Available online at www.sciencedirect.com
ScienceDirect
JOURNAL OF RARE EARTHS, Vol. 29, No. 5, May 2011, P. 484
JOURNAL OF RARE EARTHS
www.re-journal.com/en/

Ultraviolet to visible frequency-conversion properties of rare earths doped glass ceramics

Y. Hatefi[1,2], N. Shahtahmasebi[2,3], A. Moghimi[4], E. Attaran[3]

(1. Department of Physics, Imam Hossein University, Tehran, Iran; 2. Nano-Research Centre of the Ferdowsi University of Mashhad, Mashhad, Iran; 3. Department of Physics, Ferdowsi University of Mashhad, Mashhad, Iran; 4. Department of Chemistry, Imam Hossein University, Tehran, Iran)

Received 28 August 2010; revised 15 February 2011

Abstract: Nd^{3+}, Eu^{3+} and Tb^{3+} ions doped transparent chlorophosphate glass ceramics were prepared and their frequency-conversion properties were studied. X-ray diffraction (XRD) patterns evidenced the formation of expected halide nanocrystals. The absorption, excitation and emission spectra investigation indicated that some of rare earth (RE) ions were trapped in low phonon energy halide nanocrystals, and therefore an efficient down frequency-conversion was observed. The comparative spectroscopic studies of RE doped samples suggested that the glass ceramics systems are potentially applicable as efficient ultraviolet to visible frequency-conversion photonics materials.

Keywords: chlorophosphate glass; down frequency-conversion; glass ceramic; photonic devices; nanocrystal; rare earth ions

In recent years, RE ions doped glass ceramics have attracted much attention due to their potential application in optical devices such as frequency-conversion materials and solid-state lasers[1–10]. Transparent glass ceramics are two phase materials containing nanocrystalites with sizes less than 30 nm embedded in a glassy matrix[11–13].

Among various glass matrices, the phosphate glasses have several advantages, such as high thermal expansion coefficient, low melting and softening temperature and high ultraviolet transmission in comparison with conventional oxide glasses[14–16]. Phosphate glasses also act as good hosts for large concentrations of dopant RE ions with good homogeneity[15]. Furthermore, phosphate glass shows the highest emission cross-sections and highest spectral intensity[17,18]. The low phonon energy of the fluoride and chloride glasses yields low non-radiative decay and high radiative emission rates of RE ion energy levels, leading to much higher quantum efficiencies[19–21]. The host materials with low phonon energies are generally desirable in order to achieve higher emission efficiencies.

Frequency-conversion properties of Eu^{3+} doped chlorophosphate[2] and fluorophosphate[3] transparent glass ceramics were reported in our previous works. There are, however, limited number of research reports on the RE doped chlorophosphate glass and glass ceramics in the literature. In this work the Nd^{3+}, Eu^{3+} and Tb^{3+} doped chlorophosphate glass and glass ceramics were successfully prepared, and their ultraviolet to visible frequency-conversion properties have been studied.

1 Experimental

RE ions doped chlorophosphate glasses with composition in mol.% of: $45P_2O_5$, $14Na_2HPO_4$, $25CaCl_2$, 15NaCl, $1RE_2O_3$ (RE=Nd, Eu and Tb) were prepared with melting procedure. All the raw materials were anhydrous powders with high purity. The batches of raw materials were melted at 1000 ºC for 1 h in a covered alumina crucible in the normal atmosphere. The liquids were shaken at 20 min. interval during melting. The molten mixtures were transferred into stainless steel and copper molds to obtain cubic glassy rods with 3 cm length and cross sections with 0.7 cm side. The heat treatment procedures were performed at temperatures between T_g and T_c (transition and crystallization temperatures) and transparent glass ceramics samples were obtained. The Nd^{3+} and Tb^{3+} doped glass ceramics that annealed at 460 ºC for 3 h have been assigned in the text as Nd^{3+}:G-C and Tb^{3+}:G-C. The Eu^{3+} doped glass ceramics that annealed at 460 ºC for 1 and 3 h, have been assigned in the text as Eu^{3+}:G1-C and Eu^{3+}:G3-C, respectively.

