UNIVERSIDADE DE SÃO PAULO
ESCOLA DE ENGENHARIA DE SÃO CARLOS

TÁSSIA DE SOUZA GONÇALVES

**Rare earth doped fluoride-phosphate glass and glass-ceramics:
Structure-Property Relations**

São Carlos
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I dedicate this dissertation to my husband, parents and sister for all support and love during this journey.

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Abstract

GONÇALVES, T. S. **Rare earth doped fluorophosphate glass and glassceramics: Structure-Property Relations.** 99p. Dissertation (PhD)–Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, 2018.

Rare earth RE^{3+} doped fluorophosphates glasses and glass ceramics are among the most promising candidates for high efficiency laser generation in the near-infrared spectral region. Glass ceramics are polycrystalline materials of fine microstructure that are produced by the controlled crystallization (devitrification) of a glass. By developing fluorophosphate base glasses with appropriate compositions and by controlling crystal nucleation and growth in them, glass ceramics with special properties can be fabricated combining the advantages of fluorides (low phonon energy, low refractive indexes, extensive optical window, lower hygroscopicity) and oxides (high chemical and mechanical stability and high dopant solubility), resulting in enhancement of the RE^{3+} emissive properties. In this study, we present the synthesis by melting/quenching and structural/spectroscopic investigation of new glasses and glass ceramics with composition $25\text{BaF}_2 25\text{SrF}_2 (30-x)\text{Al}(\text{PO}_3)_3 x\text{AlF}_3 (20-z)\text{YF}_3: z\text{REF}_3$, where $x = 15, 20$ or 25 , $\text{RE} = \text{Er}^{3+}$ and/or Yb^{3+} and Nd^{3+} . A detailed structural investigation of a series of this glasses has been conducted, using Raman, solid-state nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) spectroscopies.

Key words: fluorophosphate glasses, rare earth ions, NMR, UV-VIS spectroscopy.

Resumo

GONÇALVES, T. S. **Vidros e vitrocerâmicas dopados com terras raras: Correlações entre estrutura e propriedades.** 99p. Tese de doutorado—Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, 2018.

Vidros e vitrocerâmicas fluorofosfatos dopados com íons terras raras (TR^{3+}) estão entre os candidatos mais promissores para a geração de laser de alta eficiência na região espectral do infravermelho próximo. As vitrocerâmicas são materiais policristalinos com microestrutura bem definida obtida a partir da cristalização controlada do vidro base. Desenvolvendo vidros base de fluorofosfato com composições apropriadas e controlando a nucleação e crescimento de cristais, vitrocerâmicas com propriedades especiais podem ser fabricadas combinando as vantagens dos fluoretos (baixa energia de fônons, baixos índices de refração, janela ótica extensa, baixa higroscopicidade) e óxidos (alta estabilidade química e mecânica e alta solubilidade dopante), resultando no aumento das propriedades emissoras dos íons TR^{3+} . Neste estudo, apresentamos a síntese por fusão/resfriamento e investigação estrutural/espectroscópica de novos vidros e vitrocerâmicas com composição $25BaF_2 25SrF_2 (30-x) Al (PO_3)_{3x} AlF_3 (20-z) YF_3: zREF_3$, onde $x = 15, 20$ ou 25 , $RE = Er^{3+}$ an / ou Yb^{3+} e Nd^{3+} . Uma investigação estrutural detalhada de uma série destes vidros foi conduzida utilizando espectroscopias Raman, de ressonância magnética nuclear de estado sólido (RMN) e de ressonância paramagnética eletrônica (EPR).

Palavras chave: vidros fluorofosfatos, íons terras raras, RMN, espectroscopia UV-VIS.

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1. INTRODUCTION

(1) Motivation

Fluoride glasses are potential candidates for Er^{3+} and Nd^{3+} doped materials because of their low phonon energy and wide optical transmission window, ranging from UV to mid-IR. However, they are fragile and they are the best host for RE^{3+} dispersion of high concentrations of rare earth ions. The addition of small quantities of selected phosphates to the glass compositions leads to much more stable glass samples with little damage to optical properties [1–4]. The optimization of the compromise between the IR optical quality loss and the improvement in mechanical properties is a challenge depending on specific applications. The growth of high optical quality crystals at large scales is costly and time consuming. The strong ionic bonding character of fluorides results in very low viscosity, at relatively low temperatures, and a large tendency to devitrification during cooling [1]. Once this step is overcome, it is possible to obtain a glass ceramic by heat treatment. Besides, significant loss of fluorine is often a problem in controlling the final fluoride glass composition and preserving the integrity of furnaces. On the other hand, phosphate glasses can have higher mechanical, chemical and thermal stability than fluorides, and usually allow high concentrations of RE dopants. Still, the phosphate glasses present high phonon energies and OH^- species at a level that can introduce high losses to the RE's quantum efficiencies via non-radiative decay processes.

Combinations of fluoride and phosphate precursors can result in glasses that possess the merits of both. Alloying melting of fluorides with even small amounts of phosphates drastically improves the glass formation ability of the melts due to introduction of more covalent bonding in the fluoride network through PO_4 groups [1]. In this case, although the addition of phosphates results in a decrease in the host's infrared transmittance and in an increase of the maximum phonon energy, the presence of fluorine guarantees that OH^- groups are kept at lower levels than in phosphate glasses.

Many papers have been published [5–7] on UV transparency of fluorophosphate glasses which have demonstrated mainly the effects of melting conditions, impurities from raw materials, crucible materials, etc. Among various glasses, fluorophosphate (FP) glass has many advantages such as long fluorescence lifetime, broad absorption and emission bands, high solubility for rare-earth ions, and tailorable properties by varying the F/P ratio [8,9].

Rare earth (RE^{3+}) doped fluoroaluminophosphate glasses and glass-ceramics are among the most promising candidates for high efficiency laser generation in the near-infrared spectral region. Glass-ceramics are advanced materials composed of one or more glassy and crystalline phases. By developing fluorophosphate glasses with appropriated compositions and by controlling their crystal nucleation and growth, glass-ceramics with special properties can be fabricated combining the advantages of fluorides and phosphates and resulting in the enhancement of the RE^{3+} emissive properties.

(2) *Glass and Glass-ceramics*

Glass is one of the oldest material the humanity knows. The chronological order of landmarks in glass developments varies from book to book. However, it is known that the first glass was obtained 400 BC. It was accidentally obtained by heating calcium carbonate stones together with sand [10]. After this first registration, only 300 years later an effective technique was developed to mold them and this technique has been used ever since. Since 1600, Newton and Galileo have promoted optical studies, and glasses have gained more importance, since they were essential in optical experiments. It is important to remember that transparent glasses were needed at that time and it was still difficult to obtain colorless glasses. In 1800, glasses were obtained from different chemical reagents, and due to the industrial revolution in 1850, the first glass factory in Jena was created in 1884. After that, the glasses have been studied continuously, from preparation to applications [11].

The most accepted definition of glass is: ***"Glass is an amorphous solid with complete absence of long range order and periodicity (Figure 1b), exhibiting a glass transition region"*** [10].

Figure 1: Two-dimensional representation: (A) of the symmetrical periodic crystal arrangement of a crystal of SiO_2 composition; (B) Representation of the glass network of the same composition [11].

Recently, Zanutto and Mauro proposed a new definition for glasses: ***“Glass is a nonequilibrium, non-crystalline condensed state of matter that exhibits a glass transition. The structure of glasses is similar to that of their parent supercooled liquids (SCL), and they spontaneously relax toward the SCL state. Their ultimate fate, in the limit of infinite time, is to crystallize”*** [12].

According Zanutto and Mauro, to understand some of the key features and the nature of glasses, it is educative to start with one of the most well-known diagrams in glass science: the enthalpy versus temperature plot, from above the melting point down to the absolute zero (Figure 2). The different regions in Figure 2 can be defined as [12]:

In equilibrium, the thermodynamically stable liquids (L) only exist above the melting point or liquidus temperature, T_m . They never crystallize. Between T_m and T_g (glass transition temperature) the supercooled liquids (SCL) exist. They are metastable and they eventually crystallize (red arrows) after a certain time; below T_g we have the glasses (G). They are thermodynamically unstable and spontaneously relax toward the supercooled liquid state at any nonzero temperature (gray arrow in Figure 2). The glass transition takes place at T_g , the temperature where the experimental or observation time, t_{obs} , is similar to the average structural relaxation time of the SCL, τ_R . On the heating path, a glass changes to a SCL at T_g . At any positive temperature, above or below T_g , for sufficiently long times ($t_{\text{obs}} \gg \tau_R$), any SCL or glass relaxes and then eventually crystallizes (arrows in Figure 2) and Crystals (C) are true solids with well-organized atomic structures at short, medium and long range, which are thermodynamically stable below T_m [12].

Figure 2: Schematic enthalpy versus temperature plot for a glass-forming substance showing four distinct states: liquid (L), supercooled liquid (SCL), glass (G), and crystal (C). T_m = melting point or liquidus temperature, T_g = glass transition temperature [12].

Glass-ceramics are polycrystalline materials of fine microstructure that are produced by the controlled crystallization (devitrification) of a glass. They can be found in nature (e.g. obsidian) or obtained artificially. The first glasses obtained were not entirely pure, but they presented certain mixtures of crystallized materials and were considered to be of poor quality of transparency. However, in the 1950s researcher Stanley Donald Stookey changed the view of glass with some crystallized phase.

Although his discovery was accidental, Stookey realized that after overheating his glass had lost its transparency and had gained superior mechanical resistance. From that point on research related to this new material was triggered and it was observed that the glass-ceramics must be obtained using controlled, very specific conditions [13]. Nevertheless, Stookey's discovery was kept secret for almost a decade, but after that time, Corning Glass Works announced the discovery of Stookey's material and thereby motivated other researchers to follow this research path.

Since the 1980s, scientists have studied glass-ceramic combining advantages of glass and crystals and focused on their synthesis to obtain transparent materials with nanocrystals, which are very important for photonic applications, such as rare earth doped materials used in optical amplifiers, fibers based on the upconversion process, infrared solid-state lasers, among others [14,15].

The first oxyfluoride glass-ceramic synthesis was reported in 1993 [16] for a glass with lead fluoride doped with erbium and ytterbium. This new composition would combine characteristics of fluoride glass with low phonon energy and oxides as a glass former.

The first article that analyzed fluoride nanocrystals in a glass-ceramic was written by Beall and Pinckney [17]. They showed the combination of the rare earth doped fluoride nanocrystals (narrow and intense emissions) with macroscopic characteristics of oxide glasses (chemical stability, mechanical stability, toughness and optical quality).

In 2011, Fedorov emphasized that transparent oxyfluoride glass-ceramics deserved the attention of researchers because they contained in their fluorine nanocrystals low phonon energy, high quantum luminescence yield and long lifetimes for metastable states. Fedorov also mentioned that the nature of these glass-ceramics prevents the agglomeration of nanoparticles allowing transparency [18].

In 2015, Fedorov published a complete review of oxyfluoride glasses, among them the fluoroaluminate glass-ceramics are the closest composition to the materials presented in this thesis, and which present high thermal stability demonstrating the possibility to obtain rare earth doped nanocrystals [14].

From a classical point of view, the processes of obtaining glass-ceramics are divided into two stages: nucleation and crystal growth. Nucleation can occur in two forms, homogeneous and heterogeneous. Superficial nucleation is heterogeneous and occurs due to the presence of defects or cracks on the surface, thus forming nucleous from the surface to the volume [19]. Volumetric nucleation occurs when the nuclei formed have the same constitutional nature of the crystals that grow on them and there is no preferential region for nucleation to occur. However, for homogeneous nucleation to occur, the matrix must have the same composition, structure, and energy. On the other hand, heterogeneous nucleation occurs more frequently than homogeneous nuclei, because the formation of nuclei originates in sites of particles of impurities or defects in glass. Among the greatest difficulties in growing crystals, there is the possibility of forming several different phases.

The most studied glasses from the point of view of the optical applications are chalcogenides, silicates, fluorides, phosphates and oxyfluorides, doped with rare earth ions (RE^{3+}). The silicates and phosphates are the most commonly studied (more traditional), however, they present high phonon energy and presence of OH groups, making the RE dopant more susceptible to non-radiative losses compared to fluoride and chalcogenide matrices with

lower phonon energy. On the other hand, the fluoride has low mechanical resistance that could compromise their applications.

Thus, interest has recently been shown for oxyfluoride glasses (usually fluorosilicate and fluorophosphate) that combine the favorable characteristics of fluoride matrices that exhibit low refractive index, low viscosity, low phonon energy ($\sim 500 \text{ cm}^{-1}$) and high transmission in the infrared spectral region and with a minimum amount of phosphates, facilitating the formation of the glass and increasing its thermal and mechanical stability .

(3) Fluoroaluminophosphate compositions

Ehrt et al. studied formation, properties and structure of glasses in different $\text{AlF}_3\text{--MF}_2$ ($\text{M}=\text{Mg, Ca, Sr, etc}$) systems and found correlations between the glass forming ability and eutectic compositions of the crystalline states. It was found that a very small amount of phosphate drastically increases the glass forming ability due to bonding more covalent PO_4 groups in the fluoroaluminate structure, and manufacturing of glasses was possible in large scale. But the phosphate groups decrease the infrared transmission due to absorption by P–O vibrations with overtones around $4.5 \text{ }\mu\text{m}$ and combination vibrations in the region of $6\text{--}7 \text{ }\mu\text{m}$. The first structural model of these glasses was proposed by comparison with the known crystal structures. The coupling of the electronic transitions of the active rare earth elements with these P–O vibrations has a large (deleterious) effect on lasing properties of fluoroaluminate glasses [9].

(3.1) Structure network

To find the best composition improving physical properties, the development of structural concepts is essential. Owing to the lack of long-range order in these glasses, we can use spectroscopy measurements to obtain structural information, such as Raman scattering and NMR spectroscopy. The short-range order of phosphate glasses is usually described in terms of Q_m^n terminology: here n is the number of P next-nearest neighbors per P tetrahedron and m is the number of next-nearest neighbor atoms in those glasses that possess additional network forming species as shown schematically in Figure 3.

Figure 3: Schematic representation of Q^n phosphate tetrahedral units.

The addition of fluoride to metaphosphate glasses is envisioned to result in network depolymerisation, the P-O-P bonds are broken to form mono- or difluorophosphate (PO_3F^- – Q^1 - units or PO_2F_2^- – Q^0 - units) [20]. Owing to this depolymerization process, the average phosphate chain length is successively decreased, as increasing amounts of fluoride species are incorporated into the metaphosphate glass structure. The process can be monitored by Raman spectroscopy where the strong bands near 1085 cm^{-1} and 990 cm^{-1} were obtained, which are assigned to the symmetric stretching modes of PO_3 and PO_4 units, respectively, of Q^1 and Q^0 phosphate tetrahedra. In addition, a broad shoulder appears near 1130 cm^{-1} suggesting the presence of Q_2 units as well. Using ^{31}P -MAS NMR we observe the same units and indicates that the Q^2 species present in pure $\text{Al}(\text{PO}_3)_3$ glass is dominantly converted into Q^1 and Q^0 species by the reaction with AlF_3 and Ba/Sr difluorides in the melting process [21]. The phonon modes coupled with rare earths and substitution of AlF_3 for $\text{Al}(\text{PO}_3)_3$ in Eu^{3+} glasses can be monitored using the phonon sideband associated with Eu^{3+} : $^5\text{D}_2 \leftarrow ^7\text{F}_0$ transition.

(3.2) Fluorophosphate glasses doped Rare Earths (RE)

Trivalent rare earth ions, with the partially filled 4f layer, are interesting for technological application because of their emissions from ultraviolet to infrared. The electrons in the 4f layer are shielded by the electrons of the more external layers (5s and 5p), so that the influence of the ligand field on the 4f-4f transitions is small, although it cannot be neglected. The shielding effects on these ions make the absorption and emission lines narrow and well defined (Blasse and Grabmaier 1994). According to Laporte's selection rules the f-f transitions are prohibited because the wavefunctions describing the 4f orbitals involved have the same parity. However, when we insert a rare earth ion into a non-symmetric crystalline field, the spherical symmetry is distorted with the mixing of opposing electronic parity configurations and consequently relaxation of the Laporte's rule occurs (HUANG, 2014).

To study the luminescent properties it is very important to understand the energetic levels presented by these ions. We can describe the total energy of a free ion by the Hamiltonian

H_0 , considering the approximation of the central field which states that each electron f is influenced by the nucleus and the other electrons, such as:

$$H_0 = \sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{i=1}^N \frac{Ze^2}{r_i}$$

However, this central field Hamiltonian H_0 does not adequately describe the total energy of the ion because it does not consider the occurrence of perturbations in multielectronic systems (electron repulsion between f electrons) that breaks the energy degeneracy of the ions in $2S + 1L$ terms, with L being the total orbital momentum and S the total spin momentum. Also it doesn't consider the spin-orbit coupling between the spin and the angular momentum of the electrons, which again results in the unfolding of the energy levels $2S + 1L$ and $J = L + S$ with denomination $2S + 1LJ$. Thus, we can write the Hamiltonian that represents the total energy of the ion in a crystalline environment as:

$$H_{\text{ion}} = H_0 + H' + H_{\text{SO}} + H_{\text{CF}}$$

The relative magnitude of each of these perturbations in the unfolding of the ion energy levels can be observed in Figure 4.

Figure 4: Effect of major disturbances on the central field Hamiltonian H_0 (HUANG, 2014).

At LEMAF – *Laboratory of Spectroscopy of Functional Materials* at IFSC/USP, we have been studying new fluoroaluminophosphate glasses with composition $\text{BaF}_2\text{-SrF}_2\text{-Al(PO}_3)_3\text{-AlF}_3\text{-YF}_3$ doped with Eu^{3+} , Nd^{3+} , Er^{3+} and/or Yb^{3+} . All of these ions are very important from the technological point of view.

The 1.5 μm emission of Er^{3+} ($^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition) is studied in a large variety of hosts for application in telecommunications. Also intense upconversion emissions in the green ($^2\text{H}_{11/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) and red ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$) spectral regions are explored in devices such as temperature sensors. Yb^{3+} is used as co-dopant because it presents significantly higher absorption cross-sections around this wavelength than Er^{3+} , it is frequently used a sensitizer of excitation radiation, with subsequent transference to Er^{3+} in Er/Yb co-doped systems increasing the upconversion emissions.

Eu^{3+} doped glasses are very useful for structural studies because of the $^7\text{F}_2 \rightarrow ^5\text{D}_0 / ^7\text{F}_1 \rightarrow ^5\text{D}_0$ transition intensity ratio, the normalized phonon sideband intensities observed in the excitation spectra, as well as excited state lifetimes, which are systematically dependent on fluoride content. The Eu^{3+} results indicated that the rare-earth ions are found in a mixed fluoride/phosphate environment, to which the fluoride ions make the dominant contribution as desired [21].

Nd^{3+} have required properties for efficient laser operation at around 1050 nm ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transition) because of its high-stimulated emission and absorption cross-sections and long enough excited state lifetime, which are significantly influenced by the material that hosts the active ion [22].

2. PURPOSE OF THIS DISSERTATION

To study the structural and spectroscopic correlations in fluorophosphate glasses we used different spectroscopic techniques such as luminescence, RAMAN, nuclear and paramagnetic resonance and conventional techniques (DSC, DRX) and different theoretical methodologies to analyze the photophysical properties. The text is divided in:

- i) Preparation of glass and glass-ceramic doped with Er^{3+} , Yb^{3+} , Nd^{3+} and co-doped with Yb^{3+} , with excellent optical and spectroscopic properties.

