Grenze International Journal of Engineering and Technology, Special Issue

Role of TeO_2 on Conduction Mechanism in $AgI\text{-}Ag_2O\text{-}B_2O_3$ Glasses

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***Abstract*—Glasses containing TeO_2 as a network former have got many applications particularly when they are mixed with super conducting halides and oxides. In the present study we have synthesized $AgI\text{-}Ag_2O\text{-}B_2O_3\text{-}TeO_2$ (SBT) glass system with different concentrations of TeO_2 by melt quenching technique and studied their electrical properties. All the prepared glasses were characterized by X-ray diffraction. X-ray diffraction confirmed the amorphous nature of the prepared samples. The DC and AC conductivity was measured for all SBT samples in the temperature region 300 to 503K and activation energies were evaluated. The AC conductivity measurements were made for all SBT glasses as a function of frequency 100 Hz to 3 MHz. The true bulk conductivity of pure sample at room temperature (σ_e =2.24 x 10^{-6} S/cm) was found to be enhanced with increase in mol % of TeO_2 and found to be maximum 1.02x10^{-2} S/cm at 503 K for 0.4 mol% of TeO_2. Both DC & AC conductivities are found to increase and activation energies decreased with increasing the concentration of TeO_2. The variation of conductivity with the TeO_2 content in the SBT system is explained using the diffusion path model, whereas the variation of conductivity with the frequency is analyzed by correlating the microscopic nature of the ionic conduction process in the SBT system.**

***Index Terms*— Silver glasses, XRD, DC, AC conductivity.**

I. INTRODUCTION

Fast ion conducting (FIC) glassy materials with exceptionally high ionic conductivity at ambient temperatures have potential applications in ionic devices, such as, solid state batteries, memory devices, capacitors, sensors, timers, fuel cells, electro chromic displays, etc.,[1,2]. Studies on silver based superionic conducting glasses have been increasingly interesting and important in the field of solid state ionics, since they exhibit high conductivity, high stability, etc., at ambient temperatures. The present investigation deals with the preparation of varying formers compositions of fast ionic conducting $55AgI\text{-}22Ag_2O\text{-}[(1\text{-}x)\ B_2O_3\text{-}xTeO_2]$ where x=0 to 0.4 in steps of 0.1 mol% glassy compounds by melt quenching technique. B_2O_3, TeO_2 are glass formers, Ag_2O is modifier and AgI is dopant salt. Also, deals with the XRD, DC and Impedance measurements respectively to study the nature, structure and electrical conductivity of all prepared SBT samples.

Tellurium oxide is also a good network former and a large number of binary and ternary tellurite systems easily form glasses. The structure of tellurite glasses has been examined by many authors [5-7] using various techniques. Tellurium oxide based glasses are mainly studied for their optical properties. The investigations

Grenze ID: 01.GIJET.4.3.52

of electrical conductivity on AgI–Ag_2O–B_2O_3-TeO_2 glass systems have been studied recently. They also exhibit high ionic conductivity on suitable modifications of the network [8-10]. In addition to all these properties, tellurite glasses exhibit less hygroscopic in nature (compared to phosphate and other oxide glasses).

The present study aims to investigate the glasses containing two glass formers (B_2O_3 and TeO_2) by replacing high conducting electrolyte material such as AgI by Ag_2O. Silver oxides has been chosen as a network modifying oxide, since silver ions possess high ionic conductivity compared to alkali modifying cations such as Li^+ ion. Keeping a constant molecular ratio of the network former, an increase of the ionic conductivity has been observed by mixing two different network modifiers. AC conductivity is one of the common methods to characterize the bulk resistance of glasses. In the present investigation complex impedance measurements are used to study AC conductivity. The frequency dependence of conductivity and dielectric relaxation has also been examined and an attempt is made to explain the conduction mechanism of these systems.

