Visible up-conversion and near-infrared luminescence of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped $\text{SbPO}_4\text{-GeO}_2$ glasses

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ABSTRACT

Recent advances in glass chemistry have led to new multifunctional optical glasses of great technological importance. Glasses containing high amounts of antimony have been studied for use in nonlinear optics, near-infrared transmission, and as hosts for rare-earth ions in photonic devices. This work describes a luminescence study of Er^{3+} and $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doping in a new $\text{SbPO}_4\text{-GeO}_2$ binary glass system. Near-infrared and visible up-conversion emissions were observed in the green and red regions, which are enhanced when the samples are co-doped with Yb^{3+} . Near-infrared emissions have good quantum efficiency and full width half maximum of 61 nm. Visible up-conversion emissions are governed by two photons and described by excited state absorption, energy transfer and cross-relaxation processes.

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1. Introduction

Rare earth (RE) doped glasses have been widely studied in glass science due to their versatility in different optical applications, such as solid-state laser materials, optical amplifiers, bar-code reading, three-dimensional displays, and remote sensing thermometers [1,2]. Among the available RE ions, Er^{3+} doped materials have drawn much attention, as excitation at 980 nm causes such materials to display low energy infrared (IR) emissions at 1550 nm, which is fundamental for applications in telecommunication systems and optical amplifier devices. They also have visible emissions in the red and green regions caused by successive absorption of IR photons, leading the population to higher energy levels by up-conversion. Both processes are enhanced when the glass host is co-doped with Yb^{3+} ions, due to their larger absorption cross section than Er^{3+} ions at 980 nm, and processes of excited state absorption as well as energy transfer from Yb^{3+} to Er^{3+} ions [3,4].

Up-conversion efficiency is higher with smaller non-radiative loss due to multiphonon relaxation, resulting in weak emission intensities in the visible range. RE doped low phonon glasses exhibit lower non-radiative decay rates. Thus, a suitable glass host for RE

ions is necessary to develop new materials for optical applications. Low phonon oxide glasses based on heavy metal oxide and tellurite glasses ($600\text{--}850\text{ cm}^{-1}$) also present high RE emission efficiencies at the visible to near infrared region. However, many of these compositions have weak mechanical strength and low thermal stability against crystallization. Although silicate glasses present high thermal stability and better mechanical properties, they have high phonon energy ($1050\text{--}1150\text{ cm}^{-1}$) which limits the efficiency of infrared emission due to highly competitive non-radiative transitions [5]. Furthermore, the pumping efficiency and the emission bandwidth for optical amplification directly depend on the chemical nature of the host matrix. Efforts for broadening the emissions in Er^{3+} doped oxide glasses have been previously made using phosphate [6], boron germanate [7] and tellurite [8,9] glasses.

Phosphate glasses containing heavy atoms have received much attention for use in laser technologies, sensing and optical transmission due to their large transparency window, which varies from 450 to 3500 nm depending on the chemical composition [10,11]. Their low melting point and high thermal stability also allow the fabrication of optical fibers [12], and their low refractive index and low dispersion are also advantageous [13]. Different phosphate glasses have been used as the host matrix for RE ions, especially those containing antimony, which have attracted much attention for photonics applications [14,15].

The strategy used in this work employs antimony

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orthophosphate, SbPO_4 , and germanium oxide, GeO_2 , as glass precursors, resulting in low multiphonon energy of $800\text{--}950\text{ cm}^{-1}$ and glasses with high thermal stability, making this new glass composition a good candidate for optical fiber production. Antimony orthophosphate-based glasses are promising materials for applications in optical systems due to their high refractive indices (linear and nonlinear), ultrafast response time [16] and low two-photon absorption [17]. Germanium antimonite-based glasses have been applied in photonics devices and for optical fiber production due to their advantages over silicate and borate glasses, such as low glass transition temperature (T_g), low softening temperature [18], high thermal expansion coefficients [18] and large transparency windows from ultraviolet to near infrared regions (up to $4\text{ }\mu\text{m}$) [19,20]. Glasses containing high concentrations of antimony are not good hosts for RE ions, and are usually present in combination with other oxides, such as Ga_2O_3 , Al_2O_3 , B_2O_3 or GeO_2 which helps the addition of RE ions into the matrix.

In this work, GeO_2 was combined with SbPO_4 in order to obtain their physical and chemical properties in one material, taking advantage of the higher RE solubility of GeO_2 -based glasses with large near-infrared transparency window ($0.4\text{--}6\text{ }\mu\text{m}$), high thermal stability against crystallization and excellent chemical durability [21]. Antimony- and lead-germanate glasses are good alternatives to tellurite glasses for near infrared applications, as both present similar phonon energies and infrared cut-off wavelengths, large thermal stability against crystallization and high glass transition temperatures [21,22].

