Up and Down Frequency-Conversion Properties of Eu^{3+} Doped Lead Fluorophosphate Nanoglass Ceramics

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Abstract – Europium doped transparent lead fluorophosphate glass ceramics successfully were prepared with heat treatment of precourse glasses at temperature above glass transition (T_g). X-ray diffraction (XRD) experiment evidenced the formation of PbF_2 nanocrystals in glassy matrix. The emission spectra investigation indicate that considerable amount of Eu^{3+} ions were trapped in crystalline phase, and therefore the efficient frequency-conversion was observed in glass ceramics samples. The investigated glass ceramics systems are potentially applicable as up and down frequency-conversion photonics materials.

KEYWORDS: Fluorophosphate glass; Frequency-conversion; Glass-ceramic; Nanocrystal; Photonics materials; Upconversion.

I. INTROCUCTION

Rare earth ions doped glass and glass ceramics with low phonon energy have been one of the most interesting fields of research due to their potential application in optical devices such as upcovversion fibers, optical amplifiers, three-dimensional displays and upconversion solid-state lasers [1-15]. Low phonon energy host material and trapping of rare earth ions within the nano-crystallites embedded in glassy matrix, can improve their optical properties and will result in considerable enhancement of emission intensities [9, 10, 13].

Among the rare earth (RE) ions, the trivalent europium ion (Eu^{3+}) is the most favorite choice that used for optically activated materials. This is because, Eu^{3+} ions have almost monochromatic light and narrow emission band and also have long lifetimes in optically active states [14-17].

The phosphates glasses have several advantages, such as low melting and softening temperature and high ultraviolet transmission in comparison with conventional oxide glasses [18-20]. Fluorophosphate glasses have low phonon energy that yields low non-radiative decay and high radiative emission rates of RE ion energy levels, leading to much higher quantum efficiencies [2, 18, 21]. The host materials with low phonon energies are generally suitable in order to achieve higher emission intensities [3-6]. In rare earth doped host material with low phonon energy, the upconversion emission is possible by non coherent excitation light such as Xe lamps [1-5].

In this work the optimized phosphate base glasses [1, 22-26] has been considered and transparent lead fluorophosphate glass ceramics were successfully prepared, and their frequency-conversion properties have been studied.

II. EXPERIMENTS

A. *Samples preparation*

Lead fluorophosphate glasses with composition in mol% of: $41.5P_2O_5$, $21Na_2HPO_4$, $21PbF_2$, 16NaF, $0.5Eu_2O_3$ were prepared with melting procedure. All the raw materials with high purity obtained from Merck. The batches of raw materials were melted at 800 °C for two hour in a covered alumina crucible in the normal atmosphere.

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The liquids were shaken at 20 min. interval during melting. The incorporation of the alkali contents reduced melting point and increased stability of the glass. The molten mixtures were transferred into steel molds to obtain cubic glass rods with 3 cm length and cross sections with 0.5 cm side. The heat treatment procedures were performed at temperatures higher than Tg and transparent glass ceramics samples were obtained. The Eu^{3+}:Glass ceramics that annealed at 310 and 320 ˚C for 2 hours have been assigned in the text as GC-310-2h and GC-320-2h, respectively.

B. *B. Characterization*

Differential thermal analysis (DTA) was carried out to confirm the T_g and the crystallized peaks temperatures (with STA 1500). XRD spectrometer (X'pert, Philips) was used to investigate the crystallization and formation of nano-particles. UV-VIS spectrometers (550 SE, Perkin Elmer) and Photoluminescence spectrometer (LS 45, Perkin Elmer) were used for absorption and emission spectroscopy studies. A Xe lamp was used as an excitation source for upconversion emission as well as the down conversion. All the measurements were carried out at room temperature.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the DTA curve of the $41.5P_2O_5$, $21Na_2HPO_4$, $21PbF_2$, 16NaF, $0.5Eu_2O_3$ glass. The T_g took place at 292 ˚C and two crystallization peaks at 417 and 454 ˚C can be observed. The heat treated temperatures of the glassy samples were above T_g and also were lower than first crystallization temperature to avoid loss of transparency for glass ceramics samples.

