Journal of Alloys and Compounds 588 (2014) 394–398

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Cerium and samarium codoped lithium aluminoborate glasses for white light emitting devices

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ARTICLE INFO

Article history:
Received 22 August 2013
Received in revised form 22 October 2013
Accepted 23 October 2013
Available online 30 October 2013

Keywords:
Borate glass
Melt quench
Optical absorption
Fluorescence
Energy transfer
X-ray diffraction

ABSTRACT

Cerium and samarium codoped lithium aluminium borate glasses are prepared by using conventional melt quench technique and their structural and spectroscopic analysis has been done. The structural studies have been done using XRD, FTIR and density measurements. The spectroscopic analysis has been done using UV–Vis absorption spectra and fluorescence emission spectra by exciting the glass samples at 380 nm and 400 nm. XRD confirms the amorphous nature of the prepared samples. The density shows an increasing trend with addition of cerium at the expense of aluminium, other components being constant. This is also confirmed by FTIR study which shows the conversion of trigonal BO_3 units into more stable tetrahedral BO_4 units. The UV–Vis absorption spectra shows an increase in intensity and a significant shift of the optical absorption edge from UV to partially visible region when cerium is added in the pure samarium containing lithium aluminium borate glass. The fluorescence spectra indicate an energy transfer from Ce^{3+} to Sm^{3+} ions. Moreover, some of the glass compositions may be found suitable for white light emitting devices as there is a simultaneous presence of red, green and blue emission.

1. Introduction

Oxide glasses have been established to be stable and attractive hosts for having effective luminescence in rare-earth (RE) ions. The RE ions are being used as dopants since 1975. These are used in glasses mainly for two reasons: (i) their well-defined and sharp absorption bands which serve as structural probes for dopant environment, (ii) the alteration of the energy level arrangement of RE ions caused by glassy environment leading to interesting applications like lasers, sensors, light converters, hole-burning high density memories, optical fibers and amplifiers [1–3]. In recent years, a lot of research work has been done for the development of rare-earth based optical devices. These materials show a strong fluorescence in wide spectral range and show upconversion and downconversion emission at low excitation power. Borate glass is frequently used as a host for RE ions as it is a proper optical material possessing high transparency, low melting temperature, high thermal stability, high chemical durability and good solubility of rare-earth ions [4,5]. Nowadays rare-earth doped/codoped materials are among hot topics of research in the development of new full colour emitting phosphor materials which possess thermal and chemical stability in air along with high emission quantum yield at room temperature [6,7] and white light emitting devices which are inviting a great attention for their applications in liquid crystal monitor screens and white light emitting diodes (W-LEDs), the so called next generation solid state lighting technology [8–10]. W-LEDs are safe, reliable, energy efficient, possess a long lifetime and are environment-friendly. These features make them attractive and versatile for the replacement of conventional incandescent and fluorescent lamps. For colour displays or white light there should be simultaneous generation of red, green and blue light. White light or individual colour emissions can be obtained by varying the concentration of rare-earth ions, their environment or by opting the multilayer approach by changing the excitation wavelength [11].

In addition to the above mentioned applications, the presence of rare-earth oxides considerably reduces the viscosity of the glass melt with a slight effect on thermal expansion, chemical durability and mechanical properties of the glass [12]. Aluminium oxide improves the chemical stability and physical properties by modifying the glass structure. It affects not only the thermo-mechanical properties but laser properties also and prevents quenching which is caused due to clustering of RE ions [13,14]. The addition of alkali like lithium decreases the viscosity of the melt and helps to lower the melting temperature [15]. In the present work, we have codoped cerium and samarium in lithium aluminium borate host to find the suitable composition for full colour/white light emission as there is very little literature available on Ce–Sm codoped glasses [16].

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http://dx.doi.org/10.1016/j.jallcom.2013.10.181

2. Experimental procedure

2.1. Sample preparation

Experimental: Glass samples having a chemical composition of x CeO_2–(9.5−x) Al_2O_3–0.5 Sm_2O_3–10Li_2CO_3–80 B_2O_3 with x varying from 0% to 2% mole fraction are prepared by using conventional melt quench technique. The raw materials of samarium oxide (Sm_2O_3), cerium oxide (CeO_2), lithium carbonate (Li_2CO_3), boric oxide (B_2O_3) and aluminium oxide (α-Al_2O_3) in appropriate amounts are mixed and grinded finely to have a batch of 15 g. This grinded mixture is melted in silica crucible in an electric furnace for one hour at a temperature of 1200 °C in normal atmosphere till the formation of a bubble free liquid. This bubble free melt is then quenched into preheated steel mould and annealed at a temperature of 400 °C to room temperature to remove thermal and mechanical stress. The nominal composition of prepared glass samples is given in Table 1.

2.2. Characterization

We have employed X-ray diffraction (XRD) study to confirm the amorphous/crystalline nature of the samples using XRD-7000 (Shimadzu) X-ray Diffractometer (Cu Kα, λ = 1.54434 Å) at the rate of 2°/min and the variation of 2θ is from 10° to 70°.

The density of glass samples is measured by using the standard Archimedes principle with the help of a sensitive microbalance and taking pure benzene as the immersion fluid.