II. EXPERIMENTAL

A. Glass Preparation

The glasses used for the present study are prepared by the melt quenching techniques. The starting materials used for the preparation of the present series of glasses were Sigma Aldrich AR grade 99.9% pure reagents (AgI, Ag_2O, B_2O_3, TeO_2); the appropriate amounts of these compounds were thoroughly mixed in an agate mortar and melted in a porcelain crucible. In the present study, 55%AgI-22%Ag_2O-23%[(1-x)B_2O_3- xTeO_2] were prepared by varying the values of 'x' from 0 to 0.4 with step 0.1 and are labelled as SBT0, SBT1, SBT2, SBT3, SBT4 respectively.

The furnace used was a PID temperature controlled furnace. The powder was melted in the temperature range 700-750^{o}C for half an hour till a bubble free liquid was formed. The glass samples were obtained by pouring the melt into a brass mould of different shapes. The samples were subsequently annealed at lower temperatures and then sliced and polished. The approximate final dimensions of the glasses used for various studies are 1cm x 1cm x 0.2cm. For dielectric measurements thin coating of silver paint was applied on either side of the glasses to serve as electrodes.

B. X–Ray Diffraction

X-ray diffraction pattern are recorded in reflection mode for all compositions of SBT samples by Panalytical X-ray Diffractometer.

C. Physical Parameters

Physical parameters like dopant ion concentration (N_i), Inter–ionic distance r_i, polaron radius (r_p), Molar volume (V_m), Oxygen packing density (O) used for characterization of the glasses are calculated from the measured value of density (d) and the average molecular weight ($\overline{M}$) and are tabulated in table 1. The density (d) of the glasses was determined by the standard principle of Archimedes using o-Xylene (99.99% pure) as the buoyant liquid. A direct reading balance (capacity 100gm, readability 0.1 mg) was used for weighing. The density of the samples was determined by weighing in the liquid and air using the equation

$$d = (W_1/ W_2) * d_0 \qquad (1)$$

W_1= weight of the sample in air, W_2=weight loss of the sample in o-Xylene, d_0=density of o-Xylene. The density results are also presented in table 1.

D. DC Conductivity

For conductivity studies, all the samples are first smoothened and silver paint is applied on both sides of the sample to act as electrodes.

Two nickel rods having an area of 1-2 sq cm are fixed to a stainless steel frame being separated electrically by silica rods. The upper electrode is fixed to a movable rod connected to a battery through an ammeter which measures the electric current through specimen. A metal shield is placed around the sample holder to maintain a uniform temperature zone. The sample holder is inserted in thermostat controlled heating chamber to carry variable temperature measurements over a range of 300 to 503K, at an interval of 5K during heating. The sample is heated slowly so that no breakage is found.

D. AC Conductivity

AC conductivity studies are carried on Wayne kerr 6440B Precision Component Analyzer. This Analyzer provides 4-termanal measurement of passive components over the frequency range 20Hz to 3MHz. The complex impedance spectroscopy measurements of AC conductivity is made on all the SBT samples by observing real and imaginary components of impedance (Z) over frequency range of 100Hz-3MHz, and temperature range of 300-503K, analyzing them in complex impedance plane. A complex impedance measurement gives information about electrical characteristics of materials and their interface with electrodes. Such studies would help in understanding dielectric nature, conduction processes and dielectric relaxations present in the material. Analysis of the complex impedance data is done by Non Least Square fit method (NLSF).

III. Results and Discussion

A. XRD

The absence of sharp peaks in Fig-1 of XRD clearly indicate the amorphous nature of these materials i.e., long-range atomic order is absent as desired. After confirming the formation of glassy material, the samples are studied for other characteristic properties.

