

STRUCTURAL AND LUMINESCENCE CHARACTERIZATION OF LITHIUM-BOROSULFOPHOSPHATE GLASSES CONTAINING DYSPROSIUM IONS

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ABSTRACT

Rare earth doped glasses have been a great deal of research interest due to their prominent applications in laser lighting technology. However, achieving highly efficient yellow light emission from these materials require the collective efforts of many researchers across the world. Hence, a series of high optical quality dysprosium doped lithium-borosulfophosphate glasses with chemical composition of $15\text{Li}_2\text{O}-30\text{B}_2\text{O}_3-15\text{SO}_3-(40-x)\text{P}_2\text{O}_5-x\text{Dy}_2\text{O}_3$ (where $x = 0.1, 0.3, 0.5, 0.7$ and 1.0 in mol%) were prepared by convectional melt quenching technique and characterized by X-Ray diffraction (XRD), Fourier Transform Infrared (FTIR) and Photoluminescence (PL) measurements. XRD pattern of the host glass confirms its amorphous nature while the results from FTIR spectra analysis indicates the presence of BO_3 , BO_4 , PO_4 and SO_4^{2-} groups in the host network structure. The photoluminescence spectral analysis revealed three emission bands at 494 nm, 585 nm and 673 nm attributed to the electronic transitions of $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$, respectively, under the excitation of 386 nm. Among all the prepared glass samples, 1.0 mol% Dy^{3+} contained glass sample exhibits an intense yellow emission at 585 nm which specifies its prospective suitability for yellow laser applications.

Keywords: Borosulfophosphate glasses, Dysprosium ions, Fourier transform infrared spectroscopy, Photoluminescence analysis

INTRODUCTION

Rare earth ions embedded in luminescent host matrices have become a new dawn in the field of advanced optical technology due to their prominent features such as easy preparation on large scale, huge variability in composition, shaping and doping flexibility of active ion concentrations (Linganna *et al.*, 2013). Owing to the unparalleled properties of these glassy materials, they have been used in diverse applications which include good laser host materials, lighting source materials, optical amplifiers, optical memories, optoelectronics and magneto-optical devices (Venkateswarlu and Rudramadevi, 2015; Vijayalakshmi *et al.*, 2014; Kiran and Kumar, 2013; Boonin *et al.*, 2016). However, to develop efficient and improved optical devices for the aforementioned applications, an appropriate selection of good host matrix is prerequisite. Recently, passionate efforts have been focused on the search of the host materials with low phonon energies, crystal-field effects and influence of local environment on the trivalent rare-earth ion, in order to reduce the multiphonon non-radiative relaxation and thus enhance the emission cross section of fluorescent levels of trivalent rare earth ion (Linganna

and Jayasankar, 2012).

Glass system with two network formers has proven to be most favourable and special candidate host material for rare earth ion because of their unified characteristics such as low dispersion, good transparency, low refractive indices from the ultraviolet to near-infrared regions, good rare earth ion solubility and better chemical stability and durability compared to many other hosts (Hua *et al.*, 2012). Among the various network formers, fusion of two strong glass formers borate (B_2O_3) and phosphate (P_2O_5) along with modifiers (alkaline oxides or sulphate) have received a considerable attention due to their promising applications in optical industry. The basic network forming units of these glasses are the trigonal BO_3 and tetrahedral PO_4 groups of the pure borate and phosphate glass respectively linked through covalent bridging oxygens (Wong *et al.*, 2014; Reddy *et al.*, 2016). Addition of modifiers to borate and phosphate glasses alters their properties and hence overcoming their individual limitations. In borate network, addition of network modifier in certain compositional ranges increases the degree of polymerization converting boron coordinate from BO_3 to BO_4 . On the contrary, introduction of modifier into phosphate network leads to depolymerisation by breaking up the P-O-P bridges and creating non-bridging oxygens (Karabulut *et al.*, 2015).