- ii) Characterization of the structural and photophysical properties using different spectroscopic techniques.
- iii) Theoretical analysis of radiative properties of rare earths.
- iv) Applications.

3. OUTLINE OF THIS DISSERTATION

This dissertation reports explorative research concerning the luminescence properties of rare earth-doped fluorophosphate glass and glass-ceramic based materials for laser applications. The focus is on searching for improved or unconventional properties in existing glass materials and, the understanding of the relationship between luminescence properties and structure/composition is a challenging part of the work as described in this thesis from a set of papers obtained during the development of the project.

This dissertation can be subdivided into the following four main parts:

Article 1: Structure-property relations in new fluorophosphate glasses singly- and co-doped with Er^{3+} and Yb^{3+} ;

Article 2: Network Structure and Rare-earth Ion Local Environments in Fluoride Phosphate Photonic Glasses Studied by Solid State NMR and EPR Spectroscopies;

Article 3: Thermo-optical spectroscopic investigation of new Nd^{3+} -doped fluoro-aluminophosphate glasses;

Article 4: Infrared to visible upconversion properties of $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped fluoro-aluminophosphate glass and glass-ceramics.

The first part shows synthesis and structural/spectroscopic investigation of new glasses with composition $25\text{BaF}_2 25\text{SrF}_2 (30-x)\text{Al}(\text{PO}_3)_3 x\text{AlF}_3 (20-z)\text{YF}_3 : z\text{REF}_3$, where $x = 20$ or 15 , $\text{RE} = \text{Er}^{3+}$ and/or Yb^{3+} , $z = 0.25 - 5.0$ mol%, initially studied during the Masters course, where we show good spectroscopic properties due to good structure properties.

The second part is a detailed study of the structure properties and spectroscopic features of glasses doped with rare earth ions. For this study we used Eu^{3+} and Yb^{3+} doped fluorophosphate glasses, because this ions offer great properties information for the advanced techniques used.

The third part studies the luminescence properties of Nd^{3+} using different spectroscopic methods to obtain quantum efficiencies values, which showed very good agreement between the experimental results and theoretical calculations. For this part, we choose our best composition $25\text{BaF}_2 25\text{SrF}_2 10\text{Al}(\text{PO}_3)_3 20\text{AlF}_3 (20-z)\text{YF}_3$ changing only the Nd^{3+} content.

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4. RESULTS

Article 1: Structure-property relations in new fluorophosphate glasses singly- and co-doped with Er^{3+} and Yb^{3+}

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Structure-property relations in new fluorophosphate glasses singly- and co-doped with Er^{3+} and Yb^{3+}

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HIGHLIGHTS

- New fluorophosphate glass composition with excellent photophysical properties.
- Detailed structural insights by multinuclear solid state NMR.
- Rare earth bonding preference to fluoride rather than phosphate ions.

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ABSTRACT

Rare earth (RE^{3+})-doped fluorophosphate glasses are among the most promising candidates for high-efficiency laser generation in the near-infrared spectral region. By proper choice of composition, these materials can combine the advantages of fluorides (low phonon energies, low refractive indices, extensive optical window, low hygroscopicity) and of oxides (high chemical and mechanical stability and high dopant solubility), resulting in enhancement of the RE^{3+} emissive properties. In this work, we present the synthesis and structural/spectroscopic investigation of new glasses with composition $25\text{BaF}_2\cdot 25\text{SrF}_2\cdot (30-x)\text{Al}(\text{PO}_3)_3\cdot x\text{AlF}_3\cdot (20-z)\text{YF}_3\cdot z\text{REF}_3$, where $x = 20$ or 15 , $\text{RE} = \text{Er}^{3+}$ and/or Yb^{3+} , $z = 0.25$ – 5.0 mol%. Results indicate considerable improvement of the emissive properties of both ions when compared to phosphate or even other fluorophosphate host compositions. Long excited state lifetimes ($\tau = 10$ ms for the Er^{3+} level $^4\text{I}_{13/2}$, and $\tau = 1.3$ ms for the Yb^{3+} level $^2\text{F}_{5/2}$) imply high fluorescence quantum efficiencies η (up to 85% for both ions). Structural characterization by Raman and multinuclear solid state NMR spectroscopies indicate that the metaphosphate-type chain structure of the $\text{Al}(\text{PO}_3)_3$ vitreous framework is partially depolymerized and dominated by $\text{Q}^{(0)}$ and $\text{Q}^{(1)}$ units crosslinked by six-coordinate Al species. As revealed by $^{27}\text{Al}\{^1\text{H}\}$ rotational echo double resonance (REDOR) NMR results the average local aluminum environment of the $x = 20$ sample comprises 1.6 phosphate and 4.4 fluoride species. These results indicate a clear bonding preference between aluminum and phosphorus, which is consistent with the desired dominance of fluoride species in the local environment of the rare earth and alkaline earth atoms in these glasses.

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Rare earth (RE^{3+})-doped fluorophosphate glasses are among the most promising candidates for high-efficiency laser generation in the near-infrared spectral region. By proper choice of composition, these materials can combine the advantages of fluorides (low phonon energies, low refractive indices, extensive optical window, low hygroscopicity) and of oxides (high chemical and mechanical stability and high dopant solubility), resulting in enhancement of the RE^{3+} emissive properties. In this work, we present the synthesis and structural/spectroscopic investigation of new glasses with composition $25\text{BaF}_2 25\text{SrF}_2 (30-x)\text{Al}(\text{PO}_3)_3 x\text{AlF}_3 (20-z)\text{YF}_3 : z\text{REF}_3$, where $x = 20$ or 15 , $\text{RE} = \text{Er}^{3+}$ and/or Yb^{3+} , $z = 0.25 - 5.0$ mol%. Results indicate considerable improvement of the emissive properties of both ions when compared to phosphate or even other fluorophosphate host compositions. Long excited state lifetimes ($\tau = 10$ ms for the Er^{3+} level $^4\text{I}_{13/2}$, and $\tau = 1.3$ ms for the Yb^{3+} level $^2\text{F}_{5/2}$) imply high fluorescence quantum efficiencies η (up to 85% for both ions). Structural characterization by Raman and multinuclear solid state NMR spectroscopies indicate that the metaphosphate-type chain structure of the $\text{Al}(\text{PO}_3)_3$ vitreous framework is partially depolymerized and dominated by $\text{Q}^{(0)}$ and $\text{Q}^{(1)}$ units crosslinked by six-coordinate Al species. As revealed by $^{27}\text{Al}\{^{31}\text{P}\}$ rotational echo double resonance (REDOR) NMR results the average local aluminum environment of the $x = 20$ sample comprises 1.6 phosphate and 4.4 fluoride species. These results indicate a clear bonding preference between aluminum and phosphorus, which is consistent with the desired dominance of fluoride species in the local environment of the rare earth and alkaline earth atoms in these glasses.

I. Introduction

When it comes to efforts to improve the infrared and visible emissions of trivalent rare earth ions (RE^{3+}) embedded in solid state host matrices, fluoride crystals and glasses, with relatively low maximum phonon energy (500 cm^{-1}) have been widely studied for a long time [1-5]. However, their poor mechanical and chemical stabilities still hinder practical applications. The growth of high optical quality crystals with large enough dimensions is costly and time consuming and, as for glasses prepared by the conventional melt-quenching technique, the strong ionic bonding character of fluorides results in very low viscosity, at relatively low temperatures, and a large tendency to devitrification during cooling[1]. Besides, significant loss of fluorine is very often a problem in maintaining control of the final glass composition and preserving the integrity of furnaces. On the other hand, oxide glasses such as silicates, borates,

tellurites and phosphates present much higher mechanical, chemical and thermal stability than fluorides, and usually allow fairly high concentrations of RE dopants. Still, these glasses present high phonon energies and OH⁻ species at a level that can introduce high losses to the RE's quantum efficiencies via non-radiative decay processes. On those bases, proper combinations of fluoride and oxide precursors can result in glasses that possess the merits of both types of glass. Alloying fluoride melts with even small amounts of phosphates drastically improves the glass forming ability of the melts due to introduction of more covalent bonding in the fluoride network through PO₄ groups [1]. In this case, although the addition of phosphates results in a decrease in the hosts' infrared transmittance and in an increase of the maximum phonon energy, the presence of fluorine guarantees that OH⁻ groups are kept at lower levels than in oxide glasses.

There have been several reports on the spectroscopic and structural properties of RE³⁺-doped oxyfluoride glasses and glass ceramics [6-12] and, more recently, special interest has been paid to various fluorophosphate compositions singly- or co-doped with Er³⁺ and Yb³⁺ [13-17]. Both of these ions are very important from the technological point of view. The 1.5 μm emission of Er³⁺ (⁴I_{13/2} → ⁴I_{15/2} transition) is studied in a large variety of hosts for application in telecommunications (waveguides and fiber amplifiers, EDFA) [18,19], and intense upconversion emissions in the green (²H_{11/2}, ⁴S_{3/2} → ⁴I_{15/2}) and red (⁴F_{9/2} → ⁴I_{15/2}) spectral regions are explored in devices such as temperature sensors [6,20-22]. All these transitions can be efficiently pumped by high power, low cost, diode lasers at 980 nm (⁴I_{15/2} → ⁴I_{11/2}). Moreover, since Yb³⁺ presents significantly higher absorption cross-sections around this wavelength than Er³⁺, it is frequently used a sensitizer of excitation radiation, with subsequent transfer to Er³⁺, in Er/Yb co-doped systems. Besides good overlap between donor (²F_{5/2}, Yb³⁺) and acceptor (⁴I_{11/2}, Er³⁺) energy levels, in order to have efficient Yb³⁺ → Er³⁺ transfer the excited state lifetime of the donor must be of the same order of magnitude or higher than that of the acceptor, in order to avoid the undesirable back transfer Er³⁺ → Yb³⁺. While the metastable emitting level ⁴I_{13/2} is populated by relaxation from ⁴I_{11/2}, the upconversion emissions are mainly excited by absorption from both of these levels to the higher energy levels ⁴F_{7/2} and ⁴F_{9/2}. From ⁴F_{7/2} there is rapid relaxation to the green (²H_{11/2} and ⁴S_{3/2}), and red (⁴F_{9/2}) emitting levels [22]. Besides its role as an efficient sensitizer to Er³⁺ and, as a matter of fact, to other RE ions as well [23], Yb³⁺ itself presents a simple two level structure which leads to intense, broadband emission around 1.0 μm (²F_{5/2} → ²F_{7/2} transition), and long excited state

lifetimes, making it a favorite for high power and femtosecond laser devices. Furthermore, it can also exhibit blue emission via cooperative upconversion mechanisms [17].

Recently, we have been studying new fluoroaluminophosphate glasses with compositions $\text{BaF}_2\text{-SrF}_2\text{-Al(PO}_3)_3\text{-AlF}_3\text{-YF}_3$ doped with Eu^{3+} , Tb^{3+} , Er^{3+} and/or Yb^{3+} . In this work, we present very promising results on samples doped and co-doped with Er^{3+} and Yb^{3+} up to 5.0 mol% REF_3 . The samples are obtained through the conventional melt quenching technique, and structure-property correlations are sought through a combination of structural and photophysical studies using various vibrational, photophysical, and nuclear magnetic resonance spectroscopic techniques. With regard to structural organization of these glasses, very little is known so far, as the NMR spectroscopic characterization of fluorophosphate glasses has been rather limited to date [24-27]. In particular, the spectroscopic consequences of omnipresent fluoride losses in these systems have not been addressed, and to date, nothing is known concerning the medium-range order of these glasses and the local environment of the rare-earth ions. Here, we present some novel NMR approaches that are able to address these questions.

II. Experimental Procedures

(1) Preparation of samples and conventional characterization.

Glasses with nominal composition $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-(}30\text{-x)Al(PO}_3)_3\text{-xAlF}_3\text{-(}20\text{-z)YF}_3\text{:zREF}_3$ with $x = 20$ or 15 , $\text{RE} = \text{Er}^{3+}$ and/or Yb^{3+} and $z = 0.25, 0.5, 1.0, 2.0, 3.0, 4.0$ and 5.0 mol% were prepared by conventional melt quenching techniques in Pt crucibles. Homogeneous mixtures of reagent grade precursors were melted at 1150°C for 5 min, quenched between copper plates and heat treated for 10h at 400°C . Densities were measured by the Archimedes method in ethylene glycol ($d = 1.114\text{g/cm}^3$ at 27°C), and crushed samples were characterized by Differential Scanning Calorimetry (DSC) between 200 and 850°C , under N_2 flux atmosphere, at a heating rate of 10°C/min , in a simultaneous TG-DSC NETZSCH calorimeter model STA 449 Jupiter F3. The samples with the higher fluorine content ($x = 20$) will be addressed hereafter as **20AlF₃** (undoped) and **20RE_z** (REF_3 -doped) and those with lower fluorine content ($x = 15$) as **15AlF₃** and **15RE_z**, respectively.

(2) Structural and photophysical characterization.

Raman spectra were measured in a Horiba Jobin–Yvon spectrophotometer model T64000 using the Ar⁺ laser line at 488 nm. ¹⁹F solid state NMR measurements were conducted in the single-pulse mode at 188.8 MHz, using a 4.65 T magnet interfaced with a Bruker DSX console. A 2.5 mm probe was used, operated at a spinning rate of 25.0 kHz. Spectra were recorded with 90° pulses of 3.2 μs length, using relaxation delays of 40 s. Chemical shifts are reported against CFCl₃, using solid AlF₃ as a secondary external standard (-172 ppm). ²⁷Al MAS-NMR studies were carried out at 130.32 MHz on a Bruker DSX 500 spectrometer, equipped with a 4 mm probe which was operated at a spinning rate of 14.0 kHz. Spectra were recorded using short pulses of 0.5 μs length and relaxation delays of 10 s. ²⁷Al triple-quantum (TQMAS) NMR data were obtained using the three-pulse z-filtering sequence [28], using hard excitation and reconversion pulses of 4 μs and 1.3 μs length and soft detection pulses of 10 μs length. Chemical shifts are reported relative to 1M Al(NO₃)₃ aqueous solutions. ³¹P MAS-NMR studies were carried out at 202.45 MHz on a Bruker DSX 500 spectrometer, equipped with a 4 mm probe which was operated at a spinning speed of 14.0 kHz. Spectra were recorded using 90° pulses of 2.0 μs length and relaxation delays of 120 s. In addition, double-quantum filtered spectra were measured using the 1-D refocused INADEQATE sequence [29]. This experiment results in the selective detection of only those ³¹P nuclei that are involved in a P-O-P linkage and therefore give rise to indirect ³¹P-³¹P spin-spin coupling (Q⁽¹⁾ and Q⁽²⁾ units) but suppress the signals of isolated Q⁽⁰⁾ units. Experimental conditions were: spinning speed 12.0 kHz, π/2 pulse length 2.6 μs, relaxation delay 150 s. The mixing time for DQ coherence creation was 16.6 ms, corresponding to a value of the indirect coupling constant ²J(³¹P-³¹P) of 30 Hz. Chemical shifts were referenced against an external 85% H₃PO₄ standard. ²⁷Al{³¹P} rotational echo double resonance (REDOR) [30] measurements were conducted under the same conditions, using π recoupling pulses on the ³¹P channel and acquisition of rotor-synchronized ²⁷Al spin echoes (6μs π pulse length). Data were acquired using the compensation method[31]. By applying a parabolic fit to the data within the range ΔS/S₀ as previously described [32] dipolar second moments were obtained from which an average number of Al-O-P linkages can be estimated. In an analogous fashion, the dipolar interaction strength between ¹⁹F and ³¹P nuclei was analyzed by ¹⁹F{³¹P} REDOR. These experiments were conducted at 11.7 T at a rotor speed of 25.0 kHz, using ³¹P-π pulses of 3.2 μs length and a 5s relaxation delay. For all

the nuclei detected, spin-lattice relaxation times were measured using the saturation recovery sequence. Lineshape analysis and deconvolutions were done using the DMFIT routine [33].

UV-VIS-NIR absorption spectra of optically polished samples were measured in a Hitachi spectrophotometer model U2800. Infrared and visible excitation, emission and excited state lifetime measurements were performed in a Horiba Jobin Yvon spectrofluorimeter model Fluorolog FL3-221. Upconversion spectra were also measured in a Fluorolog spectrofluorimeter, using as external excitation source a diode laser at 976 nm from DMC model Lasertool. Refractive index measurements were performed in cube-shaped samples in a Carl-Zeiss refractometer model Pulfrich PR2.

III. Results and Discussion

(1) Conventional characterization.

All the samples were obtained in large pieces and with excellent optical quality as judged by optical microscopy inspection (see Figure 5). The DSC curves (not shown) indicate very good thermal stability of the glasses towards crystallization. For the 20AlF₃ sample, the characteristic onset temperatures of the glass transition $T_g = 471$ °C and the crystallization exotherm, $T_x = 620$ °C, are clearly defined from the curve (not shown), leading to the thermal stability parameter $\Delta T = T_x - T_g = 149$ °C. For the 15AlF₃ sample $T_g = 510$ °C while DSC gives no clear evidence of a crystallization exotherm. In this case, the absence of a well-defined crystallization peak is in agreement with the expectation that the sample richer in phosphate exhibits higher thermal stability against crystallization [13]. These results do not vary significantly when RE dopants are present. The densities of the undoped and doped samples range from 3.9 to 4.1 g/cm³ depending on the amount of AlF₃ and the RE dopant level.

Figure 5: Representative photographs of the glasses: (a) 20Erz, (b) 20Ybz, (c) 20ErYb.

(2) Raman Spectroscopy.

Figure 6 presents the Raman spectra of undoped 20AlF₃ and 15AlF₃ samples. It is noted that except for slight intensity changes, the two spectra are rather similar and seven bands can be assigned: Band a (500 cm⁻¹) corresponds to M-F bond vibrations (M = alkaline earth),² band b (~570 cm⁻¹) corresponds to [AlF₄] vibrations [13,34], bands c and d (660 and 750 cm⁻¹) are related to symmetric stretching of P-O-P linkages involving phosphate tetrahedra associated with Q⁽²⁾ and Q⁽¹⁾ units, respectively, [2,35] bands e and f (1000 and 1080 cm⁻¹) are due to PO₄ and PO₃ stretching vibrations within Q⁽⁰⁾ and Q⁽¹⁾ type phosphate tetrahedral [34] interacting with Al. In addition, a shoulder at higher wavenumbers (band g near 1200 cm⁻¹) indicates PO₂ stretching vibrations typical of metaphosphate units [36]. It is worth noting that the data give no evidence for bands in the 800-900 cm⁻¹ region, where the P-F stretching vibration is usually observed. Thus, the Raman data give no evidence for the formation of phosphorus-fluorine bonds in significant proportions.

Figure 6: Raman scattering spectra of undoped 15Er and 20Er samples.

(3) Fluoride Quantification by ^{19}F NMR.

As fluoride losses and/or replacement by oxide species are an important issue in the preparation of oxyfluoride glasses, the total F content was quantified via NMR using a previously described standard addition method on samples containing a weighed amount of sodium fluoride, NaF [37]. These spectra were obtained as rotor synchronized Hahn spin echoes on samples spinning at 25.0 kHz. A relaxation delay of 250 s was used, which was shown to ensure fully quantitative detection. Quantification was then done via a comparison of the relative signal areas. Based on the results obtained, it was found that ca. 80% of all the fluorine is retained in the glasses under the preparation conditions used. As no significant weight losses were observed after melting, we assume that this loss is compensated by uptake of oxide or water from the furnace atmosphere.

