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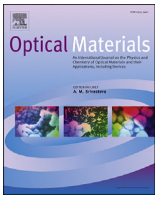

Energy transfer based photoluminescence spectra of co-doped ($Dy^{3+} + Sm^{3+}$): Li_2O-LiF-B_2O_3-ZnO glasses for orange emission

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ABSTRACT

The present paper brings out the results concerning the preparation and optical properties of Sm^{3+} and Dy^{3+} each ion separately in different concentrations (0.3, 0.5, 1.0 and 1.5 mol.%) and also together doped (x mol.% Dy^{3+} + 1.5 mol.% Sm^{3+}): Li_2O-LiF-B_2O_3-ZnO (where x = 0.5, 1.0 and 1.5 mol.%) glasses by a melt quenching method. Structural and thermal properties have been extensively studied for those glasses by XRD and TG/DTA. The compositional analysis has been carried out from FTIR spectral profile. Optical absorption spectral studies were also carried out. Sm^{3+}: LBZ glasses have displayed an intense orange emission at 603 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$) with an excitation wavelength at 403 nm and Dy^{3+}: LBZ glasses have shown two emissions located at 485 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$; *blue*) and 574 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$; *yellow*) with an excitation wavelength at 385 nm. Remarkably, it has been identified that the significant increase in the *reddish orange* emission of Sm^{3+} ions and diminished *yellow* emission pertaining to Dy^{3+} ions in the co-doped LBZ glass system under the excitation of 385 nm which relates to Dy^{3+} ions. This could be due energy transfer from Dy^{3+} to Sm^{3+}. The non-radiative energy transfer from Dy^{3+} to Sm^{3+} is explained in terms of their emission spectra, donor lifetime, energy level diagram and energy transfer characteristic factors. These significantly enhanced *orange* emission exhibited glasses could be suggested as potential optical glasses for orange luminescence photonic devices.

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1. Introduction

The study on trivalent Lanthanide (Ln^{3+}) ions doped materials gained significant importance due to their potential applications in the field of photonics as optical storage, display monitors, sensors, lasers and amplifiers for fiber optic communications [1]. Glasses doped with lanthanide (Ln^{3+}) ions are good laser materials as they emit intense radiation in visible, infrared and near infrared regions under suitable excitation conditions [2]. The optical properties of RE ions in glasses depend on the chemical composition of the glass matrix, which determines the structure and nature of the bonds [3]. Among all the classical network formers, boric oxide (B_2O_3) is one of the significant glass former and flux material, having wide applications in solar energy converters and in fabrication of number of optoelectronic devices [4]. Boron atom has an ability to generate variety of atom groups by joint with either three or four oxygen atoms [5]. Alkali fluoro borate glasses are promising hosts because of these glasses possess advantages of both fluorides and oxides such as low phonon energy, high quantum efficiencies, higher IR cutoff edge towards higher wavelength side, high transmission ability from UV to IR and low non linear refractive index [6]. They can also decrease the OH absorption because fluorine might react with OH group and forms HF. The presence of oxides imparts high mechanical and thermal stability and chemical durability [7].

In rare earth doped optical materials, fluorescence efficiency is the most important and significant parameter for their optical applications [8]. Recently research focus on RE doped glasses is not limited to infrared optical devices, but there is a growing interest in visible optical devices. With the increasing demand of various visible lasers and light sources further studies on RE ions doped glasses are becoming more important [9]. Among the Lanthanide ions, two rare earth ions (Dy^{3+} and Sm^{3+}) show line like and more intense absorption bands in NIR region and interesting emission trends in the reddish orange and yellow wavelength regions. Samarium (Sm^{3+}) ion is one of the most interesting lanthanide ion

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in which $^4G_{5/2}$ level of Sm^{3+} possesses relatively high quantum efficiency and also shows various populating as well as different quenching emission channels [10]. Sm^{3+} ion has widely used in radiation dosimeter, spectral hole burning, high-density optical storage, color displays, under sea communication [11]. Sm^{3+} ion exhibits very strong fluorescence in orange –red spectral region which has potential applications in high power lasers, LED's in visible spectral region as well as visible optical devices [9]. In addition to samarium ion, Dysprosium (Dy^{3+}) ion possesses emission in visible (yellow/blue) and NIR regions. Its visible emission is used in white light emitting diodes. Blue emission can be used in the development of blue laser diodes and mid-infrared (1.3 μm) emission of Dy^{3+} ion for the optical amplification telecommunication systems [12]. In Samarium doped optical materials, the fluorescence efficiency plays a pivotal role for numerous applications in photonic devices. However, there are several mechanisms have been established to enhance the fluorescence efficiency of the samarium ion in optical materials. Among those mechanisms, the addition of appropriate secondary rare earth ion to the samarium is found to be one of the best approaches to enhance the fluorescence efficiency of the samarium ion. Here, Sm^{3+} ion acting as an activator and Dy^{3+} ions acting as sensitizer. In our present work, we have been undertaken the Dy^{3+} ion as a secondary rare earth ion for sensitizing purpose to obtain the better performance of the Sm^{3+} ions in the host glass through energy transfer from Dy^{3+} ions to Sm^{3+} ions [7].

The excitations and interactions between unfilled 4f shells of the RE ions contribute to different emissions. Auzel et al. [13] demonstrated different mechanisms between neighboring RE ions as sensitizer (S) and activator (A) [14]. The principle interactions between two activated centers are resonant and non-resonant energy transfers and quantum cutting effect. The later phenomenon is introduced as the mechanism responsible for luminescence quenching due to energy transfer process from the luminescent to its neighboring activator [15]. Such energy transfer processes have been attracting a significant attention for its practical utility in optical devices. In the present work, we have reported the luminescence properties of Dy^{3+} and Sm^{3+} ions co-doped glass systems along with single ion doped glasses, to understand the energy transfer based photoluminescence properties using life time decay dynamics.

