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Physical, optical and luminescence properties of B_2O_3-SiO_2-Y_2O_3-CaO glasses with Sm^{3+}ions for visible laser applications

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ABSTRACT

Silicoborate glasses with composition of (BSYCaSm:(55-x)B_2O_3+ 10SiO_2 +25Y_2O_3 +10CaO + xSm_2O_3), (where, x = 0.05, 0.10, 0.20, 0.25, 0.30, 0.40, 0.50, mol%) have been synthesized by using the well-known melt quenching technique. The present work deals with physical, optical, photoluminescence, X-ray luminescence and decay time studies of silicoborate glasses. Judd-Ofelt (JO) intensity parameters (Ω_2, Ω_4 and Ω_6) and radiative properties for the important luminescent level of Sm^{3+} ions were derived by using the absorption spectrum of 0.3 mol% Sm_2O_3 doped glass. The luminescence spectra in the visible region was obtained due to $^4G_{5/2} \rightarrow {}^6H_J$ (5/2, 7/2, 9/2 and 11/2) transition of Sm^{3+} ion under 401 nm excitation. The decay profile for the $^4G_{5/2}$ level of Sm^{3+} ions was analyzed and found that for lower concentration ($\leq$ 0.20 mol%) it is single exponential in nature whereas for higher concentration ($\geq$ 0.25 mol%), it turns in to non-exponential due to the transfer of energy between donor (excited state Sm^{3+}ion) and acceptor (ground state Sm^{3+} ion). As the concentration of Sm^{3+} ions increases the decay time of $^4G_{5/2}$ state decreases. The well-known Inokuti-Hirayama (IH) model was used for fitting the non-exponential decay curves where S = 6 indicates that energy transfer process is of dipole-dipole type. Hence, in the present work, intense transition of $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (601 nm) is found to be suitable for reddish-orange laser emission. CIE chromaticity diagram has been performed for verifying the results of fluorescence in visible laser applications at 601 nm.

1. Introduction

Rare-earth (RE) ions play a vital role as active ions in many optical and light applications in the modern technology, such as optical detectors, fluorescent display devices, optical fibers, bulk lasers and waveguide lasers [1–5]. Among RE ions, Sm^{3+} is main activator in different hosts for producing strong luminescence in near-infrared regions and in the visible regions. In addition, Sm^{3+} ion is appropriate for analyzing energy transfer process, after all its lowest emitting $^4G_{5/2}$ level has comparatively high quantum efficiency and shows different quenching emission channels [6]. Moreover, greenish yellow, reddish orange and red emission band of Sm^{3+} associated to $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2 and 9/2) are suitable for high-density optical storage [7], undersea communication [8], color display [9], medical diagnostics [10], compact fiber lasers and planner wave guides [11]. Among the different oxide glasses, silicoborate glasses formed by combining the silica dioxide and boron-tri-oxide is the main glass forming constituents. These glasses have very low coefficient of thermal expansion ($\sim 3 \times 10^{-6}\,K^{-1}$ at 20 °C), resistant to thermal shock [12,13]. It is therefore, obvious that the silicoborate glass host possibly offers the best features of both silicates and borates. The insertion of the calcium oxide increases the chemical durability, strength and also increases the resistance to the hygroscopicity [14]. Likewise, yttrium oxide (Y_2O_3) as a kind of glass network modifier has drawn much attention due to its exceptional chemical and photochemical stability [13].

The current work reports the luminescence properties of the Sm^{3+} doped silicoborate glasses with different concentration (0.05, 0.10, 0.20, 0.25, 0.30, 0.40, and 0.50 mol%). The intensities of the transition are calculated by using Judd-Ofelt (JO) theory [15,16] of Sm^{3+} doped silicoborate glasses. Likewise, radiative properties which include branching ratio, radiative transition probabilities and radiative lifetime of excited states are calculated by using JO, Ω_λ (2, 4 and 6) parameters [15,16]. Similarly, the consequences of Sm^{3+} ion concentration quenching is due to energy transfer process was studied by using the Inokuti-Hirayama (IH) model [17] for explaining the non-exponential decay nature of higher concentrations.

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2. Experimental methods

2.1. Glass preparation

Silicoborate glasses doped with Sm^{3+} ion having the composition of (55-x)B_2O_3 + 10SiO_2 + 25Y_2O_3 + 10CaO + xSm_2O_3, referred as BSYCaSm0.05, BSYCaSm0.10, BSYCaSm0.20, BSYCaSm0.25, BSYCaSm0.30, BSYCaSm0.40, and BSYCaSm0.50, for x = 0.05, 0.10, 0.20, 0.25, 0.30, 0.40 and 0.50 mol%, respectively have been synthesized by convectional melt quenching technique. Approximately 20 g of each batch homogenous powders were blended wholly by using agate mortar then the powder was melted at 1400 °C in a platinum crucible for 2 h in an electrical furnace. The powders after melting instantly poured on to the brass mold baked at 450 °C and at this temperature the glass was annealed for 5 h. After this, the glass was slowly cooled down to room temperature in order to remove the thermal stress and strain during quenching process. Then, the glass samples were cut and polished for characterizing different spectroscopic properties.