XRD spectrometer (X'pert, Philips) was used to investigate the nanocrystals formation. Jenway UV-vis spectrometers and Jasco spectrofluoremeter were used for absorption, excitation and frequency conversion spectroscopy studies. A Xe lamp was used as an excitation source for down conversion emission. All the measurements were carried out at room temperature.

2 Results and discussion

2.1 XRD results

XRD patterns of the glass and glass ceramics samples are

Foundation item: Project supported by the Applied Physics Research Centre of Imam Hossein University, Tehran, Iran (180/207/531-1388/5/5)

Corresponding author: Y. Hatefi (**E-mail:** yhatefi@yahoo.com; **Tel.:** +98-21-77104932)

DOI: 10.1016/S1002-0721(10)60484-X

illustrated in Fig. 1. The glassy sample has amorphous structure. However, for glass ceramics samples the crystalline $CaCl_2$ structure (marked with *) were observed. Thus, glass ceramics containing $CaCl_2$ nanocrystals were obtained. By using Scherrer formula, the size of the nanocrystals was evaluated to be about 20 nm for glass ceramic samples that annealed at 460 ºC for 3 h. For sample that annealed at 460 ºC for 6 h (G-C 460 6 h) the size of the nanocrystals was about 35 nm and resulted more decrease in their transparency.

In the next sections, ultraviolet to visible frequency-conversion properties of Nd^{3+}, Eu^{3+} and Tb^{3+} doped glass and glass ceramics with more emphasis were reported.

2.2 Nd^{3+} doped samples

The absorption spectra of Nd^{3+}:glass and Nd^{3+}:G-C, between 300–900 nm are given in Fig. 2, which consist of some intense absorption bands located at 865, 795, 740, 580, 525 and 355 nm, corresponding to the ground state $^4I_{9/2}$ to the excited states $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$+$^4S_{3/2}$, $^4G_{5/2}$+$^2G_{7/2}$, $^2K_{13/2}$+$^4G_{7/2}$, and $^4D_{3/2}$+$^4D_{5/2}$ respectively. The absorption spectra show that both of fabricated glass and glass ceramics are transparent matrices at 300–900 nm region. Similar result has been observed for other Nd^{3+}:glasses[22–24]. And also all of absorption bands were comprised with energy level scheme of Nd^{3+} doped ceramic garnet $Y_3Al_5O_{12}$[25].

The excitation spectra of Nd^{3+} doped glass and glass ceramics, monitored at 700 nm are illustrated in Fig. 3. The spectral range from 200 to 650 nm consisted of some sharp

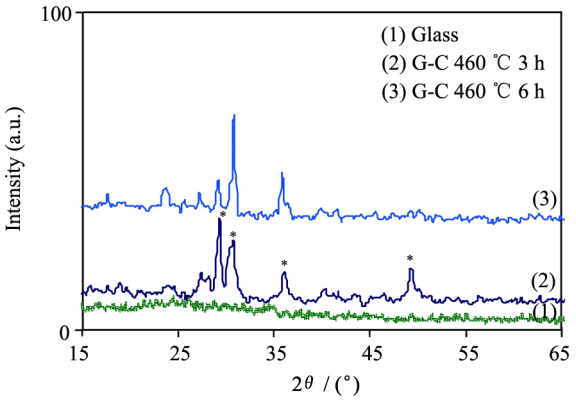

Fig. 1 XRD patterns of Glass (1), G-C 460 ºC 3 h sample with $CaCl_2$ phase (*) (2) and G-C 460 ºC 6 h (3)

