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Spectral analysis of Sm^{3+} and Dy^{3+}: B_2O_3–ZnO–PbO glasses

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Abstract

This paper reports on the spectral results of Sm^{3+} or Dy^{3+} (1.0 mol%) ions-doped B_2O_3–ZnO–PbO (BZP) glasses. Measurements of X-ray diffraction (XRD), differential scanning calorimeter (DSC) profiles of these rare-earth ion-doped glasses have been carried out. From the DSC thermograms, glass transition (T_g), crystallization (T_c) and melting (T_m) temperatures have been evaluated. Direct and indirect optical band gaps have been calculated based on the glasses UV absorption spectra. These glasses have shown strong absorption bands in the near-infrared (NIR) region and their oscillator strengths have been computed. Emission bands of $^4G_{5/2}\rightarrow{}^6H_{5/2}$ (564 nm), $^4G_{5/2}\rightarrow{}^6H_{7/2}$ (602 nm), $^4G_{5/2}\rightarrow{}^6H_{9/2}$ (647 nm) and $^4G_{5/2}\rightarrow{}^6H_{11/2}$ (710 nm) for the Sm^{3+}: glass, with excitation at $^6H_{5/2}\rightarrow{}^4I_{9/2}$ (484 nm) have been recorded. Of them, $^4G_{5/2}\rightarrow{}^6H_{7/2}$ (602 nm) has shown a bright emission. With regard to the Dy^{3+}: glass, a bright fluorescent yellow emission at 576 nm ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) has been observed, apart from $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (484 nm) and $^4F_{9/2}\rightarrow{}^6H_{11/2}$ (666 nm) emission transitions with excitation at 450 nm ($^6H_{15/2}\rightarrow{}^4I_{15/2}$) excitation wavelength. Stimulated emission cross-sections of all the emission bands of Sm^{3+} and Dy^{3+}: BZP glasses have been computed based on their measured $\Delta\lambda$ (FWHM) and measured lifetimes (τ_m).

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Keywords: RE glasses; Optical analysis

1. Introduction

Glasses based on heavy metal oxides (HMO) are becoming an important class of materials for optoelectronic applications [1–5]. The large mass, low field strength and high polarizability of lead gives some special significance to glasses that are developed. Lead oxide has the ability to form stable glasses over a wide range of concentrations due to its dual role, as glass modifier and as glass former. In our laboratory, we have recently studied the spectral properties of transition metal ions, such as Cu^{2+} [6] and Mn^{2+}, Co^{2+} and Ni^{2+} [7] ions-doped B_2O_3–ZnO–PbO (BZP) glasses. In the present work, we have undertaken these BZP glasses with Sm^{3+} and Dy^{3+} as the dopant rare-earth ions. Rare-earth ion-doped glasses have received more attention because of their potential applications towards the development of visible and near-infrared (NIR) optical lasers and amplifiers, sensors and optical switching, etc. [8–20]. Earlier, it is shown that the spectrum of Sm^{3+} ions in lead borate glasses, the heavy metal lattices, enhance the fluorescence yield of the rare earth due to their low phonon energy and give a chance of observing lasing emission [18]. Because of the fact that these two rare-earth (Sm^{3+} or Dy^{3+}) ions show line-like and more intense absorption bands in the NIR region and interesting emission trends in the reddish-orange and yellow wavelength regions; these ions have been incorporated into these BZP glasses, to understand the glass composition effects on the optical analysis of Sm^{3+} and Dy^{3+} glasses systematically, following the standard procedures.

2. Experimental studies

2.1. Glasses preparation

Following are the Sm^{3+} or Dy^{3+} ions-doped lead-based zinc borate (BZP) glasses that are developed for the present

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work, along with a reference glass:

$45B_2O_3-5ZnO-(50-x)PbO-xSm_2O_3$

$45B_2O_3-5ZnO-(50-x)PbO-xDy_2O_3$

and

$45B_2O_3-5ZnO-50PbO$ (reference glass)

where $x = 1.0$ mol% in both cases.

The starting materials used in the present work were reagent grade of H_3BO_3, ZnO, Pb_3O_4, Sm_2O_3 and Dy_2O_3. All weighed chemicals were powdered finely and mixed thoroughly before each batch (10 g) was melted in ceramic crucibles in an electrical furnace for an hour, at 950 °C. These melts were quenched in between two brass plates to obtain 2–3 cm diameter optical glass discs of 0.3 cm thickness. These glasses thus obtained were all annealed at 200 °C for an hour, to remove thermal strains in the glasses. Due to high lead content in the composition of host glass, it appeared in transparent yellow colour. Fig. 1 presents the photograph of a reference glass, Sm^{3+} and Dy^{3+} (1.0 mol%) ions-doped glasses.

