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STRUCTURAL CHARACTERIZATION OF SULFOBORATE GLASSES CONTAINING MAGNESIUM OXIDE

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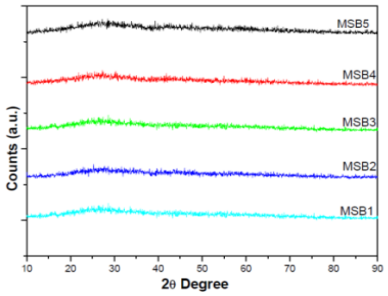
Graphical abstract



Abstract

Magnesium sulfoborate glasses of different compositions were prepared using melt quenching method with the purpose of using it for optical properties. The Fourier Transform Infra-red (FTIR) Spectroscopy, Nuclear Magnetic Resonance (NMR) and X-Ray Diffraction (XRD) have been carried out. Density and molar volume have been evaluated and analysed. From the results of XRD, the absent of discrete and continuous sharp peaks confirmed the amorphous nature of the glass compositions while the results from both FTIR and NMR revealed the existence of BO_3, BO_4 units. Addition of MgO to sulfoborate influenced the conversion of the dominant BO_3 groups to BO_4 groups. The BO_4 groups are known for creating complex defects that transform into that stable trap good for optical phenomena. It was observed that the density of glass increases while the molar volume is decreases with respect to increase in concentration of alkaline earth oxide in the glass compositions.

Keywords: SulfoBorate Glass, Infrared Spectroscopy, X-ray Diffraction, Nuclear Magnetic Resonance

1.0 INTRODUCTION

Glass is a solid that has an amorphous structure and when heated its shows a glass transition. Actually, glass is a solid formed by quick melt, it is transparent, hard and breakable [1]. Different kinds of materials are used for producing glass, such as alloys of metals, molecular liquids and aqueous solution e.t.c. Nevertheless, some elements are generally combined with common glasses to change their physical properties. Oxide glasses basically have three categories, such as the network formers, intermediates and modifiers. Network formers, form a structure of highly cross-linked chemical bond, while intermediates and modifies are generally existing as ions, alter the network system by being steady the non-bridging oxygen atoms that are covalently linkage by the glass network. The borate oxide is among the glass forming oxide that perform a special important role in electronic products [2] and offer good heat stability when compared with other oxide glasses [3], but it give better results if added with modified metal oxide. Some past research used alkaline oxides as a modifier. This is because of the chance of boron atom to joint with either three or four oxygen atoms to create a variety of atom groups [4]. Borate glasses are the most important ones for rare earth (RE) ion doping, due to their easy preparation, low melting point and good rare earth solubility [5,6]

The structural properties of lithium magnesium borate glass modified with magnesium oxide have been reported by [7]. Also, research done by Karunakaran *et al*. [8] studied the structural, optical and thermal Dy^{3+} as a dopant of lithium fluoroborate

glasses and investigated the suitability of the glasses for different physical and optical properties. Moreover, nuclear magnetic resonance (NMR) spectra earlier reported by Yun and Bray [9]. The NMR of LiO-B_2O_3 glasses of high LiO content and they observed three major different types of resonance due to boron BO_3, BO_{3S} and $BO_{3\alpha}$ units and another paper reported by [10] which determined the structural properties of IR, Raman and NMR of borate glasses. In this study, we used the methods of vibrational spectroscopy in order to determine structural elements, while methods of nuclear magnetic resonance (NMR) to determine the model of the structure of glasses as in [11], and physical properties of MgO-SO_4-B_2O_3 glasses will be discussed and reported.

2.0 EXPERIMENTAL

The samples were prepared using melt quenching method. The materials used for this study are boron oxide as glass former, magnesium and sulphur oxide as a modifier. The mixtures are mixed mechanically for an hour. Then, the mixtures was melted using alumina crucibles in an electronic furnace for about 60 minutes at 1200 ^{O}C. Next, the molten glass was poured into a steel plate and then speedy pressed with another steel plate for annealing at 400 ^{O}C for about 3 hours. After that, the samples were cooled down to room temperature of 30 ^{o}C. Lastly, white and transparent clear glasses that characterized a good quality of glasses were formed. Then, the glass samples were polished using emery paper in order to obtain smooth surfaces required for carrying out physical and mechanical test. The choice of sample composition used for this study is given in Table 1.

