



Silver lead borate glasses doped with europium ions for phosphors applications

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Abstract. Europium (Eu^{3+}) doped silver lead borate glasses with the composition of $x\text{Eu}_2\text{O}_3-(1-x)\text{Ag}_2\text{O}-29\text{PbO}-70\text{B}_2\text{O}_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5 mol%) have been successfully prepared by conventional melt quenching method. Thermal, structural and luminescence properties have been studied using thermograms, transmittance, excitation and emission spectra. From the differential scanning calorimetry studies, the glass transition temperatures (T_g) have been investigated and their values are ranging from 449 to 458°C. The investigation of Fourier transformer infrared spectra shows the presence of boron atoms in both BO_3 and BO_4 units in the glass network. In addition, it was found that new structural groups were present, such as boroxyl rings, pyro and dipenta-borate. Photoluminescence spectroscopy was used to examine down conversion emission under 394 nm excitation, which exhibits five emission bands centred at 577, 590, 612, 650 and 697 nm corresponding to ${}^5\text{D}_0-{}^7\text{F}_0$, ${}^5\text{D}_0-{}^7\text{F}_1$, ${}^5\text{D}_0-{}^7\text{F}_2$, ${}^5\text{D}_0-{}^7\text{F}_3$ and ${}^5\text{D}_0-{}^7\text{F}_4$ transitions of Eu^{3+} ions, respectively. The Commission International de l'Eclairage France 1931 chromaticity coordinates estimated from the emission spectra; it was shown that a 0.5 mol% Eu_2O_3 doped glass is quite suitable for efficient red phosphors application.

Keywords. Lead borate; DSC; FTIR; photoluminescence.

1. Introduction

In recent years, there is an emerging research that focuses on the rare earth (RE) doped oxide glasses due to their potential applications in various fields such as solid-state laser, optical amplifier, display and photo-electronic devices [1,2]. Among the RE ions, trivalent europium (Eu^{3+}) is considered as the most favourable element because of its narrow emission band producing monochromatic light, a long radiative lifetime [3] and the Eu^{3+} ions doped glasses show interesting emission spectra under near UV excitation. The visible luminescence of the Eu^{3+} ions doped glasses mainly consists of two eminent intense peaks in the orange (590 nm; ${}^5\text{D}_0-{}^7\text{F}_1$ transition) and in the red (615 nm; ${}^5\text{D}_0-{}^7\text{F}_2$ transition) wavelength regions [4]. The red wavelength region is the hypersensitive transition and strongly influenced by the environment around the ions, these kinds of Eu^{3+} doped glasses find wide range of applications in the field of an efficient red phosphor in particularly designing mercury-fluorescent lamps, LEDs and plasma displays. Glasses containing silver have been technologically interesting materials for solid-state batteries and electrochemical devices because of their valuable optical properties and high value of ionic conductivity [5]. Lead borate glasses are a research interest, owing to their structural peculiarities. The addition of PbO into the borate network brings modification of boroxol rings and formation of complex groups with one or two four-fold

co-ordinated boron atoms [6]. Lead borate glasses have several applications including radiation shields, optical and thermal properties [7,8]. Moreover, borate glasses having high phonon energies, which can be reduced by the addition of PbO into the borate network makes a reduction in non-radiative loss; thereby causing an enhancement in the luminescence efficiency [9].

In our previous work, we reported that the addition of (Eu^{3+}) ions into the silver lead borate glass matrix produces structural modification in the glass network, which leads to significant changes in the optical properties of the glass system [10]. In the present research, the authors intend to study the luminescence properties of the studied glasses through photoluminescence (PL) spectroscopy. The luminescence colour of the glass system excited at 394 nm has been demonstrated by the Commission International de l'Eclairage France (CIE) 1931 chromaticity diagram. We also studied the thermal and structural properties through differential scanning calorimetry (DSC) and Fourier transformer infrared (FTIR) spectroscopy, respectively.

2. Experimental

The raw materials of reagent grade chemicals H_3BO_3 , PbO , Ag_2O and Eu_2O_3 were used to synthesize the glass samples by conventional melt quenching method with the composition of

$x\text{Eu}_2\text{O}_3 - (1-x)\text{Ag}_2\text{O} - 29\text{PbO} - 70\text{B}_2\text{O}_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5 mol%). The detailed experimental procedure for preparation of glass is given elsewhere [10]. The glass transition temperature (T_g) was determined by DSC at nitrogen atmosphere in a Perkin Elmer's DSC-6000 in the temperature range $100\text{--}500^\circ\text{C}$. The FTIR spectra of powdered glass was recorded at room temperature by Nicolet spectrometer with a resolution of 0.2 cm^{-1} in the frequency range $400\text{--}4000\text{ cm}^{-1}$ by using the standard KBr pellet method. The excitation and emission spectra was recorded using F-2700 FL spectrophotometer with xenon flash lamp as a source.