The molar volume (V_m) is calculated with the help of following formula:

$$V_m = \sum x_i M_i / D$$

where x_i is the molar fraction of the component and M_i is its molecular weight.

The optical absorption spectra of the polished samples are recorded with the help of a UV–Vis Perkin Elmer Lambda 35 Spectrometer in the range 200–1100 nm at room temperature.

The fluorescence spectra of these samples are recorded with the help of Perkin–Elmer Fluorescence LS-Spectrometer at room temperature. The excitation wavelength for the samples is 402 nm.

The infrared transmission spectra of the prepared glass samples are measured by using Varian 660-IR FTIR Spectrophotometer in the wave number range 400–4000 cm^{-1}. The fine powder of prepared glasses is mixed with KBr in the ratio 1:100 mg (glass powder: KBr) and a pressure of 1.470×10^7 Pa is applied to the mixture to produce homogenous pellets. Then instant IR transmission measurements are made after preparing the pellets.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction pattern (Fig. 1) shows the absence of continuous or discrete sharp peaks and possesses diffused bands which indicate the amorphous/glassy nature of prepared glass samples.

3.2. Density

It is clear from Table 1 that with an increase in CeO_2 content at the expense of Al_2O_3, there is a gradual increase in density of the glass samples which shows that there is a change in structural arrangement of the atoms in the glass network. As the density of CeO_2 is 7.215 g/cm^3 and that of Al_2O_3 is 3.987 g/cm^3, there should be an increase in the density as reported in our previous study [17]. A similar trend has been observed in the present glass system which supports their increase in density.

The molar volume shows the inverse behaviour to that of density which exhibits harmony between the two physical parameters as it is clear from Fig. 2.

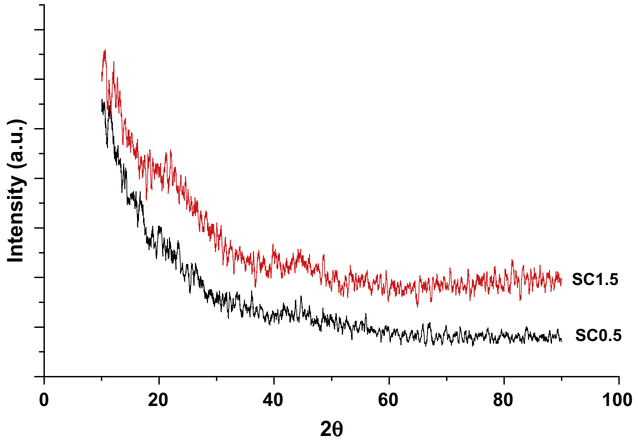

Fig. 1. XRD spectra of Sm_2O_3–CeO_2–Al_2O_3–Li_2CO_3–B_2O_3 glasses.

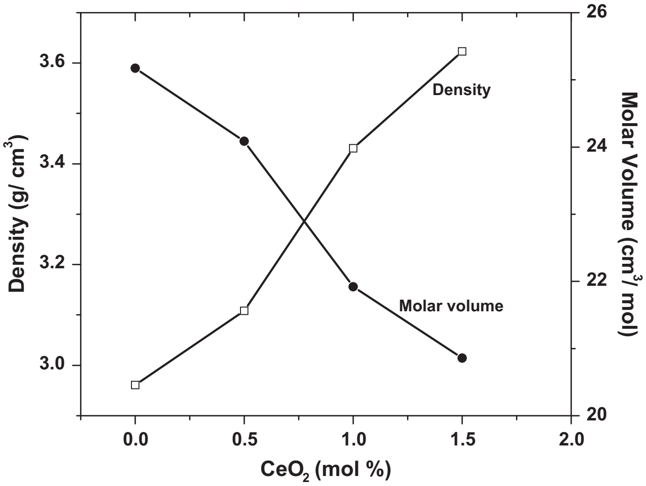

Fig. 2. Density and molar volume of Sm_2O_3–CeO_2–Al_2O_3–Li_2CO_3–B_2O_3 glasses.

3.3. FTIR

The FTIR spectra of the prepared glass samples have been shown in Fig. 3. The infrared transmittance spectra provide the information of different structural groups present and help to understand the possible changes in their rearrangement with a change in glass composition. The borate spectra have been divided as follows according to the literature survey: (i) 600–800 cm^{-1} for bending vibrations of various B–O–B segments, (ii) 800–1200 cm^{-1} for stretching vibrations of BO_4 groups and (iii) 1200–1600 cm^{-1} for B–O stretching vibrations of BO_3 groups. The other bands between 2300 and 4000 cm^{-1} are due to O–H vibrations of water groups. The band at 806 cm^{-1} is assigned to the boroxol rings. The absence of this band in the present glass system indicates that it consists only of BO_3 and BO_4 groups [18,19]. The given glass

Table 1
Nominal chemical composition (in mol%), density and molar volume of the glass samples.

S. No.	Sm_2O_3	CeO_2	Al_2O_3	Li_2CO_3	B_2O_3	Density (g/cm^3)	Molar volume (cm^3/mol)
SC0.0	0.5	0.0	9.5	10	80	2.961	25.174
SC0.5	0.5	0.5	9.0	10	80	3.108	24.088
SC1.0	0.5	1.0	8.5	10	80	3.431	21.922
SC1.5	0.5	1.5	8.0	10	80	3.623	20.857