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Investigation of europium concentration dependence on the luminescent properties of borogermanate glasses

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ABSTRACT

In order to elucidate the effect of europium content on the optical and luminescent properties of borogermanate glasses, a series of Eu^{3+} doped $30B_2O_3$-$40GeO_2$-(30-x)Gd_2O_3 glasses with various doping levels (x = 1–9 mol%) have been synthesized and studied with transmission, absorption, photoluminescence and decay time measurements. The transmission spectra proved that the title glasses maintained a high transparency about 80% in the 440 to 900 nm region. Based on the absorption spectra, the optical band gaps obtained from Tauc's plot can be narrowed by increasing content of Eu^{3+}. From the photoluminescence spectra, the strongest red emission has been observed from the $^5D_0 \to {}^7F_2$ level of Eu^{3+} ions in borogermanate glasses. The strongest emission and excitation intensities of Eu^{3+} ions are at the doping level of x = 7 mol% and then these intensities decrease due to concentration quenching. The red to orange ratio (R/O) of $^5D_0 \to {}^7F_2$ to $^5D_0 \to {}^7F_1$ transitions has been investigated to predict the local environment of Eu^{3+} ions. Judd-Ofelt (J-O) analyses have been performed from the emission spectra. The values of R/O and Ω_2 present an increase with increasing doping level, indicating the lower symmetric environment for Eu^{3+} ions and higher covalency for Eu-O bond. The emission efficiency calculated from J-O theory is 75% at x = 2 mol%. The decay time curves of $^6P_{7/2} \to {}^8S_{7/2}$ transition of Gd^{3+} ions and $^5D_0$–$^7F_2$ transition of Eu^{3+} ions confirm the energy transfer from Gd^{3+} to Eu^{3+} ions.

1. Introduction

Due to their unique optical properties, rare earth (RE) doped glasses are very attractive materials for diverse optical devices, such as advanced laser materials, plasma displays, optical waveguides, fiber amplifiers, efficient upconverters [1–4]. For the highest performance for these devices the optical properties of RE ions must be correlated with their local environment in detail [5]. In order to develop new optical devices borate, silicate and phosphate glass systems have been studied as host materials for the incorporation of trivalent RE ions [6]. In view of their high RE ion solution capacity, high thermal stability, high transparency, lower melting point, lower phonon energy, ease of shaping and low cost properties, borogermanate glasses surpass phosphate, silicate or borosilicate glass systems [7–9]. Borogermanate glasses have been used in several application areas that include scintillators, solar cells, solid state lasers and glass fibers [10–13]. Within other RE elements, Eu^{3+} ions are very effective in the investigation of the local environment of the glass materials, owing to its relatively simple energy level and hypersensitive $^7F_0 \to {}^5D_2$ transition [5,14]. Because of the properties stated above research have been conducted on Eu^{3+} doped borogermanate systems [15–17].

Glass systems doped with Gd^{3+} have been studied for various applications such as medical therapy [18], scintillator [19] and x-ray imaging [20]. In addition Gd^{3+} ion has been studied due to its significant importance in the efficient energy transfer to the incorporated ions (such as Eu^{3+}) [20–25]. Luminescent properties of glasses can be improved by energy transfer between these ions [20,26,27].

In the present work a series of europium-gadolinium co-doped borogernanate glasses have been designed for use as glass scintillators. The structural analyses of these glasses have been determined by x-ray diffraction (XRD) and Fourier transform infrared (FTIR) measurements. Absorption, transmittance, photoluminescence (PL) spectra, Judd–Ofelt analysis and decay time measurements have been evaluated in order to obtain optical and luminescent properties of borogermanate glasses as a function of Eu^{3+} concentration.

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2. Experimental methods

The glasses with composition of $30B_2O_3$-$40GeO_2$-$(30\text{-}x)Gd_2O_3$-xEu_2O_3 (x = 1,2,3,5,7,9 mol%; labeled as BGGEx) have been prepared by melt quenching method. The raw materials used for the prepared glasses were H_3BO_3 (99.99%, Alfa Aesar), GeO_2 (> 99.99%, Aldrich), Gd_2O_3 (99.9%, Aldrich) and Eu_2O_3 (99.9%, Aldrich). About 10 g batches were mixed by grinding homogeneously in an agate mortar and melted in an alumina crucible under air atmosphere at 1300~1400 °C for 3 h. The melt was poured onto a preheated stainless steel plate and pressed by another plate and then annealed at 550–600 °C for 6 h to release internal stresses and avoid cracking of the sample. Optical measurements were done on the polished glass samples with a thickness about 2.5 mm. XRD measurements were carried out using Rigaku-Rint 2200/PC (Ultima 3) diffractometer in the range of 10° and 90°. The FTIR spectrum was recorded using Perkin-Elmer BX-II FTIR spectrometer in the range of 400–4000 cm^{-1}. The glass densities were determined according to the Archimedes principle by using distilled water as an immersion liquid. Absorption and transmittance spectra were measured on a Perkin-Elmer Lambda 25 UV–vis spectrometer. The photoluminescence excitation and emission spectra were recorded by FluoroMax-4 (Horiba Jobin Yvon) spectrofluorometer equipped with a 150 W xenon lamp source. The decay time measurements were carried out using a Time Correlated Single Photon Counting (TCSPC) system (Edinburgh Instruments) with a micro second flash lamp as an excitation source. All the measurements were carried out at room temperature.