In summary, this work aims to study the photoluminescence in this new binary glass system based on $\text{SbPO}_4\text{--GeO}_2$ compositions co-doped with Er^{3+} and Yb^{3+} ions. The dependence of the visible and infrared emissions on Yb^{3+} concentration was investigated by visible up-conversion, infrared luminescence and decay time studies. Probable luminescence mechanisms are also proposed. From a fundamental point of view, the study of RE-ions doped antimony glasses are important as these glasses cannot support large amounts of RE ions. In addition, it is worth noting the potential of this composition for optical fiber production when co-doped with $\text{Yb}^{3+}/\text{Er}^{3+}$ ions, due to the high thermal stability against crystallization and high viscosity of the glass host.

2. Experimental

Glass samples were synthesized using a conventional melt-quenching method. The starting materials were germanium oxide, GeO_2 (Alfa Aesar 99.999% pure), and antimony orthophosphate, SbPO_4 (prepared as described in Ref. [11]), while RE ions were supplied using ytterbium oxide, Yb_2O_3 (99.9% pure), and erbium oxide, Er_2O_3 (99.99% pure). Raw materials were stoichiometrically measured to yield 7 g of a glass with molar composition $40\text{SbPO}_4\text{--}60\text{GeO}_2$, then mixed and loaded in a platinum crucible. The batch was melted at $1100\text{ }^\circ\text{C}$ for 40 min under air, ensuring complete elimination of adsorbed gases and good homogenization. The melt was cooled in a preheated stainless steel mould at $20\text{ }^\circ\text{C}$ below T_g , then annealed at this temperature for 2 h and slowly cooled to room temperature to minimize residual internal stress. Polished bulk glass samples were used for optical characterizations. The glass host was labeled as SG for better readability, and the samples prepared in this work are listed in Table 1.

Characteristic temperatures (T_g for glass transition and T_x for the onset of crystallization) were obtained using differential scanning calorimetry (DSC) at $300\text{--}800\text{ }^\circ\text{C}$ under N_2 at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$, using a NETZSCH Equipment DSC 404 F3 Pegasus calorimeter, with a maximum error of $\pm 2\text{ }^\circ\text{C}$ for T_g and T_x . Thermal stability against crystallization was evaluated from the stability parameter $\Delta T = T_x - T_g$.

Table 1
 Er^{3+} and Yb^{3+} co-doped SG prepared glass samples.

Sample label	Rare-earth ions concentration (mol%)		$\text{Er}^{3+}/\text{Yb}^{3+}$ conc. ratio
	Er_2O_3	Yb_2O_3	
SG01	0.10	—	—
SG01-04	0.10	0.40	0.25
SG02	0.20	—	—
SG02-03	0.20	0.30	0.66
SG03	0.30	—	—
SG03-02	0.30	0.20	1.5
SG04	0.40	—	—
SG04-01	0.40	0.10	4.0

Raman scattering spectra were acquired at room temperature in the frequency range from 100 to 1500 cm^{-1} using a HORIBA Jobin Yvon model LabRAM HR micro Raman apparatus equipped with a 632.8 nm laser of 30 mW power.

2.1. Absorption and photoluminescence measurements

Absorptions measurements were performed on the polished SG bulk glasses with $\sim 1.8\text{ mm}$ thickness from 200 to 1800 nm using a Varian Cary 5000 spectrophotometer. Linear refractive indices were obtained from polished bulk samples using prism coupling technique at 532.4 , 632.8 and 1550 nm . For a reliable comparison between the luminescence spectra between different samples, the glasses were ground and sieved to obtain similar grain size distributions from 0.063 to 0.045 mm for all samples. The emission spectra were recorded using a Spectra Pro 300i spectrometer equipped with an InGaAs detector from 800 to 1700 nm with a photomultiplier tube to collect the up-conversion emissions in the visible region. A diode laser operating at 980 nm coupled with a standard multimode fiber ($50\text{ }\mu\text{m}$ core diameter) was used as the excitation source, with variable pump power of $100\text{--}500\text{ mW}$. Photoluminescence measurements were performed at room temperature and corrected by the instrumental response. Erbium lifetime decay in the infrared region was determined from the fluorescence decay of the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition using a Fluorog 3 Horiba (Jobin Yvon Co.) equipped with a pulsed xenon lamp of 450 W and a germanium detector from 950 to 1700 nm . The sample holder used for luminescence measurements had an elliptical shape of $10\text{ mm} \times 5\text{ mm}$, and 1 mm depth, and was positioned 30° relative to the detectors. In this way, by using the same powder glass volume and grain size distribution, we expect similar scattering of the excitation light for all samples, giving more reliability to compare emissions intensities among different glass samples. Photoluminescence quantum yield (PLQY) of the samples was evaluated upon laser excitation at 930 nm line from a tunable Ti:Sapphire laser with a power of 510 mW coupled to an optical spectrum analyzer and an integrating sphere, by using an absolute method [23,24].

