

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

Y. Hatefi<sup>a</sup>, K. Anbaz<sup>b</sup>, A. Moghimi<sup>b</sup>, and B. Maddah<sup>b</sup>.

<sup>a</sup>Department of Physics, Imam Hossein University, Tehran, Iran;

<sup>b</sup>Department of Chemistry, Imam Hossein University, Tehran, Iran.

**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  $\text{PbF}_2$  nanocrystals in glassy matrix. The emission spectra investigation indicate that considerable amount of  $\text{Eu}^{3+}$  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. INTRODUCTION

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 upconversion 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 ( $\text{Eu}^{3+}$ ) is the most favorite choice that used for optically activated materials. This is because,  $\text{Eu}^{3+}$  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: 41.5 $\text{P}_2\text{O}_5$ , 21 $\text{Na}_2\text{HPO}_4$ , 21 $\text{PbF}_2$ , 16 $\text{NaF}$ , 0.5 $\text{Eu}_2\text{O}_3$  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.

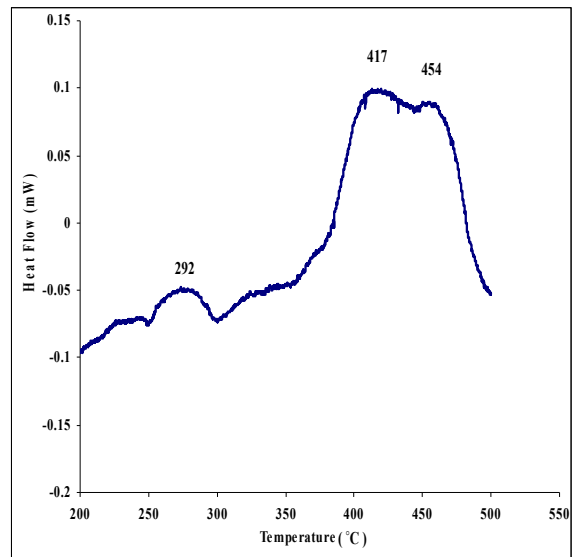
The liquids were shaken at 20 min. interval during melting. The incorporation of the alkali contents reduced melting point and increased stability of the glass. The molten mixtures were transferred into steel molds to obtain cubic glass rods with 3 cm length and cross sections with 0.5 cm side. The heat treatment procedures were performed at temperatures higher than  $T_g$  and transparent glass ceramics samples were obtained. The  $\text{Eu}^{3+}$ :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.

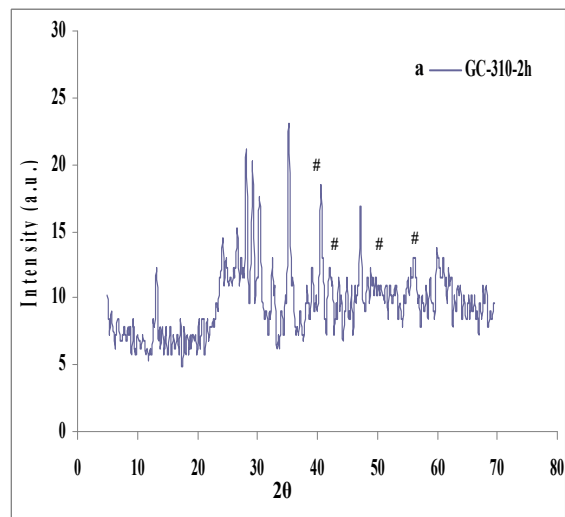
## III. RESULTS AND DISCUSSIONS

Figure 1 shows the DTA curve of the  $41.5\text{P}_2\text{O}_5$ ,  $21\text{Na}_2\text{HPO}_4$ ,  $21\text{PbF}_2$ ,  $16\text{NaF}$ ,  $0.5\text{Eu}_2\text{O}_3$  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.

