



ELECTRICAL PROPERTIES OF $\text{Ag}_2\text{O} : \text{B}_2\text{O}_3 : \text{SiO}_2$ GLASS CERAMIC FOR SENSOR APPLICATIONS

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ABSTRACT

$\text{Ag}_2\text{O} : \text{B}_2\text{O}_3 : \text{SiO}_2$ glass system is prepared by melt conventional techniques. Glass ceramics, materials prepared by controlled crystallization of these glasses, have a variety of established uses dependent on their uniform reproducible fine grain microstructures, absence of porosity, good packing density and high-strength, is synthesized, structurally and electrically characterized with a view for solid state electrochemical device application.

Key words: Glass ceramics, DTA, AC and DC conductivity, Transport number.

INTRODUCTION

The first practical glass ceramics, materials prepared by the controlled crystallization of glasses, were developed nearly sixty year ago. Since that time, a wide variety of applications of these versatile materials have been developed as a result of their many outstanding properties and have a variety of established used dependent on their uniform reproducible fine grain microstructures, absence of porosity and wide range properties which can be tailed by changes in composition and heat treatmentschedule. Since the 1970's, when it was first realized that the properties of glasses and glass ceramics could be exploited to provide the better materials for certain implant applications, the field of bioactive ceramics has expanded enormously¹. These biomaterials have been developed to be used in applications where a specific interaction with the human body is expected.

Super ion conducting glasses and glass ceramics have enormous potential for electrochemical device applications²⁻⁵. The main hurdle in this area is the availability of solid electrolyte with high ionic conductivity. It has been observed that, the efforts to increase the ionic conductivity of silver conducting glasses are always associated with their instability. The conversion of glass into glass ceramics is likely to increase the stability⁶⁻⁷. Most of the studies of ions conducting glasses carried out so far have been restricted to temperature range much below the glass transition temperature T_g ⁸⁻¹⁰. On the other hand, the electrical conductivity of glass-ceramics has been studied after conversion of glass into glass-ceramics. Nevertheless, few reports are available on the anomalous conductivity behavior of the above T_g ¹¹⁻¹⁴. The enhancement in the conductivity by two orders has been reported above T_g due to nucleation and decrease in the conductivity above crystallization temperature due to massive crystallization¹⁵.

In view above points in the present study on the synthesis, structural and electrical characterization of $\text{Ag}_2\text{O} : \text{B}_2\text{O}_3 : \text{SiO}_2$ glass ceramic for sensor applications.

EXPERIMENTAL

Glass preparation

The various compositions belonging to $\text{Ag}_2\text{O} : \text{B}_2\text{O}_3 : \text{SiO}_2$ glass systems were prepared by keeping Ag_2O content constant 'n'. The starting material silver nitrate (Ag_2NO_3), boric Acid (H_3BO_3) and silica (SiO_2) procured from Aldrich Sigma were weighed with an accuracy of 0.00001 g using Mettler balance in the required molar ratio. These materials were mixed under acetone thoroughly and dried. Then the mixture was heated in a porcelain crucible at 500°C for an hour. After evolution of the decomposition product, the melting temperature, which depends upon the composition of the different glasses was kept for 45 minutes in the temperature range of $800-1000^\circ\text{C}$. Thereafter, it was quenched in the circular shaped aluminium mould at room temperature and the glasses formed were immediately transferred to the annealing furnace previously adjusted at constant temperature of 200°C . After 24 hours annealing, the glasses were slowly cooled to room temperature. The bulk glasses were polished to smooth flat surface and to a thickness of 1-2 mm using optical grades grinding powder. They were then baked at 150°C for 2 hours for removal of mechanical stress, if any developed during polishing. The Pt was sputtered on the opposite flats surfaces in the form of a thin layer ensure good ohmic contact.