The X-ray powder diffraction (XRD) analysis was carried out using JEOL8030CX-ray diffractometer employing CuKa radiationat the scanning rate of 2degree per minute and 2θ is varied from 10 to 90°. The glass powder samples and KBr were mixed in ratio 100:1 by weight respectively, homogenized and compressed in an evacuable die until transparent discs were obtained. The surface chemistry of the transparent glass samples were studied using perkin-Elmer spectrum GX-FTIR spectrometer in absorption mode with KBr. The FTIR spectra were recorded in the 400 to 4000 cm^{-1} frequency range, after 10 scans, with resolution of 2 cm^{-1}. The position and intensities of the IR bands were processed with an in-built Spectra Analysis Software. ^{11}B NMR spectra of glass samples powder were perform by Brukker DXL 300 solid state high resolution spectrometer (B = 7.05T) conducting at 96.4 MHz. The samples ground to a nice powder with an agate mortar and pestle, then, loaded in to 3.2 mm and 5 mm (outer diameter). A rotor was employed to spin the samples at speeds of 5 KHz. The spinning side bands were specifying by virtue of their drifts when samples were spin at different speeds. Density was measured using Archimedes method and toluene as an immersion liquid. However, the density is linked to the composition of oxide glass values present in terms of the molar volume.

Table 1 The compositions of the glasses prepared in the MgO-SO_4-B_2O_3 glasses

Sample code	MgO mol%	SO_4 mol%	B_2O_3 mol%
MSB1	10	40	50
MSB2	15	35	50
MSB3	20	30	50
MSB4	25	25	50
MSB5	30	20	50

3.0 RESULTS AND DISCUSSION

To confirm that samples prepared are not crystalline and are in amorphous states, XRD were performed on the glass samples. The XRD diffraction patterns of all the glass samples are presented in Figure 1. From Figure 1 it can see that the diffraction shapes appear huge range structural disorder in the glasses. Only two huge peaks shown around 25 and 45 degree which confirm that all prepared glass samples are amorphous in nature.

Table 2 shows the calculated physical properties of MgO-SO_4-B_2O_3 glass, interested results are obtained between the density and molar volume. The results show that the density is increases with the increasing of the alkaline earth metal modifier [12]. The increases in density are linked to the conversion of sp2 planar BO_3 units to stable sp^3 tetrahedral BO_4 units. Therefore, it improved the number of oxygen-boron ratio in the glass network. The density also affects the molecular mass to be increased and cause to increases the atomic weight number. The change of density and molecular mass has influenced the molar volume. The results obtained shows that the density increases and the molar volume decreased. This workability is due to the reaction of magnesium and sulfate reaction inthe glass structure [13].

Figure 2 shows the FTIR spectra of different compositions of MgO-SO_4-B_2O_3 glasses in the region of 400-2000 cm-1 and Table 3 shows the results obtained from FTIR spectra which are closed to the previous study on the borate glass [4, 8 and 14]. From Table 3, we can be seen that existence of a low frequency cover around 696-701 cm^{-1} one absorption peak. This band is attributes to the bending vibration of B–O-B linkages in the borate network. Similar observation has also been reported by [14, 15]. The absorption band around 877 to 885 cm^{-1} is attributing to the stretching vibration of BO4 units [14]. The formation of sulfoborate structure is attributed to the formation of the bond B–O–S which is corroborated by emerging of bands at 1190 cm^{-1} which characterize asymmetric stretching vibrations of S–O of sulphate structural [16]. The bands around 1418-

1433 cm^{-1} have been assigned to the stretching relaxation of the bond between borate trigonal BO_3 and oxygen unit [16-18]. The broad band around 3430-3445 cm^{-1} is associated to the fundamental stretching vibrations of O–H ions which show the presence of hydroxyl groups in the borate glasses and peaks around 2671-2928 cm^{-1} are characteristic of hydrogen bonds in the borate glasses system [8].

Figure 3 shows ^{11}B MAS NMR spectra of different compositions of $MgO\text{-}SO_4\text{-}B_2O_3$ glasses. It exhibited a sharp resonance at around -2.06 ppm and is attributed from B_4 species and B_4 groups. The separate peak at the base of all the signals is attributed from B3 (Three coordinate boron atoms), similar work is reported by Gaguli and Rao [10]. Therefore, all the spectra have exhibited B_4 resonance peak with wings at the bottom. The region under the spectrum where the B4 and B3 present in the glass by connecting the peaks of the quadrupolar split B_3 with a uniform line. According to earlier report by Krogh-Moe [19] which gave the relationship between $N_4 = R$ for $R \leq 0.5$ and $N_4 = 0.5\text{-}0.25(R\text{-}0.5)$ for $0.5 \leq R \leq 1$ and, they compared between his values with the experimental values for the $R \leq 0.5$ region and the values of in the NMR is described as

$$N_4 = B_4/(B_3+B_4) \quad (1)$$

The compositions code of MSB2 from the Table 1 are 0.15mol fraction of MgO, 0.35mol fraction of SO_4 and 0.5 mol fraction of B_2O_3 .the experimental values of N4 given in Table 3 is 0.3, which means;

$$B_4/(B_3+B_4) = 0.3 \quad (2)$$

Where $B_3+B_4 = 2y$ and y is the mol fraction of B2O3 in the sample of glass. $B_3+B_4 = 2\times0.5 = 1.0$. Whlie, the value of B_4 is 0.3mol and B_3 is 0.7mol in the glass. Similar procedure will be follow to calculate the value of B_3 and B_4 for the remaining compositions and the calculated values of B_3 and B_4 are listed in Table 4. Since the ratio of MgO to B_2O_3 is less than 0.5 and also greater than 0.5, then, the N_4 values for $R \leq 0.5$ are expected to be less 0.5 and increases with the increased of MgO, while the N4 values for $0.5 \leq R \leq 1$ are expected to be below 0.5, decreases with an increased MgO. Table 4. Relative proportions of structural properties of $MgO\text{-}SO_4\text{-}B_2O_3$ glasses as determine from ^{11}B MAS NMR and chemical composition.