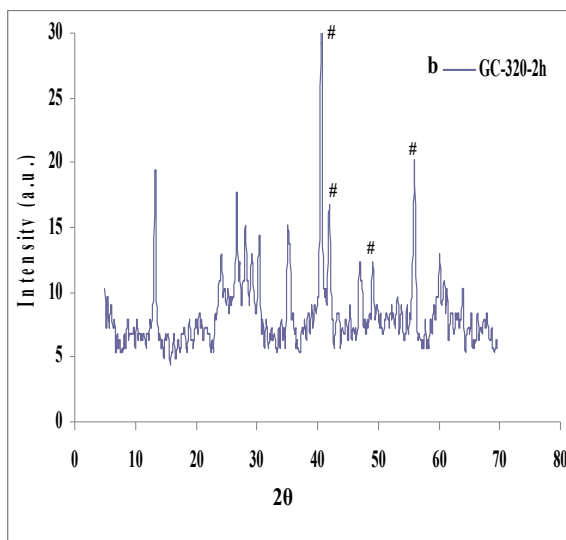


**Fig. 1** DTA curve of  $41.5\text{P}_2\text{O}_5$ ,  $21\text{Na}_2\text{HPO}_4$ ,  $21\text{PbF}_2$  -  $16\text{NaF}$  -  $0.5\text{Eu}_2\text{O}_3$  glass.

XRD patterns of glass ceramics samples are illustrated in Figure 2(a) and Figure 2(b). The crystalline phases corresponding to  $\text{Na}_4\text{Pb}(\text{PO}_3)_6$  and  $\text{PbF}_2$  structure are observed. With heat treatment at 320 °C for 2 h the crystalline  $\text{PbF}_2$  phase has been dominated. By using Scherrer formula, the average size of the  $\text{PbF}_2$  nanocrystals was evaluated to be about 22 nm for GC-310-2h and 26 nm for GC-320-2h samples.

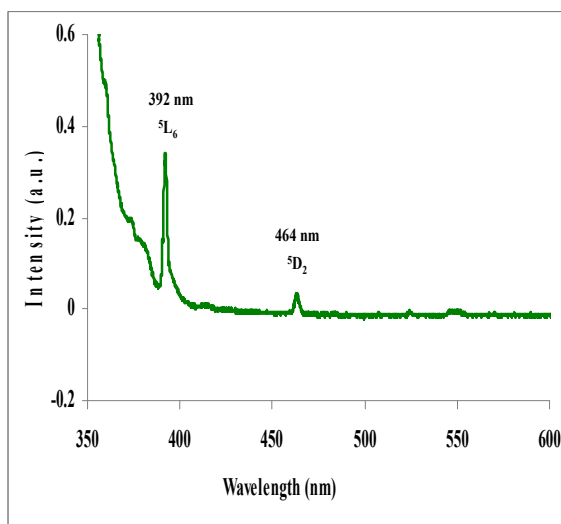


**Fig. 2** (a) XRD patterns of GC-310-2h sample with  $\text{PbF}_2$  phase (#).



**Fig. 2** (b) XRD patterns of GC-320-2h with  $\text{PbF}_2$  (#) dominated phase.

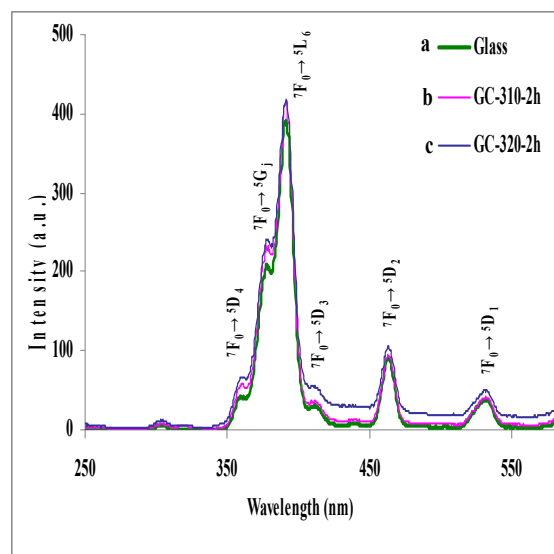
The absorption spectrum for  $\text{Eu}^{3+}$ : Glass in the wavelength region of 350-600 nm which include transitions from the  ${}^7\text{F}_0$  ground state was illustrated in Figure 3. The  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_J$  bands are spin forbidden and hence are very weak. The  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  is spin allowed and is much stronger [14, 15, 27].