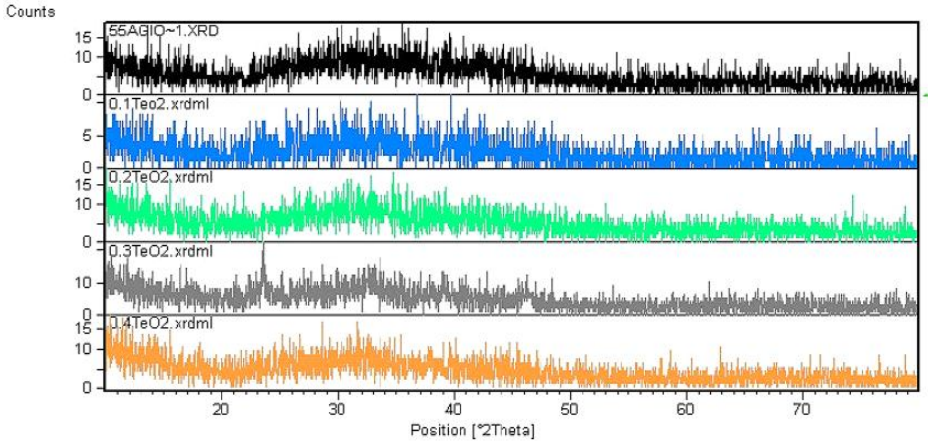

Fig. 1 XRD patterns of all the SBT samples

B. Physical Parameters

Table 1 represents the physical properties of SBT glasses. From the table 1 it can be observed that the density, average molecular weight, molar volume, oxygen packing density (OPD), polaron radius, tellurium ion concentration and inter ionic distance of tellurium ions increased with the increase in tellurium ion concentration.

The glass structure consist of three coordinated trigonal $[BO^{3/2}]^0$ and four connected tetrahedral $[BO^{4/2}]^-$ boron atoms and these $[BO^{4/2}]^-$ atoms are produced by the modification at the expense of $[BO^{3/2}]^0$ units [3, 4]. The trigonal and tetragonal conversion and formation of oxygen bridges by the oxide ion from the modifier reaches a maximum at the diborate composition. When the modifier concentration is increased further, the percentage of tetragonal boron decreases indicating a structural stability of tetrahedra in the presence of higher modifier oxide concentrations [5–7] and the notable feature is that there is no non-bridging oxygen (NBO) in the coordination of tetrahedral boron. Tellurium oxide is also a good network former and when the environment is more ionic, the addition of modifier seems to favour the formation of trigonal pyramidal, $[TeO^{3/2}]^-$ (tp) units at the expense of trigonal bipyramidal, $[TeO^{4/2}]^0$ (tbp) units [11–13].

C. DC Conductivity

Usually DC conductivity is measured to determine the conduction mechanism in these systems. DC Conductivity of the samples at room temperature ranges between 10^{-6} to 10^{-5} S/cm. From table 2 it is observed that conductivity value increases up to 10^{-2} S/cm with temperature and also increases with Tellurium ion concentration. The increase in conductivity with temperature is understood in terms of hopping of charges between the coordinating sites, local structural relaxation and segmental motion of polymer. The

TABLE I. PHYSICAL PROPERTY OF SBT GLASSES

Parameter(± error limits)	SBT0	SBT1	SBT2	SBT3	SBT4
Density (g/cm^3)	8.81	8.82	8.84	8.85	8.88
Avg.molecular weight (g)	196.1	198.1	200.2	202.3	204.3
Molar Volume (V_m)	22.2	22.4	22.5	22.8	22.9
OPD, O (g/atm l)	35.5	36.8	38.1	39.5	40.8
Polaron radius, $R_p(^0A)$	-	0.003	0.005	0.008	0.01
Te ion conc. Ni, (10^{21}/cc)	-	2.4	4.8	7.2	9.6
R_i of Te ions, R_i (^0A)	-	0.1	0.06	0.04	0.03

simultaneous addition of two network formers (B_2O_3 and TeO_2) might have formed a highly disordered network in the glass system facilitating the easy flow of charge carriers. This in turn enhanced the mobility and the conductivity increased to this particular sample.

From the graph plotted between log conductivity and $10^3/T$ (K^{-1}) (Fig-2 (a)), DC activation energies are calculated for all the samples using the Arrhenius equation and are tabulated in table 2.

$$\sigma = \sigma_0 \exp\left(\frac{-E}{KT}\right) \qquad (2)$$

where K- Boltzmann constant, E-Activation energy and σ_0- preexponantial factor.

