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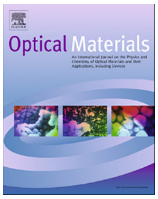

Structural, thermal and optical investigations of Dy^{3+} ions doped lead containing lithium fluoroborate glasses for simulation of white light

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ABSTRACT

Lead containing barium zinc lithium fluoroborate (LBZLFB) glasses doped with different concentrations of trivalent dysprosium ions were synthesized by conventional melt quenching method and characterized through the XRD, DSC, FTIR, FT-Raman, optical absorption, photoluminescence and decay curve analysis. X-ray diffraction studies revealed amorphous nature of the studied glass matrices. The thermal behavior has been reported by recording DSC thermograms. Coexistence of trigonal BO_3 and tetrahedral BO_4 units was evidenced by IR and Raman spectroscopy. Judd–Ofelt intensity parameters have been evaluated for 1.0 mol% Dy^{3+} ions doped LBZLFB glass. The measuring branching ratios are reasonably high for transitions $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^6H_{13/2}$ suggesting that the emission at 486 and 577 nm, respectively can give rise to lasing action in the visible region. From the visible emission spectra, the yellow to blue (Y/B) intensity ratios and chromaticity color coordinates were estimated. A combination of blue and yellow emissions has emerged in the glasses, which allows the observation of white light when the glasses are excited by the ultraviolet/blue light. These Dy^{3+} doped glasses are studied for their utility for white light generation under 454 nm excitation and the present LBZLFB glass is more suitable for generation of white light for blue LED chips.

1. Introduction

In modern lighting and display technology fields the lanthanide ions (Ln^{3+}) have vigorous research activities because of the abundant emission colors based on their 4f–4f or 4f–5d transitions. The study on Ln^{3+} ions doped materials gained significant importance due to their potential applications in the field of photonics as optical storage, display monitors, X-ray imaging, sensors, lasers, up conversion and amplifiers for fiber optic communications [1]. Glasses doped with Ln^{3+} ions are good laser materials as they emit intense radiation in the visible, infrared and near-infrared regions under suitable excitation conditions and the studies on the optical properties of the Ln^{3+} ions in glasses is essential to design optical devices such as laser, color displays, upconverters and fiber amplifiers. Advancement in telecommunications industry also demands a rapid growth in the development of suitable photonic materials for the optical fiber technology [2,3]. In recent years white light emitting diodes (WLEDs) have attracted great attention as potential candidates for the replacement of conventional incandescent fluorescent lamps. In comparison with incandescent fluorescent lamps the WLEDs have longer lifetime, higher efficiency, better reliability and eco friendly. Although commercial availability of WLEDs is currently from phosphors excited by the blue LED chip, a new trend is to realize the white light emission in glasses. The versatility of glasses regarding the possibility of a wide doping concentration, lower production cost, simple preparation procedure, halo effect and the narrow lines emission spectra of the lanthanide ions could be considered as a promising alternative approach than phosphors since the first simulation of white light in borate glass [4]. In order to identify the new optical devices for specific utility or the devices with enhanced performance active work is being carried out by selecting appropriate new hosts doped with Ln^{3+} ions.

Dy^{3+}-doped glasses and crystals have been considered as promising laser active materials and the $^6H_{11/2}$ ($^6H_{9/2}$) → $^6H_{15/2}$ transition of Dy^{3+} around 1.3 μm is found to be useful for optical fiber communication [5]. Little attention has been paid to the visible emission originating from the $^4F_{9/2}$ state situated at about 21,000 cm^{-1} [6–8] and crystal field analysis. The complicated electronic structure of the $4f^9$ configuration of Dy^{3+} ion and the large number of energy levels lying close to each other makes the crystal field analysis more cumbersome. However, tremendous progress in the development of laser diodes is going to overcome this disadvantage. Commercialization of blue laser diodes opens new possibilities of optical pumping; therefore potential laser transition in

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the visible region will be the topic of research for future interest. Among the lanthanide ions trivalent dysprosium (Dy^{3+}) doped glasses have been considered as promising materials for white light emission. Since Dy^{3+} ions possesses intense emission at blue and yellow regions, which are associated with the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions respectively. Further the later one is a hypersensitive transition which is strongly influenced by the environment. At a suitable yellow to blue (Y/B) intensity ratio, Dy^{3+} ions will emit white light. Thus the luminescent materials doped/co-doped with Dy^{3+} ions are usually used to the generation of white light both in glasses and phosphors [9–13]. Pure white light could be produced by adjusting the yellow to blue integral intensity values. The yellow to blue (Y/B) luminescence intensity ratio can be modulated by varying the composition of glass, Dy^{3+} concentration, excitation wavelength for the generation of white light [14]. A proper selection of the host will facilitate the extraction of primary colors, yellow from the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition and blue from the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition of Dy^{3+} ions.