**Fig. 3** Absorption spectrum of  $\text{Eu}^{3+}$ : Glass sample.

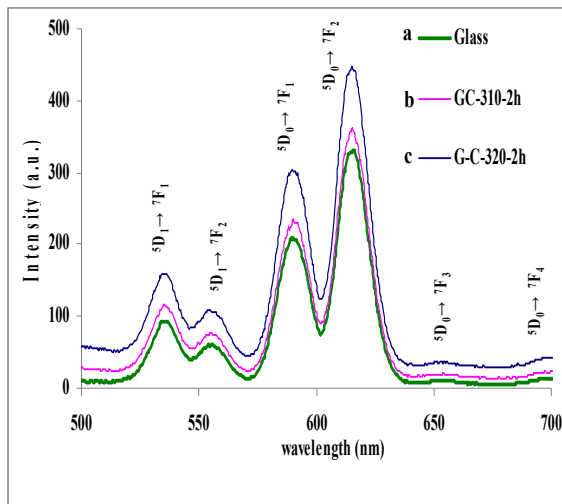
The excitation spectra of  $\text{Eu}^{3+}$  doped glass and glass ceramics samples, with emission monitored at 612 nm were depicted in Figure 4. The spectral range from 250 to 600 nm consisted of some peaks that resulted from transitions between the 4f energy levels of  $\text{Eu}^{3+}$ . The excitation bands can be assigned to

${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$  (532nm),  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$  (464nm),  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_3$  (412nm),  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  (392nm),  ${}^7\text{F}_0 \rightarrow {}^5\text{G}_j$  (378nm) and  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$  (360nm), respectively. Similar excitation spectra for  $\text{Eu}^{3+}$  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.

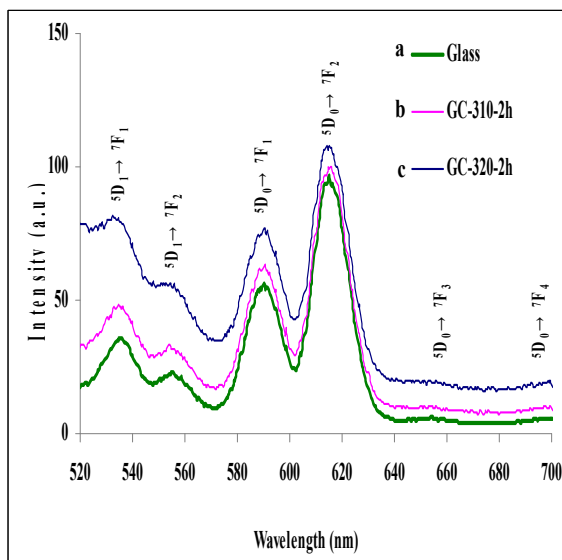


**Fig. 4** Excitation spectra of  $\text{Eu}^{3+}$  doped (a) Glass (b) GC-310-2h and (c) GC-320-2h samples (monitored at 612 nm).

Figures 5 and 6 show down conversion emission spectra (excited at 392 and 464nm) of  $\text{Eu}^{3+}$  ions in the glass and glass ceramics samples. The spectra consist of the well known  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$  ( $J=1-4$ ) and  ${}^5\text{D}_1 \rightarrow {}^7\text{F}_J$  ( $J=1, 2$ ) transitions namely  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  (588nm),  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  (610nm),  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$  (650nm),  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  (697nm),  ${}^5\text{D}_1 \rightarrow {}^7\text{F}_1$  (537nm) and  ${}^5\text{D}_1 \rightarrow {}^7\text{F}_2$  (556nm). The  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition is magnetic dipole in nature and is allowed by all selection rules, the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition is electric dipole in nature and other emission transitions  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$  ( $J=3$  and 4) are strictly forbidden and appeared with low intensities [17, 27, 29]. In Figure 5 the emission intensity of  $\text{Eu}^{3+}$ : GC-320-2h is about 1.34 times stronger than that of  $\text{Eu}^{3+}$ : Glass sample.