Process of conversion to glass-ceramics

Controlled thermal heat treatment of the prepared glass samples was carried out by glass holder using quartz boat and tube for holding the glass under crystallization inside the furnace at desired temperature and duration of time for under crystallization. Each glass sample was subjected to controlled crystallization during heat treatment schedule. The determination of the crystal growth and nucleation was done by X-ray diffraction (XRD). The main objective in this heat treatment is to achieve many nuclei growing to polycrystalline small crystals. It is accepted that the investigated silver containing glass system can exhibit self-internal nucleation without the addition of any nucleating agents. The adopted procedure is believed to give satisfactory glass-ceramic products.

Structural characterizations

The glassy and glass ceramic states of the samples were checked by means of X-ray powder diffraction (Philips 1700 X-ray powder diffractometer attached with PW1710 controlling unit) using $\text{Cu-K}\alpha$ radiation and The differential thermal analysis (DTA) was used to study the glass transition temperature (T_g). The glass transition temperature was identified by a shift of the base line in an endothermic direction while heating at $10^\circ\text{C}/\text{min}$.

Electrical characterization

The AC conductivity measurements were carried out at the different temperatures using HP 4912 LF impedance analyzer in the frequency range from 5 Hz - 13 MHz. The specimen was pressed against two silver electrodes of a spring-loaded sample holder suspended in a furnace in one fixed position. The temperature was recorded with the help of Pt-Rh thermocouple. Observations were recorded during heating as well as cooling cycles by maintaining the identical condition so as to avoid thermal hysteresis. Particularly all the measurements were restricted to the temperature range much below T_g for glasses but not for glass ceramics.

The ionic transport number of the sample was determined using Wagner's DC polarization (500 mV) technique using Keithley 617 programmable electrometer with both blocking.

RESULTS AND DISCUSSION

As seen, in entire temperature range of investigation conductivity of glasses and glass ceramics obeys the Arrhenius law -

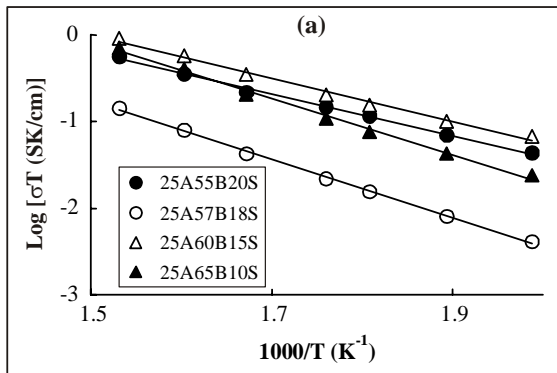
$$(\sigma T) = (\sigma T)_0 e^{\frac{-E_a}{kT}} \quad \dots(1)$$

The values of conductivity and activation energy of all glass and glass ceramics determined from above equation (Eq. 1) are summarized in Tables 1.

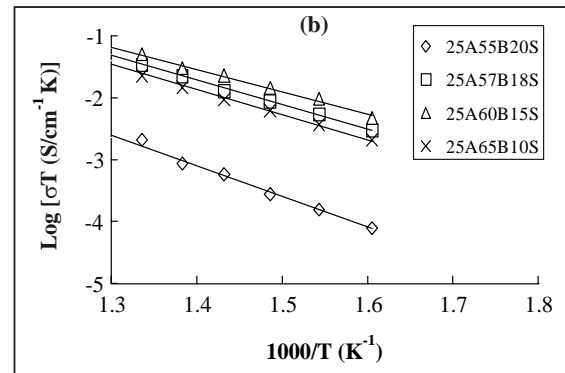
Table 1: Properties of silver-boro-silicate glass and glass ceramic

Composition	$T_g (^{\circ}C)$	$\sigma (S \times cm)^{-1} < T_g$	$E_a (eV)$	$\sigma (S \times cm)^{-1} G. C. > T_g$	$E_a (eV) G.C.$
25Ag ₂ O : 55B ₂ O ₃ : 20SiO ₂	443.6	9.96×10^{-4}	0.34	7.54×10^{-4}	0.89
25Ag ₂ O : 57B ₂ O ₃ : 18SiO ₂	428.3	2.19×10^{-4}	0.42	9.4×10^{-3}	0.79
25Ag ₂ O : 60B ₂ O ₃ : 15SiO ₂	456.7	1.52×10^{-3}	0.33	3.24×10^{-3}	0.72
25Ag ₂ O : 65B ₂ O ₃ : 10SiO ₂	440.2	2.39×10^{-3}	0.36	6.294×10^{-4}	0.81

