Physical &Dielectric Studies of MnO doped Na_2O -B_2O_3 glasses

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DECLARATION

I hereby declare that the work reported in this project entitled "***Physical and Dielectric properties of Na_2O– B_2O_3: MnOglasses***" is entirely original and was carried out by me independently in the Department of Physics,KRU Dr. MRAR College of Post Graduation StudiesNuzvid, under the supervision of **Dr. N. NarasimhaRao**. I further declare that this project has not been submitted for the award of any Degree or Diploma of any University or Institution.

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CERTIFICATE

This to certify that the present project entitled "***Physical and Dielectric properties of $Na_2O-B_2O_3$: MnO glasses***" submitted by **M. Supriya (Register No. Y21PHY245004)** towards the partial fulfillment for the award of degree of Master of Science in Physics to the KRU Dr. MRAR College of Post Graduation Studies Nuzvid, is a bonafide record of project work actually carried out by her under my guidance in the Physics Department of this institute. The results embodied in this project have not been submitted for any other degree or Diploma to any other university or institution.

16/9/2025

(Dr. N. Narasimha Rao)

Project Supervisor

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Chapter – 1

General Introduction Scope and Contents of present work

This chapter presents the general introduction, scope, contents and aim of the present work. In this chapter, the basic theory related to "Physical and Dielectric investigations on $Na_2O- B_2O_3$: MnO " glass system are presented systematically.

Chapter -1

1.1 General Introduction

Glass, one of the most ancient materials, has fascinated and attracted enormous interest both scientifically and technologically. This age-old material plays a key role in numerous applications like electronics [1], photonics [2], biomedicine [3], radioactive waste storage [4] and many others, along with classical ones like windows, architecture, lenses, containers etc. Glass which was earlier considered mainly an optical, dielectric material can now be used to make active devices like switches, memories, sensors, solar cells, catalysts etc [5]. These widespread uses reflect an ever increasing role of glass in our modern technical society and industry.

1.2 Definition of Glass

A glass is defined in ASTM [8] as 'an inorganic product of fusion, which has been cooled to rigid condition without crystallization'. According to this definition, a glass is a non- crystalline solid material obtained by a melt-quenching process. Glass is also defined as an amorphous/non-crystalline solid completely lacking in long-range periodicity and exhibit glass transition behavior [9,10]. The terms amorphous and non-crystalline are synonymous. The glass transition is a phenomenon in which a solid amorphous phase shows an abrupt change in the derivative thermodynamic properties from solid like to liquid like values with change of temperature. Nowadays, non-crystalline materials that can't be distinguished from melt-quenched glasses of the same

composition are obtainable by using various other techniques such as chemical vapor deposition, sol-gel process, etc. Therefore, most glass scientists regard the term 'glass' as covering 'all non-crystalline solids that show a glass transition' regardless of the preparation method. Glass is also defined as a configurationally frozen liquid which exhibits glass transition behavior [10].

From a thermodynamic point of view, the 'glassy' state is a meta-stable state and unlike crystalline state it is not unique. The 'glassy' state depends upon the thermal history of the melt and represents a local minimum in the free energy. Given adequate time, the system will relax to a more stable state, of lower free energy, provided the energy barrier separating these states can be crossed [11]. For practical purpose however, the time taken for relaxation of most everyday glasses is so long that the question of metastability is purely academic.

1.3 Glass Transition Phenomenon

The glass transition is an essential attribute of any glassy material. The glass transition phenomenon is quite complex and many theories have been suggested based on various parameters/properties, which characterize the glasses. These theories have been successful only to a limited extent as the glass transition is a function of many parameters like heat capacity, thermal conductivity, melting temperature, cooling rate etc. Significant variation in the value of glass transition temperature (T_g) has also been observed depending on the method used for its measurement. This is because when a melt is quenched to form a glass, the different degrees of freedom get arrested and

during heating these degrees of freedom start getting relaxed. These different degrees of freedom, corresponding to different properties, which are used to evaluate T_g, relax at different rates and result in different values of T_g being measured. When a liquid is cooled either crystallization may take place at the freezing point (or melting point 'T_m'), or else the liquid will become 'supercooled' for temperatures below T_m. This 'supercooled' liquid becomes more viscous with decreasing temperature. Although glass has atomic arrangement akin to liquid state, in terms of all other properties such as rigidity etc., glass is unequivocally a solid. This phenomenon can be understood readily by monitoring the changes in enthalpy/volume as a function of temperature (Figure1.1). The crystallization process is manifested by an abrupt change in extensive thermodynamic variables like enthalpy 'H' or volume 'V' at T_m, whereas glass formation is characterized by a gradual change in slope. The temperature range over which the change of slope occurs is called the 'glass-transformation range' [9,10]. As the transition of liquid to the glassy state is continuous, the T_g cannot be uniquely defined. However, for convenience the T_g is expressed as 'fictive' temperature 'T_f', the temperature obtained by intersection of the extrapolated liquid and glass curves (Figure 1.1). It depends on the rate of cooling of the supercooled liquid. The slower the rate of cooling, the larger is the region in which the liquid may retain supercooled state, implying lower T_f or T_g, as shown in Figure 1.1. Thus, the 'T_g' of a glass is not an intrinsic property but depends on its thermal history. Dependence of T_g on the cooling rate *q* is given as:

$$q = q_0 e^{\frac{1}{c}\left(\frac{1}{T_g} - \frac{1}{T_M}\right)} \qquad (1.1)$$

where c and q_o are constants. The experimentally measured value of T_g is not unique. The value of T_g depends on the time scale of the experiment used to observe it. The relaxation process is another very important aspect of glass transition. The configurational changes, which are responsible for the relaxation process, become increasingly slow as the temperature decreases. At T_g the material shows a solid like behaviour for observation time 't_0' which is smaller than the structural relaxation time 't_r'. For $t_r < t_0$, the material behaves like a liquid. A transition is said have taken place when the parameters corresponding to liquid like behaviour differ significantly from solid like ones, as in the case for heat capacity. In other words, T_g should occur when t_0 is equal or comparable to t_r.

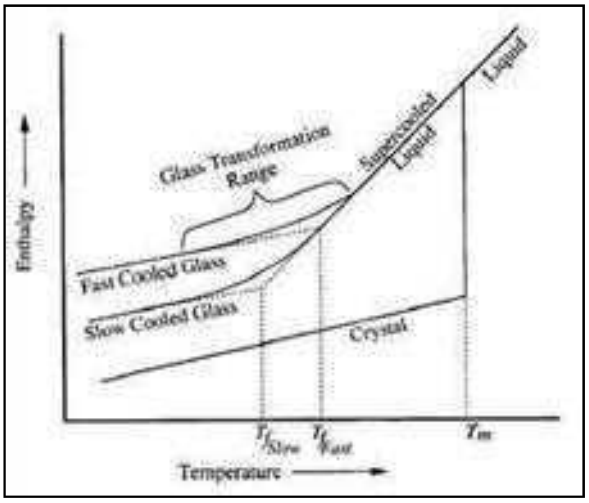

Figure 1.1: Variation in enthalpy or volume of a glass forming melt with the temperature.

The glass transition can also be expressed as a phenomenon in which a solid glassy phase shows abrupt change in the derivative thermodynamic properties such as heat capacity, thermal expansion coefficient (TEC) etc [10] at the transition

temperature. The order of a phase transition in Ehrenfest scheme is defined as the order of the lowest derivative of Gibbs free energy (G), which shows a discontinuity at the transition point. In liquid to crystal transition at freezing (or melting) temperature 'T_m' the volume 'V' and enthalpy 'H', which are the first derivative Gibbs free energy, are discontinuous. Hence, liquid to crystal transition is a first order transition. However, in liquid to glass transition, the thermodynamic variables such as volume, enthalpy and entropy are continuous and the quantities such as thermal expansion 'α_T' compressibility 'K_T' and heat capacity 'C_P', which are the second order derivative of Gibbs free energy, are discontinuous. Hence, the glass transition is a

manifestation of a second order phase transition [10].

1.4 Structural Aspects of Glasses

Good understanding of the structural arrangements of atoms in any material is a key factor to a detailed understanding of its physical and chemical properties. The structure of crystalline materials is well established and is classified according to structure of the unit cell. However,

the lack of symmetry and periodicity in amorphous materials make such approach inapplicable for them. Even though there is lack of long range periodic order, these materials often possess considerable structural order over length scale of many Á [12]. Therefore, a length scale may be arbitrarily defined, which separates microscopic structure frommacroscopic structure in amorphous solids [13].

Glass formation does not depend on the type of bonding. Besides the large class of inorganic glasses with mixed covalent ionic bonds there exist metallic glasses and

organic glasses with van der waals bonds. Therefore, determination of structure for every class of glass is a wide scientific field with a number of different theories and experimental methods to confirm them. The most important structural model for oxide glasses was proposed by Zachariasen [14] in 1932 based on continuous random network hypothesis. Continuous Random Network (CRN) model was based on the existence of the polyhedra that are linked together to form an overall random network. He suggested that the crystalline and the glassy form of an oxide should have the same type of oxygen polyhedra joined in a similar way except that in the glassy phase there is range of bond angles and bond lengths. Further, the network should be sufficiently flexible to incorporate the disorder, which is characteristic of the glassy phase, and the internal energy of both the crystalline and glassy phase should be comparable. The X-ray diffraction (XRD) studies carried out by Warren [15] supported this theory. The difference in structure of crystalline and glassy forms of a hypothetical two-dimensional oxide, say, A_2O_3 is shown in Figures 1.2(a) and 1.2(b).

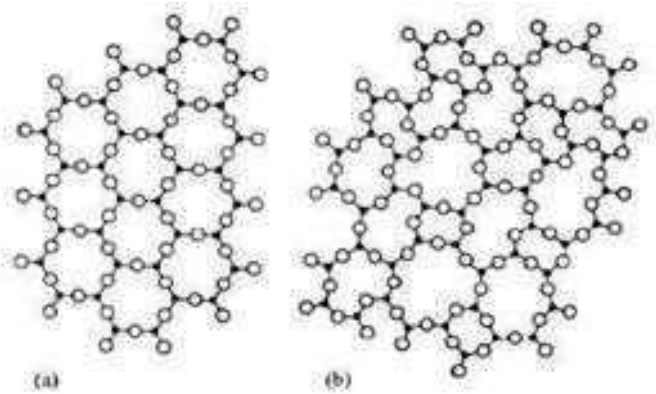

Figure 1.2: Atomic structural representation of a A_2O_3 crystal (a) and a A_2O_3 glass (b) (Filledcircles are A = cations and open circles are O = oxygen).

Thus, both the crystalline and the glassy forms are composed of AO_3 triangles

joinedto each other at corners, except that the glassy form has disorder introduced by changes in the A−O−A bond angles and A−O bond length. The triangles or O−A−O angles themselves need not be deformed much. According to the Zachariasen's CRN theory, the following criteria are valid for glass formation in simple compounds like SiO_2, B_2O_3, P_2O_5, GeO_2, As_2S_3, As_2Se_3, BeF_2, $ZnCl_2$ etc:

1. An oxide or compound tends to form a glass if it easily forms polyhedral groups as the smallest building units.
2. The cation polyhedra share only corners not edges or faces.
3. Anions (like O^{2-}, S^{2-}, Se^{2-}, F^{1-}, Cl^{1-},…) should not bind more than two central atoms (insimple glasses anions form bridges between two adjacent polyhedral).
4. The number of vertices of polyhedron should be less than six.
5. At least three vertices of a polyhedron must be shared with neighbouring polyhedral in order to form a three-dimensional (3D) network.

Zachariasen classified the cations in a glass as follows:

1. Network-formers (NWF) e.g. Si, B, P etc. with the coordination number 3 or 4.
2. Network-modifiers (NWM) e.g. Li, Na, Sr, Ba etc. with coordination numbers generally greater or equal to 6.
3. Intermediates that may either reinforce the network by cross-linking (coordination number 3 or 4) or weaken the network by depolymerization (coordination number 6-8).

1.5 Types of Glasses

Glasses have been broadly classified into two different ways. First one is based on the actual components present in them and second one, based on their end use.

Glasses based on silicate, phosphate, borate, borosilicate etc, networks belong to the first category; whereas optical glasses, sealing glasses, laser glasses etc, correspond to the second category. Other types of glasses include metallic glasses, halide glasses, organic glasses, mixed anion glasses, ionic glasses and chalcogenide glasses.

1.5.1 Borate glasses

Pure Borate glasses are difficult to prepare under normal conditions without any moisture content. Water free Borate glasses are prepared by Poch [16] by melting orthoboric acid for several hours at a pressure of 1 mm of Hg. Various structural studies carried out on pure borate glasses revealed that the structure of the glass agree well with the model proposed by Krogh-Moe [17]. According to this model B_2O_3 glasses mainly contain boroxol rings. The classic work of Krogh-Moe indicated the possible presence of 5 different types of borate species in the glass structure (Figure 1.6). Glass formation of B_2O_3 with various metal oxides has been extensively studied by various authors [18,19] and they have pointed out that some anomalous behaviour exists for these glasses. For example, in Na_2O-B_2O_3 system two separate regions of glass formation exists in the range of composition 28.5 to 33.5 mol% of B_2O_3 and 62 to 100 mol% of B_2O_3. The glass formation gap can however be removed by adding Al_2O_3 [20]. Structural aspects of binary borate glasses have been mainly investigated by ^{11}B, ^{10}B NQR

(Nuclear Quadrupole Resonance) and NMR techniques. Addition of Na_2O to B_2O_3 glass, up to 33 mol%, results in progressive conversion of trigonal boron structural units (BO_3) to tetrahedral boron structural units (BO_4). Above 33 mol% of

Na_2O, relative concentration of BO_4 structural units starteddecreasing [21].

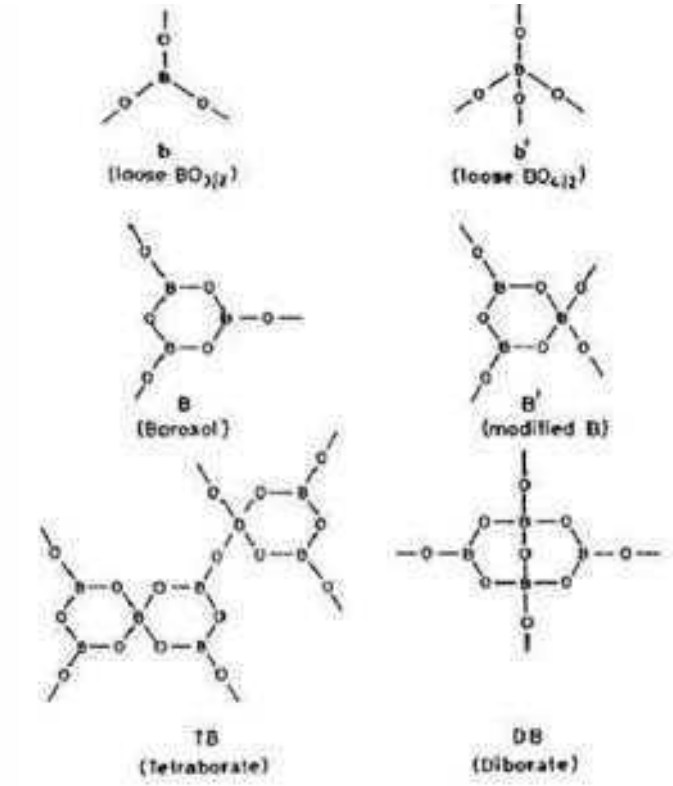

Figure 1.3: Possible borate species in the borate glass structure.

Borate glasses generally melt at lower temperatures and are frequently used as solder glasses. Primary requirement of solder glass is that, it needs to be a fluid at a temperature, which is well below the deformation temperature of the glass to be sealed. Borate glasses containing high concentration of rare earth oxides are used to manufacture lens systems with high numerical aperture and low spherical aberrations.

1.6 Scope of the Present Work

B_2O_3 glasses have attracted extensive investigation in recent years, in view of their potential applications in a number of solid state ionic devices. Several physical properties viz.,

electrical, optical, mechanical and magnetic properties of pure and various transition and rare earth metal ions doped alkali borate glasses have been under extensive investigation in recent years in view of their technological applications [22-28] especially in phosphors, lasers, solar energy converters and in a number of electronic devices. Alkali fluoro borate glasses are transparent from the near UV to the middle infrared region. They are resistant to atmospheric moisture and are capable of accepting large concentrations of transition metal ions.

The origin of the properties of alkali borate glasses has been strongly co-related to the local order around boron atoms. The coordination geometry of boron atoms has been shown to be strongly dependent on the composition of the glasses and on the chemical nature of the network modifier. For example the addition of alkali oxide like Na_2O is also expected to make the glasses more moisture resistant. It is well known that the effect of introduction of modifiers like Li_2O, Na_2O, K_2O, CaF_2 into B_2O_3 network is the conversion of sp^2 planar BO_3 units into more stable sp^3 tetrahedral BO_4 units and may also create non bridging oxygens. Each BO_4 unit is linked to two such other units and one oxygen from each unit with a metal ion and the structure leads to the formation of long chain tetrahedron.