SBT0 glass sample (pure) has high activation energy (0.162 eV). SBT4 glass sample has lowest activation energy (0.142 eV). The graph between tellurium ion mol% and activation energy is shown in Fig-2 (b). It is obvious from this figure that the activation energy decreased with increase of the TeO_2 concentration. This clearly indicates that addition of TeO_2 favours the conduction in SBT glasses. This behaviour is typical of ionic conductors. So we can conclude that the samples prepared are ionic conductors.

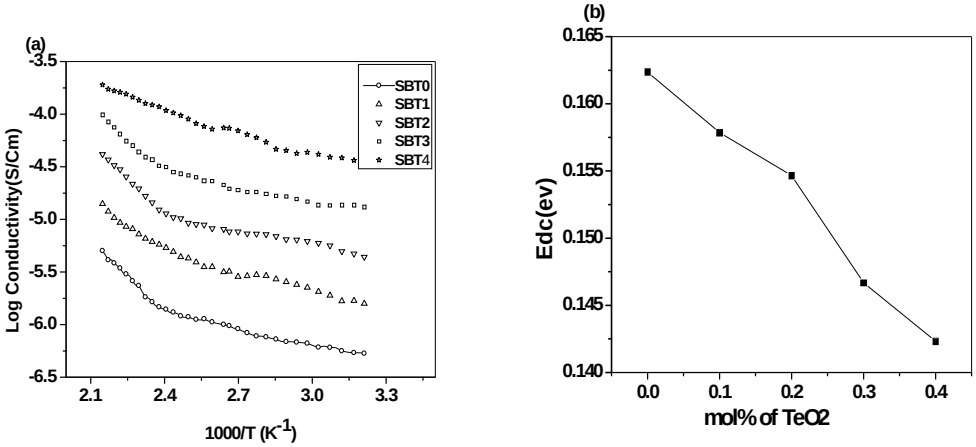

Fig.2 (a) D.C Conductivity versus temperature (b) Activation energy versus mol% of Teo_2

TABLE II. VALUES OF CONDUCTIVITY AND ACTIVATION ENERGIES

Sample	Conductivity at		E_{dc} (ev)	E_{ac} (ev)
	300K	503K		
SBT0	$2.24x10^{-6}$	$3.4\ x10^{-3}$	0.162	0.134
SBT1	$8.14x10^{-6}$	$4.7.\ x10^{-3}$	0.158	0.127
SBT2	$1.54x10^{-5}$	$7.2\ x10^{-3}$	0.155	0.122
SBT3	$3.73x10^{-5}$	$9.4x10^{-3}$	0.147	0.116
SBT4	$5.17x10^{-5}$	$1.1x10^{-2}$	0.142	0.107

D. AC Conductivity

AC conductivities are calculated from impedance data. Fig-3(a) represents variation of AC conductivity with temperature of all SBT samples. AC conductivity values are found to vary between 10^{-6} to 10^{-5} (S/cm) at room temperature. It is observed that conductivity increases with increase in temperature. AC conductivity increases with increasing TeO_2 concentration indicating that addition of TeO_2 favour the conduction in SBT glasses. The increase in conductivity with temperature is understood in terms of hopping of charges between the coordinating sites, local structural relaxation and segmental motion of polymer.

Activation energies are calculated form Arrhenius equation. AC activation energy variation with mol% of TeO_2 is also represented in Fig-3(b). AC activation energy decreases with increasing TeO_2 concentration from 0.134eV to 0.107eV indicating that addition of TeO_2 enhanced the conduction in SBT glasses.

