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Composition dependent structural and optical properties of Sm^{3+} doped boro-tellurite glasses

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ABSTRACT

Boro-tellurite glasses with the composition $(69–x)H_3BO_3+xTeO_2+15MgCO_3+15K_2CO_3+1Sm_2O_3$ (where $x=0$, 10, 20, 30 and 40 wt%) doped with trivalent samarium have been prepared and their structural and spectroscopic behavior were studied and reported. The FTIR spectra reveal the presence of BO_3 and BO_4 non-bridging oxygen as well as strong OH^- bonds in the prepared glasses. Through the optical absorption spectra, Judd–Ofelt intensity parameters (Ω_λ, $\lambda=2$, 4 and 6) have been evaluated and the same is in turn used to predict radiative properties such as radiative transition probability (A), stimulated emission cross-section (σ_P^E) and branching ratios (β_R) for the excited levels of Sm^{3+} ions corresponding to $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$, $^4G_{5/2}\rightarrow{}^6H_{9/2}$ and $^4G_{5/2}\rightarrow{}^6H_{11/2}$ transitions. Structural and spectral dependence of the Sm^{3+} ions due to the compositional changes have been examined and reported. The lifetime of the $^4G_{5/2}$ level is found to be non-exponential for all the prepared glasses indicating a cross-relaxation among the Sm^{3+} ions. The structural and spectroscopic results corresponding to compositional changes have been compared with the similar studies and reported.

1. Introduction

The optical studies of rare earth (RE) doped glasses draw much attention due to their wide applications in areas such as solid state lasers, solar concentrators, optical detectors, waveguide lasers, optical fibers, sensors, display monitor, optical data storage and undersea optical communications [1–3]. Of all the glasses, borate glass has importance due to its special physical properties like high transparency, low melting point, high thermal stability and good rare earth ions solubility [3]. Among the oxide glasses, tellurite glasses possess encouraging properties such as good mechanical strength, chemical durability, low process temperature, high dielectric constant and excellent transmission in the visible and IR wavelength regions. They also have lower phonon energy and larger refractive index, compared to other oxide glasses [4]. The origin of the extraordinary nonlinear optical properties of TeO_2 based glasses is attributed to the high hyper polarity of a lone electron pair related to the 5s orbital of the tellurium atom [5]. The tellurite based glasses possess weaker Te–O bonds, which can be easily broken and this is advantageous for accommodating rare earth ions and heavy metal oxides [6]. The pure TeO_2 is a conditional glass former and requires fast quenching to form glass. The presence of TeO_2 in the alkali borate glass matrix decreases its hygroscopic nature, improves the glass quality and enhances the IR transmission [7]. Absorption and emission analysis of lithium boro-tellurite glasses were studied and reported by Sooraj Hussain et al. [8]. Rada et al. [9] reported the structure of the TeO_2–B_2O_3 glasses through IR and DFT studies. Jamalaiah et al. [10] explored and reported that Sm^{3+} ion with $4f^5$ electronic configuration exhibit a strong orange red fluorescence in the visible region. Supriya and Buddhudu [11] reported the luminescence studies of Sm^{3+}, Dy^{3+}:TeO_2–B_2O_3–P_2O_5–Li_2O glasses.

This paper reports the structural and optical studies on Sm^{3+} doped boro-tellurite glasses. Through the XRD and FTIR measurements the structure of boro-tellurite glasses have been studied and reported. Through the absorption, luminescence and lifetime measurements, optical behavior of the prepared glasses have been discussed and compared with the similar studies. The Judd–Ofelt theory has been used to explore the radiative properties of the Sm^{3+} doped boro-tellurite glasses and the results were compared with similar reported systems.

2. Experimental

Sm^{3+} doped boro-tellurite (BnTS, where n refers 0, 1, 2, 3 and 4) glasses were prepared by the following conventional melt quenching technique. The chemicals used are H_3BO_3, TeO_2, $MgCO_3$, K_2CO_3 and Sm_2O_3 of high purity (99.99%) analytical grade.

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The batch composition (in wt%) of the Sm^{3+} doped boro-tellurite glasses and their codes are as follows:

$69B_2O_3+0TeO_2+15MgO+15K_2O+1Sm_2O_3$
———————————— B0TS

$59B_2O_3+10TeO_2+15MgO+15K_2O+1Sm_2O_3$
————————————B1TS

$49B_2O_3+20TeO_2+15MgO+15K_2O+1Sm_2O_3$
————————————B2TS

$39B_2O_3+30TeO_2+15MgO+15K_2O+1Sm_2O_3$
————————————B3TS

$29B_2O_3+40TeO_2+15MgO+15K_2O+1Sm_2O_3$
————————————B4TS

The selected composition of about 20 gm was thoroughly mixed and ground in an agate mortar to obtain homogeneous mixture. The mixture is taken into a porcelain crucible and heated at 850 °C in an electrical furnace for 45 min. The melt was poured on to a preheated brass plate and pressed by another brass plate to obtain uniform thickness of about 1.5 mm. In order to remove the strain and improve the mechanical strength, the glass samples were annealed for 7 h in another furnace maintained at 350 °C and allowed to reach the room temperature. The prepared glasses were well polished on both sides to obtain optical quality glasses.