(4) Structural Characterization by Multinuclear NMR.

Figure 7, top left, summarizes the ^{19}F MAS-NMR spectroscopic data obtained for the Er-doped $x = 10$ (20Erz) samples. Two principal resonances are observed near -51 ± 1 and -124 ± 2 ppm in an approximate ratio of 1:3. The dominant signal near -124 ppm is assigned to fluorine atoms in a mixed alkaline earth/aluminum environment as found in various Al-containing fluorophosphate [24-26] or fluoride glasses [38], as well as in corresponding crystalline model

compounds [39,40]. The signal near -51 ppm is assigned to fluorine atoms bound to yttrium atoms, based on the observation that the chemical shift of the dominant site in YF_3 is found at -45 ppm [41]. Its relative peak area varies between 23 and 30 %, but appears to be uncorrelated with the Er content. We attribute these variations to fitting errors and/or small variations in synthesis conditions. Essentially the same results are found for the $x = 15$ samples (data not shown). Consistent with the Raman spectra the ^{19}F MAS-NMR spectra give no clear evidence for P-bonded fluorine atoms, whose resonance signal would be expected near -75 ppm [24-26,42]. The possibility of P-F bonding was further examined by $^{19}\text{F}\{^{31}\text{P}\}$ rotational echo double resonance (REDOR) NMR. Figure 8 shows that both the -51 and the -124 ppm peak show comparable extents of dephasing at a dipolar evolution time of 1.5 ms. The full REDOR curves ($\Delta S/S_0$ versus the dipolar evolution time NT_r) are shown for both resonances in the bottom part of the Figure. Parabolic analysis over the initial data range ($\Delta S/S_0 < 0.2$) yielded second moment values of $M_2 = 3.3 \times 10^6 \text{ rad}^2/\text{s}^2$ for both species, indicating that the dipolar coupling strengths with ^{31}P are indistinguishable within experimental error. This result provides clear evidence for the absence of appreciable amounts of P-F bonding in these glasses. If such bonding did exist, the short P-F bond distance would result in much stronger dephasing characterized by a dipolar M_2 value on the order of $1000 \times 10^6 \text{ rad}^2/\text{s}^2$. Clearly, this is not observed in the present samples.

Figure 7: ^{19}F (top left), ^{27}Al (top right), MAS-NMR spectra of 20Erz glasses ($x = 20$), doped with zero, 0.1, 0.25 and 3% Er^{3+} respectively. Bottom: ^{31}P DQ-filtered MAS-NMR spectrum (left) and single pulse NMR spectrum (right) and proposed spectral deconvolutions. Spinning sidebands are indicated by asterisks.

Figure 7, bottom, summarizes results from ^{31}P MAS-NMR. The broad asymmetric lineshape suggests multiple contributions, however, unconstrained fitting would appear rather arbitrary. Deconvolution constraints were developed using DQ-filtered experiments as described above. The two distinct components observed in this spectrum near $-14 \pm$ and -24 ± 1 ppm can be assigned to $Q^{(1)}$ and $Q^{(2)}$ units, respectively, which are linked to aluminum atoms (left bottom trace). Comparison with the standard MAS-NMR spectrum (lower trace) reveals the presence of a third component near -7 ± 1 ppm, which is suppressed by the DQ filter. This resonance must then be assigned to $Q^{(0)}$ species linked to aluminum. Based on the final fit of the single-pulse spectrum the $Q^{(0)}:Q^{(1)}:Q^{(2)}$ ratio is $58:38:4 (\pm 2)\%$, in good qualitative agreement with the Raman spectrum.

Figure 7, top right, shows results from ^{27}Al MAS-NMR. A dominant resonance in the region of six-coordinated aluminum is observed. The resonance position is influenced by both the isotropic chemical shift and the second-order quadrupolar shift. Both contributions can be separated via Triple-quantum MAS-NMR (TQMAS), using established data analysis

procedures (data not shown) [28]. We determine the isotropic chemical shift as -1.8 ppm and the second order quadrupolar effect $P_Q = C_Q \times (1 + \eta^2/3)^{1/2}$ to 2.8 ± 0.2 MHz. In the latter expression C_Q is the ^{27}Al quadrupolar coupling constant, whereas η is the asymmetry parameter of the electric field gradient at the Al site, specifying its deviation from axial symmetry. While both MAS and TQMAS experiments suggest a minor amount of Al in five-coordination, the overwhelming majority (> 98%) of the Al species is six-coordinated.

The question to which extent fluoride and phosphate species contribute to the first coordination sphere was addressed by $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR studies. Figure 9 shows results for the undoped 20AlF_3 sample, and of the crystalline reference compound $\text{Al}(\text{PO}_3)_3$. The dipolar second moments obtained from the parabolic analyses of the initial decay regime, are $1.4 \times 10^6 \text{ rad}^2/\text{s}^2$ and $5.4 \times 10^6 \text{ rad}^2/\text{s}^2$, respectively. Considering that in crystalline aluminum metaphosphate the second coordination sphere of Al is made up by six P atoms at a distance of 3.20 Å, and assuming that in glasses the same second-nearest neighbor distance is applicable, we deduce from the ratio of the M_2 values that in the 20AlF_3 glass the average coordination comprises 1.6 phosphate and hence 4.4 fluoride species. Thus, in the first coordination sphere of aluminum the experimentally determined average P/F ratio is 0.37.

Based on these experimental results, we can develop the following structural considerations. A base glass consisting only of $\text{Al}(\text{PO}_3)_3$ and AlF_3 in a 1:2 ratio (as in the 20AlF_3 glass) would have a structure based on polymeric $Q^{(2)}$ units cross-linked by Al atoms, which are octahedrally coordinated by a variable mix of phosphate and fluoride ions. For such a glass, the batch composition predicts an average P/F ratio of 0.5 in the Al coordination environment. The components SrF_2 , BaF_2 and YF_3 can be considered network modifiers, which act to depolymerize the glass structure by breaking either P-O-P or P-O-Al linkages. Breakage of P-O-P linkages would, however, result in the formation of P-F bonds, for which our spectroscopic data give no evidence. Therefore, we conclude that these network modifiers preferentially break Al-O-P linkages, resulting in additional Al-F bonds and thus a lower P/F ratio in the coordination sphere of Al as indeed observed in the $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR experiments. While this process does occur to some extent, the experimental P/F ratio near aluminum turns out to be significantly higher than the statistically expected P/F ratios. These would be 0.14 based on the nominal glass composition (0.3 P per formula unit/2.2 F per formula unit) or 0.17 based on the actual glass composition (taking the 20% fluoride loss into consideration). Thus, our data give strong evidence for a preferential association of phosphate with aluminum species. In turn, this result implies that the local environment of the alkaline earth and yttrium species is dominated

by fluoride ions. Thus, a sizeable fraction of these fluoride species are not acting as network modifier species in these glasses but are present in the form of domains rich in Sr^{2+} , Ba^{2+} and Y^{3+} , as well as some Al^{3+} . Finally, the $\text{Q}^{(2)} \rightarrow \text{Q}^{(1)} \rightarrow \text{Q}^{(0)}$ depolymerization process evident in the ^{31}P MAS NMR data needs to be explained. In the absence of detectable P-F bonding, we relate this effect to the considerable fluoride losses noted in the quantification experiments, which we attribute to fluoride/oxide ion exchange during melting and quenching. The oxide ions produced in this fashion are highly basic and are known to depolymerize P-O-P linkages in alkali, alkaline earth and aluminum phosphate glasses. For the 20AlF_3 glass a 20% fluoride loss corresponds to 0.44 F^- ions per formula unit, to be replaced by 0.22 O^{2-} ions in the melt. This amount is certainly sufficient to convert the majority of the $\text{Q}^{(2)}$ phosphate species (whose batch concentration is 0.3 per formula unit) into $\text{Q}^{(1)}$ and $\text{Q}^{(0)}$ species in the final glasses. Finally, we note that the presence of Er^{3+} dopants also manifests itself clearly in the NMR spectra, resulting in successive paramagnetic broadening of the ^{31}P , ^{19}F , and ^{27}Al central MAS-NMR signals and an increase of the spinning sideband intensities. These spectroscopic changes reflect an increasing strength of pseudo-scalar interactions for all three nuclear species with the unpaired f-electrons of the Er^{3+} dopant. An even more sensitive parameter is the spin-lattice relaxation time of the spin-1/2 nuclei ^{19}F and ^{31}P , which is dominated by these paramagnetic interactions. For example, we measure ^{19}F (^{31}P) T_1 -values of 0.7 s (33.4 s), 0.5 s (11.3 s), 0.3 s (23.3 s), and 0.02 s (1.1 s) for the samples containing zero, 0.1, 0.25, 0.5, and 3.0 % Er, respectively. Yb^{3+} doping leads to effects of comparable magnitude. In this case the measured ^{19}F - T_1 values are 0.7 s, 0.5 s, 0.3 s, 0.14 s, 0.04 s, and 0.03 s, for samples doped with 0, 0.25, 0.5, 1.0, 3.0 and 4.0% Yb^{3+} , respectively. For the quadrupolar ^{27}Al nuclei ($I = 1/2$) these effects are less pronounced as the spin-lattice relaxation times of these spins are dominated by the vibrational modulation of local electric field gradients.

Figure 8: $^{19}\text{F}\{^{31}\text{P}\}$ REDOR results on glass with composition $x=20$ (undoped). Top: rotor synchronized echo without (black curve) and with ^{19}F dipolar dephasing (red curve), shown for a dipolar evolution time of 1.5 ms. Bottom: separately analyzed $^{19}\text{F}\{^{31}\text{P}\}$ REDOR curves for the -51 ppm (left) and the -124 ppm resonances (right). Red curves show parabolic fits to the initial data range $\Delta S/S_0 \leq 0.2$ leading to apparent dipolar second moments of $3.3 \pm 0.3 \times 10^6 \text{ rad}^2/\text{s}^2$ for both fluoride species.

Figure 9: $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR results on crystalline $\text{Al}(\text{PO}_3)_3$ and glass with composition $x = 20$ (undoped). Solid curves show parabolic fits to the initial data range $\Delta S/S_0 \leq 0.2$ leading to apparent dipolar second moments of $5.4 \times 10^6 \text{ rad}^2/\text{s}^2$ and $1.4 \times 10^6 \text{ rad}^2/\text{s}^2$.

(5) Photophysical characterization.

Only small differences were perceived between the photophysical properties of samples of the series 20Er and 15Er, 20Yb and 15Yb, and 20ErYb and 15ErYb, i.e. the 25% variation in AlF₃ content in the host matrices is not enough to result in significant spectral changes. Therefore, the spectra will be shown and discussed for representative samples of the sets 20Er, 20Yb and 20ErYb. Figure 10 presents the room temperature absorption spectrum of the 20Er3 glass where the bands referred to transitions from ground state $^4I_{15/2}$ to the excited states of Er³⁺ are indicated. The inset shows the integrated area of absorption coefficients (transitions $^4I_{15/2} \rightarrow ^2H_{11/2}, ^4S_{3/2}$), as a function of ErF₃ concentration, for both sets of samples 15Er (open circles) and 20Er (filled squares). From these spectra, the phenomenological intensity parameters Ω_2 , Ω_4 and Ω_6 were calculated by means of the Judd-Ofelt (J.O.) theory [44,45], as elsewhere described [15,46]. The calculation is based on equaling the experimental oscillator strengths P_{exp} associated to transitions between the ground state $^4I_{15/2}$ and the observed excited states, to their corresponding calculated oscillator strengths P_{calc} (which contain the $\Omega_{\lambda s}$). This way, a system of as many equations as observed transitions is obtained and solved by the least-squares fitting method, so as to result in the best Ω_{λ} ($\lambda = 2, 4$ and 6) values. The larger the number of transitions accounted for, the lower will be the error involved in the J.O. calculations. In our case, 8 equations could be analyzed for two samples of each Er-doped set yielding, as expected, very similar results, since the J.O. theory does not take into account non-radiative concentration dependent processes. Table 1 presents the results for the 20Er3 sample.

Figure 10: Representative, room temperature absorption spectra of 3 mol% ErF_3 -doped 20Er glass. The bands correspond to transitions from ground state $^4\text{I}_{15/2}$ to indicated excited states. The inset shows the integrated area of absorption coefficients (transitions $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$), as a function of doping concentration for both compositions 15Er (open circles) and 20Er (filled squares).

Table 1: Experimental (P_{exp}) and calculated (P_{calc}) oscillator strengths, and J.O. phenomenological intensity parameters Ω_λ , of representative 20Er₃ glass. The squared reduced matrix elements $[U(\lambda)]^2$ were taken from Ref. [47].

Er ³⁺ transitions, $^4\text{I}_{15/2} \rightarrow$	λ (nm)	ν (cm ⁻¹)	$P_{\text{exp}} (10^{-6})$	$P_{\text{calc}} (10^{-6})$
$^4\text{I}_{11/2}$	972	10288	0.50	0.29
$^4\text{I}_{9/2}$	800	12500	0.29	0.17
$^4\text{F}_{9/2}$	650	15385	1.77	1.24
$^4\text{S}_{3/2} + ^2\text{H}_{11/2}$	542	18450	5.21	5.51
$^4\text{F}_{7/2}$	519	19268	1.40	1.59
$^4\text{F}_{5/2} + ^4\text{F}_{3/2}$	485	20619	0.51	0.63
$^2\text{H}_{9/2}$	450	22222	0.50	0.47
$^4\text{G}_{11/2} + ^4\text{G}_{9/2} + ^2\text{G}_{7/2} + ^2\text{K}_{15/2}$	380	26316	10.0	9.27
$\Omega_2 = 4.36 \times 10^{-20} \text{ cm}^2$ $\Omega_4 = 2.29 \times 10^{-20} \text{ cm}^2$ $\Omega_6 = 1.36 \times 10^{-20} \text{ cm}^2$ $\text{rms}_{\text{error}} = 2.63\% *$				

*Calculated according to Ref. [48].

The values of the intensity parameters Ω_λ are in good agreement with those observed for other Er-doped fluorophosphate glasses (Table 2). Although there have been controversies in the literature about the meaning of such parameters, it is generally well accepted that Ω_2 is related to the covalent character of the site occupied by the lanthanide ion, whereas Ω_6 relates to the rigidity of the host matrix [49]. According to Lai et al. [15] this explains why the Ω_2 of fluorophosphate glasses is lower than in phosphates, and higher than in fluoride glasses. In phosphates, the RE is surrounded by PO_4 units through highly covalent oxygen bonding

whereas in fluorophosphates, the addition of fluorine results in progressive coordination of the RE with the less covalent –O-(F-) linkages, that is, covalence is weakened by strong attraction of F⁻ to the electrons of the RE. Besides, the attraction of F⁻ would also increase the electronic density of 5d orbitals and thus increase Ω_6 .

Table 2: Comparison of phenomenological J.O. intensity parameters Ω_λ .

Host glass composition	Ω_2 ($\times 10^{-20}$)	Ω_4 ($\times 10^{-20}$)	Ω_6 ($\times 10^{-20}$)	Refs.
BaF ₂ -SrF ₂ -Al(PO ₃) ₃ -AlF ₃ -YF ₃	4.36	2.29	1.36	This work
YF ₃ -BaF ₂ -Ba(PO ₃) ₂	4.65	1.56	1.78	[15]
Ba(PO ₃) ₂ -AlF ₃ -MgF ₂ -CaF ₂ -SrF ₂ -BaF ₂	4.36	2.01	1.14	[51]
AlF ₃ -MgF ₂ -CaF ₂ -SrF ₂ -Sr(PO ₃) ₂	4.71	1.61	1.62	[50]
ZrF ₄ -LaF ₃ -AlF ₃ -BaF ₂ -NaF	2.91	1.27	1.11	[52]
Fluorozirconate ZBLA	2.54	1.39	0.97	[53]
Mg(PO ₃) ₂ -Ca(PO ₃) ₂ -Ba(PO ₃) ₂ -Zn(PO ₃) ₂ -Al(PO ₃) ₃	5.85	1.41	0.84	[50]
Kigre phosphate	6.28	1.03	1.39	[54]

Figure 11 presents representative ground state absorption spectra of the 20Yb3 glass where the broad band corresponds to transition from the ground state $^2F_{7/2}$ to the excited state $^2F_{5/2}$. The inset shows the integrated area of this band, as a function of concentration, for both 15Yb (open circles) and 20Yb (filled squares) compositions. Similarly to the case of Er-doped samples, the linear behavior of the curves indicates the successful, progressive incorporation of Yb³⁺ as the batched YbF₃ content is increased in the samples. It is noted that for the same RE concentration (3.0 mol% YbF₃) the peak absorption cross section of the 20Yb3 sample at 980 nm is almost five times higher than that of the 20Er3 sample.

Figure 11: Representative, room temperature absorption spectrum of 3 mol% YbF_3 -doped 20Yb glass. The inset shows the integrated area of absorption coefficients ($^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$), as a function of doping concentration for both compositions 15Yb (open circles) and 20Yb (filled squares).

Figure 12: Representative luminescence spectra of 20Erz samples (right) and intensity decay curves in time (log scale).

Figure 13: Representative luminescence spectra of 20Ybz samples (right) and intensity decay curves in time (log scale). The decay curves were measured for three samples only because lifetime of Yb^{3+} is not expected to change with concentration.

Figure 12 and Figure 13 display the representative near-infrared emission spectra of samples 20Erz and 20Ybz, respectively, as well as their corresponding luminescence decay curves in time. The lineshapes and widths of the bands around 1.55 and 1.0 μm are characteristic of Er^{3+} and Yb^{3+} in glass. The emission spectra of Er^{3+} in the co-doped samples 20ErzYb4 and 15ErzYb4 (with $z = 0.25, 1.0$ and 2.0 mol%) were also measured and found to be practically identical to those in Fig. 8. Although the spectral intensity scale is not calibrated and, thus, comparisons cannot be rigorously made, care was taken in the measurements of Er-doped samples to assure that the placement of samples and volume of excitation were practically the same. Based on this premise, it can be inferred that the decrease in intensity of the 1.5 μm emission, for samples doped with more than 3.0 mol% Er^{3+} , is related to concentration quenching effects (due to ion-ion non-radiative energy transfer mechanisms such as cross relaxation and energy migration followed by non-radiative decay). This assumption is validated by the faster decaying luminescence intensity curves, which, accordingly, yield progressively smaller lifetime values, as it will be later discussed. In the case of Yb^{3+} -doped samples, the re-absorption effect, characteristic of two level systems [17], and its dependence on dopant concentration is clearly perceived by comparison of the normalized spectra (Figure 13). With increasing concentration, there is an evident decrease in the intensity of the band's higher

energy component (980 nm) with respect to the broader component around 1010 nm, even for low-power excitation. Because it was not a concern of this work, no particular actions were taken to avoid reabsorption, and the measured samples had 1-2 mm thickness. However, it is known that the effect can be minimized by employing thinner samples (with smaller optical pathlength). The intensity decay curves for samples doped with 1.0, 3.0 and 5.0 mol% Yb^{3+} are very similar, as it would be expected, and will be later discussed.

Using the Ω_λ values presented in Table II, the transition probabilities and radiative lifetime values were calculated, as described elsewhere [15,46], and are presented in Table III. The data for Yb^{3+} were calculated from the emission spectra of lowly doped samples for which reabsorption is minimized[55]. When compared to other oxyfluoride glasses [9(a), 10(a)] the values of τ_{rad} in the present work are considerably larger despite the higher refractive index ($n = 1.537$, $\lambda = 546.07$ nm) of the studied hosts.

