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Effect of the ytterbium concentration on the upconversion luminescence of Yb^{3+}/Er^{3+} co-doped $PbO–GeO_2–Ga_2O_3$ glasses

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The effect of Yb^{3+} concentration on the frequency upconversion (UPC) of Er^{3+} in $PbO–GeO_2–Ga_2O_3$ glasses is reported for the first time. Samples were prepared with 0.5 wt% of Er_2O_3 and different concentrations of Yb_2O_3 (1.0–5.0 wt%). The green (523 and 545 nm) and red (657 nm) emissions are observed under 980 nm diode laser excitation. The dependence of the frequency UPC emission intensity upon the excitation power was examined and the UPC mechanisms are discussed. An interesting characteristic of these glasses is the increase of the ratio of red to green emission, through an increase of the Yb^{3+} concentration due to an efficient energy transfer from Yb^{3+} to Er^{3+}.

1. Introduction

Rare-earth doped materials have been widely investigated for photonic applications. Erbium doped glasses have been studied and used in a variety of photonic applications, such as infrared-to-visible upconversion (UPC) infrared lasers operating in the third telecommunication window [1], and color displays and sensors [2–5]. Nevertheless, efficient pumping of this system is limited by the low absorption cross-section of Er^{3+} around 980 nm that can be improved by co-doping the material with Yb^{3+} ions [6–8]. The important property of the Yb^{3+} ion is the spectral overlap between its emission band due to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition and the absorption band of Er^{3+} due to the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transitions; this overlap allows an efficient radiative energy transfer mechanism possible, that promotes Er^{3+} ions from the ground state to the $^4I_{11/2}$ and $^4F_{7/2}$ excited states. In a next energy-transfer mechanism, Er^{3+} ions are promoted to the $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ excited states from where upconversion luminescence at 523, 545 and 657 nm is obtained, respectively [9,10].

In recent years, hosts based on heavy-metal oxides have proven to be excellent materials due to their high mechanical resistance, high chemical durability and thermal stability, large transmission window (from the visible to the mid infrared region), high refractive index (~2), which is adequate for nonlinear effects, and low maximum phonon energy (400–800 cm^{-1}) compared to silicate, borate, and phosphate glasses [11,12]. This latter feature is related to low non-radiative relaxation rates and makes the upconversion easily observable. Normally for glasses with phonon energies above 1000 cm^{-1} the UPC luminescence is not observable. In this case, by using Yb^{3+} as a sensitizer, it is possible to measure the UPC luminescence.

It has been previously reported that an increase of the Yb^{3+} concentration considerably affects the red UPC intensity in several glasses [13,14], when compared to the green UPC intensity, due to the energy transfer between Yb^{3+} and Er^{3+}. In this work we report the same phenomenon for $PbO–GeO_2–Ga_2O_3$ (PGG) glasses. Studies related to PGG glasses doped with Er^{3+} ions have been previously reported in the literature [15]. In this case the authors presented a study of the spectroscopy properties for optical amplifiers.

In this paper we present for the first time the effect of Yb^{3+} concentration on the frequency upconversion luminescence of Er^{3+} in PGG glasses. The preparation of the PGG glasses co-doped with Yb^{3+} and Er^{3+} is also described. The absorption and emission spectra in the visible range are presented and the dependence of the UPC emission intensity upon the excitation power is shown.

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2. Experimental

2.1. Preparation of glasses

To the base glass composition of PGG, 72.8PbO–17.0GeO_2–10.2Ga_2O_3 (in wt%), 0.5 wt% of Er_2O_3 and x wt% of Yb_2O_3 ($x = 0, 1, 2, 3, 4, 5$) were added and prepared by a conventional melting and quenching method. Batches of 7.0 g of high purity (99.999%) compounds were fully mixed in a platinum crucible and melted at 1200 °C for 1 h. The melts were then poured into pre-heated brass molds, in air, and annealed at 392 °C for 1 h. Finally the glasses were cooled to room temperature inside the furnace. After cooling, samples were polished to acquire an optical quality surface for absorption and emission measurements. Transparent and homogeneous glasses stable against crystallization were produced.

2.2. Measurement of optical properties

Optical absorption spectra were measured at room temperature in the 400-1700 nm range using a Varian Spectrophotometer. The visible UPC spectra were produced by optically pumping the sample with a high power diode laser emitting an average power of 7 W at 980 nm. The signal was dispersed by a monochromator and collected by a S-20 photomultiplier. All emission measurements were made at room temperature.