Basic characteristics of borate glass structures are generally agreed upon. The fundamental building block in vitreous B_2O_3 is the BO_3 groups either as a random network of boroxol rings beside some fraction of BO_3 triangles connected by B-O-B linkages [29] (bridging forms). The boroxol group is composed of three corner –sharing BO_3 triangles which form a very highly planar ring. Recent studies concluded that [30] 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 addition of alkali oxides modifies the boroxol rings, complex borate groups with

one or two four coordinated boron atoms [31]. Alkali oxide is usually incorporated in to B_2O_3 glass ironically. The initial effect upon the introduction of alkali oxide in to B_2O_3 is the conversion of sp^2 planar BO_3 units in to more stable sp^3 tetrahedral BO_4 units there by preserving the B-O bonding without the creation of non-bridging oxygen (NBO) ions. The alkali borate glasses are composed of structural groupings (boroxol, tetra borate, diborate, metaborate, pyroborate, and ortho borate) present in the various crystal structures of the alkali borate compounds. The abundance and the type of structural units present depend upon the amount of alkali oxide incorporated in to the glass.

Transition metal ions are very interesting ions to probe in the glass network because their outer d-electron orbital functions have rather broad radial distributions and their responses to surrounding actions are very sensitive; as a result these ions influence the physical properties of the glasses to a substantial extent.

Manganese ion is an interesting transition metal ion because it exists in different valence states in different glass matrices, for example as Mn^{3+} in borate glasses with octahedral coordination whereas in silicate and germanate glasses it exists in Mn^{2+} with both octahedral and tetrahedral coordination [32]. Further, among different manganese ions, Mn^{2+} and Mn^{3+} are well known paramagnetic ions and Mn^{2+} and Mn^{4+} are identified as luminescence activators [33]. Mn^{2+} has the electronic configuration $3d^5$ which corresponds to a half filled d shell. Most Mn^{2+} complexes are octahedral and have a high spin arrangement with five unpaired electrons [34]. These ions subsist in different surroundings (ionic, covalent) in glass matrices. Further, it is also quite likely for manganese ions to have link with borate groups; strengthen its structure and may raise the chemical resistance of the glass. The content of manganese in different forms in different valence states exist in the glass

depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc. Hence, the connection between the state and the position of the manganese ion and the physical properties of the glass is expected to be highly interesting.

In view of these characteristics, manganese ions are expected to influence the physical properties Na_2O-B_2O_3 glasses and may have strong bearing on electrical and mechanical properties of the glasses. Therefore, it is felt important to have some understanding over the insulating properties of these glasses. The dielectric properties and the dependence of these properties on the composition, structure and on various external factors such as humidity, radiation effect, mechanical action etc., pave the way for estimating the insulating character and mechanical strength of the glasses and such studies will help to assess the suitability of these glasses for practical applications and also help in understanding the glass structure to some extent.

This chapter is therefore devoted to investigate the influence of Mn ions on the physical and dielectric properties of Na_2O-B_2O_3 glasses.

1.6.1 Physical Parameters

Some physical parameters useful for characterization Na_2O-B_2O_3: MnO glasses are estimated from the measured value of density (d) and the average molecular weight , using the following equations [35]:

The transition metal ion concentration (N_i) in these glass matrices could be obtained from:

$$(i)\ N_i \ (10^{22}\ \text{ions}/\text{cm}^3) = \frac{N_A\, M \quad (\text{mol}\%)\, d}{\overline{M}} \qquad (1.1)$$

From the N_i values obtained, the polaron radius (r_p) and inter – ionic distance (r_i) of transition metal ions could be evaluated:

(ii) Polaron radius r_p (Å) $= \frac{1}{2}\left(\frac{1}{6N_i}\right)^{1/3}$ (1.2)

(iii) Inter – ionic distance r_i (Å) $= \left(\frac{1}{N_i}\right)^{1/3}$ (1.3)

The field strength (F_i) of transition metal ion in the glass matrix is described through the oxidation number (Z) and the ionic radii (r_p) of the transition metal ions by:

(iv) Field strength F_i (cm^{-2}) $= \frac{Z}{r_p^2}$ (1.4)

1.6.2 Dielectric Properties

When an insulating glass (a dielectric) likes Na_2O-B_2O_3: MnO glass is placed in an external electric field; two types of polarizations – the electronic and the ionic – are developed in the glass. If the dielectric contains permanent dipoles, they experience a torque in an applied field that tends to orient them in the field direction. Consequently, an orientation (or dipolar) polarization can arise. These three polarizations are due to charges locally bound in atoms, molecules or in the structures of solids (or liquids). Additionally to all these, generally there exist charge carriers that can migrate for some distance through the dielectric. Such charge carriers during their motion may be trapped in the material or on interfaces ; due to these causes, space charges and a microscopic field distortion result. Such a distortion appears as an increase in the capacitance of the sample and may be indistinguishable from a real rise of the dielectric constant. Thus a fourth polarization, called the space charge

polarization comes into play. The total polarization is sum of these four polarizations (assuming that they act independently) [36].

When the dielectric is placed in alternating fields, these polarizations are set up and the dielectric constant is a consequence of them; also a temporal phase shift is found to occur between the applied field and the resulting polarization and a loss current component appears, giving rise to the dielectric loss of the sample [37].

The complex dielectric constant, according to Debye for a material having permanent dipoles characterized by single relaxation time , given by:

$$^{*}(\quad) \quad {}_{s} \quad \frac{{}^{s}}{1 \quad i} \qquad (1.5)$$

Where $_s$ is the static dielectric constant and $_\infty$ is the dielectric constant value of the material corresponding to its electronic and atomic polarization. Separating this equation into its real and imaginary parts, one obtains:

$$(\quad) \quad \frac{{}^{s}}{1 \qquad {}^{2} \; {}^{2}} \qquad (1.6)$$

and

$$(\quad) \quad \frac{(\quad {}_{s} \qquad)}{1 \qquad {}^{2} \; {}^{2}} \qquad (1.7)$$

The dielectric loss of the material (generally expressed by tan) is given by the expression:

$$\tan \quad = \quad \frac{"(\quad)}{'(\quad)} = \quad \frac{(\quad {}_{s} - \quad)}{{}_{s} + \qquad {}^{2}} \qquad (1.8)$$

If the conductivity ($_{ac}$) of the sample is also taken into account, it can be shown that

$$Tan \qquad \frac{4}{(\quad)} \quad \frac{(\quad {}_{s} \qquad)}{{}_{s} \qquad {}^{2} \; {}^{2}} \qquad (1.9)$$

By plotting log (tan) as a function of log ( ), information regarding d.c conductivity as well as the behavior of the dipoles present if any can be obtained.

1.7 Aim of the Present Work

Increased demand on diverse applications of modern electronic devices has led to the search for new materials, which will meet the specific requirements. Addition of Na_2O into borate glass network expected to show significant improvement in chemical durability while maintaining low glass transformation temperature and softening points. Due to the possibility that a large variety of properties are adjustable by composition and excellent chemical durability close to that of window glasses, these glasses have potential applications in sealing as well as optical purposes. Though few studies on certain physical properties of some borate glasses are available in the recent years, a thorough survey of the literature on these glasses show that a detailed investigations on electrical properties of MnO doped Na_2O-B_2O_3 glasses in particular are not available. Study on the dielectric properties helps in estimating the insulating strength of these glasses and will also throw some light on the structural information of these glasses.

1.8 Contents of the present work

The glasses used for the present studies are:

$G_{0:}$ 20 Na_2O -80 B_2O_3

G_1: 20 Na_2O -79.50 B_2O_3: 0.5 MnO

$G_{2:}$ 20 Na_2O -79.00 B_2O_3: 1.0 MnO

$G_{3:}$ 20 Na_2O -78.50 B_2O_3: 1.5 MnO

$G_{4:}$ 20 Na_2O -78.00 B_2O_3: 2.0 MnO

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Chapter – 2

Experimental Methods

This chapter gives the description of experimental methods employed in the preparation and characterization of MnO doped $Na_2O- B_2O_3$ glasses. The details of the apparatus used for synthesizing the samples and the techniques adopted for measuring Physical and Dielectric are described in detail in this chapter.

hapter – 2

Experimental Methods

2.1 Introduction

In this chapter, a detailed description of the methods which used in the perpetration of Na_2O -B_2O_3: MnO glasses are presented. Various measurement techniques employed for determining density etc, are also discussed. The description of the apparatus used and detailed procedure for studying dielectric properties of Na_2O-B_2O_3 glasses are also included.

2. 2 Glass Preparation

Within the glass-forming region of Na_2O-B_2O_3: MnO glass system, the following particular compositions with successive increase in the concentration of MnO are chosen for the present study:

$G_{0:}$ 20 Na_2O -80 B_2O_3
G_1: 20 Na_2O -79.50 B_2O_3: 0.5 MnO
$G_{2:}$ 20 Na_2O -79.00 B_2O_3: 1.0 MnO
$G_{3:}$ 20 Na_2O -78.50 B_2O_3: 1.5 MnO
$G_{4:}$ 20 Na_2O -78.00 B_2O_3: 2.0 MnO

The glasses used for the present study were prepared by the melting and quenching techniques [1-3]. Appropriate amounts (all in mol %) of reagent grades of Na_2O, B_2O_3 and MnO powders were thoroughly mixed in an agate mortar and melted in a thick walled platinum crucible in the temperature range 900-950 ºC . The furnace used was a PID temperature controlled furnace (Fig. 2.1).

Fig. 2.1 Schematic images of PID controlled furnace and annealing chamber

The glasses were melted in a thick walled platinum crucible for an hour till a bubble free liquid was formed. The resultant melt was poured on a rectangular brass mould (having smooth polished inner surface) held at room temperature and subsequently annealed at 200 oC in another furnace. The weight of the glass obtained always agreed with that anticipated in the batch, with an error of 0.2 to 0.5 % wt loss in each case. The results indicate that the actual glass compositions are essentially equal to those based on the glass batch. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for present study are 1 cm x 1 cm x 0.2 cm. For dielectric and dielectric breakdown measurements thin coating of silver paint was applied on either side of the glasses, to serve as electrodes.

2.3 Physical Properties

The density (d) of the glasses was determined by the standard principle of Archimedis' using o-xylene (99.99 % pure) as the buoyant liquid. A direct reading balance (capacity 100 g, readability 0.1 mg) was used for weighing. The bulk glass was suspended on a very thin

copper strand kept in the immersion liquid container and weighed in the liquid and air.

Using density and average molecular weight, other physical parameters such as copper ion concentration N_i , the polaron radius r_P , the field strength F_i of these glasses are evaluated.

2.4 X-ray diffraction

The amorphous state of the prepared glasses was checked by X-ray diffraction spectra recorded on SEIFEERT Diffractometer Model SO – DEBYE FLUX 202 fitted with copper target and nickel filter operated at 40 kV, 30m A.

2.5 Dielectric Measurements

The dielectric measurements on the Na_2O-B_2O_3: MnO glasses were carried out on HP 4263B LCR Meter in the frequency range 10^2 - 10^5 Hz [4] in the temperature range 30 – 300^o C.

2.5.1 HP 4263 B LCR Meter

Capacitance measurements were made with HP 4263B LCR Meter. The HP 4263B LCR Meter is a fully automatic high performance test instrument used to measure a wide range of parameters .The measurement speed of the instrument is 29 ms, it has a very test quick recovery and got built in comparator. It can measure the capacitance to a high accuracy and wide measurement range, which allows us to make precise measurements at five frequencies 100 Hz, 120 Hz, 1 kHz, 10 kHz and 100 kHz. The two measurement display sections, capacitance (C) and dissipation factor (D) provide the direct read out of the parameters .The instrument has got two modes of measurement viz., normal mode and average mode; in normal mode operation the instrument performs measurements at very high

speed where as in the average mode it has short, medium or long range rate to average the measurement results. The second mode, adopted in the present measurements, gives a high reliable and repeatable value than in the normal mode of the measurement.

2. 5. 2 Sample Holders

Two different types of sample holders have been used for room and high temperature dielectric measurements:

I) For measurements at room temperature on HP 4263 B LCR Meter a laboratory made sample holder with teflon base and micrometer arrangement [Fig 2.2(a)] was used.

II) For the temperature variation of the dielectric properties at a fixed frequency the sample holder shown in Fig 2.2(b) has been used .

Fig. 2.2 (a) HP 4263 B LCR micrometer arrangement and **Fig 2.2(b)** Sample holder

The sample was put in between two silver electrodes and a 200 W nichrome heater heated the holder. Adjusting the current with a variac controlled the heating. The readings were taken when the sample attained the steady temperature. A chromel – alumel thermo-couple was attached to the sample holder vary near the sample. The thermo e.m.f. Developed across the junction was measured using digital PID temperature controller.

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Chapter – 3

The primary objective of this study is to characterize the Dielectric properties viz., Dielectric constant and Dielectric loss of $Na_2O- B_2O_3$: MnO glasses

Chapter -3

Physical &Dielectric Studies of MnO doped Na_2O -B_2O_3 glasses

3.1 Introduction

Study on radiation induced defect centers in glasses has been an interesting subject of investigation in recent years, since such studies help for examining the suitability of the glasses for radiation dosimetry applications. Extensive studies on the activating or killing effect of luminescence due to some transition metal ions like Fe2+, Cu2+, Ti4+etc, in amorphous materials are available in literature [1-2]. In recent years Pontuschka et al. have done a commendable work on thermo luminescence mechanisms in borate glasses [3]. Borate glasses are very advantageous materials for the radiation dosimetry applications in view of the fact that their effective atomic number is very close to that of human tissue. However, pure borate glasses have certain disadvantages to use in radiation dosimetry since they are highly hygroscopic and exhibit weak glow peak at relatively low temperatures. Alkali oxy borate glasses are considered as good materials for dosimetry applications since they are relatively moisture resistant when compared with the pure borate glasses.

Manganese ion, is yet an another interesting transition metal ion because it exists in different valence states in different glass matrices, for example in silicate and germanate glasses it exists in Mn^{2+} with both octahedral and tetrahedral coordination [4]. Further, among different manganese ions, Mn^{2+} and Mn^{3+} are well known paramagnetic ions and Mn^{2+} and Mn^{4+} are identified as luminescence activators [5]. Further, it is also quite likely for manganese ions to have link with borate groups; strengthen its structure and may raise the

chemical resistance of the glass. The content of manganese in different forms in different valence states exist in the glass depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc. Hence, the connection between the state and the position of the manganese ion and the physical properties of the glass is expected to be highly interesting.

Mn^{2+} has the electronic configuration $3d^5$ which corresponds to a half filled d shell. Most Mn^{2+} complexes are octahedral and have a high spin arrangement with five unpaired electrons [6]. In view of these characteristics, manganese ions are expected to influence the physical properties of Na_2O-B_2O_3 glasses and may have strong bearing on electrical and mechanical properties of the glasses.

A large number of interesting studies are available on the environment of manganese ion in various inorganic glass systems. These ions subsist in different surroundings (ionic, covalent) in glass matrices. Manganese ions seem to exist in Mn^{2+} and Mn^{3+} states in Na_2O-B_2O_3 glass network. The most probable local structure likely to occur for Mn^{3+} in these glasses is as a MnO_6 octahedron entwined with a BO_4 tetrahedron $MnBO_9$ where all the oxygens are bridging. The presence of such complexes obviously increases the stability of the glass network. Even though a number of recent investigations are available on the environment of manganese ions in a variety of inorganic glass systems [7-12], no dedicated studies are available on the influence of manganese ions on Na_2O - B_2O_3 glass systems in particular. This chapter is therefore devoted to investigate the influence of Mn ions on the structure and physical properties of Na_2O-B_2O_3 glasses.

Thus the clear objective of this chapter is to have a comprehensive understanding over the influence of manganese ions on physical and the insulating character of Na_2O–B_2O_3: MnO

glass system by a systematic study of dielectric properties (dielectric constant ε', loss and tan δ) over a moderately wide range of frequency and temperature. Glasses of the following composition are chosen for the present study:

$G_{0:}$ 20 Na_2O -80 B_2O_3

G_1: 20 Na_2O -79.50 B_2O_3: 0.5 MnO

$G_{2:}$ 20 Na_2O -79.00 B_2O_3: 1.0 MnO

$G_{3:}$ 20 Na_2O -78.50 B_2O_3: 1.5 MnO

$G_{4:}$ 20 Na_2O -78.000 B_2O_3: 2.0 MnO

3.2 Results

3.2.1 XRD

The glasses under investigation of X-RD patterns are shown in Fig. 3.1. 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 3.1).

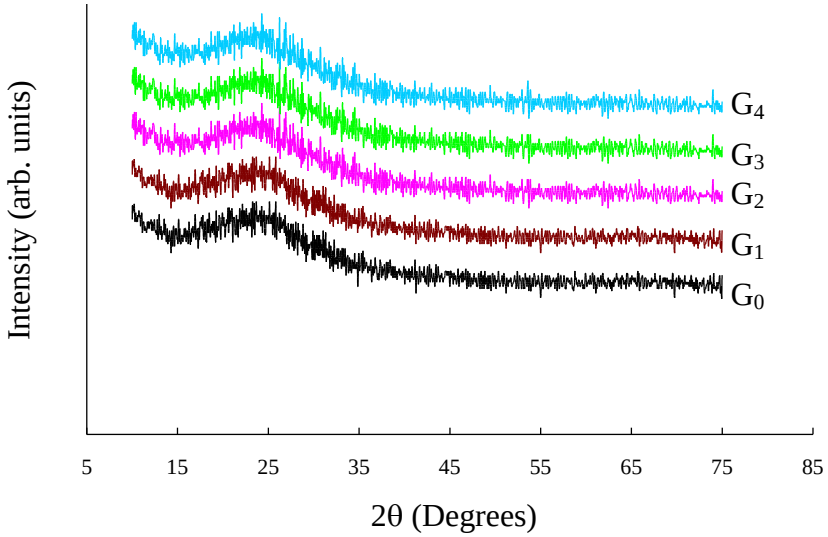

Fig.3.1. XRD pattern of Na_2O− B_2O_3: MnO glasses

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

Table 3.1 : Experimental data obtained from X-RD patterns

Sample Code	**Percent Crystallinity**	**Remark**
G_0	Nil	All Samples are amorphous in nature
G_1	Nil	
G_2	Nil	
G_3	Nil	
G_4	Nil	

3.3.2 Physical Parameters

Some physical variables that can be used to characterize Na_2O-B_2O_3: MnO glasses are calculated using the average molecular weight (M) and the measured value of density (d) [13]. Table 3.2 lists the physical characteristics of these glasses after evaluation.