The amorphous nature of the prepared glasses was confirmed through X-ray diffraction studies using JEOL 8530C X-ray diffractometer employing CuK_α radiation. The FTIR spectra of the glasses were recorded using Perkin-Elmer Paragon 500 spectrometer with a spectral resolution of 4 cm^{-1} following the KBr pellet technique. Optical absorption spectra were recorded in the wavelength region 350–1750 nm using CARY 500 spectrophotometer with a spectral resolution of $\pm$0.1 nm. The luminescence spectra of the prepared glasses were measured between the wavelength 500–750 nm using Perkin-Elmer LS55 spectrometer with a spectral resolution of $\pm$1.0 nm. The lifetime measurements were carried out using a Sciencetech modular spectrophotometer using a xenon flash lamp as an excitation source. All these measurements were carried out at room temperature only.

The refractive indices of the prepared glasses were measured through Abbe refractometer at sodium wavelength using mono bromonaphthalin as a contact liquid. The density of the prepared glasses was measured following Archimedes method using xylene as an immersion liquid. The physical properties of the Sm^{3+} doped boro-tellurite glasses are presented in Table 1.

3. Results and discussion

3.1. XRD and FTIR spectral analysis

The XRD pattern of the Sm^{3+}:B0TS glass shown in Fig. 1 exhibits broad scattering at lower angles, which is the characteristic long range structural disorder and confirms the amorphous nature of the prepared glasses.

The FTIR spectra of the Sm^{3+} doped boro-tellurite glasses shown in Fig. 2 contain several peaks broad or moderate in bandwidth specifying the local structure and their peak assignments are shown in Table 2. The bands found in the region 3375–3560 cm^{-1} belong to hydroxyl groups due to OH stretching vibrations. The peaks observed between 2800 and 2900 cm^{-1} are due to the characteristic of hydrogen bond in the glasses. The boron atoms are connected to the three oxygen atoms (BO_3 units) and the band around 1658 cm^{-1} reveal the stretching vibration of borate triangles [12–14]. All the spectra exhibit peaks around 1463 cm^{-1}, which are due to $B–O^-$ vibrations attached to the large segments of borate network. The bands around 1020 cm^{-1} is attributed to B–O bond stretching vibrations in BO_4 tetrahedra from tri-, tetra- and penta-borate groups [9,14,15]. The band around 839 cm^{-1} is attributed to B–O bond stretching vibration in BO_4 tetrahedra from diborate groups. The band around 717 cm^{-1} is attributed to Te–O bending vibration in TeO_3 and TeO_6 units. The peak positions around 450 cm^{-1} reveal the Te–O–Te or O–Te–O linkage bending vibrations [16,17] and all these assignments are in good agreement with the reported literature [9,14,16].

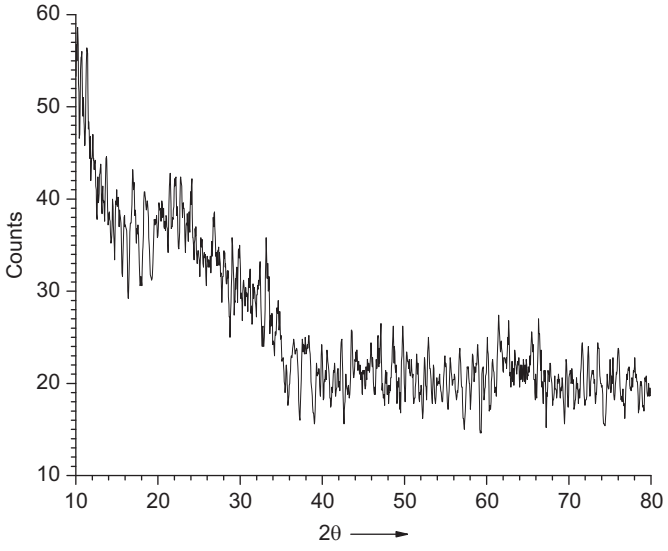

Fig. 1. XRD Pattern of the Sm^{3+}:B0TS glass.

Table 1
Physical properties of the Sm^{3+}-doped boro-tellurite glasses.

Sl. No.	Physical properties	B0TS	B1TS	B2TS	B3TS	B4TS
1	Density, ρ (g/cm^3)	2.93	3.42	4.17	4.77	5.59
2	Sample thickness (mm)	1.50	1.58	1.52	1.54	1.55
3	Refractive index, n_d (589.3 nm)	1.594	1.626	1.682	1.701	1.725
4	Rare earth ion concentration, N (10^{20} ions/cm^3)	4.243	4.431	4.890	5.107	5.506
5	Polaron radius, r_p (A°)	5.359	5.284	5.114	5.040	4.916
6	Inter ionic distance, r_i (A°)	13.302	13.116	12.692	12.510	12.200
7	Field strength, F (10^{14} cm^{-2})	1.695	1.743	1.862	1.916	2.015
8	Electronic polarizability, α_e ($10-^{22}$ cm^3)	1.909	1.908	2.041	1.809	1.722
9	Molar refractivity, R_m (cm^3)	8.376	7.726	6.664	5.887	5.201
10	Dielectric constant (ε)	2.541	2.644	2.829	2.893	2.976
11	Reflection losses, R (%)	5.244	5.683	6.466	6.736	7.079