2.2. Measurements

Glass densities were measured with toluene as an immersion liquid from the Archimedes's principle. Abbe refractometer was used to measure the glass refractive index at Na (589.3 nm) lamp wavelength. Powder X-ray diffraction (XRD) spectra were obtained on Shimadzu XD 3A diffractometer with a Ni filter and Cu-Kα (1.5418 Å) radiation with an applied voltage of 30 KV and 20 mA anode current calibrated with Si at the rate of 2° min^{-1}. Differential scanning calorimeter (DSC) profiles were carried out on Netzsch STA 409C in the temperature range 30°–1200 °C, at the rate of 10 °C min^{-1}, under N_2-gas atmosphere. The optical absorption spectra (400–2500 nm) were measured on a Varian-Cary Win spectrometer. The excitation and emission spectra were obtained on a SPEX Fluorolog-2 Fluorimeter (Model II) with Data max software to acquire the data with a Xe-arc lamp (150 W) as the excitation source. A Xe-flash lamp with a phosphorimeter attachment was used to measure the lifetimes of the emission transitions of these glasses. Table 1 presents the physical properties of Sm^{3+} and Dy^{3+} ions-doped glasses. From the DSC profile, the values of T_g, T_c and T_m were evaluated and from these the values of glass stability factor (S) and Hruby's parameter (K_{gl}) were calculated and the results are given in Table 1. The glass stability factors reveal that these glasses are more stable. Hruby's parameter gives information on the stability of the glass against devitrification.

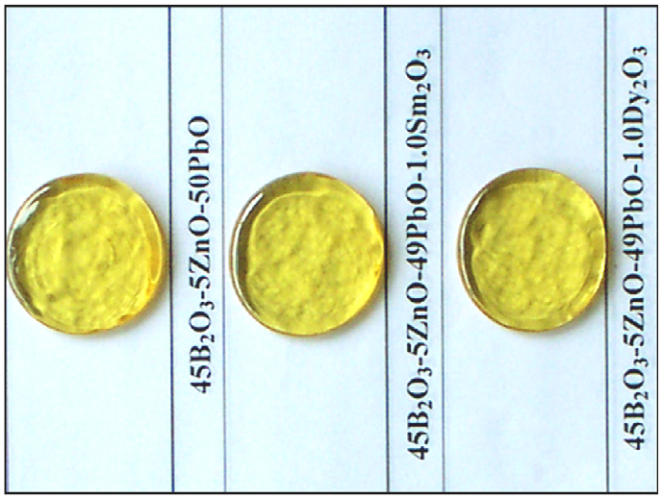

Fig. 1. Photograph of Sm^{3+} and Dy^{3+} (1.0 mol%) ions-doped glasses along with reference glass.

Table 1
Physical properties of Sm^{3+} and Dy^{3+} (1.0 mol%): $45B_2O_3$–5ZnO–49PbO glasses

Physical quantities	Data	
	Sm^{3+} (1.0 mol%)	Dy^{3+} (1.0 mol%)
Average molecular weight, M (g)	374.811	375.054
Density, d (g/cm^3)	5.774	5.775
Refractive index, n_d (589.3 nm)	2.1582	2.1584
Number Density, N (ions/cm^3)10^{20}	0.9278	0.9272
Polaron radius, r_p (Å)	1.9175	1.9179
Interionic distance, r_i (Å)	4.7589	4.760
Field strength, F (10^{16} cm^{-2})	0.8159	0.8155
Direct optical band gap (eV)	2.60	2.57
Indirect optical band gap (eV)	2.49	2.47
Glass transition temperature, T_g (°C)	359.3	407.3
Crystallization temperature, T_c (°C)	519.7	598.2
Temperature of melting, T_m (°C)	829.0	865.2
Glass stability factor, $S = T_c - T_g$ (°C)	160.4	190.9
Hruby's parameter, $k_{gl} = ((T_c - T_g)/(T_m - T_c))$	0.518	0.715

3. Results and discussion

3.1. Sm^{3+} glass

The XRD pattern of the glass (1.0 mol% Sm^{3+}: $45B_2O_3$–5ZnO–49PbO) is shown in Fig. 2, which confirms its amorphous nature. The DSC thermogram for the Sm^{3+}: glass is shown in Fig. 3. From this profile, we have identified two crystallization peaks at 519.7 °C (T_{c1}), 592.8 °C (T_{c2}). Due to the high lead content in the host matrix, a high thermal stability was noticed with the glass; based on the T_g, T_c and T_m, as presented in Table 1. Both direct and indirect optical band gaps have been calculated from the UV absorption spectrum of Sm^{3+}: glass, following the procedure given earlier [6], and the results are listed out in Table 1. The VIS–NIR absorption spectrum of Sm^{3+} ion is shown in Fig. 4, with strong absorption bands in the NIR region. The rare-earth ions