In the recent years, special interest has been devoted to Dy^{3+} -doped host materials among the different rare earth ions. Depending on the host material, Dy^{3+} is one of the best luminescent ion which emits an intense blue (470-500 nm) and yellow (570-600 nm) and a moderate red (620-780 nm) emission in the visible light spectrum. The hypersensitive yellow emission attributed to the transition $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ in Dy^{3+} -doped materials is prospective for the development of solid state lighting devices including automobile brake lights, traffic signals and all manners of architectural spotlights (Narukawa, 2004). In view of the significant promising applications of glass host materials containing dysprosium ions, the present work has been undertaken to explore the synthesis and characterizations of Dy^{3+} -doped lithium borosulfophosphate glasses. The structural features and luminescence properties of these glasses are clearly demonstrated in this study for their potential utility in white LEDs and laser applications.

EXPERIMENTAL PROCEDURES

Glass samples Preparation

Dy^{3+} doped lithium-borosulfophosphate glasses with chemical compositions $15\text{Li}_2\text{O}-30\text{B}_2\text{O}_3-15\text{SO}_3-(40-x)\text{P}_2\text{O}_5-x\text{Dy}_2\text{O}_3$ (where $x = 0.1, 0.3, 0.5, 0.7$ and 1.0 in mol %) were prepared using a

convictional melt quenching method. The starting materials used are lithium carbonate (Li_2CO_3), boric acid (H_3BO_3), sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4) and dysprosium oxide (Dy_2O_3) of analytical grade (sigma Aldrich) with 99.99% high purity. The corresponding masses of the starting materials in batches (20g) were weighed via analytical balance and mixed thoroughly in porcelain crucible. The homogeneous mixture of the samples were placed in an electrical furnace and preheated at 300°C for 45 min to facilitate the vaporisation of water (H_2O) and carbon dioxide (CO_2) and melted by increasing the furnace temperature to 950°C with heating rate at $25^\circ\text{C}/\text{min}$ and maintained for 1hr until the mixture became molten and homogeneous. The resultant bubble-free molten was poured on a stainless steel plate in another furnace and subsequently annealed at 350°C for 3hr in order to remove strain. Upon completing the annealing process, the furnace is switched off and gradually cooled down to room temperature.

Glass samples Characterization

The amorphous nature of the prepared glass samples are confirmed via Siemens X-Ray Diffractometer D5000 which uses $\text{CuK}\alpha$ radiation ($\lambda=1.54\text{\AA}$) operating at 40kV and 30mA under normal operating conditions with ranges of 2θ from 10° to 80° . The structural features of the glasses were analysed using FTIR measurements. The measurements were carried out by KBr pellets method. FTIR spectra of glasses were recorded by Perin-Elmer spectrum one FTIR spectrometer in the range of $4000\text{--}400\text{cm}^{-1}$ at room temperature using 100 scans at 4cm^{-1} resolution. In order to investigate the luminescence properties of the prepared glasses, the samples were polished using emery paper to ensure smooth surfaces. The photoluminescence properties were measured by Perkin Elmer LS55 luminescence spectrophotometer and the corresponding excitation and emission spectra of the samples were examine at 585 nm emission 386 nm and excitation wavelength.

RESULTS AND DISCUSSION

X-ray Diffraction Analysis

To verify the noncrystallinity of the prepared samples, XRD was performed on the glass samples. The XRD pattern of Dy^{3+} doped lithium-borosulfophosphate glasses are illustrated in Figure 1. It is observed from Figure 1 that each glass sample contains broad hump at low angles without any crystalline sharp peaks which confirms the amorphous nature of the prepared samples.

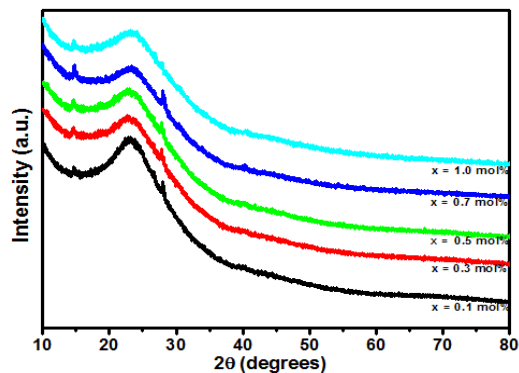


Figure 1. XRD pattern of $15\text{Li}_2\text{O}\text{--}30\text{B}_2\text{O}_3\text{--}15\text{SO}_3\text{--}(40\text{--}x)\text{P}_2\text{O}_5$ glasses doped with different concentration (in mol%) of Dy_2O_3 ions.

