_6$, respectively, 521, 544 and 662 nm which correspond to Er³⁺: $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$. Green emission in TZYb-00-03 sample is predominant, and decreases when doped with Tm₂O₃, indicating an ET process from Er³⁺ to Tm³⁺ as well as the blue emission of TZYb-10-00 and TZYb-20-00 samples, indicating ET from Tm³⁺ to Er³⁺. Further, Tm³⁺: $^1G_4 \rightarrow ^3H_6$ band in TZYb-20-00 glass decreases with respect to TZYb-10-00, showing a fluorescence quenching in the UC emission intensity and might be attributed to a change in the glass structure discussed in the JO analysis and the refractive index results.

As Er³⁺ presents an emission band in ~488 nm (Er³⁺: $^4F_{7/2} \rightarrow ^4I_{15/2}$ transition), a deconvolution for each 472 nm band was performed as illustrated in Figure 10b – e. All samples doped with Tm³⁺ present the deconvoluted bands 462, 470, 474 and 476 nm, and for triply doped samples, the ~ 488 nm contribution is small when compared with other bands. In sample TZYb-10-03, the integrated area of 488 nm deconvoluted band represents ~2.73% of the 472 nm peak area, and in sample TZYb-20-03 this represents the ~2.00%. Therefore, the crystal field potential generated by the tellurite-zinc host favours the green and red emission of Er³⁺, and the weak blue emission could be attributed to the ET of Er³⁺ to other REI.

The UC spectra under 980 nm of samples TZYb-10-03 and TZYb-20-03 at different excitation intensities are illustrated in Figure 11. In both samples, blue emission is intense because the concentration of Tm₂O₃ is greater than the concentration of Er₂O₃, however, TZYb-20-03 exhibits a lesser emission intensity when compared with sample TZYb-10-03. Furthermore, the number of IR photons involved in each emission band is the slope of the curves plotted in double logarithmic scale of I_{UC} VS I_{exc} (see insets of Figure 11a and b). As n must be an integer, the emission band centred at 472 nm is related to three photons and for the bands centred at 521, 544, 662 and 692 nm two photons are involved. Besides, three or two photons are involved in band centred at 651 nm considering the error of the fitting and can be due to the Er³⁺: $^2H_{11/2} \rightarrow ^4I_{15/2}$, as mentioned above, or Tm³⁺: $^1G_4 \rightarrow ^3F_4$ transition. This occurs for both samples.

The CIE-1931 chromaticity diagram showed in Figure 12 illustrates the white to blue light emission by increasing the excitation intensity from 127 to 637 W/cm². White light was obtained in sample TZYb-10-03 with an excitation intensity of 127 W/cm² and is near to the correlated colour temperature (CCT) of 6000 K. The tendency of the (x, y) CIE coordinates indicates that cool white light could be obtained when decreasing the excitation intensity, however, this implicates collect undesirable noisy data.

Figure 10 – a) Normalized up-conversion spectra of the TZYb glasses excited with 980 nm and a pump intensity of 637 W/cm². Deconvolution of the 472 nm band of b) TZYb-10-00, c) TZYb-10-03, d) TZYb-20-00 and TZYb-20-03 samples. All spectra are normalized.

Figure 11 – Up-conversion spectra of the a) TZYb-10-03 and b) TZYb-20-03 glasses excited under 980 nm varying the excitation intensity from 127 to 637 W/cm². Inset: Log-log plot of the integrated emission intensity as a function of the excitation intensity for TZYb. Legends include emission bands, slope values and their standard error.

Source: By the author.

Figure 12 – a) CIE-1931 chromaticity diagram of the TZYb-10-03 and TZYb-20-03 glasses showing the (x,y) coordinates of the mixed RGB light at different input intensities. The arrow indicates the increment of excitation intensity. Photograph of the b) TZYb-10-03 and c) TZYb-20-03, both excited under 980 nm and with a pump intensity of 2546 W/cm² emitting bluish white light.

Source: By the author.

4.2.4.2 Luminescence spectroscopy

In order to further understand the ET mechanism, the luminescence spectroscopy for visible and NIR region were performed under 405 nm excitation. First, luminescence spectra in the VIS-NIR region (in the wavelength region 450 – 900 nm) is plotted in Figure 13a), where the most representative bands are Er³⁺: ²H_{11/2} → ⁴I_{15/2} and ⁴S_{3/2} → ⁴I_{15/2}, which correspond to the green emission. The intensity of this band decreases with the addition of Tm₂O₃ when compared TZYb-00-03 with TZYb-10-03, and can be concluded that there is ET from Er³⁺ to Tm³⁺, specifically to the Tm³⁺: ³F₃ → ⁴H₆ band. Moreover, the magnitude of the reduction is lesser than the UC emission (see Figure 10a). This last indicates that the ET process from Er³⁺ to Tm³⁺ is more efficient when the glasses are pumped with 980 nm than with 405 nm and might be due to the fact that with $\lambda_{exc} = 405$ nm, the population of ²H_{11/2} and ⁴S_{3/2} levels is greater than exciting with 980 nm, and the probability of decay is greater than an electron jumps to another level. Other observed bands in TZYb-00-03 sample are Er³⁺: ⁴F_{9/2} → ⁴I_{15/2} and Er³⁺: ⁴I_{9/2} → ⁴I_{15/2} (centred at ~850 nm). Tm³⁺ does not present an absorption band centred at 405 nm, however, Tm³⁺: ³H₄ → ³H₆ band and a broad emission band centred in ~650 nm with low intensity in the range 560 – 750 nm were observed. This ~650 nm broad band might be attributed to the Te⁴⁺ centres (Te³⁺: ³T_{1u} → ¹A_{1g} band) present in the glass matrix as reported in other tellurite glasses.^{72,73}

Figure 13 – Normalized luminescence spectra of the TZYb-00-03, TZYb-10-00 and TZYb-10-03 excited with 405 nm and a pump intensity of 1273 W/cm² in the a) visible and b) near-infrared emission. Inset: a) Emission bands in the range 550 – 750 nm and b) excitation spectrum of the TZYb-10-00 sample monitoring 1010 nm emission.

Source: By the author.

In Figure 13b, the luminescence spectra in the NIR region (in the wavelength region 900 – 1800 nm) is showed. The emission centred at ~ 1010 nm is due to the Yb³⁺: $4F_{5/2} \rightarrow 4F_{7/2}$ transition in sample TZYb-10-00, and for samples TZYb-00-03 and TZYb-10-03 are attributed to Yb³⁺: $4F_{5/2} \rightarrow 4F_{7/2}$ and Er³⁺: $4I_{13/2} \rightarrow 4I_{15/2}$. This band present an

intensity reduction when increasing the doping concentration, where TZYb-00-03 sample exhibits the highest value. Additionally, Er^{3+} -doped glasses present an emission band centred at 1550 nm, which correspond to the $\text{Er}^{3+}: {}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ transition, which was not appreciated in the absorption spectra.

Concerning the TZYb-10-00 sample, excitation spectroscopy for the $\text{Yb}^{3+}: {}^4\text{F}_{5/2} \rightarrow {}^4\text{F}_{7/2}$ was performed and is illustrated in the inset of Figure 13b, where a broad excitation band ranging from 300 to 410 nm was found. As 405 nm is within this range, $\text{Yb}^{3+}: {}^4\text{F}_{5/2} \rightarrow {}^4\text{F}_{7/2}$ emission band is obtained under this excitation wavelength, and suggest that there is ET from Te^{4+} to Yb^{3+} and from Tm^{3+} to Yb^{3+} . Finally, Figure 14 illustrates the CIE-1931 chromaticity diagram for luminescence under 405 nm of TZYb-00-03 and TZYb-10-03 samples. As expected, green emission was predominant for both samples, and the (x,y) coordinates of the TZYb-10-03 glass shows a slight deviation down to the red region and is due to the $\text{Tm}^{3+}: {}^3\text{F}_3 \rightarrow {}^3\text{H}_6$ transition.

Figure 14 – CIE-1931 chromaticity diagram of the TZYb-00-03 and TZYb-10-03 glasses excited under 405 nm showing a predominant green emission.

Source: By the author.

4.2.5 Lifetime measurements

In order to find the excitation wavelength for lifetime measurements of each UC emission band, excitation spectroscopy was performed and is illustrated in Figure 15 for triply-doped samples. For blue emission, which is entirely due to Tm^{3+} contribution, the excitation wavelength corresponds to the $\text{Tm}^{3+}: {}^1\text{D}_2 \rightarrow {}^3\text{H}_6$ transition (359 nm), which means that the Tm^{3+} will be excited to ${}^1\text{D}_2$ state and then will decay until the ${}^1\text{G}_4$ state, from which blue emission is achieved. Due to proximities between 522 and 544 nm

emission bands, both lifetimes will be measured exciting the samples with 379 nm, which corresponds to the $\text{Er}^{3+}: {}^4\text{G}_{11/2} \rightarrow {}^4\text{I}_{15/2}$. Furthermore, for emission band centred at 651 nm, the glasses which are doped with Tm^{3+} have to be excited with 472 nm ($\text{Tm}^{3+}: {}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ transition) and for emission band centred at 662 nm, the samples doped with Er^{3+} have to be excited with 521 nm ($\text{Er}^{3+}: {}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ transition). It must be mentioned that it was not possible to measure the lifetime for 488 and 692 nm bands because the emission intensities are weak, therefore no decay signal was encountered.

Figure 15 – Excitation spectra of the samples a) TZYb-10-03 and b) TZYb-20-03, showing the principles wavelengths for each RGB emissions.

Source: By the author.

It was found that decay curves exhibit deviations of an exponential behaviour as can be seen (as illustration) in Figure 16a and b for $\text{Tm}^{3+}: {}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ transition and for $\text{Er}^{3+}: {}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$, respectively. This non-exponential nature is due to the effect of the ET and the multi-phonon relaxation on the decay of Tm^{3+} and Er^{3+} .