2.2. Physical properties

The important physical properties of this material are density, average molecular weight, molar volume and refractive index. Here, density was measured by Archimedes principle where water is used as an immersion liquid and refractive index by Atago abbe refractometer at sodium wavelength (589.3 nm) with 1-bromonapthelene ($C_{10}H_7Br$) as contact liquid. The other important physical parameter is compactness of the glass due to doping concentration of samarium ion was determined by calculating polaron radius and inter-ionic separation using the following Eqs. (1) and (2), respectively:

$$r_p = \frac{1}{2}\left(\frac{\pi}{6N}\right)^{\frac{1}{3}} \tag{1}$$

where N is the number of rare earth ions per unit volume

$$r_i = \left(\frac{1}{N}\right)^{\frac{1}{3}} \tag{2}$$

Similarly, field strength (F) has been calculated as follows

$$F = \frac{z}{(r_p)^2} \tag{3}$$

Here 'z' is the atomic mass for rare earth ions. All the calculated physical parameters are shown in Table 1. The density of the BSYCaSm glasses decrease with the increase in concentration up to 0.25 mol% and then increases for higher concentration of Sm_2O_3. The probable reason for decrease in density may be the arrangement of non-bridging oxygen (NBO's) atoms bonded to the lower concentration of samarium oxide. Similarly, the density increases for higher concentration because of conversion of $[BO3]^{-3}$ triangles to Bo^{-4} tetrahedral and increase of molar mass [18]. The molar volume which is mainly depends on the density of glasses shows opposite behavior with respect to density in the current work. Such unexpected behavior of density and molar volume could be due to the creation of excess of NBO's which open up the structure of glass networks [19]. From Table 1, it is found that the polaron radius decreases with the increase in concentration of Sm^{3+} ions. Similarly, relationship between the inter-ionic separation and field strength is shown in Fig. 1, indicating that the inter-ionic separation decreases as the field strength increases. Because of this, there is stronger bonding between Sm-O, producing stronger field around Sm^{3+} ions.

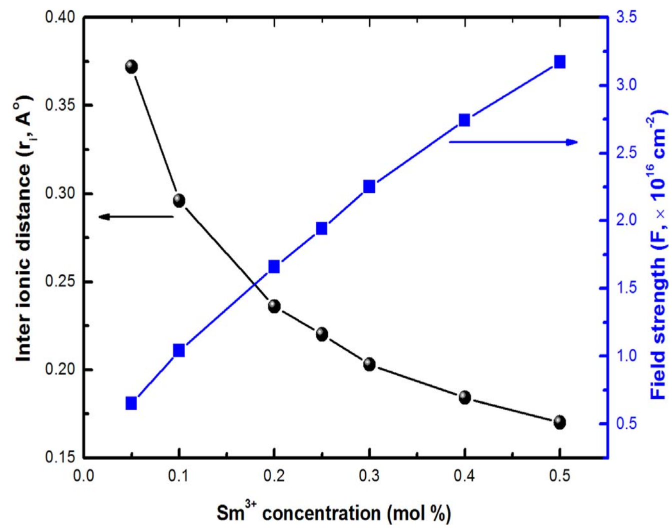

Fig. 1. Inter ionic separation (ri, Å) and Field strength (F, × 10^{16} cm^{-2}) as a function of Sm^{3+} concentration.

2.3. Optical measurements

The optical absorption spectrum was studied with a UV–visible-NIR spectrophotometer (Shimadzu UV-3600) having one nm spectral resolution in the spectral range of 350–2500 nm. The excitation, emission and decay time measurement were analyzed by using a fluorescence spectrophotometer (Aligent Cary-Eclipse) having xenon lamp as an excitation source. The X-ray induced luminescence was measured by using X-ray as the excitation source (DRGEM Co.) and the spectrum was collected by QE65000 spectrometer (Ocean Optics Co.) through optical fiber. The energy used for X-ray source was 100 kV and 2 mA.

3. Results and discussion

3.1. Optical absorption and Judd-Ofelt study for BSYCaSm0.30 glass

The experimental oscillator strength of the absorption is evaluated by using the area under the absorption curve using the relation [20]

$$f_{exp} = 4.32\times 10^{-9}\int \mathscr{E}(\nu)d\nu \tag{4}$$

where: $\mathscr{E}$ is the molar absorptivity at a wavenumber υ (cm^{-1}). Similarly, the theoretical oscillator strength of an induced electric-dipole transition from the ground state ΨJ to excited state Ψ'J' is calculated by

Table 1
Physical properties of the Sm^{3+}-doped silicoborate glasses.

S.N.	Physical properties	BSYCa Sm0.05	BSYCaSm0.10	BSYCaSm0.20	BSYCaSm0.25	BSYCaSm0.30	BSYCaSm0.40	BSYCaSm0.50
1	Density (ρ, g/cm^3)	3.443	3.399	3.389	3.444	3.577	3.603	3.605
2	Average molecular weight (g)	106.50	106.64	106.92	107.06	107.20	107.48	107.75
3	Molar volume (cm^3/mol)	30.93	31.37	31.55	31.30	29.97	29.83	29.89
4	Refractive index at 589.3 nm (n)	–	–	–	–	1.5461	–	–
5	Concentration (N_0,10^{20} ions/cm^3)	0.19	0.38	0.76	0.94	1.20	1.61	2.02
6	Polaron radius (r_p, Å)	15.03	11.97	9.52	8.88	8.19	7.42	6.87
7	Inter ionic distance (r_i Å)	37.3	29.7	25.84	22.04	20.31	18.42	17.08
8	Field strength (F, 10^{16} cm^{-2})	0.65	1.04	1.66	1.94	2.25	2.74	3.17