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Structural and luminescence properties of samarium doped lead alumino borate glasses

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ABSTRACT

The study reports the effect of samarium concentration on the physical, structural and spectroscopic characteristics of samarium doped lead alumino borate glasses having composition *20PbO-(10-x)Al_2O_3-70B_2O_3-xSm_2O_3; x = 0.1, 0.5, 1.0 and 2.0 mol %*. The glasses were fabricated by conventional melt-quenching technique and then characterized by XRD, FTIR, optical absorption and fluorescence spectra. X-ray diffraction studies confirmed the amorphous nature of the prepared glasses. FTIR spectra indicate the presence of BO_3, BO_4, AlO_6 and a few other structural groups. Various physical properties such as density, molar volume, refractive index, rare earth ion concentration, boron-boron distance and polarizability etc. were determined using conventional methods and standard formulae. The Judd-Ofelt theory was applied on the optical absorption spectra of the glasses to evaluate the three phenomenological intensity parameters Ω_2, Ω_4 and Ω_6. The value of Ω_2 was found to be highest for glass with 1 mol% Sm_2O_3 and attributed to the asymmetry of the ligand field at the rare earth ion site and the rare earth oxygen (Sm-O) covalency. The calculated intensity parameters and fluorescence spectra were further used to predict the radiative transition probability (A), radiative lifetime (τ_R), branching ratio (β_R), peak wavelength (λ_p), effective line widths ($\Delta\lambda_{eff}$) and stimulated emission cross-section (σ) for the characteristic $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ transitions of the Sm^{3+} ion. Concentration quenching was observed for 2 mol% concentration of Sm_2O_3 and ascribed to energy transfer through various cross-relaxation channels between Sm^{3+} ions. Reasonably high values of branching ratios and stimulated emission cross-section for the prepared glasses points towards their utility in the development of visible lasers emitting in the reddish-orange spectral region. However, the glass with 1 mol% Sm_2O_3 was found to show better radiative properties.

1. Introduction

Rare-earth doped glasses have gathered extensive interest in the research arena because of their practical applications in several optoelectronic devices such as high power solid-state lasers, high-density memory devices, sensors, optical fibers and amplifiers etc. [1–4]. The spectroscopic properties of rare earth (RE) ions in the glasses are very sensitive to their local environment and the distribution of the doped ions in the glass matrix, which further depends on the chemical composition of the host material [5,6]. This composition dependence can be investigated using the Judd-Ofelt theory [7,8], a powerful tool for the systematic investigation and selection of glasses for specific applications.

Out of the various hosts undertaken for rare earth doping, oxide glasses especially borate glasses have turned up as favorable hosts because of their high transparency, good RE ion solubility, ease for mass production, flexibility in shape and low melting point [9]. However, borate glasses have high phonon energy, which result in non-radiative decays. But this non-radiative transition probability can be reduced by the incorporation of heavy metal ions in the glass matrix and hence the quantum efficiency can be increased substantially [10]. The heavy metal lattices enhance the fluorescence yield of the rare earth ions due to their low phonon energy thereby giving a chance of observing lasing emission [11]. Also, large phonon energy is not detrimental to Sm^{3+} ion emissions, so borate glasses are of substantial interest for doping Sm^{3+} ions [12].

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Sm^{3+} doped glasses are of special interest because of their intense emissions in the visible region through different emission channels. Especially, the reddish orange emission originating from the $^4G_{5/2}$ level of Sm^{3+}ion possess strong luminescence intensity, large stimulated emission cross section, high quantum efficiency and very less probability for non-radiative decay, which are desirable features for laser applications. Sm^{3+} doped glasses extend plausible applications in high density optical storage, visible solid state lasers, color displays, photodynamic therapy (PDT) light sources and undersea communication [13–16]. Also the $^4G_{5/2}$ level of Sm^{3+} ion exhibits different quenching emission levels, thus facilitating the study of energy transfer process.

The structural, optical and spectroscopic properties of Sm^{3+} ions in various hosts such as sodium fluoroborate glasses containing alkali/alkaline earth metal oxides [4], sodium borate and fluoroborate glasses [12], heavy metal gallate glasses [16], zinc bismuth borate glasses [17], various oxide and fluoride glasses [18], lead zinc phosphate glasses [19], zinc fluorophosphate glasses [20], niobium borotellurite glasses [21], zinc phosphate glasses [22], lead fluoroborate glasses [23], zinc alumino bismuth borate glasses [24], lithium borate and lithium fluoroborate glasses [25] have been studied in the recent past. Active work is being carried out to identify new hosts which are appropriate for doping of Sm^{3+} ions, hence facilitating the fabrication of new optical devices with specific utility and enhanced performance.