Infrared Spectra Analysis

Figure 2 shows the FTIR spectra of lithium-borosulfophosphate glasses activated with different concentrations of Dy^{3+} ions. The studied based glasses consist of two network forming oxides B_2O_3 and P_2O_5 and two network modifiers Li_2O and SO_3 . The impact of Dy^{3+} ions on the network structure of the based glasses has been examined. The FTIR spectra analysis revealed that as Dy^{3+} concentrations increases from 0.1 to 1.0 mol%, the band position do not show any significant change. The summary of the observed band positions and their corresponding band assignments are listed in Table 1. The well-defined band observed at $512\text{--}529\text{cm}^{-1}$ is attributed to the bending vibration of O-P-O in Q^1 groups (Karabulut *et al.*, 2015; Srinivasulu *et al.*, 2012) while the shoulder around $747\text{--}764\text{cm}^{-1}$ is a characteristic of Q^1 groups as it arises from the symmetric stretching vibration of P-O-P and the bending vibration of B-O-B linkages in the borate network (Saitoh *et al.*, 2015; Thieme *et al.*, 2015). The observed band at $910\text{--}960\text{cm}^{-1}$ can be ascribed to the symmetric stretching vibration of the PO_4^{3-} tetrahedra. This region is also consisting of bands due to pyrophosphate groups $\text{PO}_4^{4-}/\text{BO}_4$ units (Kumar *et al.*, 2012a). Another band located around $1057\text{--}1074\text{cm}^{-1}$ is assigned to asymmetric stretching vibration of P-O-P (Suresh *et al.*, 2016; Qian *et al.*, 2013). In the spectral region, $1179\text{--}1203\text{cm}^{-1}$ observed vibration bands corresponds to bending and asymmetric modes of SO_4^{2-} group (Kumar *et al.*, 2012b; Dalhatu *et al.*, 2016). The band observed around $1447\text{--}1464\text{cm}^{-1}$ is due to the symmetric stretching relaxation vibration of B-O in BO_3 units from metaborate, pyroborate and orthoborate groups. The strong band located in the range of $1642\text{--}1651\text{cm}^{-1}$ can be ascribed to the stretching of O-H, P-O-H and B-O-H groups in different structural site (Srinivasulu *et al.*, 2012) and the peaks at $2261\text{--}2423\text{cm}^{-1}$ indicates the presence of hydrogen bonding. The relatively weak bands from $3245\text{--}3659\text{cm}^{-1}$ are attributed to the fundamental stretching vibration of O-H groups or water groups (Deepa *et al.*, 2016). The appearance of water group bands look strange as the sample under investigation does not contain H_2O as unit in the network. However, the bands accounted for water molecule in the spectra could be as a result of the hygroscopic nature of the glass powder sample. Furthermore, powder potassium bromide (KBr) can absorb moisture and remained in the disc surface during sample preparation by pellet method for FTIR analysis.

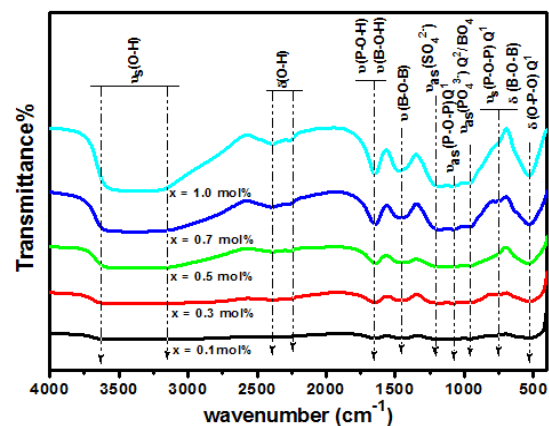


Figure 2. FTIR spectra of $15\text{Li}_2\text{O}\text{--}30\text{B}_2\text{O}_3\text{--}15\text{SO}_3\text{--}(40\text{--}x)\text{P}_2\text{O}_5$ glasses doped with different concentration (in mol%) of Dy_2O_3 ions.