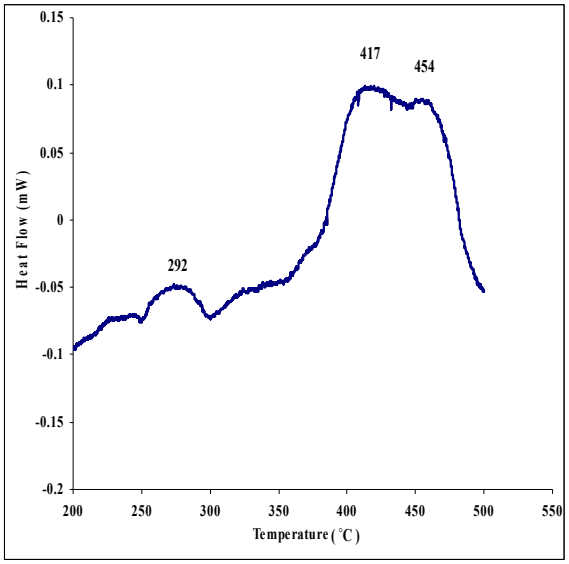

Fig. 1 DTA curve of $41.5P_2O_5$, $21Na_2HPO_4$, $21PbF_2$ - 16NaF - $0.5Eu_2O_3$ glass.

XRD patterns of glass ceramics samples are illustrated in Figure 2(a) and Figure 2(b). The crystalline phases corresponding to $Na_4Pb(PO_3)_6$ and PbF_2 structure are observed. With heat treatment at 320 ˚C for 2 h the crystalline PbF_2 phase has been dominated. By using Scherrer formula, the average size of the PbF_2 nanocrystals was evaluated to be about 22 nm for GC-310-2h and 26 nm for GC-320-2h samples.

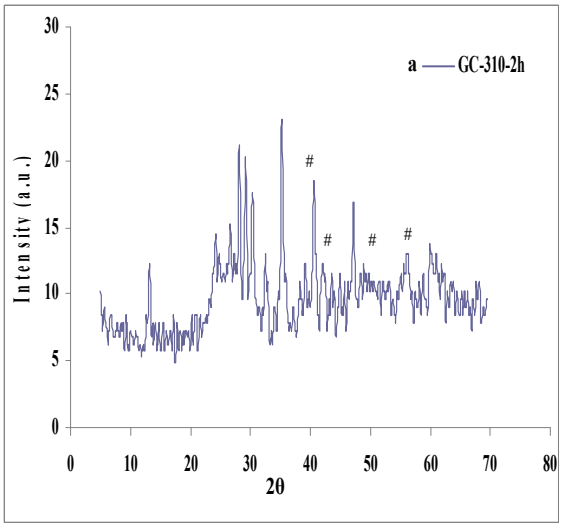

Fig. 2 (a) XRD patterns of GC-310-2h sample with PbF_2 phase (#).

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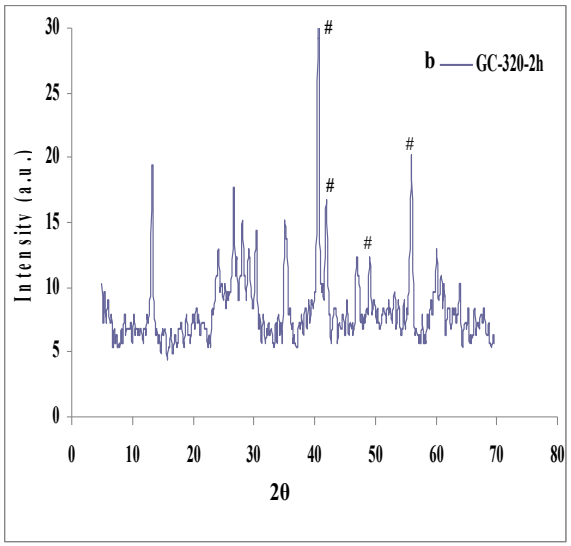

Fig. 2 (b) XRD patterns of GC-320-2h with PbF_2 (#) dominated phase.

The absorption spectrum for Eu^{3+}: Glass in the wavelength region of 350-600 nm which include transitions from the $^7F_0$ ground state was illustrated in Figure 3. The $^7F_0 \rightarrow {}^5D_J$ bands are spin forbidden and hence are very weak. The $^7F_0 \rightarrow {}^5L_6$ is spin allowed and is much stronger [14, 15, 27].