3. Results and discussion

Colorless undoped samples and slightly pink doped samples were obtained from the binary $40\text{SbPO}_4\text{--}60\text{GeO}_2$ glass system. Homogeneous samples without bubbles and crystallites were produced. The maximum amount of RE oxides accepted by the binary system $60\text{SbPO}_4\text{--}40\text{GeO}_2$ to avoid devitrification is $0.5\text{ mol\%}$. Above this concentration the samples easily crystallize, enabling the production of bulk glass. Thus, the highest RE oxide concentration used was in consideration of the total amount of Er_2O_3 and Yb_2O_3 , as related in Table 1.

DSC curves for SG undoped and SG doped (SG04-01) samples are shown in Fig. 1. The characteristics temperatures T_g , T_x and ΔT are unchanged at 410 °C, 610 °C and 200 °C, respectively, even when the RE oxide concentration is at its maximum (0.5 mol%), showing that low concentrations of dopant not cause glass structural modification. It is worth noting that the value of the thermal stability parameter against crystallization is comparable with those found in tellurites [9], lead germanates [22] and phosphates glasses [12], making 40SbPO₄-60GeO₂ a promising candidate for optical fiber production and optical applications. Moreover, the fact that this antimony-containing glass can accept certain amounts of RE ions, unusual behavior for this type of glass, means it can be used for many photonics applications.

Raman spectra for SG, SG04-01 and SG01-04 glass samples are shown in Fig. 2, which exhibit several Raman features used to evaluate the structural dependence of composition as a function of RE oxide concentration. As expected, any strong structural changes are observed at low concentrations of dopants. All samples showed a weak broad band from 900 to 1300 cm⁻¹ assigned to asymmetric and symmetric stretching of O–P–O bridges associated with orthophosphate tetrahedral units linked by the oxygen in SbPO₄ and GeO₂ units [25]. Another weak band at ~850 cm⁻¹ is assigned to the Ge–O–Ge asymmetric stretching of GeO₄ units. The region from 500 to 700 cm⁻¹ is assigned to the overlap of GeO₄ (Ge–O–Ge at 600 cm⁻¹), PO₄ and SbO₄ tetrahedral units (symmetric bending of SbO₄ at 546 cm⁻¹) bands. The most intense band centered at ~450 cm⁻¹ is assigned to the Ge–O–Ge symmetric stretching of six-member rings of GeO₄ tetrahedral units [26], overlapping with the band at ~460 cm⁻¹ assigned to the asymmetric bending of PO₄ units. A shoulder observed at ~320 cm⁻¹ is assigned to a group of vibration modes present in SbPO₄ [26].

Similar to the thermal behavior, no changes are observed in the linear refractive indices n_0 , as a function of Er₂O₃ and Yb₂O₃ ion concentration. The refractive indices at 532.4 nm, 632.8 nm and 1550 nm were 1.73, 1.72 and 1.69, respectively, regardless the amount of dopant.

Fig. 1. Differential scanning calorimetric curves (DSC) of SG (undoped) and SG04-01 glass samples.

Fig. 2. Raman spectra of SG (undoped), SG01-04 and SG04-01 glass samples.

Absorptions spectra of the SG undoped and SG-doped glass samples are shown in Fig. 3. The RE absorption bands originate from electronic transitions of Er³⁺ and Yb³⁺ ions from their fundamental levels to excited ones. Erbium ions have bands close in energy, and for an accurate investigation of the up-conversion mechanism, the excitation light was focused on the surface of the powdered samples to ensure similar light scattering from all glass samples (same grain size distribution), and then reducing re-absorption of the emitted photons by ground state Er³⁺ ions.

The transitions of Er³⁺ ions are labeled in the inset of Fig. 3, considering the absorptions from the ⁴I_{15/2} ground state level to the ⁴G_{11/2} at 390 nm, ⁴F_{7/2} at 490 nm, ²H_{11/2} at 521 nm, ⁴S_{3/2} at 546 nm, ⁴F_{9/2} at 652 nm, ⁴I_{9/2} at 800 nm, ⁴I_{11/2} at 980 nm and to ⁴I_{13/2} at 1550 nm. The absorption at 980 nm is assigned to Yb³⁺ ion absorption from the ²F_{7/2} ground state to the ²F_{5/2} excited state.