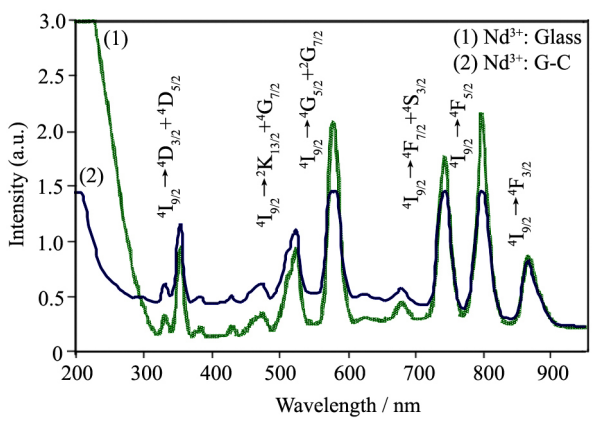

Fig. 2 Absorption spectra of Nd^{3+}: glass (1) and Nd^{3+}: G-C samples (2)

lines at 238, 300 and 355 nm which resulted from transitions between the 4f energy levels of Nd^{3+} ions. For Nd^{3+}: G-C sample, very intense emissions were observed at 238 nm in comparison with Nd^{3+}: glass and this wavelength is very suitable for down frequency conversion.

Fig. 4 shows the down conversion emission spectra of Nd^{3+} ions in the glass and glass ceramic samples. The emission bands were achieved in visible region at 472, 484, 703 and 715 nm. For Nd^{3+}: glass sample, weak luminescence peaks were observed, while intense luminescence was observed for glass ceramic sample. The measured down conversion emission intensity from the Nd^{3+}: G-C at 472 nm is about 14 times that of the Nd^{3+}: glass sample at 484 nm. For the crystallized sample the emission bands centers shift to lower wavelengths side. The band shift can be related for the transformation of environmental structure of Nd^{3+} site from amorphous to ordered crystalline, which confirms the incorporation of Nd^{3+} ions into $CaCl_2$ nanocrystals during crystallization.

2.3 Eu^{3+} doped samples

The excitation spectra of Eu^{3+} emission monitored at 615 nm of $^5D_0 \rightarrow {}^7F_2$ transition are depicted in Fig. 5. The excitation bands in the spectral range from 220 to 600 nm, can be assigned to $^7F_0 \rightarrow {}^5D_0$ (592 nm), $^7F_0 \rightarrow {}^5D_1$ (534 nm), $^7F_0 \rightarrow {}^5D_2$ (465 nm), $^7F_0 \rightarrow {}^5D_3$ (414 nm), $^7F_0 \rightarrow {}^5L_6$ (396 nm), $^7F_0 \rightarrow {}^5G_3$ (383 nm) and $^7F_0 \rightarrow {}^5D_4$ (364 nm) respectively. Similar excitation spectra for Eu^{3+} doped glasses and glass ceramics previously were reported[12,21,26–28]. The strongest peak at 396 nm for Eu^{3+}: glass and particular strong peaks for Eu^{3+} doped glass ceramics samples at 311 nm were obtained. Thus, the

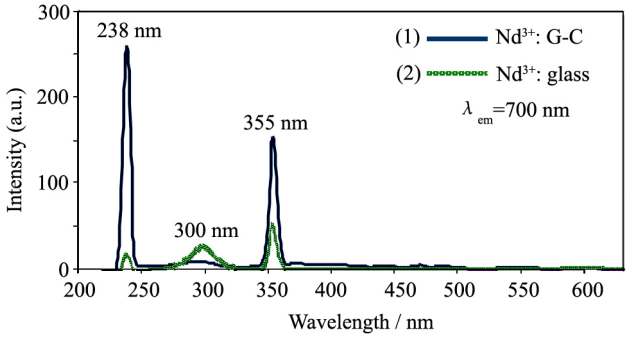

Fig. 3 Excitation spectra of Nd^{3+}: G-C (1) and Nd^{3+}: glass (2) samples (monitored at 700 nm)

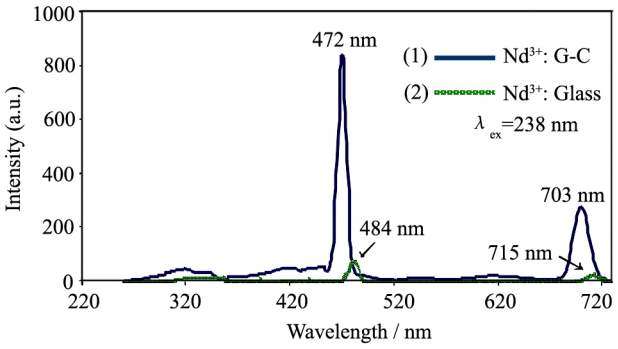

Fig. 4 Down conversion luminescences of Nd^{3+}: G-C (1) and Nd^{3+}: glass (2) samples (excited at 238 nm)

