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Abstract:

Glass samples belonging to the general chemical formula $60B_2O_3$ -(40-x)Na₂O-xMnO₂ with x=5, 10,15, 20, and 25 mol % are prepared by melt quench method. Characterization of the system was carried out using XRD, SEM and FTIR. The structural changes with composition of the glasses have been studied by FT-IR spectroscopy. FT-IR spectra analysis indicates that MnO_2 is preferentially incorporated into the borate network. Amorphous nature of the system was confirmed by XRD and SEM is used to study the morphology of the glass samples.

Kev Words: Borate glasses, XRD, SEM & FTIR

1. Introduction:

Glasses are studied nowadays mainly because of the large applications that they period. B₂O₃ is one of the most common glass former and is present in almost all commercially important glasses. It is often used as a dielectric and insulating materials and because of the occurrence of boron anomaly [1] B₂O₃ can be considered to posses highest glass formation tendency because molten B₂O₃ does not crystalline by itself even when cooled at a slowest rate. The size of B3+ ion is very small and it can fit into the trigonal void created by three oxide ions in mutual contact, forming a BO₃ units. BO₃ units are the primary building blocks in all borate glasses [2]. Alkali borate glass systems like sodium borate glasses are good candidates for ion conduction and suitable for the fabrication of solid state batteries. The role of Na₂O in the B_2O_3 network is to modify the host structure through the transformation of the structural units of the borate network. There have been several studies, which deal with the structure of sodium borate glasses [3]. The study of oxide glasses doped with Transition Metal Ions (TMI) has received considerable attention in nowadays due to their attractive combination of physical and chemical properties. Continued effort for the development of new glassy materials either by doping or by adding TMI, and the study of their novel properties is highly relevant due to their potential applications in various technological fields [4, 5] Glasses doped with transition metal ions like Cu2+ and Mn2+ have attracted considerable interest because of their memory and photo conducting properties [6] The influence of manganese ions on optical, magnetic and electrical properties of various inorganic glass systems has been under extensive investigation in recent years [7]. The borate glasses are very often investigated by a lot of methods because they are relatively easy to obtain and moreover because in their structure appear a large variety of structural units over a wide range of modifier concentration [8].

2. Experimental:

The glass samples having the general chemical formula $60B_2O_3$ (40-x)Na₂O-xMnO₂ with x=5, 10, 15, 20 and 25 mol% were prepared by rapid melt quench method using the starting materials as B_2O_3 , Na₂O and MnO₂ of reagent purity grade. The required amount in mol% of different chemicals in powder form were weighed using single pan balance having an accuracy of ± 0.001 g and mixed in a mortar. The mixtures corresponding to the desired compositions were melted in porcelain crucible in a muffle furnace. Melting is carried out under controlled conditions at temperature from 750 to 900°C for all the compositions. The molten sample is cast into a copper mould having dimensions of 10mm diameter and 6mm thickness. Then the glass samples are annealed for two hours to avoid the mechanical strain developed during the quenching process. The samples prepared are chemically stable and non-hygroscopic. The samples are polished and the surfaces are made perfectly plane and smoothened by diamond disc and diamond powder. The nominal composition of BNM glass samples are given in Table 1.

Snooimon	Nominal Composition in Mol%	Domonka
Specifien	B_2O_3 -Na ₂ O-MnO ₂	Kemarks
BNM1	60-35-05	P.O. constant
BNM2	60-30-10	B_2O_3 constant,
BNM3	60-25-15	and increase in
BNM4	60-20-20	MnO mol%
BNM5	60-15-25	10170 million

Table 1: Nomenclature composition of glass samples

3. Results and Discussion:

3.1 XRD Analysis:

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Figure 1: XRD spectrum of BNM1, BNM5 glass samples