Table 1. Summary of the Infrared band assignments for lithium-borosulfophosphate glasses doped with different concentrations (in mol %) of Dy₂O₃ ions.

Observed values (cm ⁻¹)					Band Assignments
x=0.1	0.3	0.5	0.7	1.0	
512	520	520	529	520	O-P-O bending mode in Q ¹
747	756	747	740	764	P-O-P symmetric vibration/B-O-B bending vibration
927	910	943	951	960	Asymmetric stretching of (PO ₄ ³⁻) in Q ² groups / bending vibration in BO ₄ units
1057	1065	1057	1065	1074	Asymmetric stretching of P-O-P in Q ¹ groups
1179	1188	1203	1195	1195	Asymmetric stretching mode of SO ₄ ²⁻ units
1447	1447	1464	1455	1455	Stretching vibration mode of B-O-B in BO ₃ units
1651	1651	1642	1651	1651	Stretching vibration mode of P-O-H/B-O-B groups
2285	2261	2269	2261	2261	Deformation mode of O-H groups
2414	2407	2414	2423	2414	
-	-	-	-	3245	Stretching vibration mode of O-H groups
3650	3659	3643	3618	3623	

Luminescence Spectra Analysis

Figure 3 and 4 shows the excitation and emission spectra of 15Li₂O-30B₂O₃-15SO₃-(40-x)P₂O₅ glasses doped with different concentrations of Dy³⁺ ions. The excitation spectra was monitored at the emission wavelength of 585 nm in the range of 300-500 nm and the spectra reveals a total of seven 4f-4f transition bands at 320 nm, 346 nm, 362 nm, 386 nm, 422 nm, 450 nm and 471 nm attributed to transitions originating from the ⁶H_{15/2} ground state to ⁶P_{3/2}, ⁶P_{7/2}, ⁶P_{5/2}, ⁴K_{17/2}, ⁴G_{11/2}, ⁴H_{15/2} and ⁴F_{9/2} of Dy³⁺ ions. Among all the transitions, ⁶H_{15/2}→⁴K_{17/2} transition at 386 nm is more prominent and is therefore used for the measurement of emission spectra.

The visible emission spectra under excitation of 386 nm in the region 480-700 nm consists of two intense bands at 494 nm (blue) and 585 nm (yellow) and with a very weak band at 675 nm corresponding to the transitions ⁴F_{9/2}→⁶H_{15/2}, ⁴F_{9/2}→⁶H_{13/2} and ⁴F_{9/2}→⁶H_{11/2}, respectively. Higher emission wavelength was observed in this present study which is in agreement with the previous investigations on Dy³⁺-doped glasses reported elsewhere (Zhang *et al.*, 2012). The yellow emission due to ⁴F_{9/2}→⁶H_{13/2} transition is electric dipole transition (hypersensitive) which obeys the selection rule of ΔL = ±2 and ΔJ = ±2. This transition is highly influenced by the surrounding environment and its intensity depends on the host. Meanwhile, the blue emission at 494 nm is a magnetic dipole transition which follows the selection rule ΔJ = 0, ±1 and 0 ↔ 0 is forbidden transition. This magnetic dipole transition is less sensitive to the glass host environment compared to the electric dipole transition. However, the weak red emission at 675 nm is an electric dipole transition. The emission intensities for each glass sample increase with increase in Dy³⁺ ions concentrations from 0.1 to 1.0 mol%.

Figure 5 represents the partial energy level diagram of Dy³⁺ ions which describes the excitations, emissions and other processes such as radiative and non-radiative energy transfer. First, the Dy³⁺ ions are excited by 386 nm radiation from the ground state ⁶H_{15/2} to most excited level ⁴K_{17/2} which then decay non-radiatively to ⁴F_{9/2} states before making ⁴F_{9/2}→⁶H_{15/2}, ⁴F_{9/2}→⁶H_{13/2} and ⁴F_{9/2}→⁶H_{11/2} downward transition radiatively giving blue, yellow and red emissions, respectively.