Figure 16 – Fluorescence decay curves of a) $\text{Tm}^{3+}: {}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ (472 nm) transition and b) $\text{Er}^{3+}: {}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ (662 nm) transition of the TZYb glasses.

Source: By the author.

The radiative lifetimes τ_{exp} and the fluorescence quantum efficiency for each UC emission band in TZYb glasses are listed in Table 8. Changes in the lifetime values give information about the ET process and distinguish between donor and acceptor:

- i. In band centred at 472 nm, τ_{exp} of TZYb-10-00 is greater than TZYb-10-03, hence there is ET from Tm^{3+} to Er^{3+} , likewise in samples TZYb-20-00 and TZYb-20-03.
- ii. In bands centred at 521, 544 and 662 nm, the τ_{exp} of TZYb-00-03 are larger than the triply-doped ones, hence there is ET from Er^{3+} to Tm^{3+} .
- iii. In band centred at 651 nm, the τ_{exp} of TZYb-10-03 is greater than sample TZYb-10-00, hence there is ET from Er^{3+} to Tm^{3+} , likewise in samples TZYb-20-03 and TZYb-20-00.

Larger quantum efficiency values are attributed to the large spontaneous emission probabilities and to the low phonon energy of the glass matrix. In Table 8, quantum efficiency of the Er^{3+} : $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and Tm^{3+} : $^1\text{G}_4 \rightarrow ^3\text{H}_6$ exhibit larger values which means less multi-phonon losses in the emission of these bands, and their lower values corresponds to the Er^{3+} : $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition. Additionally, η values decrease with the increment of concentration of REI, except for the Tm^{3+} : $^3\text{F}_2 \rightarrow ^3\text{H}_6$ emission band.

Table 8 – Radiative lifetimes τ_{exp} (in μs) and quantum efficiency η of the TZYb glasses for each UC emission band λ_{em} (in nm).

Sample	Band	λ_{em}	τ_{exp}	η
TZYb-00-03	Er^{3+} : $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$	521	55.30	0.848
	Er^{3+} : $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	544	55.34	0.082
	Er^{3+} : $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$	662	51.44	0.116
TZYb-10-00	Tm^{3+} : $^1\text{G}_4 \rightarrow ^3\text{H}_6$	472	100.8	0.654
	Tm^{3+} : $^3\text{F}_2 \rightarrow ^3\text{H}_6$	651	21.07	0.064
TZYb-10-03	Tm^{3+} : $^1\text{G}_4 \rightarrow ^3\text{H}_6$	472	90.81	0.635
	Er^{3+} : $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$	521	51.10	0.781
	Er^{3+} : $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	544	51.37	0.076
	Tm^{3+} : $^3\text{F}_2 \rightarrow ^3\text{H}_6$	651	24.23	0.074
	Er^{3+} : $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$	662	45.15	0.101
TZYb-20-00	Tm^{3+} : $^1\text{G}_4 \rightarrow ^3\text{H}_6$	472	88.20	0.592
	Tm^{3+} : $^3\text{F}_2 \rightarrow ^3\text{H}_6$	651	21.29	0.067
TZYb-20-03	Tm^{3+} : $^1\text{G}_4 \rightarrow ^3\text{H}_6$	472	82.18	0.537
	Er^{3+} : $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$	521	47.80	0.739
	Er^{3+} : $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	544	47.75	0.072
	Tm^{3+} : $^3\text{F}_2 \rightarrow ^3\text{H}_6$	651	25.90	0.079
	Er^{3+} : $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$	662	41.75	0.095

Source: By the author.

The energy level diagram of Er^{3+} , Yb^{3+} and Tm^{3+} in TZYb glasses with possible ET in the visible region is illustrated in Figure 17. As 488 nm emission (Er^{3+} : $^4\text{F}_{7/2} \rightarrow ^4\text{I}_{15/2}$ transition) is weak, is supposed to be the responsible for emissions via ET to Tm^{3+} and even to Er^{3+} . The $^4\text{F}_{7/2}$ level can be populated via $\text{ET}_{\text{Tm} \rightarrow \text{Er}}$ (Tm^{3+} : $^1\text{G}_4 \xrightarrow{\text{ET}} \text{Er}^{3+}$: $^4\text{F}_{7/2}$), due to three 980 nm photons via ET_1 , ET_2 and ET_3 , or due to two 980 nm photons via ET_1 and ET_3/ESA_3 , and finally can be depopulated to the $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ or $^4\text{F}_{9/2}$ levels as

a consequence of NR decays. Additionally, $\text{Er}^{3+}: {}^4\text{F}_{9/2}$ level can be populated involving two 980 nm photons via ET_1 and ET_2 , as well as $\text{Er}^{3+}: {}^2\text{H}_{11/2} / {}^4\text{S}_{3/2}$ via ET_1 and ET_3 .

Three 980 nm photons are involved in the emission of the $\text{Tm}^{3+}: {}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ band via ET_4 , ET_5 and ET_6 , likewise for $\text{Tm}^{3+}: {}^1\text{G}_4 \rightarrow {}^3\text{F}_4$ emission band centred at 651 nm. $\text{Tm}^{3+}: {}^3\text{F}_{2,3}$ level can be populated via RET ($\text{Er}^{3+}: {}^4\text{F}_{9/2} \xrightarrow{\text{RET}} \text{Tm}^{3+}: {}^3\text{F}_{2,3}$) or via ET_4 and ET_5 . Moreover, the excitation spectra show that the $\text{Er}^{3+}: {}^2\text{H}_{11/2}, {}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ transition is responsible for the population of $\text{Tm}^{3+}: {}^3\text{F}_{2,3}$ level via $\text{ET}_{\text{Er} \rightarrow \text{Tm}}$ ($\text{Er}^{3+}: ({}^2\text{H}_{11/2}, {}^4\text{S}_{3/2}) \xrightarrow{\text{ET}} \text{Tm}^{3+}: {}^3\text{F}_{2,3}$).

Figure 17 – Proposed energy level diagram of $\text{Er}^{3+}\text{-Yb}^{3+}\text{-Tm}^{3+}$ -doped zinc-tellurite glasses with the mechanism of energy transfer in the visible region for white light generation. Downward arrows (dashed lines) indicate non-radiative transitions.

Source: By the author.

4.2.6 Energy transfer micro-parameters

Absorption and emission cross-sections spectra of Yb^{3+} in TZYb glasses are plotted in Figure 18, as well as the energy transfer coefficients and critical radii for each sample. The spontaneous transition probability were calculated by using Equation 3.15 and are approximately 1141.4, 1141.8, 1153.1, 1153.9, 1061.9 and 1179.3 s^{-1} for TZYb-00-00,

TZYb-00-03, TZYb-10-00, TZYb-10-03, TZYb-20-00 and TZYb-20-03 samples, respectively. Additionally, the σ_{abs} for all samples centred at ~ 980 nm are $\sim 1.6 \times 10^{-20} \text{ cm}^2$, except for sample TZYb-20-00, which $\sigma_{abs} \approx 1.4 \times 10^{-20} \text{ cm}^2$.

Figure 18 – Absorption and emission cross section and energy transfer micro-parameters of the 980 nm band for samples a) TZYb-00-00, b) TZYb-00-03, c) TZYb-10-00, d) TZYb-10-03, e) TZYb-20-00 and f) TZYb-20-03 in the wavelength region 580 – 1050 nm. The shaded region is the overlapping area.

Source: By the author.

Regarding to the ET micro-parameters of Yb^{3+} , it can be seen that the critical radius of each one almost remains the same and is probably due to the high concentration of Yb_2O_3 . Further, C_{DD} is proportional to the ET probability, and their values are similar, excluding TZYb-20-00 sample, which value is the lowest in this band. The values of the

σ_{em} for samples TZYb-00-00, TZYb-00-03 and TZYb-10-03 are about $2.27 \times 10^{-20} \text{ cm}^2$ and slightly increase in samples TZYb-10-03 and TZYb-20-03 to $\sim 2.31 \times 10^{-20} \text{ cm}^2$. This increment might be attributed to a small Er^{3+} contribution because, as Yb^{3+} , possesses a band centred at 980.

Figure 19 – Absorption and emission cross section and energy transfer micro-parameters of the 472 nm band for samples a) TZYb-10-00, b) TZYb-10-03, c) TZYb-20-00 and d) TZYb-20-03 in the wavelength region 450 – 500 nm. The shaded region is the overlapping area.

Source: By the author.

In the case of $\text{Tm}^{3+}: {}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ band (see Figure 19), the emission cross-section was determined using the Fchtbauer–Ladenburg model (Equation 2.31), and can be seen that the critical radius is almost invariable with the addition of Er_2O_3 , and the ET coefficient decreases when compared TZYb-10-00 with TZYb-10-03, and TZYb-10-00 with TZYb-20-00, and conversely when compared TZYb-20-00 with TZYb-20-03. Decrements in C_{DD} suggest that the probability of ET from the ${}^1\text{G}_4$ level is reduced and the populated electrons in such level decay to generate red emission as showed in the excitation spectra (Figure 15).

Figure 20 – Absorption and emission cross section and energy transfer micro-parameters of the 522-544 nm bands for samples a) TZYb-00-03, b) TZYb-10-03 and c) TZYb-20-03 in the wavelength region 510 – 570 nm. The shaded region is the overlapping area.

Source: By the author.

Figure 20 illustrates the absorption and emission cross-sections for both Er^{3+} : $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and Er^{3+} : $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions, where σ_{em} was determined using the Fchtbauer–Ladenburg model. The difference between the values of the critical radii is small when compared both green bands for each sample, moreover, there is a slight difference between the C_{DD} values in Er^{3+} : $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ band. However, the C_{DD} value of the sample TZYb-20-03 in the Er^{3+} : $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ band is larger when compared TZYb-00-03 and TZYb-10-03. This effect can be observed in the decrement of the measured lifetime in the 521 and 544 nm band (see Table 8), and based on the C_{DD} values, Er^{3+} transfers energy with major degree in sample TZYb-20-03.