Table 3.2 Data on Physical properties of $Na_2O- B_2O_3$: MnO glasses

Sample Code	Density d (g/cm^3)	Avg. Mol. wt	Mn^{2+} ion concentration N_I (10^{21}ions/cm^3)	Inter ionic distance R_I (nm)	Molar Volume cc/mol
G_0	2.422	68.08	....	..	28.11
G_1	2.436	68.174	4.31	0.61	27.98
G_2	2.451	68.261	8.65	0.48	27.84
G_3	2.465	68.348	13.01	0.42	27.72
G_4	2.480	68.434	17.51	0.38	27.59

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 27.59cc/mol as noted in a table. Increased in modifier contents introduce NBO containing borate triangles [14]. 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 [15, 16].

Variations in ρ and V_m of the glasses as a function of MnO content (x) are shown in Figure 3.2. The ρ increases up to 2.0 mol%, however, the V_m decrease. The observed variation up to 1.0 mol% MnO contents, is in contrary to one's expectation as the molecular weight of B_2O_3 and MnO are 69.61 g/mol and 86.93 g/mol, respectively and replacement of B_2O_3 by MnO is expected to increase the ρ and decrease the V_m. Observed variation in the above properties indicates that the MnO polyhedra form some new interconnections within the network up to 2.0 mol%. This indicates that up to 1.0 mol% MnO content, interconnections provided by MnO polyhedra are sufficient to overcome the depolymerization of borate network and result in increase in ρ and decrease in the V_m. The results of measurement also support the observation that glass structure becomes more stable and rigid up to 2.0 mol% MnO

3.2.3 Dielectric Properties

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 in Figures 3.3 and 3.4. 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. 3.3 & Fig.3.4).

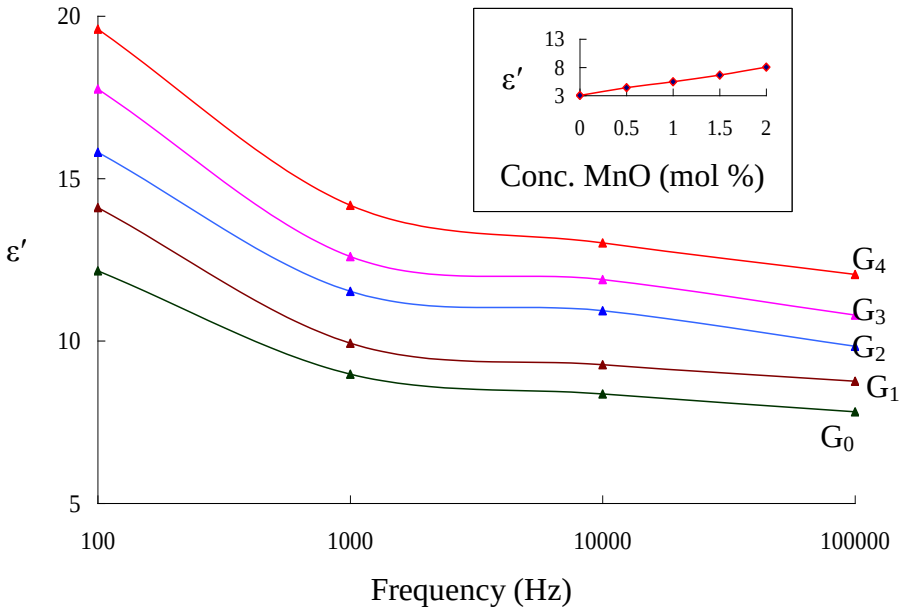

Fig.3.3. Variation of dielectric constant with frequency at room temperature of Na_2O - B_2O_3: MnO glasses. Inset represents the variation of tan δ with the concentration of MnO at 100 kHz.

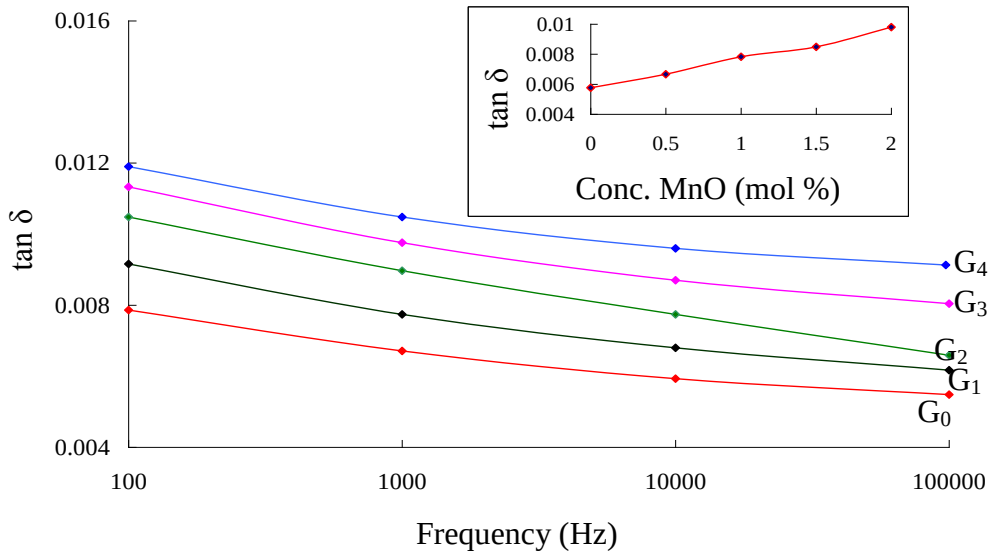

Fig.3.4. Variation of dielectric loss with frequency at room temperature of Na_2O -B_2O_3: MnO glasses. Inset represents the variation of tan δ with the concentration of MnO at 100 kHz.

The temperature dependence of Na_2O-B_2O_3 glasses doped with various amounts of MnO was recorded at 10 kHz, is shown as a comparison figure 3.5. 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 inset of Fig. 3.5.

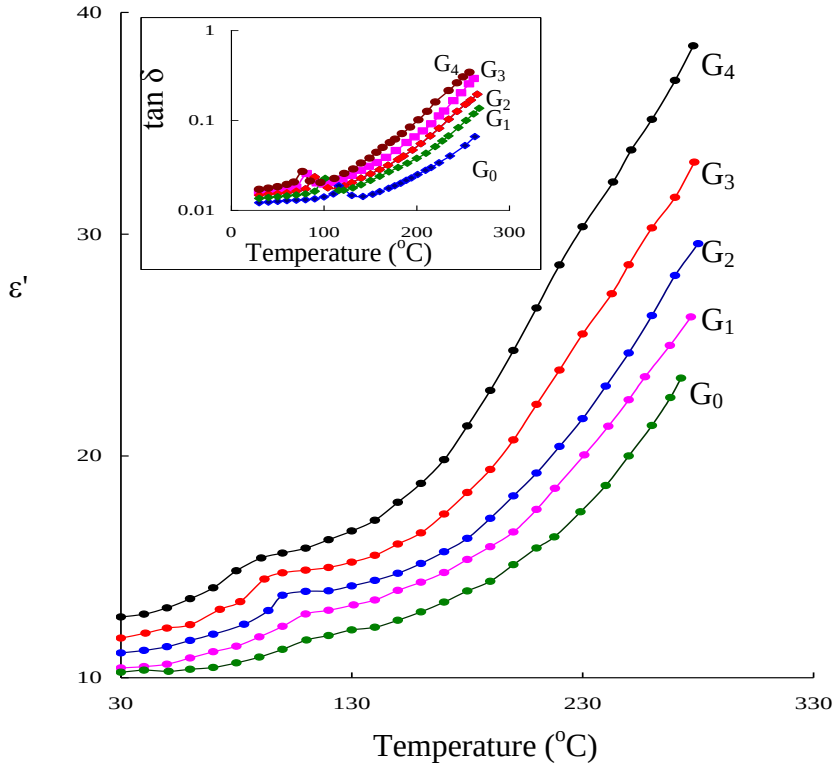

Fig. 3.5. Comparison plot of Variation of dielectric constant with temperature measured at 10 kHz for Na_2O -B_2O_3: MnO glasses. Inset represents the variation dielectric loss with temperature measured at 10 kHz

Table 3.3 summaries information on the dielectric constant and loss of Na_2O-B_2O_3: MnO glasses. With increasing temperature, the frequency maximum of the temperature dependent dielectric loss tan δ 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%.

Table 3.3 Data on dielectric properties of $Na_2O- B_2O_3$: MnO glasses

Glass	Temp (^oC)	Dielectric constant			Dielectric Loss		
		1kHz	10kHz	100kHz	1kHz	10kHz	100kHz
G_0	30	4.10	3.02	2.13	0.010	0.008	0.006
	100	6.34	4.73	3.10	0.014	0.010	0.008
	200	16.05	10.10	6.85	0.032	0.024	0.015
G_1	30	5.31	4.42	3.09	0.012	0.011	0.009
	100	7.09	6.13	4.72	0.017	0.013	0.010
	200	18.70	13.02	10.07	0.044	0.028	0.019
G_2	30	7.82	5.46	4.10	0.016	0.014	0.012
	100	9.67	7.20	5.92	0.026	0.019	0.016
	200	20.70	13.50	11.14	0.050	0.041	0.020
G_3	30	9.41	6.65	5.03	0.026	0.018	0.015
	100	11.03	9.12	7.86	0.032	0.021	0.017
	200	23.27	15.09	13.21	0.078	0.060	0.035
G_4	30	10.91	8.04	6.01	0.029	0.022	0.019
	100	13.81	10.08	8.10	0.053	0.036	0.024
	200	26.92	17.13	15.04	0.091	0.080	0.047

3.3 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 [17]. 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 [18, 19]. 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 [20, 21]. At higher frequencies, where this form of polarization reduces noticeably with frequency, the change in ε' and tan δ 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 δ 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 δ 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.

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Chapter – 4

Summary and Conclusions

This chapter contains a brief outline and conclusions drawn from the investigation carried out on physical and Dielectric properties of $Na_2O - B_2O_3$: MnO glasses. The outlines of of glass system are also presented.

Chapter -4

Summary and Conclusions

4.1 Summary

A systematic study on dielectric properties of manganese metal ions doped Na_2O-B_2O_3 glasses has been presented.

The compositions of the glasses used for the present study are:

$G_{0:}$ 20 Na_2O -80 B_2O_3

G_1: 20 Na_2O -79.50 B_2O_3: 0.5 MnO

$G_{2:}$ 20 Na_2O -79.00 B_2O_3: 1.0 MnO

$G_{3:}$ 20 Na_2O -78.50 B_2O_3: 1.5 MnO

$G_{4:}$ 20 Na_2O -78.00 B_2O_3: 2.0 MnO

The glasses were prepared by the usual melting, quenching and subsequent annealing techniques. Dielectric properties, viz., dielectric constant ε' and loss Tan δ in the frequency range 10^2 to 10^5 Hz and in the temperature range 30 to 300^o C were made

4.2 Conclusions

The main **conclusions drawn** from the results of above studies are:

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 G0 to G4 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.

Physical &Dielectric Studies of MnO doped Na_2O -B_2O_3 glasses

Dissertation submitted to
KRISHNA UNIVERSITY
Forthe partial fulfillment for the award of Degree of
MASTER OF SCIENCE IN PHYSICS

By
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September - 2023

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DECLARATION

I hereby declare that the work reported in this project entitled "***Physical and Dielectric properties of Na_2O– B_2O_3: MnOglasses***" is entirely original and was carried out by me independently in the Department of Physics,KRU Dr. MRAR College of Post Graduation StudiesNuzvid, under the supervision of **Dr. N. NarasimhaRao**. I further declare that this project has not been submitted for the award of any Degree or Diploma of any University or Institution.

S. Bhagya Sri

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KRISHNA UNIVERSITY

CERTIFICATE

This to certify that the present project entitled "***Physical and Dielectric properties of Na_2O–B_2O_3: MnO glasses***" submitted by **S. Bhagya Sri (Register No. Y21PHY245005)** towards the partial fulfillment for the award of degree of Master of Science in Physics to the KRU Dr. MRAR College of Post Graduation Studies Nuzvid, is a bonafide record of project work actually carried out by her under my guidance in the Physics Department of this institute. The results embodied in this project have not been submitted for any other degree or Diploma to any other university or institution.

16/9/2023

(Dr. N. Narasimha Rao)

Project Supervisor

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S. Bhagya Sri

Contents

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Chapter – 1

General Introduction Scope and Contents of present work

This chapter presents the general introduction, scope, contents and aim of the present work. In this chapter, the basic theory related to "Physical and Dielectric investigations on $Na_2O- B_2O_3$: MnO " glass system are presented systematically.

Chapter -1

1.1 General Introduction

Glass, one of the most ancient materials, has fascinated and attracted enormous interest both scientifically and technologically. This age-old material plays a key role in numerous applications like electronics [1], photonics [2], biomedicine [3], radioactive waste storage [4] and many others, along with classical ones like windows, architecture, lenses, containers etc. Glass which was earlier considered mainly an optical, dielectric material can now be used to make active devices like switches, memories, sensors, solar cells, catalysts etc [5]. These widespread uses reflect an ever increasing role of glass in our modern technical society and industry.

1.2 Definition of Glass

A glass is defined in ASTM [8] as 'an inorganic product of fusion, which has been cooled to rigid condition without crystallization'. According to this definition, a glass is a non- crystalline solid material obtained by a melt-quenching process. Glass is also defined as an amorphous/non-crystalline solid completely lacking in long-range periodicity and exhibit glass transition behavior [9,10]. The terms amorphous and non-crystalline are synonymous. The glass transition is a phenomenon in which a solid amorphous phase shows an abrupt change in the derivative thermodynamic properties from solid like to liquid like values with change of temperature. Nowadays, non-crystalline materials that can't be distinguished from melt-quenched glasses of the same

composition are obtainable by using various other techniques such as chemical vapor deposition, sol-gel process, etc. Therefore, most glass scientists regard the term 'glass' as covering 'all non-crystalline solids that show a glass transition' regardless of the preparation method. Glass is also defined as a configurationally frozen liquid which exhibits glass transition behavior [10].

From a thermodynamic point of view, the 'glassy' state is a meta-stable state and unlike crystalline state it is not unique. The 'glassy' state depends upon the thermal history of the melt and represents a local minimum in the free energy. Given adequate time, the system will relax to a more stable state, of lower free energy, provided the energy barrier separating these states can be crossed [11]. For practical purpose however, the time taken for relaxation of most everyday glasses is so long that the question of metastability is purely academic.

1.3 Glass Transition Phenomenon

The glass transition is an essential attribute of any glassy material. The glass transition phenomenon is quite complex and many theories have been suggested based on various parameters/properties, which characterize the glasses. These theories have been successful only to a limited extent as the glass transition is a function of many parameters like heat capacity, thermal conductivity, melting temperature, cooling rate etc. Significant variation in the value of glass transition temperature (T_g) has also been observed depending on the method used for its measurement. This is because when a melt is quenched to form a glass, the different degrees of freedom get arrested and

during heating these degrees of freedom start getting relaxed. These different degrees of freedom, corresponding to different properties, which are used to evaluate T_g, relax at different rates and result in different values of T_g being measured. When a liquid is cooled either crystallization may take place at the freezing point (or melting point 'T_m'), or else the liquid will become 'supercooled' for temperatures below T_m. This 'supercooled' liquid becomes more viscous with decreasing temperature. Although glass has atomic arrangement akin to liquid state, in terms of all other properties such as rigidity etc., glass is unequivocally a solid. This phenomenon can be understood readily by monitoring the changes in enthalpy/volume as a function of temperature (Figure1.1). The crystallization process is manifested by an abrupt change in extensive thermodynamic variables like enthalpy 'H' or volume 'V' at T_m, whereas glass formation is characterized by a gradual change in slope. The temperature range over which the change of slope occurs is called the 'glass-transformation range' [9,10]. As the transition of liquid to the glassy state is continuous, the T_g cannot be uniquely defined. However, for convenience the T_g is expressed as 'fictive' temperature 'T_f', the temperature obtained by intersection of the extrapolated liquid and glass curves (Figure 1.1). It depends on the rate of cooling of the supercooled liquid. The slower the rate of cooling, the larger is the region in which the liquid may retain supercooled state, implying lower T_f or T_g, as shown in Figure 1.1. Thus, the 'T_g' of a glass is not an intrinsic property but depends on its thermal history. Dependence of T_g on the cooling rate *q* is given as:

$$q = q_0 e^{\frac{1}{c}\left(\frac{1}{T_g} - \frac{1}{T_M}\right)} \qquad (1.1)$$

where c and q_o are constants. The experimentally measured value of T_g is not unique. The value of T_g depends on the time scale of the experiment used to observe it. The relaxation process is another very important aspect of glass transition. The configurational changes, which are responsible for the relaxation process, become increasingly slow as the temperature decreases. At T_g the material shows a solid like behaviour for observation time 't_0' which is smaller than the structural relaxation time 't_r'. For $t_r < t_0$, the material behaves like a liquid. A transition is said have taken place when the parameters corresponding to liquid like behaviour differ significantly from solid like ones, as in the case for heat capacity. In other words, T_g should occur when t_0 is equal or comparable to t_r.

