JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 16 No 2, 02020(4pp) (2024)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 16 № 2, 02020(4cc) (2024)

REGULAR ARTICLE

OPEN ACCESS

Effect of Additive (MnO) on Dielectric Constant and Dielectric Loss of Na_2O-B_2O_3 Glasses

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(Received 10 December 2023; revised manuscript received 17 April 2024; published online 29 April 2024)

Glass samples of composition Na_2O-B_2O_3:MnO were synthesized by the method of melt quenching (MQT). Dielectric permeability and dielectric loss for the samples were studied as a characteristic of temperature at different frequencies. The influence of the alloying oxide modifier on the studied parameters is interpreted. It was found that the dielectric constant of all studied samples depends on the composition, and the development of dipole relaxation in the studied glasses was also revealed. MnO-containing sodium glasses show an increasing presence of Mn^{2+} ions in glasses from C_0 to C_4, which function as modifiers. The dielectric constant of glass varies significantly with temperature, especially at lower frequencies.

Keywords: B_2O_3 glasses, Dielectric constant, Dielectric loss, Mn^{2+} ions.

DOI: 10.21272/jnep.16(2).02020 PACS numbers: 61.43.Fs, 72.80.Ng, 77.22.Gm

1. INTRODUCTION

In general, borate glass formations share some fundamental properties. The basic component of vitreous B_2O_3 is the BO_3 groups, which can either take the form of a random network of boroxol rings or a portion of BO_3 triangles joined by B-O-B linkages [1]. Three corner-sharing BO_3 triangles that together constitute the boroxol group produce an extremely highly planar ring. Recent studies concluded that [2] any model which attempts to give a full description of the structure of B_2O_3 must include a high concentration of boroxol group. The boroxol rings split off as the temperature of glass transition approaches, resulting in a more open structure. Glasses behavior as a host material is heavily influenced by its open structure, allowing sites to accommodate host ions over a much greater range of size and coordination number. The boroxol rings are altered by the addition of alkali oxides [3]. Alkali borate glasses have rapid thermal expansion, low chemical durability, and low melting temperatures, which are important in some particular applications like sealing and soldering procedures [4, 5]. The conversion of sp^2 planar BO_3 units into more stable sp^3 tetrahedral BO_4 units, which preserves the B-O bonding without producing non-bridging oxygen (NBO) ions, is the initial result of adding alkali oxide to B_2O_3.

Manganese ion is an interesting transition metal ion, because it appears in several valence states in various glass matrices, such as Mn^{3+} in borate glasses with octahedral coordination and Mn^{2+} in silicate and germanate glasses with both octahedral and tetrahedral coordination [6]. Further, among different manganese ions, Mn^{2+} and Mn^{3+} are well known paramagnetic ions [7]. Glass matrices contain these ions in a variety of environments (ionic, covalent). Therefore, it is considered to comprehend the insulating capabilities of these glasses. This papers clear objective is to understanding of how MnO affects the insulating properties of Na_2O-B_2O_3 glass by the analysis of dielectric constant and dielectric loss over a range of frequency and temperature.

2. EXPERIMENTAL

The melting and quenching processes were employed to prepare the glasses for the current study [8-10]. Within the glass-forming region of Na_2O-B_2O_3: MnO glass system, the compositions with successive increase in the concentration of MnO are chosen for the present study $20Na_2O$–$(80\text{-}x)B_2O_3$: x MnO (with $x = 0.5$, 1.0, 1.5 and 2.0 all in ml %)) and the glass samples are labeled as C_0, C_1, C_2, C_3 and C_4 respectively.

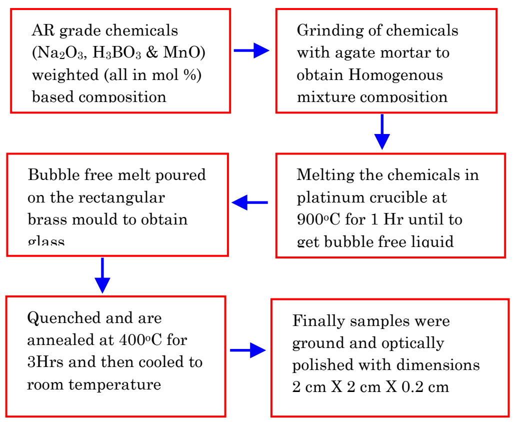

Fig. 1 – Flow chart of various step involved in preparation of glass samples

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Cite this article as: N.N. Rao et al, *J. Nano- Electron. Phys.* 16 No 2, 02020 (2024) https://doi.org/10.21272/jnep.16(2).02020

The Philips PW 1830 X-ray diffraction spectrometer was used to record the XRD patterns. The dielectric measurements were completed using an HP 4263B LCR Meter with frequencies between 10^2 and 10^5 Hz in the temperature range 30 – 300°C.

