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Antiquenching effect of modifying cations on samarium clustering: Physical, structural and luminescent behavior of heavy metal borate glass systems

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ABSTRACT

In this paper an attempt has been made to correlate the structural modifications and luminescence efficiencies by changing the environment of the glass network by modifying oxides. Sm^{3+} doped lead borate (SPB) and lead cadmium alumino borate (SCPB) glasses have been fabricated by melt quench technique at high temperature. The glass samples are characterized by XRD, FTIR, optical absorptions, fluorescence and density measurements. The effect of Sm^{3+} ion and glass host interaction on the emission spectra has been discussed in the view of the ionicity and covalency of hosts. The ratio of the intensities of electric to magnetic dipole emissions are calculated by varying both the concentration of the Sm^{3+} ion and the composition of the glass matrix. The XRD profile of all the glasses confirms their amorphous nature and FTIR spectrum shows the presence of BO_3 and BO_4 groups. These glasses have shown strong absorption bands in the visible (VIS and NIR) region and emit strong orange red wavelengths when excited by ultraviolet light. The concentration quenching has been noticed and ascribed to energy transfer through cross-relaxation between Sm^{3+} ions. Shifting of UV absorption edge towards longer wavelength with addition of Sm_2O_3 concentration has been observed. Incorporation of Al_2O_3 and CdO in 2nd glass system is responsible for strong effect on luminescence of the present glass system. Based on these results, an attempt has been made to throw some light on the relationship between the structural modifications and luminescence efficiencies in two different glass hosts as a laser active medium in the visible region. Moreover the optical basicity values were theoretically determined along with covalent behavior of two glass systems.

1. Introduction

Among various oxide glass compositions, heavy metal glasses seem to be attractive systems for making of more efficient laser systems because of low phonon energy, wide transmission range of light, large ion polarizabilities which results in large values of refractive indices and higher covalency. This tags them as suitable host lattices for rare earth (RE) ion incorporation [1,2].

Heavy metal glass (HMG) also helps to enhance radiative or quantum efficiencies of rare earth ions [3,4]. Borate based glasses have attracted considerable interest over the past few years in the development of optoelectronic devices as it is a suitable optical material with high transparency, low melting point, high thermal stability and good rare earth solubility [5,6]. A remarkable characteristic feature of the borate glasses is the fluctuations in its structural properties when modifiers or intermediate are introduced. The structure of the borate glasses is not a random distribution of BO_3 triangles and BO_4 tetrahedra, but a gathering of these units to form well defined and stable borate groups such as diborate, triborate, and tetraborate, which constitute the random three-dimensional network. Because of these reasons, borate glasses are the best choice for RE doping. Also the B_2O_3-based glasses are well known due to their larger (even larger than crystals) photo-induced second order non-linear optical effects that have strong bearing on luminescent efficiencies of these glasses [7]. From polarizability approach for simple oxides, it is known that B_2O_3 belongs to semi covalent group of metal oxides with strong interionic interaction, whereas PbO is classified as very ionic metal oxide with very weak interaction.

$Sm^{3+}(4f^5)$ has been emerged as one of the most interesting rare earth ion for its increasing demand in color displays, various fluorescent devices and temperature sensors [8]. Spectroscopic properties of rare earth ions are mainly associated with 4f

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transitions and are governed by chemical composition of glass systems. Also among different rare earth ions samarium is one of the most interesting rare earth ions to analyses the fluorescence in spite of its high lying 4f–5d charge transfer states resulting in poor absorption strength in near UV or visible range. Currently it has become one of the most interesting rare earth ion because of its growing interest in visible optical systems (orange-reddish phosphors) as it is used for red-emitting phosphors incorporated in crystalline materials, thin films, glasses, dosimetry and high resolution radiation detection [9–13]. Moreover $^4G_{5/2}$ level of Sm^{3+} has high quantum efficiency due to high energy gap between its low lying $^6F_{11/2}$ levels which is approx. 7000 cm^{-1}. It means that probability of non-radiative decay is very less likely to occur [14].