The representative upconversion spectra of the sample 20Er4, as a function of excitation power (100, 500 and 1000 W) at 976 nm, are presented in Figure 14. The excitation light was delivered through an optical fiber positioned at 5 mm distance from the sample. Via excited state absorption from the metastable levels $^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$ the characteristic emission bands of Er^{3+} in the green ($^2\text{H}_{11/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) and red ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$) are observed. As the excitation power increases, the intensity of the peak in 530 nm increases with respect to that of the peak at 555 nm. This well-known effect is thermal in nature, that is, with increasing excitation power the sample experiences heating and the emitting levels $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ are thermally coupled due to the small energy difference ($\Delta E \approx 680 \text{ cm}^{-1}$) between them [22]. This way, the upper level $^2\text{H}_{11/2}$, which otherwise would present low emission intensity due to highly probable nonradiative decay to $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$, is efficiently populated yielding intense emission. This result is also confirmed by the experiment in which the distance between the optical fiber and the sample is varied between 5 cm to 5 mm (Figure 15). In this case, when the optical fiber is at the closer distance the heating effect is more pronounced, and the intensity of $^2\text{H}_{11/2}$ emission increases. The emission spectrum of the “cold” sample (with excitation at 5 cm) resembles the spectrum obtained with direct excitation at 377 nm. Even though this wavelength corresponds to enough energy to populate the upper level $^2\text{H}_{11/2}$, the pronounced non-radiative decay of the latter results in lower intensity for its emission.

Table 3: Radiative properties (W_{rad} = total radiative transition rate, τ_{rad} = radiative lifetime value obtained from the J.O. formalism). Only the transitions of interest to this work are represented. Data of 20Yb and 15Yb were calculated as in Ref. [55].

Transition	λ (nm)	ν (cm ⁻¹)	W_{rad} (s ⁻¹)	τ_{rad} (ms)
$^4I_{13/2} \rightarrow ^4I_{15/2}$	1530	6536	82.77 (20Er)	12.0 (20Er)
			89.56 (15Er)	11.2 (15Er)
$^4F_{9/2} \rightarrow ^4I_{15/2}$	660	15152	988.9 (20Er)	1.01 (20Er)
			1117 (15Er)	0.90 (15Er)
$^4S_{3/2} \rightarrow ^4I_{15/2}$	545	18349	1051 (20Er)	0.95 (20Er)
			1137 (15Er)	0.88 (15Er)
$^2H_{11/2} \rightarrow ^4I_{15/2}$	524	19084	1718 (20Er)	0.58 (20Er)
			1131 (15Er)	0.88 (15Er)
$^2F_{7/2} \rightarrow ^2F_{5/2}$	1000	10000	767.1 (20Yb)	1.30 (20Yb)
			903.0 (15Yb)	1.11 (15Yb)

The lifetime values depicted in Table IV were determined from the decay curves in Figure 12 and Figure 13 as the time at which the intensity drops by a factor $1/e$. This procedure is often used to determine an “average” lifetime value for systems in which a large distribution of sites and a moderate contribution of non-radiative decay processes compromise the fit with exponential functions. Still, a comparison with the values obtained by single exponential fits shows a discrepancy in τ of less than 15%. The values are significantly longer than those reported in the literature for phosphate and fluorophosphate glasses. For instance, the lifetimes of the near-infrared state $^4I_{13/2}$ of Er^{3+} reported in the literature are 9.5 ms for the fluoride phosphate FP20, and 7.9 ms for the well-known Kigre QX phosphate glass [11]. Such values are lower or comparable to those measured for our samples. These results are nicely corroborated by the NMR and Raman findings that fluorine is preferentially bonded to the REs and alkaline metals, excluding OH^- species and lowering the local vibrational frequency, which minimizes non-radiative decays and turns out to be ideal for RE emission. As for concentration dependent ion-ion energy transfer, in the case of Er^{3+} -doped samples, the comparison of lifetime values allows more reliable conclusions than mere emission intensity measurements. Up to 4.0 mol% doping the lifetime variation is within a maximum of 20%, for both sets, whereas for the sample doped with 5.0 mol%, the lifetime is about half of the maximum value. This result is very promising because it means that fairly high concentrations of RE can be employed with still large enough fluorescence quantum efficiencies η , which vary in the range 85 to 43%. The lifetimes of ytterbium’s upper state $^2F_{7/2}$ in singly doped samples range from 1.7-1.5 ms, again higher than the values reported for several hosts in the literature measured at similar thicknesses and ionic concentrations [1,17]. The high lifetime values lead to apparent fluorescence quantum

efficiencies $\eta > 1$. Obviously, this has no physical meaning other than suggesting 100% efficiency, as it is indeed expected for a two-level system with minimized vibrational or energy transfer losses. Probably, the apparently long lifetimes are also a consequence of the reabsorption process, which constitutes an additional excitation mechanism of the $^2F_{7/2}$ emitting level. For the co-doped samples however, the lifetime values of Yb^{3+} decrease with increasing Er^{3+} concentration while, concomitantly, those of Er^{3+} increase. These results give clear evidence that Yb^{3+} to Er^{3+} energy transfer is active upon excitation at 980 nm. Still, because the lifetime value of the donor level $^2F_{7/2}$ is one order of magnitude smaller than that of the acceptor level $^4I_{11/2}$, the reverse $Er^{3+} \rightarrow Yb^{3+}$ transfer cannot be excluded. One way to investigate this assumption is to calculate the transfer rates in both directions, which will be presented in a future work.

Figure 14: Representative upconversion spectra of sample 20Er4. The 976 nm excitation beam was delivered by an optical fiber positioned 5 mm from the sample and varying the nominal laser power by 100, 500 and 1000 mW.

Figure 15: (a) Upconversion spectra ($\lambda_{exc} = 976$ nm) of the sample 20Er4 measured with the excitation optical fiber close to the sample (5 mm) and far from the sample (5 cm); (b) Emission spectrum of the same sample obtained with direct excitation at 377 nm.

Table 4: Excited state lifetime (τ_{exp}) and fluorescence quantum efficiency (η) values for singly-doped (Er^{3+} or Yb^{3+}) and co-doped samples of both compositional sets studied. To obtain η the radiative lifetime values of Er^{3+} $\tau_{rad} = 12.01$ ms for the 20Er set, and $\tau_{rad} = 11.16$ ms for 15Er, calculated from the J.O. theory, were used.

Singly-doped samples	RE = Er^{3+}		RE = Yb^{3+}	
	τ_{exp} (ms)	η (τ_{exp}/τ_{rad})	τ_{exp} (ms)	η (τ_{exp}/τ_{rad})
20RE0.25	9.14	0.76	-	-
20RE0.5	9.83	0.82	-	-
20RE1	9.02	0.75	1.70	1.31
20RE2	8.36	0.69	-	-
20RE3	7.63	0.64	1.69	1.3
20RE4	7.92	0.66	-	-
20RE5	5.18	0.43	1.58	1.2
15RE0.25	8.55	0.76	-	-
15RE0.5	7.76	0.69	-	-
15RE1	8.56	0.76	1.45	1.31
15RE2	9.13	0.82	-	-
15RE3	8.83	0.79	1.5	1.35

15RE4	8.14	0.73	-	-
15RE5	6.42	0.57	1.53	1.38
Co-doped samples				
20Er0.25Yb4	8.98	0.75	0.88	0.68
20Er1Yb4	9.02	0.75	0.9	0.69
20Er2Yb4	10.16	0.85	0.49	0.38
15Er0.25Yb4	8.18	0.73	0.9	0.81
15Er1Yb4	8.83	0.79	0.91	0.82
15Er2Yb4	9.22	0.83	0.48	0.43

IV. Conclusions

New fluorophosphate glasses singly- and co-doped with Er^{3+} and Yb^{3+} were obtained with excellent optical and spectroscopic properties such as long lifetimes and high fluorescence quantum efficiencies. Detailed structural investigation through Raman and NMR show that the improvements with respect to other phosphate and fluorphosphate compositions are related to the local coordination of the rare-earth ions with fluoride rather than phosphate species. The NMR results give clear evidence for the preferential association of phosphate species with the aluminum atoms in the glass inventory. Thus, we may also conclude that the local coordination of the alkaline-earth and the rare-earth ions is dominated by fluoride ions, which corresponds exactly to the desired effect. The presence of fluorine in the first coordination sphere of the REs means exclusion of OH^- species, which can cause severe non-radiative depopulation of excited states. A more rigorous quantification of bonding preferences would be available on the basis of $^{31}\text{P}\{^{27}\text{Al}\}$ rotational echo adiabatic passage double resonance (REAPDOR) and/or $^{89}\text{Y}\{^{31}\text{P}\}$ or $^{89}\text{Y}\{^{19}\text{F}\}$ REDOR experiments. Such experiments are currently under consideration in our laboratory. For the co-doped samples, there is clear evidence of the well-known energy transfer from Yb^{3+} to Er^{3+} however, the back transfer cannot be excluded and is under current investigation for a future work.

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Article 2: Network Structure and Rare-earth Ion Local Environments in Fluoride Phosphate Photonic Glasses Studied by Solid State NMR and EPR Spectroscopies

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Network Structure and Rare-Earth Ion Local Environments in Fluoride Phosphate Photonic Glasses Studied by Solid-State NMR and Electron Paramagnetic Resonance Spectroscopies

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Supporting Information

ABSTRACT: A detailed structural investigation of a series of fluoride phosphate laser glasses with nominal composition $25\text{BaF}_2\text{--}25\text{SrF}_2\text{--}(30-x)\text{Al}(\text{PO}_3)_3\text{--}x\text{AlF}_3\text{--}(20-z)\text{YF}_3\text{:zREF}_3$ with $x = 25, 20, 15$ and 10 , $\text{RE} = \text{Yb}$ and Eu , and $0 \leq z \leq 1.0$ has been conducted using Raman, solid-state nuclear magnetic resonance (NMR), and electron paramagnetic resonance (EPR) spectroscopies. The network structure is dominated by the preferred formation of aluminum-to-phosphorus linkages, which have been quantified by means of $^{27}\text{Al}/^{31}\text{P}$ NMR double-resonance techniques. The fluoride ions are found in mixed $\text{Al}/\text{Y}/\text{Ba}/\text{Sr}$ environments accommodating the luminescent dopant species as well. The local environments of the rare-earth species have been studied by pulsed EPR spectroscopy of the Yb^{3+} spin probe ($S = 1/2$), revealing composition-dependent echo-detected lineshapes and strong hyperfine coupling with ^{19}F nuclei in hyperfine sublevel correlation (HYSCORE) spectra consistent with the formation of $\text{Yb}^{3+}\text{--F}$ bonds. In addition, photoluminescence spectra of Eu^{3+} -doped samples reveal that the $^5\text{D}_0 \rightarrow ^7\text{F}_2/^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions intensity ratio, the normalized phonon sideband intensities in the excitation spectra, and excited state $^5\text{D}_0$ lifetime values are systematically dependent on fluoride content. Altogether, these results indicate that the rare-earth ions are found in a mixed fluoride/phosphate environment, to which the fluoride ions make the dominant contribution. Nevertheless, even at the highest fluoride levels ($x = 25$), the data suggest residual rare-earth–phosphate coordination.

A detailed structural investigation of a series of fluoride phosphate laser glasses with nominal composition $25\text{BaF}_2\text{--}25\text{SrF}_2\text{--}(30-x)\text{Al}(\text{PO}_3)_3\text{--}x\text{AlF}_3\text{--}(20-z)\text{YF}_3\text{:zREF}_3$ with $x = 25, 20, 15$ and 10 , $\text{RE} = \text{Yb}$ and Eu and $0 \leq z \leq 1.0$ has been conducted, using Raman, solid-state nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) spectroscopies. The network structure is dominated by the preferred formation of aluminum-to-phosphorus

linkages, which have been quantified by means of $^{27}\text{Al}/^{31}\text{P}$ NMR double resonance techniques. The fluoride ions are found in mixed Al/Y/Ba/Sr environments accommodating the luminescent dopant species as well. The local environments of the rare-earth species have been studied by pulsed EPR spectroscopy of the Yb^{3+} spin probe ($S=1/2$), revealing composition dependent echo-detected lineshapes, and strong hyperfine coupling with ^{19}F nuclei in hyperfine sublevel correlation (HYSCORE) spectra consistent with the formation of $\text{Yb}^{3+}\text{-F}$ bonds. In addition, photoluminescence spectra of Eu^{3+} -doped samples reveal that the $^7\text{F}_2 \rightarrow ^5\text{D}_0 / ^7\text{F}_1 \rightarrow ^5\text{D}_0$ transition intensity ratio, the normalized phonon sideband intensities in the excitation spectra as well as excited state lifetimes are systematically dependent on fluoride content. Altogether, these results indicate that the rare-earth ions are found in a mixed fluoride/phosphate environment, to which the fluoride ions make the dominant contribution. Nevertheless, even at the highest fluoride levels ($x = 25$) the data suggest residual rare-earth-phosphate coordination.

I. INTRODUCTION

Rare earth (RE) ion doped glasses and transparent ceramics remain at the focus of much current attention for the development of improved solid state lasers and other optical devices. Efficient dispersal of the luminescent species can be accomplished by a wide variety of glassy matrices, including phosphates, chalcogenides and fluorides [1-3]. Each of these matrices presents its characteristic advantages and disadvantages. Chalcogenide glasses, with low phonon energy, produce high absorption and emission cross sections, excellent quantum yields and long excited state lifetimes, but suffer from the drawbacks of poor atmospheric, thermal and mechanical stability, and laborious procedures for obtaining materials of sufficient purity. Oxide-based glasses are easier to manufacture and present higher mechanical stabilities, however, quantum yields and excited state lifetimes are generally lower owing to effective excited state deactivation via multiphonon relaxation. Fluoride glasses also present excellent photophysical characteristics [4], but generally suffer from low mechanical stabilities and difficulties in fiber drawing. Regarding these apparently conflicting materials requirements, it is important to realize that they involve different length scales. While the photophysical properties are dominated by the local environments (nearest neighbour coordinations) of the luminescent rare-earth ions, the mechanical properties are controlled by structural features on a much longer distance scale. Based on this realization, it appears possible to combine, in an ideal way, the low-phonon energy characteristic of a fluoride coordination environment with

the high mechanical strength and chemical stability of oxide-based frameworks, by designing oxyfluoride-based host materials. This design principle has been successfully demonstrated in a number of high-performance glass-ceramics generated from PbF_2 /aluminosilicate glasses [5] or LaF_3 /alumino-silicate-based systems [6], doped with rare-earth ions, which substitute in the PbF_2 and LaF_3 lattices of the crystallized component. For the development of high-power lasers, however, higher dopant ion concentrations are required, while still maintaining homogenous ionic dispersion to prevent concentration quenching effects. For this reason, the search for new RE-doped glasses is still at the focus of much current attention, not only as laser active media but also as constituents of several other optical devices such as amplifiers, detectors, waveguides and sensors.

Fluoroaluminophosphate glasses play an important role in this endeavor and numerous promising RE-doped compositions have been developed, characterized with regard to their local structures and photophysical properties, and functionally tested [7-17]. Nevertheless, the local bonding preferences of the emitting rare earth ions in these glasses are still uncertain. As some of the transitions of Eu^{3+} are particularly sensitive to the ligand environment, detailed spectroscopic studies of Eu-doped glasses have been carried out with systematic compositional variation [18-21]. Qualitative insights have also come from phonon sideband intensities [21,22] and Mössbauer spectra [22], whereas the method of electron spin resonance utilizing rare-earth spin probes has been greatly under-utilized in this field [23]. Unfortunately, rare-earth ion environments cannot be studied directly by standard solid-state NMR methods, as their $4f^n$ -paramagnetism broadens their NMR signals beyond detectability. It is, however, possible to record NMR spectra of the nuclei close to the paramagnetic dopants, using pulsed electron paramagnetic resonance (EPR) techniques. The effect arises as a consequence of non-secular electron–nuclear spin interactions and manifests itself by a modulation of the electron spin echo intensity when recorded as a function of evolution time [24]. In the weak coupling limit (where the nuclear-electron hyperfine coupling constant is zero or negligible), the modulation frequency is given by the Zeeman frequencies of those nuclei that exhibit magnetic dipole-dipole interactions with the electron spins [24]. Stronger couplings manifest themselves in more complicated spectra that can frequently be disentangled by a two-dimensional pulsed EPR technique called hyperfine sublevel correlation spectroscopy (2D-HYSCORE) [25-28]. While some qualitative studies on crystalline and glassy laser host materials have shown the general feasibility of this approach [29-33], no work on rare-earth doped fluoride phosphate glasses has been reported so far, to the best of our knowledge.

In the present work we will apply these magnetic resonance techniques for the characterization of a new promising series of rare-earth doped fluoroaluminophosphate glasses in the system $\text{BaF}_2\text{-SrF}_2\text{-Al(PO}_3)_3\text{-AlF}_3\text{-YF}_3$ [15-34]. The AlF_3 to $\text{Al(PO}_3)_3$ molar ratios are systematically varied to examine the effect of the anion (fluoride versus phosphate) inventory on the framework structure and the rare-earth ion local environments. The question of interest is whether, and to what extent, the proposed synergy of fluoride phosphate glasses is indeed realized, i.e. how dominant the Al-O-P linkages in the framework are and whether there is any desired preferential ligation of the rare-earth ion by fluoride species. Advanced solid state NMR techniques will be used to examine the details of the short- and medium-range order in the framework, while information about the local environments of the rare-earth dopants will be sought by applying pulsed EPR, ESEEM and HYSCORE techniques to Yb^{3+} doped samples. The results will be correlated with the photophysical properties of glasses doped with variable levels of Eu^{3+} emitters.

II. EXPERIMENTAL SECTION

(1) Sample Preparation and Characterization.

Glasses with nominal composition $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-(}30\text{-x)Al(PO}_3)_3\text{-xAlF}_3\text{-(}20\text{-z)YF}_3\text{:zREF}_3$ with $x = 25, 20, 15$ and 10 , $\text{RE} = \text{Yb}$ and Eu and $z = 0, 0.20$ or 0.25 , and 1.0 mol% were prepared by conventional melt quenching techniques in Pt crucibles. Homogeneous mixtures of reagent grade precursors were melted at 1100°C for 5 min, quenched between copper plates and heat treated for 8 h at 400°C . Differential scanning calorimetry was done on $20\text{-}50$ mg samples on a NETZSCH DSC-204 instrument, using a heating rate of 10°C/min . Glass transition temperatures are reported as onset temperatures of the apparent heat capacity changes. Quantitative fluoride contents were determined by a ^{19}F single-pulse solid state NMR procedure, using a known quantity of NaF as an internal quantification standard. Table 5 summarizes the glass compositions, glass transition temperatures and the fraction of fluoride retained in the glass. Raman scattering measurements were performed at room temperature using a Jobin-Yvon T64000 triple monochromator with a CCD detector. The 514.5 nm exciting light from an argon laser was focused on the samples by an optical microscope using a long work distance 50X objective.

(2) Solid State NMR.