3. Results

3.1. Absorption spectra

The absorption spectra of the co-doped PGG glasses in the visible and near-infrared regions are presented in Fig. 1. The absorption bands are attributed to 4f–4f transitions of Er^{3+} from the ground state $^4I_{15/2}$ to the excited states. We observe seven peaks related to the absorption of Er^{3+} at: 490, 522, 545, 654, 800, 980 and 1532 nm. These absorption bands are related to the following transitions: $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$. The intense absorption band around 980 nm is also related to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} that overlaps the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition of the Er^{3+} ion. An enhancement of the intensity of this band is observed with increasing Yb_2O_3 concentration.

3.2. UPC fluorescence spectra

Fig. 2 shows the spectra of the UPC luminescence emission of Er^{3+}–Yb^{3+} co-doped PGG glasses. The emission bands centered at 523, 545, and 657 nm correspond to $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions, respectively. We measured five co-doped glasses and just one Er^{3+}-doped glass. As a result the increase of the Yb_2O_3 concentration resulted in an enhancement of the frequency UPC emission in the visible region. For all samples, the shapes of the spectra are similar and the red emission is stronger than the green one for the 5.0% of Yb_2O_3. This phenomenon was previously reported [13–14,16] and it is observed in other Er^{3+}/Yb^{3+} co-doped glasses pumped at 980 nm.

The tendency of the integrated intensity ratio (Fig. 3) shows that the red emission at 657 nm augments more than the green, at 557 nm, when the Yb_2O_3 concentration is increased. A similar behavior is observed when comparing the red emission with the emission at 523 nm. The emission at 523 nm increases less than at 545 nm, when the Yb_2O_3 concentration is increased, as can be observed in Fig. 2.

4. Discussion

4.1. Analysis of the frequency UPC mechanisms

The intensity of the frequency UPC luminescence is enhanced by the presence of the sensitizer Yb^{3+}. The incorporation of Yb^{3+} causes an increase of the green emissions because the Yb^{3+} ion absorbs light with the wavelength of 980 nm effectively. The relative integral intensities of the red (657 nm) and green emissions (545 nm) increase approximately 40 and 4 times, respectively, when the concentration is changed from 1.0 to 5.0 wt% of Yb_2O_3 (Fig. 2). These results shows that Yb^{3+} ions are playing a role in the energy transfer process and that the influence of Yb^{3+} in the red emission is more intense than in the green emission.

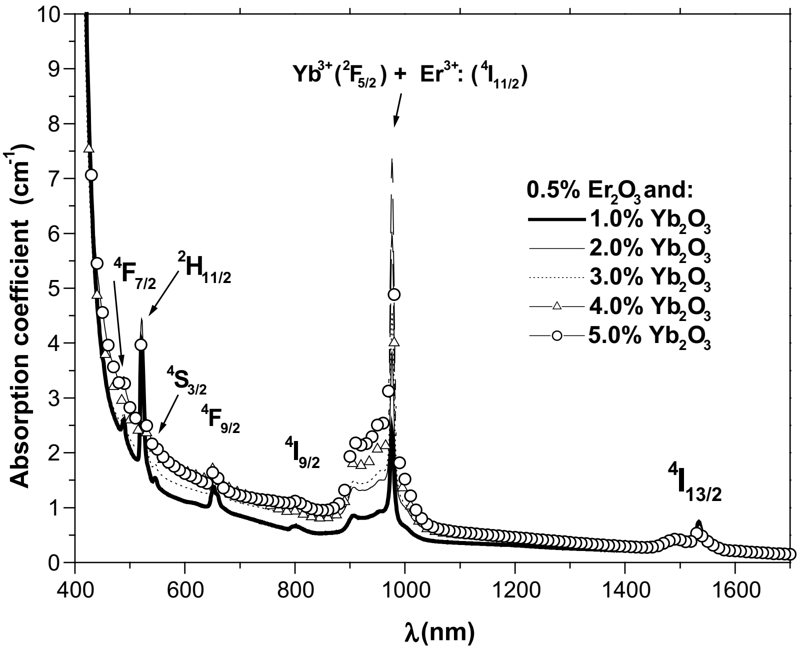

Fig. 1. Absorption spectra of Er^{3+}/Yb^{3+} co-doped PGG glasses at room temperature.