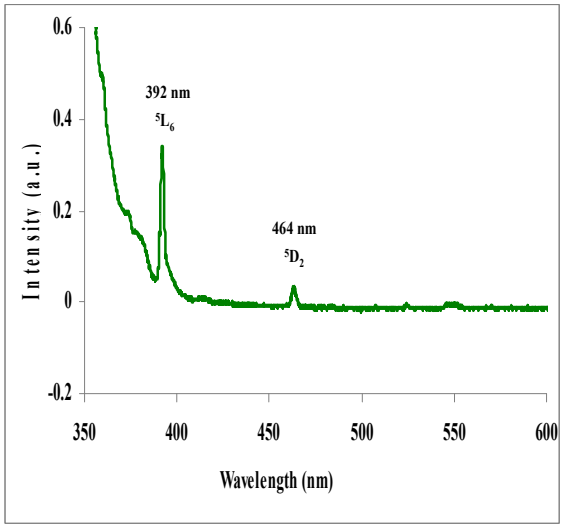

Fig. 3 Absorption spectrum of Eu^{3+}: Glass sample.

The excitation spectra of Eu^{3+} doped glass and glass ceramics samples, with emission monitored at 612 nm were depicted in Figure 4. The spectral range from 250 to 600 nm consisted of some peaks that resulted from transitions between the 4f energy levels of Eu^{3+}. The excitation bands can be assigned to $^7F_0 \rightarrow {}^5D_1$ (532nm), $^7F_0 \rightarrow {}^5D_2$ (464nm), $^7F_0 \rightarrow {}^5D_3$ (412nm), $^7F_0 \rightarrow {}^5L_6$ (392nm), $^7F_0 \rightarrow {}^5G_j$ (378nm) and $^7F_0 \rightarrow {}^5D_4$ (360nm), respectively. Similar excitation spectra for Eu^{3+} doped glass and glass ceramics were reported in other works [13, 15, 16, 27-30]. The absorption and excitation spectra (Figures 3 and 4) show that, 392 and 464 nm are suitable wavelengths for down frequency conversion excitation.

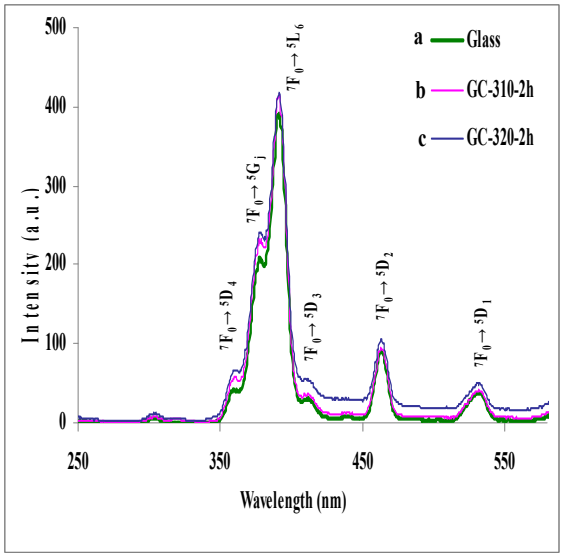

Fig. 4 Excitation spectra of Eu^{3+}doped (a) Glass (b) GC-310-2h and (c) GC-320-2h samples (monitored at 612 nm).

Figures 5 and 6 show down conversion emission spectra (excited at 392 and 464nm) of Eu^{3+} ions in the glass and glass ceramics samples. The spectra consist of the well known $^5D_0 \rightarrow {}^7F_J$ (J=1-4) and $^5D_1 \rightarrow {}^7F_J$ (J=1, 2) transitions namely $^5D_0 \rightarrow {}^7F_1$ (588nm), $^5D_0 \rightarrow {}^7F_2$ (610nm), $^5D_0 \rightarrow {}^7F_3$ (650nm), $^5D_0 \rightarrow {}^7F_4$ (697nm), $^5D_1 \rightarrow {}^7F_1$ (537nm) and $^5D_1 \rightarrow {}^7F_2$ (556nm). The $^5D_0 \rightarrow {}^7F_1$ transition is magnetic dipole in nature and is allowed by all selection rules, the $^5D_0 \rightarrow {}^7F_2$ transition is electric dipole in nature and other emission transitions $^5D_0 \rightarrow {}^7F_J$ (J=3 and 4) are strictly forbidden and appeared with low intensities [17, 27, 29]. In Figure 5 the emission intensity of Eu^{3+}: GC-320-2h is about 1.34 times stronger than that of Eu^{3+}: Glass sample.