Previously, we have compared the optical properties of cerium lead borate and lead aluminium borate glass systems [15] and now we are investigating absorption and luminescent emission properties of the Sm^{3+} doped lead borate and lead aluminium cadmium borate glasses as Sm—O bond is sensitive to structural changes in borate glass. In these borate glasses, the oxides i.e. PbO and CdO are acting as the network modifiers (NWMs) resulting in conversion of three co-ordinated trigonal boron atoms to four coordinated tetrahedral B4 atoms and also changes the non-bridging oxygen ions. Also CdO is considered as promising candidate for its development as potential optical materials [16]. CdO being a heavy metal oxide, the addition of it is expected to increase the gamma ray shielding properties of the glass systems. Among the glass intermediates, Al_2O_3 has received significant consideration as the most likely matrix element due to its high solubility of rare-earth ions [15,17] by making structural changes around rare earth ions. As Re_2O_3 and Al_2O_3 has alike structure, in which the RE ions have a preference for eightfold or nine fold coordination which supports to limit concentration quenching effects on photoluminescence thereby improving the optical response of the material. Thus investigation of absorption and luminescent emission properties of the Sm^{3+} [18,19] ions have indicated that the optical properties of these rare earth ions are affected by the host glass compositions, thus opening up the possibility of engineering applications. Also Oxide glasses are stable hosts for obtaining efficient luminescence in rare earth ions.

Presently, Sm^{3+} doped lead borate (SPB) and lead cadmium alumino borate glasses (SCPB) are prepared in normal atmosphere and Sm^{3+} ions act as spectroscopic probe of local structure of the glass systems. The structural, physical and optical properties of the given composition of glasses are carried out. The physical and structural properties are studied by using XRD (X-ray diffraction), FTIR (Fourier transform infrared spectroscopy), density and molar volume techniques. The optical properties are investigated by UV–Vis spectroscopy and Fluorescence.

2. Experimental details

The glass samples studied here have the following composition:

$$20PbO - (80\text{-}x)B_2O_3 - xSm_2O_3 \ (\textbf{SPB})$$

$$20PbO - (5\text{-}x)Al_2O_3 - 5CdO\text{-}70B_2O_3\text{-}xSm_2O_3 \ (\textbf{SCPB})$$

where x = 0, 0.50, 1.00, 1.5 and 2 mol%.

The raw materials samarium oxide (Sm_2O_3), lead Oxide (PbO), borate (B_2O_3) cadmium oxide (CdO) and aluminium oxide (Al_2O_3) in proper amounts 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 a temperature of 400 °C to room temperature automatically 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, λ = 1.54434 Å) at the rate of 2°/min and the variation of 2θ is from 10° to 70°. The differential scanning calorimetry (DSC) for glass samples was carried out on a SDT Q600 (TA instruments) thermal analyzer in the 50–1000 °C temperature range. A heating rate of 10 °C min^{-1} was used under ordinary air atmosphere using aluminium pan with accuracy ±3 °C. 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.

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

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:

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

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 fluorescence spectra of prepared samples are recorded with the help of Perkin-Elmer Fluorescence LS 45 spectrophotometer with a resolution of ±1.0 nm. The excitation wavelength for the samples is 402 nm. The infra-red 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 1.470×10^7 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. Results and discussion

4.1. X-ray diffraction

X-ray diffraction pattern of SPB and SCPB glass samples (Fig. 1) shows no continuous or discrete sharp peaks but consists of diffused halo which reflects the characteristics of amorphous nature of glass samples.

4.2. FTIR (Fourier transform infrared spectroscopy)

4.2.1. $PbO—Sm_2O_3—B_2O_3$ glasses:

The FTIR spectra of Sm_2O_3 doped $PbO—B_2O_3$ have been given in Fig. 2(a). Infrared spectra of borate glasses can be divided into mainly four regions [20,21].

(I) 600–800 cm^{-1} for the B—O—B vibrations.
(II) 800–1200 cm^{-1} for BO_4 groups.
(III) 1200–1600 cm^{-1} for BO_3 groups.
(IV) The near infrared bands in region 3000–4000 cm^{-1} due the presence of water groups' vibration [22].