3. RESULTS

Some physical variables that can be used to characterize Na_2O-$B2O_3$: MnO glasses are calculated using the average molecular weight (M) and the measured value of density (*d*) [11]. Table 1 lists the physical characteristics of these glasses after evaluation. From the table it has been noted that the density of glass increases from 2.422 to 2.480 g/cm3 and molar volume decreases from 28.11 to 27.59 cc/mol as noted in a table. Increased in modifier contents introduce NBO containing borate triangles [12]. With rising MnO the molar volume decreases, it indicates that replacement of B_2O_3 by Mn^{2+} ions, these findings are well-concordant with past findings [13, 14].

Table 1 – Data on Physical properties of Na_2O– B_2O_3: MnO glasses

Sample Code	Density d (g/cm³)	Avg. Mol. wt	Mn^{2+} ion concentration N_I (10^{21} ions/cm³)	Inter ionic distance R_i (nm)	Molar Volume cc/mol
C_0	2.422	68.08	…	…	28.11
C_1	2.436	68.174	4.31	0.61	27.98
C_2	2.451	68.261	8.65	0.48	27.84
C_3	2.465	68.348	13.01	0.42	27.72
C_4	2.480	68.434	17.51	0.38	27.59

The glasses under investigation of X-RD patterns are shown in Fig. 2. It is commonly recognized that the lack of a sharp peak in a curve implies the glass sample is amorphous. As no peaks can be determined in X-ray diffraction spectra, all of the glass samples examined are amorphous in form (Table 2).

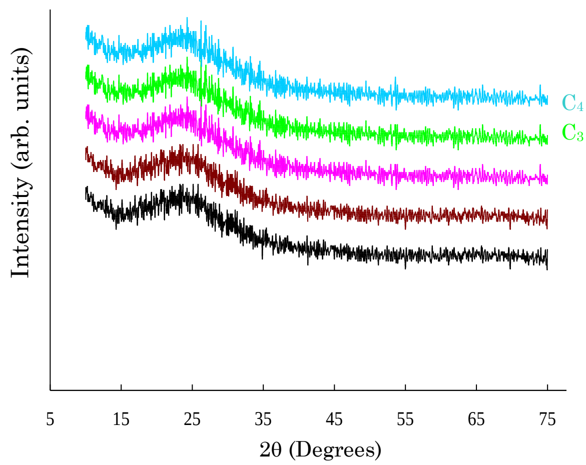

Fig. 2 – XRD pattern of Na_2O– B_2O_3: MnO glasses

Moreover, the XRD patterns of all studied samples exhibit a hump at an angle 20° – 30°, confirming the presence of short-range atomic periodicity in the glass samples

Table 2 – Experimental data obtained from X-RD patterns

Sample Code	Percent Crystallinity	Remark
C_0	Nil	All Samples are amorphous in nature
C_1	Nil	
C_2	Nil	
C_3	Nil	
C_4	Nil	

Na_2O-B_2O_3 glasses infused with different amounts of MnO show variations in dielectric constant and loss with frequency observed at ambient temperature (Fig. 3 and 4). The inclusions of MnO, the values are seen to increases. Additionally, constant ε' displays strong frequency dependence, with bigger values appearing at lower frequencies. At 2.0 mol% of MnO, it is discovered that loss as well as constant exhibit their highest levels (inset of Fig. 2 and Fig. 3).

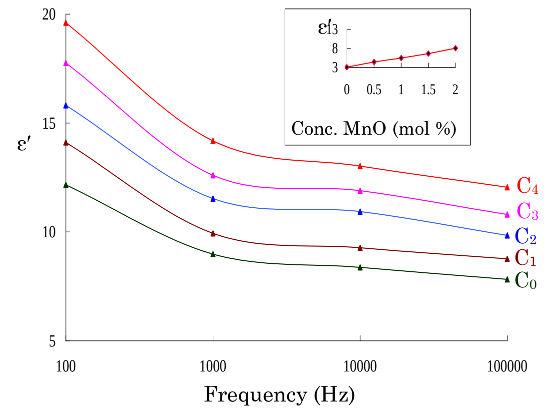

Fig. 3 – Variation of dielectric constant with frequency at room temperature of Na_2O-B_2O_3:MnO glasses. Inset represents the variation of ε' with the concentration of MnO at 100 kHz.