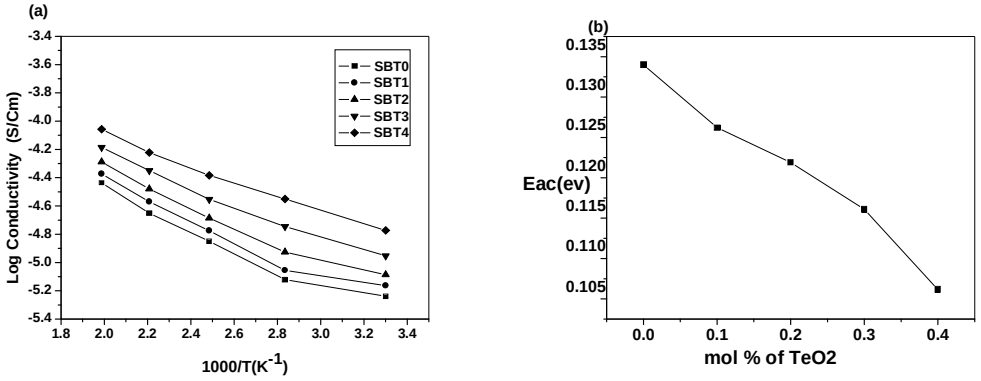

Fig.3 (a) Variation of A.C conductivity with temperature (b) E_{ac} variation with Mol% of TeO_2

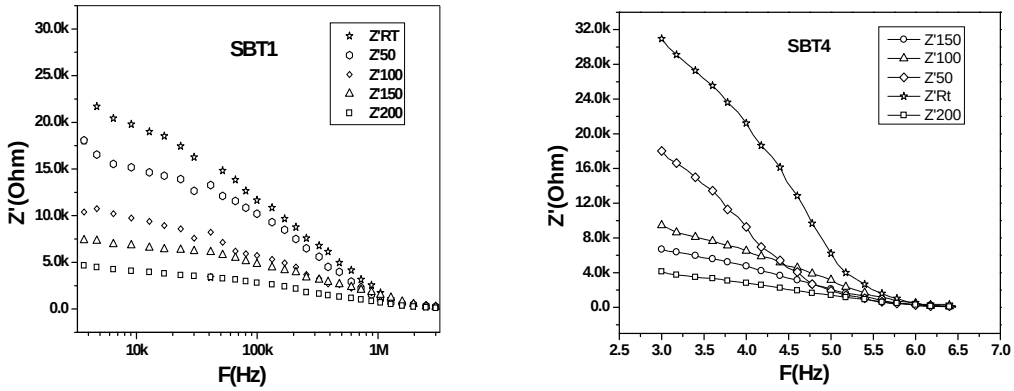

Fig. 4 (a), (b) Real impedance (Z') versus frequency of SBT1, SBT4 samples

Variation of real impedance with frequency at different temperatures of SBT1, SBT4 samples is represented.in Fig-4(a, b). It is observed that real impedance decrease with the increase frequency, and they merged around 300 kHz. At higher temperatures energy distribution in the network become more uniform and the variation of impedances at higher frequencies become less. This makes real and imaginary impedances to converge at higher frequencies indicating that at higher frequencies conductivity and impedance become independent of temperature.

Variation of Imaginary impedance with frequency at different temperatures of SBT1, SBT4 samples is represented in Fig-4(c, d). It is observed that imaginary impedance decreased with the increasing the temperature in low frequency region, and merged at higher frequencies for all temperatures. A peak is found at lower frequency region, as the temperature increases the peak shift towards higher frequency region.

The popular forms of data presentation are complex impedance plots (Z' verses Z''). Sample data for SBT1, SBT4 samples at different temperatures is represented in Fig-5(a, b). The observed peaks within the range studied depend on the strength of dielectric relaxation. In addition to semi-circle, careful examination of the graph reveals a spike at low frequencies, which is the characteristic of a double layer capacitance (C_{dl}). The