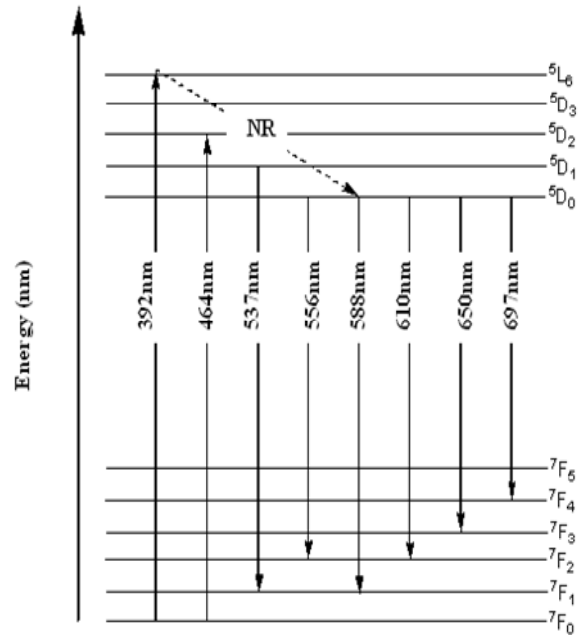


**Fig. 5** Down conversion emission spectra of  $\text{Eu}^{3+}$  doped (a) Glass, (b) GC-310-2h, and (c) GC-320-2h samples (excited at 392 nm).



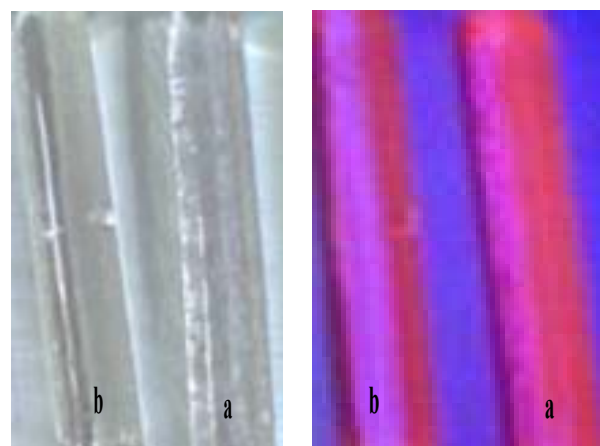
**Fig. 6** Down conversion emission spectra of  $\text{Eu}^{3+}$  doped (a) Glass, (b) GC-310-2h, and (c) GC-320-2h samples (excited at 464 nm).

Figure 7 shows the energy diagram of  $\text{Eu}^{3+}$  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  $\text{Eu}^{3+}$  ions in glass and glass ceramics and due to high non-radiative transitions from excited states of energy level higher than  $^5\text{D}_0$  states, some strong emission bands in the range of 500-650 nm are caused by the  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  and  $^5\text{D}_1 \rightarrow ^7\text{F}_j$  ( $j=1-2$ ) transitions.



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

Figure 8 shows two photographs of fabricated  $\text{Eu}^{3+}$  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  $\text{Eu}^{3+}$  ions medium in the glass ceramics sample.