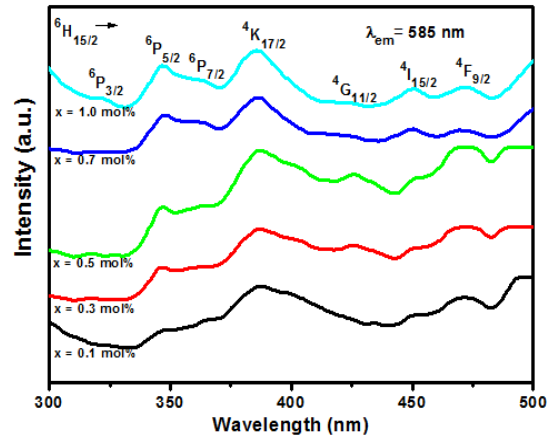


Figure 3. Excitation of 15Li₂O-30B₂O₃-15SO₃-(40-x)P₂O₅ glasses doped with different (in mol%) of Dy₂O₃ ions.

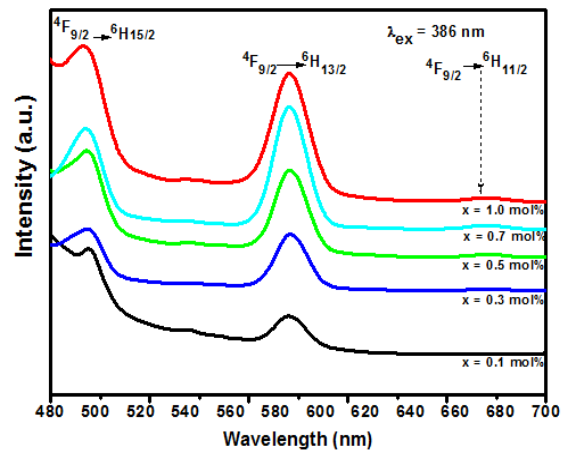


Figure 4. Emission spectra of 15Li₂O-30B₂O₃-15SO₃-(40-x)P₂O₅ glasses doped with different concentration (in mol%) of Dy₂O₃ ions.

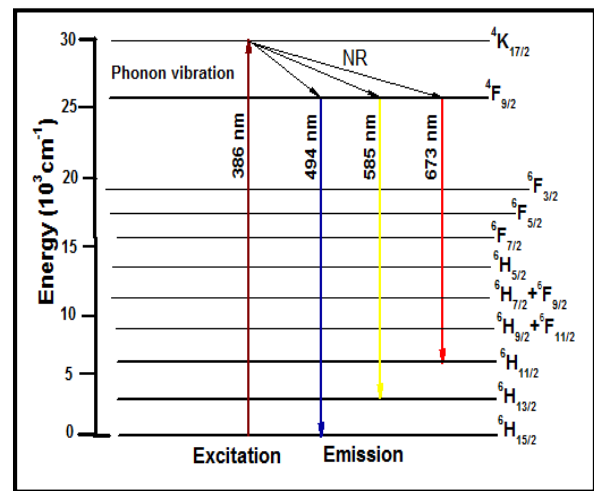


Figure 5. The partial energy level diagram of Dy³⁺ ions showing the possible emission transitions and non-radiative (NR) decay in 15Li₂O-30B₂O₃-15SO₃-(40-x)P₂O₅ glasses doped with different concentration (in mol%) of Dy₂O₃ ions.

Conclusion

A series of high optical transparent lithium-borosulfophosphate glasses doped with Dy³⁺ ions have been prepared by convectional melt quenching method and their structural and luminescence properties were studied. The X-ray diffraction pattern strongly confirmed the amorphous nature of the prepared glasses whereas the presence of BO₃, BO₄, PO₄ and SO₄²⁻ groups from the interaction between borate, sulfate and phosphate units were elucidated by FTIR spectra analysis. Upon excitation with 386 nm, a remarkable yellow emission intensities at 585 nm from photoluminescence spectra analysis increases proportionally with Dy³⁺ ions concentrations without any account for quenching phenomenon even at higher concentration up to 1.0 mol%. Thus, these prepared glasses could be suggested as promising luminescent host materials with potential ability for yellow laser applications.

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