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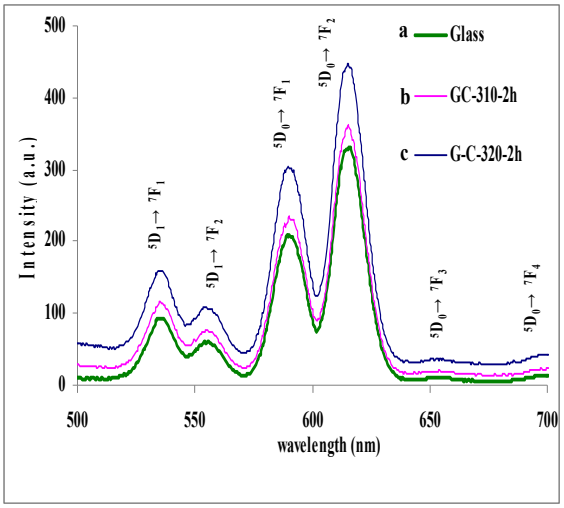

Fig. 5 Down conversion emission spectra of Eu^{3+} doped (a) Glass, (b) GC-310-2h, and (c) GC-320-2h samples (excited at 392 nm).

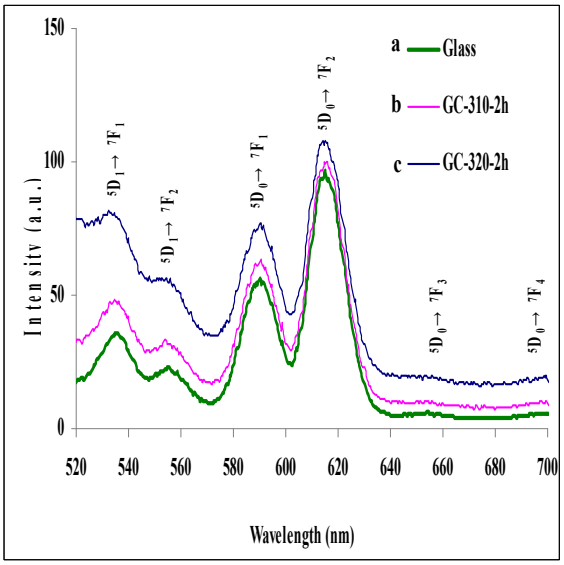

Fig. 6 Down conversion emission spectra of Eu^{3+} doped (a) Glass, (b) GC-310-2h, and (c) GC-320-2h samples (excited at 464 nm).

Figure 7 shows the energy diagram of Eu^{3+} ions, based on the excitation and emission processes that illustrated in Figures 5 and 6. The non-radiative transitions, related to the low energy environment of the Eu^{3+} ions in glass and glass ceramics and due to high non-radiative transitions from excited states of energy level higher than $^5D_0$ states, some strong emission bands in the range of 500-650 nm are caused by the $^5D_0 \rightarrow {}^7F_j$ and $^5D_1 \rightarrow {}^7F_j$ (j=1-2) transitions.

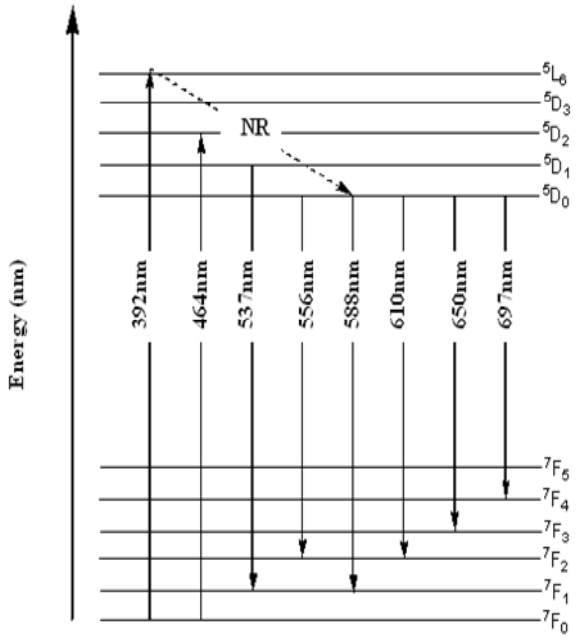

Fig. 7 Excitation and emission energy diagram of Eu^{3+} doped lead fluorophosphate glass and glass ceramics.