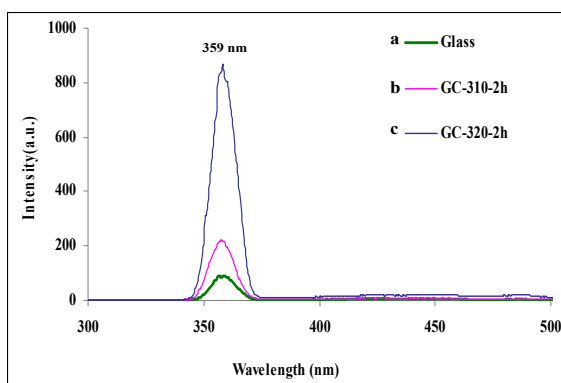


**Fig. 8** Transparent  $\text{Eu}^{3+}$  doped glass (a) and glass ceramic (b) at ordinary light (left), under UV lamp (right).

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

samples.  $\text{Eu}^{3+}$  doped glass ceramics have very intensive emissions in comparison with  $\text{Eu}^{3+}$ : Glass sample. The emission bands were achieved at 359 nm and two photons absorption process was occurred. The upconversion emission intensity of  $\text{Eu}^{3+}$ : GC-320-2h is about 10 times stronger than that of  $\text{Eu}^{3+}$ : 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  $\text{Eu}^{3+}$  ions in  $\text{PbF}_2$  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  $\text{Eu}^{3+}$  doped (a) Glass, (b) GC-310-2h, and (c) GC-320-2h samples (excited at 710nm).

#### IV. CONCLUSION

Transparent  $\text{Eu}^{3+}$  doped lead fluorophosphate glass ceramics containing  $\text{PbF}_2$  nanocrystals have been obtained from  $\text{P}_2\text{O}_5\text{-Na}_2\text{HPO}_4\text{-PbF}_2\text{-NaF-Eu}_2\text{O}_3$  composition. After crystallization process, some of the  $\text{Eu}^{3+}$  ions are incorporated in to the  $\text{PbF}_2$  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  $\text{Eu}^{3+}$  site from amorphous to ordered crystalline medium with lower phonon energies. This study shows that the investigated  $\text{Eu}^{3+}$  doped glass ceramics could be potentially applicable for efficient up and down frequency conversion optical devices.

#### ACKNOWLEDGMENT

This work was supported by Applied Physics Research centre and Applied Chemistry Research centre of Imam Hossein University, Tehran, Iran.

#### REFERENCES

- [1] Y. Hatefi, N. Shahtahmasebi, A. Moghimi, and E. Attaran, "Frequency- conversion properties of  $\text{Eu}^{3+}$  doped chlorophosphate glass ceramics containing  $\text{CaCl}_2$  nanocrystals," To be submitted to J. Lumin.
- [2] B. Karmakar and K. Annapurna, "Blue, green and red upconversions  $\text{Ho}_2\text{O}_3$  -doped fluorophosphate glasses," J. Non-Cryst. Solids, Vol. 353, pp. 1377-1382, 2007.
- [3] T. Som and B. Karmakar, "Infrared-to-red upconversion luminescence in samarium -doped antimony glasses," J. Lumin. Vol. 128, pp. 1989 -1996, 2008.
- [4] T. Som and B. Karmakar, "Green and red fluorescence upconversion in neodymium-doped low phonon antimony glasses," J. Alloys Compd. Vol. 476, pp. 383-389, 2009.
- [5] Q. Xiang, Y. Zhou, Y.L. Lam, Y.C. Chan, C.H. Kam, B.S. Ooi, H.X. Zhang, and S. Buddhudu, "Up-conversion emission in violet from yellow in  $\text{Nd}^{3+}$ :  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$  sol-gel glasses," Mat. Res. Bull. Vol. 35, pp. 1571-1578, 2000.
- [6] A.S. Gouveia-Neto, E.B. da Costa, L.A. Bueno, and S.J.L. Ribeiro, "Upconversion luminescence in transparent glass ceramics containing  $\beta\text{-PbF}_2$  nanocrystals doped with erbium," J. Alloys Compd. Vol. 375, pp. 224-228, 2004.
- [7] M. J. Dejneka, "The luminescence and structure of novel transparent oxyfluoride glass-ceramics," J. Non-Cryst. Solids, Vol. 239, pp. 149-155, 1998.