Table 9 – Absorption and emission cross sections (in $\times 10^{-20} \text{ cm}^2$), energy transfer coefficients C_{DD} (in $\times 10^{-40} \text{ cm}^6\text{s}^{-1}$) and critical radii R_C (in nm) of the TZYb glasses for the analysed bands λ (in nm).

Sample	Donor–Donor	λ	σ_{abs}	σ_{em}	C_{DD}	R_C
TZYb-00-00	$\text{Yb}^{3+} \rightarrow \text{Yb}^{3+}$	980	1.58	2.27	155.1	1.54
	$\text{Yb}^{3+} \rightarrow \text{Yb}^{3+}$	980	1.58	2.28	156.3	1.55
TZYb-00-03	$\text{Er}^{3+} \rightarrow \text{Er}^{3+}$	522	3.14	4.02	276.1	1.07
		544	2.52	3.39	124.3	0.94
TZYb-10-00	$\text{Yb}^{3+} \rightarrow \text{Yb}^{3+}$	980	1.58	2.27	159.3	1.55
	$\text{Tm}^{3+} \rightarrow \text{Tm}^{3+}$	472	0.17	0.83	6.72	0.65
TZYb-10-03	$\text{Yb}^{3+} \rightarrow \text{Yb}^{3+}$	980	1.60	2.31	159.3	1.55
		522	2.98	4.16	274.8	1.06
	$\text{Er}^{3+} \rightarrow \text{Er}^{3+}$	544	2.76	3.77	124.6	0.93
		472	0.18	0.93	6.36	0.63
TZYb-20-00	$\text{Yb}^{3+} \rightarrow \text{Yb}^{3+}$	980	1.45	2.07	129.8	1.52
	$\text{Tm}^{3+} \rightarrow \text{Tm}^{3+}$	472	0.11	1.02	4.89	0.59
TZYb-20-03	$\text{Yb}^{3+} \rightarrow \text{Yb}^{3+}$	980	1.62	2.31	155.1	1.54
		522	2.84	4.14	277.1	1.05
	$\text{Er}^{3+} \rightarrow \text{Er}^{3+}$	544	2.55	3.95	135.9	0.93
		472	0.15	1.01	5.99	0.61

Source: By the author.

All ET micro-parameters and absorption/emission cross sections are summarized in Table 9. As previously stated, σ_{abs} of 980 nm band maintains its value except for TZYb-20-00 sample, which additionally exhibits the lowest σ_{em} value. Hence, absorption

and emission of Yb^{3+} in this sample is not favourable when compared with the other ones, however, their values increase with addition of Er_2O_3 and might be attributed to the Er^{3+} contribution in the 980 nm band.

The largest σ_{abs} correspond to 522 nm band ($\text{Er}^{3+}: {}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$), which is a hypersensitive transition, for all samples doped with Er^{3+} , and its value decreases with addition of Tm_2O_3 . Conversely, σ_{em} increases with addition of Tm_2O_3 , and might be attributed to the ET from Tm^{3+} to Er^{3+} . Finally, 980 nm band possesses the largest R_C values between Yb^{3+} ions when compared with Er^{3+} and Tm^{3+} . As the R_C is larger, it can be assumed that the Yb^{3+} transfers its energy preferentially to the other REI than itself, which is the aim of this research.

5 CONCLUSIONS

The goal of this dissertation is the generation of white light in tellurite-zinc glass doped with Er^{3+} - Yb^{3+} - Tm^{3+} via up-conversion, and it was obtained based on the colour mixing of red, green and blue light. Additionally, modifying the excitation intensity, white to blue emission can be achieved. For this purpose, the TZYb-10-03 sample has the optimal concentration, i.e. 3.0% of Yb_2O_3 , 0.10% of Tm_2O_3 and 0.03% of Er_2O_3 , because the sample TZYb-20-03 with 0.20% of Tm_2O_3 presents luminescence quenching, although it is capable to emit white light. The energy transfer between those rare-earth ions was evidenced in the up-conversion spectroscopy, the overlapping of the absorption and emission cross-sections, also in changes in the lifetimes.

We shown that the glass structure in samples with rare-earth concentration greater than 3.13 mol% was modified and was evidenced with the increment of the refractive index, changes in density and in the Judd-Ofelt parameters. Additionally, the experimental oscillator strengths are in agreement with the calculated values, as well as the branching ration in the emission bands, since the blue emission is principally due to the $\text{Tm}^{3+}: {}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ electronic transition.

The luminescence spectroscopy was helpful to explain the difference in the energy transfer between Er^{3+} and Tm^{3+} when the glasses are excited with 980 nm and 405 nm. Under 405 nm, the population of the Er^{3+} energy levels is greater than exciting with 980 nm, and therefore, more electrons decay radiatively than transfer its energy to Tm^{3+} . Possible emission of Te^{4+} centres peaked at ~ 650 nm ($\text{Te}^{4+}: {}^3\text{T}_{1u} \rightarrow {}^1\text{A}_{1g}$ broadband) was observed and contribute to the energy transfer process to Yb^{3+} .

Experimental data, the spectroscopic parameters determined by the Judd-Ofelt theory, McCumber, Dexter and Fchtbauer–Ladenburg models were capable to give a comprehensive explanation of the energy transfer process of these rare-earth ions in the visible region, even for singly, doubly and triply doped glasses. However, in the analysis of the Yb^{3+} cross sections, despite only posses one excited level, there is no enough data to give an accurate study of its band because Er^{3+} and Yb^{3+} exhibit a 980 nm transition.

The future perspectives of this research involve structural characterization in order to support the Judd-Ofelt analysis of these glasses. Further, synthesis of new samples modifying the composition and doping concentration should be made to study the $\text{Te}^{4+}: {}^3\text{T}_{1u} \rightarrow {}^1\text{A}_{1g}$ band emission, as well as their influence in the energy transfer process with different rare-earth ions. Samples singly doped with Er^{3+} or Yb^{3+} can be fabricated to investigate the contribution of the 980 nm band of each rare-earth ion. Regarding to the lifetime measurements, a pulsed 980 nm laser should be used to obtain the decay curve of

all transition bands found in the up-conversion spectra because all peaks present enough intensity values to be recorded in a spectrofluorimeter. The high refractive index of the TZYb glasses, as well as their spectroscopic properties, suggest that those materials are propitious candidates for photonic devices, wave-guides, plasmonics, solid-state lighting and in non-linear applications.

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Appendix

APPENDIX A – MATHEMATICA PROGRAMS

A.1 Judd-Ofelt parameters calculation

This program was developed to determinate the Judd-Ofelt intensity parameters (Ω_λ), calculated oscillator strength (f_{cal}), transition probabilities (A), calculated lifetimes (τ_{cal}) and the branching ratio (β).

```
ClearAll;
```

Preliminars

```
SetDirectory[NotebookDirectory[]];
(*Constants*)
h = 6.62606885 * 10-27 (*[g cm2 s-1]*);
c = 29979245800 (*[cm s-1]*);
m = 9.10938215 * 10-28 (*[g]*);
e = 4.80320427 * 10-10 (*[cm3/2 g1/2 s-1]*);
(*Reading data*)
OscillatorEr = Import["Oscillator_Er.txt", "Table"];
(*Experimental oscillator strengths for Er*)
OscillatorTm = Import["Oscillator_Tm.txt", "Table"];
(*Experimental oscillator strengths for Tm*)
MEr = Import["AbsMatrixElements_Er.txt", "Table"];
(*Matrix elements for Er from its ground state*)
MTm = Import["AbsMatrixElements_Tm.txt", "Table"];
(*Matrix elements for Tm from its ground state*)
EMEr = Import["EmMatrixElements_Er.txt", "Table"];
(*Matrix elements for Er from intermediate state*)
EMTm = Import["EmMatrixElements_Tm.txt", "Table"];
(*Matrix elements for Tm from intermediate state*)
Sellmeier = Import["Sellmeier.txt", "Table"]; (*Sellmeier coefficients for all samples*)
λEr = Drop[OscillatorEr[[All, 1]], 1]; (*[nm]*)
λTm = Drop[OscillatorTm[[All, 1]], 1]; (*[nm]*)
(*Oscillator strength values*)
fEr = Drop[Drop[OscillatorEr, 0, 1], 1];
fEr0003 = fEr[[All, 1]];
fEr1003 = fEr[[All, 2]];
fEr2003 = fEr[[All, 3]];
fTm = Drop[Drop[OscillatorTm, 0, 1], 1];
fTm1000 = fTm[[All, 1]];
fTm1003 = fTm[[All, 2]];
fTm2000 = fTm[[All, 3]];
fTm2003 = fTm[[All, 4]];
(*Sellmeier coefficients*)
Ai = Drop[Sellmeier[[All, 2]], 1];
Bi = Drop[Sellmeier[[All, 3]], 1];
(*J and wavenumber values for emission*)
J1Er = EMEr[[All, 1]];
νEr = EMEr[[All, 7]];
JLSνEr = Drop[Drop[EMEr, 0, 0], 0, -3];
EMEr = Drop[Drop[EMEr, 0, 1], 0, 6];
J1Tm = EMTm[[All, 1]];
νTm = EMTm[[All, 7]];
JLSνTm = Drop[Drop[EMTm, 0, 0], 0, -3];
EMTm = Drop[Drop[EMTm, 0, 1], 0, 6];
```

Refractive indices and line strengths

(*Refractive index of each sample in function of λ *)

$$n0000[\lambda_]:= \text{Sqrt}\left[1 + \frac{\text{Ai}[[1]]}{1 - \text{Bi}[[1]]/\lambda^2}\right];$$

$$n0003[\lambda_]:= \text{Sqrt}\left[1 + \frac{\text{Ai}[[2]]}{1 - \text{Bi}[[2]]/\lambda^2}\right];$$

$$n1000[\lambda_]:= \text{Sqrt}\left[1 + \frac{\text{Ai}[[3]]}{1 - \text{Bi}[[3]]/\lambda^2}\right];$$

$$n1003[\lambda_]:= \text{Sqrt}\left[1 + \frac{\text{Ai}[[4]]}{1 - \text{Bi}[[4]]/\lambda^2}\right];$$

$$n2000[\lambda_]:= \text{Sqrt}\left[1 + \frac{\text{Ai}[[5]]}{1 - \text{Bi}[[5]]/\lambda^2}\right];$$

$$n2003[\lambda_]:= \text{Sqrt}\left[1 + \frac{\text{Ai}[[6]]}{1 - \text{Bi}[[6]]/\lambda^2}\right];$$

