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Journal of Luminescence

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Frequency-conversion properties of Eu^{3+} doped chlorophosphate glass ceramics containing CaCl_2 nanocrystals

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ARTICLE INFO

Article history:

Received 28 June 2009

Received in revised form

12 April 2010

Accepted 22 September 2010

Available online 29 September 2010

Keywords:

Chlorophosphate glass

Glass ceramic

Frequency conversion

Upconversion

Photonics devices

ABSTRACT

Eu^{3+} ion doped chlorophosphate glass ceramics containing nanocrystals were successfully prepared, and their spectroscopic characterizations were done using absorption, excitation and emission spectra. For the crystallized samples, X-ray diffraction (XRD) and transmission electron microscopy (TEM) experiments evidenced the formation of CaCl_2 nanocrystals. The absorption and emission spectra investigations indicate that a considerable amount of Eu^{3+} ions was trapped in CaCl_2 nanocrystals, and therefore an efficient up- and down-frequency conversion was observed. The comparative spectroscopic studies of Eu^{3+} doped samples suggest that the investigated glass ceramics systems are potentially applicable as frequency-conversion photonics devices.

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1. Introduction

Glass ceramics containing rare earth ions have been one of the most interesting fields of research during the past decade, due to their potential application in optical devices such as photon upconversion materials and solid-state lasers [1–7]. Transparent glass ceramics are composite materials containing nanocrystallites with sizes less than 30 nm embedded in a glassy matrix [8–10]. The trapping of rare earth ions within the nanocrystallites can improve their optical properties and result in considerable enhancement of up and down-conversion intensities in the doped glass ceramics [4,5,11].

The trivalent europium ion Eu^{3+} is the most favored choice among the rare earth (RE) ions used to optically activate glass matrices. This is because Eu^{3+} ions have a narrow emission band, producing almost monochromatic light, and also long lifetimes of their optically active states [12–15].

The phosphate glasses, among various glass matrices, have several advantages over conventional silicate and borate glasses. These advantages come from their superior physical properties, such as high thermal expansion coefficient, low melting and softening temperatures, and high ultraviolet transmission [16–18].

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Furthermore, among the four (Li, Na, K and Ca) alkali elements for glass matrices, calcium phosphate glass shows the highest emission cross-sections and highest spectral intensity [19]. Phosphate glasses act as good hosts for large concentrations of dopant rare earth ions with good homogeneity [18]. The low phonon energy of the halide phosphate glasses yields low non-radioactive decay and high radiative emission rates of RE ion energy levels, leading to much higher quantum efficiencies [17,20,23]. Host materials with lower maximum phonon energies are generally desirable in order to achieve higher emission efficiencies.

There are, however, limited number of research reports on Eu^{3+} doped chlorophosphate glass and glass ceramics in the literature. Considering the above points, we were motivated to perform this work on the synthesis and study of the structural and frequency-conversion properties of Eu^{3+} doped chlorophosphate glass and glass ceramics.

2. Experimental

Eu^{3+} ion doped chlorophosphate glasses with composition in mol% of $45\text{P}_2\text{O}_5$, $14\text{Na}_2\text{HPO}_4$, 25CaCl_2 , 15NaCl and $1\text{Eu}_2\text{O}_3$ were prepared. All the raw materials were obtained from Merck. The batches of raw materials were melted at 1000°C for 1 h in a covered alumina crucible in the normal atmosphere. In order to obtain bubble-free glass and to ensure homogeneity, the liquids were

shaken at 20 min-intervals during melting. Incorporation of the alkali contents reduced the melting point and increased the stability of the glass. The molten mixtures were transferred into stainless steel molds to obtain cubic glass rods with 3 cm length and cross-sections with 0.7 cm side.

The heat treatment procedures for some of the samples were performed at temperatures higher than T_g and transparent glass ceramics samples were obtained. The Eu^{3+} :Glass ceramics that were annealed at 460 °C for 3 h have been designated in the text as Eu^{3+} :G-C 460, 3 h (or Eu^{3+} :G-C).

In order to investigate the crystallization and formation of nano-particles, an X'pert XRD spectrometer was used. For further structural analysis TEM (Leo AB 120 KV Zeiss) images were prepared. The TEM and selected area electron diffraction (SAED) images were performed for the Eu^{3+} :G-C sample. Jenway UV-vis spectrometers and a Jasco spectrofluorometer were used for absorption and frequency conversion spectroscopy studies. All the measurements were carried out at room temperature.