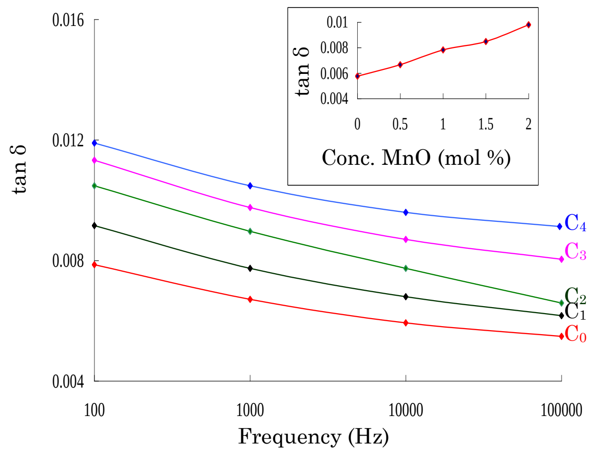

Fig. 4 – Variation of dielectric loss with frequency at room temperature of Na_2O -B_2O_3: MnO glasses. Inset represents the variation of tan δ with the concentration of MnO at 100 kHz.

The temperature dependence of dielectric constant of Na_2O–B_2O_3 glasses doped with various amounts of MnO was recorded at 10 kHz, is shown as a comparison Fig. 5. The glasses with 2.0 mol% of MnO are found to have the fastest rate of growth with temperature. The temperature dependency of the tanδ for the glasses doped with various concentrations of MnO, as determined at 10 kHz, is shown in Fig. 6.

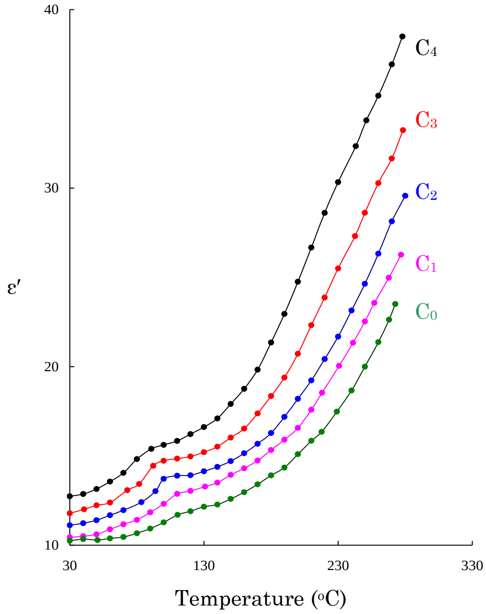

Fig. 5 – Comparison plot of Variation of dielectric constant with temperature measured at 10 kHz for Na_2O -B_2O_3: MnO glasses.

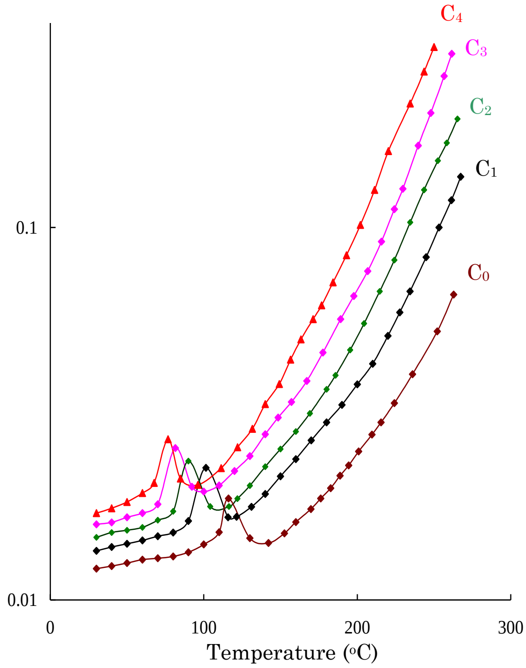

Fig. 6 – Comparison plot of variation of dielectric loss with temperature measured at 10 kHz

Table 3 and Table 4 summaries information on the dielectric constant and dielectric loss of Na_2O-B_2O_3: MnO glasses.

Table 3 – Data on dielectric constant of Na_2O–B_2O_3:MnO glasses

Glass	T (°C)	Dielectric constant		
		1 kHz	10 kHz	100 kHz
C_0	30	4.10	3.02	2.13
	100	6.34	4.73	3.10
	200	16.05	10.10	6.85
C_1	30	5.31	4.42	3.09
	100	7.09	6.13	4.72
	200	18.70	13.02	10.07
C_2	30	7.82	5.46	4.10
	100	9.67	7.20	5.92
	200	20.70	13.50	11.14
C_3	30	9.41	6.65	5.03
	100	11.03	9.12	7.86
	200	23.27	15.09	13.21
C_4	30	10.91	8.04	6.01
	100	13.81	10.08	8.10
	200	26.92	17.13	15.04