(*Electric-dipole line strength S_{ED} *)

SEDEr0003 =

$$\text{Table}\left[\frac{3 h \lambda \text{Er}[[i]] * 10^{-7} (2 J + 1) n0003[\lambda \text{Er}[[i]]]}{8 \text{Pi}^2 m c} \left(\frac{3}{n0003[\lambda \text{Er}[[i]]]^2 + 2}\right)^2 f\text{Er}0003[[i]], \{i, 1, \text{Length}[\lambda \text{Er}]\} \right] /. J \rightarrow 15/2;$$

$$\text{SEDEr1003} = \text{Table}\left[\frac{3 h \lambda \text{Er}[[i]] * 10^{-7} (2 J + 1) n1003[\lambda \text{Er}[[i]]]}{8 \text{Pi}^2 m c} \left(\frac{3}{n1003[\lambda \text{Er}[[i]]]^2 + 2}\right)^2 f\text{Er}1003[[i]], \{i, 1, \text{Length}[\lambda \text{Er}]\} \right] /. J \rightarrow 15/2;$$

$$\text{SEDEr2003} = \text{Table}\left[\frac{3 h \lambda \text{Er}[[i]] * 10^{-7} (2 J + 1) n2003[\lambda \text{Er}[[i]]]}{8 \text{Pi}^2 m c} \left(\frac{3}{n2003[\lambda \text{Er}[[i]]]^2 + 2}\right)^2 f\text{Er}2003[[i]], \{i, 1, \text{Length}[\lambda \text{Er}]\} \right] /. J \rightarrow 15/2;$$

$$\text{SEDTm1000} = \text{Table}\left[\frac{3 h \lambda \text{Tm}[[i]] * 10^{-7} (2 J + 1) n1000[\lambda \text{Tm}[[i]]]}{8 \text{Pi}^2 m c} \left(\frac{3}{n1000[\lambda \text{Tm}[[i]]]^2 + 2}\right)^2 f\text{Tm}1000[[i]], \{i, 1, \text{Length}[\lambda \text{Tm}]\} \right] /. J \rightarrow 6;$$

$$\text{SEDTm1003} = \text{Table}\left[\frac{3 h \lambda \text{Tm}[[i]] * 10^{-7} (2 J + 1) n1003[\lambda \text{Tm}[[i]]]}{8 \text{Pi}^2 m c} \left(\frac{3}{n1003[\lambda \text{Tm}[[i]]]^2 + 2}\right)^2 f\text{Tm}1003[[i]], \{i, 1, \text{Length}[\lambda \text{Tm}]\} \right] /. J \rightarrow 6;$$

$$\text{SEDTm2000} = \text{Table}\left[\frac{3 h \lambda \text{Tm}[[i]] * 10^{-7} (2 J + 1) n2000[\lambda \text{Tm}[[i]]]}{8 \text{Pi}^2 m c} \left(\frac{3}{n2000[\lambda \text{Tm}[[i]]]^2 + 2}\right)^2 f\text{Tm}2000[[i]], \{i, 1, \text{Length}[\lambda \text{Tm}]\} \right] /. J \rightarrow 6;$$

$$\text{SEDTm2003} = \text{Table}\left[\frac{3 h \lambda \text{Tm}[[i]] * 10^{-7} (2 J + 1) n2003[\lambda \text{Tm}[[i]]]}{8 \text{Pi}^2 m c} \left(\frac{3}{n2003[\lambda \text{Tm}[[i]]]^2 + 2}\right)^2 f\text{Tm}2003[[i]], \{i, 1, \text{Length}[\lambda \text{Tm}]\} \right] /. J \rightarrow 6;$$

(*Magnetic-dipole line strengths S_{MD} *)

$$\text{SMD}[J1_ , L1_ , S1_ , J2_ , L2_ , S2_ , v_] := \left(\frac{e h}{4 \text{Pi} m c}\right)^2 * \text{If}[J1 == J2 \&\& S1 == S2 \&\& L1 == L2,$$

$$\left(1 + \frac{J1 (J1 + 1) + S1 (S1 + 1) - L1 (L1 + 1)}{2 J1 (J1 + 1)}\right)^2 (J1 (J1 + 1) (2 J1 + 1)),$$

$$\text{If}[J2 == J1 - 1 \&\& S1 == S2 \&\& L1 == L2, \frac{1}{4 J1} (S1 + L1 + J1 + 1) (S1 + L1 - J1 + 1) (S1 + J1 - L1) (L1 + J1 - S1),$$

$$\text{If}[J2 == J1 + 1 \&\& S1 == S2 \&\& L1 == L2, \frac{1}{4 (J1 + 1)} (S1 + L1 + J1 + 2) (S1 - L1 + J1 + 1) (L1 - S1 + J1 + 1) (L1 - J1 + S1), 0]]];$$

Judd - Ofelt intensity parameters calculation

(*Equations to be solved by least squares method*)

```

ΩEr0003 = LeastSquares[MER, SEDEr0003];
ΩEr1003 = LeastSquares[MER, SEDEr1003];
ΩEr2003 = LeastSquares[MER, SEDEr2003];
ΩTm1000 = LeastSquares[MTm, SEDTm1000];
ΩTm1003 = LeastSquares[MTm, SEDTm1003];
ΩTm2000 = LeastSquares[MTm, SEDTm2000];
ΩTm2003 = LeastSquares[MTm, SEDTm2003];

```

(*Line Strength δ_{rms} calculation*)

```

SEDEr0003CAL = Table[Sum[ΩEr0003[[i]] * MER[[j]][[i]], {i, 1, 3}], {j, 1, Length[MER]}];
SEDEr1003CAL = Table[Sum[ΩEr1003[[i]] * MER[[j]][[i]], {i, 1, 3}], {j, 1, Length[MER]}];
SEDEr2003CAL = Table[Sum[ΩEr2003[[i]] * MER[[j]][[i]], {i, 1, 3}], {j, 1, Length[MER]}];
SEDTm1000CAL = Table[Sum[ΩTm1000[[i]] * MTm[[j]][[i]], {i, 1, 3}], {j, 1, Length[MTm]}];
SEDTm1003CAL = Table[Sum[ΩTm1003[[i]] * MTm[[j]][[i]], {i, 1, 3}], {j, 1, Length[MTm]}];
SEDTm2000CAL = Table[Sum[ΩTm2000[[i]] * MTm[[j]][[i]], {i, 1, 3}], {j, 1, Length[MTm]}];
SEDTm2003CAL = Table[Sum[ΩTm2003[[i]] * MTm[[j]][[i]], {i, 1, 3}], {j, 1, Length[MTm]}];

```

δSEDEr0003 =

```

Sqrt[Sum[(SEDEr0003CAL[[i]] - SEDEr0003[[i]])^2, {i, 1, Length[λEr]}] / (Length[λEr] - 3)];
δSEDEr1003 = Sqrt[Sum[(SEDEr1003CAL[[i]] - SEDEr1003[[i]])^2, {i, 1, Length[λEr]}] /
  (Length[λEr] - 3)];
δSEDEr2003 = Sqrt[Sum[(SEDEr2003CAL[[i]] - SEDEr2003[[i]])^2, {i, 1, Length[λEr]}] /
  (Length[λEr] - 3)];
δSEDTm1000 = Sqrt[Sum[(SEDTm1000CAL[[i]] - SEDTm1000[[i]])^2, {i, 1, Length[λTm]}] /
  (Length[λTm] - 3)];
δSEDTm1003 = Sqrt[Sum[(SEDTm1003CAL[[i]] - SEDTm1003[[i]])^2, {i, 1, Length[λTm]}] /
  (Length[λTm] - 3)];
δSEDTm2000 = Sqrt[Sum[(SEDTm2000CAL[[i]] - SEDTm2000[[i]])^2, {i, 1, Length[λTm]}] /
  (Length[λTm] - 3)];
δSEDTm2003 = Sqrt[Sum[(SEDTm2003CAL[[i]] - SEDTm2003[[i]])^2, {i, 1, Length[λTm]}] /
  (Length[λTm] - 3)];
δSED = {δSEDEr0003, δSEDEr1003, δSEDEr2003, δSEDTm1000,
  δSEDTm1003, δSEDTm2000, δSEDTm2003} * 1020;

```

(*Judd-Ofelt parameters with σ_{rms} *)

```

TableForm[{{"TZYb-00-03", ΩEr0003[[1]] * 1020, ΩEr0003[[2]] * 1020,
  ΩEr0003[[3]] * 1020, ΩEr0003[[2]] / ΩEr0003[[3]], δSED[[1]]},
{"TZYb-10-03", ΩEr1003[[1]] * 1020, ΩEr1003[[2]] * 1020,
  ΩEr1003[[3]] * 1020, ΩEr1003[[2]] / ΩEr1003[[3]], δSED[[2]]},
{"TZYb-20-03", ΩEr2003[[1]] * 1020, ΩEr2003[[2]] * 1020,
  ΩEr2003[[3]] * 1020, ΩEr2003[[2]] / ΩEr2003[[3]], δSED[[3]]}],
TableHeadings → {{{"For Er3+"}, {"Sample", "Ω2 (×10-20)",
  "Ω4 (×10-20)", "Ω6 (×10-20)", "Ω4/Ω6", "δrms (×10-20)"}]}
TableForm[{{"TZYb-10-00", ΩTm1000[[1]] * 1020, ΩTm1000[[2]] * 1020,
  ΩTm1000[[3]] * 1020, ΩTm1000[[2]] / ΩTm1000[[3]], δSED[[4]]},
{"TZYb-10-03", ΩTm1003[[1]] * 1020, ΩTm1003[[2]] * 1020,
  ΩTm1003[[3]] * 1020, ΩTm1003[[2]] / ΩTm1003[[3]], δSED[[5]]},
{"TZYb-20-00", ΩTm2000[[1]] * 1020, ΩTm2000[[2]] * 1020,
  ΩTm2000[[3]] * 1020, ΩTm2000[[2]] / ΩTm2000[[3]], δSED[[6]]},
{"TZYb-20-03", ΩTm2003[[1]] * 1020, ΩTm2003[[2]] * 1020,
  ΩTm2003[[3]] * 1020, ΩTm2003[[2]] / ΩTm2003[[3]], δSED[[7]]}],
TableHeadings → {{{"For Tm3+"}, {"Sample", "Ω2 (×10-20)",
  "Ω4 (×10-20)", "Ω6 (×10-20)", "Ω4/Ω6", "δrms (×10-20)"}]}