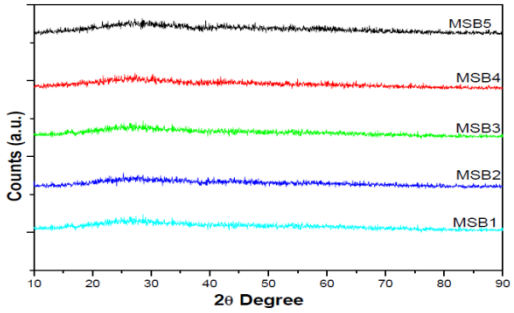


Figure 1 XRD pattern of $MgO\text{-}SO_4\text{-}B_2O_3$ glasses

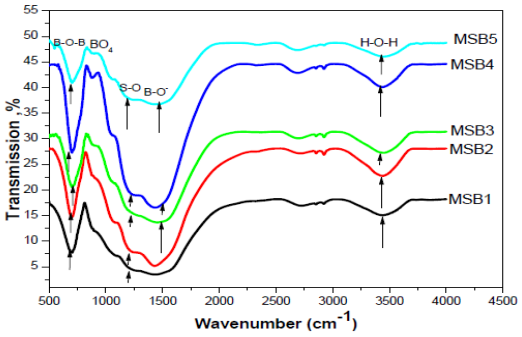


Figure 2 FTIR spectra of $MgO\text{-}SO_4\text{-}B_2O_3$ glasses.

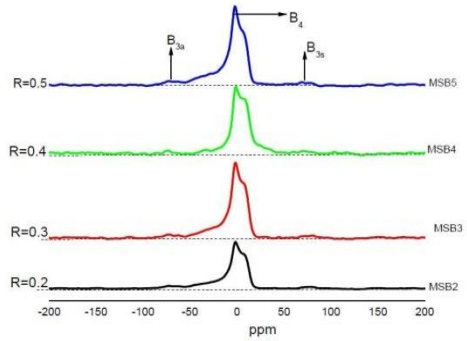


Figure 3 ^{11}B MAS NMR spectra of the $MgO\text{-}SO_4\text{-}B_2O_3$ glasses

Table 2 Physical properties of magnesium sulfoborate glasses

Measurements	MSB1	MSB2	MSB3	MSB4	MSB5
Average molecular weight, M (g)	123.22	115.43	107.63	99.84	92.05
Density, ρ (g/cm^3)	2.49	2.51	2.53	2.55	2.57
Molar volume, V_m (cm^3/mol)	49.49	45.99	42.54	39.15	35.82

Table 3 The FTIR absorption peaks position of $MgO\text{-}SO_4\text{-}B_2O_3$ glasses

S/No.	Assnment	MSB1	MSB2	MSB3	MSB4	MSB5
1	H-O-H	3430	3438	3438	3438	3445
2	Hydrogen bonding	2920	2927	2920	2920	2928
3	Hydrogen bonding	2671	2687	2687	2701	2701
4	B-O- Vibrations	1418	1433	1418	1418	1426
5	Asymmetric stretching of S-O	1190	1190	1185	1190	1190
6	Stretching vibration of BO_4 units	877	877	887	885	885
7	B-O-B Linkages	701	701	696	697	697

Table 4 Relative proportions of structural properties **of** $MgO\text{-}SO_4\text{-}B_2O_3$ glasses as determine from ^{11}B MAS NMR and Chemical composition

Sample code	R=mol%MgO/mol%B2O3	N4 (NMR)	B4	B3
MSB2	0.3	0.3	0.3	0.7
MSB3	0.4	0.4	0.4	0.6
MSB4	0.5	0.5	0.5	0.5
MSB5	0.6	0.48	0.48	0.52

4.0 CONCLUSION

The different compositions of $MgO\text{-}SO_4\text{-}B_2O_3$ glasses were prepared using melt quenching method. The XRD pattern confirmed the glasses are amorphous materials while from FTIR and ^{11}B MAS NMR spectra analyses showed an evidence of retention of BO_3 and BO_4 units from interaction between borate and sulfate units. The results obtained from physical calculation revealed that the density of the glass samples increases with decrease in molar volume as the concentration of alkaline earth oxide increases in the glass compositions.

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