2. Experimental studies

Glasses in the chemical composition of Li_2O-LiF-B_2O_3-ZnO (LBZ) separately doped with Sm^{3+} and Dy^{3+} ions in different concentrations (0.3, 0.5, 1and 1.5 mol.%) and also co-doped with fixed 1.5 mol.% concentration of Sm^{3+} and Dy^{3+}concentration varied from 0.5 to 1.5 mol.% were prepared by a melt quenching method. The glass sample chemical composition as follows.

i. $30Li_2O$-20LiF-$45B_2O_3$-5ZnO (LBZ host glass)
ii. $30Li_2O$-20LiF-(45-x) B_2O_3-5ZnO-xSm_2O_3 (Sm^{3+}: LBZ glass), (where x = 0.3, 0.5, 1.0, 1.5 and 2 mol.%)
iii. $30Li_2O$-20LiF-(45-y) B_2O_3-5ZnO-yDy_2O_3 (Dy^{3+}: LBZ glass), (where y = 0.3, 0.5, 1.0 and 1.5 mol.%)
iv. $30Li_2O$-20LiF-(45-x-y)B_2O_3-5ZnO-xDy_2O_3-ySm_2O_3((Sm^{3+}+Dy^{3+}): LBZ glass), (where x = 0.5, 1.0 and 1.5 mol.% and y = 1.5 mol.%).

Standard chemicals from Sigma Aldrich, such as H_3BO_3, Li_2CO_3, LiF, ZnO, Sm_2O_3, and Dy_2O_3 were used in the preparation of both host and rare earth ions doped glasses. All these chemicals were weighed separately in 10 g batch each, thoroughly mixed and finely powdered using an agate mortar and pestle. Each batch of chemicals mix was transferred into porcelain crucibles and each of those was sintered separately in electric furnace for an hour at 950 °C in order to ensure homogenous melts and then these melts were quenched in between two smooth surfaced brass plates to obtain circular glass discs of 2–3 cm in diameter and 0.3 cm as thickness. These prepared glasses were taken for further characterization. By incorporating the rare earth ions (Sm^{3+} and Dy^{3+}), each ion separately and also together in (LBZ) glasses have exhibited orange, blue/yellow and reddish-orange emissions under an UV lamp.

The density of glass samples was measured using Archimedes principle with water as an immersion liquid. The refractive indices were measured at 589.3 nm (sodium wavelength) using an Abbe refractometer with mono-bromo-naphthalene as the contact liquid. For all the glass samples, the physical parameters like density, thickness and refractive indices have been measured. XRD profile of the host glass was recorded on a *Seifert X-ray diffractometer (model 3003 TT)* with CuK$_\alpha$ radiation ($\lambda = 1.5406$ Å) at 40 KV and 30 mA with a Si detector, where 2θ range from 10° to 60° at the rate of two degrees per minute. A simultaneous measurement of TGA and DTA were carried out on *NetZsch STA 409* at a heating rate of 10 °C/min with N_2 as the purging gas was obtained to correlate the results for a better understanding of the trends. FT-IR spectrum of the host glass was recorded on a *Nicolet -5700 FT-IR spectrometer* using KBr pellet technique in the range of 4000–400 cm^{-1}. The optical absorption spectra of Dy^{3+}, Sm^{3+} doped and co-doped LBZ glasses were recorded on a *Varian-Cary-Win* Spectrometer (*JASCO V-570*). The excitation and emission spectra of singly doped Sm^{3+}, Dy^{3+} and co-doped (Sm^{3+} and Dy^{3+}) glasses were recorded at room temperature on a *SPEX Flurolog-3* (*Model-II*) Spectrophotometer, attached with an Xe-arc lamp (450 W) as the excitation source. This system is employed with a Datamax software for acquiring the data and emission decay-curve (lifetime measurement) data using a Phosphorimeter attached with a Xe-flash lamp.

3. Results and discussion

3.1. Host Li_2O-LiF-B_2O_3-ZnO (LBZ) glass

3.1.1. Structural analysis

The X-ray diffraction pattern of the above titled host Li_2O-LiF-B_2O_3-ZnO (LBZ) glass exhibits a broad hollow peak (diffused peak) between 20° and 30° which confirms the amorphous nature of the glass [16] as shown in Fig. 1. Similar behavior has also been observed in rare earth ions doped and co-doped LBZ glasses.

3.1.2. Thermal analysis

TG and DTA profiles are simultaneously measured for the Li_2O-LiF-B_2O_3-ZnO (LBZ) precursor chemical mix as shown in Fig. 2. TG profile displays that the weight loss of the sample takes place in a multistep process in the temperature range of 39 °C – 700 °C. Initial weight loss of the sample takes place between 39 °C and 135 °C due to the decomposition of the organic compounds which were used during the grinding of chemicals mix [17], it has been found to be 4.1%. The second weight loss is noticed in the temperature range of 135 °C – 177 °C, due to the transformation of boric acid (H_3BO_3) into meta-boric acid (HBO_2) at 135 °C with a weight loss of 7.0%. Upon further heating, the third weight loss has occurred in the temperature range of 177 °C – 462 °C. This is due to conversion of HBO_2 as tetraboric acid or pyroboric acid, which in turn further become as anhydrous oxide as boron trioxide (B_2O_3) in crystalline form. It melts at 462 °C, the corresponding weight loss has been found to be 7.5%. The final weight loss has been observed in the range of 460 °C – 595 °C due to decomposition of Li_2CO_3 into Li_2O and CO_2 with its elimination by forming constituent oxides [18], the

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