Journal of Alloys and Compounds 557 (2013) 209–217

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Optical and structural investigation of Eu^{3+} ions in Nd^{3+} co-doped magnesium lead borosilicate glasses

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ARTICLE INFO

Article history:
Received 13 December 2012
Received in revised form 29 December 2012
Accepted 31 December 2012
Available online 7 January 2013

Keywords:
$MgO–PbO–B_2O_3–SiO_2–Nd_2O_3$ glasses
Eu^{3+} ions
UV–Vis–NIR absorption
Luminescence
J–O parameters

ABSTRACT

The Eu^{3+} ions doped $MgO–PbO–B_2O_3–SiO_2–Nd_2O_3$ glasses have been prepared by melt-quenching technique. The optical and the structural characterizations are carried out for these glass samples. UV–Vis–NIR absorption spectra have prominent absorption bands in the Vis–NIR regions because of spectra materials Eu^{3+}, Nd^{3+} ions in the glass network. Luminescence spectra are recorded with an excited wavelength of 355 nm; the Eu^{3+} doped glasses have seven luminescence bands. The Judd–Ofelt intensity parameters, radiative transition probabilities and branching ratios are estimated for the observed Eu^{3+} luminescence bands in the spectra and compared with other literature data for Eu^{3+} in various compounds. The influence of Eu^{3+} ions on structure of the glass network has been studied by means of Fourier transform infrared (FT-IR) and Raman spectroscopy. The polymerization of the glass network takes place by the addition of Eu^{3+} ions due to the replacement of bonds B–O–B, Si–O–Si with more resistant B–O–Si, Si–O–Pb bonds. Along with spectroscopic parameters some physical parameters like density and refractive index are measured for these glasses.

1. Introduction

Borosilicate glasses are one of the important glasses offering attracted extensive research in the fields such as optoelectronics, solar energy technology, astronomical reflecting telescope, in microelectromechanical systems and sealing glasses to nuclear waste immobilization [1–5]. Moreover the high density of these glasses makes suitable for radiation shielding materials. The wide applications of the glasses takes place by their interesting properties as low thermal expansion, high softening temperature, high resistance to chemical attack, high refractive index with low dispersion and mechanical strength. Martens and Muller-Warmuth [6], Zhao et al. [7] and other researchers extensively investigated on structure of borosilicate glasses. They concluded that modifiers used in the network are influenced the physical properties and the structural changes in borosilicate glasses. Lead oxide (PbO) is widely used as intermediate oxide because it improves the chemical durability, enhances the resistance against diversification and reduces the melting temperature.

In modern technology, rare earth (RE) ions have attractive role as active ions in many optical materials due to large number of the absorption and emission bands arising from the transitions between the energy levels [8,9]. Among different lanthanides, europium is one of the effective materials which can be found to be in two oxidation states i.e. Eu^{2+}, Eu^{3+} depending upon the preparation conditions and it is the only lanthanide ion in which the ground state has $J = 0$, exceptional restrictions exists on the induced electric-dipole transitions originating from the ground state. The energy level structure of Eu^{3+} ion is found to be very sensitive to surrounding environs. The addition of Eu^{3+} ion in oxide glass matrix usually induces significant changes in its magnetic behavior and for the studies of the host–guest effects due to is relatively weak radiation-less transitions.

Co-doping of RE ions (Nd^{3+}) leads to an effective enhancement in the intensity of fluorescence (sensitized luminescence) for understanding of the basic mechanisms involved in formation of spectra and also to resolve the structure surrounding the RE ions in host matrix [10]. In present investigation, an attempt is made to study how the optical and structural features are changed with varying Eu^{3+}ions content in the $MgO–PbO–B_2O_3–SiO_2–Nd_2O_3$ glass network by means of UV–Vis–NIR absorption, luminescence, FT-IR and Raman spectral analysis.

2. Experimental

Various compositions of the glasses used for the present work are mentioned in Table 1. Melt-quenching technique is used for synthesis of the specified glasses. In this technique, appropriate amounts of analytical grade reagents are systematically mixed in agate mortar. Then it is taken in the silica crucible and placed in an automatic temperature controlled (ATC) furnace at a temperature range 1180–1220 °C for 20 min. The molten form of the material is poured on the brass mold for the re-

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http://dx.doi.org/10.1016/j.jallcom.2012.12.162

Table 1
Glass compositions.

