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Characterization of Fe^{3+} doped mixed alkali zinc borate glasses — Physical and spectroscopic investigations

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ABSTRACT

The glasses of $19.9ZnO + xLi_2O + (30-x)Na_2O + 50B_2O_3$ $(5 \le x \le 25)$ (ZLNB) doped with 0.1 mol% of paramagnetic Fe_2O_3 impurity are prepared by melt quench technique. Physical parameters of all the glasses are evaluated and they reveal a non-linear behavior with respect to the composition. Powder XRD pattern has not revealed any crystalline peak which indicates its amorphous nature. The optical band gap and Urbach energies exhibited the mixed alkali effect. All the prepared glass samples are found to be strong and stable in structure with low values of Urbach energy which lie between 0.010 and 0.022 eV. Electron paramagnetic resonance exhibited three resonance signals around g values at 2.06, 4.24 and 8.34 in the all Fe^{3+} doped glasses. The optical absorption spectrum of the samples exhibited three bands which are characteristic of Fe^{3+} in distorted octahedral symmetry. The crystal field parameter (Dq) and Racah inter electronic repulsion parameters (B, C) are evaluated. The FT-IR spectra of Fe^{3+} doped glasses exhibited characteristic vibrations of BO_3 and BO_4 units.

1. Introduction

Oxide glasses formed with transition metal ions have received significant attention owing to their interesting optical applications. All the properties of glasses which are strongly affected by long-range motions of ions, show large deviations from a simple additive behavior upon mixing of two different types of mobile ions; this phenomenon is known as mixed alkali effect (MAE) [1]. While the mixed alkali effect might be of limited value for technological application, it is important in understanding the general problem of ionic transport in glasses. Borate glasses are particularly interesting model systems as they exhibit a variety of structural changes with alkali content. ZnO enters in the glass structure in the form of both network former and network modifier. Since, zinc containing glasses have low melting point, they have been used as good sintering agents [2–5].

Though the spectroscopic investigations are meager, they are important and useful to gain insight into the microscopic mechanism responsible for the effect. Recent progress in understanding the mixed alkali effect has been initiated by the development of the dynamic structure model [6]. For alkali borate glasses, the abrupt property changes are observed near 15–20 mol% modified oxide [7]. This peculiar behavior is referred to as 'borate anomaly'. On the other hand, the spectroscopic investigations such as EPR and optical absorption techniques are valuable to gain insight into the microscopic origin of the MAE.

Glasses containing Fe_2O_3 are used in electrochemical, electronic and electro-optic devices [8,9]. The stability and semiconductor properties of Fe_2O_3 allow it to be used as a photocatalyst [9]. At low concentrations, the ions act as modifiers similar to the alkali metals or alkaline earths [10]. EPR spectra of Fe^{3+} in various glasses have been extensively studied. It is found that trivalent iron ions can take two different coordination sites, i.e., tetrahedral [11,12] or octahedral [13,14] in glasses. Recently effects of transition metal ions doped alkali zinc borate glasses are reported and they exhibit the mixed alkali effect [15–22]. No EPR study of Fe^{3+} in alkali zinc borate glasses have been reported so far, the aim of the present study is to observe the physical and structural behavior of the new quaternary system of trivalent ion, Fe^{3+} doped $19.9\ ZnO + xLi_2O + (30-x)Na_2O + 50B_2O_3$ $(5 \le x \le 25)$ (hereafter referred as ZLNB) glasses by using spectroscopic techniques and to correlate their properties.

2. Experimental

2.1. Preparation

Glass samples are prepared by the melt quench technique. 0.1 mol% of Fe^{3+} doped mixed alkali zinc borate glasses is prepared by using analar grade chemicals of ZnO, Li_2CO_3, Na_2CO_3, B_2O_3 and Fe_2O_3 as

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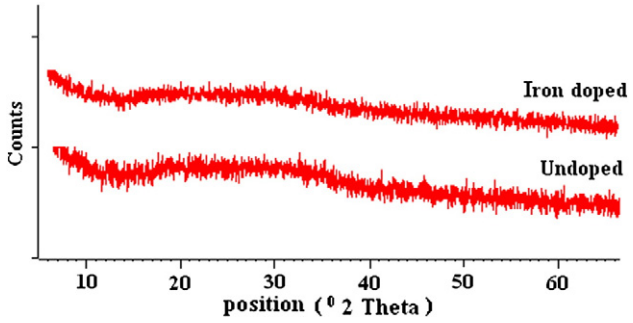

Fig. 1. Powder X-ray diffraction patterns of Fe^{3+} doped and undoped ZLNB glasses.