It is worth to note from Figure 1 (a, b) and Table 1 that 25Ag₂O : 60B₂O₃ : 15SiO₂ glass exhibits maximum conductivity as well as high T_g along with the minimum activation energy for ion conductivity. Same composition, interesting, when converted into glass ceramic offering maximum conductivity with activation energy amongst all glass-ceramics under study. A comparison of Figures 1a and 1b as well as Table 1 clearly reveals that the glasses offer higher conductivity vis-à-vis glass-ceramic counterparts. Although, glass-ceramic is inferior in terms of conductivity compared to glass, the glass-ceramics provide superior electrolyte-electrode interface contact in comparison with the glass.



**Fig.1(a): Arrhenius plots for glasses
i.e. before heat treatment**



**Fig.1(b): Arrhenius plots for glass ceramics
i.e. after heat treatment**

The enhancement in σ in the space charge layer across the hetero-junction can be better understood in the light of dispersed phase theory of two phase mixture, $MX/M'X$ ¹⁶⁻¹⁷. Since the system under consideration is a heterogeneous, there exist sudden structural and chemical compositions. The redistribution

of ionic and electronic constituents taking place across the interface leads to the formation of diffused space charge layers across it¹⁶.

Two significant interfaces participating in the conduction are assumed to be homo-junction (Ag^+ -glass/ Ag^+ -glass) and hetero-junction (Ag^+ -glass/ Ag_2SiO_3 or $\text{Ag}_2\text{Si}_2\text{O}_7$). For simplicity, here the interface at Ag^+ -glass/ Ag_2SiO_3 and Ag^+ -glass/ $\text{Ag}_2\text{Si}_2\text{O}_7$ is considered to be identical to first approximation. In glass/glass interface, in concurrence with the space charge theory, an interfacial surface reaction at homo-junction may give increase in interstitial Ag^+ concentration adjacent to the surface of one glass particle and equivalent Ag^+ vacancy concentration adjacent to the surface of other glass particle in contact. The surface interaction at Ag^+ -glass/ Ag_2SiO_3 hetero-junction is considered analogous to that at the moderate ion-conductor/ insulator interface. Here, it is also presumed that an attractive interaction at Ag^+ -glass/ Ag_2SiO_3 interface has a consequence that the Ag^+ would be sucked out of glass thereby, creates equivalent vacancies adjacent to glass surface. On the other hand, repulsive interaction drives Ag^+ from Ag_2SiO_3 into glass, thereby enhancing the interstitial ion concentration, both quasi-chemical reactions increases Ag^+ vacancies and interstitial ions adjacent the glass surface at the hetero-junction interface whereby creating highly disordered structure in the vicinity of interface under consideration. Such highly distorted regions are known as the space charge layers. The variation of relative vacancy concentration (C/C_0) (where C and C_0 are the defect concentration in the space charge region and in bulk, respectively) and consequently conductivity with distance inside the glass from the interface. The large variance in defect concentration in the homo- and the hetero-junctions results into a considerable difference in corresponding σ as well as activation enthalpy (E_a). In the simplest case, space charge layers across the interface, being highly conducting short circuits the conduction through the crystalline grains. Thus, the major contribution to the total conductivity of the composite systems is from hetero-junctions.