S. No.	Glass codes	MgO	PbO	B_2O_3	SiO_2	Nd_2O_3	Eu_2O_3
		mol%	mol%	mol%	mol%	mol%	mol%
1	Pure	9.5	40.0	25.0	25.0	0.5	–
2	Eu_1	9.0	40.0	25.0	25.0	0.5	0.5
3	Eu_2	8.5	40.0	25.0	25.0	0.5	1.0
4	Eu_3	8.0	40.0	25.0	25.0	0.5	1.5
5	Eu_4	7.5	40.0	25.0	25.0	0.5	2.0

quired shape. Simultaneously it is placed in the annealing furnace kept about 350 °C and subsequently cooled to room temperature for removing thermal stress in the glasses. Finally the glasses were polished to dimensions 1 cm × 1 cm × 0.2 cm.

The X-ray diffraction spectra are measured on a diffractometer with copper target (XRDARLX'TRA) and nickel filter operated at 40 kV, 30 mA. The optical absorption (UV–Vis–NIR) spectra of these glasses are recorded from 300 to 2400 nm for using a recording spectrophotometer type JASCO, V-570 with spectral resolution of 0.1 nm. The luminescence spectra are recorded at room temperature on a Photon Technology International (PTI) spectrofluorometer with exited wavelength of 355 nm from 350 to 1200 nm, using this data and MATLAB color coordinates program; emitting color coordinates are estimated. Fourier transform infrared spectra are recorded on a JASCO-FT/IR-5300 spectrophotometer with resolution of 0.1 cm^{-1} in the spectral range 400–1500 cm^{-1} using KBr pellets (300 mg) containing pulverized sample (1.5 mg). The Raman spectra (model Nexus 670 Nicolet–Madison–WI USA) have been recorded on Fourier Transform Raman spectrometer with resolution of 4 cm^{-1} in the range 200–2000 cm^{-1}.

The refractive index of the glasses is measured using Abbe's Refractometer and monobromo naphthalene as the contact layer between the glass and the refractometer prism. Archimedes' principle is used for the density measurement with an accuracy of ±0.001 by means of *o*-xylene (99.99% pure) as the buoyant liquid.

3. Results

Thermal conductivity, elastic properties and other important parameter of the materials (glasses) can be investigated by means of density; it is one of the important physical properties of the material. Using predictable formulae [11–14], density and refractive index; several other physical parameters such as Eu^{3+} ion concentration (N_i), mean separation (r_i), polaron radius (r_p), field strength (F_i), electronic polarizability (α), reflection loss as well as optical dielectric constant (ε_0) in the present glass network can be estimated and mentioned in Table 2. Figs. 1 and 2 show the variation of density, refractive index, reflection loss and molar reflectivity as a function of glass samples. The density of glasses is increased with content of Eu_2O_3 in the glass network because MgO is replacing by Eu_2O_3 which has relatively high density. But in case of Eu_3, it is slightly decreased due to the formation of non-bridging oxygen atom in glass structure.

Table 2
Physical parameters of $MgO–PbO–B_2O_3–SiO_2–Nd_2O_3–Eu_2O_3$ glasses.

S. No.	Physical properties	Glasses				
		Pure	Eu_1	Eu_2	Eu_3	Eu_4
1	Density D (g/cm^3) (±0.004)	5.2248	5.2788	5.2816	5.3076	5.3102
2	Rare earth ion concentration N_i (10^{21} ions/cm^3) (±0.005)	–	1.24	2.45	3.60	4.79
3	Interionic distance r_i (Å) (±0.005)	–	9.32	7.41	6.52	5.93
4	Polaron radius r_p (Å) (±0.005)	–	3.76	2.99	2.63	2.39
5	Field strength F_i (10^{15} cm^{-2}) (±0.005)	–	2.13	3.363	4.36	5.25
6	Electronic polarizability α_e (10^{-21} ions/cm^3) (±0.005)	–	8.32	4.21	2.78	2.13
7	Refractive index n (±0.0001)	1.7862	1.7963	1.7964	1.7966	1.7972
8	Reflection loss	0.07962	0.08109	0.08111	0.08114	0.08122
9	Molar reflectivity R_M (cm^{-3}) (±0.005)	10.2759	10.3868	10.4621	10.6471	10.7153
10	Optical dielectric constant ε_0 (±0.005)	3.1905	3.2267	3.2271	3.2278	3.2299