starting materials with 99.9% of purity. Appropriate amounts of these starting materials are weighed and thoroughly mixed and ground in an agate mortar and pestle for about an hour. The batch mixture was transferred to a silica crucible and it is sintered at 750 K and melted in an electric furnace in a silica crucible around 1250 K for nearly 1 h. The silica crucible containing the melt was occasionally swirled inside the furnace for a few minutes to homogenize the glass melt. The melt is then quenched at room temperature in air to form a glass. The glass samples are quickly transferred to another furnace previously kept at 700 K, and annealed at this temperature for 1 h to reduce thermal stresses generated by rapid cooling. All glass samples are disk-shaped (about 1 cm diameter and thickness of 1–2 mm). The opposite faces of the samples are ground and polished with different grades of emery powder for UV–Visible spectroscopic measurements. The glass compositions are taken as $19.9ZnO + xLi_2O + (30 - x)\ Na_2O + 50B_2O_3 + 0.1\ Fe_2O_3$ ($5 \le x \le 25$ or $x = 5$, 10, 15, 20, 25 mol%), hereafter named as ZLNB glass systems prepared at the temperatures 1175, 1188, 1213, 1223 and 1223 K respectively.

2.2. Characterization

The densities (ρ) of all glass samples are measured by using Archimedes method with xylene as an immersion fluid. Refractive indices of prepared glasses are measured by using Atago Abbe's refractometer. Bruker FT-IR Spectrophotometer is used for recording the FT-IR spectra of the prepared samples in the region of 500–2000 cm^{-1}. X-ray diffraction patterns of powdered glass samples are recorded on PANalytical Xpert Pro diffractometer with Cu K_α wavelength of 1.5406 Å. EPR spectra of powder samples are recorded at room temperature on JEOL JES TE100 ESR spectrometer at X-band frequency with 100 kHz field modulation. The optical absorption spectra of polished glass samples are recorded on JASCO V-670 spectrophotometer in the region of 200–1400 nm.

3. Results

3.1. Powder X-ray diffraction studies

The X-ray diffraction patterns do not contain any sharp peaks which is a sign of amorphous material. All the prepared glass samples confirm the glassy nature. Fig. 1 shows the X-ray diffraction patterns of undoped and iron doped glasses.

3.2. Physical properties

The calculated values of densities and refractive indices of the prepared Fe^{3+} doped ZLNB glass systems are given in Table 1 along with some other physical parameters. The error in density measurements and refractive indices are estimated to be ± 0.004 g/cm^3 and ± 0.0001. The effect of Li_2O content on density and refractive index of Fe^{3+} doped ZLNB glass systems is shown in Fig. 2. For Fe^{3+} doped ZLNB glasses, ionic concentration and electronic polarizability are correlated with respect to Li_2O content and depicted in Fig. 3.

3.3. FT-IR studies

FT-IR spectra of Fe^{3+} doped $(19.9ZnO + xLi_2O + (30 - x)\ Na_2O + 50B_2O_3, (5 \le x \le 25))$ glasses are shown in Fig. 4. B–O–B bending vibrations are observed at 551 and 553 cm^{-1}. B–O symmetric stretching vibrations of BO_4 units are observed in the region 1042–1085 cm^{-1}. B–O stretching vibrations of trigonal BO_3 units are observed in the region 1270–1500 cm^{-1}.The obtained absorption bands and their assignments are summarized in Table 2.

3.4. Optical absorption studies

The optical absorption spectra of Fe^{3+} doped ZLNB glass systems are shown in Fig. 5. The spectrum exhibits three bands around 450, 519 and 686 nm that represent the characteristic absorption of

Table 1
Physical properties of $19.9ZnO + xLi_2O + (30 - x)Na_2O + 50B_2O_3 + 0.1Fe_2O_3$ ($5 \le x \le 25$) glass systems at room temperature.

Sl. No	physical parameter (units)	Glass code				
		ZLNB1 X = 5	ZLNB2 X = 10	ZLNB3 X = 15	ZLNB4 X = 20	ZLNB5 X = 25
1.	Average molecular weight (g/mol)	81.3562	79.7514	78.1465	76.5419	74.9365
2.	Density (ρ) (g/cm^3) (± 0.004)	2.6779	2.8217	2.7193	2.8443	2.8247
3.	Refractive index (μ) (± 0.0001)	1.6552	1.6551	1.6556	1.6555	1.6554
4.	Optical dielectric Constant (ε)	2.7397	2.7393	2.7410	2.7406	2.7403
5.	Reflection loss	0.0608	0.0608	0.0609	0.0609	0.0609
6.	Molar refractivity (R_M) (cm^{-3}) (± 0.005)	11.1510	10.3728	10.5532	9.8810	9.7397
7.	Iron ion concentration (N) (10^{22} ions/cm^3)(± 0.005)	0.3165	0.3403	0.3346	0.3574	0.3625
8.	Electronic polarizability (α_e) (10^{-24} ions/cm^3) (± 0.005)	27.6921	25.7593	26.2072	24.5381	24.1872
9.	Inter-ionic distance (r_i) (Å) (± 0.005)	6.8103	6.6483	6.6852	6.5405	6.5094
10.	Polaron radius (r_p) (Å) (± 0.005)	2.7440	2.6788	2.6936	2.6353	2.6228