

Optical and Electrical Studies of Silver Boro Tellurite Glasses

Abstract- Super ion conducting glasses of composition $55\text{AgI}-22\text{Ag}_2\text{O}-23[(1-x)\text{B}_2\text{O}_3-x\text{TeO}_2]$ where $x=0$ to 1 in steps of 0.2 mol% were prepared by melt quenching technique. XRD, FTIR investigations were carried out on all glasses to understand physical characteristics of the prepared glasses. Electrical characterization is done in terms of AC and DC conductivities, activation energy, break down strength, transport number, and equivalent R-C circuits. DC conductivity at room temperature increased from 10^{-4} to 10^{-2} S/cm with increasing concentration of TeO_2 . DC activation energy (E_{ac}) is found to decrease from 0.36 to 0.19 eV with increasing concentration of TeO_2 . The breakdown strength of all the samples is found to be in the range of 2.3 to 1.6 kV/cm. From the Impedance spectroscopy, real and imaginary impedances (Z' , Z'') were calculated, and equivalent R-C circuit parameters were obtained from Nyquist plots for all the samples. AC conductivity is observed to increase whereas the AC activation energy (E_{ac}) is observed to decrease from 0.23 to 0.14 eV with increasing concentration of TeO_2 . The quantitative analysis of these results indicates that the electrical conductivity of silver borate glasses is enhanced by addition of TeO_2 . These glasses are identified as superionic conductors, with in which conduction is carried by hopping mechanism.

Index Terms-Fast ion conducting glasses, XRD, FTIR, DC and AC conductivities, break down strength.

1. INTRODUCTION

Several electrical studies on glassy materials revealed that glasses under certain circumstances can be super ionic conductors [1–3]. These glassy materials are of technological interest in view of their applications such as biosensors, storage batteries and fuel cells etc.,. The conductivity depends on the nature and content of the modifier oxide and also glass former compositions [4, 5]. The incorporation of alkali halides or metal halides in to the mixed glass formers [6, 7] is considered to be predominant factor playing the role of enhancing the conductivity of the conventional glasses to reach the values of super ionic materials.

The nature of the interaction between metal ions (Ag^+) and amorphous molecules is usually studied by different techniques. The structure and the electrical properties of silver ion-conducting borate-based glasses have been reported in the literature [8, 9]. The mobility of Ag^+ ions associated with an iodide environment is considered to be higher and based on the fact that increase in the percentage of AgI in the glass gives rise to higher conductivities [10-12]. One of the most widely used glass formers for the synthesis of super ionic conducting glass is B_2O_3 .

It has been observed that in many cases the conductivity can be enhanced by mixing two different glass formers [10, 11, 21-23] with different coordination polyhedrons. But such mixtures have a strong tendency to phase separation at low modifier oxide molar ratio. Therefore, the complete substitution of one network former by another one has not always been possible [11].

Tellurium oxide is also a good network former and a large number of binary and ternary tellurite systems easily form glasses [13, 14]. The structure of tellurite glasses has been examined by many authors [15-17] using various techniques. Electrical conductivity investigation on $\text{AgI}-\text{Ag}_2\text{O}-\text{B}_2\text{O}_3-\text{TeO}_2$ glass systems have been started recently. They also exhibit high ionic conductivity on suitable modifications of the network [18-20]. Tellurite glasses exhibit low glass transition temperature, high thermal expansion coefficient and are less hygroscopic in nature (compared to phosphate and other oxide glasses).

The present study aims to investigate the conductivity of the glasses containing high conducting electrolyte material such as AgI and Ag_2O by changing the concentrations of glass formers B_2O_3 and TeO_2 . Silver oxide 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 modifiers, an increase of the ionic conductivity has been observed by mixing two different network formers. AC conductivity is one of the common

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methods to characterize the bulk resistance of glasses. In the present investigation complex impedance measurements are used to study AC conductivity.

2. MATERIALS AND METHODS

2.1. Sample Preparation

Silver BoroTellurite [SBT] glasses of various compositions were prepared by melt quenching method. $\text{AgI-Ag}_2\text{O}[(1-x)\text{B}_2\text{O}_3-x\text{TeO}_2]$, $x=0$ to 1 in steps of 0.2. Sample with $x=0$ is termed as SBT0 and sample with $x=0.2$ is termed as SBT2 and so on. Starting compounds AgI, Ag_2O , B_2O_3 and TeO_2 are taken according to their molecular weight percentage (mol.wt.%) and mixed thoroughly in a porcelain crucible. This mixture is heated gradually to 750°C and maintained at that temperature for about 30 min. The melt was poured onto a stainless steel plate and pressed with another plate to obtain a thin disc (0.1–0.15 cm in thickness). For XRD, FTIR studies the obtained glasses are crushed into fine powders using pestle and mortar. For conductivity studies this powder is made into pellet formed by high compression method and silver paste is applied for better electrode contact.