```

Theoretical oscillator strengths calculation

(*Calculated Oscillator Strength ($\times 10^{-6}$ *)

$$f_{Er0003CAL} = \text{Table}\left[\frac{8 \pi^2 m c}{3 h \lambda_{Er}[[i]] * 10^{-7} (2 J + 1) n_{0003}[\lambda_{Er}[[i]]]}\right. \\ \left.\left(\frac{n_{0003}[\lambda_{Er}[[i]]]^2 + 2}{3}\right)^2 \text{SEDEr0003CAL}[[i]], \{i, 1, \text{Length}[\lambda_{Er}]\}\right] /. J \rightarrow 15/2;$$

$$f_{Er1003CAL} = \text{Table}\left[\frac{8 \pi^2 m c}{3 h \lambda_{Er}[[i]] * 10^{-7} (2 J + 1) n_{1003}[\lambda_{Er}[[i]]]}\right. \\ \left.\left(\frac{n_{1003}[\lambda_{Er}[[i]]]^2 + 2}{3}\right)^2 \text{SEDEr1003CAL}[[i]], \{i, 1, \text{Length}[\lambda_{Er}]\}\right] /. J \rightarrow 15/2;$$

$$f_{Er2003CAL} = \text{Table}\left[\frac{8 \pi^2 m c}{3 h \lambda_{Er}[[i]] * 10^{-7} (2 J + 1) n_{2003}[\lambda_{Er}[[i]]]}\right. \\ \left.\left(\frac{n_{2003}[\lambda_{Er}[[i]]]^2 + 2}{3}\right)^2 \text{SEDEr2003CAL}[[i]], \{i, 1, \text{Length}[\lambda_{Er}]\}\right] /. J \rightarrow 15/2;$$

$$f_{Tm1000CAL} = \text{Table}\left[\frac{8 \pi^2 m c}{3 h \lambda_{Tm}[[i]] * 10^{-7} (2 J + 1) n_{1000}[\lambda_{Tm}[[i]]]}\right. \\ \left.\left(\frac{n_{1000}[\lambda_{Er}[[i]]]^2 + 2}{3}\right)^2 \text{SEDTm1000CAL}[[i]], \{i, 1, \text{Length}[\lambda_{Tm}]\}\right] /. J \rightarrow 6;$$

$$f_{Tm1003CAL} = \text{Table}\left[\frac{8 \pi^2 m c}{3 h \lambda_{Tm}[[i]] * 10^{-7} (2 J + 1) n_{1003}[\lambda_{Tm}[[i]]]}\right. \\ \left.\left(\frac{n_{1003}[\lambda_{Er}[[i]]]^2 + 2}{3}\right)^2 \text{SEDTm1003CAL}[[i]], \{i, 1, \text{Length}[\lambda_{Tm}]\}\right] /. J \rightarrow 6;$$

$$f_{Tm2000CAL} = \text{Table}\left[\frac{8 \pi^2 m c}{3 h \lambda_{Tm}[[i]] * 10^{-7} (2 J + 1) n_{2000}[\lambda_{Tm}[[i]]]}\right. \\ \left.\left(\frac{n_{2000}[\lambda_{Er}[[i]]]^2 + 2}{3}\right)^2 \text{SEDTm2000CAL}[[i]], \{i, 1, \text{Length}[\lambda_{Tm}]\}\right] /. J \rightarrow 6;$$

$$f_{Tm2003CAL} = \text{Table}\left[\frac{8 \pi^2 m c}{3 h \lambda_{Tm}[[i]] * 10^{-7} (2 J + 1) n_{2003}[\lambda_{Tm}[[i]]]}\right. \\ \left.\left(\frac{n_{2003}[\lambda_{Er}[[i]]]^2 + 2}{3}\right)^2 \text{SEDTm2003CAL}[[i]], \{i, 1, \text{Length}[\lambda_{Tm}]\}\right] /. J \rightarrow 6;$$

(*Oscillator Strength δ_{rms} calculation ($\times 10^{-8}$ *)

$$\delta f_{Er0003} = \sqrt{\text{Sum}[(f_{Er0003CAL}[[i]] - f_{Er0003}[[i]])^2, \{i, 1, \text{Length}[\lambda_{Er}]\}] / (\text{Length}[\lambda_{Er}] - 3)};$$

$$\delta f_{Er1003} = \sqrt{\text{Sum}[(f_{Er1003CAL}[[i]] - f_{Er1003}[[i]])^2, \{i, 1, \text{Length}[\lambda_{Er}]\}] / (\text{Length}[\lambda_{Er}] - 3)};$$

$$\delta f_{Er2003} = \sqrt{\text{Sum}[(f_{Er2003CAL}[[i]] - f_{Er2003}[[i]])^2, \{i, 1, \text{Length}[\lambda_{Er}]\}] / (\text{Length}[\lambda_{Er}] - 3)};$$

$$\delta f_{Tm1000} = \sqrt{\text{Sum}[(f_{Tm1000CAL}[[i]] - f_{Tm1000}[[i]])^2, \{i, 1, \text{Length}[\lambda_{Tm}]\}] / (\text{Length}[\lambda_{Tm}] - 3)};$$

$$\delta f_{Tm1003} = \sqrt{\text{Sum}[(f_{Tm1003CAL}[[i]] - f_{Tm1003}[[i]])^2, \{i, 1, \text{Length}[\lambda_{Tm}]\}] / (\text{Length}[\lambda_{Tm}] - 3)};$$

$$\delta f_{Tm2000} = \sqrt{\text{Sum}[(f_{Tm2000CAL}[[i]] - f_{Tm2000}[[i]])^2, \{i, 1, \text{Length}[\lambda_{Tm}]\}] / (\text{Length}[\lambda_{Tm}] - 3)};$$

$$\delta f_{Tm2003} = \sqrt{\text{Sum}[(f_{Tm2003CAL}[[i]] - f_{Tm2003}[[i]])^2, \{i, 1, \text{Length}[\lambda_{Tm}]\}] / (\text{Length}[\lambda_{Tm}] - 3)};$$

$$\delta f = \{\delta f_{Er0003}, \delta f_{Er1003}, \delta f_{Er2003}, \delta f_{Tm1000}, \delta f_{Tm1003}, \delta f_{Tm2000}, \delta f_{Tm2003}\} * 10^6;$$

(*Oscillator Strengths with σ_{rms} *)

$$\text{TableForm}\left[\text{Table}\left[\text{If}[i \leq \text{Length}[\lambda_{Er}], \{\lambda_{Er}[[i]] * 10^{-6}, f_{Er0003}[[i]], f_{Er0003CAL}[[i]], f_{Er1003}[[i]],\right.\right. \\ \left.\left.f_{Er1003CAL}[[i]], f_{Er2003}[[i]], f_{Er2003CAL}[[i]]\} * 10^6,\right. \\ \left.\{\text{"}\delta_{rms}\text{": "}, \delta f[[1]], \text{" "}, \delta f[[2]], \text{" "}, \delta f[[3]], \text{" "}\}, \{i, 1, \text{Length}[\lambda_{Er}] + 1\}\right], \\ \text{TableHeadings} \rightarrow \{\{\text{"For Er}^{3+}\}, \\ \{\text{"}\lambda \text{ (nm)"}, \text{"}f_{exp0003}\text{"}, \text{"}f_{cal0003}\text{"}, \text{"}f_{exp1003}\text{"}, \text{"}f_{cal1003}\text{"}, \text{"}f_{exp2003}\text{"}, \text{"}f_{cal2003}\text{"}\}\}\} \\ \text{TableForm}\left[\text{Table}\left[\text{If}[i \leq \text{Length}[\lambda_{Tm}], \{\lambda_{Tm}[[i]] * 10^{-6}, f_{Tm1000}[[i]], f_{Tm1000CAL}[[i]], f_{Tm1003}[[i]], f_{Tm1003CAL}[[i]],\right.\right. \\ \left.\left.f_{Tm2000}[[i]], f_{Tm2000CAL}[[i]], f_{Tm2003}[[i]], f_{Tm2003CAL}[[i]]\} * 10^6,\right. \\ \left.\{\text{"}\delta_{rms}\text{": "}, \delta f[[4]], \text{" "}, \delta f[[5]], \text{" "}, \delta f[[6]], \text{" "}, \delta f[[7]], \text{" "}\}, \{i, 1, \text{Length}[\lambda_{Tm}] + 1\}\right], \\ \text{TableHeadings} \rightarrow \{\{\text{"For Tm}^{3+}\}, \{\text{"}\lambda \text{ (nm)"}, \text{"}f_{exp1000}\text{"}, \text{"}f_{cal1000}\text{"}, \\ \text{"}f_{exp1003}\text{"}, \text{"}f_{cal1003}\text{"}, \text{"}f_{exp2000}\text{"}, \text{"}f_{cal2000}\text{"}, \text{"}f_{exp2003}\text{"}, \text{"}f_{cal2003}\text{"}\}\}\}$$

Transition probabilities calculation

(*Sum terms*)