Table 4- Data on dielectric loss of Na_2O– B_2O_3: MnO glasses

Glass	T (°C)	Dielectric constant		
		1 kHz	10 kHz	100 kHz
C_0	30	0.010	0.008	0.006
	100	0.014	0.010	0.008
	200	0.032	0.024	0.015
C_1	30	0.012	0.011	0.009
	100	0.017	0.013	0.010
	200	0.044	0.028	0.019
C_2	30	0.016	0.014	0.012
	100	0.026	0.019	0.016
	200	0.050	0.041	0.020
C_3	30	0.026	0.018	0.015
	100	0.032	0.021	0.017
	200	0.078	0.060	0.035
C_4	30	0.029	0.022	0.019
	100	0.053	0.036	0.024
	200	0.091	0.080	0.047

With increasing temperature, the frequency maximum of the temperature dependent dielectric loss tanδ of pure and MnO-doped Na_2O–B_2O_3 glasses changes towards higher frequencies, suggesting the dielectric relaxation character of the dielectric loss of these glasses. The relaxation intensity is found to rise with an increase in MnO concentration up to 2.0 mol%.

4. DISCUSSION

Electrically insulating substances that are capable of being polarized by an external electric field are referred to as dielectric materials. When the dielectric material is placing in electric field, Dielectric polarization results from electric charge carriers that are slightly shifting from their average equilibrium locations rather than flowing through the material as they would in an electrical conductor. The temperature has a complicated influence on the dielectric constant. The increase in ionic distance caused by temperature increases influences the ionic and electronic polarizations. The contribution of space charge is determined by the purity and perfection of the glasses. It has a negligible effect at very low temperatures and is noticeable in the low frequency region [15].

We have seen spreading of relaxation with a set of relaxation periods when the glasses are doped with manganese ions, indicating that different forms of dipoles are responsible for the relaxation effects [16, 17]. Increases in MnO concentration up to 2.0 mol% are associated with increases in Mn^{2+} ion concentration as evidenced by an increase in the relaxation's intensity. The low intensity relaxation peaks for lower MnO concentrations show that the majority of the manganese ions in these glasses are in the Mn^{3+} state. Recalling the results, it is possible to attribute the minor increase in the dielectric constant and loss at room temperature, particularly at low frequencies for pure and MnO-doped $Na_2O–B_2O_3$ glasses, to imperfections formed in the glass network that support the polarization of the space charge [18, 19]. At higher frequencies, where this form of polarization reduces noticeably with frequency, the change in ε' and $\tan\delta$ with temperature is less pronounced.

The glasses with 2.0 mol% content of MnO are found to have the largest variation of ε' and $\tan\delta$ with temperature. This suggests a rise in the distortion in the $Na_2O–B_2O_3$ glass network, which leads to an enhancement of the space charge polarization and, in turn, a bigger increase in the observed ε' and $\tan\delta$ values. These oxides (MnO) act as modifiers by rupturing B-O-B bonds and introducing dangling bonds into the glass network. The resulting bonding flaws provide simple paths for the migration of charges that would otherwise build up space charge polarization, increasing the dielectric properties of the glasses.

5. CONCLUSIONS

MnO-containing sodium borate glasses were successfully made using the melt annealing process. The values of the dielectric constant and loss are observed to increase up to 2.0 mol% with the addition of MnO to the $Na_2O–B_2O_3$ glass matrix, showing an increasing presence of Mn^{2+} ions in glasses C_0 to C_4 that function as modifiers. The dielectric constant of $Na_2O–B_2O_3$: MnO glass varies significantly with temperature, especially at lower frequencies. Dipolar relaxation effects were visible in the fluctuation of dielectric loss with temperature of pure and MnO doped $Na_2O–B_2O_3$ glasses. Summarizing all of the research reported here, it is concluded that the degree of disorder in the glass network increases when MnO is present at higher concentrations (2.0 mol %) because manganese ions primarily adopt network-modifying positions.

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Вплив домішки MnO на діелектричну проникність та діелектричні втрати скла $Na_2O-B_2O_3$

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Зразки скла складу $Na_2O-B_2O_3$:MnO синтезували методом гартування розплаву. Досліджено діелектричну проникність і діелектричні втрати для зразків як характеристику температури на різних частотах. Інтерпретовано вплив модифікатора легуючого оксиду на досліджувані параметри. Встановлено залежність діелектричної проникності всіх досліджуваних зразків від складу, а також виявлено розвиток дипольної релаксації в досліджуваних стеклах. MnO-вмісні натрієві скла показують зростаючу присутність іонів Mn^{2+} у склах від C_0 до C_4, які виконують функцію модифікаторів. Діелектрична проникність скла значно змінюється в залежності від температури, особливо на нижчих частотах.

Ключові слова: B_2O_3 стекла, Діелектрична стала, Діелектричні втрати, Mn^{2+} іони.