2.2. Experimental

All the samples are characterized by using XRD, FTIR and electrical characterisation is done by impedance spectroscopy over a frequency range of 1kHz-3MHz and between 300K and 423K.

In the present investigation, X-ray diffraction measurements were carried out for all the samples using Rigaku miniflex diffractometer with $\text{Cu K}\alpha$ -radiation of wavelength $\lambda = 1.5418\text{\AA}$ between 10° and 90° of 2θ .

The FTIR spectra for all the samples are recorded on Shimadzu FTIR-8000 spectrometer. Pellets made with the mixture of SBT powder and KBr are used to record FTIR spectra in the range of $600\text{--}4000\text{ cm}^{-1}$ with 4 cm^{-1} resolution.

2.3. Electrical Characterisation

For DC and AC characterization pellets of the glass samples (dia=1cm, thickness=1.5mm approximately) both sides painted with silver for better electrode contact were used.

For DC conductivity measurement the silver coated pellets were sandwiched between two spring loaded stainless steel blocking electrodes of surface area 3.14 cm^2 . The sample holder is placed in a thermostat controlled furnace and temperature

is varied from 30°C to 150°C (423K) at an interval of 50°C . DC conductivity measurements were carried out using Keithly 6485 pico ammeter in the temperature range of 303-523K for all SBT samples.

For AC electrical conductivity, impedance measurements were carried out by Waynekerr LCR-6440B impedance analyser from 1kHz to 3MHz over the temperature range of 303–423K for all SBT samples. The impedance data was analysed by nonlinear curve fit method, and from those curves AC conductivity, activation energy, R-C values and relaxation values were calculated.

2.4. Break down Strength

The study on the electric breakdown of glass dielectrics is extreme importance in deciding the insulating character of the glass. Breakdown strength E_b is nothing but the destruction of the dielectric by the force of an electric field. An electric breakdown develops as a result of interaction of free charge particles (electrons, ions) accelerated by an electric field with the particles of a dielectric, or as a result of inelastic displacement of bound charges in a dielectric under the action of an external electric field.

The electric breakdown is distinguished by:

- A short time of development of breakdown (commonly of the order of micro seconds and even less)
- A small dependence of E_b on the frequency of the applied voltage
- A small dependence of electric strength on temperature
- A comparatively little pronounced (at any rate with a uniform electric field) dependence of electric strength on the dimensions of the dielectric and the electrodes.

Dielectric breakdown strength for all these glasses at room temperature in air medium were determined using a high AC voltage insulation breakdown tester ITL (Instruments techniques Pvt. Ltd., Hyderabad) Model BDV-5 operated with an input voltage of 250V and a frequency of 50 Hz. The sample holder for breakdown tester is just similar to the one used for room temperature dielectric measurements.

3. RESULTS AND DISCUSSIONS

3.1. XRD

Fig. 1 shows the XRD spectra of all the compositions of SBT glasses prepared by melt

quench technique and the absence of any sharp peak confirms that all the samples are amorphous in nature.