Fig. 3.1(a) and Fig. 3.2(b) show the X-ray Diffraction pattern (XRD) of BNM1 and BNM5 glass samples respectively. The XRD shows no continuous or distinct sharp peak but exhibit broad halo hump around $2\theta\approx30^{\circ}$ [9], which reflects the characteristics of amorphous glass structure. The appearance of broad profile around $2\theta\approx30^{\circ}$, also suggests that some short range order in the sodium borate glasses are conserved. The absence of long-range atomic arrangement is a clear indication of glassy nature of the glass sample. **3.2 SEM Analysis:**



Figure 2: SEM images of BNM3 glass sample

The microstructure of the powdered glass samples were examined using Scanning Electron Microscope (SEM). The SEM photograph of the BNM3 sample was given in Fig. 3.2 respectively. It consists of densely packed grains free from holes. Some sphere-like agglomerates are found to be spreading due to deposition of amorphous apatite which clearly indicates the glassy nature of the samples [10].

3.3 FTIR Spectra Analysis:

Infrared spectroscopy has proved to be an important tool for the investigation of structure and dynamics of disorder materials. IR spectra of materials may help to get the idea of the nature of vibration in a disorder system [11]. The FT–IR spectra of BNM glass samples are shown in Fig.3.3.1



Figure 3: FT-IR Spectra of prepared glass samples

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In the infrared spectral region, the vibration modes of the borate network have four distinct frequency regions [12]. (a) The first group of bands, which occur at $1200-1600 \text{ cm}^{-1}$ is due to the asymmetric stretching vibration of the B–O bonds in BO₃ units. (b) The second group lies between 800 and 1200 cm⁻¹ and is due to the B–O stretching of the tetrahedral BO₄ units. (c) The third group is observed around 700 cm⁻¹ and is due to the bending of B–O–B linkages in the borate network. Deformation modes of both types of units are active between 600 and 800 cm⁻¹ [13]. The band at 1390 cm⁻¹ was assigned to B-O stretching vibrations of trigonal (BO₃) units in meta borate, pyro borate and ortho borate grups [14]. The intensity of this band is decreasing with the increasing of MnO content. The band at 1210 cm⁻¹ was assigned to B–O stretching vibrations of trigonal (BO₃) units in boroxol rings [15]. The intensity of this band increases with the increase of MnO mol%; for higher concentrations, the amplitude of this band decreases. The weak bands evidenced at 1045 cm⁻¹, 1013 and at 984 cm^{-1} was assigned to stretching vibrations of B–O bonds of BO₄ units from tri-, tetra- and penta- borate groups [16]. The band at 1013 cm⁻¹ gradually disappears with the increase of MnO content by merging into band centred at 1045 cm⁻¹. The band at 760 cm⁻¹ is assigned to the B-O-B bending vibration of bridges containing one trigonal and one tetrahedral boron and has approximate the same intensity for all the compositional range. In all the IR spectra appears a band at 700 cm⁻¹ relative to the band at 715 cm⁻¹ from the spectrum of vitreous B_2O_3 , which is due to the bending vibration of B-O-B linkage in borate network [17]. The intensity of this band increases with the increase of MnO content up to 10 mol%; for higher concentrations, the amplitude of this band decreases. The band at 630 cm⁻¹ is due to specific vibrations of Mn-O bonds. It can be noticed that the intensity of the band at 624 cm⁻¹ increases with the increase of MnO content up to 5 mol% and for higher concentrations of MnO almost disappears, while the intensity of the band at 474 cm⁻¹ is approximately the same for all compositional range.

Conclusion:

The glass system $60B_2O_3$ -(40-x) Na₂O-xMnO₂ with x=5, 10, 15, 20 and 25 mol % have been synthesized successfully by rapid melt quenching method. From the present investigation the following conclusions are drawn. Morphological analysis of SEM and XRD patterns have been confirmed their amorphous nature of the prepared glass samples. FTIR spectra of these glasses have been analyzed in order to identify the spectral contribution of component on the structure and to point out the role of the manganese ions as a modifier of the glass network. The shape of the spectrum revealed a significant disorder in our glasses for higher content of MnO.

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