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# Optical studies of $Sm^{3+}$ ions doped Zinc Alumino Bismuth Borate glasses

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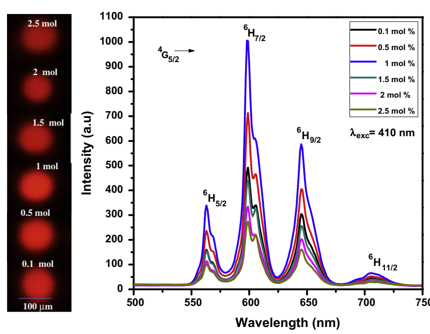
## HIGHLIGHTS

- ZnAlBiB glasses were prepared by conventional melt quenching technique.
- Emission data coupled with JO analysis were used to measure radiative properties.
- Quantum efficiency of ZnAlBiB glasses were measured from decay curves.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Zinc Alumino Bismuth Borate (ZnAlBiB) glasses doped with different concentrations of samarium ($Sm^{3+}$) ions were prepared by using melt quenching technique and characterized for their lasing potentialities in visible region by using the techniques such as optical absorption, emission and emission decay measurements. Radiative properties for various fluorescent levels of $Sm^{3+}$ ions were estimated from absorption spectral information using Judd–Ofelt (JO) analysis. The emission spectra and con-focal photoluminescence images obtained by 410 nm laser excitation demonstrates very distinct and intense orange–red emission for all the doped glasses. The suitable concentration of $Sm^{3+}$ ions in these glasses to act as an efficient lasing material has been discussed by measuring the emission cross-section and branching ratios for the emission transitions. The quantum efficiencies were also been estimated from emission decay measurements recorded for the $^4G_{5/2}$ level of $Sm^{3+}$ ions. From the measured emission cross-sections, branching ratios, strong photoluminescence features and CIE chromaticity coordinates, it was found that 1 mol% of $Sm^{3+}$ ions doped ZnAlBiB glasses are most suitable for the development of visible orange–red lasers.



## Introduction

In recent years, there has been an increasing interest to the lanthanide ions doped in different hosts to achieve favorable optical devices such as lasers, fiber amplifiers, light converters, sensors

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and hole burning high density memories [1,2]. The optical spectrum of lanthanide ion is closely related to the particular local symmetry of the environment occupied by this ion in solid matrices. In glasses, they usually in homogeneously broadened band due to site-to-site variations in the local field action on the ions [3]. Glasses doped with rare-earth ions are proving to be the best luminescent materials as they have high emission efficiencies. While the emission is originated from both 4f–4f as well as 4f-5d electronic transitions, the 4f–4f transitions gives sharp emission lines covering wide range of spectral region, from the ultraviolet (UV) to the infrared region (IR). These sharp emissions attracted potential applications in solid state lasers, optical fiber amplifiers and three dimensional display devices [4–6]. The emission quantum efficiencies of the rare-earth ions are strongly dependent on phonon energy of the host material and active ion concentration. In recent years, among other oxide based glasses, borate glasses have been the subject of interest due to their high transparency, low melting point, high thermal stability and capability of accommodating large concentrations of rare earth ions [7–9].

The structure of the borate glasses is the gathering of $BO_3$ triangles and $BO_4$ tetrahedral units to form well defined and stable borate groups such as di borate, tri borate and tetra borate, resulting into random three-dimensional network [10]. Because of these reasons borate glasses are the best choice for rare earth ion doping. However, borate glasses have large phonon energies due to the stretching vibrations of network-forming oxides, resulting into enhanced non-radiative processes there by reduction in the luminescence efficiency. Such high phonon energies possessed by the borate glasses can be conveniently reduced by adding heavy metal oxides (HMO) such as bismuth and lead oxides [11]. Furthermore, HMO containing glasses show extremely high radioactive resistance because of their high density and atomic number. Bismuth trioxide alone cannot be considered as network former due to small field strength of $Bi^{3+}$ ion [11]. Furthermore, introducing $Al_2O_3$ as network modifier in a glass improves the chemical stability, thermo-mechanical stability and other emission properties of the rare-earth doped glass [12]. Zinc oxide in a glass host can act as a network former/modifier and gives better chemical durability, low glass transition temperature and wider glass forming compositional range [13]. Hence, for the present work we have prepared a borate glass with the other important oxide based network modifiers containing $B^{3+}$, $Bi^{3+}$, $Zn^{2+}$ and $Al^{3+}$ ions.