Figure 8 shows two photographs of fabricated Eu^{3+} doped glass and glass ceramic rods. Both samples are transparent under ordinary light. With exciting under UV irradiation at 350 nm, red emission luminescence were observed. There is a significant difference between the colors of glassy (a) and glass ceramic (b) samples under UV lamp, which demonstrates the changes in Eu^{3+} ions medium in the glass ceramics sample.

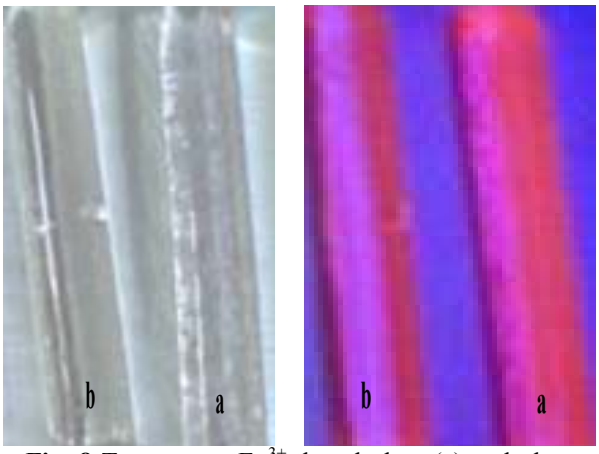

Fig. 8 Transparent Eu^{3+} doped glass (a) and glass ceramic (b) at ordinary light (left), under UV lamp (right).

Figure 9 shows the upconversion emission spectra (excited at 710 nm) of Eu^{3+} doped

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samples. Eu^{3+} doped glass ceramics have very intensive emissions in comparison with Eu^{3+}: Glass sample. The emission bands were achieved at 359 nm and two photons absorption process was occurred. The upconversion emission intensity of Eu^{3+}: GC-320-2h is about 10 times stronger than that of Eu^{3+}: Glass sample. The changes in the emission intensities between the glass and glass ceramics evidenced a new environment around the rare earth ions in the glass ceramics and trapping of active ions with in crystalline phase which does not exist in the glass samples [9, 11, 13].

The trapping of Eu^{3+} ions in PbF_2 nanocrystals, resulted very high intense upconversion emission. Similar frequency upconversion properties of rare earth doped glass ceramics were reported in previous works [1, 6, 9, 10, 31, 32].

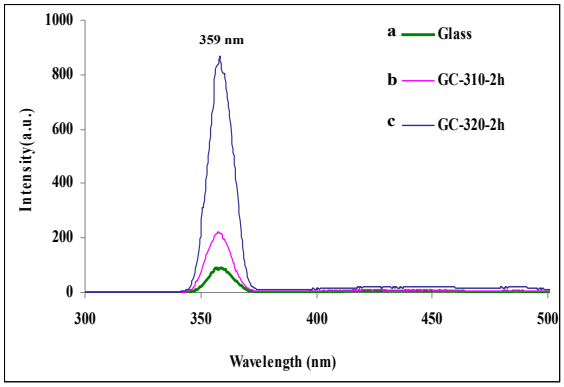

Fig. 9 Upconversion emission spectra of Eu^{3+} doped (a) Glass, (b) GC-310-2h, and (c) GC-320-2h samples (excited at 710nm).

IV. CONCLUSION

Transparent Eu^{3+} doped lead fluorophosphate glass ceramics containing PbF2 nanocrystals have been obtained from P_2O_5-Na_2HPO_4-PbF_2-NaF-Eu_2O_3 composition. After crystallization process, some of the Eu^{3+} ions are incorporated in to the PbF2 nanocrystals. The glass ceramic matrix provides a medium with lower phonon energy compared to precourse glass and minimizes the non-radiative losses. The intense up and down frequency conversion emission for the crystallized samples can be related to the transformation of environmental structure of Eu^{3+} site from amorphous to ordered crystalline medium with lower phonon energies. This study shows that the investigated Eu^{3+} doped glass ceramics could be potentially applicable for efficient up and down frequency conversion optical devices.

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