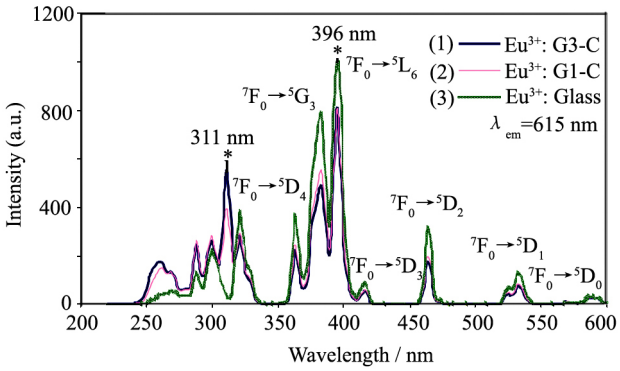

Fig. 5 Excitation spectra of Eu^{3+}: G3-C (1), Eu^{3+}: G1-C (2) and Eu^{3+}: glass (3) samples (monitored at 615 nm)

396 and 311 nm are ideal pump wavelengths to generate down conversion emission from these samples.

Fig. 6 shows ultraviolet to visible frequency-conversion emission spectra of Eu^{3+} ions in the glass and glass ceramics samples that excited at 396 nm. These spectra consist of the well known $^5D_0 \rightarrow {}^7F_J$ (J=0–4) transitions namely $^5D_0 \rightarrow {}^7F_0$ (554 nm), $^5D_0 \rightarrow {}^7F_1$ (588 nm), $^5D_0 \rightarrow {}^7F_2$ (611 nm), $^5D_0 \rightarrow {}^7F_3$ (652 nm) and $^5D_0 \rightarrow {}^7F_4$ (696 nm). For Eu^{3+}: G1-C sample the highest intensity has been obtained and with increasing the time of heat treatment (for Eu^{3+}: G3-C) emission intensities were decreased. The excitation beams at region 392-396 nm (corresponding to $^5L_6 \rightarrow {}^7F_0$ transition) have been suggested as ideal wavelengths to generate brightly red luminescent in different Eu^{3+} doped glasses[2,3,12,27–31].

Fig.7 shows the emission spectra of Eu^{3+} doped samples at $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions that excited at 311 nm. The intense emission was achieved at 614 nm for Eu^{3+}: G3-C. For $^5D_0 \rightarrow {}^7F_1$ transition at 591 nm, weak emission peak was appeared. The emission intensity of Eu^{3+}: G3-C and Eu^{3+}: G1-C are about 13.4 and 10.2 times stronger than of Eu^{3+}: glass at 614 nm respectively. The probability of the $^5D_0 \rightarrow {}^7F_2$ transition is very sensitive to changes in the chemical surroundings of the Eu^{3+} ions[2,3,12] which indicated that the Eu^{3+} ions have been incorporated into $CaCl_2$ nanocrystals.

2.4 Tb^{3+} doped samples

The excitation spectra of Tb^{3+} doped glass and glass ceramics emission monitored at 592 nm are illustrated in Fig. 8.

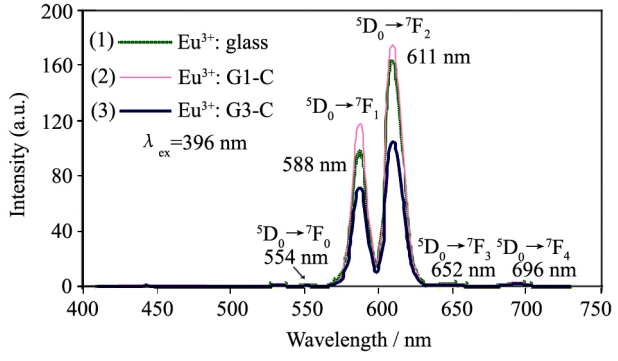

Fig. 6 Emission spectra of Eu^{3+}: glass (1), Eu^{3+}: G1-C (2) and Eu^{3+}: G3-C (3) (excited at 396 nm)