Solid state ^{31}P and ^{27}Al NMR studies were carried out on a Bruker Avance III spectrometer operating at 400 MHz, equipped with a 4 mm probe which was operated at spinning speeds up to 14.0 kHz. ^{19}F MAS-NMR spectra were recorded at 188.345 MHz in a 2.5 mm rotor spinning near 30.0 kHz on a Bruker DSX 500 console interfaced with a 4.65 T magnet, using 90° pulses of 3.35 μs length and relaxation delays of 20 s (one pulse) or 2150 s (for quantification studies with NaF standard included). Chemical shifts are reported relative to CFCl_3 using solid AlF_3 as a secondary reference (-172 ppm). ^{27}Al MAS-NMR spectra were recorded using short pulses of 1 μs length and a relaxation delay of 10 s. ^{27}Al triple-quantum (TQMAS) NMR data were obtained using the three-pulse z-filtering sequence,³⁵ using hard excitation and reconversion pulses of 5 μs and 2 μs length and soft detection pulses of 10 μs length. Chemical shifts are reported relative to a 1M $\text{Al}(\text{NO}_3)_3$ aqueous solution. ^{31}P MAS-NMR spectra were recorded using 90° pulses of 3.0 μs length and a relaxation delay of 150 s. In addition, double-quantum (DQ) filtered spectra were measured using the 1-D refocused INADEQATE sequence [36]. This experiment results in the selective detection of only those ^{31}P nuclei that are involved in a P-O-P linkage ($\text{Q}^{(1)}$ and $\text{Q}^{(2)}$ units) and therefore give rise to the excitation of a double quantum coherence through indirect ^{31}P - ^{31}P spin-spin coupling. In contrast, the signals of isolated $\text{Q}^{(0)}$ units are suppressed by this pulse sequence. Experimental conditions were: spinning speed 12.0 kHz, $\pi/2$ pulse length 2.6 μs , relaxation delay 150 s. The mixing time for DQ coherence creation was 16.6 ms, corresponding to a value of the indirect spin-spin coupling constant $^2J(^{31}\text{P}\text{-}^{31}\text{P})$ of 30 Hz. Chemical shifts were referenced against an external 85% H_3PO_4 standard. $^{27}\text{Al}\{^{31}\text{P}\}$ rotational echo double resonance (REDOR) [37] measurements were conducted under the same conditions, using π recoupling pulses on the ^{31}P channel and acquisition of rotor-synchronized ^{27}Al spin echoes (the π pulse length was 6 μs in these experiments). Data were acquired using the compensation method [38]. The second moment of the ^{27}Al - ^{31}P dipolar interaction ($M_{2\text{AlP}}$) was obtained by applying a parabolic fit to the data within the range $\Delta S/S_0 < 0.2$, according to the expression [39]

$$\frac{\Delta S}{S_0} = \frac{4}{3\pi^2} (NT_R)^2 M_{2\text{AlP}}. \quad (1)$$

The experiments were performed at MAS frequencies of 12.0 and 14.0 kHz, in order to have a considerable number of data points for short dephasing times. From the obtained $M_2(^{27}\text{Al}\{^{31}\text{P}\})$ an average number of Al-O-P linkages can be estimated. $^{31}\text{P}\{^{27}\text{Al}\}$ rotational echo adiabatic passage (REAPDOR) [40,41] experiments were performed using a typical value for ^{31}P π -pulse duration of 5.8 μs and a spinning frequency of 12.0 kHz. A recycle delay of 120 s was applied in combination with a pre-saturation train of 10 $\pi/2$ pulses. In order to get quantitative information, the $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR dephasing curves were simulated using the SIMPSON package [42], based on the actual experimental values of the parameters used in the pulse sequence and the quadrupolar coupling constants deduced from the ^{27}Al TQMAS experiments. The dipolar coupling was calculated based on the same internuclear distance (327 pm) as found in crystalline $\text{Al}(\text{PO}_3)_3$ and both ^{31}P - ^{27}Al two- and $^{31}\text{P}(^{27}\text{Al})_2$ three-spin systems (pseudo-tetrahedral geometry) were calculated. For all the nuclei detected, spin-lattice relaxation times were measured using the saturation recovery sequence. Lineshape analysis and deconvolutions were done using the DMFIT routine [43].

(3) Solid State EPR.

Pulsed solid-state EPR experiments were carried out on the Yb-doped ($z = 0.2$) glass samples at 6.5 K on an E-580 BRUKER ELEXIS X-band EPR spectrometer. Owing to very fast spin-spin relaxation no electron spin echo was observable at temperatures above 12 K. Electron spin echo envelope modulation (ESEEM) spectra were obtained at external field strengths of 550 and 700 mT using the three-pulse sequence $(t_p) - \tau - (t_p) - T - (t_p) - \text{echo}$ [24,44], with a $\pi/2$ pulse $t_p = 8$ ns. The delay between first and second pulse, τ , was set to 140 ns (different τ values were tested to examine the possible occurrence of blind spots). The time interval T was incremented in 12-ns steps starting with $T = 300$ ns; 300 acquisitions were accumulated for each increment with repetition times of 300 μs and up to 20 scans were added up for signal averaging. A four step phase cycling of the first and second pulse was used for echo detection to avoid unwanted primary echoes and FID distortions [24]. The resulting data were processed in the following way: the modulated echo decay was fitted to a biexponential function, which in turn is subtracted from the experimental data in order to isolate the oscillatory component. Following further apodization and zero-filling, the oscillating signal was Fourier-transformed, resulting in the ESEEM spectrum. The echo detected absorption spectra were recorded using the three-pulse sequence. The integrated echo intensities were measured as a

function of the magnetic field strength over a range of 10 – 1200 mT. The pulse spacing between the first two pulses (π) was set to 100 ns, and the time between the second and the third pulse (T) was 10 μ s in order to suppress nuclear frequency modulation effects. HYSCORE experiments were conducted at external magnetic field strengths of 450, 550, and 700 mT using the four-pulse sequence $(t_p) - \tau - (t_p) - t_1 - (2t_p) - t_2 - (t_p) - echo$ [24], with $\tau = 140$ ns. The echo intensity was measured as a function of t_1 and t_2 , where t_1 and t_2 were incremented in steps of 16 ns from the initial values of 300 ns. Pulses of $t_p = 8$ ns for the $\pi/2$ pulse and $2t_p = 16$ ns for the π pulse were used to record a 160×160 matrix. Following further apodization and zero-filling (to 256×256 points), the oscillating signal was Fourier-transformed in both dimensions, resulting in the HYSCORE spectrum. A 4-step phase cycle was used to eliminate unwanted echoes.

Solid state HYSCORE data were simulated by the function “saffron” of the software package EasySpin® implemented in MATLAB (MathWorks, Inc) [45]. The simulations consider the static spin Hamiltonian for electron-nucleus spin pairs in the solid state, given by

$$\mathcal{H} = \beta_e \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \sum_j g_{nj} \beta_n \mathbf{H} \cdot \mathbf{I}_j + \sum_j \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}_j, \quad (2)$$

where the summations are over the nuclear species considered in the simulation, the first two terms are the electronic and nuclear Zeeman interactions, respectively, where $\mathbf{g}$ is a symmetric tensor that can be represented by six independent components, for example, its principal values, g_{xx} , g_{yy} and g_{zz} , and three Euler angles describing the orientation of its principal axes relative to a molecular coordinate system. In the case of glassy systems we expect a distribution of Euler angles and principal values for $\mathbf{g}$. Owing to lacking orientational information (which would only be available from single-crystal studies) in this work a simplified approach was taken to the simulations: all angles were considered zero (coincident $\mathbf{g}$ and molecular frame orientations), and strains were used in the $\mathbf{g}$ -parameter to represent the disorder found in glasses. The third term represents the electron-nucleus hyperfine coupling interaction. In this work axial symmetry was considered for the hyperfine tensors $\mathbf{A}$, which can be described by the principal values $A_{\perp}$, $A_{\parallel}$, with $A_{iso} = (2 A_{\perp} + A_{\parallel})/3$. The $\mathbf{A}$ - and $\mathbf{g}$ - principal axis systems were considered coincident, due to lack of theoretical and/or experimental evidence of their relative orientation.

(4) Photophysical Characterization.

UV-VIS-NIR absorption spectra of optically polished samples were measured in a Perkin-Elmer spectrophotometer model Lambda 1050. Infrared and visible excitation, emission, and excited state lifetime measurements, on Eu-doped samples were carried out in a Horiba Fluorolog spectrofluorimeter, equipped with CW and pulsed Xe lamps, as well as Delta Diodes as excitation sources. The signals were collected by a photodiode detector model PPD-850 in the visible and by a Hamamatsu photomultiplier in the infrared. The spectra were corrected by the lamp profile and detector response.

III. RESULTS AND DISCUSSION

(1) Glass Preparation and Analysis.

Table 5 summarizes the glass compositions, experimentally determined mass losses, and fluoride contents (in wt.%) as determined via the NMR procedure outlined above. Note that, even though weight losses were found to be minimal, in glasses with $x = 15, 20$, and 25 the fluoride content seems to be systematically depleted. This apparently contradictory result may arise from some fluoride/oxide exchange in the furnace atmosphere. For glasses with $x = 10$, the fluoride content was found higher than batched. This effect may be attributed to some P_2O_5 volatilization. At this phosphate-rich composition, no Eu-doped glasses could be prepared. Glass transition temperatures show a maximum value at $x=15$ and tend to decrease towards higher fluoride contents.

Table 5: Compositions, glass transition temperatures, mass losses, and % fluoride retained in the glasses under study.

x	Composition, mole %					T_g / K	Δm , %	wt.% F	
	$Al(PO_3)_3$	AlF_3	BaF_2	SrF_2	YF_3			calc.	exp.
10	20	10	25	25	20	758	Not det.	21.8	25.1
15	15	15	25	25	20	795	1.1%	24.9	19.2
20	10	20	25	25	20	754	0.7%	28.3	25.7
25	05	25	25	25	20	726	0.6%	32.2	30.0

(2) Raman Spectroscopy.

Figure 16 shows the Raman spectra of these glasses. The relevant features include strong bands near 1085 cm^{-1} and 990 cm^{-1} , which are assigned to the symmetric stretching modes of the PO_3 and PO_4 units, respectively, of $\text{Q}^{(1)}$ and $\text{Q}^{(0)}$ phosphate tetrahedral [46]. In addition, a broad shoulder appears near 1130 cm^{-1} suggesting the presence of $\text{Q}^{(2)}$ units as well. The spectra show no evidence for P-F linkages which would be expected to exhibit a band near 900 cm^{-1} . The band observed at 750 cm^{-1} can be attributed to the P-O-P stretching mode involving the bridging oxygen species of $\text{Q}^{(1)}$ and (to a minor extent) some $\text{Q}^{(2)}$ species. Altogether the spectra show little compositional dependence, indicating that the framework structure of these glasses remains constant throughout the compositional series.

Figure 16: Raman spectra of $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-(}30\text{-x)Al(PO}_3\text{)}_3\text{-xAlF}_3\text{-}20\text{YF}_3$ glasses.

(3) ^{19}F MAS-NMR.

Figure 17: ^{19}F MAS-NMR spectra of $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-(}30\text{-x)Al(PO}_3\text{)}_3\text{-xAlF}_3\text{-}20\text{YF}_3$ glasses. Spinning sidebands are indicated by asterisks. shows the ^{19}F MAS-NMR spectra for the entire set of compositions. Two principal resonances are observed near -50 ± 2 and -122 ± 3 ppm in an approximate ratio of 1:3, independent of composition. The dominant signal near -122 ppm is assigned to fluorine atoms in a mixed alkaline earth/aluminum environment, as found in various Al-containing fluoride phosphate [47-49], or fluoride glasses [50], as well as in corresponding crystalline model compounds [51,52]. The signal near -50 ppm is assigned to fluorine atoms

bound to yttrium atoms, based on the observation that the chemical shift of the two crystallographic sites in YF_3 are found at -57 and -68 ppm [53]. No clear evidence is observed for P-bonded fluorine atoms, whose resonance signal would be expected near -75 ppm [54,55]. As documented by previously published $^{19}\text{F}\{^{31}\text{P}\}$ REDOR experiments on the $x = 20$ sample [34], no rapidly decaying signal owing to P-bonded F-atoms could be observed. Based on this result, we conclude that these species do not make a significant contribution to the glass structure.

Figure 17: ^{19}F MAS-NMR spectra of $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-(}30\text{-}x\text{)Al(PO}_3\text{)}_3\text{-}x\text{AlF}_3\text{-}20\text{YF}_3$ glasses. Spinning sidebands are indicated by asterisks.

Table 6: ^{19}F NMR spectral deconvolution of $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-(}30\text{-}x\text{)Al(PO}_3\text{)}_3\text{-}x\text{AlF}_3\text{-}20\text{YF}_3$ glasses

x	$\delta\text{-}^{19}\text{F}$ (± 0.5 ppm)	line width (± 0.5 ppm)	Area (± 0.5 %)	$\delta\text{-}^{19}\text{F}$ (± 0.5 ppm)	line width (± 0.5 ppm)	Area (± 0.5 %)
10	-122.2	39.8	71.5	-49.3	53.8	28.5
15	-119.6	41.0	73.9	-47.80	53.7	26.1
20	-122.0	40.2	68.8	-49.6	57.2	31.2
25	-125.1	36.9	67.3	-51.7	52.6	32.7

(4) ^{31}P -MAS NMR.

Figure 18a shows results from single pulse ^{31}P MAS NMR experiments for the set of samples investigated. In agreement with data reported in the literature in related fluoride phosphate glasses [47-49, 54-57], the spectra exhibit a broad asymmetric lineshape, indicating multiple contributions. As unconstrained fitting would appear rather arbitrary deconvolution constraints were developed using DQ filtered spectra (Figure 18b) obtained with the refocused INADEQUATE technique. In all the spectra in Figure 18b two distinct components can be observed, with positions varying from -12.5 to -13.5 ppm for the first one, and from -22.2 to -23.6 ppm for the second one (see Table 7). These components can be assigned to $\text{Q}^{(1)}$ and $\text{Q}^{(2)}$ units, respectively, which are linked to aluminum atoms. Comparison with the standard MAS-NMR spectra (Figure 18a) reveals the presence of a third component with position varying from -6.0 to -7.3 ppm, which is suppressed by the DQ filter. This resonance must then be assigned to $\text{Q}^{(0)}$ species linked to aluminum. Based on the final fit of the single-pulse spectra the intensity ratio for the three components ($\text{Q}^{(0)}$, $\text{Q}^{(1)}$ and $\text{Q}^{(2)}$) can be obtained, as shown in Table 7. As previously discussed for the $x = 20$ sample [34], the ^{31}P MAS NMR spectra indicate that the $\text{Q}^{(2)}$ species present in pure $\text{Al}(\text{PO}_3)_3$ glass is dominantly converted into $\text{Q}^{(1)}$ and $\text{Q}^{(0)}$ species by the reaction with AlF_3 and the Ba/Sr difluorides in the melt. Part of this effect may also be related to fluoride losses caused by partial fluoride/oxide ion exchange during the melting and quenching process. The oxide ions produced in this fashion are highly basic and are known to depolymerize P-O-P linkages in alkali, alkaline earth and aluminum phosphate glasses.

Figure 18: Experimental ^{31}P MAS NMR spectra obtained by single pulse (a) and refocused INADEQUATE (b) techniques for the glasses under study. Red curves denote the de-convolutions into individual Gaussian components (blue curves). Black curves denote experimental data.

Table 7: ^{31}P isotropic chemical shifts and relative areas of the individual $Q(n)$ phosphate species, determined from the deconvolution of the single pulse ^{31}P MAS-NMR spectra of Figure 16Figure 1, and ^{27}Al isotropic chemical shift $\delta_{\text{iso}}^{\text{CS}}$ and second-order quadrupolar effects SOQE determined from TQMAS experiments.

x	$Q^{(0)}$		$Q^{(1)}$		$Q^{(2)}$		$C_Q(^{27}\text{Al})$ (± 0.2 MHz)	$\delta_{\text{iso}}^{\text{CS}}(^{27}\text{Al})$ (± 0.5 ppm)
	δ_{iso} (± 0.2 ppm)	Area (± 0.5 %)	δ_{iso} (± 0.1 ppm)	Area (± 0.5 %)	δ_{iso} (± 0.4 ppm)	Area (± 0.5 %)		
10	-7.3	42.8	-13.5	55.0	-26.3	2.2	3.9	-4.7
15	-6.6	62.3	-13.4	36.2	-25.3	1.6	3.8	-3.4
20	-6.7	57.8	-13.4	38.2	-23.4	4.0	4.0	-3.1
25	-6.0	59.0	-12.5	37.6	-22.2	3.4	3.9	-3.0

(5) ^{27}Al -MAS NMR.

Figure 19a shows results from ^{27}Al MAS-NMR. A dominant resonance in the region of six-coordinated aluminum is observed for all the samples. The resonance position is influenced by both the isotropic chemical shift ($\delta_{\text{iso}}^{\text{CS}}$) and the second-order quadrupolar shift. Both contributions can be separated via triple-quantum MAS-NMR (TQMAS), using established data analysis procedures (data available as supplementary material) [58]. Table 3 details the

isotropic chemical shifts and the quadrupolar coupling constants (C_Q) obtained from this procedure. The C_Q values were obtained from the second order quadrupolar effect $SOQE = C_Q \times (1 + \eta^2/3)^{1/2}$, assuming an average value of 0.5 for the asymmetry parameter η . It is well-known that the ^{27}Al chemical shifts are quite sensitive to both the aluminum coordination number and the nature of the ligands to which these alumina coordination polyhedra are linked. For example in a series of fluoride phosphate glasses prepared by sol-gel chemistry the ^{27}Al chemical shift decreases with increasing phosphate ligation at aluminum [57]. For the sample with $x = 10$ the $\delta_{\text{iso}}^{\text{cs}}$ value suggests that the coordination sphere of aluminum contains a mix of ^{31}P and ^{19}F species. For increasing x the ^{27}Al isotropic chemical shift values tend to increase, indicating an increasingly strong interaction with ^{19}F nuclei (see *Figure 19b*). This behavior is consistent with our ^{27}Al - ^{31}P double NMR results discussed in the following section.

Figure 19: (a) ^{27}Al MAS NMR spectra for undoped 25BaF_2 - 25SrF_2 -($30-x$) $\text{Al}(\text{PO}_3)_3$ - $x\text{AlF}_3$ - 20YF_3 glasses. (b) ^{27}Al isotropic chemical shifts, obtained from the TQMAS experiments, as a function of the AlF_3 content (x).

(6) $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR and $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR.

The question to which extent fluoride and phosphate species contribute to the first coordination sphere was addressed by $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR studies.

Figure 20 shows results for the set of samples, and for the crystalline reference compound $\text{Al}(\text{PO}_3)_3$. Dipolar second moments were obtained from parabolic analyses of the initial decay regime [38,39] (see Table 8). Considering that in crystalline aluminum metaphosphate the second coordination sphere of Al is made up by six P atoms at a distance of 3.2 Å, and assuming that in glasses the same second-nearest neighbor distance is applicable,

the average number of P atoms (N_P) in the Al coordination environment can be deduced from the ratio $M_2(\text{glass})/M_2(\text{AlPO}_3)_3$, as shown in Table 8. Since the large majority of the Al atoms are six-coordinated, the average number of F atoms (N_F) neighboring Al can be estimated ($N_F=6-N_P$). From these values the N_P/N_F ratio can be experimentally determined for the first coordination sphere of aluminum; the values are shown in Table 8.

Figure 21 shows $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR dephasing curves (squares) for the studied set of samples. The solid curves correspond to SIMPSON simulations considering two different spin systems. The blue curves represent simulations for a three spin-system involving one ^{31}P and two neighboring ^{27}Al nuclei, assuming the P-Al average distance observed in the $\text{Al}(\text{PO}_3)_3$ crystal (3.27 Å) and an Al-P-Al angle of 109.4° , which is based on the O-P-O angle in the phosphorus tetrahedron, assuming linear P-O-Al linkages. The red curves represent simulations for a two-spin system involving one ^{31}P and one neighboring ^{27}Al nucleus, assuming the same P-Al average distance of 3.27 Å as in the three-spin simulation.