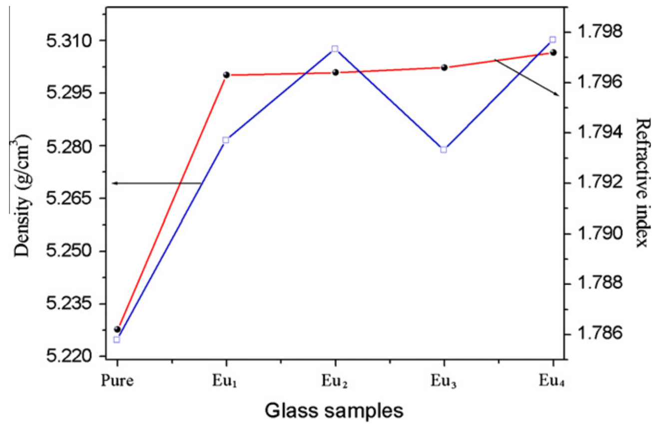

Fig. 1. Variation of density and refractive index with glass samples.

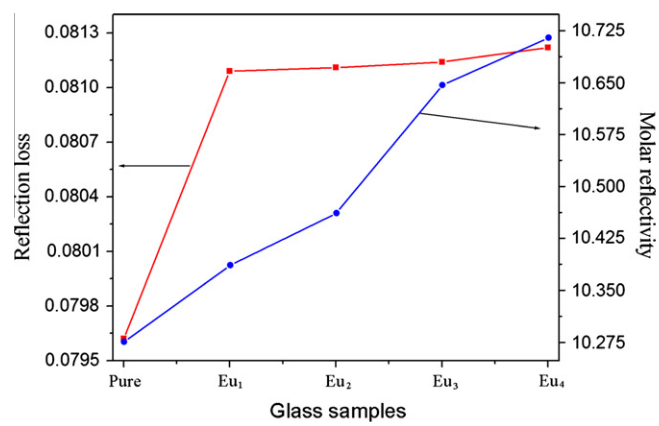

Fig. 2. Variation of reflection loss and molar reflectivity with glass samples.

Fig. 3 is the characteristic X-ray diffraction spectra of the specified glasses. The spectra of each glass samples contains abroad bump located at 31° (=2θ) and no shape line are observed in the spectra which suggested that all the prepared glass samples confirm the amorphous (glassy) nature.

Fig. 4 shows the UV–Vis–NIR absorption spectra of Eu^{3+} ions doped $MgO–PbO–B_2O_3–SiO_2–Nd_2O_3$ glasses. The host (Eu^{3+} ions free) glass shows absorption bands at ~431, ~473, ~512, ~526, ~583, ~624, ~683, ~747, ~804 and ~876 nm in the range 350–950 nm which correspond to Nd^{3+} ion transitions originating from the ground $^4I_{9/2}$ level to number closely spaced higher energy levels in the glass network and assigned as follows $^4I_{9/2} \rightarrow {}^2P_{1/2}$, $^4G_{11/2} + {}^2G_{9/2} + {}^2D_{3/2} + {}^2K_{15/2}$, $^4G_{9/2}$, $^4G_{7/2}$, $^2G_{7/2} + {}^4G_{5/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2} + {}^4S_{3/2}$, $^2H_{9/2} + {}^4F_{5/2}$ and $^4F_{3/2}$ respectively. Inhomogeneous broad absorption features are also observed in the range 1000–1800 nm (not shown in the figure) due to lack of long-range order and may be host glass absorption [15–18].

In connection with this Eu^{3+} ions introduced into glass network additional bands are observed at around ~390, ~2094 and ~2206 nm; these supplementary bands attributed to transitions