- [8] V. Lavín, I. Iparraguirre, J. Azkargorta, A. Mendioroz, J. González-Platas, R. Balda, and J. Fernández, "Stimulated and upconverted emissions of  $\text{Nd}^{3+}$  in a transparent oxyfluoride glass-ceramic," *Opt. Mater.* Vol. 25, pp. 201-208, 2004.
- [9] F. Lahoz, I.R. Martín, U.R. Rodríguez-Mendoza, I. Iparraguirre, J. Azkargorta, A. Mendioroz, R. Balda, J. Fernández, and V. Lavín, "Rare earths in nanocrystalline glass-ceramics," *Opt. Mater.* Vol. 27, pp. 1762-1770, 2005.
- [10] X. Qiao, X. Fan, and M. Wang, "Luminescence behavior of  $\text{Er}^{3+}$  in glass ceramics containing  $\text{BaF}_2$  nanocrystals," *Scripta mater.* Vol. 55, pp. 211-214, 2006.
- [11] J. Pisarska, W. Ryba-Romanowski, G. Dominiak-Dzik, T. Goryczka, and W.A. Pisarski, "Nd-doped oxyfluoroborate glasses and glass-ceramics for NIR laser applications," *J. Alloys Compd.* Vol. 451, pp. 223-225, 2008.
- [12] D. Deng, S. Xu, S. Zhao, C. Li, H. Wang, and H. Ju, "Enhancement of upconversion luminescence in  $\text{Tm}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$  -co doped glass ceramic containing  $\text{LiYF}_4$  nanocrystals," *J. Lumin.* Vol. 129, pp. 1266-1270, 2009.
- [13] D. Zhao, X. Qiao, X. Fan, and M. Wang, "Local vibration around rare earth ions in  $\text{SiO}_2\text{-PbF}_2$  glass and glass ceramics using  $\text{Eu}^{3+}$  probe," *Physica B*, Vol. 396, pp. 10-15, 2007.
- [14] S. Balaji, P. Abdul Azeem, and R. R. Reddy, "Absorption and emission properties of  $\text{Eu}^{3+}$  ions in Sodium fluoroborate glasses," *Physica B*, Vol. 394, pp. 62-68, 2007.
- [15] K. Annapurna, M. Das, P. Kundu, R.N. Dwivedi, and S. Buddhudu, "Spectral properties of  $\text{Eu}^{3+}$ :  $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$  glasses," *J. Mol. Struct.* Vol. 741, pp. 53-60, 2005.
- [16] Y. Cong, B. Li, B. Lei, X. Wang, C. Liu, J. Liu, and W. Li, "Enhancement of luminescence intensity and increase of emission lifetime in  $\text{Eu}^{3+}$  -doped  $3\text{CdO-Al}_2\text{O}_3\text{-3SiO}_2$  amorphous system," *J. Lumin.* Vol. 128, pp. 105-109, 2008.
- [17] V. Venkatramu, D. Navarro-Urrios, P. Babu, C.K. Jayasankar, and V. Lavín, "Fluorescence line narrowing spectral studies of  $\text{Eu}^{3+}$  -doped lead borate glass," *J. Non-Cryst. Solids*, Vol. 351, pp. 929-935, 2005.
- [18] K.U. Kumar, P. Babu, K.H. Jang, H. J. Seo, C. K. Jayasankar, and A.S. Joshi, "Spectroscopic and 1.06  $\mu\text{m}$  laser properties of  $\text{Nd}^{3+}$  -doped K-Sr-Al phosphate and fluorophosphate glasses," *J. Alloys Compd.* Vol. 458, pp. 509-516, 2008.
- [19] M. Seshadri, K. Venkata Rao, J.L. Rao, and Y.C. Ratnakaram, "Spectroscopic and laser properties of  $\text{Sm}^{3+}$  -doped different phosphate glasses," *J. Alloys Compd.* Vol. 476, pp. 263-270, 2009.
- [20] G.N. Hemantha Kumar, J.L. Rao, K. Ravindra Prasad, and Y.C. Ratnakaram, "Fluorescence and Judd-Ofelt analysis of  $\text{Nd}^{3+}$  doped  $\text{P}_2\text{O}_5\text{-Na}_2\text{O-K}_2\text{O}$  glass," *J. Alloys Compd.* Vol. 480, pp. 208-215, 2009.
- [21] G.V. Prakash and R. Jagannathan, "Fluorescence Properties of  $\text{Eu}^{3+}$  doped lead bearing fluoro-chloro phosphate glasses," *Spectrochim. Acta A*, Vol. 55, pp. 1799-1808, 1999.
- [22] Y.C. Ratnakaram, A.V. Reddy, and R.P.S. Chakradhar, "Electronic absorption spectra and energy gap studies of  $\text{Er}^{3+}$  ions in different chlorophosphate glasses," *Spectrochimica Acta Part A*, Vol. 58, pp. 1809-1822, 2002.
- [23] Y. Hatefi, "Influence of  $\text{SiO}_2$  on absorption and emission properties of chlorophosphate laser glasses," 13<sup>th</sup> Annual Iranian Conference on optics and photonics. 6-8, Feb, 2007.
- [24] Y. Hatefi, M. Shafinia, N. Shahtahmasebi, R. Malekfar, and M. Vaezzadeh, "Transparent Nano Glass-Ceramics Containing Lanthanide Ions," Annual Physics Conference of Iran 25-28, Aug 2008.
- [25] Y. Hatefi and N. Shahtahmasebi, "Optical properties of rare earth ions in glass-ceramics containing  $\text{CaCl}_2$  nanocrystals," 15<sup>th</sup> Iranian Conference on Optics and Photonics, University of Isfahan, January 27-29, 2009.
- [26] Y. Hatefi, "Upconversion properties of  $\text{Nd}^{3+}$  and  $\text{Eu}^{3+}$  doped oxychlorophosphate glass ceramics containing  $\text{CaCl}_2$  nanocrystals," 2<sup>nd</sup> Iran-India Joint Conference on Nanotechnology, University of Isfahan 5-7 May, 2009.
- [27] M. Dejneka, E. Snitzer, R.E. Riman, "Blue, green and red fluorescence and energy transfer of  $\text{Eu}^{3+}$  in fluoride glasses," *J. Lumin.* Vol. 65, pp. 227-245, 1995.