STAEDer0003[j_] :=

$$\frac{64 \text{Pi}^4 e^2 (\text{vEr}[[j]])^3}{3 \text{h} (2 \text{J1Er}[[j]] + 1)} \left(\frac{n0003[10^7/\text{vEr}[[j]]] (n0003[10^7/\text{vEr}[[j]]]^2 + 2)^2}{9} \right) *$$

Sum[EMEr[[j]][[i]] * $\Omega\text{Er0003}[[i]]$, {i, 1, 3}]

STAEDer1003[j_] := $\frac{64 \text{Pi}^4 e^2 (\text{vEr}[[j]])^3}{3 \text{h} (2 \text{J1Er}[[j]] + 1)}$

$$\left(\frac{n1003[10^7/\text{vEr}[[j]]] (n1003[10^7/\text{vEr}[[j]]]^2 + 2)^2}{9} \right) *$$

Sum[EMEr[[j]][[i]] * $\Omega\text{Er0003}[[i]]$, {i, 1, 3}]

STAEDer2003[j_] := $\frac{64 \text{Pi}^4 e^2 (\text{vEr}[[j]])^3}{3 \text{h} (2 \text{J1Er}[[j]] + 1)}$

$$\left(\frac{n2003[10^7/\text{vEr}[[j]]] (n2003[10^7/\text{vEr}[[j]]]^2 + 2)^2}{9} \right) *$$

Sum[EMEr[[j]][[i]] * $\Omega\text{Er0003}[[i]]$, {i, 1, 3}]

STAEDTm1000[j_] := $\frac{64 \text{Pi}^4 e^2 (\text{vTm}[[j]])^3}{3 \text{h} (2 \text{J1Tm}[[j]] + 1)}$

$$\left(\frac{n1000[10^7/\text{vTm}[[j]]] (n1000[10^7/\text{vTm}[[j]]]^2 + 2)^2}{9} \right) *$$

Sum[EMTm[[j]][[i]] * $\Omega\text{Tm1000}[[i]]$, {i, 1, 3}]

STAEDTm1003[j_] := $\frac{64 \text{Pi}^4 e^2 (\text{vTm}[[j]])^3}{3 \text{h} (2 \text{J1Tm}[[j]] + 1)}$

$$\left(\frac{n1003[10^7/\text{vTm}[[j]]] (n1003[10^7/\text{vTm}[[j]]]^2 + 2)^2}{9} \right) *$$

Sum[EMTm[[j]][[i]] * $\Omega\text{Tm1000}[[i]]$, {i, 1, 3}]

STAEDTm2000[j_] := $\frac{64 \text{Pi}^4 e^2 (\text{vTm}[[j]])^3}{3 \text{h} (2 \text{J1Tm}[[j]] + 1)}$

$$\left(\frac{n2000[10^7/\text{vTm}[[j]]] (n2000[10^7/\text{vTm}[[j]]]^2 + 2)^2}{9} \right) *$$

Sum[EMTm[[j]][[i]] * $\Omega\text{Tm1000}[[i]]$, {i, 1, 3}]

STAEDTm2003[j_] := $\frac{64 \text{Pi}^4 e^2 (\text{vTm}[[j]])^3}{3 \text{h} (2 \text{J1Tm}[[j]] + 1)}$

$$\left(\frac{n2003[10^7/\text{vTm}[[j]]] (n2003[10^7/\text{vTm}[[j]]]^2 + 2)^2}{9} \right) *$$

Sum[EMTm[[j]][[i]] * $\Omega\text{Tm1000}[[i]]$, {i, 1, 3}]

(*Transition probabilities due to electric-dipole transition*)

AEDer0003[α_, β_] := Sum[STAEDer0003[j], {j, α, β}];

AEDer1003[α_, β_] := Sum[STAEDer1003[j], {j, α, β}];

AEDer2003[α_, β_] := Sum[STAEDer2003[j], {j, α, β}];

AEDTm1000[α_, β_] := Sum[STAEDTm1000[j], {j, α, β}];

AEDTm1003[α_, β_] := Sum[STAEDTm1003[j], {j, α, β}];

AEDTm2000[α_, β_] := Sum[STAEDTm2000[j], {j, α, β}];

AEDTm2003[α_, β_] := Sum[STAEDTm2003[j], {j, α, β}];

```

(*Transition probabilities due to magnetic-dipole transition*)
TAMDEr0003[J1_, L1_, S1_, J2_, L2_, S2_, v_] :=
  
$$\frac{64 \pi^4 v^3}{3 h (2 J_1 + 1)} n_{0003} [10^7 / v]^3 \text{SMD}[J1, L1, S1, J2, L2, S2, v];$$

TAMDEr1003[J1_, L1_, S1_, J2_, L2_, S2_, v_] :=
  
$$\frac{64 \pi^4 v^3}{3 h (2 J_1 + 1)} n_{1003} [10^7 / v]^3 \text{SMD}[J1, L1, S1, J2, L2, S2, v];$$

TAMDEr2003[J1_, L1_, S1_, J2_, L2_, S2_, v_] :=
  
$$\frac{64 \pi^4 v^3}{3 h (2 J_1 + 1)} n_{2003} [10^7 / v]^3 \text{SMD}[J1, L1, S1, J2, L2, S2, v];$$

TAMDTm1000[J1_, L1_, S1_, J2_, L2_, S2_, v_] :=
  
$$\frac{64 \pi^4 v^3}{3 h (2 J_1 + 1)} n_{1000} [10^7 / v]^3 \text{SMD}[J1, L1, S1, J2, L2, S2, v];$$

TAMDTm1003[J1_, L1_, S1_, J2_, L2_, S2_, v_] :=
  
$$\frac{64 \pi^4 v^3}{3 h (2 J_1 + 1)} n_{1003} [10^7 / v]^3 \text{SMD}[J1, L1, S1, J2, L2, S2, v];$$

TAMDTm2000[J1_, L1_, S1_, J2_, L2_, S2_, v_] :=
  
$$\frac{64 \pi^4 v^3}{3 h (2 J_1 + 1)} n_{2000} [10^7 / v]^3 \text{SMD}[J1, L1, S1, J2, L2, S2, v];$$

TAMDTm2003[J1_, L1_, S1_, J2_, L2_, S2_, v_] :=
  
$$\frac{64 \pi^4 v^3}{3 h (2 J_1 + 1)} n_{2003} [10^7 / v]^3 \text{SMD}[J1, L1, S1, J2, L2, S2, v];$$

STMDer0003 = TAMDEr0003[###] &@@@ JLSvEr;
STMDer1003 = TAMDEr1003[###] &@@@ JLSvEr;
STMDer2003 = TAMDEr2003[###] &@@@ JLSvEr;
STMDTm1000 = TAMDTm1000[###] &@@@ JLSvTm;
STMDTm1003 = TAMDTm1003[###] &@@@ JLSvTm;
STMDTm2000 = TAMDTm2000[###] &@@@ JLSvTm;
STMDTm2003 = TAMDTm2003[###] &@@@ JLSvTm;

AMDEr0003[α_, β_] := Sum[STMDer0003[[i]], {i, α, β}];
AMDEr1003[α_, β_] := Sum[STMDer1003[[i]], {i, α, β}];
AMDEr2003[α_, β_] := Sum[STMDer2003[[i]], {i, α, β}];
AMDTm1000[α_, β_] := Sum[STMDTm1000[[i]], {i, α, β}];
AMDTm1003[α_, β_] := Sum[STMDTm1003[[i]], {i, α, β}];
AMDTm2000[α_, β_] := Sum[STMDTm2000[[i]], {i, α, β}];
AMDTm2003[α_, β_] := Sum[STMDTm2003[[i]], {i, α, β}];

AEDer[a_, b_, i_] := {λEr[[i]], AEDer0003[a, b], AEDer1003[a, b], AEDer2003[a, b]};
AMDEr[a_, b_, i_] := {λEr[[i]], AMDEr0003[a, b], AMDEr1003[a, b], AMDEr2003[a, b]};

AEDTm[a_, b_, i_] :=
  {λTm[[i]], AEDTm1000[a, b], AEDTm1003[a, b], AEDTm2000[a, b], AEDTm2003[a, b]};
AMDTm[a_, b_, i_] := {λTm[[i]], AMDTm1000[a, b],
  AMDTm1003[a, b], AMDTm2000[a, b], AMDTm2003[a, b]};

(*Electric dipole transition probabilities*)
TableForm[AEDerTable =
  AEDer[###] &@@@ {{1, 4, 1}, {5, 9, 2}, {10, 15, 3}, {16, 22, 4}, {23, 30, 5}, {31, 39, 6}},
  TableHeadings → {"ED for Er3+",
    {"λ (nm)", "AED-00-03 (s-1)", "AED-10-03 (s-1)", "AED-20-03 (s-1)"}]}
TableForm[AEDTmTable = AEDTm[###] &@@@
  {{1, 2, 1}, {3, 5, 2}, {6, 9, 3}, {10, 14, 4}, {15, 20, 5}},
  TableHeadings → {"ED for Tm3+", {"λ (nm)", "AED-10-00 (s-1)",
    "AED-10-03 (s-1)", "AED-20-00 (s-1)", "AED-20-03 (s-1)"}]}

(*Magnetic dipole transition probabilities*)
TableForm[AMDErTable =
  AMDEr[###] &@@@ {{1, 4, 1}, {5, 9, 2}, {10, 15, 3}, {16, 22, 4}, {23, 30, 5}, {31, 39, 6}},
  TableHeadings → {"MD for Er3+",
    {"λ (nm)", "AMD-00-03 (s-1)", "AMD-10-03 (s-1)", "AMD-20-03 (s-1)"}]}
TableForm[AMDTmTable = AMDTm[###] &@@@
  {{1, 2, 1}, {3, 5, 2}, {6, 9, 3}, {10, 14, 4}, {15, 20, 5}},
  TableHeadings → {"MD for Tm3+", {"λ (nm)", "AMD-10-00 (s-1)",
    "AMD-10-03 (s-1)", "AMD-20-00 (s-1)", "AMD-20-03 (s-1)"}]}