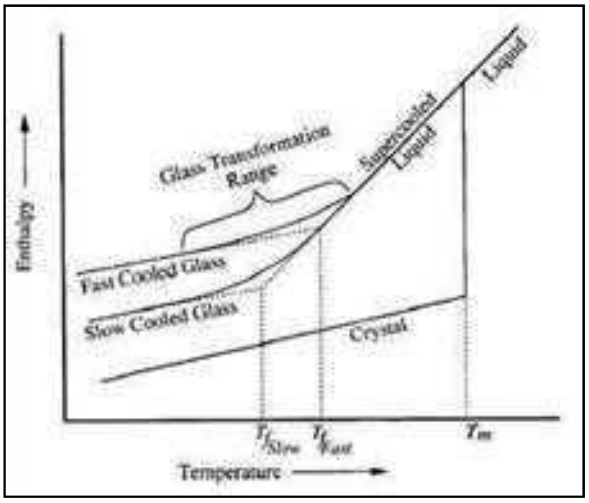

Figure 1.1: Variation in enthalpy or volume of a glass forming melt with the temperature.

The glass transition can also be expressed as a phenomenon in which a solid glassy phase shows abrupt change in the derivative thermodynamic properties such as heat capacity, thermal expansion coefficient (TEC) etc [10] at the transition

temperature. The order of a phase transition in Ehrenfest scheme is defined as the order of the lowest derivative of Gibbs free energy (G), which shows a discontinuity at the transition point. In liquid to crystal transition at freezing (or melting) temperature 'T_m' the volume 'V' and enthalpy 'H', which are the first derivative Gibbs free energy, are discontinuous. Hence, liquid to crystal transition is a first order transition. However, in liquid to glass transition, the thermodynamic variables such as volume, enthalpy and entropy are continuous and the quantities such as thermal expansion 'α_T' compressibility 'K_T' and heat capacity 'C_P', which are the second order derivative of Gibbs free energy, are discontinuous. Hence, the glass transition is a

manifestation of a second order phase transition [10].

1.4 Structural Aspects of Glasses

Good understanding of the structural arrangements of atoms in any material is a key factor to a detailed understanding of its physical and chemical properties. The structure of crystalline materials is well established and is classified according to structure of the unit cell. However,

the lack of symmetry and periodicity in amorphous materials make such approach inapplicable for them. Even though there is lack of long range periodic order, these materials often possess considerable structural order over length scale of many Á [12]. Therefore, a length scale may be arbitrarily defined, which separates microscopic structure frommacroscopic structure in amorphous solids [13].

Glass formation does not depend on the type of bonding. Besides the large class of inorganic glasses with mixed covalent ionic bonds there exist metallic glasses and

organic glasses with van der waals bonds. Therefore, determination of structure for every class of glass is a wide scientific field with a number of different theories and experimental methods to confirm them. The most important structural model for oxide glasses was proposed by Zachariasen [14] in 1932 based on continuous random network hypothesis. Continuous Random Network (CRN) model was based on the existence of the polyhedra that are linked together to form an overall random network. He suggested that the crystalline and the glassy form of an oxide should have the same type of oxygen polyhedra joined in a similar way except that in the glassy phase there is range of bond angles and bond lengths. Further, the network should be sufficiently flexible to incorporate the disorder, which is characteristic of the glassy phase, and the internal energy of both the crystalline and glassy phase should be comparable. The X-ray diffraction (XRD) studies carried out by Warren [15] supported this theory. The difference in structure of crystalline and glassy forms of a hypothetical two-dimensional oxide, say, A_2O_3 is shown in Figures 1.2(a) and 1.2(b).

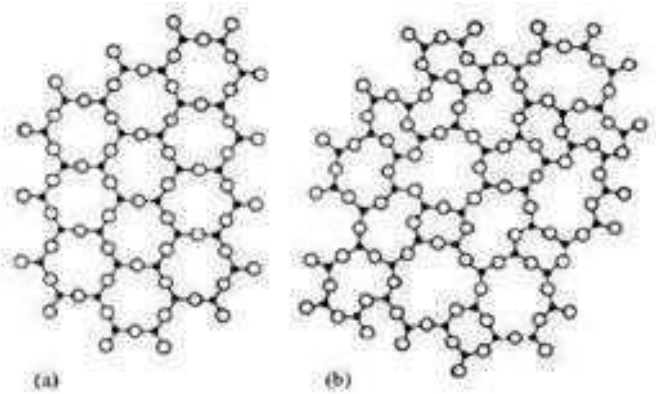

Figure 1.2: Atomic structural representation of a A_2O_3 crystal (a) and a A_2O_3 glass (b) (Filledcircles are A = cations and open circles are O = oxygen).

Thus, both the crystalline and the glassy forms are composed of AO_3 triangles

joinedto each other at corners, except that the glassy form has disorder introduced by changes in the A−O−A bond angles and A−O bond length. The triangles or O−A−O angles themselves need not be deformed much. According to the Zachariasen's CRN theory, the following criteria are valid for glass formation in simple compounds like SiO_2, B_2O_3, P_2O_5, GeO_2, As_2S_3, As_2Se_3, BeF_2, $ZnCl_2$ etc:

1. An oxide or compound tends to form a glass if it easily forms polyhedral groups as the smallest building units.
2. The cation polyhedra share only corners not edges or faces.
3. Anions (like O^{2-}, S^{2-}, Se^{2-}, F^{1-}, Cl^{1-},…) should not bind more than two central atoms (insimple glasses anions form bridges between two adjacent polyhedral).
4. The number of vertices of polyhedron should be less than six.
5. At least three vertices of a polyhedron must be shared with neighbouring polyhedral in order to form a three-dimensional (3D) network.

Zachariasen classified the cations in a glass as follows:

1. Network-formers (NWF) e.g. Si, B, P etc. with the coordination number 3 or 4.
2. Network-modifiers (NWM) e.g. Li, Na, Sr, Ba etc. with coordination numbers generally greater or equal to 6.
3. Intermediates that may either reinforce the network by cross-linking (coordination number 3 or 4) or weaken the network by depolymerization (coordination number 6-8).

1.5 Types of Glasses

Glasses have been broadly classified into two different ways. First one is based on the actual components present in them and second one, based on their end use.

Glasses based on silicate, phosphate, borate, borosilicate etc, networks belong to the first category; whereas optical glasses, sealing glasses, laser glasses etc, correspond to the second category. Other types of glasses include metallic glasses, halide glasses, organic glasses, mixed anion glasses, ionic glasses and chalcogenide glasses.

1.5.1 Borate glasses

Pure Borate glasses are difficult to prepare under normal conditions without any moisture content. Water free Borate glasses are prepared by Poch [16] by melting orthoboric acid for several hours at a pressure of 1 mm of Hg. Various structural studies carried out on pure borate glasses revealed that the structure of the glass agree well with the model proposed by Krogh-Moe [17]. According to this model B_2O_3 glasses mainly contain boroxol rings. The classic work of Krogh-Moe indicated the possible presence of 5 different types of borate species in the glass structure (Figure 1.6). Glass formation of B_2O_3 with various metal oxides has been extensively studied by various authors [18,19] and they have pointed out that some anomalous behaviour exists for these glasses. For example, in Na_2O-B_2O_3 system two separate regions of glass formation exists in the range of composition 28.5 to 33.5 mol% of B_2O_3 and 62 to 100 mol% of B_2O_3. The glass formation gap can however be removed by adding Al_2O_3 [20]. Structural aspects of binary borate glasses have been mainly investigated by ^{11}B, ^{10}B NQR

(Nuclear Quadrupole Resonance) and NMR techniques. Addition of Na_2O to B_2O_3 glass, up to 33 mol%, results in progressive conversion of trigonal boron structural units (BO_3) to tetrahedral boron structural units (BO_4). Above 33 mol% of

Na_2O, relative concentration of BO_4 structural units starteddecreasing [21].

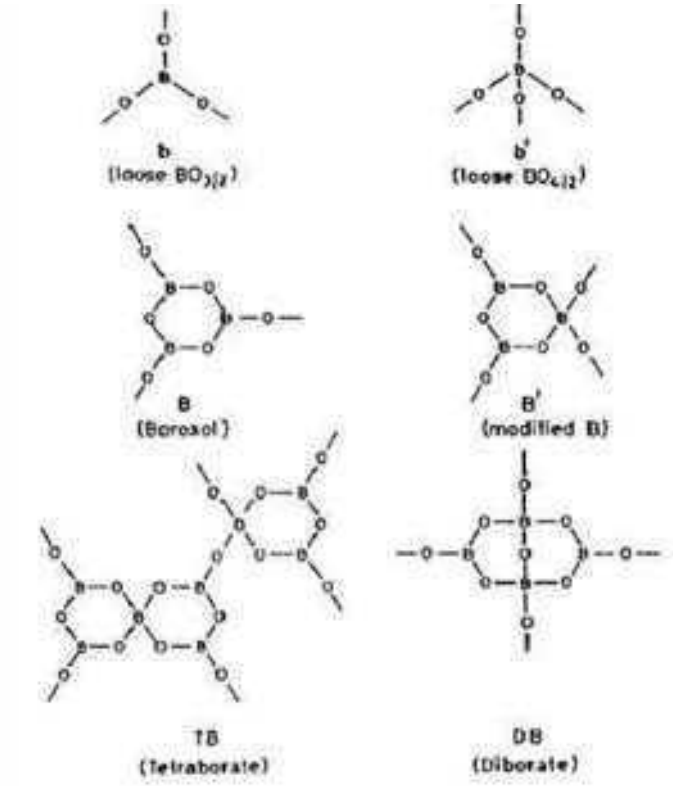

Figure 1.3: Possible borate species in the borate glass structure.

Borate glasses generally melt at lower temperatures and are frequently used as solder glasses. Primary requirement of solder glass is that, it needs to be a fluid at a temperature, which is well below the deformation temperature of the glass to be sealed. Borate glasses containing high concentration of rare earth oxides are used to manufacture lens systems with high numerical aperture and low spherical aberrations.

1.6 Scope of the Present Work

B_2O_3 glasses have attracted extensive investigation in recent years, in view of their potential applications in a number of solid state ionic devices. Several physical properties viz.,

electrical, optical, mechanical and magnetic properties of pure and various transition and rare earth metal ions doped alkali borate glasses have been under extensive investigation in recent years in view of their technological applications [22-28] especially in phosphors, lasers, solar energy converters and in a number of electronic devices. Alkali fluoro borate glasses are transparent from the near UV to the middle infrared region. They are resistant to atmospheric moisture and are capable of accepting large concentrations of transition metal ions.

The origin of the properties of alkali borate glasses has been strongly co-related to the local order around boron atoms. The coordination geometry of boron atoms has been shown to be strongly dependent on the composition of the glasses and on the chemical nature of the network modifier. For example the addition of alkali oxide like Na_2O is also expected to make the glasses more moisture resistant. It is well known that the effect of introduction of modifiers like Li_2O, Na_2O, K_2O, CaF_2 into B_2O_3 network is the conversion of sp^2 planar BO_3 units into more stable sp^3 tetrahedral BO_4 units and may also create non bridging oxygens. Each BO_4 unit is linked to two such other units and one oxygen from each unit with a metal ion and the structure leads to the formation of long chain tetrahedron.

Basic characteristics of borate glass structures are generally agreed upon. The fundamental building block in vitreous B_2O_3 is the BO_3 groups either as a random network of boroxol rings beside some fraction of BO_3 triangles connected by B-O-B linkages [29] (bridging forms). The boroxol group is composed of three corner –sharing BO_3 triangles which form a very highly planar ring. Recent studies concluded that [30] 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 addition of alkali oxides modifies the boroxol rings, complex borate groups with

one or two four coordinated boron atoms [31]. Alkali oxide is usually incorporated in to B_2O_3 glass ironically. The initial effect upon the introduction of alkali oxide in to B_2O_3 is the conversion of sp^2 planar BO_3 units in to more stable sp^3 tetrahedral BO_4 units there by preserving the B-O bonding without the creation of non-bridging oxygen (NBO) ions. The alkali borate glasses are composed of structural groupings (boroxol, tetra borate, diborate, metaborate, pyroborate, and ortho borate) present in the various crystal structures of the alkali borate compounds. The abundance and the type of structural units present depend upon the amount of alkali oxide incorporated in to the glass.

Transition metal ions are very interesting ions to probe in the glass network because their outer d-electron orbital functions have rather broad radial distributions and their responses to surrounding actions are very sensitive; as a result these ions influence the physical properties of the glasses to a substantial extent.

Manganese ion is an interesting transition metal ion because it exists in different valence states in different glass matrices, for example as Mn^{3+} in borate glasses with octahedral coordination whereas in silicate and germanate glasses it exists in Mn^{2+} with both octahedral and tetrahedral coordination [32]. Further, among different manganese ions, Mn^{2+} and Mn^{3+} are well known paramagnetic ions and Mn^{2+} and Mn^{4+} are identified as luminescence activators [33]. Mn^{2+} has the electronic configuration $3d^5$ which corresponds to a half filled d shell. Most Mn^{2+} complexes are octahedral and have a high spin arrangement with five unpaired electrons [34]. These ions subsist in different surroundings (ionic, covalent) in glass matrices. Further, it is also quite likely for manganese ions to have link with borate groups; strengthen its structure and may raise the chemical resistance of the glass. The content of manganese in different forms in different valence states exist in the glass

depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc. Hence, the connection between the state and the position of the manganese ion and the physical properties of the glass is expected to be highly interesting.

In view of these characteristics, manganese ions are expected to influence the physical properties Na_2O-B_2O_3 glasses and may have strong bearing on electrical and mechanical properties of the glasses. Therefore, it is felt important to have some understanding over the insulating properties of these glasses. The dielectric properties and the dependence of these properties on the composition, structure and on various external factors such as humidity, radiation effect, mechanical action etc., pave the way for estimating the insulating character and mechanical strength of the glasses and such studies will help to assess the suitability of these glasses for practical applications and also help in understanding the glass structure to some extent.

This chapter is therefore devoted to investigate the influence of Mn ions on the physical and dielectric properties of Na_2O-B_2O_3 glasses.

1.6.1 Physical Parameters

Some physical parameters useful for characterization Na_2O-B_2O_3: MnO glasses are estimated from the measured value of density (d) and the average molecular weight M, using the following equations [35]:

The transition metal ion concentration (N_i) in these glass matrices could be obtained from:

$$(i)\ N_i \ (10^{22}\ \text{ions}/\text{cm}^3) = \frac{N_A\, M \quad (\text{mol}\%)\, d}{\overline{M}} \qquad (1.1)$$

From the N_i values obtained, the polaron radius (r_p) and inter – ionic distance (r_i) of transition metal ions could be evaluated:

(ii) Polaron radius r_p (Å) $= \frac{1}{2}\left(\frac{\pi}{6N_i}\right)^{1/3}$ (1.2)

(iii) Inter – ionic distance r_i (Å) $= \left(\frac{1}{N_i}\right)^{1/3}$ (1.3)

The field strength (F_i) of transition metal ion in the glass matrix is described through the oxidation number (Z) and the ionic radii (r_p) of the transition metal ions by:

(iv) Field strength $F_i\,(cm^{-2}) = \frac{Z}{r_p^2}$ (1.4)

1.6.2 Dielectric Properties

When an insulating glass (a dielectric) likes Na_2O-B_2O_3: MnO glass is placed in an external electric field; two types of polarizations – the electronic and the ionic – are developed in the glass. If the dielectric contains permanent dipoles, they experience a torque in an applied field that tends to orient them in the field direction. Consequently, an orientation (or dipolar) polarization can arise. These three polarizations are due to charges locally bound in atoms, molecules or in the structures of solids (or liquids). Additionally to all these, generally there exist charge carriers that can migrate for some distance through the dielectric. Such charge carriers during their motion may be trapped in the material or on interfaces ; due to these causes, space charges and a microscopic field distortion result. Such a distortion appears as an increase in the capacitance of the sample and may be indistinguishable from a real rise of the dielectric constant. Thus a fourth polarization, called the space charge

polarization comes into play. The total polarization is sum of these four polarizations (assuming that they act independently) [36].

When the dielectric is placed in alternating fields, these polarizations are set up and the dielectric constant is a consequence of them; also a temporal phase shift is found to occur between the applied field and the resulting polarization and a loss current component appears, giving rise to the dielectric loss of the sample [37].

The complex dielectric constant, according to Debye for a material having permanent dipoles characterized by single relaxation time τ, given by:

$$\varepsilon^{*}(\omega) = \varepsilon_s + \frac{\varepsilon_s - \varepsilon}{1 + i\omega\ \tau} \qquad (1.5)$$

Where ε_s is the static dielectric constant and ε_∞ is the dielectric constant value of the material corresponding to its electronic and atomic polarization. Separating this equation into its real and imaginary parts, one obtains:

$$\varepsilon\ (\omega) = \frac{\varepsilon_s - \varepsilon}{1 + \omega^2\tau^2} \qquad (1.6)$$

and

$$\varepsilon\ \ (\omega) = \frac{(\varepsilon_s - \varepsilon\ \ )\omega\tau}{1 + \omega^2\tau^2} \qquad (1.7)$$

The dielectric loss of the material (generally expressed by tan δ) is given by the expression:

$$\tan\delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} = \frac{(\varepsilon_s - \varepsilon\ )\ \omega\tau}{\varepsilon_s + \varepsilon\ \ \omega^2\tau^2} \qquad (1.8)$$

If the conductivity (σ_{ac}) of the sample is also taken into account, it can be shown that

$$Tan\delta = \frac{4\pi\sigma}{\omega\varepsilon\ (\omega)} + \frac{(\varepsilon_s - \varepsilon\ )\omega\tau}{\varepsilon_s + \varepsilon\ \ \omega^2\tau^2} \qquad (1.9)$$

By plotting log (tan δ) as a function of log (ω), information regarding d.c conductivity as well as the behavior of the dipoles present if any can be obtained.