3. Results and discussion

XRD patterns of the glass samples represented no significant peak, indicating an amorphous structure. However, for the Eu^{3+} :G-C sample the expected peaks corresponding to the crystalline CaCl_2 structure were observed with the occurrence of crystallization (Fig. 1). Thus, glass ceramics containing CaCl_2 nanocrystals were obtained. Using Scherrer's formula, the size of the nanocrystals was evaluated to be about 20 nm.

Fig. 2 and the inset graphs show TEM and SAED images of the Eu^{3+} :G-C samples. The sizes of nanocrystals embedded in the glass matrix were found to be 5–20 nm. The size of observed nanocrystals agrees with that evaluated from XRD patterns. The associated SAED patterns for crystalline and glassy phases were also demonstrated.

The absorption spectra for Eu^{3+} :Glass and Eu^{3+} :G-C samples in the wavelength region 270–950 nm, which include transitions from the 7F_0 ground state, were illustrated in Fig. 3. The $^7F_0 \rightarrow ^5D_j$ ($j=1-4$) bands are spin forbidden and are hence very weak; $^7F_0 \rightarrow ^5L_6$ is spin allowed and is much stronger [12,13,21]. The absorption intensity of Eu^{3+} :G-C in comparison with the Eu^{3+} :Glass sample was increased up to 650 nm and was decreased in the 650–900 nm region. The changes in absorption intensities can be related to a new environment around the Eu^{3+} ions in the glass ceramic, which does not exist in the

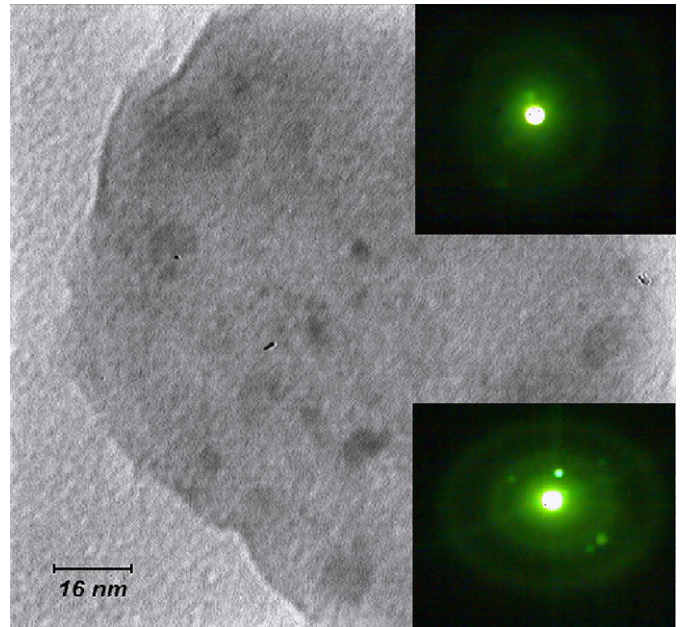


Fig. 2. TEM image of glass ceramic sample. Inset: SAED for glassy area (up) and for crystallized area (down).

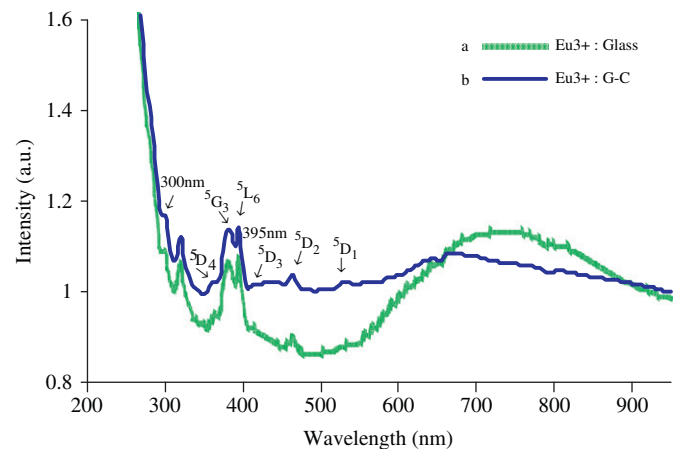


Fig. 3. Absorption spectra for Eu^{3+} doped glass and glass ceramics samples.