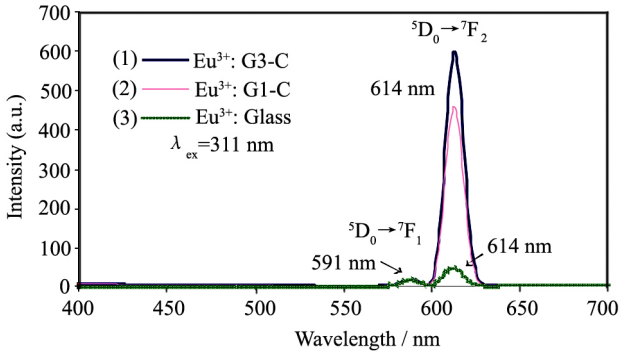

Fig. 7 Emission spectra of Eu^{3+}: G3-C (1), Eu^{3+}: G1-C (2) and Eu^{3+}: glass (3) samples (excited at 311 nm)

The spectral range from 220 to 600 nm consisted of some intense excitation at 255 and 300 nm. For Tb^{3+}: G-C sample, very intense emission was observed at 300 nm in comparison with Tb^{3+}: glass and this wavelength is very suitable for down frequency conversion.

Fig. 9 shows the down conversion emission spectra (excited at 300 nm) of Tb^{3+} doped samples. The emission bands were achieved at 490, 543 and 592 nm. For Tb^{3+}: glass sample, weak luminescence peak were observed, while intense down conversion luminescence was observed for glass ceramic sample at 592 nm, the down conversion emission intensity of Tb^{3+}: G-C is about 66 times stronger than of Tb^{3+}: glass sample at this wavelength.

For all of RE doped glass ceramics samples, the increasing of down conversion emission intensities indicates that $CaCl_2$ nanocrystals have a great influence on these favorable changes. After crystallization process of thermal treatment, some of the rare earths ions could be trapped in the $CaCl_2$ nanocrystals. The glass ceramic matrix provides the distinct

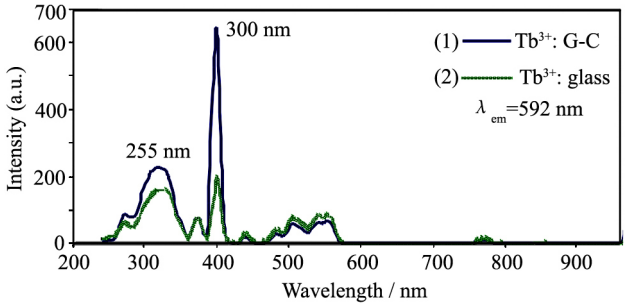

Fig. 8 Excitation spectra of Tb^{3+}: G-C (1) and Tb^{3+}: Glass (2) samples (monitored at 592 nm)

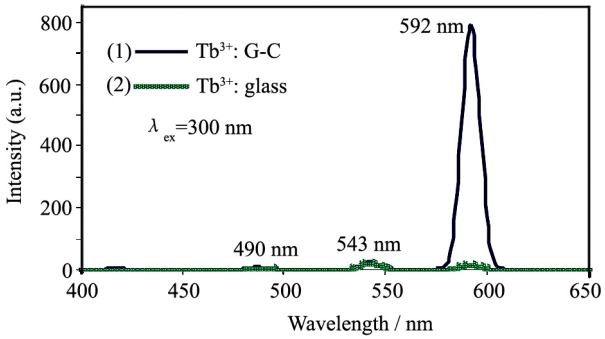

Fig. 9 Emission spectra of Tb^{3+}: G-C (1) and Tb^{3+}: Glass (2) samples (excited at 300 nm)

advantage of low phonon frequencies compared to glass materials and minimizes the non-radiative losses and therefore more efficient emission intensities can be observed.