The luminescence phenomenon is the process of absorbing incident energy and converting it into visible light. 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 phosphors, solar energy converters and in the fabrication of number of optoelectronic devices. The luminescence studies on borate compounds have been started since 1967 [15]. Considerable studies have to focus on the borate glasses to improve and enhance its emission by photoluminescence. Consequently, these enhancements make the host network more stable and acquire specific properties, which have significant impact on medical and industrial disciplines. It is well known that the ability of boron atom to joint with either three or four oxygen atoms to generate a variety of atom groups. Alkali/alkaline earth oxides were frequently applied as modifiers, consequently, these oxides shift up the boroxol rings, and the active groups in the mixture, to form tri- and tetra-bond on the host [16]. The borate glasses offer good heat stability and lower melting temperature compared with other glasses [17]. However, it is difficult to realize efficient infrared to visible upconversion emission in borate based glasses due to high vibrational energy. The introduction of heavy metal compounds such as PbO and PbF_2, in conventional glasses like silicate and borate, is of interest for realization of more efficient laser systems as their presence improves the effective fluorescence. The addition of lead oxide (PbO) decreases the host phonon energy and there by suppress the non-radiative losses [18,19]. The presence of structurally different groups such as BO_3 and BO_4 in the PbO–B_2O_3 glass network gives rise to a variety of spectroscopic properties to be investigated. The lead borate glasses are optically transparent from visible to NIR region. The spectroscopic and luminescence properties of RE ions are strongly influenced by the presence of highly polarizable Pb^{2+} ions due to the strong and direct nature of Pb–O bond [20,21]. Because of a dual role such as network modifier (when Pb–O is ionic) and network former (when Pb–O is covalent with PbO_3 and PbO_4 structural units) of Pb^{2+} in the glass structure, the PbO can form stable glasses and make them more moisture resistant [22]. Because of above facts, lead borate glasses are significant in the field of solid state lasers.

Though different spectroscopic characterization have been significantly studied by the modification of chemical composition or ion concentration to improve the performance of laser hosts, still there is a demand for new host materials with high efficiency. On the basis of the above mentioned considerations, the authors have designed, synthesized and characterized the LBZLFB glasses to meet the needs of present photonic devices and was reported by doping Sm^{3+} ions for visible solid state lasers [23]. In continuation of spectroscopic studies of LBZLFB glasses, the authors are extended the work by doping with Dy^{3+} ions to produce solid state lasers suitable for visible region and for simulation of white light at 454 nm excitation i.e., for blue LED chip.

2. Experimental methods

2.1. Glass preparation

The glass samples were prepared with chemical composition of $20PbO + 5BaO + 5ZnO + 10LiF + (60 - x)B_2O_3 + xDy_2O_3$, (where $x = 0.1, 0.5, 1.0, 1.5$ and 2.0 mol%). Approximately 10 g batches of homogeneous mixture of reagent grade Pb_3O_4, $BaCO_3$, ZnO, LiF, H_3BO_3 and Dy_2O_3 were mixed and grinded in required proportions in an agate mortar and melted in an electric furnace at 950 °C in porcelain crucible for about 1 h. The melt was poured into preheated brass molds and annealed at 300 °C for 5 h to remove thermal strains. The glass samples were slowly cooled to the room temperature, shaped and polished to measure their physical and optical properties.

2.2. Physical properties

For concentration determination, density measurements were made by the Archimedes's method using distilled water as the immersion liquid. Refractive index was measured with an Abbe's refractometer with sodium vapor lamp using 1-bromonapthalene as the contact liquid and the thickness (optical path length) was measured by a screw gauge. From the measured values of refractive index (1.581), sample thickness (0.3 cm) and density (5.84 g/cc), the rare earth ion concentration (1.499×10^{20} ions/cc) was estimated for 1.0 mol% of Dy^{3+}-doped LBZLFB glasses. The various measured and calculated physical properties of the 1.0 mol% Dy^{3+}-doped LBZLFB glasses are presented in Table 1.

2.3. Spectral measurements

The X-ray diffraction (XRD) profile was recorded using Seifert X-ray diffractometer. Differential scanning calorimeter (DSC) profile on a Netzsch DSC 204 differential scanning calorimeter in the temperature range of 0–500 °C, at the rate of 10 °C/min, under N_2 gas atmosphere was recorded. FT-IR spectrum in the range 450–4000 cm^{-1} using Perkin–Elmer Spectrum One FTIR spectrophotometer by the standard KBr pellet technique was recorded.

FT-Raman spectra in the range 50–5000 cm^{-1} with Bruker RFS 27 stand alone Raman spectrometer using 1064 nm light from Nd:YAG laser on glass powders were recorded in back scattering geometry with a resolution of 2 cm^{-1}. The absorption spectra were recorded using a double beam Perkin Elmer Lambda 950 spectrophotometer in the wavelength range 250–2500 nm. The excitation,

Table 1
Measured and calculated physical properties for 1.0 mol% Dy^{3+}-doped LBZLFB glass.

Physical quantities	LBZLFB
Sample thickness (cm)	0.300
Refractive index (n)	1.581
Density (g/cc)	4.840
Concentration (mol/l)	0.249
Concentration (ions $cm^{-3} \times 10^{20}$)	1.499
Average molecular weight (g)	193.850
Dielectric constant (ε)	2.500
Molar volume V_m (cm^3/mol)	40.000
Glass molar refractivity (cm^{-3})	13.350
Electronic polarizability α_e ($\times 10^{-24}$ cm^3)	5.290
Reflection losses R (%)	5.070
Polaron radius r_p (Å)	7.500
Inter ionic distance r_i (Å)	18.824
Field strength F ($\times 10^{14}$ cm^{-2})	5.300