3. Result and discussion

The DSC patterns for different composition glasses are shown in figure 1, for a heating rate of 5°C min^{-1} and their obtained values are presented in table 1. It can be seen from figure 1 that all glass samples showed an endothermic peak, which shifts to lower temperature by adding 0.1 mol% of Eu_2O_3 and by further increasing the concentration of Eu_2O_3 up to 0.5 mol%, the glass T_g increases linearly. We are well aware

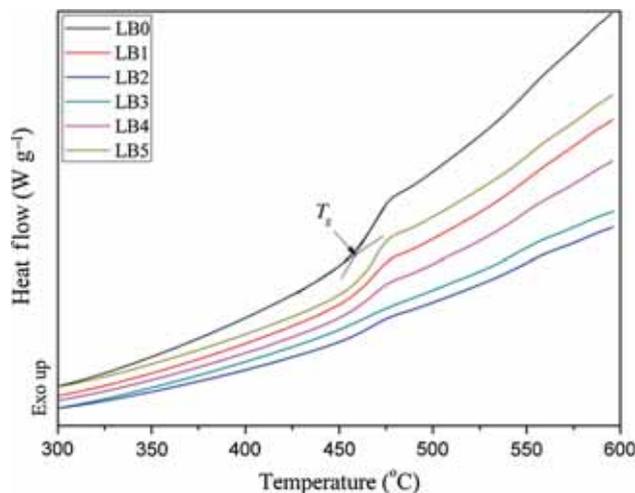


Figure 1. DSC thermograms of the $\text{Eu}_2\text{O}_3 - \text{Ag}_2\text{O} - \text{PbO} - \text{B}_2\text{O}_3$ glass system.

that the glass T_g is rigorously linked to the density of cross-linking and bond strength. It is clear that when a higher density of cross-link and higher bond strength of the structure are obtained because of the incorporation of the dopant; the mean bond strength and network connectivity increases, resulting in the increase in glass T_g [11]. When the thermograms of all the samples were re-measured from cooled down to room temperature, the same kind of endothermic peak reappeared for all samples. These results confirm that the first measured glass T_g was not permanent, but reversible. From the DSC results we conclude that the rigidity of glasses increases with the increase in Eu_2O_3 mol% from 0.2 to 0.5 mol%.

The FTIR spectra of the glass system as depicted in figure 2 and their assignments of the bands are presented in table 2. The broad composite band extending from 3200 to 3600 cm^{-1} is attributed to hydroxyl (OH) or water group [12]. The broad water bands have been classified into three categories: (i) the peak around $3600\text{--}3750\text{ cm}^{-1}$ is originating from OH-groups, (ii) the peak from 3200 to 3500 cm^{-1} is originating from the molecular water and (iii) the peak from 2700 to 3000 cm^{-1} is originating from hydrogen bonding. In figure 2, it can be seen that a strong broad band appeared in the range of $1346\text{--}1377\text{ cm}^{-1}$, which is attributed to B-O asymmetric stretching of the trigonal BO_3 unit and the shoulder at 1234 cm^{-1} may arise from B-O stretching vibrations of $(\text{BO}_3)^{3-}$ units in metaborates, pyroborates and orthoborates [13]. Similarly the bands around $1087\text{--}1113\text{ cm}^{-1}$ is because of the vibration of some boron atoms attached to non-bridging oxygen in the form of BO_4 units [14] and the absorption peaks around $1087\text{--}1113\text{ cm}^{-1}$ is attributed to the formation of diborate in the glass system. The absorption peaks were around $947\text{--}971\text{ cm}^{-1}$ probably due to the stretching vibrations of tetrahedral BO_4 units and the band at 993 cm^{-1} in the spectra may also be assigned to a stretching vibration of B-O-Pb linkage. The band, which is around 710 cm^{-1} is assigned to bond bending vibrations of B-O-B linkages of the boron-oxygen network [12]. The absorption band at 692 cm^{-1} is assumed to be due to combined vibration of BO_4 and PbO_4 groups and the band, which is around 699 cm^{-1} indicates that oxygen bridges two trigonal boron atoms. The spectral domain $400\text{--}760\text{ cm}^{-1}$ is dominated by the band centred at

Table 1. The glass samples composition with glass transition temperature (T_g) for $\text{Eu}_2\text{O}_3 - \text{Ag}_2\text{O} - \text{PbO} - \text{B}_2\text{O}_3$ glass system.