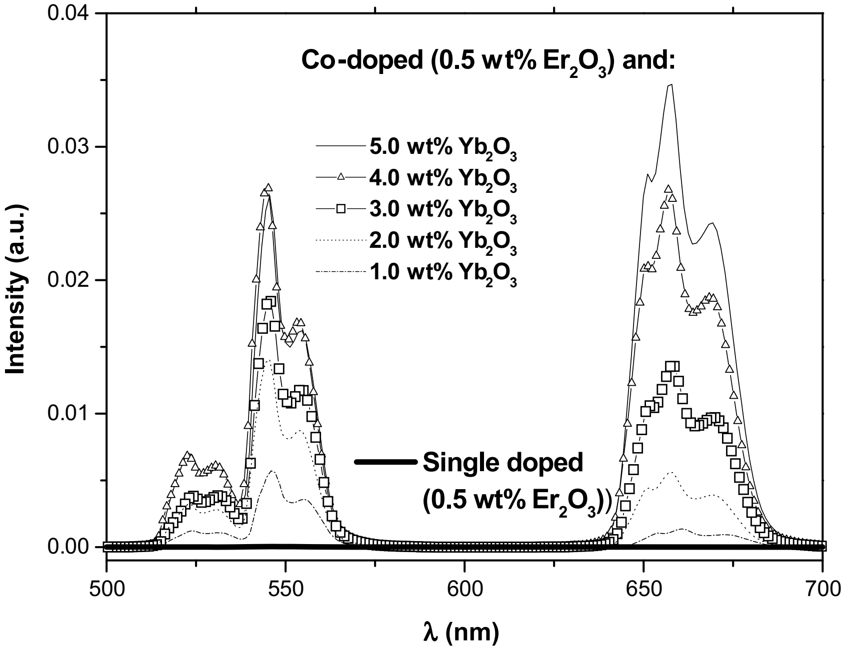

Fig. 2. Frequency UPC emission spectra of PGG glasses with different concentrations of Yb_2O_3 under 980 nm excitation.

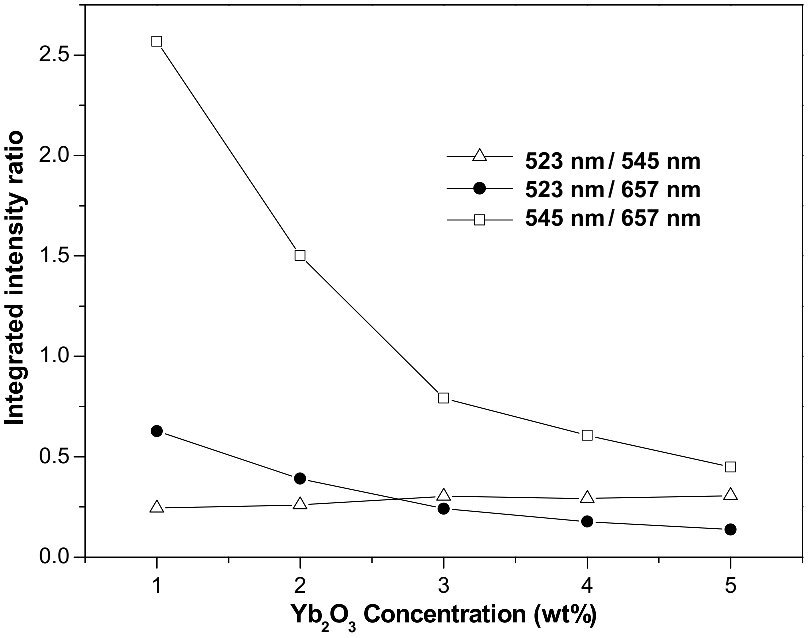

Fig. 3. Integrated intensity ratios as a function of Yb_2O_3 concentration in PGG glasses.

The UPC emission intensity, I_{UPC}, is proportional to the infrared pump power, I_{IR}, and this proportionality can be expressed as $I_{UPC} \propto I_{IR}^n$, where n represents the number of absorbed photons that are required to populate the emitting state [11,12]; it is determined from the slope of the line of intensity versus pump power in a log–log plot.

Fig. 4 presents the I_{UPC} of the 545 nm (Fig 4(a)) and 657 nm (Fig 4(b)) emission as a function of the pump excitation in a log–log plot. [11,12]. In all cases the slope is around 2, indicating that two photons are absorbed in the UPC process. Non-radiative process may participate in some cases and contribute to the decrease of the slope.

Fig. 5 presents the simplified energy level diagram of Er^{3+}/Yb^{3+}. The UPC processes of Er^{3+} doped glasses have been previously discussed [11,12]; in Er^{3+}/Yb^{3+} co-doped glasses the electronic population in $^4S_{3/2}$ and $^4F_{9/2}$ levels is accomplished through two successive energy transfers from Yb^{3+} ions as indicated in Fig. 5 by (1) and (2). Another possible channel for the electronic population of the $^4F_{9/2}$ level is indicated by (3) in Fig. 5 [13].