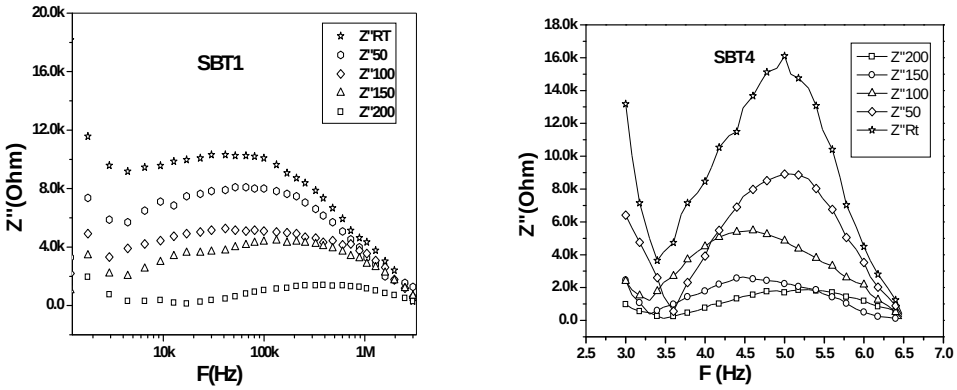

Fig. 4 (c), (d) Imaginary impedance versus frequency of SBT1 and SBT4 samples

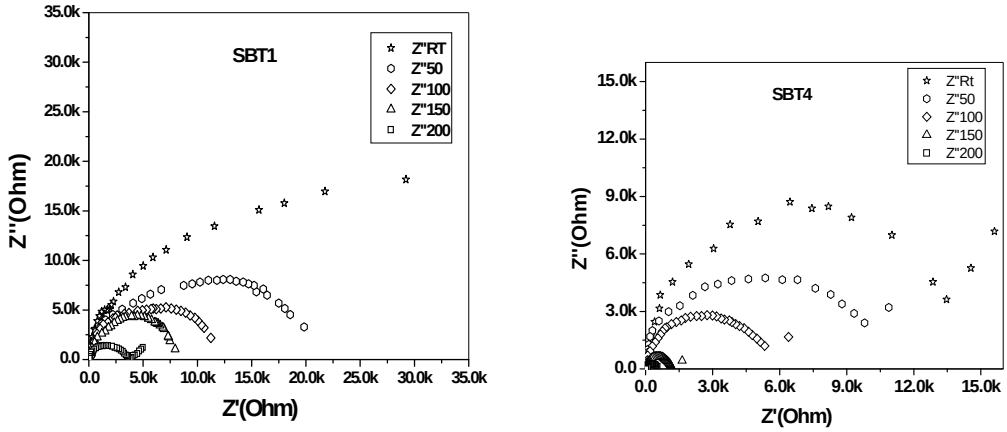

Fig-5 (a, b) Cole-Cole plots for SBT1, SBT4 samples at different temperatures

spike is attributed to the diffusion limited Warburg impedance, which is present at low frequencies and these clearly indicate the presence of space charge polarization. It is observed that the intercept of the semicircle with the real axis shifts towards the low resistance region with an increase in temperature. The intercept of the inclined straight line with the real axis gives the DC resistance for each composition and at each temperature. DC resistance decreases with increase in temperature.

For all samples from complex impedance plots, relaxation frequencies are calculated at different temperatures and tabulated below in table 3. Any specific trend is not observed in the relaxation frequencies. The migration of mobile ions is described by the relaxation times. The existence of distribution of relaxation times in disorder solids is commonly reported [14].

TABLE III. RELAXATION FREQUENCIES IN KHZ

Temp(^{0}C)	SBT0	SBT1	SBT2	SBT3	SBT4
30	6.2	6.2	6.2	314	37.6
50	6.2	188	628	75	37
100	6.2	157	251	314	188
150	12.5	502	188	251	502
200	251	942	125	251	125

IV. Conclusions

Conductivity increased with increase in temperature, this reflects ionic conducting property of the samples. Impedance spectroscopy shows the presence of relaxation by showing semi-circle in mid frequency range. This also reflects the involvement of conducting ions. In all the samples DC values is lower than AC values. In all the samples the impedances are observed to decrease not only with increase in temperature, but also with increase in concentration of TeO_2.

The fast ion conducting glasses are characterized by greater freedom of movement of Ag+ ions because these ions are not held in the lattice sites or anion cages firmly. Hence addition of network modifier such as TeO_2 introduces ionic bonds usually associating non-bridging oxygen ions with modifying cations.

Acknowledgements

The authors are thankful to the University Grants Commission, New Delhi, for financial assistance to carry out this work.

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