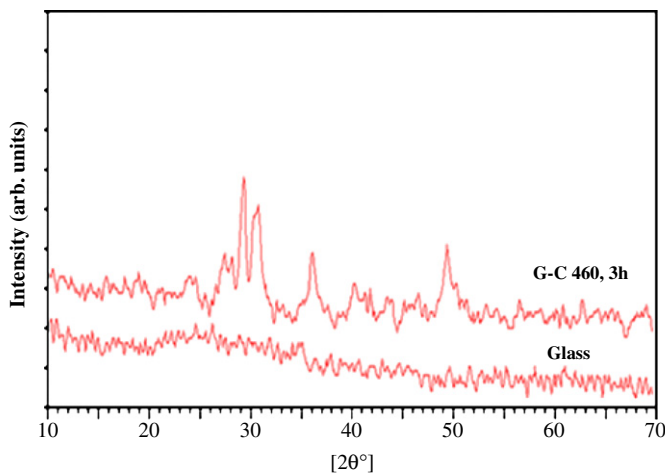


Fig. 1. XRD patterns of glass and glass ceramic samples. Corresponding peaks of the CaCl_2 structure appeared in the glass ceramic sample.

precursor glass. The reason for the absorption intensity decrease (650–900 nm region) is that Eu^{3+} ions are trapped within the nanocrystals, and the nanocrystals medium is treated as an obstacle in the way of the input beam with an absorption wavelength of the Eu^{3+} ions. These results are in agreement with those found in previous reports [4,5,22,27] for rare earth doped glass ceramics. The reason for absorption intensity increase at shorter wavelengths (270–650 nm) is still a matter of discussion. However, it can improve the down-conversion luminescence of Eu^{3+} doped glass ceramic samples.

The excitation spectra of Eu^{3+} emission monitored at 590 and 615 nm of $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions are depicted in Figs. 4 and 5, respectively. The spectral range from 250 to 570 nm consists of sharp lines, which resulted from transitions between the 4f energy levels of Eu^{3+} . The excitation bands can be assigned to $^7F_0 \rightarrow ^5D_1$ (534 nm), $^7F_0 \rightarrow ^5D_2$ (465 nm), $^7F_0 \rightarrow ^5D_3$ (414 nm), $^7F_0 \rightarrow ^5L_6$ (395 nm), $^7F_0 \rightarrow ^5G_3$ (383 nm) and $^7F_0 \rightarrow ^5D_4$ (364 nm). All of these transitions are in agreement with the assigned absorption bands in Fig. 3. Similar excitation spectra for Eu^{3+} doped glasses

and glass ceramics were reported in previous works [9,13,14,21,24–26]. The strongest peak at 395 nm for Eu^{3+} :Glass and particularly strong peaks for Eu^{3+} doped glass ceramics samples at 300 nm in Fig. 4 and at 310 nm in Fig. 5 were achieved. Thus, we consider 395, 300 and 310 nm to be ideal pump wavelengths to generate emission from these prepared samples.

Fig. 6 shows the emission spectra (excited at 395) of Eu^{3+} ions in the glass and glass ceramics samples. The spectra consist of well known ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J=0-4$) transitions namely ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$

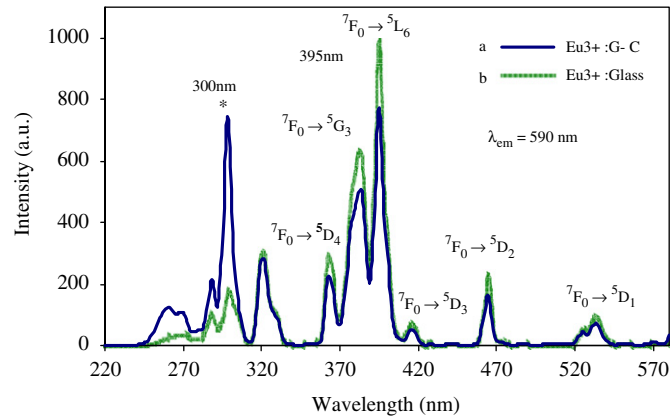


Fig. 4. Excitation spectra of (a) Eu^{3+} :G-C and (b) Eu^{3+} :Glass samples (monitored at 590 nm).