Glass code	Glass composition (mol%)				Glass transition temperature (T_g)($^\circ\text{C}$)
	Eu_2O_3	Ag_2O	PbO	B_2O_3	
LB0	0	1	29	70	456
LB1	0.1	0.9	29	70	449
LB2	0.2	0.8	29	70	454
LB3	0.3	0.7	29	70	455
LB4	0.4	0.6	29	70	457
LB5	0.5	0.5	29	70	458

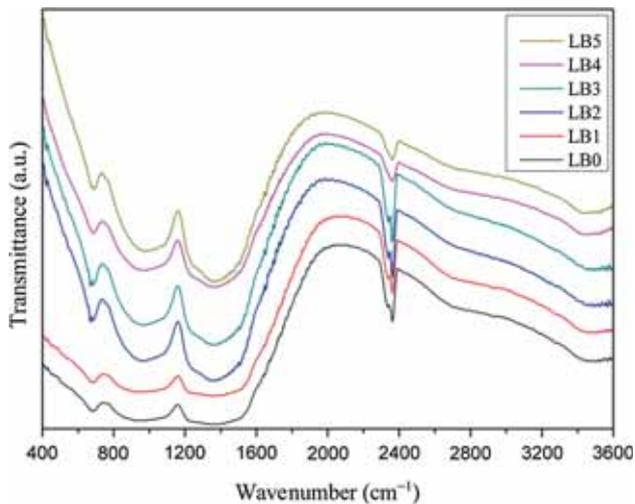


Figure 2. FTIR spectra of the $\text{Eu}_2\text{O}_3\text{-Ag}_2\text{O-PbO-B}_2\text{O}_3$ glass system.

Table 2. Wavenumbers and their assignments for FTIR spectra of the $\text{Eu}_2\text{O}_3\text{-Ag}_2\text{O-PbO-B}_2\text{O}_3$ glass system.

Wavenumber (cm^{-1})	Assignments
3600–3750	OH- group
3200–3500	Molecular water
2700–3000	Hydrogen bonding
1346–1377	B–O asymmetric stretching of trigonal BO_3 unit
1234	B–O stretching vibrations of $(\text{BO}_3)^{3-}$ units in metaborates, pyroborates and orthoborates
993	Stretching vibration of B–O–Pb linkage
710	Bending vibrations of B–O–B linkages of the boron–oxygen network
670	Pb–O bond vibrations and O–B–O bond bending vibrations

670 cm^{-1} , which is attributed to Pb–O bond vibrations and O–B–O bond bending vibrations [15]. It was detected that there was no characteristic vibration of modes of bonds from Eu_2O_3 and Ag_2O oxides in the FTIR spectra.

The down conversion (fluorescence) property of Eu^{3+} ions in silver lead borate glass was examined. The excitation spectra of Eu^{3+} was monitored at $\lambda_{\text{em}} = 590$ and 612 nm of ${}^5\text{D}_0\text{-}{}^7\text{F}_1$ and ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ transitions that are depicted in figure 3. The spectral range from 200 to 600 nm consists of sharp lines, which is attributed to transitions among the 4f energy levels of Eu^{3+} . The excitation bands can be assigned to 362 nm (${}^7\text{F}_0\text{-}{}^5\text{D}_4$), 381 nm (${}^7\text{F}_0\text{-}{}^5\text{G}_3$), 394 nm (${}^7\text{F}_0\text{-}{}^5\text{L}_6$), 414 nm (${}^7\text{F}_0\text{-}{}^5\text{D}_3$), 465 nm (${}^7\text{F}_0\text{-}{}^5\text{D}_2$) and 533 nm (${}^7\text{F}_0\text{-}{}^5\text{D}_1$). All the assigned transition values are in good agreement with excitation values of Eu^{3+} ions as reported in the literature [16]. The excitation spectra shows the