3 Conclusions

Nd^{3+}, Eu^{3+} and Tb^{3+} doped transparent chlorophosphate glass ceramics containing $CaCl_2$ nanocrystals were obtained from P_2O_5-Na_2HPO_4-$CaCl_2$-NaCl-RE_2O_3 composition. All of the experiments demonstrated suitable changes in glass ceramics host medium and resulted in further improvements in emission intensities of RE doped glass ceramics. Spectroscopy studies showed that considerable amount of RE ions were incorporated into the crystalline phase and resulted in much stronger emission in glass ceramics samples and therefore implied them as a potential material for ultraviolet to visible frequency-conversion photonics materials.

References:

[1] Clara Gonçalves M, Santos Luis F, Almeida Rui M. Rare-earth-doped transparent glass ceramics. *C. R. Chimie*, 2002, **5**: 845.

[2] Hatefi Y, Shahtahmasebi N, Moghimi A, Attaran E. Frequency-conversion properties of Eu^{3+} doped chlorophosphate glass ceramics containing $CaCl_2$ nanocrystals. *J. Lumin.*, 2011, **131**: 114.

[3] Hatefi Y, Anbaz K, Moghimi A, Maddah B. Up and down frequency-conversion properties of Eu^{3+} doped lead fluorophosphate nanoglass ceramics. *International Journal of Optics and Photonics* (IJOP in Iran), Winter-Spring, 2010, **4**: 57.

[4] Dejneka M J. The luminescence and structure of novel transparent oxyfluoride glass-ceramics. *J. Non-Cryst. Solids,* 1998, **239**: 149.

[5] Lavin V, Iparraguirre I, Azkargorta J, Mendioroz A, Gonzalez-Platas J, Balda R, Fernandez J. Stimulated and upconverted emissions of Nd^{3+} in a transparent oxyfluoride glass-ceramic. *Opt. Mater.*, 2004, **25**: 201.

[6] Gouveia-Neto A S, da Costa E B, Bueno L A, Ribeiro S J L. Upconversion luminescence in transparent glass ceramics containing β-PbF_2 nanocrystals doped with erbium. *J. Alloys Compd.*, 2004, **375**: 224.

[7] Lahoz F, Martςn I R, Rodriguez-Mendoza U R, Iparraguirre I, Azkargorta J, Mendioroz A, Balda R, Fernandez J, Lavin V. Rare earths in nanocrystalline glass-ceramics. *Opt. Mater.*, 2005, **27**: 1762.

[8] Qiao X, Fan X, Wang M. Luminescence behavior of Er^{3+} in glass ceramics containing BaF_2 nanocrystals. *Scripta Mater.*, 2006, **55**: 211.

[9] Pisarska J, Ryba-Romanowski W, Dominiak-Dzik G, Goryczka T, Pisarski W A. Nd-doped oxyfluoroborate glasses and glass-ceramics for NIR laser applications. *J. Alloys Compd.*, 2008, **451**: 223.

[10] Deng D, Xu S, Zhao S, Li C, Wang H, Ju H. Enhancement of upconversion luminescence in Tm^{3+}/Er^{3+}/Yb^{3+}-co doped glass ceramic containing $LiYF_4$ nanocrystals. *J. Lumin.*, 2009, **129**: 1266.

[11] Edgar A. Optical Properties of Condensed Matter and Applications", Edited by Singh J, John Wiley & Sons Ltd, 2006: 159.

[12] Zhao D, Qiao X, Fan X, Wang M. Local vibration around rare earth ions in SiO_2-PbF_2 glass and glass ceramics using Eu^{3+} probe. *Physica B,* 2007, **396**: 10.

[13] Shepilov M P. On light scattering in fluorozirconate glass-ceramics containing $BaCl_2$ nano-crystals. *Opt. Mater.,* 2008, **30**: 839.

[14] Kumar K U, Babu P, Jang K H, Seo H J, Jayasankar C K, Joshi A S. Spectroscopic and 1.06 μm laser properties of Nd^{3+}-doped K-Sr-Al phosphate and fluorophosphate glasses. *J. Alloys Compd*., 2008, **458**: 509.