Figure 20: $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR dephasing curves of undoped $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-(}30\text{-x)Al(PO}_3)_3\text{-xAlF}_3\text{-}20\text{YF}_3$ glasses and for an $\text{Al(PO}_3)_3$ crystalline sample. Triangles and squares represent experimental points obtained under MAS spinning speed of 14.0 kHz and 12.0 kHz, respectively. Solid curves are parabolic fits to the data, analyzed within the data range $\Delta S/S_0 < 0.2$ (for the compound $\text{Al(PO}_3)_3$ a SIMPSON simulation considering a two spin system is shown).

Figure 21: $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR dephasing curves of undoped $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-(}30\text{-x)Al(PO}_3)_3\text{-xAlF}_3\text{-}20\text{YF}_3$ glasses. (a) $x = 10$; (b) $x = 15$; (c) $x = 20$; (d) $x = 25$. Solid curves represent SIMPSON simulations of the REAPDOR curves for ^{31}P interacting with one (red curves) or two (blue curves) ^{27}Al neighbors at a distance of $3.27 \text{ \AA}$. For the simulations ^{27}Al CQ values were taken from TQMAS results. Dashed lines are combinations of both simulated curves (for one or two ^{27}Al neighbors) considering 50% of each contribution.

The value of C_Q used in this calculation is identical with the one measured with ^{27}Al TQMAS, shown in Table 7. The dashed curves in Figure 21 correspond to weighted superpositions of the simulated curves for one and two Al atoms in the P coordination environment, with 50% of contribution from each one. The good agreement with the experimental data indicates that the average number of P-O-Al bonds per phosphate unit is 1.5 ± 0.2 , and this number is practically independent of the sample composition.

Table 8 shows the total numbers of P-O-Al linkages, obtained either by multiplying the average number of P connected to Al (from REDOR experiments) by the Al content of the glass (30 mol %), or by multiplying the average number of Al connected to P (from REAPDOR experiments) by the P content ($3 \times [30-x]$ mol %). Except for the sample with $x=10$, these values, obtained via two independent experiments, are in excellent agreement with each other, thereby validating the above analysis. Table 8 also shows the theoretical N_P/N_F ratio expected for a glass consisting only of $\text{Al(PO}_3)_3$ and AlF_3 in a $(30-x):x$ ratio. In this case we would have a structure based on polymeric $Q^{(2)}$ units cross-linked by Al atoms, which are octahedrally coordinated by a mix of phosphate and fluoride ions in a $(30-x):x$ ratio. The components SrF_2 , BaF_2 and YF_3 may be considered as network modifiers, which might act to depolymerize the

glass structure by breaking either P-O-P or P-O-Al linkages. As neither the ^{19}F MAS NMR, the Raman spectra nor the (previously reported) $^{19}\text{F}\{^{31}\text{P}\}$ REDOR data show any evidence of P-F bonding [34], we can conclude that no significant breakage of P-O-P linkages by these fluoride modifier species occurs. Glass network depolymerization by BaF_2 , SrF_2 or YF_3 might also arise from the breakage of Al-O-P linkages, and would result in $N_{\text{P}}/N_{\text{F}}$ ratios in the first coordination sphere of Al that are lower than those predicted from the $\text{Al}(\text{PO}_3)_3/\text{AlF}_3$ ratios alone. This is indeed observed to some minor extent in the $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR experiments for the samples with $x = 15, 20$ and 25 , whereas for the sample with $x = 10$ the experimental $N_{\text{P}}/N_{\text{F}}$ ratio is somewhat higher than that predicted by the $\text{Al}(\text{PO}_3)_3/\text{AlF}_3$ ratio. Overall, Table 8 indicates, however, that the experimental $N_{\text{P}}/N_{\text{F}}$ ratio in the Al coordination environment is significantly higher than the statistically expected $N_{\text{P}}/N_{\text{F}}$ ratios (considering all species in the glass formula) for the whole set of samples. This result indicates that there is no randomization of fluoride/phosphate anions in the glass structure, but that the aluminum species preferentially associate with phosphate anions. This result confirms that the framework is still dominated by P-O-Al (and some P-O-P) linkages. It implies further that the local environment of the alkaline earth and yttrium species would be dominated by fluoride ions (see below). We conclude that a sizeable fraction of these fluoride ions are not acting as classical network modifier species in these glasses but are present in the form of domains rich in Sr^{2+} , Ba^{2+} and Y^{3+} , as well as some Al^{3+} .

Table 8: Values of second moment $M_{2\text{AlP}}$ obtained from $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR experiments and connectivity data on undoped $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-(}30\text{-}x\text{)Al}(\text{PO}_3)_3\text{-}x\text{AlF}_3\text{-}20\text{YF}_3$ glasses. N_{P} and $(N_{\text{P}}/N_{\text{F}})_{\text{exp}}$ are respectively the number of P atoms and the fraction of P to F atoms in the Al coordination environment, obtained experimentally from REDOR results. $(N_{\text{P}}/N_{\text{F}})_{\text{AlPF}}$ is the P/F fraction considering only the fluoride atoms connected to aluminum in the nominal composition. $(N_{\text{P}}/N_{\text{F}})_{\text{Stat}}$ is the statistically expected P/F ratio. $N_{\text{P-O-Al}}^{\text{REDOR}}$ and $N_{\text{P-O-Al}}^{\text{REAPDOR}}$ are the total number of P-O-Al linkages obtained from the $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR and $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR experiments respectively.

X	$M_{2\text{AlP}}$ ($10^6 \text{ rad}^2 \text{ s}^{-2}$)	N_{P}	$(N_{\text{P}}/N_{\text{F}})_{\text{exp}}$	$(N_{\text{P}}/N_{\text{F}})_{\text{AlPF}}$	$(N_{\text{P}}/N_{\text{F}})_{\text{Stat}}$	$N_{\text{P-O-Al}}^{\text{REDOR}}$	$N_{\text{P-O-Al}}^{\text{REAPDOR}}$
10	3.7 ± 0.6	4.4	2.75	2.0	0.32	132	90
15	2.2 ± 0.6	2.6	0.76	1.0	0.22	78	68
20	$1.4 \pm 0.2^{\text{a}}$	1.6	0.37	0.5	0.14	48	45
25	0.8 ± 0.1	1.0	0.20	0.2	0.06	30	23
$\text{Al}(\text{PO}_3)_3^{\text{b}}$	5.0 ± 0.1	6	-	-	-	-	-

^a extracted from Ref. 34 ^b crystalline model compound.

(7) Pulsed EPR spectroscopy on Yb-doped samples.

Pulsed EPR techniques were used to study the RE coordination environment in samples doped with Yb^{3+} ions ($z = 0.2$ mol %). Yb^{3+} is an $S = 1/2$ ion. The 4f configuration gives rise to a $^2F_{7/2}$ term in the ground state and a $^2F_{5/2}$ term in the first excited state. As the energy difference is 10000 cm^{-1} for the free Yb^{3+} ion the $^2F_{5/2}$ term has little effect on the magnetic properties. Owing to the low dopant concentrations used (0.2 mol %), inter-atomic dipole interactions can be neglected. Figure 22 shows the echo detected field sweep EPR (EDFS) lineshape, recorded by mapping the echo intensity as a function of the magnetic field strength at 6.5 K. No signal was observed over the temperature range 5-20 K on an undoped control sample of glass with composition $x = 20$. Contrary to the situation of Yb^{3+} doped GeO_2 glass, no electron spin echo is detected at zero field, consistent with the absence of rare-earth clustering [59]. In agreement with the discussion given by Sen and coworkers [59] we attribute the main lineshape features to the isotopologues without nuclear spin, which comprise about 70% of the natural abundance, as no specific features attributable to ^{171}Yb and ^{173}Yb nuclear hyperfine interaction can be discerned. Figure 22 indicates systematic variations in these lineshapes as a function of the fluoride content of these glasses. The spectral lineshape is most likely dominated by the g-anisotropy, however, owing to the likely existence of g-tensor parameter distribution effects no unique fit to the complex lineshapes of these EDFS spectra can be accomplished. Rather, we must consider these spectra as “fingerprint” data sensitive to the mixed local fluoride/phosphate environments of the rare-earth ions. We attribute the large changes in these apparent g-tensor parameters (corresponding to field strengths of about 5 kG) to a systematic change of the oxide to fluoride ligand ratio around the Yb^{3+} ion. Such large changes might seem surprising at first, however, literature data on doped crystalline fluorides have also shown that the g-tensor parameters for Yb^{3+} centers are very sensitive to the geometry and composition of the Yb coordination environment [60,61]. In addition, Deschamps et al. have shown that Yb^{3+} dopants in $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ glass fibers show variations of comparable magnitude (~ 3 kG) in ligand environments dominated solely by oxygen [62]. Figure 22 indicates further that for the samples with the highest fluoride content ($x=20$ or 25) some lineshape convergence is observed. To the best of our knowledge, no relevant literature data are available for comparison of the present EPR spectra with those of Yb^{3+} ions in pure fluoride glass environments. While the relatively small change of the spectra with increasing fluoride to phosphate ratio from $x=20$ to $x=25$ might suggest that Yb^{3+} ions are dominantly coordinated by fluoride ions in these glasses, the

photophysical data, to be discussed below, still indicate that phosphate ligands contribute to some extent to the rare-earth ions' coordination sphere. The EPR spectra of the samples with lower fluoride contents appear systematically shifted towards lower magnetic fields, suggesting increasing contributions of phosphate ligands to the first coordination sphere of the Yb^{3+} ions. Figure 22 also includes two simulated EPR spectra that consider only the g anisotropy, g -strain and isotropic line broadening. The red dashed line represents the powder spectrum expected for isolated Yb^{3+} ions in a pure oxide environment, based on the data of Sen et al [59]; while the black dashed line is a tentative simulation to reproduce the low field region of the spectrum of the $x=15$ sample. For this last simulation an axial g tensor was considered with $g_{\perp} = 1.4$ and $g_{\parallel} = 0.5$, Gaussian g -strain parameters $\Delta g_{\perp} = 0.9$ and $\Delta g_{\parallel} = 0.3$, and an isotropic Gaussian line broadening parameter of 150 mT.

Figure 22: Echo detected absorption spectra for $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-(}30\text{-}x\text{)Al(PO}_3\text{)}_3\text{-}x\text{AlF}_3\text{-}19.75\text{-YF}_3\text{-}0.25\text{YbF}_3$ glasses (solid curves). The black dashed curve corresponds to a simulation considering an axial g -tensor, with $g_{\perp} = 1.4$ and $g_{\parallel} = 0.5$, Gaussian g -strain parameters $\Delta g_{\perp} = 0.9$ and $\Delta g_{\parallel} = 0.3$, and an isotropic Gaussian line broadening parameter of 150 mT (4.2 kHz peak-to-peak linewidth). The red dashed curve is a simulation based on Yb^{3+} in a pure oxide environment, based on the literature [59].

Figure 23 shows the ESEEM spectra for the different glasses, at magnetic field strengths of 550 mT (a) and 700 mT (b), using an interpulse delay (τ) of 140 ns. Clearly, the spectra reveal the Larmor frequencies of ^{89}Y (1.15 MHz and 1.46 MHz, respectively), ^{27}Al (6.1 MHz and 7.8 MHz, respectively), ^{31}P (9.5 MHz and 12.0 MHz, respectively) and ^{19}F (22 MHz and 28 MHz, respectively), suggesting that all four types of nuclei are interacting with the electron

spins residing in the 4f orbitals of the Yb atoms in the *weak coupling limit*, where the hyperfine coupling constants (in Hz) are small compared to the nuclear Zeeman frequencies. Therefore, we conclude that these signals belong to nuclei in the second or in higher order Yb³⁺ coordination spheres (distance range 4-8 Å). Besides these resonances at the Larmor frequencies of the different isotopes, hyperfine sublevel correlation (HYSCORE) experiments described below show ¹⁹F signals experiencing significant hyperfine splittings (see Figure 24, Figure 25 and Figure 26). This splittings are not resolved in the ESEEM spectra, possibly because the modulation pattern, which is influenced by the anisotropy of the hyperfine couplings, decays much faster than the overall amplitude of the echo, owing to destructive interference of different resonance frequencies. As discussed below, this problem can be overcome by the four-pulse sequence used in HYSCORE, where an additional π pulse between the second and third $\pi/2$ pulses of the ESEEM experiments serves to interchange the nuclear coherence between the electron spin α and β manifolds [63]. Figure 23 also shows simulated ESEEM spectra for the two magnetic fields. These simulations were performed with exactly the same parameters as used in the HYSCORE simulations described below and reproduce in excellent agreement the above-cited lack of resolution for the signal of the strongly coupled ¹⁹F nuclei in the ESEEM spectra.

Each set of ESEEM spectra in Figure 23a and Figure 23b were measured under identical conditions, which allow us to compare the relative peak intensities of the observed resonances. As expected, the ²⁷Al/⁸⁹Y peak amplitude ratio remains constant for all samples, while the ²⁷Al/³¹P ratio increases and the ²⁷Al/¹⁹F ratio decreases with increasing AlF₃ content (x), as expected from the batch compositions. This behavior indicates that the Yb³⁺ ions are well dispersed in the glass matrix, i.e. there is no evidence of phase segregation.

Figure 23: Simulated and experimental three-pulse ESEEM spectra for $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-(}30\text{-}x\text{)Al(PO}_3\text{)}_3\text{-}x\text{AlF}_3\text{-}19.75\text{YF}_3\text{-}0.25\text{YbF}_3$ glasses. The spectra were measured at magnetic field strengths of 550 mT (a) and 700 mT (b). Resonances are marked with the correspondent nuclear species. Simulation parameters are described in the text and in the caption of Figure 26.

Figure 24, Figure 25 and Figure 26 show the HYSCORE spectra obtained at 450, 550 mT and 700 mT for the Yb-doped samples. All the resonances are observed in the (+,+) quadrant of the spectra. The three diagonal peaks correspond to the Zeeman frequencies of ^{89}Y , ^{27}Al and ^{31}P nuclei at the respective field strengths. Such resonances in the diagonal region of the spectra indicate that the electron-nucleus interaction for these species fulfill the conditions of the weak coupling-limit, in agreement with the ESEEM data discussed above. In addition, the ^{19}F hyperfine splittings (presumably arising from Yb^{3+} ions involved in direct Yb-F bonding) are also quite visible in the HYSCORE data at 550 and 700 mT, giving rise to a pair of off-diagonal resonances (maximum positions $[\nu_\alpha, \nu_\beta]$ and $[\nu_\beta, \nu_\alpha]$ with $\nu_\alpha = 20$ MHz and 27 MHz and $\nu_\beta = 25$ MHz and 30 MHz for 550 mT and 700 mT respectively), which are symmetrically displaced from the diagonal position corresponding to the ^{19}F Zeeman frequency. They are less clearly visible in the spectra at 450 mT. The hyperfine interaction parameters in this case can be obtained through appropriate computer simulations, which are reproduced in Figure 27 for the three magnetic field strengths considered. The simulations are based on an axial g -tensor, with parameters $g_\perp = 1.4$ and $g_\parallel = 0.5$, which reproduce the low-field region of the EPR spectra of the sample with $x=15$, as shown in Figure 22 (black dashed curve). No substantial changes are observed in the HYSCORE simulations for a variation of ± 0.5 in $g_\perp$ and ± 0.2 in $g_\parallel$, therefore, in terms of the g -tensor, the simulations in Figure 27 can be compared to the experimental data of the whole set of samples. In order to reproduce the

experimental data in both ESEEM and HYSCORE experiments, the simulations should consider that each Yb^{3+} ion is interacting with two distinct types of ^{19}F nuclei: a strongly coupled one, giving rise to the split signal and a weakly coupled one, with its resonance at the ^{19}F nuclear Zeeman frequency. The number of weakly coupled ^{19}F nuclei is expected to be considerably larger, due to the larger volume of the interaction sphere considered. Although only information regarding the ^{19}F species can be experimentally quantified in the HYSCORE spectra, weak electron-nucleus hyperfine interaction with ^{27}Al , ^{31}P and ^{89}Y was considered in the simulations to reproduce possible peak suppressions and blind spots.

For the simulations an axial ^{19}F hyperfine tensor was considered, with $A_{\perp} = -0.5 \pm 0.5$ MHz and $A_{\parallel} = 14 \pm 3$ MHz, where $A_{\perp}$ and $A_{\parallel}$ are respectively the perpendicular and parallel components of the tensor. The simulations are sensitive to the relative signal between both components, but the absolute signs cannot be determined. Although simplified, this model results in hyperfine parameters that are close to those observed in the literature for Yb-F interactions in crystalline systems [64-66]. For all three magnetic field strengths the HYSCORE simulated spectra (Figure 26) are in excellent agreement with the experimental data for all samples. The simulations also reproduce the experimental observation that the hyperfine splitting owing to the strongly coupled nuclei is not clearly observed at 450 mT, while it is clearly evident at 550 and 700 mT. In contrast, simulations based on a broad distribution of isotropic hyperfine coupling constants and low anisotropies did not lead to satisfactory agreement with the experimental data.

The ESEEM relative intensities between the ^{19}F resonances and the other nuclei could not be reproduced in a single EasySpin® simulation considering the five nuclei involved. In such a simulation the ^{19}F signal is very attenuated due to the cross-suppression effect [67], arising as a consequence of the product rule [24], which may suppress shallower modulations in the presence of modulations that are significantly stronger. The stronger ^{19}F signal intensity observed experimentally is strong evidence of preferential coordination of the Yb^{3+} ions with F atoms. Each Yb^{3+} ion interacts with both strongly-coupled and weakly coupled ^{19}F nuclei, however their relative numbers are not known. In the simulations we adopted a simplified model, considering one Yb^{3+} coupled to one strongly- and one weakly coupled ^{19}F species, and a second Yb^{3+} species, presumed to be exclusively in the weak coupling limit. The relative intensities of these two species were then varied to reproduce the experimentally observed intensity profiles.

Figure 24: 2D-HYSCORE spectra recorded at a magnetic field strength of 450 mT for $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-(}30\text{-x)Al(PO}_3\text{)}_3\text{-xAlF}_3\text{-}19.75\text{YF}_3\text{-}0.25\text{YbF}_3$ glasses. The anti-diagonal dashed lines cross the diagonal at the nuclear Zeeman frequencies for the isotopes indicated in the plots.

Figure 25: 2D-HYSCORE spectra recorded at a magnetic field strength of 550 mT for 25BaF_2 - 25SrF_2 -($30-x$) $\text{Al}(\text{PO}_3)_3$ - $x\text{AlF}_3$ - 19.75YF_3 - 0.25YbF_3 glasses. The anti-diagonal dashed lines cross the diagonal at the nuclear Zeeman frequencies for the isotopes indicated in the plots.

Figure 26: 2D-HYSCORE spectra recorded at a magnetic field strength of 700 mT for 25BaF_2 - 25SrF_2 -($30-x$) $\text{Al}(\text{PO}_3)_3$ - $x\text{AlF}_3$ - 19.75YF_3 - 0.25YbF_3 glasses. The anti-diagonal dashed lines cross the diagonal at the nuclear Zeeman frequencies for the isotopes related in the plots. The peak at the 33 MHz diagonal position is an artifact.