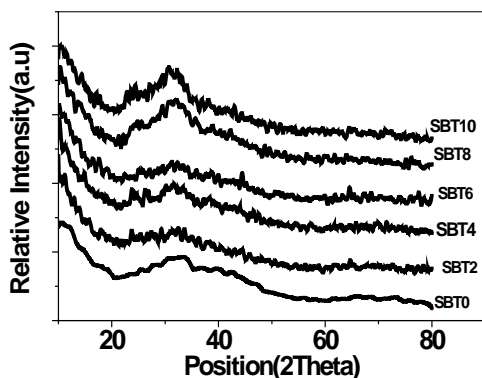


Fig. 1. XRD patterns of SBT glasses

3.2. Fourier Transforms Infrared (FTIR) spectra

Fig. 2 shows the FTIR spectra of all compositions of SBT samples and the observed major IR bands are at 660, 721, 914, 1223, 1360 and 1741 cm^{-1} . The 1741 cm^{-1} band is attributed to the ν_3 vibration mode of Te-O bond of TeO_4 group. The 721 cm^{-1} is due to ν_1 normal vibration mode of TeO_4 polyhedral. The broad band between 960 and 914 cm^{-1} is attributed to B-O bond stretching of tetrahedral BO_4 and 1223 cm^{-1} asymmetric stretching vibration of B_2O . The 1360 cm^{-1} band is due to B-O bond stretching of trigonal BO_3 and 660 cm^{-1} band is due to the stretching vibrations of the Te-O_{ax} (axial) and Te-O_{eq} (equatorial) bonds in deformed TeO_4 groups. As shown in Fig. 2 there is a shift in IR bands positions of B_2O_3 and TeO_2 with the mixing of two formers in different compositions. Also, it is observed that the intensity of IR bands of B_2O_3 decreases with decreasing B_2O_3 content in SBT glasses, which may also confirm the formation of proper structured network, according to the composition. Hence, from FTIR results, it is confirmed that TeO_2 and B_2O_3 compounds resulted in the formation of mixed network in SBT glassy samples. Table-1 gives the observed major band positions and their assignments of all SBT samples along with the band positions of pure B_2O_3 , AgI, Ag_2O and TeO_2 and also reported band positions of other B_2O_3 , AgI, Ag_2O and TeO_2 glasses. The band positions and functional groups are tabulated in table-1.

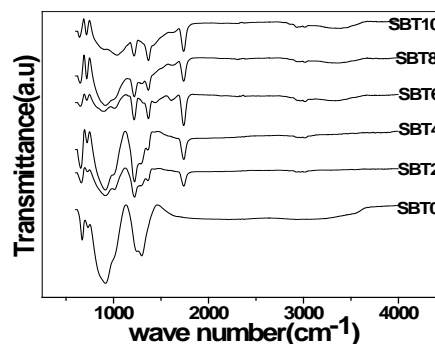


Fig. 2. FTIR spectra of SBT glasses

TABLE-1. The observed major IR band positions and their assignments of SBT samples.

Peak position (cm^{-1})	Assignment
660	Stretching vibrations of the Te-O_{ax} (axial) and Te-O_{eq} (equatorial) bonds in deformed TeO_4 groups.
721	ν_1 normal vibration mode of TeO_4 polyhedral
914	B-O bond stretching of tetrahedral BO_4
1223	Asymmetric stretching vibration of B_2O
1360	B-O bond stretching of tri-gonal BO_3
1741	ν_3 vibration mode of Te-O bond of TeO_4 group

3.3. DC Conductivity

Usually DC conductivity is measured to determine the ionic conductivity in these systems. Ion transport in these materials under a DC potential leads to a build-up of charge at the electrolyte-electrode inter phase if the ions are not replenished at the electrodes. From DC volt ampere characteristics DC conductivity is obtained at various temperatures. Conductivity of the samples at room temperature ranges between 10^{-4} to 10^{-1} S/cm from SBT0 to SBT10. Conductivity is found to increase with increase in temperature. The increase in conductivity with temperature is understood in terms of hopping of charges between the coordinating sites, local structural relaxation and

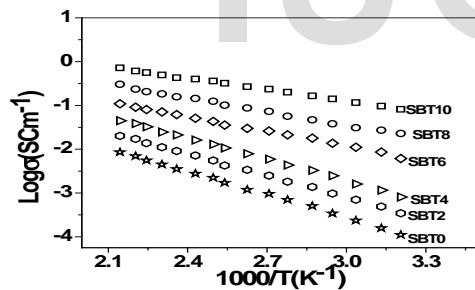
segmental motion of glass. From table-2 it is observed that conductivity value increases with temperature and also increases with tellurium ion concentration.

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

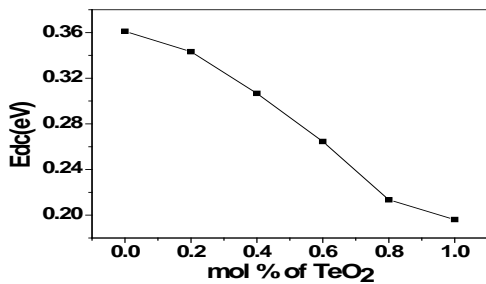
$$\sigma = \sigma_0 \exp\left(\frac{-E}{kT}\right)$$

Where k is Boltzmann constant, E is activation energy, and σ_0 is pre exponential factor.