1.7 Aim of the Present Work

Increased demand on diverse applications of modern electronic devices has led to the search for new materials, which will meet the specific requirements. Addition of Na_2O into borate glass network expected to show significant improvement in chemical durability while maintaining low glass transformation temperature and softening points. Due to the possibility that a large variety of properties are adjustable by composition and excellent chemical durability close to that of window glasses, these glasses have potential applications in sealing as well as optical purposes. Though few studies on certain physical properties of some borate glasses are available in the recent years, a thorough survey of the literature on these glasses show that a detailed investigations on electrical properties of MnO doped Na_2O-B_2O_3 glasses in particular are not available. Study on the dielectric properties helps in estimating the insulating strength of these glasses and will also throw some light on the structural information of these glasses.

1.8 Contents of the present work

The glasses used for the present studies are:

$G_{0:}$ 20 Na_2O -80 B_2O_3

G_1: 20 Na_2O -79.50 B_2O_3: 0.5 MnO

$G_{2:}$ 20 Na_2O -79.00 B_2O_3: 1.0 MnO

$G_{3:}$ 20 Na_2O -78.50 B_2O_3: 1.5 MnO

$G_{4:}$ 20 Na_2O -78.00 B_2O_3: 2.0 MnO

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Chapter – 2

Experimental Methods

This chapter gives the description of experimental methods employed in the preparation and characterization of MnO doped $Na_2O- B_2O_3$ glasses. The details of the apparatus used for synthesizing the samples and the techniques adopted for measuring Physical and Dielectric are described in detail in this chapter.

hapter – 2

Experimental Methods

2.1 Introduction

In this chapter, a detailed description of the methods which used in the perpetration of Na_2O -B_2O_3: MnO glasses are presented. Various measurement techniques employed for determining density etc, are also discussed. The description of the apparatus used and detailed procedure for studying dielectric properties of Na_2O-B_2O_3 glasses are also included.

2. 2 Glass Preparation

Within the glass-forming region of Na_2O-B_2O_3: MnO glass system, the following particular compositions with successive increase in the concentration of MnO are chosen for the present study:

$G_{0:}$ 20 Na_2O -80 B_2O_3
G_1: 20 Na_2O -79.50 B_2O_3: 0.5 MnO
$G_{2:}$ 20 Na_2O -79.00 B_2O_3: 1.0 MnO
$G_{3:}$ 20 Na_2O -78.50 B_2O_3: 1.5 MnO
$G_{4:}$ 20 Na_2O -78.00 B_2O_3: 2.0 MnO

The glasses used for the present study were prepared by the melting and quenching techniques [1-3]. Appropriate amounts (all in mol %) of reagent grades of Na_2O, B_2O_3 and MnO powders were thoroughly mixed in an agate mortar and melted in a thick walled platinum crucible in the temperature range 900-950 ºC . The furnace used was a PID temperature controlled furnace (Fig. 2.1).

Fig. 2.1 Schematic images of PID controlled furnace and annealing chamber

The glasses were melted in a thick walled platinum crucible for an hour till a bubble free liquid was formed. The resultant melt was poured on a rectangular brass mould (having smooth polished inner surface) held at room temperature and subsequently annealed at 200 oC in another furnace. The weight of the glass obtained always agreed with that anticipated in the batch, with an error of 0.2 to 0.5 % wt loss in each case. The results indicate that the actual glass compositions are essentially equal to those based on the glass batch. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for present study are 1 cm x 1 cm x 0.2 cm. For dielectric and dielectric breakdown measurements thin coating of silver paint was applied on either side of the glasses, to serve as electrodes.

2.3 Physical Properties

The density (d) of the glasses was determined by the standard principle of Archimedis' using o-xylene (99.99 % pure) as the buoyant liquid. A direct reading balance (capacity 100 g, readability 0.1 mg) was used for weighing. The bulk glass was suspended on a very thin

copper strand kept in the immersion liquid container and weighed in the liquid and air.

Using density and average molecular weight, other physical parameters such as copper ion concentration N_i , the polaron radius r_P , the field strength F_i of these glasses are evaluated.

2.4 X-ray diffraction

The amorphous state of the prepared glasses was checked by X-ray diffraction spectra recorded on SEIFEERT Diffractometer Model SO – DEBYE FLUX 202 fitted with copper target and nickel filter operated at 40 kV, 30m A.

2.5 Dielectric Measurements

The dielectric measurements on the Na_2O-B_2O_3: MnO glasses were carried out on HP 4263B LCR Meter in the frequency range 10^2 - 10^5 Hz [4] in the temperature range 30 – 300^o C.

2.5.1 HP 4263 B LCR Meter

Capacitance measurements were made with HP 4263B LCR Meter. The HP 4263B LCR Meter is a fully automatic high performance test instrument used to measure a wide range of parameters .The measurement speed of the instrument is 29 ms, it has a very test quick recovery and got built in comparator. It can measure the capacitance to a high accuracy and wide measurement range, which allows us to make precise measurements at five frequencies 100 Hz, 120 Hz, 1 kHz, 10 kHz and 100 kHz. The two measurement display sections, capacitance (C) and dissipation factor (D) provide the direct read out of the parameters .The instrument has got two modes of measurement viz., normal mode and average mode; in normal mode operation the instrument performs measurements at very high

speed where as in the average mode it has short, medium or long range rate to average the measurement results. The second mode, adopted in the present measurements, gives a high reliable and repeatable value than in the normal mode of the measurement.

2. 5. 2 Sample Holders

Two different types of sample holders have been used for room and high temperature dielectric measurements:

I) For measurements at room temperature on HP 4263 B LCR Meter a laboratory made sample holder with teflon base and micrometer arrangement [Fig 2.2(a)] was used.

II) For the temperature variation of the dielectric properties at a fixed frequency the sample holder shown in Fig 2.2(b) has been used .

Fig. 2.2 (a) HP 4263 B LCR micrometer arrangement and **Fig 2.2(b)** Sample holder

The sample was put in between two silver electrodes and a 200 W nichrome heater heated the holder. Adjusting the current with a variac controlled the heating. The readings were taken when the sample attained the steady temperature. A chromel – alumel thermo-couple was attached to the sample holder vary near the sample. The thermo e.m.f. Developed across the junction was measured using digital PID temperature controller.

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Chapter – 3

The primary objective of this study is to characterize the Dielectric properties viz., Dielectric constant and Dielectric loss of $Na_2O- B_2O_3$: MnO glasses

Chapter -3

Physical &Dielectric Studies of MnO doped Na_2O -B_2O_3 glasses

3.1 Introduction

Study on radiation induced defect centers in glasses has been an interesting subject of investigation in recent years, since such studies help for examining the suitability of the glasses for radiation dosimetry applications. Extensive studies on the activating or killing effect of luminescence due to some transition metal ions like Fe2+, Cu2+, Ti4+etc, in amorphous materials are available in literature [1-2]. In recent years Pontuschka et al. have done a commendable work on thermo luminescence mechanisms in borate glasses [3]. Borate glasses are very advantageous materials for the radiation dosimetry applications in view of the fact that their effective atomic number is very close to that of human tissue. However, pure borate glasses have certain disadvantages to use in radiation dosimetry since they are highly hygroscopic and exhibit weak glow peak at relatively low temperatures. Alkali oxy borate glasses are considered as good materials for dosimetry applications since they are relatively moisture resistant when compared with the pure borate glasses.

Manganese ion, is yet an another interesting transition metal ion because it exists in different valence states in different glass matrices, for example in silicate and germanate glasses it exists in Mn^{2+} with both octahedral and tetrahedral coordination [4]. Further, among different manganese ions, Mn^{2+} and Mn^{3+} are well known paramagnetic ions and Mn^{2+} and Mn^{4+} are identified as luminescence activators [5]. Further, it is also quite likely for manganese ions to have link with borate groups; strengthen its structure and may raise the

chemical resistance of the glass. The content of manganese in different forms in different valence states exist in the glass depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc. Hence, the connection between the state and the position of the manganese ion and the physical properties of the glass is expected to be highly interesting.

Mn^{2+} has the electronic configuration $3d^5$ which corresponds to a half filled d shell. Most Mn^{2+} complexes are octahedral and have a high spin arrangement with five unpaired electrons [6]. In view of these characteristics, manganese ions are expected to influence the physical properties of Na_2O-B_2O_3 glasses and may have strong bearing on electrical and mechanical properties of the glasses.

A large number of interesting studies are available on the environment of manganese ion in various inorganic glass systems. These ions subsist in different surroundings (ionic, covalent) in glass matrices. Manganese ions seem to exist in Mn^{2+} and Mn^{3+} states in Na_2O-B_2O_3 glass network. The most probable local structure likely to occur for Mn^{3+} in these glasses is as a MnO_6 octahedron entwined with a BO_4 tetrahedron $MnBO_9$ where all the oxygens are bridging. The presence of such complexes obviously increases the stability of the glass network. Even though a number of recent investigations are available on the environment of manganese ions in a variety of inorganic glass systems [7-12], no dedicated studies are available on the influence of manganese ions on Na_2O - B_2O_3 glass systems in particular. This chapter is therefore devoted to investigate the influence of Mn ions on the structure and physical properties of Na_2O-B_2O_3 glasses.

Thus the clear objective of this chapter is to have a comprehensive understanding over the influence of manganese ions on physical and the insulating character of Na_2O–B_2O_3: MnO

glass system by a systematic study of dielectric properties (dielectric constant ε', loss and tan δ) over a moderately wide range of frequency and temperature. Glasses of the following composition are chosen for the present study:

$G_{0:}$ 20 Na_2O -80 B_2O_3

G_1: 20 Na_2O -79.50 B_2O_3: 0.5 MnO

$G_{2:}$ 20 Na_2O -79.00 B_2O_3: 1.0 MnO

$G_{3:}$ 20 Na_2O -78.50 B_2O_3: 1.5 MnO

$G_{4:}$ 20 Na_2O -78.000 B_2O_3: 2.0 MnO

3.2 Results

3.2.1 XRD

The glasses under investigation of X-RD patterns are shown in Fig. 3.1. 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 3.1).

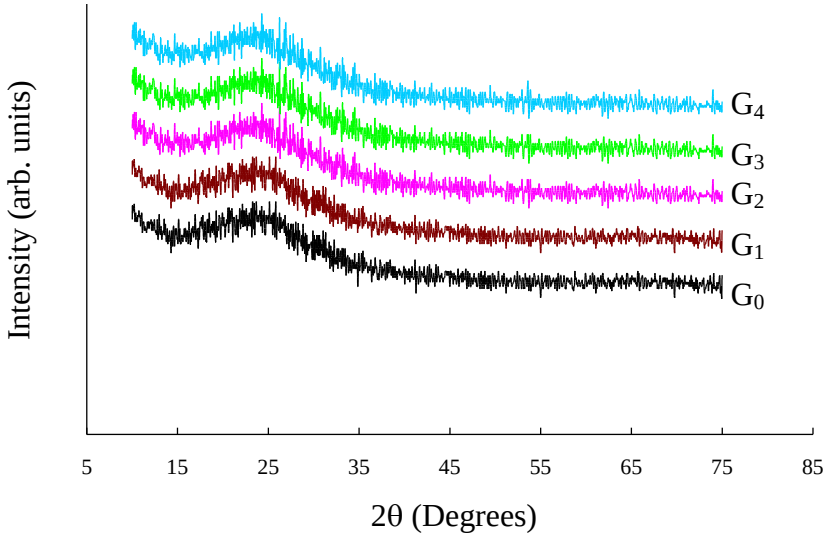

Fig.3.1. XRD pattern of Na_2O− B_2O_3: MnO glasses

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

Table 3.1 : Experimental data obtained from X-RD patterns

Sample Code	**Percent Crystallinity**	**Remark**
G_0	Nil	All Samples are amorphous in nature
G_1	Nil	
G_2	Nil	
G_3	Nil	
G_4	Nil	

3.3.2 Physical Parameters

Some physical variables that can be used to characterize Na_2O-B_2O_3: MnO glasses are calculated using the average molecular weight (M) and the measured value of density (d) [13]. Table 3.2 lists the physical characteristics of these glasses after evaluation.

Table 3.2 Data on Physical properties of $Na_2O- B_2O_3$: MnO glasses

Sample Code	Density d (g/cm^3)	Avg. Mol. wt	Mn^{2+} ion concentration N_I (10^{21}ions/cm^3)	Inter ionic distance R_I (nm)	Molar Volume cc/mol
G_0	2.422	68.08	....	..	28.11
G_1	2.436	68.174	4.31	0.61	27.98
G_2	2.451	68.261	8.65	0.48	27.84
G_3	2.465	68.348	13.01	0.42	27.72
G_4	2.480	68.434	17.51	0.38	27.59

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 27.59cc/mol as noted in a table. Increased in modifier contents introduce NBO containing borate triangles [14]. 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 [15, 16].

Variations in ρ and V_m of the glasses as a function of MnO content (x) are shown in Figure 3.2. The ρ increases up to 2.0 mol%, however, the V_m decrease. The observed variation up to 1.0 mol% MnO contents, is in contrary to one's expectation as the molecular weight of B_2O_3 and MnO are 69.61 g/mol and 86.93 g/mol, respectively and replacement of B_2O_3 by MnO is expected to increase the ρ and decrease the V_m. Observed variation in the above properties indicates that the MnO polyhedra form some new interconnections within the network up to 2.0 mol%. This indicates that up to 1.0 mol% MnO content, interconnections provided by MnO polyhedra are sufficient to overcome the depolymerization of borate network and result in increase in ρ and decrease in the V_m. The results of measurement also support the observation that glass structure becomes more stable and rigid up to 2.0 mol% MnO

3.2.3 Dielectric Properties

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 in Figures 3.3 and 3.4. 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. 3.3 & Fig.3.4).

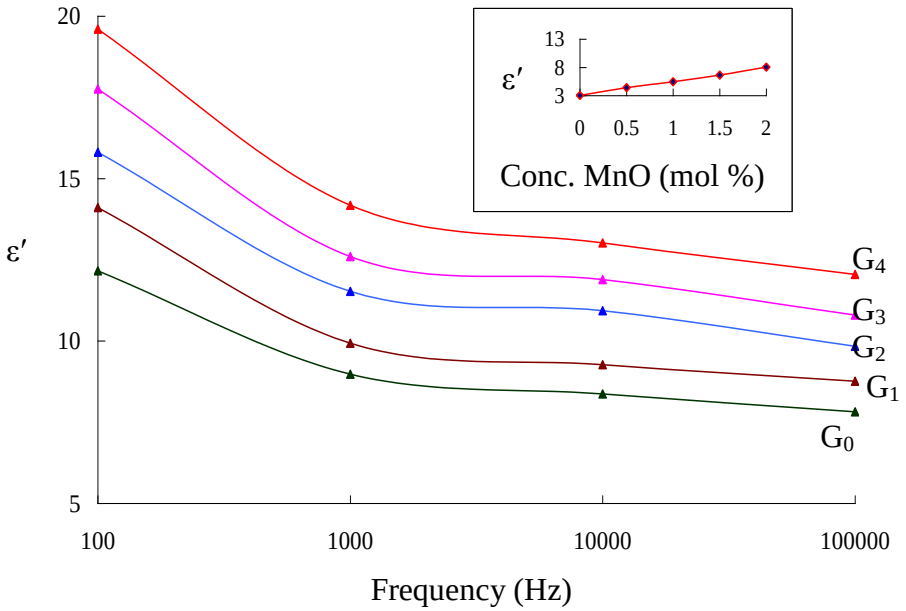

Fig.3.3. Variation of dielectric constant with frequency at room temperature of Na_2O - B_2O_3: MnO glasses. Inset represents the variation of tan δ with the concentration of MnO at 100 kHz.

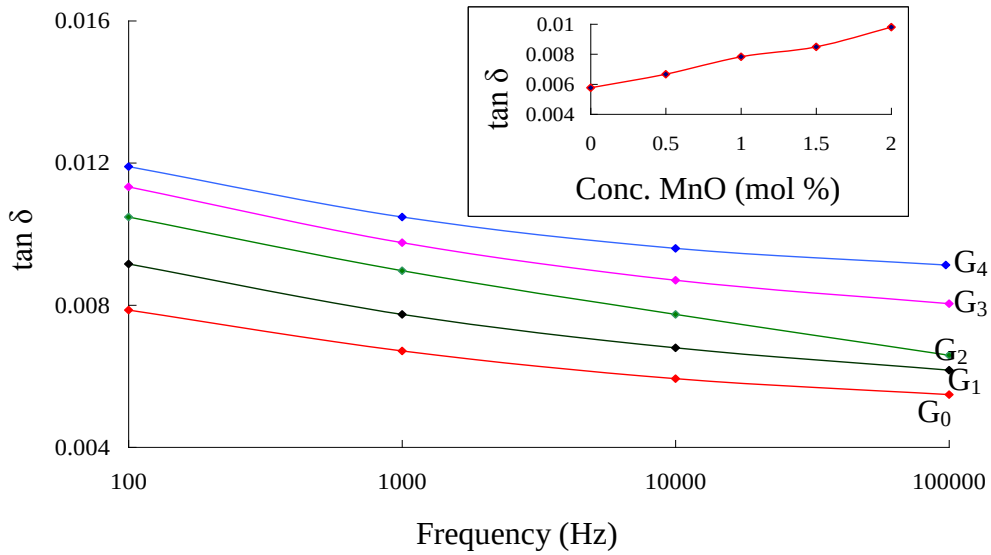

Fig.3.4. Variation of dielectric loss with frequency at room temperature of Na_2O -B_2O_3: MnO glasses. Inset represents the variation of tan δ with the concentration of MnO at 100 kHz.