The green emissions are originated from the following process: the Yb^{3+} is excited from the $^2F_{7/2}$ level to the $^2F_{5/2}$ level under 980 nm pumping, and then transfers its energy to the Er^{3+} ion that is excited from the $^4I_{15/2}$ ground state to the $^4I_{11/2}$ excited state, and then promoted to the $^4F_{7/2}$ level (processes 1 and 2) [14]. After that,

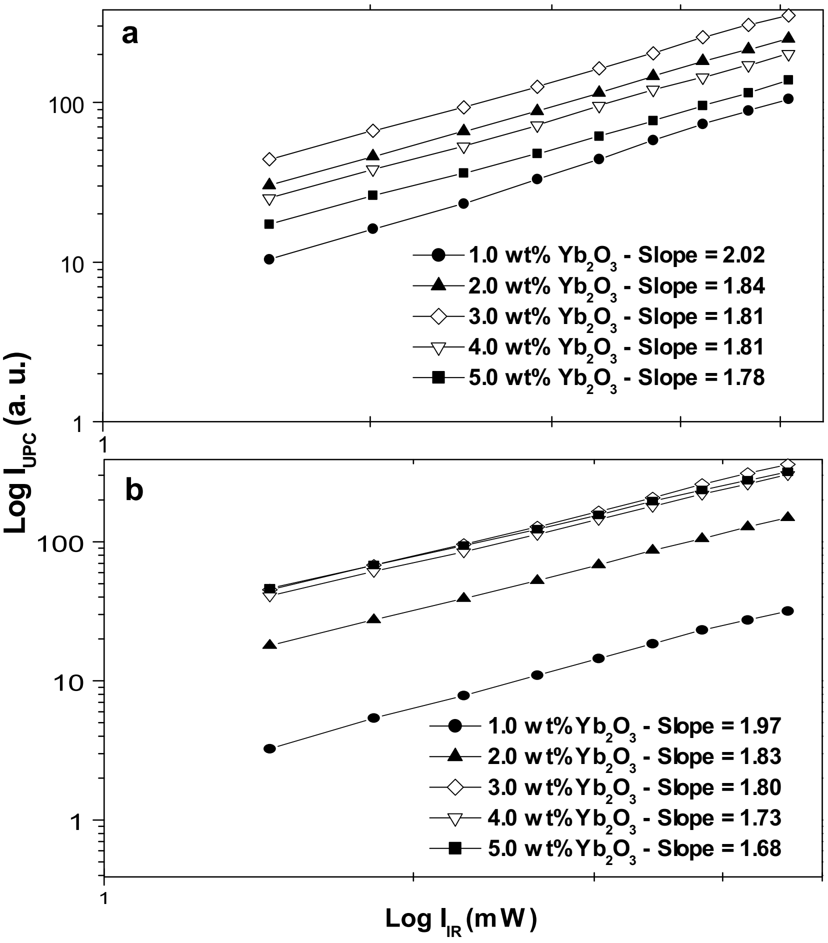

Fig. 4. UPC emission as a function of the pump power intensity for different Yb_2O_3 concentration in PGG glasses: (a) at 545 nm and (b) at 657 nm.