Figure 27: 2D-HYSCORE simulated spectra (blue/yellow contours) considering magnetic field strengths of 450 mT (a) 550 mT (b) and 700 mT (c). Parameters used in both simulations are: $\tau = 140$ ns; $A_{\perp} = -0.5$ MHz and $A_{\parallel} = 1$ MHz for ^{27}Al ; $A_{\perp} = -1$ MHz and $A_{\parallel} = 2$ MHz for ^{31}P ; $A_{\perp} = -0.15$ MHz and $A_{\parallel} = 0.3$ MHz for ^{89}Y ; $A_{\perp} = -0.5$ MHz and $A_{\parallel} = 14$ MHz for strongly coupled ^{19}F ; and $A_{\perp} = -0.3$ MHz and $A_{\parallel} = 0.6$ MHz for weakly coupled ^{19}F . The anti-diagonal dashed lines cross the diagonal at the nuclear Zeeman frequencies for the isotopes indicated in the plots. Experimental spectra are plotted as green contours for the sake of comparison.

(8) Photophysical Properties.

For developing an understanding of the emissive properties of the rare-earth ions in these glass matrices, we measured the emission and excitation spectra as well as the excited state lifetimes of samples doped with 0.2 and 1.0 mol% Eu^{3+} . Figure 28 summarizes the emission spectra of a set of Eu-doped glasses, containing $z = 1.0$ mol% Eu^{3+} . Table 9

summarizes the spectroscopic observables deduced from these spectra, as well as from the spectra of the $x = 0.2$ set, data given in parentheses). The emission spectra are comparable to those reported in the literature for other fluoride phosphate glasses and dominated by $^5D_0 \rightarrow ^7F_1$ transitions [18-23, 69]. The hypersensitive, electric dipole, $^5D_0 \rightarrow ^7F_2$ transition is highly dependent on the chemical environment of Eu, whereas the intensity of the magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition does not depend on the local ligand field. Therefore, it is a common procedure to employ the ratio $\alpha = I(^5D_0 \rightarrow ^7F_2) / I(^5D_0 \rightarrow ^7F_1)$ as an indicator of the symmetry of the Eu site [70,71]. Increased $^5D_0 \rightarrow ^7F_2$ transition probabilities (and hence higher α values) are generally observed for Eu^{3+} in ligand environments that are more distorted and/or characterized by a higher degree of covalency. As the non-bridging oxygen atoms of the phosphate ligands generate higher ligand field strength and bonding covalency than the fluoride ligands, higher α values are expected for phosphate glasses than for fluoride glasses in general. A review of the literature on Eu-doped fluoride phosphate glasses indicates α values near unity in glasses with high F contents and values near 2.5 to 3.0 in pure phosphate glasses [18-23, 68, 72-75]. In the present system we observe α -values near 1.6, 1.9, and 2.3 in glasses with $x = 25$, 20, and 15, respectively, containing 1.0 % Eu. Thus, our data suggest that the local bonding environment of the Eu ions in these two glasses continues to evolve with increasing x , towards a more fluoride-rich environment. The same conclusion can be drawn from the excited state lifetimes monitored for the $^5D_0 \rightarrow ^7F_2$ transitions (see Table 9), which also increase proportionally to x . For Eu embedded in pure phosphate matrices one typically observes lifetime values within the range 2.0 ± 0.5 ms [65,66], whereas for Eu in pure fluoride glass matrices, values of up to 6.8 ms have been reported [20]. Further evidence for a mixed fluoride/phosphate environment comes from the phonon sideband peaks associated with the excitation spectra of the monitored $^5D_0 \rightarrow ^7F_2$ transition: While the most intense excitation line lies at 464 nm, the excitation spectra also present a weak phonon sideband at 441 nm, which can be attributed to the anti-Stokes band reflecting the vibrational wavenumber near 1100 cm^{-1} which contributes to the multiphonon relaxation. By comparison with the spectra in Figure 16, one can see that the wavenumber value corresponds to the dominant high-frequency Raman scattering band, attributed to the $Q^{(1)}$ phosphate species found in these glasses. As indicated by Figure 29 and Table 9, the ratio of the phonon sideband peak intensity to the main excitation peak decreases with increasing AlF_3 content x , suggesting once again that the average phosphate-to-fluoride ratio of the Eu coordination environment keeps evolving. Nevertheless, the fact that the phonon sideband is present even in the glass with the highest fluoride content ($x = 25$), strongly suggests that

phosphate ligands still contribute to the Eu coordination environment to some extent, even at the highest fluoride concentration studied in the present system.

Figure 28: Emission spectra (a) of the $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-(}30\text{-x)Al(PO}_3\text{)}_3\text{-xAlF}_3\text{-}19\text{YF}_3\text{-}1.0\text{EuF}_3$ glasses as a function of composition ($x = 0.15, 0.20$, and 0.25). In order to highlight the variations in the α ratio, the spectra are internally normalized to the peak intensity at 595 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition).

Figure 29: Excitation spectra recorded by monitoring the $^7\text{F}_2 \rightarrow ^5\text{D}_0$ transition at 612 nm in $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-(}30\text{-x)Al(PO}_3\text{)}_3\text{-xAlF}_3\text{-}19\text{YF}_3\text{-}1.0\text{EuF}_3$ glasses as a function of composition ($x = 0.15, 0.20$, and 0.25). The inset shows an expansion of the internally normalized phonon sideband (anti-Stokes) transition at 441 nm.

Table 9: Photophysical data obtained on the fluoride phosphate glasses containing 1 mole% (and 0.2 mole%, data in parentheses) Eu as a function of composition. The wavelengths of the two most intense emission bands are given, as well as the wavenumber ν of the phonon sideband. The intensity ratio of the phonon sideband to the excitation band at 464 nm is denoted R, and the intensity ratio of the emissions at 612 and 595 nm ($^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$) is denoted α . The average excited state 5D_0 lifetime values are given for samples doped with 1 mol% and 0.2 mol% (values in parentheses).

X	λ_1/nm	λ_2/nm	ν/cm^{-1}	$10^3 R$	α	$\tau(\text{ms})$
0.15	590	612	1100	11.4(10.8)	2.3	3.8 (3.6)
0.20	590	612	1085	8.4(9.6)	1.9	4.1(4.4)
0.25	590	612	1085	5.7(8.9)	1.6	5.2(5.5)

IV. CONCLUSIONS

In summary, this comprehensive structural study of a new series of fluoride phosphate potential laser glasses provides detailed insights into the network organization and rare-earth coordination both in the undoped state, as well as doped with the EPR probe Yb^{3+} and the optical probe Eu^{3+} . The solid-state NMR results indicate that the network structure is dominated by Al-O-P linkages, which can be consistently quantified by $^{27}\text{Al}/^{31}\text{P}$ double resonance NMR techniques. The EPR and optical spectroscopic properties indicate that the local environment of the rare-earth ions is characterized by a mixed phosphate/fluoride environment, and a preference for fluoride ligation, which evolves with composition in the expected manner. However, consistent with previous literature reports on related systems [18-23], the limiting case of an exclusive fluoride environment is not realized in these glasses, even at the highest fluoride contents. What remains to be accomplished is a definitive quantification of the average ligand distribution for the rare-earth ions in the same way as has been done here for the ^{27}Al nuclei. In principle, this could be done on diamagnetic mimic nuclei such as ^{45}Sc and ^{89}Y in these glasses. Corresponding REDOR experiments addressing this question are currently under consideration in our laboratory. The long excited state lifetime values of Eu^{3+} in these glasses are noteworthy, which give strong evidence that these fluorophosphate glasses show promise as active media in lasing and other lighting devices.

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Article 3: Thermo-optical spectroscopic investigation of new Nd³⁺-doped fluoro-aluminophosphate glasses

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ABSTRACT

Fluorophosphate glasses in the compositional system 25BaF₂-25SrF₂-10Al(PO₃)₃-20AlF₃-(20-z)YF₃:zNdF₃ with z = 0.5, 1, 2, 4 and 8 mol % were prepared and characterized from the spectroscopic point of view, as potential laser active media. The thermal optical properties of the glasses were evaluated using the Thermal Lens Technique and from the analysis of the heat generated upon excitation (and the consequent change in refractive index), the fluorescence quantum efficiencies η were determined for samples doped with different Nd³⁺ concentrations. These values were then compared to those obtained by employing the radiative lifetime values determined from the Judd Ofelt theory and a very good agreement was verified between the experimental and theoretical results. A nearly zero change in optical pathlength $ds/dT = 2.5 \times 10^{-6} \text{ K}^{-1}$ and thermal conductivity values ranging from $(12-7) \times 10^{-3} \text{ W/Kcm}$, favorable for laser action, were determined for samples doped with 0.5–8 mol %.

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Fluorophosphate glasses in the compositional system 25BaF₂-25SrF₂-10Al(PO₃)₃-20AlF₃-(20-z)YF₃:zNdF₃ with z = 0.5, 1, 2, 4 and 8 mol% were prepared and characterized from the spectroscopic point of view, as potential laser active media. The thermal optical properties of the glasses were evaluated using the Thermal Lens Technique and from the analysis of the heat generated upon excitation (and the consequent change in refractive index), the fluorescence quantum efficiencies η were determined for samples doped with different Nd³⁺ concentrations. These values were then compared to those obtained by employing the radiative lifetime values determined from the Judd Ofelt theory and a very good agreement was verified between the

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experimental results and theory. A nearly zero change in optical pathlength $ds/dT = 2.5 \times 10^{-6} \text{ K}^{-1}$ and thermal conductivity values ranging from $(12 - 7) \times 10^{-3} \text{ W/Kcm}$, favorable for laser action, were determined for samples doped with 0.5-8 mol %.

I. Introduction

Neodymium (Nd^{3+}) is one of the most efficient luminescence activators among the trivalent rare earth (RE) ions with various possibilities of optical and spectroscopic applications such as near infrared low and high power solid state lasers around 1060 nm, temperature sensors, and fiber amplifiers in telecommunications at around 1325 nm [23,24]. Among the required properties for efficient laser operation at around 1050 nm ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transition) are high-stimulated emission and absorption cross-sections and long enough excited state lifetime, which are significantly influenced by the material that hosts the active ion. The rare earth ion's non-radiative decay probability is directly dependent on the host's phonon energy and on the ionic concentration (which rules non radiative energy transfer processes). Thus, studies of the best possible host-ion combinations are justified aiming at an optimized choice of composition and the development of appropriately doped materials for efficient laser action. [23]

To this end, fluorophosphate glasses have been largely studied [25–29] due to their ability to combine the advantages of oxide glasses (easy fabrication in different shapes and sizes, higher RE solubility, higher mechanical and thermal strength, etc) with those of fluoride glasses (lower phonon energy, higher absorption and emission cross sections, low non-linear refractive index and possible crystallization of RE-containing fluoride phases) [27,30]. Nd^{3+} -doped fluorophosphate glasses show relatively high degree of inhomogeneous spectral line broadening and smooth line shapes that can result in relatively shorter laser pulses. Because of these advantages, fluorophosphate glasses have often been suggested as ideal host materials for several rare earth dopants aiming at laser applications and lighting [23,24,30]. Besides optical and spectroscopic characteristics, for practical laser applications it is also important to characterize the thermal loading properties of the material which can severely prevent laser action.

In our research group, we have been studying RE doped glasses and glass ceramics in the compositional system $\text{BaF}_2\text{-SrF}_2\text{-Al(PO}_3)_3\text{-AlF}_3\text{-YF}_3\text{:REF}_3$ ($\text{RE} = \text{Er}^{3+}, \text{Nd}^{3+}, \text{Eu}^{3+}$) which have shown promising characteristics for laser action in the infrared and visible spectral regions [29,31]. In this work, we extend the investigation of Nd^{3+} -doped glasses employing the Thermal

Lens technique (TL) [32] to explore the thermal-optical characteristics of lowly and highly doped samples (up to 8 mol %). A comprehensive study is presented combining the results of TL with those of UV-VIS spectroscopy, photoluminescence and excited state lifetime (τ_{exp}) measurements. The Judd Ofelt theory is employed to calculate the phenomenological intensity parameters ($\Omega_{\lambda=2,4,6}$) and the excited state $^4F_{3/2}$ radiative lifetime (τ_{rad}) value, which allow the calculation of the fluorescence quantum efficiencies ($\eta = \tau_{\text{exp}}/\tau_{\text{rad}}$), as a function of Nd^{3+} concentration. The calculated η values were compared to those determined by the mode-mismatched TL technique in good agreement, validating the employed methodology.

II. Theoretical background

The thermal lens effect takes place when a laser beam passes through an absorbing medium. The absorbed energy causes thermal expansion and induces a refractive index gradient in the medium changing the wave front curvature of a second laser beam (probe beam) at a non-absorbing wavelength. Thus, the sample acts like a lens, focusing or defocusing the probe beam, with a transversal phase shift whose amplitude is given by [33–36].

$$\theta = -\varphi \frac{P_{\text{abs}}}{K\lambda_p} \frac{ds}{dT} \quad (1)$$

where φ , P_{abs} , K , λ_p , and ds/dT are, respectively, the fraction of absorbed energy converted into heat, the absorbed pump power, the thermal conductivity, the probe beam wavelength and the temperature coefficient of the optical path length.

The fluorescence quantum efficiency, η , of a given energy level, can be obtained from φ through the relation:

$$\varphi = 1 - \eta \frac{\langle \nu_{\text{em}} \rangle}{\nu_{\text{exc}}} \quad (2)$$

where $\langle \nu_{\text{em}} \rangle$ is the average emission frequency of the level under consideration and ν_{exc} is the excitation frequency. Eq. (2) is valid for systems with one emitting level and the η factor includes all types of down converting energy transfer processes, which reduce the lifetime of the emitting level while increasing the value of φ .

On analyzing the TL temporal response, two parameters are of interest: the characteristic lens formation time (t_c) and θ . Since θ is proportional to P_{abs} , it is convenient to use the normalized parameter (Θ) [36,37]

$$\Theta = \frac{\theta}{P_{abs}} = C\varphi \quad (3)$$

Where $C=(\lambda_p K)^{-1} ds/dT$. For materials doped with fluorescent ions, part of the absorbed excitation is converted into heat and part into fluorescence. The φ value can be obtained using a TL method, by determining Θ . Since the C parameter is usually unknown, Eq.(3) presents two unknown parameter in the right hand side. The multiwavelength TL overcomes this difficulty by using several excitation wavelength [38], but it is very time consuming. The normalized lifetime method [39], uses the lifetime τ_{exp} data of a series of samples with different doping concentration (N_t) assuming that $\eta = \tau_{exp}/\tau_{rad}$ and all samples share the same value of radiate lifetime (τ_{rad}) Considering that η strongly depends on N_t , the relation $\eta(N_t) = \eta^* \Gamma(N_t)$ is obtained, where $\Gamma(N_t) = \tau/\tau^*$ is the normalized lifetime parameter and η^* is the quantum efficiency of one particular sample (a reference sample) with lifetime τ^* is obtained using an empirical formula for the radiative lifetime. Thus, through equations (2) and (3) a linear relationship between Θ and Γ is obtained:

$$\Theta(N_t) = C \left[1 - \eta^* \frac{\langle \nu_{em} \rangle}{\nu_{exc}} \Gamma(N_t) \right] \quad (4)$$

Assuming that $\langle \nu_{em} \rangle$ and C are constant for all samples, Eq. (4) predicts a linear decrease of $\Theta(N_t)$ with $\Gamma(N_t)$, where both parameters are experimentally determined. The parameters C and η^* can be determined from the linear fit of the data using Eq.(4). It should be noticed that the choice of the reference sample is totally arbitrary. This strategy has been successfully employed to determine η for Nd^{3+} and Yb^{3+} doped glasses with ionic concentrations up to 10^{21} cm^{-3} [10,12–14]. However, in some cases it was observed a significant variation of the thermal diffusivity with ion concentration, so it is interesting to rewrite Eq.(4) as:

$$D\Theta = C' \left[1 - \eta^* \frac{\langle \nu_{em} \rangle}{\nu_{exc}} \Gamma \right], \quad (5)$$

where $C'=(\lambda_p \rho c)^{-1} ds/dT$, ρ is the sample density and c is the specific heat. Eq. (5) indicates that both C' and η^* can be obtained from the fit of $D\Theta$ versus Γ . Although D may vary with concentration, it is assumed that τ_{rad} , $\langle \nu_{em} \rangle$ and C' are nearly constants. The use of Eq. (5)

instead of Eq.(4) is advantageous because, in most cases, the product ρc is approximately independent on concentration [13].

III. Experimental

(1) Sample preparation and conventional characterization

Glasses with nominal composition $25\text{BaF}_2\text{-}25\text{SrF}_2\text{-}10\text{Al(PO}_3)_3\text{-}20\text{AlF}_3\text{-(}20\text{-}z\text{)YF}_3\text{:}z\text{NdF}_3$ with $z = 0.5, 1, 2, 4$ and 8 mol % were prepared by the conventional melt quenching technique in Pt crucibles. Homogeneous mixtures of reagent grade precursors were melted at 1100°C for 5 min, quenched between steel plates and heat treated for 8 h at 400°C . The samples in blade form were subjected to meticulous and lengthy polishing to minimize surface roughness and ensure that the sides were parallel. Prior to spectroscopic characterization, all the samples were verified by XRD (not shown) to verify the amorphous nature of the glasses [31].

(2) Spectroscopic and thermal lens investigations

The UV–VIS–NIR absorption spectra were measured in a Perkin Elmer spectrophotometer model Lambda 1050. Infrared and visible excitation, emission, and excited-state lifetime measurements of Nd^{3+} -doped samples were recorded using a Horiba Fluorolog spectrofluorimeter model FL-1050, equipped with CW and pulsed Xe lamps as excitation sources. The signals were collected by a photodiode detector, model PPD-850, in the visible spectral region, and by a Hamamatsu photomultiplier in the infrared. The spectra were corrected by the lamp profile and detector's response. The luminescence decay curves of the glasses were measured with a built-in decay-by-delay phosphorimeter and the excited state lifetime values of different RE concentrations were determined by fitting the curves with exponential decay functions.

The TL experiments were performed using the time-resolved mode-mismatched configuration. An Ar^+ laser at 514 nm was used as the excitation source and a He-Ne laser at 632.8 nm as the probe beam for the TL effect. The pump signal was modulated at 8 Hz to ensure enough time to induce TL effect in the gain medium and to observe the system reaching the stationary state. The temporal evolution of the on-axis probe beam intensity, $I(t)$, was measured

in the far field using a circular aperture in front of a photodiode [33–35]. According to Shen et al. [40], the Fresnel diffraction theory was used to determine an analytical expression for the probe beam intensity at the detector:

$$I(t) = I(0) \left[1 + \frac{\theta}{2} \tan^{-1} \left(\frac{2mV}{\left[(1+2m)^2 + V^2 \right] \left(\frac{t_c}{2t} \right) + 1 + 2m + V^2} \right) \right]^2, \quad (6)$$

where $m = (w_p/w_e)^2$ and $V = (Z/Z_{cp})$ are experimental geometrical parameters. Most of measurements were performed with probe beam radius, $w_p = 169 \times 10^{-4}$ cm, the excitation beam radius, $w_e = 28.5 \times 10^{-4}$ cm at the sample and the position of the sample with relation to the probe beam waist $Z = 3.1$ cm. The characteristic TL response time, t_c , given by:

$$t_c = \frac{w_o^2 e}{4D}, \quad (7)$$

where D is the sample's thermal diffusivity. Further details of the experimental arrangement can be found in Refs. [33,34,41]

IV. Results and discussions

The representative absorption spectrum of the 4 mol % Nd^{3+} -doped glass can be seen in Figure 30. From the graphs, one can see the characteristic transitions of Nd^{3+} from ground state $^4I_{9/2}$ to the indicated excited states. The absorption coefficient increases linearly with the Nd^{3+} concentration up to 4 mol %, indicating the successful incorporation of the Nd^{3+} ions in the glasses in this concentration range, which corresponds to $0 - 6.5 \times 10^{20} \text{ cm}^{-3}$. The sample with nominal 8 mol% concentration presents absorption slightly smaller than predicted by this linear behavior, so we estimated that the actual concentration is ~ 6.3 mol % ($10.5 \times 10^{20} \text{ cm}^{-3}$).