The temperature dependence of Na_2O-B_2O_3 glasses doped with various amounts of MnO was recorded at 10 kHz, is shown as a comparison figure 3.5. 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 inset of Fig. 3.5.

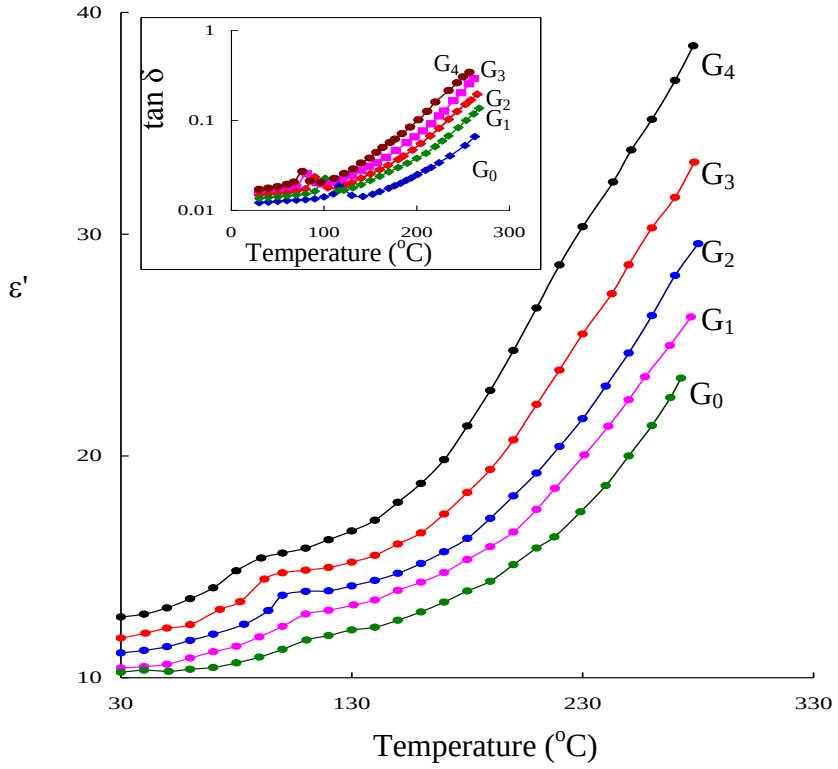

Fig. 3.5. Comparison plot of Variation of dielectric constant with temperature measured at 10 kHz for Na_2O -B_2O_3: MnO glasses. Inset represents the variation dielectric loss with temperature measured at 10 kHz

Table 3.3 summaries information on the dielectric constant and loss of Na_2O-B_2O_3: MnO glasses. With increasing temperature, the frequency maximum of the temperature dependent dielectric loss tan δ 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%.

Table 3.3 Data on dielectric properties of $Na_2O- B_2O_3$: MnO glasses

Glass	Temp (^oC)	Dielectric constant			Dielectric Loss		
		1kHz	10kHz	100kHz	1kHz	10kHz	100kHz
G_0	30	4.10	3.02	2.13	0.010	0.008	0.006
	100	6.34	4.73	3.10	0.014	0.010	0.008
	200	16.05	10.10	6.85	0.032	0.024	0.015
G_1	30	5.31	4.42	3.09	0.012	0.011	0.009
	100	7.09	6.13	4.72	0.017	0.013	0.010
	200	18.70	13.02	10.07	0.044	0.028	0.019
G_2	30	7.82	5.46	4.10	0.016	0.014	0.012
	100	9.67	7.20	5.92	0.026	0.019	0.016
	200	20.70	13.50	11.14	0.050	0.041	0.020
G_3	30	9.41	6.65	5.03	0.026	0.018	0.015
	100	11.03	9.12	7.86	0.032	0.021	0.017
	200	23.27	15.09	13.21	0.078	0.060	0.035
G_4	30	10.91	8.04	6.01	0.029	0.022	0.019
	100	13.81	10.08	8.10	0.053	0.036	0.024
	200	26.92	17.13	15.04	0.091	0.080	0.047

3.3 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 [17]. 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 [18, 19]. 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 [20, 21]. At higher frequencies, where this form of polarization reduces noticeably with frequency, the change in ε' and tan δ 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 δ 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 δ 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.

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Chapter – 4

Summary and Conclusions

This chapter contains a brief outline and conclusions drawn from the investigation carried out on physical and Dielectric properties of $Na_2O - B_2O_3$: MnO glasses. The outlines of of glass system are also presented.

Chapter -4

Summary and Conclusions

4.1 Summary

A systematic study on dielectric properties of manganese metal ions doped Na_2O-B_2O_3 glasses has been presented.

The compositions of the glasses used for the present study are:

$G_{0:}$ 20 Na_2O -80 B_2O_3

G_1: 20 Na_2O -79.50 B_2O_3: 0.5 MnO

$G_{2:}$ 20 Na_2O -79.00 B_2O_3: 1.0 MnO

$G_{3:}$ 20 Na_2O -78.50 B_2O_3: 1.5 MnO

$G_{4:}$ 20 Na_2O -78.00 B_2O_3: 2.0 MnO

The glasses were prepared by the usual melting, quenching and subsequent annealing techniques. Dielectric properties, viz., dielectric constant ε' and loss Tan δ in the frequency range 10^2 to 10^5 Hz and in the temperature range 30 to 300^o C were made

4.2 Conclusions

The main **conclusions drawn** from the results of above studies are:

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 G0 to G4 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.

Physical &Dielectric Studies of MnO doped Na_2O -B_2O_3 glasses

Dissertation submitted to
KRISHNA UNIVERSITY
For the partial fulfillment for the award of Degree of
MASTER OF SCIENCE IN PHYSICS

By
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NUZVID 521201

September - 2023

DECLARATION

I hereby declare that the work reported in this project entitled "***Physical and Dielectric properties of $Na_2O-B_2O_3:MnO$ glasses***" is entirely original and was carried out by me independently in the Department of Physics, KRU Dr. MRAR College of Post Graduation Studies Nuzvid, under the supervision of **Dr. N. Narasimha Rao**. I further declare that this project has not been submitted for the award of any Degree or Diploma of any University or Institution.

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CERTIFICATE

This to certify that the present project entitled "*Physical and Dielectric properties of Na_2O–B_2O_3: MnO glasses*" submitted by **M. Mahesh Babu (Register No. Y21PHY245003)** towards the partial fulfillment for the award of degree of Master of Science in Physics to the KRU Dr. MRAR College of Post Graduation Studies Nuzvid, is a bonafide record of project work actually carried out by him under my guidance in the Physics Department of this institute. The results embodied in this project have not been submitted for any other degree or Diploma to any other university or institution.

N. Rao

(Dr. N. Narasimha Rao)

Project Supervisor

16/9/2023

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M. Mahesh Babu

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Chapter – 1

General Introduction Scope and Contents of present work

This chapter presents the general introduction, scope, contents and aim of the present work. In this chapter, the basic theory related to "Physical and Dielectric investigations on $Na_2O- B_2O_3$: MnO " glass system are presented systematically.

Chapter -1

1.1 General Introduction

Glass, one of the most ancient materials, has fascinated and attracted enormous interest both scientifically and technologically. This age-old material plays a key role in numerous applications like electronics [1], photonics [2], biomedicine [3], radioactive waste storage [4] and many others, along with classical ones like windows, architecture, lenses, containers etc. Glass which was earlier considered mainly an optical, dielectric material can now be used to make active devices like switches, memories, sensors, solar cells, catalysts etc [5]. These widespread uses reflect an ever increasing role of glass in our modern technical society and industry.

1.2 Definition of Glass

A glass is defined in ASTM [8] as 'an inorganic product of fusion, which has been cooled to rigid condition without crystallization'. According to this definition, a glass is a non- crystalline solid material obtained by a melt-quenching process. Glass is also defined as an amorphous/non-crystalline solid completely lacking in long-range periodicity and exhibit glass transition behavior [9,10]. The terms amorphous and non-crystalline are synonymous. The glass transition is a phenomenon in which a solid amorphous phase shows an abrupt change in the derivative thermodynamic properties from solid like to liquid like values with change of temperature. Nowadays, non-crystalline materials that can't be distinguished from melt-quenched glasses of the same

composition are obtainable by using various other techniques such as chemical vapor deposition, sol-gel process, etc. Therefore, most glass scientists regard the term 'glass' as covering 'all non-crystalline solids that show a glass transition' regardless of the preparation method. Glass is also defined as a configurationally frozen liquid which exhibits glass transition behavior [10].

From a thermodynamic point of view, the 'glassy' state is a meta-stable state and unlike crystalline state it is not unique. The 'glassy' state depends upon the thermal history of the melt and represents a local minimum in the free energy. Given adequate time, the system will relax to a more stable state, of lower free energy, provided the energy barrier separating these states can be crossed [11]. For practical purpose however, the time taken for relaxation of most everyday glasses is so long that the question of metastability is purely academic.

1.3 Glass Transition Phenomenon

The glass transition is an essential attribute of any glassy material. The glass transition phenomenon is quite complex and many theories have been suggested based on various parameters/properties, which characterize the glasses. These theories have been successful only to a limited extent as the glass transition is a function of many parameters like heat capacity, thermal conductivity, melting temperature, cooling rate etc. Significant variation in the value of glass transition temperature (T_g) has also been observed depending on the method used for its measurement. This is because when a melt is quenched to form a glass, the different degrees of freedom get arrested and

during heating these degrees of freedom start getting relaxed. These different degrees of freedom, corresponding to different properties, which are used to evaluate T_g, relax at different rates and result in different values of T_g being measured. When a liquid is cooled either crystallization may take place at the freezing point (or melting point 'T_m'), or else the liquid will become 'supercooled' for temperatures below T_m. This 'supercooled' liquid becomes more viscous with decreasing temperature. Although glass has atomic arrangement akin to liquid state, in terms of all other properties such as rigidity etc., glass is unequivocally a solid. This phenomenon can be understood readily by monitoring the changes in enthalpy/volume as a function of temperature (Figure1.1). The crystallization process is manifested by an abrupt change in extensive thermodynamic variables like enthalpy 'H' or volume 'V' at T_m, whereas glass formation is characterized by a gradual change in slope. The temperature range over which the change of slope occurs is called the 'glass-transformation range' [9,10]. As the transition of liquid to the glassy state is continuous, the T_g cannot be uniquely defined. However, for convenience the T_g is expressed as 'fictive' temperature 'T_f', the temperature obtained by intersection of the extrapolated liquid and glass curves (Figure 1.1). It depends on the rate of cooling of the supercooled liquid. The slower the rate of cooling, the larger is the region in which the liquid may retain supercooled state, implying lower T_f or T_g, as shown in Figure 1.1. Thus, the 'T_g' of a glass is not an intrinsic property but depends on its thermal history. Dependence of T_g on the cooling rate *q* is given as:

$$q = q_0 e^{\frac{1}{c}\left(\frac{1}{T_g} - \frac{1}{T_M}\right)} \qquad (1.1)$$

where c and q_o are constants. The experimentally measured value of T_g is not unique. The value of T_g depends on the time scale of the experiment used to observe it. The relaxation process is another very important aspect of glass transition. The configurational changes, which are responsible for the relaxation process, become increasingly slow as the temperature decreases. At T_g the material shows a solid like behaviour for observation time 't_0' which is smaller than the structural relaxation time 't_r'. For $t_r < t_0$, the material behaves like a liquid. A transition is said have taken place when the parameters corresponding to liquid like behaviour differ significantly from solid like ones, as in the case for heat capacity. In other words, T_g should occur when t_0 is equal or comparable to t_r.

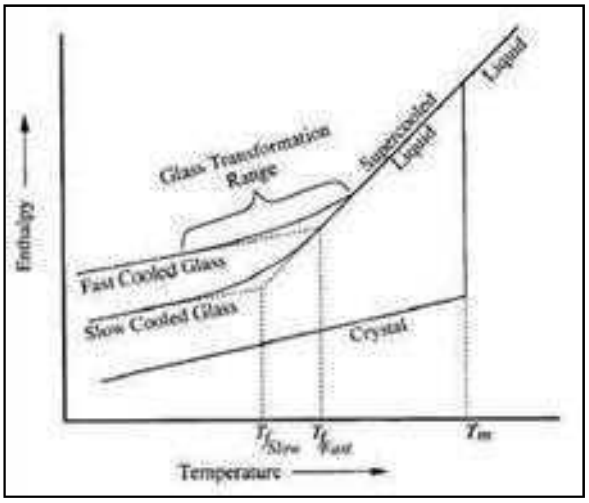

Figure 1.1: Variation in enthalpy or volume of a glass forming melt with the temperature.

The glass transition can also be expressed as a phenomenon in which a solid glassy phase shows abrupt change in the derivative thermodynamic properties such as heat capacity, thermal expansion coefficient (TEC) etc [10] at the transition

temperature. The order of a phase transition in Ehrenfest scheme is defined as the order of the lowest derivative of Gibbs free energy (G), which shows a discontinuity at the transition point. In liquid to crystal transition at freezing (or melting) temperature 'T_m' the volume 'V' and enthalpy 'H', which are the first derivative Gibbs free energy, are discontinuous. Hence, liquid to crystal transition is a first order transition. However, in liquid to glass transition, the thermodynamic variables such as volume, enthalpy and entropy are continuous and the quantities such as thermal expansion 'α_T' compressibility 'K_T' and heat capacity 'C_P', which are the second order derivative of Gibbs free energy, are discontinuous. Hence, the glass transition is a

manifestation of a second order phase transition [10].

1.4 Structural Aspects of Glasses

Good understanding of the structural arrangements of atoms in any material is a key factor to a detailed understanding of its physical and chemical properties. The structure of crystalline materials is well established and is classified according to structure of the unit cell. However,

the lack of symmetry and periodicity in amorphous materials make such approach inapplicable for them. Even though there is lack of long range periodic order, these materials often possess considerable structural order over length scale of many Á [12]. Therefore, a length scale may be arbitrarily defined, which separates microscopic structure frommacroscopic structure in amorphous solids [13].

Glass formation does not depend on the type of bonding. Besides the large class of inorganic glasses with mixed covalent ionic bonds there exist metallic glasses and

organic glasses with van der waals bonds. Therefore, determination of structure for every class of glass is a wide scientific field with a number of different theories and experimental methods to confirm them. The most important structural model for oxide glasses was proposed by Zachariasen [14] in 1932 based on continuous random network hypothesis. Continuous Random Network (CRN) model was based on the existence of the polyhedra that are linked together to form an overall random network. He suggested that the crystalline and the glassy form of an oxide should have the same type of oxygen polyhedra joined in a similar way except that in the glassy phase there is range of bond angles and bond lengths. Further, the network should be sufficiently flexible to incorporate the disorder, which is characteristic of the glassy phase, and the internal energy of both the crystalline and glassy phase should be comparable. The X-ray diffraction (XRD) studies carried out by Warren [15] supported this theory. The difference in structure of crystalline and glassy forms of a hypothetical two-dimensional oxide, say, A_2O_3 is shown in Figures 1.2(a) and 1.2(b).

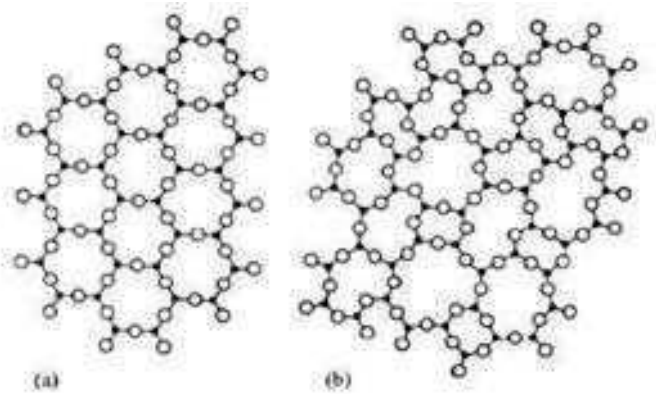

Figure 1.2: Atomic structural representation of a A_2O_3 crystal (a) and a A_2O_3 glass (b) (Filledcircles are A = cations and open circles are O = oxygen).

Thus, both the crystalline and the glassy forms are composed of AO_3 triangles

joinedto each other at corners, except that the glassy form has disorder introduced by changes in the A−O−A bond angles and A−O bond length. The triangles or O−A−O angles themselves need not be deformed much. According to the Zachariasen's CRN theory, the following criteria are valid for glass formation in simple compounds like SiO_2, B_2O_3, P_2O_5, GeO_2, As_2S_3, As_2Se_3, BeF_2, $ZnCl_2$ etc:

1. An oxide or compound tends to form a glass if it easily forms polyhedral groups as the smallest building units.
2. The cation polyhedra share only corners not edges or faces.
3. Anions (like O^{2-}, S^{2-}, Se^{2-}, F^{1-}, Cl^{1-},…) should not bind more than two central atoms (insimple glasses anions form bridges between two adjacent polyhedral).
4. The number of vertices of polyhedron should be less than six.
5. At least three vertices of a polyhedron must be shared with neighbouring polyhedral in order to form a three-dimensional (3D) network.