3.1. Visible up-conversion emissions of Er³⁺ doped and Er³⁺/Yb³⁺ co-doped SG glasses

Visible up-conversion emissions were weakly detected in the green (500–600 nm) and red (620–700 nm) regions for single Er³⁺ doped SG samples, with very low signal/noise ratios even under excitation power of 500 mW. The weak visible emissions intensities of the single doped samples are related to the low absorption cross section at 980 nm of Er³⁺ ions. These emissions are explained by the successive absorptions of one or more 980 nm photons, leading the electron population to higher energy levels. In order to increase the visible emissions intensities, Er³⁺/Yb³⁺ co-doped glass samples were prepared and labeled SG01-04, SG02-03, SG03-02 and SG04-01, as shown in Table 1.

Fig. 4(a) show the visible up-conversion spectra for the co-doped samples. The green emissions are attributed to bands centered at 544 nm and 522 nm, assigned to the ⁴S_{3/2} → ⁴I_{15/2} and ²H_{11/2} → ⁴I_{15/2} transitions, respectively. For the red emission, a large band centered at 652 nm is attributed to the ⁴F_{9/2} → ⁴I_{15/2}

Fig. 3. Absorption spectra of SG, SG04 and SG01-04 glass samples. Er^{3+} and Yb^{3+} excited levels are labeled, considering absorptions from the ground states $^4\text{I}_{15/2}$ and $^2\text{F}_{5/2}$, respectively.

transition. Both emissions are broad due to the inhomogeneous broadening characteristic of amorphous materials and Starks splitting.

According to Fig. 4(a), the highest visible intensity occurred in

the sample containing 0.2 mol% of Er^{3+} and 0.3 mol% Yb^{3+} . For an efficient interaction between Yb^{3+} and Er^{3+} ions, one emitter ion have to be sensitized by two sensitizer ions (Yb^{3+}). For the highest Er^{3+} and lowest Yb^{3+} concentrations (SG03-02 and SG04-01),

Fig. 4. (a) Visible up-conversion emissions spectra of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped SG glasses (SG-01-04, SG-02-03, SG-03-02 and SG-04-01) from 500 to 720 nm under 980 nm excitation; and (b) up-conversion emission spectra of SG-02-03 glass sample under 980 nm excitation with pump power of 100–500 mW.

insufficient energy transfer from Yb^{3+} to Er^{3+} decreases the radiative emissions as erbium ions weakly absorb 980 nm light. In the case of sample SG01-04, due to the low concentration of Er^{3+} ions, they are placed far away from the sensitizer ion (Yb^{3+} ions), leading to an inefficient interaction between them that weakens the up-conversion emissions. High intensity up-conversion emissions were observed in SG-02-03, as shown in Fig. 4(b). The visible emissions intensities increase as a function of excitation power, and the assigned transitions are shown in Fig. 4.

Infrared lifetime decay times were calculated with a first order exponential fitting of SG-02 and SG-02-03 spectra obtained by excitation at 520 nm while monitoring the 1550 nm emission. The lifetimes were 5.3 and 5.7 ms respectively, which are comparable with values obtained from silicate [27], fluoride [28] and tellurite [29] glass compositions.

To better understand the involved up-conversion mechanisms, the dependence of the integrated band intensities for each visible emission as a function of pump power is plotted in Fig. 5. Generally speaking, in up-conversion processes the emission intensity I_{UC} is proportional to I_{ex}^n , where I_{ex} is the intensity of the infrared excitation, and n is the number of infrared photons absorbed per visible photon emitted [30], which is determined from the slope obtained by the linear fit of $\log(I_{UC})$ vs. $\log(I_{ex})$. Fig. 5 shows the logarithmic plots of I_{UC} vs. I_{ex} for the three emissions, showing good linear adjustments with the experimental values for all wavelengths

Fig. 5. Visible up-conversion emission intensities as a function of excitation power at 980 nm for SG02-03.

($R = 0.998$). The number of involved photons for green (522 and 544 nm) and red (652 nm) emissions for the SG-02-03 sample are 1.81, 1.74 and 1.72, respectively. From these results, the proposed up-conversion mechanism indicates an average of two photons involved in the frequency up-conversion process. While we expect a two-photon process, these lower values indicate a temperature dependence of the emitter levels of Er^{3+} . The temperature was increased by the excitation light, owing to the relatively high power used for the luminescence measurements.