3. Results and discussion

Various physical properties including molecular weight (M), density (ρ), refractive index (n), molar volume (V_m), packing density (PD), rare earth-ion concentration (N), polaron radius (r_p) and critical distance (R_c) for Eu^{3+} doped borogermanate glasses have been provided in Table 1. The refractive indexes of glasses have been calculated using Gladstone-Dale relation [28]. The critical distances (R_c) and other calculated physical properties of glasses have been obtained according to literature [29,30], respectively.

As the molecular mass of Eu^{3+} ion is less than Gd^{3+} ion, the glass density decreases gradually by the increase in content of Eu^{3+} ions. The critical distance between Eu^{3+} ions is higher than the polaron radius for all samples. Both the values of R_c and r_p reduce with the increase of Eu^{3+} ion content [22]).

3.1. Structural analysis

The XRD pattern of x = 1 mol% Eu^{3+} doped borogermanate glass is shown in Fig. 1. The spectrum exhibits a broad scattering at around 25° and 55° and lacks the presence of specific crystalline peaks, indicating the amorphous nature of network structure.

As a representative case, the IR spectra of BGGE1 glass (Fig. 2) has been evaluated to identify the structural formation. The typical absorption band of OH^- group is centered at 3400 cm^{-1}, which reveals

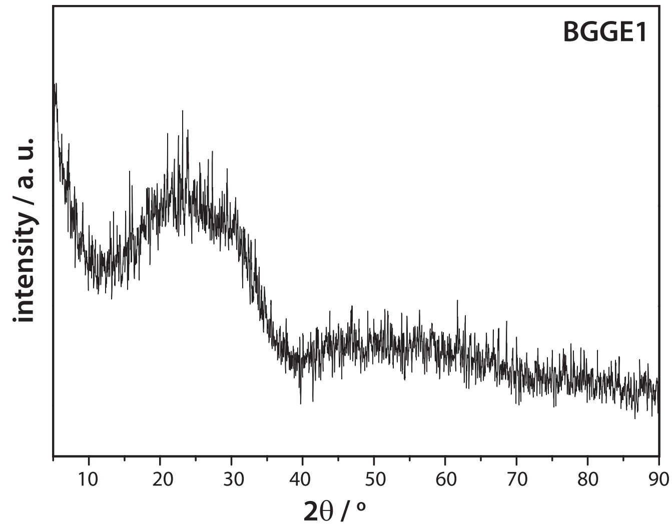

Fig. 1. XRD pattern of BGGE1 glass.

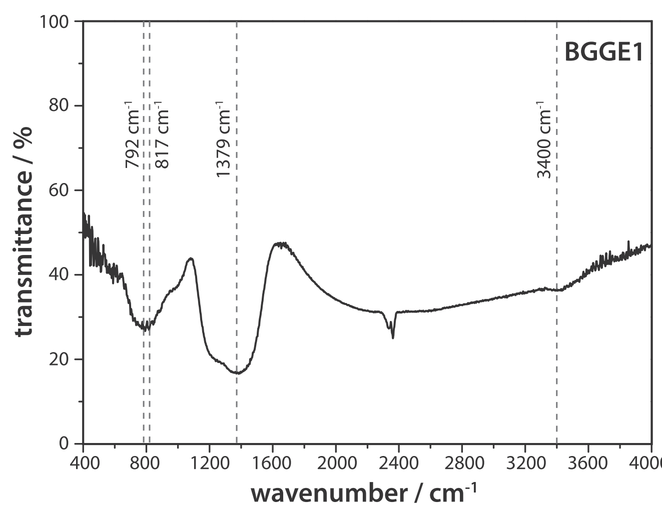

Fig. 2. Infrared transmission spectrum of BGGE1 glass.

Table 1
The digital photographs, molecular weight (M), density (ρ), refractive index (n), molar volume (V_m), packing density (PD), rare earth-ion concentration (N), polaron radius (r_p) and critical distance (R_c).

	BGGE1	BGGE2	BGGE3	BGGE5	BGGE7	BGGE9
						
M (g/mol)	171.585	171.279	171.173	170.962	170.751	170.539
ρ (g/cm^3)	4.807	4.824	4.818	4.764	4.778	4.732
n	1.700	1.702	1.701	1.693	1.695	1.689
V_M (cm^3/mol)	35.694	35.505	35.527	35.886	35.736	36.039
PD ($x10^{22}$ ions/cm^3)	1.687	1.696	1.695	1.678	1.685	1.671
N ($x10^{20}$ ions/cm^3)	1.687	3.392	5.085	8.390	11.795	15.038
r_p (Å)	7.292	5.777	5.048	4.272	3.813	3.516
R_c (Eu^{+3}-Eu^{+3}) (Å)	14.364	11.380	9.943	8.415	7.511	6.927
R_c (Gd^{+3}-Eu^{+3}) (Å)	4.622	4.614	4.615	4.631	4.624	4.637