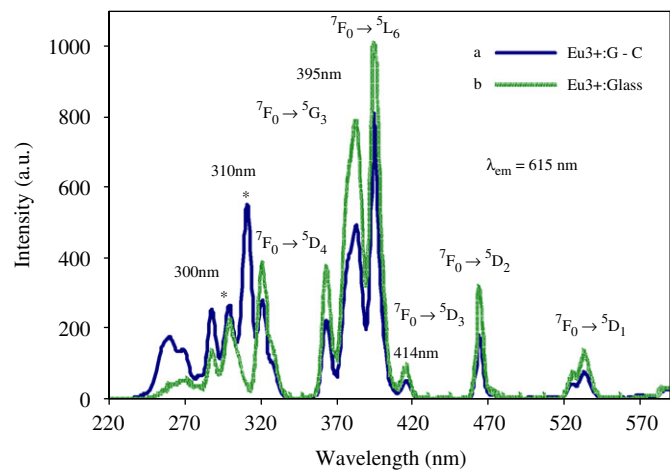


Fig. 5. Excitation spectra of (a) Eu^{3+} :G-C and (b) Eu^{3+} :Glass samples (monitored at 615 nm).

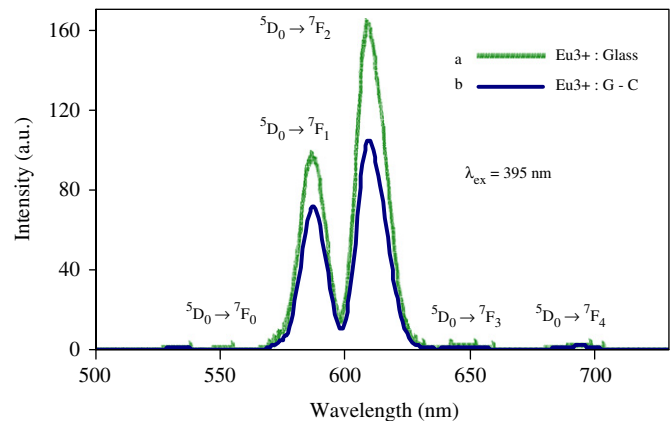


Fig. 6. Emission spectra of (a) Eu^{3+} :Glass and (b) Eu^{3+} :G-C (excited at 395 nm).

(554 nm), ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (588 nm), ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (610 nm), ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ (650 nm) and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ (697 nm). Similar transitions were reported in previous works [12–15]. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition is magnetic dipole in nature and is allowed by all selection rules, whereas the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition is electric dipole in nature and other emission transitions, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J=0, 3$ and 4), are strictly forbidden [15,21,24,25] and appear with low intensities. The excitation beam at 395 nm has been suggested to be an ideal one to demonstrate europium glass as a brightly red luminescent optical material [9,13,14,25]. In excitation spectra (Figs. 4 and 5) Eu^{3+} :Glass shows the highest intensities at 395 nm in comparison with Eu^{3+} :G-C.

Figs. 7 and 8 show the emission spectra (excited at 300 and 310 nm) of Eu^{3+} doped samples due to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions, respectively. In Fig. 7 intense emissions were observed for Eu^{3+} :G-C at 591 and 611 nm. The emission intensity at 591 nm for the glass ceramic sample is about 4.1 times stronger than that for Eu^{3+} :Glass. The emission band at 591 nm for the glass ceramic sample appeared to be much more sensitive than that at 611 nm, which can be related to the presence of Eu^{3+} in the crystalline phases [9]. As shown in Fig. 8, on choosing a longer excitation beam (at 310 nm instead of 300 nm), an intense emission band was achieved at 614 nm for Eu^{3+} :G-C; for ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition at 590 nm some weak emission peaks

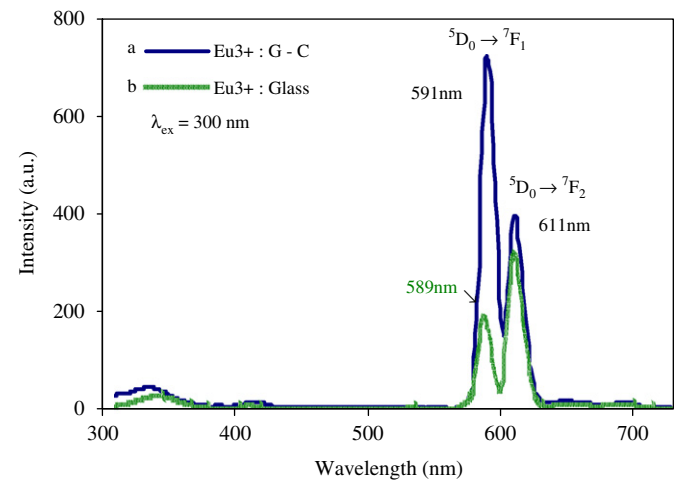


Fig. 7. Emission spectra of (a) Eu^{3+} :G-C and (b) Eu^{3+} :Glass samples (excited at 300 nm).