Three possible up-conversion mechanisms for $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped SG glasses are by excited state absorption (ESA), energy transfer (ET) and cross-relaxation (CR) [31]. Fig. 6 shows the energy level diagram of Er^{3+} and Yb^{3+} as well as the possible mechanisms involved. For green emissions, a two-step up-conversion mechanism may occur. (a) First, the Er^{3+} excited state $^4I_{11/2}$ level is directly excited with 980 nm pump light from the ground state $^4I_{15/2}$ (GSA) and also by energy transfer (ET) from the Yb^{3+} excited state $^2F_{5/2}$,

Fig. 6. Energy level diagram of Er^{3+} and Yb^{3+} ions under excitation at 980 nm.

Fig. 7. Infrared emission spectra for (a) SG02 and SG02-03 glass samples under excitation at 980 nm; and (b) normalized emission spectra around of SG02 and SG02-03 glass samples under excitation at 980 nm.

due to the absorption of 980 nm photons by the ground state $^2F_{7/2}$ level: $^2F_{5/2}(\text{Yb}^{3+}) + ^4I_{15/2}(\text{Er}^{3+}) \rightarrow ^2F_{7/2}(\text{Yb}^{3+}) + ^4I_{11/2}(\text{Er}^{3+})$. Note that ET from Yb^{3+} to Er^{3+} ions is prevalent over the direct excitation of $^4I_{11/2}$ level of Er^{3+} , due to the large absorption cross-section of Yb^{3+} than Er^{3+} ions at 980 nm; (b) second, the excitation processes involving electrons at $^4I_{11/2}$ (Er^{3+}) excited state by different mechanisms: (i) by ESA, where the excited Er^{3+} ion absorbs a second 980 nm photon, raising the electrons to the highest energy level $^2F_{7/2}$ of Er^{3+} ions: $^4I_{11/2}(\text{Er}^{3+}) \rightarrow ^4F_{7/2}(\text{Er}^{3+})$; and (ii) by energy transfer (ET), where excited Yb^{3+} ions ($^2F_{5/2}$ level) transfer this energy to Er^{3+} ions, promoting their excited electrons from $^4I_{11/2}$ to $^4F_{7/2}$: $^2F_{5/2}(\text{Yb}^{3+}) + ^4I_{11/2}(\text{Er}^{3+}) \rightarrow ^2F_{7/2}(\text{Yb}^{3+}) + ^4F_{7/2}(\text{Er}^{3+})$. Then, the excited electrons in the $^4F_{7/2}$ level relax through matrix multiphonon processes to drop to the energy level $^2H_{11/2}$, emitting at 522 nm by a radiative energy decay to the ground state $^4I_{15/2}$: $^2H_{11/2}(\text{Er}^{3+}) \rightarrow \text{green emission} + ^4I_{15/2}(\text{Er}^{3+})$; and at 544 nm by a non-radiative decay from $^2H_{11/2}$ to $^4S_{3/2}$ and then radiative decay to the ground level: $^4S_{3/2}(\text{Er}^{3+}) \rightarrow \text{green emission} + ^4I_{15/2}(\text{Er}^{3+})$.

For green emissions, a CR mechanism may occur in excited Yb^{3+} ($^2F_{7/2} + h\nu_{980\text{nm}} \rightarrow ^2F_{5/2}$) and Er^{3+} ions, promoting the latter to the $^4I_{11/2}$ excited state. The 980 nm photon absorbed by Er^{3+} ($^4I_{15/2}$

$+ h\nu_{980\text{nm}} \rightarrow ^4I_{11/2}$) then promotes the electrons to the $^4F_{7/2}$ level, followed by a multiphonon relaxation to luminescent Er^{3+} levels $^2H_{11/2}$ ($^4F_{7/2} \rightarrow \text{multiphonon relaxation} + ^2H_{11/2} \rightarrow \text{green emission} + ^4I_{15/2}$) and $^4S_{3/2}$ ($^4F_{7/2} \rightarrow \text{non-radiative decay} + ^4S_{3/2} \rightarrow \text{green emission} + ^4I_{15/2}$), giving green emissions at 522 and 544 nm, respectively.