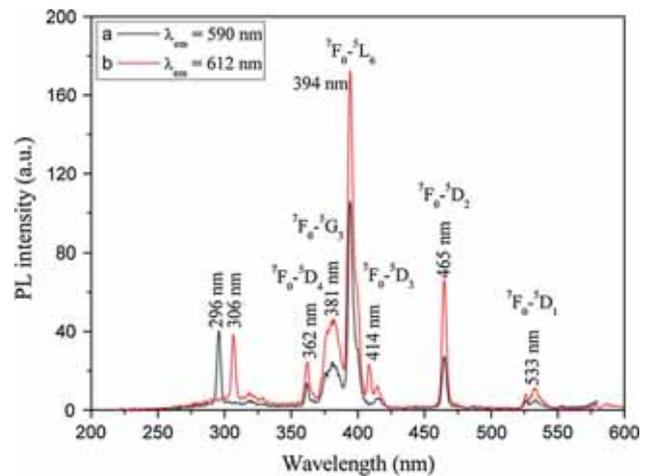


Figure 3. Typical excitation spectra of the Eu^{3+} glass monitored at $\lambda_{\text{em}} = 590$ and 612 nm .

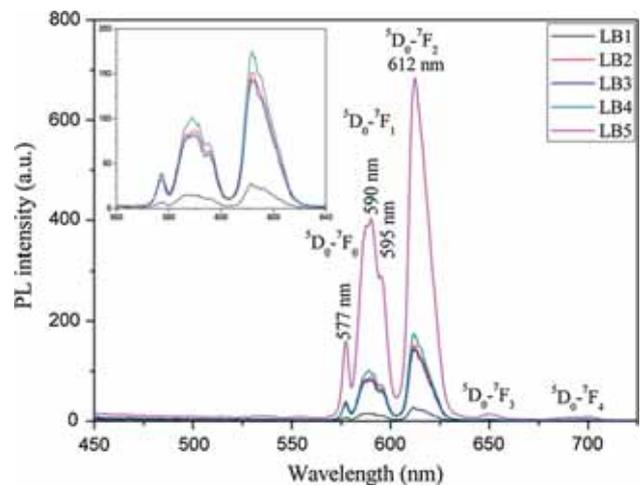


Figure 4. The emission spectra of the $\text{Eu}_2\text{O}_3\text{-Ag}_2\text{O-PbO-B}_2\text{O}_3$ glass system monitored at $\lambda_{\text{ex}} = 394\text{ nm}$.

strongest peak at 394 nm for Eu^{3+} and also found peaks at 296 and 306 nm for $\lambda_{\text{em}} = 590$ and 612 nm , respectively. A peak shift has been observed from 296 to 306 nm in the different emission values of Eu^{3+} . Thus, we consider 394, 306 and 296 nm to be ideal pump wavelengths to generate emission from the prepared samples and the emission spectra shows the most efficient emission peak at $\lambda_{\text{ex}} = 394\text{ nm}$. Figure 4 shows the emission spectra monitored at $\lambda_{\text{ex}} = 394\text{ nm}$ of Eu^{3+} ions in the glasses. It was clearly seen that the emission spectra consists of a number of peaks in the spectral range 450–725 nm, which corresponds to ${}^5\text{D}_0\text{-}{}^7\text{F}_J$ ($J = 0, 1, 2, 3$ and 4) transitions of Eu^{3+} . In glasses, due to the absence of a centre of symmetry and long-range periodicity of atoms, amalgamation of the 4f orbitals with an opposite parity orbital takes place [17]. This rise to the electric dipole allowed transitions. The ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ emission transition is forced by the crystal field

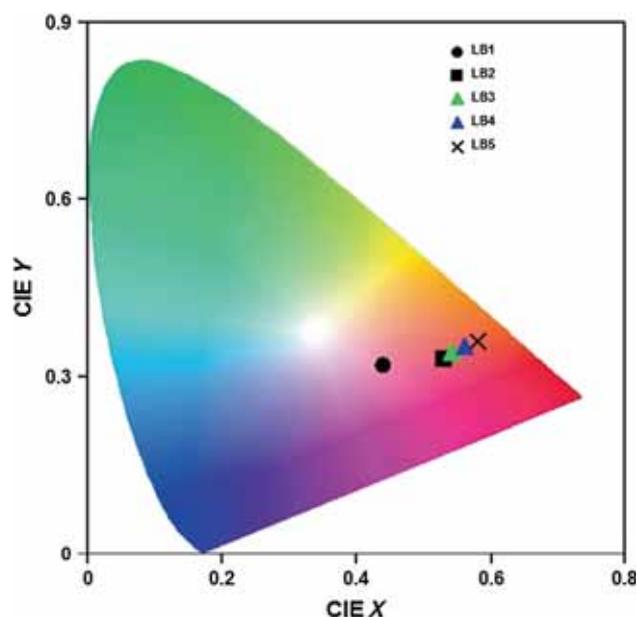


Figure 5. The luminescence colour space chromaticity diagram of the $\text{Eu}_2\text{O}_3\text{-Ag}_2\text{O-PbO-B}_2\text{O}_3$ glass system.