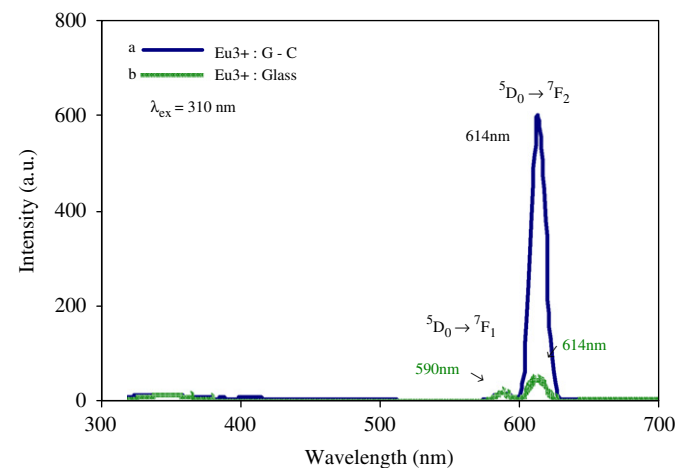


Fig. 8. Emission spectra of (a) Eu^{3+} :G-C and (b) Eu^{3+} :Glass samples (excited at 310 nm).

appeared. The emission intensity of Eu^{3+} :G-C is about 13.3 times stronger than that of Eu^{3+} :Glass at 614 nm.

Figs. 9 and 10 show the upconversion emission spectra (excited at 587 and 720 nm) of Eu^{3+} doped samples. Eu^{3+} doped glass ceramics have very intense emissions in comparison to Eu^{3+} :Glasses. According to the upconversion emission in Fig. 9, the emission bands were achieved at 296 and 298 nm for Eu^{3+} :G-C and Eu^{3+} :Glass, respectively. In this frequency conversion, two photon absorption processes occurred. The upconversion emission intensity of Eu^{3+} :G-C is about 45 times stronger than that of the Eu^{3+} :Glass sample, which indicates that CaCl_2 nanocrystals have a great influence on emission intensities of doped glass ceramics. The shifted frequency can be related to a new environment around the Eu^{3+} ions in the glass ceramic.

According to the upconversion emission in Fig. 10, the emission bands were achieved at 363 and 365 nm for Eu^{3+} :G-C and Eu^{3+} :Glass, respectively. The trapping of Eu^{3+} ions in CaCl_2 nanocrystals resulted in very high intense upconversion emissions, and shift frequency at 363 nm. Ordinary emissions for $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions also appeared at 588 and 610 nm. Similar frequency upconversion properties of rare earth doped glass ceramics were reported in previous works [2–5,28,29].

Fig. 11 shows a photograph of luminescence in transparent Eu^{3+} :Glass and Eu^{3+} :G-C samples excited with a UV lamp at 350 nm. There is a significant difference between the colors of glass and glass ceramics samples under UV irradiation, which demonstrates the changes in Eu^{3+} ions medium in the glass

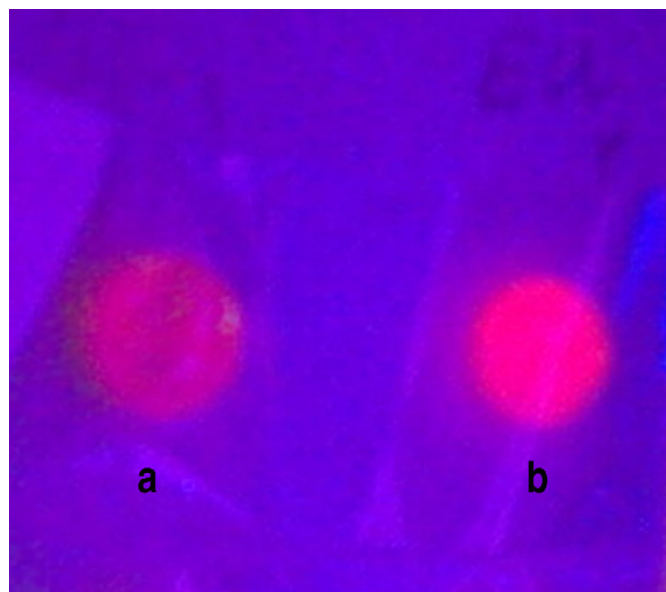


Fig. 11. Photograph of the photoluminescence in (a) Eu^{3+} :G-C and (b) Eu^{3+} :Glass samples.