The relative populations in the emitting Er^{3+} levels $^2H_{11/2}$ and $^4S_{3/2}$ are temperature dependent as $k_B T$, where k_B is the Boltzmann constant and T the absolute temperature, reflecting on the intensity ratio between the two green emissions at 522 and 544 nm. The red emission is obtained when the $^4F_{9/2}$ energy level of Er^{3+} ions is populated and radiative decays to the ground $^4I_{15/2}$ level, emitting 652 nm light in two possible ways: (i) Yb^{3+} and Er^{3+} ions are simultaneously excited to the $^2F_{5/2}$ and $^4I_{11/2}$ levels, respectively, by absorption of 980 nm photons. In turn, the electrons of Er^{3+} undergo non-radiative decay as $^4I_{11/2} \rightarrow ^4I_{13/2} + \text{non-radiative process}$. Then, the $^4F_{9/2}$ level can be populated by absorption of one more 980 nm photon or by energy transfer from Yb^{3+} ions at excited state: $^2F_{5/2}(\text{Yb}^{3+}) + ^4I_{13/2}(\text{Er}^{3+}) \rightarrow ^2F_{7/2}(\text{Yb}^{3+}) + ^4F_{9/2}(\text{Er}^{3+}) + \text{ET}$. The $^4F_{9/2}$ level can also be occupied by non-radiative

Fig. 8. Bar graph relating the IR emission intensities at different pump powers (100–500 mW) for the $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped glass samples.

Fig. 9. Infrared emission spectra from 1400 to 1700 nm of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped $\text{SbPO}_4\text{-GeO}_2$ glasses under excitation at 980 nm, varying the excitation power from 100 to 500 mW.

Fig. 10. Absolute photoluminescence spectra of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped SG02-03 sample up on 980 nm excitation with an excitation power of 510 mW under A, B and C conditions. Condition A: An incident photons collected with OSA without the sample; condition B: An emitted photons collected when the sample is placed inside an integrating sphere and the laser beam is incident on the sample with diffused light; condition C: An emitted photons collected when the sample with in an integrating sphere and the laser beam is directed on it.

decay from $^4\text{S}_{3/2}$, contrary to what occurs for green emissions at 544 nm (assigned to the $^4\text{S}_{3/2}$ energy level), where a non-radiative process occurs as $^4\text{F}_{9/2}(\text{Er}^{3+}) \rightarrow ^4\text{I}_{15/2}(\text{Er}^{3+}) + \text{red emission}$. The red emission at 652 nm has a higher intensity compared to the green emission due to the preferable non-radiative decay from the $^4\text{S}_{3/2}$ and $^2\text{H}_{11/2}$ excited levels to $^4\text{F}_{9/2}$, followed by a radiative decay to the Er^{3+} ground state level.

3.2. Infrared emission

For optimized applications, the most important emission of Er^{3+} occurs in the IR region (at 1550 nm), which can be used for optical amplifier applications. Indeed, erbium doped glass matrixes have been extensively studied due to their broad IR emissions which cover all telecom wavelengths located along the 3rd telecom window. For Er^{3+} ions, the luminescence from the excited $^4\text{I}_{13/2}$ state to the ground $^4\text{I}_{15/2}$ state results in a broad band centered at approximately 1550 nm. Similarly for visible up-conversion emission behavior, the presence of Yb^{3+} ions enhances the IR emission intensity at 1538 nm, as exemplified in Fig. 7(a) for samples SG02 and SG02-03 when excited at 980 nm radiation of 300 mW. In this case, the center IR band (1538 nm) almost doubles in intensity when co-doped with Yb^{3+} .

Among the $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped samples, regardless the excitation power, the enhanced emission intensity is also prominent in SG-02-03 as shown in Fig. 8, which was chosen for further infrared luminescence studies.

Fig. 9 shows the IR emissions spectrum for SG02-03 at 1400–1700 nm, varying the excitation power from 100 to 500 mW. As expected, the emission intensity increases with pump power, and a broadening of the full width half maximum (FWHM) from 41 to 61 nm is observed, which is related to the excitation power and the sensitization of Yb^{3+} co-doping Er^{3+} in antimonite germanium-phosphate glasses.

The infrared emissions spectra for SG02 and SG02-03 are presented together in Fig. 7(b) for better comparison of the FWHM and relative luminescence intensities. $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped samples show a slightly broader band with FWHM = 61 nm, due to Yb^{3+} ions acting as sensitizers and absorbing 980 nm photons more

efficiently than Er^{3+} ions, transferring energy to Er^{3+} and enhancing the emission at 1538 nm, as previously shown in Fig. 6.