[15] Hemantha Kumar G N, Rao J L, Ravindra Prasad K, Ratnakaram Y C. Fluorescence and Judd-Ofelt analysis of Nd^{3+} doped P_2O_5-Na_2O-K_2O glass. *J. Alloys Compd*., 2009, **480**: 208.

[16] Seshadri M, Venkata Rao K, Rao J L, Ratnakaram Y C. Spectroscopic and laser properties of Sm^{3+}-doped different phosphate glasses. *J. Alloys Compd*., 2009, **476**: 263.

[17] Ratnakaram Y C, Viswanadha Reddy A, Sreekanth Chakradhar R P. Electronic absorption spectra and energy gap studies of Er^{3+} ions in different chlorophosphate glasses. *Spectrochim. Acta A*, 2002, **58**: 1809.

[18] Weber M J. Science and technology of laser glass, *J. Non-Cryst. Solids,* 1990, **123**: 208.

[19] Karmakar B, Annapurna K. Blue, green and red upconversions Ho_2O_3-doped fluorophosphate Glasses. *J. Non-Cryst. Solids,* 2007, **353**: 1377.

[20] Prakash G V, Jagannathan R. Fluorescence properties of Eu^{3+} doped lead bearing fluorochloro phosphate glasses. *Spectrochim. Acta A*, 1999, **55**: 1799.

[21] Annapurna K, Dwivedi R N, Buddhudu S. Emission properties of Eu^{3+} ions in $ZnCl_2$-$BaCl_2$-KCl glass. *Mater. Lett*., 2002, **53**: 359.

[22] Koepke Cz, Wisniewski K, Sikorski L, Piatkowski D, Kowalska K, Naftaly M. Upconverted luminescence under 800 nm laser diode excitation in Nd^{3+}-activated fluoroaluminate glass. *Opt. Mater.*, 2005, **28**: 129.

[23] Nie Q, Li X, Dai S, Xu T, Chen Y, Zhang X. Investigation of 1.3 μm emission in Nd^{3+}-doped bismuth-based oxide glasses. *Physica B,* 2007, **400**: 88.

[24] Ratnakaram Y C, Reddy A V. Electronic spectra and optical band gap studies in neodymium chlorophosphate glasses. *J. Non-Cryst. Solids*, 2000, **277**: 142.

[25] Gruber J B, Sardar D K, Yow R M, Allik T H, Zandi B. Energy-level structure and spectral analysis of $Nd^{3+}(4f^3)$ in polycrystalline ceramic garnet $Y_3Al_5O_{12}$. *J. Appl. Phys*., 2004, **96**(6): 3050.

[26] Dejneka M, Snitzer E, Riman R E. Blue, green and red fluorescence and energy transfer of Eu^{3+} in fluoride glasses. *J. Lumin*., 1995, **65**: 227.

[27] Kam C H, Buddhudu S. Photoluminescence properties of Eu^{3+}: ZrF_4-BaF_2-LaF_3-YF_3-AlF_3-NaF Glasses. *Physica B,* 2004, **344**: 182.

[28] Luo Q, Qiao X, Fan X, Liu S, Yang H, Zhang X. Reduction

and luminescence of europium ions in glass ceramics containing SrF_2 nanocrystals. *J. Non-Cryst. Solids*, 2008, **354**: 4691.

[29] Balaji S, Abdul Azeem P, Reddy R. Absorption and emission properties of Eu^{3+} ions in sodium fluoroborate glasses. *Physica B,* 2007, **394**: 62.

[30] Cong Y, Li B, Lei B, Wang X, Liu C, Liu J, Li W. Enhancement of luminescence intensity and Increase of emission lifetime in Eu^{3+}-doped 3CdO- Al_2O_3-3SiO_2 amorphous system. *J. Lumin.*, 2008, **128**: 105.

[31] You Hongpeng, Hong Guangyan. The change of Eu^{3+}-surroundings in the system Al_2O_3-B_2O_3 containing Eu^{3+} ions. *J. Phys. Chem. Solids,* 1999, **60**: 325