environment in the vicinity of the Eu^{3+} ions. It is a hypersensitive ($\Delta J = 2$) transition and its intensity is very sensitive to the local environment. The second strongest peak at 590 nm is in the orange region corresponding to $^5\text{D}_0\text{-}^7\text{F}_1$ emission transition (magnetic dipole, $\Delta J = 1$) of Eu^{3+} ions, which is spin-forbidden under selection rules. It is allowed due to spin-orbit interaction and its intensity is independent of the host environment. It is also found that in figure 4, there is a small stark splitting at 590 and 595 nm depending upon the ligand fields being experienced by them and other emissions $^5\text{D}_0\text{-}^7\text{F}_J$ ($J = 0, 3$ and 4) are strictly forbidden and appear with low intensities [18–20]. Among all the emission transitions, the most prominent and intense peak is the one from $^5\text{D}_0\text{-}^7\text{F}_2$ transition at 612 nm. As can be seen from figure 4, an increase in the luminescence intensity is observed, with increasing Eu_2O_3 concentration up to 0.2 mol% and slight decrease of 0.3 mol%, further increasing the concentration of Eu_2O_3 up to 0.5 mol%, which increases luminescence intensity. The enhanced emission intensities in the glass system suggested that Eu^{3+} ions possess lower symmetry and a strong covalent nature of the bonds between the Eu^{3+} ions and other constituents in the glass network. The intensity distributions of the $^5\text{D}_0\text{-}^7\text{F}_J$ ($J = 0, 1, 2, 3$ and 4) transition levels depend on the symmetry of the local environment around the Eu^{3+} ions and its covalence [21]. It can be observed from figure 4 that the optimum dopant concentration of Eu^{3+} ions in the silver lead borate glass system was about 0.5 mol%. The PL concentration quenching effect has also been observed in the glass system at 0.3 mol% of Eu_2O_3 . The luminescence intensity slightly reduces as concentration quenching occurs due to the lack of phonon-assisted process. In addition, it may be due to higher symmetry and a lower Eu-O covalence in the

glass network. The luminescence colour of the glasses excited at 394 nm has been demonstrated by the CIE 1931 chromaticity diagram as depicted in figure 5. The obtained chromaticity coordinates (x, y) for LB1, LB2, LB3, LB4 and LB5 are (0.44, 0.32), (0.53, 0.33), (0.54, 0.34), (0.56, 0.35) and (0.58, 0.36) respectively, which falls in the pink to red light region of CIE 1931 chromaticity diagram. It is observed from figure 5 that the obtained highest chromaticity coordinates (0.58, 0.36) of 0.5 mol% of Eu_2O_3 produce efficient red light. The other coordinates appearing in the pink to red region, can be used as pink to red colour phosphors applications and have several potential applications in photonic devices as well.

4. Conclusions

Silver lead borate glasses, doped with Eu^{3+} trioxide were successfully synthesized by conventional melt quenching method. DSC results concluded that increasing of the rigidity of the glasses occurs with an increase in Eu_2O_3 concentration in the host matrix. The investigation of FTIR spectra revealed that in the glass matrix various borate groups are randomly interconnected. We observed the presence of boron atoms in both BO_3 trigonal units and BO_4 tetrahedral units with new complex structural groups such as diborate, triborate, tetra borate and penta borate units in the glass network. No change was observed in the glass structure with the variation of Eu_2O_3 and addition of Ag_2O in the host matrix. From the PL studies of the glass system it is found to be an intense red emission peak for 0.5 mol% of Eu^{3+} ions, which is suitable for efficient red phosphor applications. However, we found that concentration quenching effect at 0.3 mol% of Eu^{3+} ions is because of the lack of phonon-assisted process. The CIE 1931 chromaticity coordinates x and y were found to be in the pink to red light region. These kinds of luminescence functionality novel phosphor glasses are promising materials for practical applications in mercury-fluorescent lamps, LEDs and plasma displays.

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