In order to gain more insight in the spectroscopic properties of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped $\text{SbPO}_4\text{-GeO}_2$ glasses, Judd–Ofelt modeling was performed by using the absorption spectrum of SG02-03 (shown in Fig. 3). The experimental oscillator strength f_{exp} for the Er^{3+} transitions were calculated from the integrated area of the absorption bands as $f_{\text{exp}} = 4.31 \times 10^{-9} \int \epsilon(\nu) d\nu$, where $\epsilon(\nu)$ is the molar extinction coefficient at the corresponding frequency ν (cm^{-1}). Judd–Ofelt parameters [32,33] Ω_2 , Ω_4 and Ω_6 were determined as 5.58×10^{-20} , 1.30×10^{-20} and $6.14 \times 10^{-21} \text{ cm}^2$, respectively, similar to those found in other phosphate glasses [34]. The radiative lifetime (τ_r) of the $^4\text{I}_{13/2}$ level was calculated from the Judd–Ofelt parameters and the experimental value (τ_f) was estimated around 9.7 ms.

Absolute photoluminescence spectra of the Yb^{3+} and Er^{3+} co-doped SG02-03 sample up on 930 nm laser excitation is shown in Fig. 10. The photoluminescence quantum yield of Er^{3+} ion and Yb^{3+} ion found to be 32% and 37%, respectively, for the best sample (SG02-03). The higher PLQY for Yb^{3+} due to in-band pumping that compared to the Er^{3+} (out of the band), as the Er^{3+} has no resonant absorption at the pumping wavelength. The obtained PLQY for Er^{3+} is due to the energy transfer from Yb^{3+} to Er^{3+} . This low PLQY can be explained by the fact that the glasses synthesized under ambient atmosphere which increases the free OH^- vibrations in the structure thus favoring non-radiative processes. To achieve high PLQY (close to unity) and low background absorption, the synthesis can be performed under controlled N_2 atmosphere, and also the usage of purified starting materials. Future work will focus on the synthesis of low OH^- content purified glasses can be investigated for laser cooling applications.

4. Conclusions

In this work we obtained Er^{3+} doped and $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped antimonite germanium-phosphate glasses with composition $\text{SbPO}_4\text{-GeO}_2$ by using melt quenching techniques. Despite the difficulties of incorporating RE ions into antimonite based glasses, our system featured enough RE ions to obtain luminescence and to propose photonics applications according to the potential shown by these glass hosts. The luminescence in the visible and infrared ranges was evaluated using absorption and luminescence studies. Potential up-conversions processes involve ESA, ET and CR mechanisms.

We evaluated the influence of Yb^{3+} ions on the enhancement of infrared, green and red up-conversion emissions at 1538 nm, (522 and 544 nm) and 652 nm, respectively. The composition reported in this work indicates that this glass can be used to manufacture optical devices operating as optical amplifier into the telecom C-band. Due to the intense visible emissions, this new glass also has potential for use in many applications in photonics, such as solid-state laser materials to develop up-converting compact visible lasers. Another interesting point of view is that up-conversion materials emitting in the visible range by excitation at IR would be useful in high capacity data storage optical devices, bar-code reading, laser printing, biomedical instruments and temperature sensing.

In general, the infrared and up-conversion emissions observed in $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped antimonite germanium-phosphate glasses are very interesting for an extended range of photonic applications, due to the efficient emission of RE ions in this matrix. In addition to the high thermal stability against crystallization and large transparent window, combined with the aforementioned luminescent properties, this composition is suitable for the production of optical fibers.