The graph between tellurium ion mol% and DC activation energy is shown in Fig. 3(b). The SBT0, SBT10 glass samples has activation energies of 0.36eV and 0.19eV respectively. It is obvious from this figure that the activation energy decreases with increasing the TeO₂ concentration. This clearly indicates that addition of TeO₂ favours the conduction in SBT glasses. Variation of increasing conductivity with increasing temperature is characteristic of ionic conductors. So we can conclude that the samples prepared are ionic conductors.



(a)



(b)

Fig. 3(a).DC conductivity versus temperature (b) DC activation energy versus mol% of TeO₂

TABLE-2.DC and AC conductivities and activation energies for all samples at room temperature.

SNo.	Sample	$\sigma_{dc}(S/cm)$ RT(300K)	E_{dc} (eV)	$\sigma_{ac}(S/cm)$ RT(300K)	E_{ac} (eV)
1	SBT0	5.80×10^{-4}	0.36	1.50×10^{-4}	0.23
2	SBT2	6.80×10^{-4}	0.34	2.20×10^{-4}	0.2
3	SBT4	2.80×10^{-3}	0.3	1.78×10^{-3}	0.19
4	SBT6	8.30×10^{-3}	0.26	4.17×10^{-2}	0.18
5	SBT8	6.94×10^{-2}	0.21	4.55×10^{-2}	0.16
6	SBT10	1.23×10^{-1}	0.19	1.03×10^{-1}	0.14

3.4. Electrical Impedance

The real (Z') and imaginary (Z'') parts of the impedance are calculated from the measured data of impedance $|Z|$ and phase angle. The temperature dependence of impedance, and Nyquist plots (Z' Vs Z'') are shown in Fig. 4 (e), (f) for SBT0 and SBT10 samples of the SBT glassy system. DC resistance decreases with increase in temperature. This is in agreement with the result obtained from the DC measurements.

The real and imaginary parts of the impedance plots of the sample in a complex phase and their frequency dispersion curves gives the information about the effects of electrolyte-electrode interface, bulk resistance, grain boundary resistance etc.

The straight line at the low frequency region represent a capacitance effect at the electrode and electrolyte interface and it is called double layer capacitance (C_{dl}). Further, it is stated that the inclination in the low frequency straight line is due to the presence of the asymmetric nature of the distributed elements in the electrode and electrolyte interface.

Variations of real impedance with frequency at different temperatures for SBT0, SBT10 samples are represented in Fig. 4 (a), (b). It is observed that real impedance decrease with the increase in frequency, and they merged around 100kHz, 70kHz respectively. A value of Real impedance is found to decrease with the increase in temperature. 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. Variations of

value of Imaginary impedance with frequency at different temperatures for SBT0, SBT10 samples are represented in Fig. 4(c), (d). It is observed that imaginary impedance decreased with the increasing the temperature at 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[26].

Fig. 4(g) shows Nyquist plots of all SBT glasses at 303K (RT) SBT0 glass has lowest conductivity and

SBT10 glass has highest conductivity and for remaining glasses conductivity is in-between these two glasses.

AC Conductivity values are found to vary between 10^{-4} (SBT0) to 10^{-1} (SBT10) (S/cm) at room temperature. It is observed from conductivity graph Fig. 5(a) that conductivity increased with increase of temperature. Higher temperatures favour the conduction in SBT glasses.