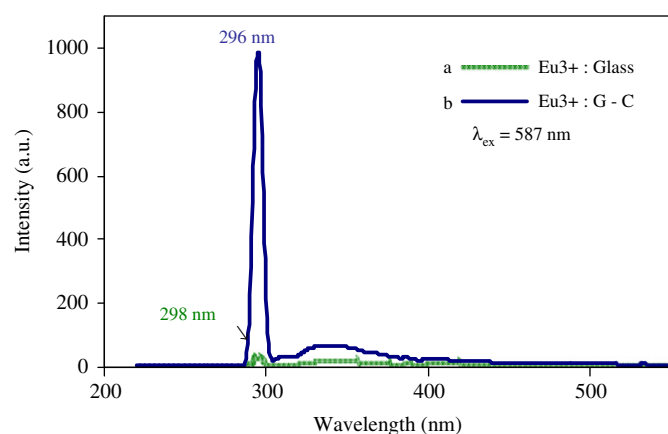


Fig. 9. Upconversion emission spectra of (a) Eu^{3+} :Glass and (b) Eu^{3+} :G-C samples (excited at 587 nm).

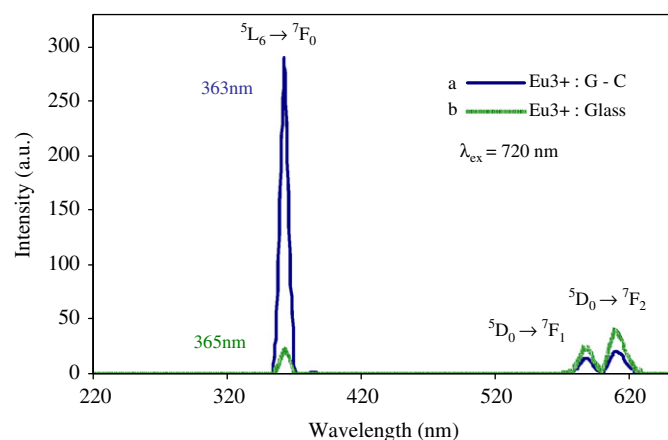


Fig. 10. Upconversion emission spectra of (a) Eu^{3+} :Glass and (b) Eu^{3+} :G-C samples (excited at 720 nm).

ceramics sample. In fact, it can be related to the trapping of Eu^{3+} ions into the CaCl_2 nanocrystals.

The emission enhancement in the Eu^{3+} doped glass ceramic samples can be explained as follows: during the crystallization process of thermal treatment, some of the Eu^{3+} ions could be incorporated into the CaCl_2 nanocrystals. The glass ceramic matrix provides the distinct advantage of low phonon frequencies compared to glass materials and minimizes the non-radiative losses and multi-phonon relaxation, and more efficient emission intensities can be observed. The shifted band for the crystallized samples can be related to the transformation of the environmental structure of Eu^{3+} sites from the amorphous to ordered crystalline state.

4. Conclusions

New transparent Eu^{3+} doped chlorophosphate glass ceramics containing CaCl_2 nanocrystals have been obtained from the P_2O_5 - Na_2HPO_4 - CaCl_2 - NaCl - Eu_2O_3 composition. All of the experiments demonstrate suitable changes in the glass ceramics host medium and result in further improvements in emission bands of doped glass ceramics. Absorption, excitation and emission spectroscopy studies show that Eu^{3+} ions were incorporated into the crystallized phase and resulted in much stronger emissions in glass ceramics samples for up- and down-frequency conversion and therefore implicating them as a potential material for frequency-conversion photonics devices.

Acknowledgment

This work was supported by Applied Physics Research centre of Imam Hossein University, Tehran, Iran and Nano-Research centre of the University of Ferdowsi, Mashhad, Iran.

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