Figure 30: Representative room temperature absorption spectrum of the 0.5-8 mol % Nd^{3+} doped fluorophosphates glass.

Based on the absorption spectra, the Judd-Ofelt theory [42,43] has been widely employed to calculate the oscillator strength for transitions between ground and excited states of RE ions embedded in different hosts. In this method, the phenomenological intensity parameters Ω_λ ($\lambda = 2, 4, 6$ for Nd^{3+}) are calculated from a least-square fitting procedure of a system of equations that equal the theoretical and experimental oscillator strengths. The Ω_λ values, calculated for some typical Nd^{3+} doped glasses, are presented in Table 10.

Table 10: Phenomenological J-O parameters Ω_λ (10^{-20} cm^2) for some Nd^{3+} -doped glasses.

Ω_λ (10^{-20} cm^2)	Fluorophosphate	PKBAN (fluorophosphate)	PKBAFN (fluorophosphate)
Ω_2	3.13	9.23	6.60
Ω_4	8.76	7.00	6.36
Ω_6	9.58	8.74	7.30
Ref.	Present work	[44]	[44]

The intensity parameters provide information on the symmetry and bonding of rare-earth ions in local environment [45]. Usually, Ω_2 is associated with the covalence and symmetry of the ligand field around Nd^{3+} ions [46,47]. As it is shown in Table 10, Ω_2 obtained for the fluorophosphates glasses in this work is lower than the typical values for fluorophosphate glasses, this value is lower because our composition has higher amount of fluorine compared with others. Emission intensity could be also characterized by the Ω_4 and Ω_6 parameters. The ratio χ ($=\Omega_4/\Omega_6$), defined as a the spectroscopic quality parameter, is found to be 0.91 in being

compared with those of other host materials reported [44]. Figure 31 presents the emission spectrum of the glasses doped with different Nd^{3+} concentrations and excited at 800 nm. As indicated by the bands, the characteristic transitions at 880, 1050 and 1350 nm are due to the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$, $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$ transitions, respectively. From the absorption and emission spectra it was possible to calculate the radiative transition probabilities and the radiative lifetime value $\tau_{\text{rad}} = 528 \mu\text{s}$ for the emitting level $^4\text{F}_{3/2}$.

Figure 31: Room temperature near infrared luminescence spectra of fluorophosphate glasses doped with 0.5 to 8 mol % NdF_3 excited at 800 nm.

The decay profile curves of the $^4\text{F}_{3/2}$ excited state, measured by monitoring the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transition are shown in Figure 32 for the samples doped with up to 5.0 mol % Nd^{3+} . For higher dopant concentrations low fluorescence intensity and very rapid decays prevented accurate measurements. From the curves, the average fluorescence lifetime values (τ_{exp}) of the excited state were taken from single exponential fits and, for the sake of comparison, as those corresponding to a $1/e$ decrease of the normalized fluorescence intensity presented in Figure 32. The progressive decrease in lifetime values as a function of increasing dopant ion concentration is known as self-quenching [12], and it is due to ion-ion non-radiative energy transfer mechanisms such as the cross relaxations and energy migration responsible for additional depopulation of the emitting level.

Figure 32: Fluorescence decay curves of Nd³⁺-doped fluorophosphate glasses ($\lambda_{exc} = 800$ nm, $\lambda_{em} = 1050$ nm). The excited state $^4F_{3/2}$ lifetime values were determined by single exponential fitting and as the time at which intensity decreases by a factor 1/e.

The dependence of self-quenching on dopant ion concentration can be adjusted by the empirical expression: [48]

$$\tau_{exp} = \frac{\tau_0}{1 + \left(\frac{N_t}{Q} \right)^p}, \quad (8)$$

where τ_0 is the lifetime value in the limit of zero doping concentration, N_t is the Nd³⁺ ion concentration, Q is the quenching parameter corresponding to the concentration for which η decreases by a factor 2 and p is an adjustable parameter [23]. Figure 33 presents the experimental lifetime values, obtained by simple exponential decay as a function of Nd³⁺ ion concentration. The curve is well fitted by Eq.(7) resulting in $\tau_0 = (477 \pm 33) \mu$ s, $Q = (3.5 \pm 0.5) \times 10^{20}$ ions/cm³ which corresponding to 2.1 mol % and $p \approx 1.5$ value, in agreement with previous data of fluorophosphates glasses [49]. Most studies estimate the quantum efficiency of Nd³⁺-doped glasses using $\eta = \tau_{exp}/\tau_{rad}$, where τ_{exp} is the measured decay time and τ_{rad} is the value calculated by the Judd–Ofelt method. Since the values of τ_{rad} and τ_0 are in good agreement (< 9 % difference), we arbitrarily chose to use τ_0 , for which the attributed error is smaller.

Figure 33: Experimental lifetime values versus Nd^{3+} concentration for Nd^{3+} -doped fluorophosphates glasses.

(1) TL measurements: thermal diffusivity, quantum efficiency, and ds/dT

Figure 34 presents a typical normalized TL transient signal for the 1.0 mol % doped glass. In the present case, the decrease of the signal reveals a divergent character of the induced thermal lens, so in this material $ds/dT < 0$. The solid line represents the theoretical fit using Eq. (6) [37], which provides two parameters: $\theta = (5.02 \pm 0.02) \times 10^{-2}$ rad and $t_c = (4.99 \pm 0.05) \times 10^{-4}$ s.

Figure 34: TL transient signal for $P_{ex} = 133$ mW, $\lambda_{exc} = 514$ nm and $\lambda_p = 632.8$ nm. The solid line corresponds to the fitting using Eq.6. The curve fitting provide θ and t_c of Eq. = $(5.02 \pm 0.02) \times 10^{-2}$ rad and $t_c = (4.99 \pm 0.05) \times 10^{-4}$ s for 90F10P:1NdF3 glass.

In order to accurately determine D several transients signal were taken as a function of P up to ~ 200 mW. Figure 35 shows the power dependence of TL signal and t_c for the same 1.0 mol% doped sample. The t_c values remained approximately constant, resulting in values with ~ 6 % accuracy. A linear increase of θ versus P was observed, as expected by Eq.(1). This assures that in the studied intensity regime nonlinear effects such as absorption saturation or energy transfer between a pair of excited ions (Auger upconversion [50]) are not observed even for higher concentrations. The same analysis was performed for all samples and the resulting values are presented in Table 11.

Table 11: Spectroscopic and TL parameters for Nd^{3+} -doped fluorophosphate glasses.

Nd^{3+} mol%	Nd^{3+} $\times 10^{20} \text{ cm}^{-3}$	L cm	t_c $\times 10^{-4} \text{ s}$	$\Theta = \theta/P_{\text{abs}}$ (rad/W)	A(514nm) cm^{-1}	τ_{exp} μs	D $\times 10^{-3} \text{ cm}^2/\text{s}$
0.5	0.80	0.195	4.7 ± 0.2	1.9 ± 0.1	0.36 ± 0.02	489	4.3 ± 0.3
1	1.62	0.190	5.2 ± 0.3	2.9 ± 0.1	0.69 ± 0.03	289	3.9 ± 0.2
2	3.27	0.187	5.7 ± 0.3	3.2 ± 0.2	1.22 ± 0.06	267	3.6 ± 0.2
3	4.90	0.199	6.4 ± 0.3	4.1 ± 0.2	1.92 ± 0.06	187	3.2 ± 0.2
4	6.55	0.197	6.8 ± 0.3	4.5 ± 0.2	2.5 ± 0.2	133	3.0 ± 0.2
8	13.25	0.243	7.7 ± 0.4	3.5 ± 0.3	5.0 ± 0.3	30	2.7 ± 0.4

Figure 35: Power dependence of TL parameters, θ and t_c for the 1.0 mol % doped glass.

In some cases, the doping rate can reach several tens of percent or more, and highly doped laser materials have elicited interest. Figure 36 presents the strong decrease of thermal diffusivity with the increase of Nd^{3+} concentration, as commonly observed in rare earth doped

crystals and glasses [29,30]. In the case of crystals, this behavior is attributed to the difference between the masses of rare earth ion and the atom which is substituted. In glasses the dopant ion acts as network modifiers and in most cases can decrease the phonons mean free path and oxygen vacancies can cause the same effect. From Figure 36 plot we extrapolate $D \sim 4.8 \times 10^{-3} \text{ cm}^2/\text{s}$ for the undoped sample, D decreases $\sim 44 \%$ for the highest concentration. In order to compare this behavior with other rare earth doped materials, we considered that D decreases by 25 % in the interval $0 - 3 \times 10^{20} \text{ ions/cm}^3$, which is the typical concentration of Nd doped glasses. In the same Nd concentration range D decreases 25 % in Nd:YAG polycrystalline ceramics [14,31], 7.3 % in borosilicate glasses and 3.5 % in aluminosilicate glasses [32]. However, it is interesting to note that in aluminosilicates, the D decrease is stronger for Er^{3+} compared to Nd [32].

Heat removal is critical in many photonic devices. For instance, in quasi-three-level laser systems, such as Nd^{3+} and Yb^{3+} ($\sim 900\text{--}950 \text{ nm}$), a temperature rise increases the population of the terminal laser level. The temperature gradient in the laser rods induces thermal lensing and other deleterious effects [12, 28]. The most important physical parameter for heat remove is K , which can be calculated from the experimental D values by $K = rCD$. We used the factor $rC = 2.5 \text{ J/K.cm}^3$ from data of a fluorophosphates glass [33]. Therefore, we estimate a decrease of K from $12\text{--}7 \times 10^{-3} \text{ W/K.cm}$, for the concentration range shown in Figure 36. For a concentration of $3 \times 10^{20} \text{ cm}^3$, typical of most Nd^{3+} doped glasses, we estimate $K \sim 9.1 \times 10^{-3} \text{ W/K.cm}$ which is similar to $K \sim 8.8 \times 10^{-3} \text{ W/K.cm}$ of IRG9 and other fluorophosphates glasses [33], phosphates [34] and fluorides [35].

Figure 36: Thermal diffusivity for the fluorophosphates glasses, as a function of the Nd^{3+} concentration. The dashed line is guide to the eyes.

The experimental decays presented in Figure 32 are given by the sum of radiative and nonradiative lifetime contributions. The lifetime decrease, usually observed in Nd^{3+} -doped solids, is mainly attributed to nonradiative cross relaxation processes. Thus, an excited ion, decay non-radiatively to an intermediate state, transfers part of its energy to a nearby ion in the ground state, promoting it to the same or another intermediated excited state. Subsequently, both donor and acceptor ions quickly decay nonradiatively to the ground state and, consequently, there is a decrease in quantum efficiency. To estimate the ψ factor, we consider the heat generated due to absorption of a photon in the green ($\lambda_{\text{exc}} = 514 \text{ nm}$) by Nd^{3+} ion. In this case, the excited ion rapidly decays to the metastable $^4\text{F}_{3/2}$ level, from which it decays radiatively. The $\langle v_{\text{em}} \rangle$ value presented in Eq.(2) can be obtained from the emission spectra in Figure 31, considering that $\langle v_{\text{em}} \rangle / v_{\text{exc}} \sim \lambda_{\text{exc}} / \langle \lambda_{\text{em}} \rangle = 0.49$, calculated with average emission wavelength $\langle \lambda_{\text{em}} \rangle = 1050 \text{ nm}$, obtained from the emission spectrum of the 1.0 mol % doped glass.

The plot of the product $D \cdot \Theta$ (thermal diffusivity with the normalized TL phase shift) versus the parameter Γ (normalized lifetime parameter) is shown in Figure 37. The sample with the lowest concentration (0.5 mol %) was chosen as reference sample, the one for which $\Gamma = 1$ and $\tau^* = 489 \mu\text{s}$. Figure 36 shows that $D \cdot \Theta$ decreases linearly with Γ as predicted by Eq.(4). It should be noticed that the lowest lifetime (nominal concentration 8 mol %) does not fit in this general trend indicating that it does not have the same physical properties of the others, so this

data point was not included in fit. From the the linear fit shown in Figure 36, we obtained the parameters $C' = (1.55 \pm 0.01) \times 10^{-2} \text{ cm}^2/\text{J}$ and $\eta^* = (0.93 \pm 0.03)$, which is the quantum efficiency of the reference sample. The η values for the other samples are obtained by $\eta = \eta^* \cdot \Gamma = \eta^* \cdot (\tau/\tau^*)$ as shown in Figure 38. A very good agreement of these η values were obtained with the ones obtained by Judd-Ofelt $\eta_{JO} = \tau/\tau_{rad}$. Alternatively we can use η^* to estimate the radiative lifetime by $t_{rad} = \tau^*/\eta^* = (526 \pm 14) \mu\text{s}$ in fair agreement with $\tau_{rad} = 533 \mu\text{s}$, obtained by Judd-Ofelt calculations. Furthermore, within the uncertainty, both values also agree with $\tau_o = (477 \pm 33) \mu\text{s}$, the experimental lifetime in the limit of zero Nd^{3+} concentration. Thus the effect of eventual impurities or hydroxyl groups on the quantum efficiency should be very small.

From the definition of C' factor (Eq.5) the factor $ds/dQ = (\rho c)^{-1} ds/dT = -9.8 \cdot 10^{-7} \text{ K}^{-1}$, which indicates the optical path change per heat since $dQ = \rho c \cdot dT$. Moreover, we can use the $\rho C = 2.5 \text{ J/K} \cdot \text{cm}^3$, from Schott IRG9 fluorophosphates glass, in order to estimate $ds/dT = -2.5 \times 10^{-6} \text{ K}^{-1}$. The optical path change depends on dn/dT (temperature coefficient of refractive index), thermal expansion and thermal stress. Since the expansion term is always positive, the negative value of ds/dT is due to a negative value of dn/dT , which is characteristic of fluorine compounds. Negative dn/dT values are found mainly in fluoride glasses and also in phosphates glasses [34,51]. Our results suggest that by small changes in the composition studied in this paper it is possible to achieve, for instance, and athermal glass with ds/dT near zero.

Figure 37: Dependence of photothermal parameter $D\Theta$ with the normalized lifetime $\Gamma = \tau_{exp}/\tau^*$, where τ^* is the lifetime of the sample with the lowest ion concentration.

Figure 38: Comparison of fluorescence quantum efficiency values for Nd³⁺-doped fluorophosphate glasses obtained by Judd-Ofelt (JO) and Thermal Lens (TL) methods.

V. Conclusions

When studying new optical materials and, particularly, in order to choose hosts that may be promising for high-power laser applications, there is a need to relate the chemical and optical characteristics of the material to its thermal properties. Nd³⁺ doped fluorophosphate glasses have been prepared and characterized from the spectroscopic point of view using UV-VIS, photoluminescence and TL techniques. The thermo-optical properties have been obtained: the thermal diffusivity D and a positive ds/dT , whose value is near zero and favorable for laser glasses, were determined.

Our results show that the D value strongly decreases (about 40 %) for the Nd³⁺ doped fluorophosphate glass doped with 8 mol%. Using the thermal diffusivity values, the fluorescence quantum efficiencies of $^4F_{3/2}$ level were determined and compared to the values obtained by the theoretical methodology indicating good agreement. The results also indicate that η decreases from 0.93 to 0.07 for T.L. as the doping concentration increases from 0.5–8 mol %, showing that significant concentration quenching starts around 2 mol % doping. This strong decrease in η values is attributed to the interaction between pairs of Nd³⁺ ions that is

boosted by increasing the ionic concentration. Furthermore, it is interesting to validate the quantum efficiency calculations obtained by the J.O. method ($\eta = \tau_{exp}/\tau_{rad}$) by direct comparison with a photothermal (TL) η determination.

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Article 4: Infrared to visible upconversion properties of Yb³⁺/Er³⁺ co-doped fluoro-aluminophosphate glass and glass-ceramics

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5. CONCLUSIONS AND PERSPECTIVES

New fluorophosphate glasses doped with REs were obtained with excellent optical and spectroscopic properties such as long lifetimes and high fluorescence quantum efficiencies. Detailed structural insights into the network organization and rare-earth coordination both in the undoped state.

The solid-state NMR results indicate that the network structure is dominated by Al-O-P linkages, which can be consistently quantified by $^{27}\text{Al}/^{31}\text{P}$ double resonance NMR techniques. The EPR and optical spectroscopic properties indicate that the local environment of the rare-earth ions is characterized by a mixed phosphate/fluoride environment, and a preference for fluoride ligation, which evolves with composition in the expected manner. However, consistent with previous literature reports on related systems, the limiting case of an exclusive fluoride environment is not realized in these glasses, even at the highest fluoride contents. What remains to be accomplished is a definitive quantification of the average ligand distribution for the rare-earth ions in the same way as has been done here for the ^{27}Al nuclei. In principle, this could be done on diamagnetic mimic nuclei such as ^{45}Sc and ^{89}Y in these glasses.

Materials promising for high-power laser applications request some chemical and optical characteristics of the material such as thermal properties. Nd^{3+} doped fluorophosphate glasses have been characterized from the spectroscopic point of view using UV-VIS, photoluminescence and TL techniques. The thermo-optical properties have been obtained: the thermal diffusivity D and a positive ds/dT , whose value is near zero and favorable for laser glasses, were determined.

The fluorescence quantum efficiencies of $^4\text{F}_{3/2}$ level were determined and compared to the values obtained by the theoretical methodology indicating good agreement. The results also indicate that η decreases from 0.93 to 0.07 for T.L. as the doping concentration increases from 0.5–8 mol %, showing that significant concentration quenching starts around 2 mol % doping. This strong decrease in η values is attributed to the interaction between pairs of Nd^{3+} ions that is boosted by increasing the ionic concentration. Furthermore, it is interesting to validate the quantum efficiency calculations obtained by the J.O. method ($\eta = t_{\text{exp}}/t_{\text{rad}}$) by direct comparison with a photothermal (TL) h determination.

Transparent doped glass-ceramics has been prepared by heat treatment of precursor glass. The XRD results together luminescence spectra suggested that Er^{3+} and Yb^{3+} ions had efficiently enriched in SrF_2 nanocrystals in the glass-ceramic. The lifetime of excited states

could be used to reveal the surroundings of luminescent Er^{3+} and Yb^{3+} . The green UC emission bands observed around 520 nm and 540 nm assigned to the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} ion, respectively, have been explored for possible application in optical temperature sensors by the fluorescence intensity ratio technique. It wasn't possible to obtain Nd^{3+} glass-ceramic using the same treatment for Er^{3+} suggesting that crystallization process depends on the rare earth, the samples obtained for Nd^{3+} was translucent and increase your emissions.

The observations and conclusions of this dissertation have provided valuable insight into the properties and behavior of the material systems studied, but have also raised new questions and left others outstanding. Therefore, future efforts should be directed toward answering the following questions:

- Study non linearities for fluorophosphate doped Yb^{3+} , because they present good properties as laser fiber application;
- Measure laser action for Nd^{3+} samples;
- Characterize codoped samples $\text{Nd}^{3+}\text{-Yb}^{3+}$ studying your luminescence and possible application;
- Study the better conditions to obtain Nd^{3+} transparent glassceramic.