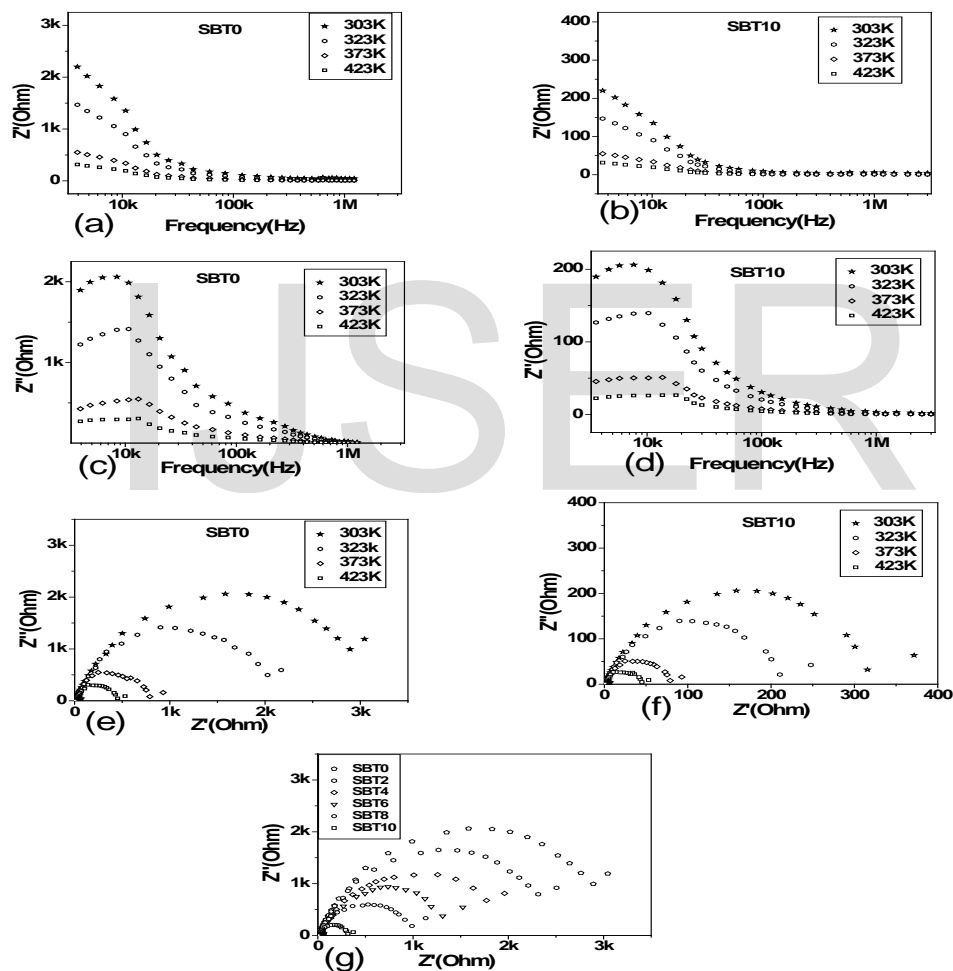


Fig. 4 (a), (b) Nyquist plots, (c), (d) Frequency versus real Z, (e), (f) Frequency versus imaginary Z of SBT0, SBT-10 samples respectively.(g) Nyquist plots of all SBT glass system.

AC conductivity increases with increasing TeO₂ concentration indicating that addition of TeO₂ favour the conduction in SBT glasses.

Activation energies are calculated from Arrhenius equation. AC activation energy variation with mol% of TeO₂ is also represented in Fig. 5(b). From the graph it is observed that AC activation energy decreases with increasing TeO₂ concentration from 0.24 to 0.14eV indicating that addition of TeO₂ enhanced the conduction in SBT glasses. The AC conductivity and AC activation energies values are shown in table-2.

AC activation energy decrease depends on increase in temperature at selected frequency. This behaviour is a characteristic of conductors with hopping charge carriers.

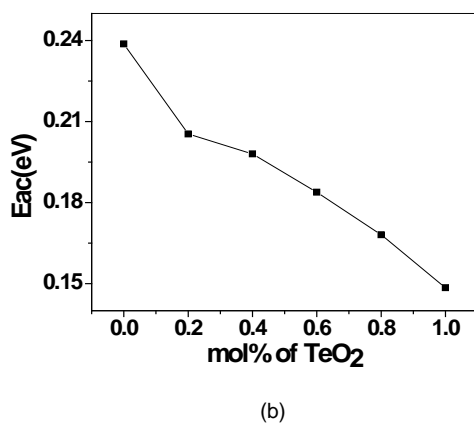
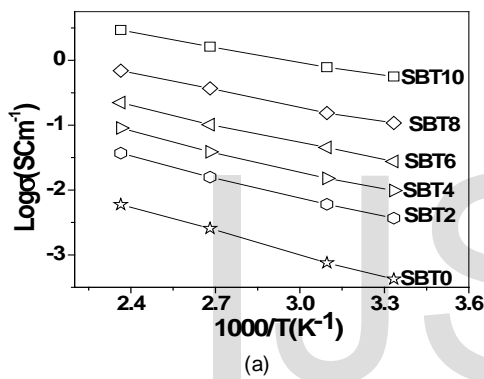


Fig.5(a).AC conductivity versus temperature (b) AC activation energy versus mol% of Teo₂

The migration of mobile ions is described by the relaxation times. Relaxation times are calculated at all temperatures from frequency versus imaginary part of impedance of SBT0 and SBT10 samples and values are tabulated in table-

3. Relaxation time decreases with increase in temperature and found to small increase from SBT0 to SBT10 at higher temperatures. These values are in the order of mille seconds.