```


Transition probabilities

```

AEr = Table[If[j == 1, λEr[[i]], AEDerTable[[i, j]] + AMDerTable[[i, j]]],
  {i, 1, Length[λEr]}, {j, 1, Length[AEDerTable[[1, All]]]};
ATm = Table[If[j == 1, λTm[[i]], AEDTmTable[[i, j]] + AMDTmTable[[i, j]]],
  {i, 1, Length[λTm]}, {j, 1, Length[AEDTmTable[[1, All]]]};

TableForm[AEr, TableHeadings →
  {{{"For Er3+"}, {"λ (nm)", "A-00-03 (s-1)", "A-10-03 (s-1)", "A-20-03 (s-1)"}}}]
TableForm[ATm, TableHeadings → {{{"For Tm3+"},
  {"λ (nm)", "A-10-00 (s-1)", "A-10-03 (s-1)", "A-20-00 (s-1)", "A-20-03 (s-1)"}}}]

```

Calculated lifetimes

```

τEr = Table[If[j == 1, λEr[[i]], 103 (AEDerTable[[i, j]] + AMDerTable[[i, j]])-1],
  {i, 1, Length[λEr]}, {j, 1, Length[AEDerTable[[1, All]]]};
τTm = Table[If[j == 1, λTm[[i]], 103 (AEDTmTable[[i, j]] + AMDTmTable[[i, j]])-1],
  {i, 1, Length[λTm]}, {j, 1, Length[AEDTmTable[[1, All]]]};

TableForm[τEr, TableHeadings →
  {{{"For Er3+"}, {"λ (nm)", "τ-00-03 (ms)", "τ-10-03 (ms)", "τ-20-03 (ms)"}}}]
TableForm[τTm, TableHeadings → {{{"For Tm3+"},
  {"λ (nm)", "τ-10-00 (ms)", "τ-10-03 (ms)", "τ-20-00 (ms)", "τ-20-03 (ms)"}}}]

```

Luminescence branching ratio

```

βEr[a_, b_, c_] := Table[{vEr[[i]], 10.7/vEr[[i]],
  STAEder0003[i],
  STMDer0003[[i]],
  (STAEder0003[i] + STMDer0003[[i]]) * τEr[[c, 2]] * 10-1,
  STAEder1003[i],
  STMDer1003[[i]],
  (STAEder1003[i] + STMDer1003[[i]]) * τEr[[c, 3]] * 10-1,
  STAEder2003[i],
  STMDer2003[[i]],
  (STAEder2003[i] + STMDer2003[[i]]) * τEr[[c, 4]] * 10-1}, {i, a, b}];

βTm[a_, b_, c_] := Table[{vTm[[i]], 10.7/vTm[[i]],
  STAEDTm1000[i],
  STMDTm1000[[i]],
  (STAEDTm1000[i] + STMDTm1000[[i]]) * τTm[[c, 2]] * 10-1,
  STAEDTm1003[i],
  STMDTm1003[[i]],
  (STAEDTm1003[i] + STMDTm1003[[i]]) * τTm[[c, 3]] * 10-1,
  STAEDTm2000[i],
  STMDTm2000[[i]],
  (STAEDTm2000[i] + STMDTm2000[[i]]) * τTm[[c, 4]] * 10-1,
  STAEDTm2003[i],
  STMDTm2003[[i]],
  (STAEDTm2003[i] + STMDTm2003[[i]]) * τTm[[c, 5]] * 10-1}, {i, a, b}];

TableForm[Transpose[βEr[###]] & @@@
  {{1, 4, 1}, {5, 9, 2}, {10, 15, 3}, {16, 22, 4}, {23, 30, 5}, {31, 39, 6}},
  TableHeadings → {{{"For Er3+"}, {"ν (cm-1)", "λ (nm)", "AED-00-03",
    "AMD-00-03", "β-00-03 (%)", "AED-10-03", "AMD-10-03",
    "β-10-03 (%)", "AED-20-03", "AMD-20-03", "β-20-03 (%)"}}}]

TableForm[
  Transpose[βTm[###]] & @@@ {{1, 2, 1}, {3, 5, 2}, {6, 9, 3}, {10, 14, 4}, {15, 20, 5}},
  TableHeadings → {{{"For Tm3+"}, {"ν (cm-1)", "λ (nm)", "AED-10-00", "AMD-10-00",
    "β-10-00 (%)", "AED-10-03", "AMD-10-03", "β-10-03 (%)", "AED-20-00",
    "AMD-20-00", "β-20-00 (%)", "AED-20-03", "AMD-20-03", "β-20-03 (%)"}}}]

```

A.2 CIE-1931 chromaticity diagram

This program was developed to determinate the CIE-1931 (x, y) coordinates.

```
ClearAll;
```

Preliminars

```
res = Input["Resolution"]; (*Setting spectrometer resolution*)
SetDirectory[NotebookDirectory[]];
(*Reading data*)
CCTdata = Import["CCT.txt", "Table"];
CIEboundary = Import["CIE_Boundary.txt", "Table"];
CIEwavelengths = Import["CIE_Wavelengths.txt", "Table"];
CMF = Import["CMF.txt", "Table"];
TZYb1003 = Import["TZYb-10-03.txt", "Table"];
TZYb2003 = Import["TZYb-20-03.txt", "Table"];

(*UC spectra data and Colour Matching Function (CMF) variables*)
CCT = CCTdata[[All, 1]]; (*Correlated colour temperature*)
CCTx = CCTdata[[All, 2]]; (*CCT abscissa*)
CCTy = CCTdata[[All, 3]]; (*CCT ordinate*)
bCIEx = CIEboundary[[All, 2]]; (*CIE boundary abscissas*)
bCIEy = CIEboundary[[All, 3]]; (*CIE boundary ordinates*)
λCIE = CIEwavelengths[[All, 1]]; (*Spectral locus wavelength*)
λCIEx = CIEwavelengths[[All, 2]]; (*Spectral locus abscissa*)
λCIEy = CIEwavelengths[[All, 3]]; (*Spectral locus ordinate*)
λCMF = CMF[[All, 1]]; (*CMF wavelengths*)
rCMF = CMF[[All, 2]]; (*CMF  $\bar{x}$  → red*)
gCMF = CMF[[All, 3]]; (*CMF  $\bar{y}$  → green*)
bCMF = CMF[[All, 4]]; (*CMF  $\bar{z}$  → blue*)
λUC1 = TZYb1003[[All, 1]]; (*Data: wavelength*)
λUC2 = TZYb2003[[All, 1]]; (*Data: wavelength*)
iUC1 = Table[TZYb1003[[All, i]], {i, 2, Length[TZYb1003[[1, All]]]};
iUC2 = Table[TZYb2003[[All, i]], {i, 2, Length[TZYb2003[[1, All]]]};

(*Interpolating the CMF*)
frCMF = Interpolation[Table[{λCMF[[i]], rCMF[[i]]}, {i, 1, Length[λCMF]}]];
fgCMF = Interpolation[Table[{λCMF[[i]], gCMF[[i]]}, {i, 1, Length[λCMF]}]];
fbCMF = Interpolation[Table[{λCMF[[i]], bCMF[[i]]}, {i, 1, Length[λCMF]}]];
fCMF = Table[{i, frCMF[i], fgCMF[i], fbCMF[i]}, {i, First[λCMF], Last[λCMF], res}];
λCMF = fCMF[[All, 1]]; (*Interpolated CMF wavelengths*)
rCMF = fCMF[[All, 2]]; (*Interpolated CMF  $\bar{x}$  → red*)
gCMF = fCMF[[All, 3]]; (*Interpolated CMF  $\bar{y}$  → green*)
bCMF = fCMF[[All, 4]]; (*Interpolated CMF  $\bar{z}$  → blue*)
```