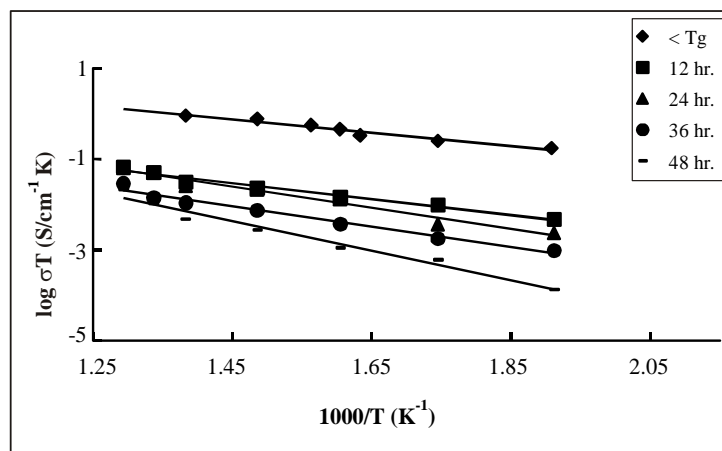


Fig. 2: Variation of Arrhenius plot of glass and corresponding glass ceramic obtained by varying sintering time

A typical variation of DC conductivity as a parametric function of temperature for 25 Ag_2O : 60 B_2O_3 : 15 SiO_2 is depicted in Figure 3. As seen, initially the conductivity decreases rapidly with time, after 20-minute laps the conductivity sets towards the saturation value. Extremely large value of zero time conductivity, taken as σ_∞ , is due to contribution from both the ions and the electrons present in the solid under test. As time lapses Ag^+ moves from Pt electrode towards the reversible silver electrode. Platinum being irreversible or unable to deliver Ag ions to electrolyte; consequently the number of charge carrier concentration decreases thereby, the conductivity. An exponential behavior of conductivity with time is understood to be due to the variation in the relaxation times of mobile Ag^+ , immobile Ag^+ and immobile oxide groups. After polarization of all above-mentioned ions, only electrons contribute to the conductivity,

which are not only less in number but also limited. Therefore, the conductivity saturates to very low conductivity value. Identical results were obtained for the optimized glass and glass ceramics. The transport number determined at temperatures 450 and 500°C for optimized samples are summarized in Table 2.

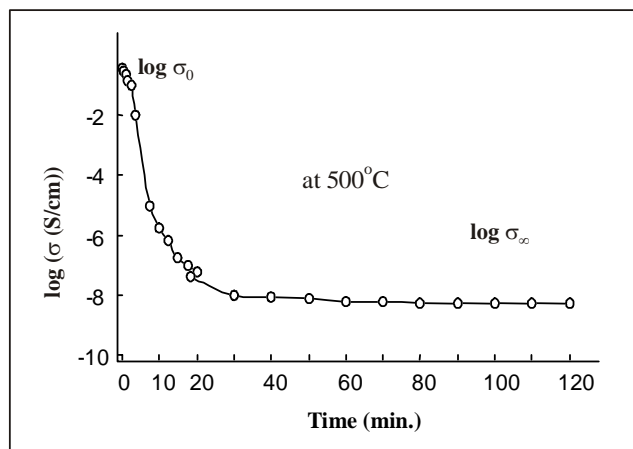


Fig. 3: Variation of $\log(\sigma_{dc})$ with time at 500°C

Table 2: Ionic transport number for optimized glass at 450°C along with for glass ceramic at 450 and 500°C

Composition	Nature	Transport number (t_I)	
		at 450°C	at 500°C
25Ag ₂ O : 60B ₂ O ₃ : 15SiO ₂	Glass	0.999	
25Ag ₂ O : 60B ₂ O ₃ : 15SiO ₂	Glass-ceramics	0.9975	0.9998

From the table it is clear that all-solid electrolyte under investigation exhibit negligible electronic contribution to the total conductivity, suggesting their viability in sensor applications.

CONCLUSION

The present studies show that the conductivity of $Ag_2O : B_2O_3 : SiO_2$ glass and glass ceramics enhances with increase in temperature. The transport number, which is nearly equal to unity, thereby proves the particular glass system as an ionic conductor and conduction is due to mobile Ag^+ carrier. Ag^+ glass ceramics, which is, dispersed in Ag_2SO_4 acts as solid electrolyte material. This may provide a new route for the development of solid electrolyte for solid state electrochemical SO_2 gas sensor.

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