Journal of Luminescence 180 (2016) 190–197

Contents lists available at ScienceDirect

Journal of Luminescence

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

Full Length Article

White light emission of Ce^{3+} sensitized Sm^{3+} doped lead alumino borate glasses

Simranpreet Kaur, Parvinder Kaur, Gurinder Pal Singh, Deepawali Arora, Sunil Kumar, D.P. Singh *

Department of Physics, Guru Nanak Dev University, Amritsar 143005, India

ARTICLE INFO

Article history:
Received 1 July 2015
Received in revised form
10 August 2016
Accepted 12 August 2016
Available online 20 August 2016

Keywords:
Energy transfer
Optical properties
Activators, Ce^{3+} White LED glasses

ABSTRACT

In present work, Ce^{3+} activated Sm^{3+} doped lead alumino borate glasses have been synthesized by melt quench method. Photoluminescence spectra were measured under different excitation wavelengths. The co-doped samples show enhanced Sm^{3+} ions emission at the cost of Ce^{3+} emission with the increasing Ce^{3+} ions concentration which shows that Ce^{3+} is acting as a sensitizer. This kind of luminescent behavior is discussed with respect to energy transfer process. The investigation based on excitation spectra and decay curves demonstrated that the energy transfer is nonradiative in nature taking place between Ce^{3+} and Sm^{3+} clusters. It is governed by dipole–dipole interactions as explained in terms of donor lifetime. The results showed that the white light has been achieved under excitation at 400 nm when concentration of Ce^{3+} is in the range of 0.5–1.0 mol%. An efficient energy transfer from Ce^{3+} to Sm^{3+} ions (up to around 42%) with decay times approaching 22 ns has been observed at 400 nm excitation. The UV–Vis absorption spectra shows an increase in intensity and a significant red-shift of the optical absorption edge with increasing rare earth ions concentration in lead alumino borate glass and the FTIR study depicts the conversion of trigonal BO_3 units into more stable tetrahedral BO_4 units.

1. Introduction

The ions of rare earth elements retain their discrete electronic energy levels when incorporated into crystalline or glassy host materials which makes them useful for solid state lasers. RE ions are being used as dopants in glasses since 1975 and these are used mainly for two reasons: (i) their well-defined and sharp absorption bands which function as structural probes for dopant surroundings, (ii) the modification of the energy level arrangement of RE ions in glassy environment which is helpful for lasers, sensors, light converters, hole-burning high density memories, optical fibers and amplifiers [1–3]. Rare-earth doped/codoped materials are also being used in the development of new color emitting phosphor materials which possess good thermal and chemical stability in air along with high emission yield at room temperature [4,5]. White light emitting devices have attracted great attention for their use in liquid crystal monitor screens and white light emitting diodes (W-LEDs), the so called next generation solid state lighting technology [6–8]. Various efforts are being done to simulate the white light emission by adjusting the intensities of red–green–blue (RGB) colors which have been reported by many researchers using RE ions codoped in different lattices since W-LEDs are harmless, consistent, energy-efficient, have a long lifetime and are environment friendly. These features make them smart and versatile for the replacement of conventional incandescent and fluorescent lamps. White light emission or single wavelength color emission can be acquired by changing the rare-earth ion concentration, their environment or by selecting the multilayer approach by altering the excitation wavelength [9]. But the fluorescence quenching is one of the setbacks in the luminescence yield of rare earth ions due to their clustering tendency and non-radiative relaxations. Heavy metal oxide glasses are most likely to be used for photonics and optoelectronics due to of their effective luminescence in rare-earth (RE) ions. These glasses display wide range transmission of light, small phonon energy, large ion polarizabilities resulting in high values of refractive index and higher covalency [10,11]. Heavy metal glass (HMG) helps to raise radiative or quantum efficiencies of rare earth ions [12,13] as they have steady glass structure with weak ionicity and lower phonon energy. Addition of aluminum oxide helps in improving the chemical stability and physical properties by altering the glass structure. It not only improves thermo-mechanical properties but also affects laser properties and thus prevents quenching caused by

---

* Corresponding author.
E-mail address: dpsinghdr@yahoo.com (D.P. Singh).

http://dx.doi.org/10.1016/j.jlumin.2016.08.027
0022-2313/© 2016 Elsevier B.V. All rights reserved.

clustering of RE ions. Ce^{3+} can be used as either sensitizer or activator because of its efficient broad band luminescence. The white light emission has been achieved by various investigators by means of tuning the content of RE ions in different cerium doped glassy hosts such as borate, oxyfluoroborate, silicate and metaphosphate glasses [14–21]. The Ce^{3+}/Sm^{3+}co-doped Na_2O–Y_2O_3–SiO_2 glass and Sm^{3+}/Ce^{3+} in barium fluoroborate glasses which could be used as a potential matrix material for ultraviolet light emitting diode (LED) chip based white LEDs. [22,23]. Interestingly Shen et al. and Velázquez et al. demonstrated the role of Ce^{3+} in Ce^{3+}/Sm^{3+} in barium fluoroborate glasses and Ce^{3+}/Tb^{3+} nano glass-ceramics respectively for UV→Vis photon conversion layer for solar cells [24,25]. Various researchers also studied Ce^{3+}/Sm^{3+} doped Lu_2SiO_5–Gd_2SiO_5 solid solution crystals [26], Y_2SiO_5:Ce^{3+}/Sm^{3+} [27] and CaS:Ce, Sm nanophosphors for wLEDs [28].