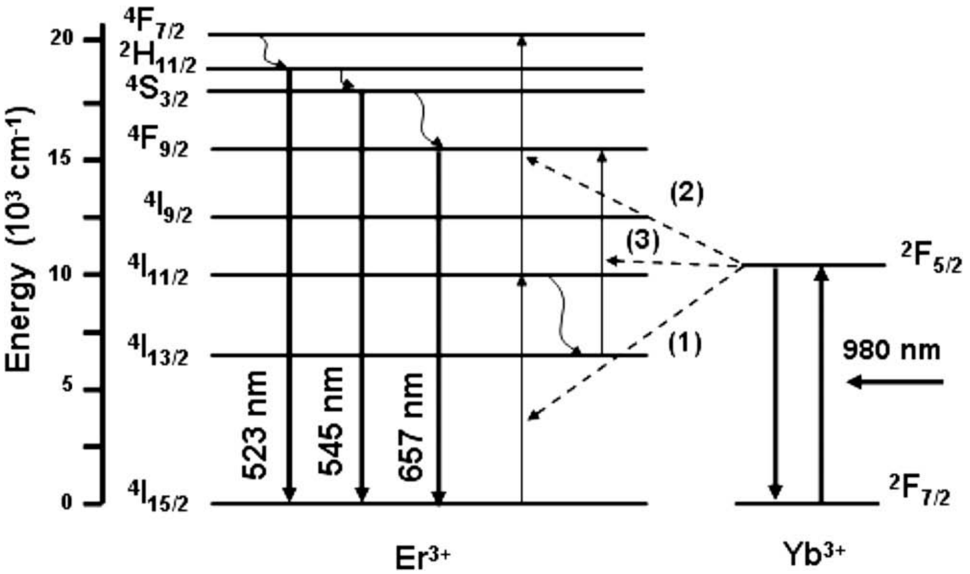

Fig. 5. Simplified energy level diagram of Er^{3+}/Yb^{3+} ions and possible UPC luminescence mechanisms for Er^{3+}/Yb^{3+} co-doped glasses [13]. Solid straight lines with upward and down arrows indicate pumping and UPC transitions, and radiative transitions, respectively; dot lines and wavy arrows denote energy transfer and non-radiative relaxation, respectively.

the Er^{3+} ion relaxes non-radiatively to the $^2H_{11/2}$ and $^4S_{3/2}$ levels and the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions occur, which are responsible for the green emissions, respectively. The red emission at 667 nm comes from the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. The population of the $^4F_{9/2}$ level is possible by two different channels. The first channel follows the processes 1 and 2 and then relaxes non-radiatively from the $^4S_{3/2}$ level to the $^4F_{9/2}$ level. The other channel is related to the $^4I_{13/2}$ level, populated by non-radiative relaxation after the process 1 from the $^4I_{11/2}$ excited state. The Er^{3+} ion in the $^4I_{13/2}$ level can be excited to the $^4F_{9/2}$ level (process 3) by the same energy transfer from Yb^{3+} mentioned above.

The experimental evidence of the enhancement of the red emission when compared to the green emission can be explained by this third energy transfer channel shown in Fig. 5.

The number of Er^{3+} ions in the $^4I_{11/2}$ level relaxing non-radiatively to the lower $^4I_{13/2}$ level are much greater than those excited to the upper $^4F_{7/2}$ level via the first channel. The much longer lifetime of $^4I_{13/2}$ state when compared with the lifetime of the $^4I_{11/2}$ state [7,15,17] makes the second channel dominant over the first one for the red emission. The green emission cannot be populated by the second channel (process 3).

Moreover, as mentioned before, the phonon energy also plays an important role and it can affect the UPC intensity: with the increase of the phonon energy in Er^{3+}/Yb^{3+} co-doped glasses the red emission increases more than the green by means of the second channel (process 3) [13]. The presence of Ga_2O_3 also contributes to the relative enhancement of the red emission when compared to the green, as previously reported [18].

The same phenomenon was previously observed for Er^{3+}/Yb^{3+} co-doped lead germanate oxyfluoride, lead telluride oxyfluoride, lead borate oxyfluoride glasses [13], silicate glasses [14] and lead telluride germanate glasses [19]. In all cases the intensity of both green and red emissions enhances with the increase of Yb^{3+} concentration and the red emission is always more affected than the green one. We remark that for silicate oxyfluoride glasses this effect is even more intense because, as explained before, the phonon energy is higher ($1100\ cm^{-1}$) when compared to germanate and telluride glasses ($700–800\ cm^{-1}$). For silicate oxyfluoride glasses with 2 mol% of Yb^{3+}, the red emission becomes higher than the green one.

5. Conclusions

We report for the first time on the enhancement of the Er^{3+} visible UPC in PGG glasses. The red emission is more influenced than the green emissions and this is attributed to the fact that the probability of Er^{3+} ions relaxing non-radiatively from the $^4F_{11/2}$ level to the lower $^4I_{13/2}$ level is much higher than the probability of upconversion to the upper $^4F_{7/2}$ level as a result of the longer lifetime of the $^4I_{13/2}$ level compared to the lifetime of the $^4I_{11/2}$ level, which makes the non-radiative relaxation $^4I_{11/2} \rightarrow {}^4I_{13/2}$ more easily to occur. Power dependent studies reveal that both green and red emissions are related to two-photon processes. The main characteristic of PGG glasses is its capacity of increasing the red emission compared to the green emission through an increase of the Yb^{3+} concentration. For Yb_2O_3 concentrations higher than 4 wt%, red emission dominates over green emission. The presence of Ga_2O_3 also contributes and favors the red emission. This effect expands the applications of this glass to other developments in photonic devices, like e.g. the study of red up-conversion lasers.

Acknowledgements

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