TABLE-3. Variation of relaxation time with temperature.

Temperature (K)	Relaxation time (mSec)	
	SBT0	SBT10
303	0.13	0.13
323	0.098	0.099
373	0.072	0.073
423	0.056	0.057

3.5. Electrical equivalent circuit

The Cole-Cole plots of SBT0 and SBT10 are shown in figure 6(a), (b). Nonlinear least square fit method is applied to these Cole-Cole plots to fit R-C equivalent circuit or CPE. From these graphs bulk resistance (R_b) and bulk capacitances (C_b) are calculated and are tabulated below in table-4. In the semi-circle of the impedance plot is the characteristic of the parallel combination of a resistance and a capacitance, which are respectively, the bulk resistance R_b and the bulk capacitance C_b of the solid electrolyte [24, 25].

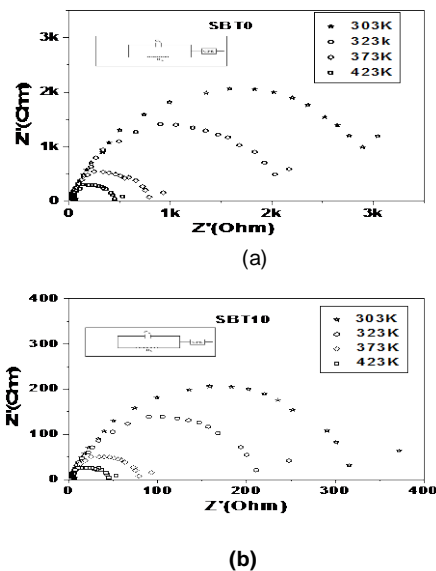


Fig. 6(a), (b). Z' versus Z'' (Cole-Cole) plots of SBT0, SBT10 samples

TABLE –4.RC values for SBT0, SBT10 glasses.

Temp(K)	SBT0		SBT10	
	R _b (ohm)	C _b (nf)	R _b (ohm)	C _b (nf)
303	29659	0.671	3112	6.39
323	20872	0.762	2075	7.67
373	9179	1.445	778	17.05
423	5245	2.023	444	23.87

We can observe from table-4, as increasing the concentration of TeO₂resistance values are decreasing, capacitance values are increasing and as increasing the temperature resistance values are decreasing, capacitance values are increasing that this favours conductivity increases in this system.

3.6. Break down strength

When the dielectric is placed in an electric field, the heat of dielectric loss is liberated. In a dielectric across which the voltage is applied, heat is liberated, the temperature of the dielectric then rises and the loss increases still more. The measured values of breakdown strengths of SBT glasses are presented in table-5.The breakdown strengths are determined at room temperature the heat liberated during the breakdown raises the temperature of the glass and hence raises the conductivity value.The breakdown strength values are decreasing with increasing the concentration of TeO₂in all SBT glass system. So the prepared glasses are fast ion conducting glasses. It is observed that the values of breakdown strength are maximum for SBT0 glass and minimum for SBT10 glass.

TABLE -5.Breakdown strength values of SBT glass system.

S. No.	Sample	Break down strength(KV/cm)
1	SBT0	2.3
2	SBT2	2.1
3	SBT4	1.9
4	SBT6	1.8
5	SBT8	1.7
6	SBT10	1.6

4. Conclusions

- An ideal mixing of both the glass formers TeO₄ and B₂O₃ along with iodine and silver ions to form the mixed network in SBT glassy samples is confirmed by FTIR spectra.
- Breakdown strength values are decreasing with the increasing the concentration of TeO₂. DC and AC Conductivity results show linear dependency of conductivity with temperature. This reflects ionic conducting property of the samples.
- In all the glasses both the conductivities are observed to increase not only with increase in temperature, but also with increase in concentration of TeO₂.
- DC and AC activation energy values are found to decrease with increase in temperature and also with increase in the concentration of TeO₂. Also, it is found that the highest conductivity composition has minimum activation energy.
- The FTIR spectra and breakdown voltage results support that increase of TeO₂ concentration favour better amorphous network in SBT glasses.
- Addition of network modifier such as TeO₂ introduces ionic bonds usually associating non-bridging oxygen ions with modifying cations.
- We can conclude that Te⁺ions are influence the electrical properties of glass system.
- High ionic conductivity shows thatthese glasses can be used as electrolytes in solid state batteries.

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