- [28] K. Annapurna, R. N. Dwivedi, and S. Buddhudu, "Emission properties of  $\text{Eu}^{3+}$  ions in  $\text{ZnCl}_2\text{-BaCl}_2\text{-KCl}$  glass," *Mater. Lett.* Vol. 53, pp. 359-363, 2002.
- [29] C.H. Kam and S. Buddhudu, "Photoluminescence properties of  $\text{Eu}^{3+}:\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-YF}_3\text{-AlF}_3\text{-NaF}$  glasses," *Physica B*, Vol. 344, pp. 182-189, 2004.
- [30] Q. Luo, X. Qiao, X. Fan, S. Liu, H. Yang, and X. Zhang, "Reduction and luminescence of europium ions in glass ceramics containing  $\text{SrF}_2$  nanocrystals," *J. Non-Cryst. Solids*, Vol. 354, pp. 4691-4694, 2008.
- [31] Y. Kishi and S. Tanabe, "Infrared-to-visible upconversion of rare-earth doped glass ceramics containing  $\text{CaF}_2$  crystals," *J. Alloys Compd.* Vol. 408-412, pp. 842-844, 2006.
- [32] A.S. Gouveia-Neto, E.B. da Costa, L.A. Bueno, and S.J.L. Ribeiro, "Intense red upconversion emission in infrared excited holmium-doped  $\text{PbGeO}_3\text{-PbF}_2\text{-CdF}_2$  transparent glass ceramic," *J. Lumin.* Vol. 110, pp. 79-84, 2004.

THIS PAGE IS INTENTIONALLY LEFT BLANK.