In recent times, glasses containing $Sm^{3+}$ ions have stimulated extensive interest due to their potential application for high-density optical storage, under sea communication and color displays [14,15]. Additionally, the $Sm^{3+}$ ions exhibit broad emission bands due to $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2, 11/2) transitions in any host matrix. Moreover, the phonon energies of hosts are not so critical to the orange–red emission at ~600 nm, because of the large energy difference of $^4G_{5/2}$ meta-stable level to its next lower lying levels [16,17]. The large gap between the $^4G_{5/2}$ level and its sublevels permits the applications of $sm^{3+}$ ions in different glass hosts with large phonon energy. It is also well known that the intensities of emission bands of $Sm^{3+}$ ion in glasses depend on its concentration and glass composition [18]. In order to obtain optimum emission characteristics for device applications, the characteristic features of host as well as concentration dependent studies of $Sm^{3+}$ are essential.

The present work reports, the preparation and characterization of a new series of trivalent samarium doped Zinc Alumino Bismuth Borate (ZnAlBiB) glasses, by using the techniques such as XRD, FT-IR, optical absorption, luminescence and decay curve measurements. The present study mainly focus on absorption, steady-state and time-resolved emission measurements of $Sm^{3+}$ ions in ZnAlBiB glasses to select a good host material for solid state laser devices.

## Experimental

The glasses having composition $20ZnO - 10Al_2O_3 - (10 - x) Bi_2O_3 - 60B_2O_3 + xSm_2O_3$, ($x$ = 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 mol%) were prepared by using normal melt-quenching technique. The glasses were abbreviated as ZnAlBiBSm01, ZnAlBiBSm05, ZnAlBiBSm10, ZnAlBiBSm15, ZnAlBiBSm20, and ZnAlBiBSm25. Analytical reagents of ZnO, $Al_2O_3$, $Bi_2O_3$, $B_2O_3$, and $Sm_2O_3$ were used as starting materials to prepare the glasses. The reagents were fully mixed and about 10 g batches were taken in a crucible and were put in an electric furnace at a temperature of 1200 °C for 30 min. The melt was stirred frequently for homogeneous mixing of all the constituents. The glass samples were obtained by pouring and quenching the melt in-between two brass plates kept at room temperature (RT). Clear, bubble free and transparent glasses were obtained. Disk shaped samples were polished with different grades of emery powder. The densities and refractive indices were estimated by Archimedes' principle and Brewster angle technique respectively. The absorption spectra were obtained from a JASCO model V-670 UV–vis–NIR spectrophotometer from 800 to 1700 nm with a resolution of 0.1 nm. The photoluminescence (PL) emission and excitation spectra for all these glasses were recorded at room temperature using RF-5301 PC Spectrofluorophotometer. The emission from sample was coupled into a monochromator (Acton SP2300) coupled to CCD (charge coupled detector) through the appropriate lenses and filters. The high-resolution PL images were obtained from a modified 410 nm CW diode laser coupled con-focal microscope (Olympus, BX51) equipped with XY-piezo stage. Time-resolved PL measurements were recorded using an Edinburgh luminescence spectrometer (model F900) equipped with a microsecond xenon flash lamp as the source of excitation at 401 nm.

## Result and discussions

### *XRD spectral analysis*

In order to check the amorphous nature of the prepared glasses, the XRD spectral measurement were taken up for an undoped glass using XPERT-PRO diffractometer with Cu K$\alpha_1$ radiation ($\lambda$ = 1.5406 Å) in the 2$\theta$ angle range 5°–70° with step size 0.02° $s^{-1}$ and is shown in Fig. 1. The XRD spectrum shows a broad hump which is continuous in appearance. It is well known that, an amorphous material with short range order will always give a featureless broad hump. Hence the prepared ZnAlBiB glasses have amorphous nature.

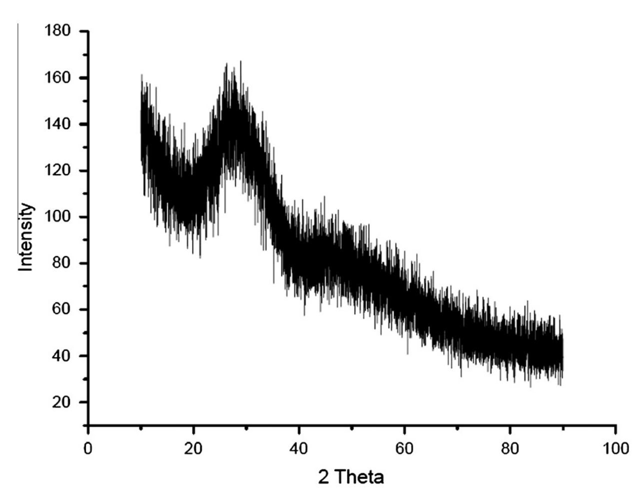


**Fig. 1.** XRD spectrum for an undoped ZnAlBiB Glass.