Zachariasen classified the cations in a glass as follows:

1. Network-formers (NWF) e.g. Si, B, P etc. with the coordination number 3 or 4.
2. Network-modifiers (NWM) e.g. Li, Na, Sr, Ba etc. with coordination numbers generally greater or equal to 6.
3. Intermediates that may either reinforce the network by cross-linking (coordination number 3 or 4) or weaken the network by depolymerization (coordination number 6-8).

1.5 Types of Glasses

Glasses have been broadly classified into two different ways. First one is based on the actual components present in them and second one, based on their end use.

Glasses based on silicate, phosphate, borate, borosilicate etc, networks belong to the first category; whereas optical glasses, sealing glasses, laser glasses etc, correspond to the second category. Other types of glasses include metallic glasses, halide glasses, organic glasses, mixed anion glasses, ionic glasses and chalcogenide glasses.

1.5.1 Borate glasses

Pure Borate glasses are difficult to prepare under normal conditions without any moisture content. Water free Borate glasses are prepared by Poch [16] by melting orthoboric acid for several hours at a pressure of 1 mm of Hg. Various structural studies carried out on pure borate glasses revealed that the structure of the glass agree well with the model proposed by Krogh-Moe [17]. According to this model B_2O_3 glasses mainly contain boroxol rings. The classic work of Krogh-Moe indicated the possible presence of 5 different types of borate species in the glass structure (Figure 1.6). Glass formation of B_2O_3 with various metal oxides has been extensively studied by various authors [18,19] and they have pointed out that some anomalous behaviour exists for these glasses. For example, in Na_2O-B_2O_3 system two separate regions of glass formation exists in the range of composition 28.5 to 33.5 mol% of B_2O_3 and 62 to 100 mol% of B_2O_3. The glass formation gap can however be removed by adding Al_2O_3 [20]. Structural aspects of binary borate glasses have been mainly investigated by ^{11}B, ^{10}B NQR

(Nuclear Quadrupole Resonance) and NMR techniques. Addition of Na_2O to B_2O_3 glass, up to 33 mol%, results in progressive conversion of trigonal boron structural units (BO_3) to tetrahedral boron structural units (BO_4). Above 33 mol% of

Na_2O, relative concentration of BO_4 structural units starteddecreasing [21].

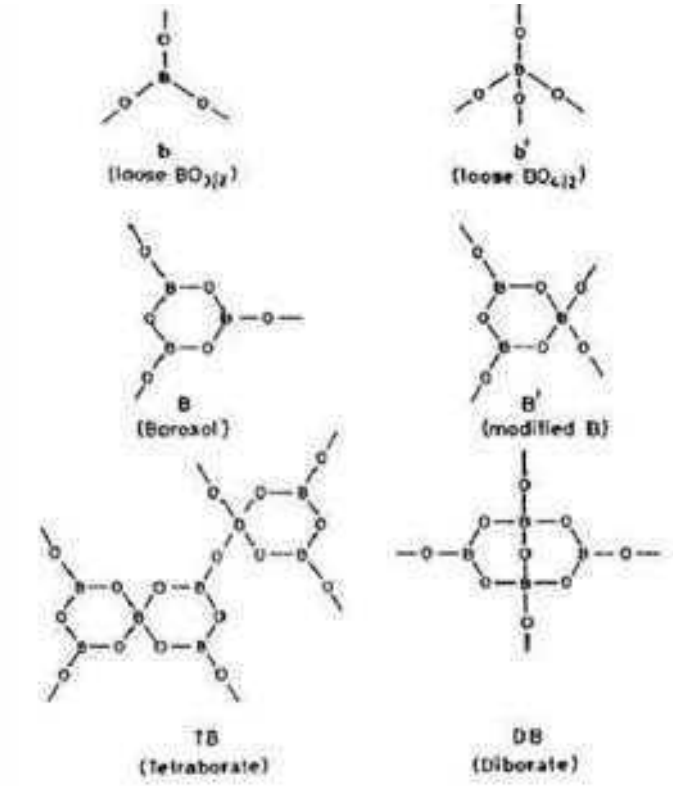

Figure 1.3: Possible borate species in the borate glass structure.

Borate glasses generally melt at lower temperatures and are frequently used as solder glasses. Primary requirement of solder glass is that, it needs to be a fluid at a temperature, which is well below the deformation temperature of the glass to be sealed. Borate glasses containing high concentration of rare earth oxides are used to manufacture lens systems with high numerical aperture and low spherical aberrations.

1.6 Scope of the Present Work

B_2O_3 glasses have attracted extensive investigation in recent years, in view of their potential applications in a number of solid state ionic devices. Several physical properties viz.,

electrical, optical, mechanical and magnetic properties of pure and various transition and rare earth metal ions doped alkali borate glasses have been under extensive investigation in recent years in view of their technological applications [22-28] especially in phosphors, lasers, solar energy converters and in a number of electronic devices. Alkali fluoro borate glasses are transparent from the near UV to the middle infrared region. They are resistant to atmospheric moisture and are capable of accepting large concentrations of transition metal ions.

The origin of the properties of alkali borate glasses has been strongly co-related to the local order around boron atoms. The coordination geometry of boron atoms has been shown to be strongly dependent on the composition of the glasses and on the chemical nature of the network modifier. For example the addition of alkali oxide like Na_2O is also expected to make the glasses more moisture resistant. It is well known that the effect of introduction of modifiers like Li_2O, Na_2O, K_2O, CaF_2 into B_2O_3 network is the conversion of sp^2 planar BO_3 units into more stable sp^3 tetrahedral BO_4 units and may also create non bridging oxygens. Each BO_4 unit is linked to two such other units and one oxygen from each unit with a metal ion and the structure leads to the formation of long chain tetrahedron.

Basic characteristics of borate glass structures are generally agreed upon. The fundamental building block in vitreous B_2O_3 is the BO_3 groups either as a random network of boroxol rings beside some fraction of BO_3 triangles connected by B-O-B linkages [29] (bridging forms). The boroxol group is composed of three corner –sharing BO_3 triangles which form a very highly planar ring. Recent studies concluded that [30] 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 addition of alkali oxides modifies the boroxol rings, complex borate groups with

one or two four coordinated boron atoms [31]. Alkali oxide is usually incorporated in to B_2O_3 glass ironically. The initial effect upon the introduction of alkali oxide in to B_2O_3 is the conversion of sp^2 planar BO_3 units in to more stable sp^3 tetrahedral BO_4 units there by preserving the B-O bonding without the creation of non-bridging oxygen (NBO) ions. The alkali borate glasses are composed of structural groupings (boroxol, tetra borate, diborate, metaborate, pyroborate, and ortho borate) present in the various crystal structures of the alkali borate compounds. The abundance and the type of structural units present depend upon the amount of alkali oxide incorporated in to the glass.

Transition metal ions are very interesting ions to probe in the glass network because their outer d-electron orbital functions have rather broad radial distributions and their responses to surrounding actions are very sensitive; as a result these ions influence the physical properties of the glasses to a substantial extent.

Manganese ion is an interesting transition metal ion because it exists in different valence states in different glass matrices, for example as Mn^{3+} in borate glasses with octahedral coordination whereas in silicate and germanate glasses it exists in Mn^{2+} with both octahedral and tetrahedral coordination [32]. Further, among different manganese ions, Mn^{2+} and Mn^{3+} are well known paramagnetic ions and Mn^{2+} and Mn^{4+} are identified as luminescence activators [33]. Mn^{2+} has the electronic configuration $3d^5$ which corresponds to a half filled d shell. Most Mn^{2+} complexes are octahedral and have a high spin arrangement with five unpaired electrons [34]. These ions subsist in different surroundings (ionic, covalent) in glass matrices. Further, it is also quite likely for manganese ions to have link with borate groups; strengthen its structure and may raise the chemical resistance of the glass. The content of manganese in different forms in different valence states exist in the glass

depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc. Hence, the connection between the state and the position of the manganese ion and the physical properties of the glass is expected to be highly interesting.

In view of these characteristics, manganese ions are expected to influence the physical properties Na_2O-B_2O_3 glasses and may have strong bearing on electrical and mechanical properties of the glasses. Therefore, it is felt important to have some understanding over the insulating properties of these glasses. The dielectric properties and the dependence of these properties on the composition, structure and on various external factors such as humidity, radiation effect, mechanical action etc., pave the way for estimating the insulating character and mechanical strength of the glasses and such studies will help to assess the suitability of these glasses for practical applications and also help in understanding the glass structure to some extent.

This chapter is therefore devoted to investigate the influence of Mn ions on the physical and dielectric properties of Na_2O-B_2O_3 glasses.

1.6.1 Physical Parameters

Some physical parameters useful for characterization Na_2O-B_2O_3: MnO glasses are estimated from the measured value of density (d) and the average molecular weight M, using the following equations [35]:

The transition metal ion concentration (N_i) in these glass matrices could be obtained from:

$$(i)\ N_i \ (10^{22}\ \text{ions}/\text{cm}^3) = \frac{N_A\, M \quad (\text{mol}\%)\, d}{\overline{M}} \qquad (1.1)$$

From the N_i values obtained, the polaron radius (r_p) and inter – ionic distance (r_i) of transition metal ions could be evaluated:

(ii) Polaron radius r_p (Å) $= \frac{1}{2}\left(\frac{\pi}{6N_i}\right)^{1/3}$ (1.2)

(iii) Inter – ionic distance r_i (Å) $= \left(\frac{1}{N_i}\right)^{1/3}$ (1.3)

The field strength (F_i) of transition metal ion in the glass matrix is described through the oxidation number (Z) and the ionic radii (r_p) of the transition metal ions by:

(iv) Field strength $F_i\,(cm^{-2}) = \frac{Z}{r_p^2}$ (1.4)

1.6.2 Dielectric Properties

When an insulating glass (a dielectric) likes Na_2O-B_2O_3: MnO glass is placed in an external electric field; two types of polarizations – the electronic and the ionic – are developed in the glass. If the dielectric contains permanent dipoles, they experience a torque in an applied field that tends to orient them in the field direction. Consequently, an orientation (or dipolar) polarization can arise. These three polarizations are due to charges locally bound in atoms, molecules or in the structures of solids (or liquids). Additionally to all these, generally there exist charge carriers that can migrate for some distance through the dielectric. Such charge carriers during their motion may be trapped in the material or on interfaces ; due to these causes, space charges and a microscopic field distortion result. Such a distortion appears as an increase in the capacitance of the sample and may be indistinguishable from a real rise of the dielectric constant. Thus a fourth polarization, called the space charge

polarization comes into play. The total polarization is sum of these four polarizations (assuming that they act independently) [36].

When the dielectric is placed in alternating fields, these polarizations are set up and the dielectric constant is a consequence of them; also a temporal phase shift is found to occur between the applied field and the resulting polarization and a loss current component appears, giving rise to the dielectric loss of the sample [37].

The complex dielectric constant, according to Debye for a material having permanent dipoles characterized by single relaxation time τ, given by:

$$\varepsilon^{*}(\omega) = \varepsilon_s + \frac{\varepsilon_s - \varepsilon}{1 + i\omega\ \tau} \qquad (1.5)$$

Where ε_s is the static dielectric constant and ε_∞ is the dielectric constant value of the material corresponding to its electronic and atomic polarization. Separating this equation into its real and imaginary parts, one obtains:

$$\varepsilon\ (\omega) = \frac{\varepsilon_s - \varepsilon}{1 + \omega^2\tau^2} \qquad (1.6)$$

and

$$\varepsilon\ \ (\omega) = \frac{(\varepsilon_s - \varepsilon\ \ )\omega\tau}{1 + \omega^2\tau^2} \qquad (1.7)$$

The dielectric loss of the material (generally expressed by tan δ) is given by the expression:

$$\tan\delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} = \frac{(\varepsilon_s - \varepsilon\ )\ \omega\tau}{\varepsilon_s + \varepsilon\ \ \omega^2\tau^2} \qquad (1.8)$$

If the conductivity (σ_{ac}) of the sample is also taken into account, it can be shown that

$$Tan\delta = \frac{4\pi\sigma}{\omega\varepsilon\ (\omega)} + \frac{(\varepsilon_s - \varepsilon\ )\omega\tau}{\varepsilon_s + \varepsilon\ \ \omega^2\tau^2} \qquad (1.9)$$

By plotting log (tan δ) as a function of log (ω), information regarding d.c conductivity as well as the behavior of the dipoles present if any can be obtained.

1.7 Aim of the Present Work

Increased demand on diverse applications of modern electronic devices has led to the search for new materials, which will meet the specific requirements. Addition of Na_2O into borate glass network expected to show significant improvement in chemical durability while maintaining low glass transformation temperature and softening points. Due to the possibility that a large variety of properties are adjustable by composition and excellent chemical durability close to that of window glasses, these glasses have potential applications in sealing as well as optical purposes. Though few studies on certain physical properties of some borate glasses are available in the recent years, a thorough survey of the literature on these glasses show that a detailed investigations on electrical properties of MnO doped Na_2O-B_2O_3 glasses in particular are not available. Study on the dielectric properties helps in estimating the insulating strength of these glasses and will also throw some light on the structural information of these glasses.

1.8 Contents of the present work

The glasses used for the present studies are:

$G_{0:}$ 20 Na_2O -80 B_2O_3

G_1: 20 Na_2O -79.50 B_2O_3: 0.5 MnO

$G_{2:}$ 20 Na_2O -79.00 B_2O_3: 1.0 MnO

$G_{3:}$ 20 Na_2O -78.50 B_2O_3: 1.5 MnO

$G_{4:}$ 20 Na_2O -78.00 B_2O_3: 2.0 MnO

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Chapter – 2

Experimental Methods

This chapter gives the description of experimental methods employed in the preparation and characterization of MnO doped $Na_2O- B_2O_3$ glasses. The details of the apparatus used for synthesizing the samples and the techniques adopted for measuring Physical and Dielectric are described in detail in this chapter.

hapter – 2

Experimental Methods

2.1 Introduction

In this chapter, a detailed description of the methods which used in the perpetration of Na_2O -B_2O_3: MnO glasses are presented. Various measurement techniques employed for determining density etc, are also discussed. The description of the apparatus used and detailed procedure for studying dielectric properties of Na_2O-B_2O_3 glasses are also included.

2. 2 Glass Preparation

Within the glass-forming region of Na_2O-B_2O_3: MnO glass system, the following particular compositions with successive increase in the concentration of MnO are chosen for the present study:

$G_{0:}$ 20 Na_2O -80 B_2O_3
G_1: 20 Na_2O -79.50 B_2O_3: 0.5 MnO
$G_{2:}$ 20 Na_2O -79.00 B_2O_3: 1.0 MnO
$G_{3:}$ 20 Na_2O -78.50 B_2O_3: 1.5 MnO
$G_{4:}$ 20 Na_2O -78.00 B_2O_3: 2.0 MnO

The glasses used for the present study were prepared by the melting and quenching techniques [1-3]. Appropriate amounts (all in mol %) of reagent grades of Na_2O, B_2O_3 and MnO powders were thoroughly mixed in an agate mortar and melted in a thick walled platinum crucible in the temperature range 900-950 ºC . The furnace used was a PID temperature controlled furnace (Fig. 2.1).

Fig. 2.1 Schematic images of PID controlled furnace and annealing chamber

The glasses were melted in a thick walled platinum crucible for an hour till a bubble free liquid was formed. The resultant melt was poured on a rectangular brass mould (having smooth polished inner surface) held at room temperature and subsequently annealed at 200 oC in another furnace. The weight of the glass obtained always agreed with that anticipated in the batch, with an error of 0.2 to 0.5 % wt loss in each case. The results indicate that the actual glass compositions are essentially equal to those based on the glass batch. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for present study are 1 cm x 1 cm x 0.2 cm. For dielectric and dielectric breakdown measurements thin coating of silver paint was applied on either side of the glasses, to serve as electrodes.

2.3 Physical Properties

The density (d) of the glasses was determined by the standard principle of Archimedis' using o-xylene (99.99 % pure) as the buoyant liquid. A direct reading balance (capacity 100 g, readability 0.1 mg) was used for weighing. The bulk glass was suspended on a very thin

copper strand kept in the immersion liquid container and weighed in the liquid and air.

Using density and average molecular weight, other physical parameters such as copper ion concentration N_i , the polaron radius r_P , the field strength F_i of these glasses are evaluated.

2.4 X-ray diffraction

The amorphous state of the prepared glasses was checked by X-ray diffraction spectra recorded on SEIFEERT Diffractometer Model SO – DEBYE FLUX 202 fitted with copper target and nickel filter operated at 40 kV, 30m A.

2.5 Dielectric Measurements

The dielectric measurements on the Na_2O-B_2O_3: MnO glasses were carried out on HP 4263B LCR Meter in the frequency range 10^2 - 10^5 Hz [4] in the temperature range 30 – 300^o C.

2.5.1 HP 4263 B LCR Meter

Capacitance measurements were made with HP 4263B LCR Meter. The HP 4263B LCR Meter is a fully automatic high performance test instrument used to measure a wide range of parameters .The measurement speed of the instrument is 29 ms, it has a very test quick recovery and got built in comparator. It can measure the capacitance to a high accuracy and wide measurement range, which allows us to make precise measurements at five frequencies 100 Hz, 120 Hz, 1 kHz, 10 kHz and 100 kHz. The two measurement display sections, capacitance (C) and dissipation factor (D) provide the direct read out of the parameters .The instrument has got two modes of measurement viz., normal mode and average mode; in normal mode operation the instrument performs measurements at very high

speed where as in the average mode it has short, medium or long range rate to average the measurement results. The second mode, adopted in the present measurements, gives a high reliable and repeatable value than in the normal mode of the measurement.