In the present work, the authors report the physical, structural, optical and luminescence properties of Sm^{3+} doped lead alumino borate glasses. This work is an extension to our previous work [26–29], wherein the radiative properties of Nd^{3+} doped glasses were studied using Judd-Ofelt theory. It was highlighted that the addition of PbO to borate matrix results in an increase in density and refractive index and also reduces its phonon energy, which in turn helps in the reduction of non-radiative decays and an enhancement in the quantum efficiency of the glass system. The addition of small amount of Al_2O_3 to this system can increase the glass stability [30] and the solubility of the rare earth ions [31] by making structural changes around the RE ions. The Al^{3+} ions are found to affect the thermo-mechanical as well as the lasing properties of the material in which they are incorporated [32]. On the whole, PbO-Al_2O_3-B_2O_3 glass system is stable, moisture resistant, has good rare earth ion solubility, high refractive index and low phonon energy. Considering these points, the authors have chosen this host to incorporate Sm^{3+} ions. The effect of samarium concentration on the physical and structural properties as well as the absorption and emission spectra has been discussed taking into account the interaction among the Sm^{3+} ions, which leads to energy transfer through cross-relaxation. To the best of our knowledge, the spectroscopic properties of Sm^{3+} doped PbO-Al_2O_3-B_2O_3 glass system using the Judd-Ofelt theory have not been reported so far.

2. Experimental details

2.1. Glass synthesis

Samarium doped lead alumino borate glasses of the composition (in mol%) *20PbO-(10-x)Al_2O_3-70B_2O_3-xSm_2O_3* where $x = 0.1$, 0.5, 1.0 and 2.0 mol%, were prepared by the conventional melt quenching technique. The glasses were labeled according to their composition as follows.

PABS1: 20PbO- 9.9Al_2O_3-70B_2O_3- 0.1Sm_2O_3
PABS2: 20PbO - 9.5Al_2O_3- 70B_2O_3- 0.5Sm_2O_3
PABS3: 20PbO - 9.0Al_2O_3-70B_2O_3- 1.0Sm_2O_3
PABS4: 20PbO - 8.0Al_2O_3- 70B_2O_3- 2.0Sm_2O_3

Appropriate amount of analar grade reagents of lead oxide (PbO), aluminium oxide (Al_2O_3), borate (B_2O_3) and samarium oxide (Sm_2O_3) of high purity (99.9%) were mixed thoroughly in an agate mortar and a batch of 15 g each was obtained. This batch of mixture was then heated under normal atmospheric conditions, in a platinum crucible at a temperature of 1100^{O}C for 1 h, in an electric furnace. The melt was stirred frequently for homogeneous mixing of all the constituents. The melt was then air quenched by pouring it onto a preheated stainless steel mould. Thereafter it was annealed at a temperature of 400^{O}C for 12 h in order to remove thermal strains and then allowed to cool to room temperature. The glass samples so obtained were then ground using different grades of SiC and polished with cerium oxide to obtain flat surfaces for optical measurements. Fig. 1 presents a schematic illustration of different steps of glass preparation by melt quenching technique along with the photograph of the prepared samples.

2.2. Physical and spectroscopic measurements

In order to check the amorphous nature of the prepared glass samples, XRD patterns of the powdered glass samples were recorded using XRD-7000 Shimadzu X-ray diffractometer (Cu K_α, $\lambda = 1.504$ A^o) at the scanning rate of 2°/min and 2θ was varied from 10° to 90°. The densities of the prepared samples were determined by employing the Archimedes' principle. Pure benzene having density $\rho_b = 0.8765$ g/cm^3 was used as the immersion liquid (buoyant) and the relation used was

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b \quad (1)$$

where W_a is the weight of sample in air and W_b is the weight of sample in the buoyant. The refractive indices of the prepared glass samples were measured ~ at 30 °C using an Abbe refractometer with mono-bromonaphthalene as an adhesive coating. The estimated error in the measurements was ±0.001.

Fourier Transform Infrared (FTIR) spectra of all the powdered samples were measured in the wavenumber range 400–4000 cm^{-1}, using a Varian 660-IR FTIR spectrophotometer having a spectral resolution of 4 cm^{-1}.1.0 mg of each powdered glass sample was mixed with 100 mg of KBr in an agate mortar and then pressed to a pressure of 150 kg/cm^2 resulting in homogeneous pellets which were instantly used to record the spectra. For each sample the spectrum represents an average of 20 scans, which were normalized to the spectrum of the blank KBr pellet. Optical absorption spectra of the prepared samples were recorded using a UV–Vis–NIR Perkin Elmer Lambda 35 Spectrometer with a spectral resolution of ±1.0 nm, in the wavelength range 200–2500 nm at normal incidence. The fluorescence spectra of the prepared glasses were recorded with the help of Perkin-Elmer Fluorescence LS 45 spectrophotometer, with a spectral resolution of ±1 nm, at an excitation wavelength of 402 nm.

3. Results and discussion

3.1. Physical properties

The recorded X-ray diffraction (XRD) pattern of the prepared glasses does not exhibit any sharp Bragg peaks, rather a few broad diffused peaks are observed. This indicates a long range structural disorder (*i.e.* a random arrangement of atoms) and confirms the amorphous nature of the prepared samples. The probability of finding the atoms is therefore not uniform inside the prepared glass matrices and also there are large variations in the interatomic distances, as a result of which the peaks get broader. As an