Computing XYZ from spectra data

```
(*Normalizing the UC intensity spectra*)
iUC1 = Table[iUC1[[i]] / Max[iUC1[[i]]], {i, 1, Length[TZYb1003[[1, All]]] - 1};
iUC2 = Table[iUC2[[i]] / Max[iUC2[[i]]], {i, 1, Length[TZYb2003[[1, All]]] - 1};

(* X, Y and Z are the CIE tristimulus values*)
(* $X = \int I(\lambda) \bar{x}(\lambda) d\lambda$      $Y = \int I(\lambda) \bar{y}(\lambda) d\lambda$      $Z = \int I(\lambda) \bar{z}(\lambda) d\lambda$  *)
CIEEX1 = Table[DeleteCases[
  Table[If[λCMF[[i]] == λUC1[[j]], rCMF[[i]] * iUC1[[k]][[j]], {i, 1, Length[λCMF]},
    {j, 1, Length[λUC1]]} // Flatten, Null], {k, 1, Length[TZYb1003[[1, All]]] - 1}];
CIEY1 = Table[DeleteCases[Table[If[λCMF[[i]] == λUC1[[j]], gCMF[[i]] * iUC1[[k]][[j]],
  {i, 1, Length[λCMF]}, {j, 1, Length[λUC1]]} // Flatten,
  Null], {k, 1, Length[TZYb1003[[1, All]]] - 1}];
CIEZ1 = Table[DeleteCases[Table[If[λCMF[[i]] == λUC1[[j]], bCMF[[i]] * iUC1[[k]][[j]],
  {i, 1, Length[λCMF]}, {j, 1, Length[λUC1]]} // Flatten,
  Null], {k, 1, Length[TZYb1003[[1, All]]] - 1}];
λ1 = DeleteCases[Table[If[λCMF[[i]] == λUC1[[j]], λUC1[[j]],
  {i, 1, Length[λCMF]}, {j, 1, Length[λUC1]]} // Flatten, Null];
CIEEX2 = Table[DeleteCases[Table[If[λCMF[[i]] == λUC2[[j]], rCMF[[i]] * iUC2[[k]][[j]],
  {i, 1, Length[λCMF]}, {j, 1, Length[λUC2]]} // Flatten,
  Null], {k, 1, Length[TZYb2003[[1, All]]] - 1}];
CIEY2 = Table[DeleteCases[Table[If[λCMF[[i]] == λUC2[[j]], gCMF[[i]] * iUC2[[k]][[j]],
  {i, 1, Length[λCMF]}, {j, 1, Length[λUC2]]} // Flatten,
  Null], {k, 1, Length[TZYb2003[[1, All]]] - 1}];
CIEZ2 = Table[DeleteCases[Table[If[λCMF[[i]] == λUC2[[j]], bCMF[[i]] * iUC2[[k]][[j]],
  {i, 1, Length[λCMF]}, {j, 1, Length[λUC2]]} // Flatten,
  Null], {k, 1, Length[TZYb2003[[1, All]]] - 1}];
λ2 = DeleteCases[Table[If[λCMF[[i]] == λUC2[[j]], λUC2[[j]],
  {i, 1, Length[λCMF]}, {j, 1, Length[λUC2]]} // Flatten, Null];
```

```

X1 = Table[Table[{λ1[[i]], CIEX1[[j]][[i]]}, {i, 1, Length[λ1]}],
  {j, 1, Length[TZYb1003[[1, All]]] - 1}];
Y1 = Table[Table[{λ1[[i]], CIEY1[[j]][[i]]}, {i, 1, Length[λ1]}],
  {j, 1, Length[TZYb1003[[1, All]]] - 1}];
Z1 = Table[Table[{λ1[[i]], CIEZ1[[j]][[i]]}, {i, 1, Length[λ1]}],
  {j, 1, Length[TZYb1003[[1, All]]] - 1}];
X2 = Table[Table[{λ2[[i]], CIEX2[[j]][[i]]}, {i, 1, Length[λ2]}],
  {j, 1, Length[TZYb2003[[1, All]]] - 1}];
Y2 = Table[Table[{λ2[[i]], CIEY2[[j]][[i]]}, {i, 1, Length[λ2]}],
  {j, 1, Length[TZYb2003[[1, All]]] - 1}];
Z2 = Table[Table[{λ2[[i]], CIEZ2[[j]][[i]]}, {i, 1, Length[λ2]}],
  {j, 1, Length[TZYb2003[[1, All]]] - 1}];

fx1 = Table[Interpolation[X1[[i]]], {i, 1, Length[TZYb1003[[1, All]]] - 1};
fy1 = Table[Interpolation[Y1[[i]]], {i, 1, Length[TZYb1003[[1, All]]] - 1};
fz1 = Table[Interpolation[Z1[[i]]], {i, 1, Length[TZYb1003[[1, All]]] - 1};
fx2 = Table[Interpolation[X2[[i]]], {i, 1, Length[TZYb2003[[1, All]]] - 1};
fy2 = Table[Interpolation[Y2[[i]]], {i, 1, Length[TZYb2003[[1, All]]] - 1};
fz2 = Table[Interpolation[Z2[[i]]], {i, 1, Length[TZYb2003[[1, All]]] - 1};

(*Tristimulus values*)
XX1 =
  Table[Integrate[fx1[[i]][x], {x, First[X1[[i]][[All, 1]]], Last[X1[[i]][[All, 1]]]}],
    {i, 1, Length[TZYb1003[[1, All]]] - 1};
YY1 = Table[Integrate[fy1[[i]][x], {x, First[Y1[[i]][[All, 1]]],
  Last[Y1[[i]][[All, 1]]]}], {i, 1, Length[TZYb1003[[1, All]]] - 1};
ZZ1 = Table[Integrate[fz1[[i]][x], {x, First[Z1[[i]][[All, 1]]],
  Last[Z1[[i]][[All, 1]]]}], {i, 1, Length[TZYb1003[[1, All]]] - 1};
XX2 = Table[Integrate[fx2[[i]][x], {x, First[X2[[i]][[All, 1]]],
  Last[X2[[i]][[All, 1]]]}], {i, 1, Length[TZYb2003[[1, All]]] - 1};
YY2 = Table[Integrate[fy2[[i]][x], {x, First[Y2[[i]][[All, 1]]],
  Last[Y2[[i]][[All, 1]]]}], {i, 1, Length[TZYb2003[[1, All]]] - 1};
ZZ2 = Table[Integrate[fz2[[i]][x], {x, First[Z2[[i]][[All, 1]]],
  Last[Z2[[i]][[All, 1]]]}], {i, 1, Length[TZYb2003[[1, All]]] - 1};

(*Normalizing (x,y,z) coordinates*)
xyz1 = Table[{
  
$$\frac{XX1[[i]]}{XX1[[i]] + YY1[[i]] + ZZ1[[i]]}, \frac{YY1[[i]]}{XX1[[i]] + YY1[[i]] + ZZ1[[i]]}, \frac{ZZ1[[i]]}{XX1[[i]] + YY1[[i]] + ZZ1[[i]]}$$

}, {i, 1, Length[iUC1]}];
x1 = xyz1[[All, 1]];
y1 = xyz1[[All, 2]];

xyz2 = Table[{
  
$$\frac{XX2[[i]]}{XX2[[i]] + YY2[[i]] + ZZ2[[i]]}, \frac{YY2[[i]]}{XX2[[i]] + YY2[[i]] + ZZ2[[i]]}, \frac{ZZ2[[i]]}{XX2[[i]] + YY2[[i]] + ZZ2[[i]]}$$

}, {i, 1, Length[iUC2]}];
x2 = xyz2[[All, 1]];
y2 = xyz2[[All, 2]];

```

Chromaticity diagram

```

cie = ChromaticityPlot["RGB", "CIE31", BoundaryStyle → None, WhitePoint → None, Frame → True,
  FrameLabel → {Style["x", FontFamily → "Times", Black, 20],
    Style["y", FontFamily → "Times", Black, 20]},
  FrameTicks → {{Table[If[Mod[i, 2] == 0 && i > 0, {N[i/10], N[i/10], {0, 0.02}},
    {N[i/10], " ", {0, 0.01}}], {i, 0, 9, 0.5}], None},
    {Table[If[Mod[i, 2] == 0, {N[i/10], NumberForm[i/10, {2, 1}], {0, 0.02}},
    {N[i/10], " ", {0, 0.01}}], {i, 0, 9, 0.5}], None}},
  FrameStyle → Directive[Black, 16, FontFamily → "Times"],
  PlotRange → {{-0.045, 0.8}, {0, 0.91}}];

title =
  Graphics[{Text[Style["CIE 1931", Black, 22, Bold, FontFamily → "Times"], {0.2, 0.9}]}];

(* (x,y) point *)
point1 = ListPlot[Table[{x1[[i]], y1[[i]]}, {i, 1, Length[iUC1]}],
  PlotMarkers → {"■", 16},
  PlotStyle → Black,
  PlotLegends → Placed[
    {Style["TZYb-10-03", FontFamily → "Times", 20]}, {Scaled[{1, 0.90}], {1.1, 1}}];

```

```

point2 = ListPlot[Table[{x2[[i]], y2[[i]]}, {i, 1, Length[iUC2]}],
  PlotMarkers -> {"▲", 16},
  PlotStyle -> Black,
  PlotLegends -> Placed[
    {Style["TZYb-20-03", FontFamily -> "Times", 20]}, {Scaled[{1, 0.84}], {1.1, 1}}];

(*Wavelengths located in the outer curved boundary*)
wavelength = ListPlot[Table[{λCIEx[[i]], λCIEy[[i]]}, {i, 1, Length[λCIEx]}] ->
  Table[Style[λCIE[[i]], 18, FontFamily -> "Times"], {i, 1, Length[λCIE]}],
  LabelingFunction -> Center];
lines = Graphics[{Line[{0.14396, 0.0297}, {0.12947, 0.01592}],
  Line[{0.09129, 0.1327}, {0.07255, 0.12572}],
  Line[{0.00817, 0.53842}, {-0.01175, 0.53659}],
  Line[{0.0743, 0.8338}, {0.07035, 0.85341}],
  Line[{0.22962, 0.75433}, {0.24193, 0.77009}],
  Line[{0.3731, 0.62445}, {0.38703, 0.63881}],
  Line[{0.51249, 0.48659}, {0.52661, 0.50075}],
  Line[{0.62704, 0.37249}, {0.64115, 0.38667}],
  Line[{0.6915, 0.30834}, {0.70563, 0.3225}]}];

b1 = ListLinePlot[Table[{bCIEx[[i]], bCIEy[[i]]}, {i, 1, Length[bCIEx]}],
  PlotStyle -> Black];
b2 = ListLinePlot[{bCIEx[[1]], bCIEy[[1]]}, {Last[bCIEx], Last[bCIEy]}],
  PlotStyle -> Black];

(*Correlated colour temperature curve*)
cct = ListPlot[Table[{CCTx[[i]], CCTy[[i]]}, {i, 1, Length[CCT]}] ->
  Table[Style[CCT[[i]], 10, Bold, FontFamily -> "Times"], {i, 1, Length[CCT]}],
  LabelingFunction -> Bottom,
  PlotStyle -> Black,
  PlotMarkers -> {Automatic, 6}];

f = Interpolation[Table[{CCTx[[i]], CCTy[[i]]}, {i, 1, Length[CCT]}]];

pf = Plot[f[x], {x, First[CCTx], Last[CCTx]},
  PlotStyle -> Directive[Thickness[0.002], Black]];

ar = Graphics[{Thickness[0.003], Arrowheads[0.03], Arrow[{0.27, 0.47}, {0.23, 0.38}]},
  {Thickness[0.003], Arrowheads[0.03], Arrow[{0.29, 0.38}, {0.25, 0.30}]}];

λexc =
  Graphics[{Text[Style["λexc = 980 nm", Black, 20, FontFamily -> "Times"], {0.67, 0.87}]}];

(*CIE 1931 diagram with (x,y) coordinates*)
img = Show[cie, title, ar, λexc, point1,
  point2, wavelength, lines, b1, b2, cct, pf, ImageSize -> Large]
Export["CIE_TZYb.png", img, ImageResolution -> 300];

```