2. 5. 2 Sample Holders

Two different types of sample holders have been used for room and high temperature dielectric measurements:

I) For measurements at room temperature on HP 4263 B LCR Meter a laboratory made sample holder with teflon base and micrometer arrangement [Fig 2.2(a)] was used.

II) For the temperature variation of the dielectric properties at a fixed frequency the sample holder shown in Fig 2.2(b) has been used .

Fig. 2.2 (a) HP 4263 B LCR micrometer arrangement and **Fig 2.2(b)** Sample holder

The sample was put in between two silver electrodes and a 200 W nichrome heater heated the holder. Adjusting the current with a variac controlled the heating. The readings were taken when the sample attained the steady temperature. A chromel – alumel thermo-couple was attached to the sample holder vary near the sample. The thermo e.m.f. Developed across the junction was measured using digital PID temperature controller.

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Chapter – 3

The primary objective of this study is to characterize the Dielectric properties viz., Dielectric constant and Dielectric loss of $Na_2O- B_2O_3$: MnO glasses

Chapter -3

Physical &Dielectric Studies of MnO doped Na_2O -B_2O_3 glasses

3.1 Introduction

Study on radiation induced defect centers in glasses has been an interesting subject of investigation in recent years, since such studies help for examining the suitability of the glasses for radiation dosimetry applications. Extensive studies on the activating or killing effect of luminescence due to some transition metal ions like Fe2+, Cu2+, Ti4+etc, in amorphous materials are available in literature [1-2]. In recent years Pontuschka et al. have done a commendable work on thermo luminescence mechanisms in borate glasses [3]. Borate glasses are very advantageous materials for the radiation dosimetry applications in view of the fact that their effective atomic number is very close to that of human tissue. However, pure borate glasses have certain disadvantages to use in radiation dosimetry since they are highly hygroscopic and exhibit weak glow peak at relatively low temperatures. Alkali oxy borate glasses are considered as good materials for dosimetry applications since they are relatively moisture resistant when compared with the pure borate glasses.

Manganese ion, is yet an another interesting transition metal ion because it exists in different valence states in different glass matrices, for example in silicate and germanate glasses it exists in Mn^{2+} with both octahedral and tetrahedral coordination [4]. Further, among different manganese ions, Mn^{2+} and Mn^{3+} are well known paramagnetic ions and Mn^{2+} and Mn^{4+} are identified as luminescence activators [5]. Further, it is also quite likely for manganese ions to have link with borate groups; strengthen its structure and may raise the

chemical resistance of the glass. The content of manganese in different forms in different valence states exist in the glass depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc. Hence, the connection between the state and the position of the manganese ion and the physical properties of the glass is expected to be highly interesting.

Mn^{2+} has the electronic configuration $3d^5$ which corresponds to a half filled d shell. Most Mn^{2+} complexes are octahedral and have a high spin arrangement with five unpaired electrons [6]. In view of these characteristics, manganese ions are expected to influence the physical properties of Na_2O-B_2O_3 glasses and may have strong bearing on electrical and mechanical properties of the glasses.

A large number of interesting studies are available on the environment of manganese ion in various inorganic glass systems. These ions subsist in different surroundings (ionic, covalent) in glass matrices. Manganese ions seem to exist in Mn^{2+} and Mn^{3+} states in Na_2O-B_2O_3 glass network. The most probable local structure likely to occur for Mn^{3+} in these glasses is as a MnO_6 octahedron entwined with a BO_4 tetrahedron $MnBO_9$ where all the oxygens are bridging. The presence of such complexes obviously increases the stability of the glass network. Even though a number of recent investigations are available on the environment of manganese ions in a variety of inorganic glass systems [7-12], no dedicated studies are available on the influence of manganese ions on Na_2O - B_2O_3 glass systems in particular. This chapter is therefore devoted to investigate the influence of Mn ions on the structure and physical properties of Na_2O-B_2O_3 glasses.

Thus the clear objective of this chapter is to have a comprehensive understanding over the influence of manganese ions on physical and the insulating character of Na_2O–B_2O_3: MnO

glass system by a systematic study of dielectric properties (dielectric constant ε', loss and tan δ) over a moderately wide range of frequency and temperature. Glasses of the following composition are chosen for the present study:

$G_{0:}$ 20 Na_2O -80 B_2O_3

G_1: 20 Na_2O -79.50 B_2O_3: 0.5 MnO

$G_{2:}$ 20 Na_2O -79.00 B_2O_3: 1.0 MnO

$G_{3:}$ 20 Na_2O -78.50 B_2O_3: 1.5 MnO

$G_{4:}$ 20 Na_2O -78.000 B_2O_3: 2.0 MnO

3.2 Results

3.2.1 XRD

The glasses under investigation of X-RD patterns are shown in Fig. 3.1. 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 3.1).

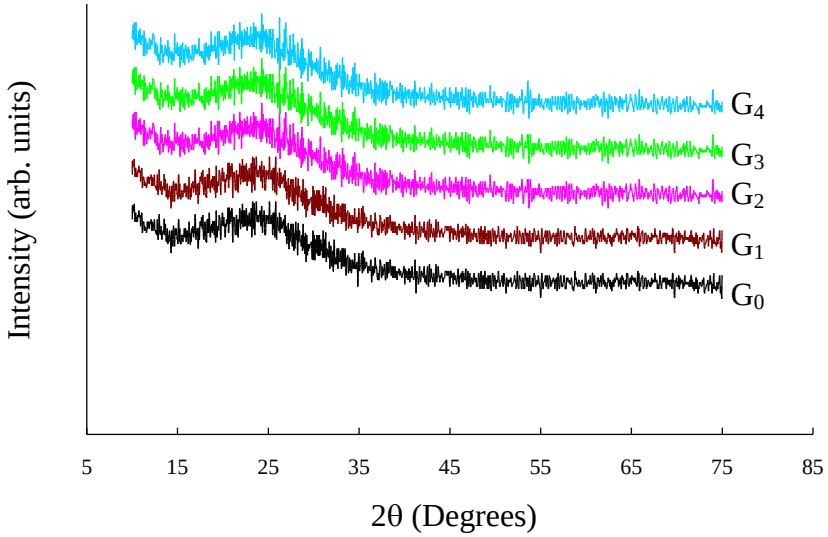

Fig.3.1. XRD pattern of Na_2O− B_2O_3: MnO glasses

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

Table 3.1 : Experimental data obtained from X-RD patterns

Sample Code	**Percent Crystallinity**	**Remark**
G_0	Nil	All Samples are amorphous in nature
G_1	Nil	
G_2	Nil	
G_3	Nil	
G_4	Nil	

3.3.2 Physical Parameters

Some physical variables that can be used to characterize Na_2O-B_2O_3: MnO glasses are calculated using the average molecular weight (M) and the measured value of density (d) [13]. Table 3.2 lists the physical characteristics of these glasses after evaluation.

Table 3.2 Data on Physical properties of $Na_2O- B_2O_3$: MnO glasses

Sample Code	Density d (g/cm^3)	Avg. Mol. wt	Mn^{2+} ion concentration N_I (10^{21}ions/cm^3)	Inter ionic distance R_I (nm)	Molar Volume cc/mol
G_0	2.422	68.08	....	..	28.11
G_1	2.436	68.174	4.31	0.61	27.98
G_2	2.451	68.261	8.65	0.48	27.84
G_3	2.465	68.348	13.01	0.42	27.72
G_4	2.480	68.434	17.51	0.38	27.59

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 27.59cc/mol as noted in a table. Increased in modifier contents introduce NBO containing borate triangles [14]. 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 [15, 16].

Variations in ρ and V_m of the glasses as a function of MnO content (x) are shown in Figure 3.2. The ρ increases up to 2.0 mol%, however, the V_m decrease. The observed variation up to 1.0 mol% MnO contents, is in contrary to one's expectation as the molecular weight of B_2O_3 and MnO are 69.61 g/mol and 86.93 g/mol, respectively and replacement of B_2O_3 by MnO is expected to increase the ρ and decrease the V_m. Observed variation in the above properties indicates that the MnO polyhedra form some new interconnections within the network up to 2.0 mol%. This indicates that up to 1.0 mol% MnO content, interconnections provided by MnO polyhedra are sufficient to overcome the depolymerization of borate network and result in increase in ρ and decrease in the V_m. The results of measurement also support the observation that glass structure becomes more stable and rigid up to 2.0 mol% MnO

3.2.3 Dielectric Properties

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 in Figures 3.3 and 3.4. 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. 3.3 & Fig.3.4).

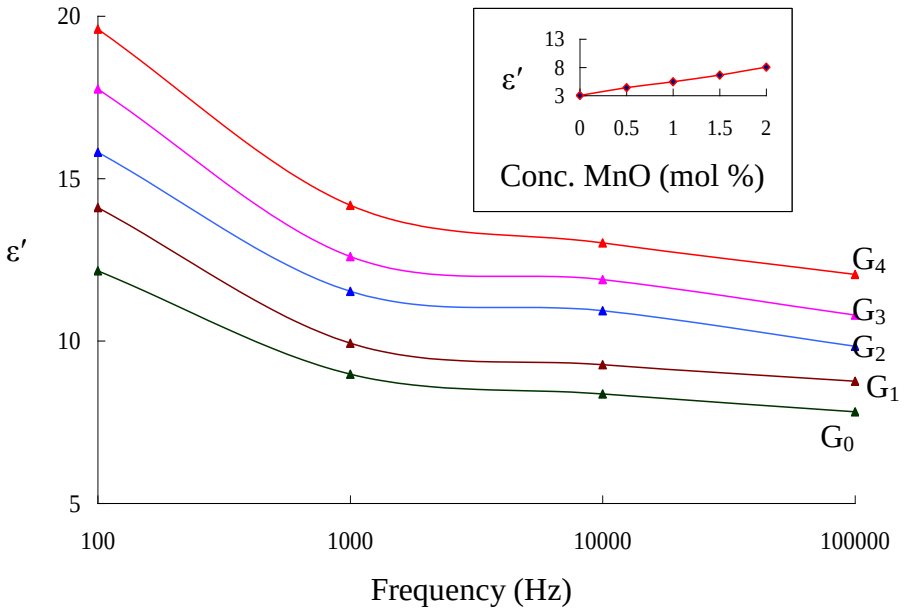

Fig.3.3. Variation of dielectric constant with frequency at room temperature of Na_2O - B_2O_3: MnO glasses. Inset represents the variation of tan δ with the concentration of MnO at 100 kHz.

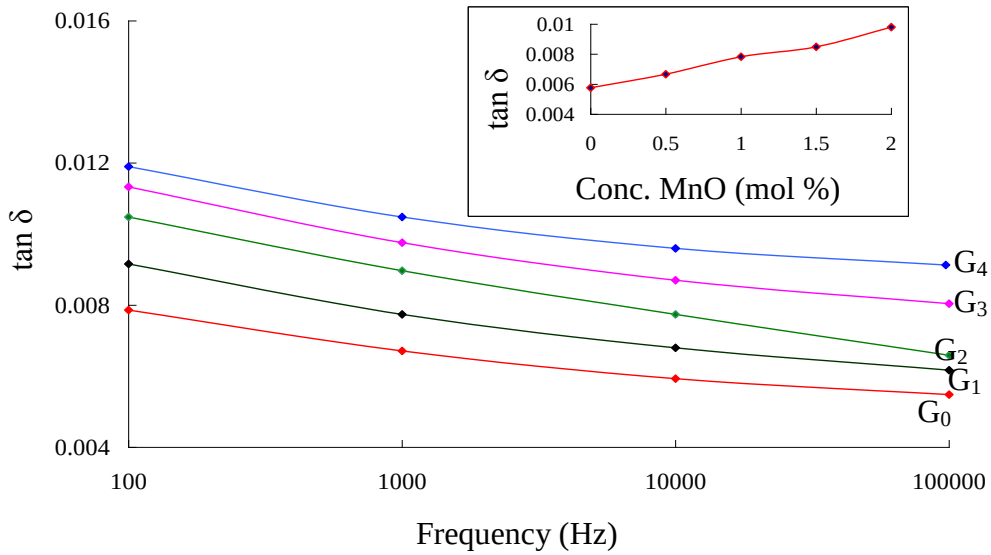

Fig.3.4. Variation of dielectric loss with frequency at room temperature of Na_2O -B_2O_3: MnO glasses. Inset represents the variation of tan δ with the concentration of MnO at 100 kHz.

The temperature dependence of Na_2O-B_2O_3 glasses doped with various amounts of MnO was recorded at 10 kHz, is shown as a comparison figure 3.5. 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 inset of Fig. 3.5.

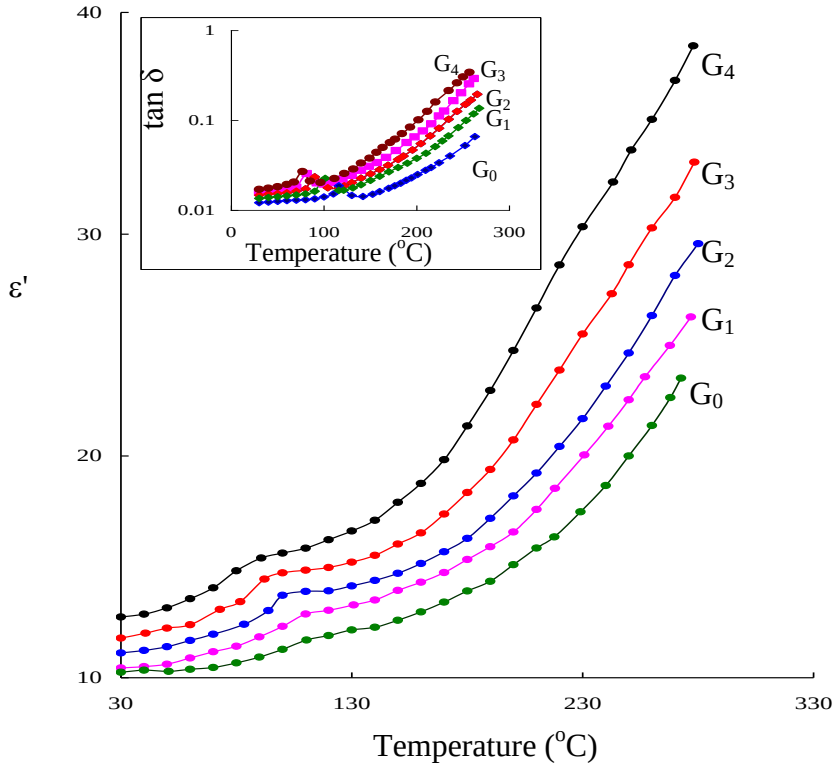

Fig. 3.5. Comparison plot of Variation of dielectric constant with temperature measured at 10 kHz for Na_2O -B_2O_3: MnO glasses. Inset represents the variation dielectric loss with temperature measured at 10 kHz

Table 3.3 summaries information on the dielectric constant and loss of Na_2O-B_2O_3: MnO glasses. With increasing temperature, the frequency maximum of the temperature dependent dielectric loss tan δ 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%.

Table 3.3 Data on dielectric properties of $Na_2O- B_2O_3$: MnO glasses

Glass	Temp (^oC)	Dielectric constant			Dielectric Loss		
		1kHz	10kHz	100kHz	1kHz	10kHz	100kHz
G_0	30	4.10	3.02	2.13	0.010	0.008	0.006
	100	6.34	4.73	3.10	0.014	0.010	0.008
	200	16.05	10.10	6.85	0.032	0.024	0.015
G_1	30	5.31	4.42	3.09	0.012	0.011	0.009
	100	7.09	6.13	4.72	0.017	0.013	0.010
	200	18.70	13.02	10.07	0.044	0.028	0.019
G_2	30	7.82	5.46	4.10	0.016	0.014	0.012
	100	9.67	7.20	5.92	0.026	0.019	0.016
	200	20.70	13.50	11.14	0.050	0.041	0.020
G_3	30	9.41	6.65	5.03	0.026	0.018	0.015
	100	11.03	9.12	7.86	0.032	0.021	0.017
	200	23.27	15.09	13.21	0.078	0.060	0.035
G_4	30	10.91	8.04	6.01	0.029	0.022	0.019
	100	13.81	10.08	8.10	0.053	0.036	0.024
	200	26.92	17.13	15.04	0.091	0.080	0.047

3.3 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 [17]. 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 [18, 19]. 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 [20, 21]. At higher frequencies, where this form of polarization reduces noticeably with frequency, the change in ε' and tan δ 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 δ 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 δ 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.

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Chapter – 4

Summary and Conclusions

This chapter contains a brief outline and conclusions drawn from the investigation carried out on physical and Dielectric properties of $Na_2O - B_2O_3$: MnO glasses. The outlines of of glass system are also presented.

Chapter -4

Summary and Conclusions

4.1 Summary

A systematic study on dielectric properties of manganese metal ions doped Na_2O-B_2O_3 glasses has been presented.

The compositions of the glasses used for the present study are:

$G_{0:}$ 20 Na_2O -80 B_2O_3

G_1: 20 Na_2O -79.50 B_2O_3: 0.5 MnO

$G_{2:}$ 20 Na_2O -79.00 B_2O_3: 1.0 MnO

$G_{3:}$ 20 Na_2O -78.50 B_2O_3: 1.5 MnO

$G_{4:}$ 20 Na_2O -78.00 B_2O_3: 2.0 MnO

The glasses were prepared by the usual melting, quenching and subsequent annealing techniques. Dielectric properties, viz., dielectric constant ε' and loss Tan δ in the frequency range 10^2 to 10^5 Hz and in the temperature range 30 to 300^o C were made

4.2 Conclusions

The main **conclusions drawn** from the results of above studies are:

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 G0 to G4 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.