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References

- [1] B. Karmakar, R.N. Dwivedi, *J. Non-Cryst. Solids* 342 (2004) 132.
- [2] S.F.H. Correia, V.Z. Bermudez, S.J.L. Ribeiro, P.S. André, R.A.S. Ferreira, L.D. Carlos, *J. Mater. Chem. A* 2 (2014) 5580.
- [3] L.A. Gomez, L.D. Menezes, C.B. de Araújo, R.R. Gonçalves, S.J.L. Ribeiro, Y. Messaddeq, *J. Appl. Phys.* 107 (2010), 113508–113508-5.
- [4] A. Chiasera, M. Montagna, C. Tosello, S. Pelli, G.C. Righini, M. Ferrari, L. Zampedri, A. Monteil, P. Lazzeri, *Opt. Mater.* 25 (2004) 117.
- [5] M. Li, G. Bai, Y. Guo, L. Hu, J. Zhang, *J. Lumin.* 132 (7) (2012) 1830.
- [6] A.F. Obaton, C. Labbé, P. Le Bsoulanger, B. Elouadi, G. Boulon, *Spectrochim. Acta, Part A* 55 (1999) 263.
- [7] G.E. Malashkevich, V.N. Sigaev, N.V. Golubev, V.I. Savinkov, P.D. Sarkisov, I.A. Khodasevich, V.I. Dashkevich, A.V. Mudryi, *J. Non-Cryst. Solids* 357 (2011) 67.
- [8] I. Jlassi, H. Elhouichet, M. Ferid, C. Barthou, *J. Lumin.* 130 (2010) 2394.
- [9] D. Manzani, J.L. Ferrari, F.C. Polachini, Y. Messaddeq, S.J.L. Ribeiro, *J. Mater. Chem.* 22 (2012) 16540.
- [10] D. Manzani, C.B. de Araújo, G. Boudebs, Y. Messaddeq, S.J.L. Ribeiro, *J. Phys. Chem. B* 117 (2013) 408.
- [11] M. Nalin, M. Poulain, S.J.L. Ribeiro, Y. Messaddeq, *J. Non-Cryst. Solids* 284 (2001) 110.
- [12] E. Mura, J. Lousteau, D. Milanese, S. Abrate, V.M. Sglavo, *J. Non-Cryst. Solids* 362 (2013) 147.
- [13] R. Praveena, V. Venkatramu, P. Babu, C.K. Jayasankar, *Phys. B* 403 (2008) 3527.
- [14] P. Petkova, M.T. Soltani, S. Petkov, J. Tacheva, V. Nedkov, *Phys. Scr.* T149 (2012) 014057.
- [15] D. Dorosz, J. Zmojd, M. Kochanowicz, *Opt. Mater.* 35 (2013) 2577.
- [16] E.L. Falcao, C.A.C. Bosco, G.S. Maciel, C.B. Araujo, M. Nalin, Y. Messaddeq, *Appl. Phys. Lett.* 83 (2003) 1292.
- [17] E.L. Falcão-Filho, C.B. de Araújo, C.A.C. Bosco, G.S. Maciel, L.H. Acioli, M. Nalin, Y. Messaddeq, *J. Appl. Phys.* 97 (2005) 013505.
- [18] M. Nalin, Y. Messaddeq, S.J.L. Ribeiro, M. Poulain, V. Briois, G. Brunklaus, C. Rosenhahn, B.D. Mosel, H. Eckert, *J. Mater. Chem.* 14 (2014) 3398.
- [19] R.K. Brown, *J. Non-Cryst. Solids* 263&264 (2000) 1.
- [20] J.H. Campbell, T.I. Suratwala, *J. Non-Cryst. Solids* 263&264 (2000) 318.
- [21] H. Takahashi, I. Sugimoto, *J. Light. Technol.* 5 (1984) 613.
- [22] H.T. Munasinghe, A. Winterstein-Beckmann, C. Schiele, D. Manzani, L. Wondraczek, S. Afshar, T.M. Monro, H. Ebendorff-Heidepriem, *Opt. Mater. Express* 3 (9) (2013) 1488.
- [23] J.C. de Mello, H.F. Wittmann, R.H. Friend, An improved experimental determination of external photoluminescence quantum efficiency, *Adv. Mater.* 9 (1997) 230.
- [24] E.S. de Lima Filho, K. Venkata Krishnaiah, Y. Ledemi, Y.-J. Yu, Y. Messaddeq, G. Nemova, R. Kashyap, Ytterbium-doped glass-ceramics for optical refrigeration, *Opt. Express* 23 (2015) 4630.
- [25] G.S. Henderson, R.T. Amos, *J. Non-Cryst. Solids* 328 (2003) 1.
- [26] E.I. Kamitsos, Y.D. Yiannopoulos, M.A. Karakassides, G.D. Chryssikos, H. Jain, *J. Phys. Chem.* 100 (1996) 11755.
- [27] Z. Wei, F. Chen, Y. Tian, S. Xu, *Opt. Commun.* 315 (2014) 199.
- [28] F. Huang, L. Hua, D. Chena, *Ceram. Int.* 41 (2015) 189.
- [29] S. Hocde, S. Jiang, X. Peng, N. Peyghambarian, T. Luo, M. Morrell, *Opt. Mater.* 25 (2004) 149.
- [30] D.C. Yeh, W.A. Sibley, M. Suscavage, M.G. Drexhage, *J. Appl. Phys.* 62 (1987) 266.
- [31] F. Auzel, *Chem. Rev.* 104 (2004) 139.
- [32] B.R. Judd, *Phys. Rev.* 127 (1962) 750.
- [33] G.S. Ofelt, *J. Chem. Phys.* 37 (1962) 511.
- [34] K. Ouannes, M.T. Soltani, M. Poulain, G. Boulon, G. Alombert-Goget, Y. Guyot, A. Pillonnet, K. Lebbou, *J. Alloy. Compd.* 603 (2014) 132.