In this paper Ce^{3+}/Sm^{3+} codoped glasses have been prepared and their photoluminescence properties were investigated. We reported the results based on observation that the change of excitation wavelength between 350 nm and 400 nm affect's the color of emitted light in $20PbO$–$(9.5-x)\ Al_2O_3$–$70B_2O_3$–$0.5Sm_2O_3$–$xCeO_2$ where $x=0.25$, 0.5, 1, 1.5% glasses using Ce^{3+} ions as the multi-sensitizers, which were synthesized in air atmosphere. Energy transfer (ET) processes of $Ce^{3+}\rightarrow Sm^{3+}$ has also been investigated. Our results indicate the potential applications of these glasses in the fabrication of white-LEDs.

2. Experimental details

The glass samples studied here have the following composition:

$20PbO$–$(9.5-x)\ Al_2O_3$–$70B_2O_3$–$0.5Sm_2O_3-xCeO_2$

where $x=$ 0.25, 0.5, 1, 1.5%.

The raw materials samarium oxide (Sm_2O_3), lead Oxide (PbO), borate (B_2O_3) and aluminum oxide (Al_2O_3) in stoichiometric ratios are mixed and grinded finely to get a batch of 15 g. This grinded mixture was melted in silica crucible for 1 h in an electric furnace at a temperature of 1200 °C in normal atmosphere till the formation of a bubble free liquid. The melt is then quenched into preheated steel mold and annealed at 400 °C to room temperature to eliminate thermal and mechanical stress. The obtained samples are then ground using different grade of SiC and polished with cerium oxide to have maximum flatness and make them amenable to spectroscopic studies.

3. Characterization

To confirm the amorphous/crystalline nature of the samples, we have used X-ray diffraction (XRD) study using XRD-7000 Shimadzu X-ray Diffractometer (Cu K_α, $\lambda=1.54434$ Å) at the rate of 2°/min and the variation of 2θ is from 10° to 70°. The standard Archimedes principle is used to find the density of glass samples by using a sensitive microbalance with pure benzene as the immersion fluid.

$$D=\left[W_A/(W_A-W_B)\right]d, \quad (1)$$

where W_A is the weight of sample in air, W_B weight of the sample in benzene, and d is density of the benzene.

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

$$V_m=\Sigma x_i M_i/d \quad (2)$$

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 at room temperature with the help of a (UV–Vis–NIR) Perkin Elmer Lambda 35 Spectrometer in the range 200–1100 nm with a spectral resolution of ±1 nm. The optical band gap (E_g) was calculated by model proposed by Mott and Davis for indirect transitions observed in case of glasses due to long range geometrical disorder [29]. The fluorescence spectra of prepared samples are recorded with the help of Perkin-Elmer Fluorescence LS 45 spectro- photometer with a resolution of ±1.0 nm Spectrometer. The time-resolved fluorescence spectra were recorded with a BH-CHRONOS time resolved fluorescence spectrophotometer using UV LED. The excitation wavelength for the samples is 349 nm, 386 nm and 400 nm. The infrared transmission spectra of the samples are measured by using Varian 660-IR FTIR Spectrophotometer with spectral resolution of 4 cm^{-1} in the wavenumber range 400–4000 cm^{-1}. The fine powder of prepared glasses is mixed with KBr in the ratio 1:100 (glass powder: KBr) and a pressure of $1.470\ \times 10^7$ Pa is applied to the mixture to get homogenous pellets. The IR transmission measurements are made instantly after preparing the pellets to avoid moisture.

4. Experimental results and discussion

4.1. X-ray diffraction of CeO_2–Sm_2O_3–PbO–Al_2O_3–B_2O_3

X-ray diffraction spectra of the obtained CS samples (Fig. 1) shows no continuous or discrete sharp peaks but consist of diffused halo that reflects their glassy structure.

4.2. FTIR of CeO_2–Sm_2O_3–PbO–Al_2O_3–B_2O_3

The FTIR spectra of the prepared glass samples prepared at room temperature are shown Fig. 2. It makes us available the information about the presence of different structural groups along with the variations occurring in their arrangements with variation in the glass composition. The spectra of borates have been mainly divided as follows: (i) 600–800 cm^{-1} is ascribed to bending vibrations of different B–O–B bonding, (ii) 800–1200 cm^{-1} is for BO4 groups stretching vibrations and (iii) 1200–1600 cm^{-1} presents the B–O stretching vibrations of BO3 groups. The band at 806 cm^{-1} has been due to boroxol rings which are absent in present glass system showing only the presence of BO_3 and BO_4 groups [30,31].

The prepared glass system displays various infrared transmission bands at around 690, 989, 1050, 1236 and 1389 cm^{-1}. The

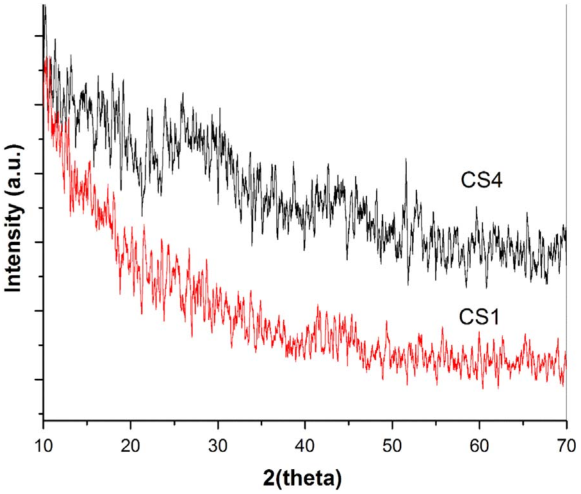

Fig. 1. XRD patterns of samples CS1 and CS4.