



SYNTHESIS OF Ag^+ CONDUCTING GLASS SYSTEM FOR ELECTROCHEMICAL SO_2 GAS SENSOR

AJAY LAD*

Department of Physics, Amolakchand Mahavidyalaya, YAVATMAL (M.S.) INDIA

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ABSTRACT

$\text{Ag}_2\text{O} : \text{B}_2\text{O}_3 : \text{SiO}_2$ Glass System for $n = \frac{B + Si}{Ag}$ and $y = \frac{B}{B + Si}$ $0.7 \leq y \leq 0.94$ is synthesized, structurally and

electrically characterized with a view to have high glass transition temperature (T_g) for solid state electrochemical SO_2 gas sensor operating at 400^0 - 500^0C . The glass $25\text{Ag}_2\text{O} : 60\text{B}_2\text{O}_3 : 15\text{SiO}_2$ gave maximum conductivity value of the order of 10^{-3} S/cm at 450^0C (less than T_g) and low activation energy ($E_a = 0.33$) due to mixed former effect.

Key words: Glassy solid electrolyte, XRD, DTA, Conductivity, Gas sensor.

INTRODUCTION

Super ionic conducting glasses are of great interest because of their isotropic conduction, ease of preparation in requiring shape and size, high ionic conductivity (depending on the nature and content of the modifier oxide, dopant, and glass former). The well-known glass formers are the tri, tetra, and pentavalent metal oxide (M_2O_3 , MO_2 , M_2O_5) where, M-O bonds are covalent enough to create simple local structure (units) and ionic enough to allow deformation of bond angles. This consequently leads to the destruction of long-range order¹. The oxides are most typical glass formers having different electro-negativity in range of 1.9-2.2².

In view of the above points in the present paper we report an investigation on the synthesis, structural and electrical characterization of the $\text{Ag}_2\text{O} : \text{B}_2\text{O}_3 : \text{SiO}_2$ glass system (composition $n = 3$ for $0.7 \leq y \leq 0.94$ where, $n = \frac{B + Si}{Ag}$ and $y = \frac{B}{B + Si}$). Also the electrical transport number is determined to estimate the magnitude of ionic and electronic conductivities for throwing some light on the utility of these glasses as electrolyte or electrode material in electrochemical gas sensor application.

EXPERIMENTAL

$\text{Ag}_2\text{O} : \text{B}_2\text{O}_3 : \text{SiO}_2$ glass system with high T_g were prepared by melting at 1000^0C together appropriate molar fraction of the initial ingredients; Silver nitrate (Ag_2NO_3), Boric Acid (H_3BO_3) and Silica

(SiO₂) followed by quenching it in an aluminum mould kept at room temperature. The details of preparations and characterizations of glass system are discussed elsewhere³

RESULTS AND DISCUSSION

Structural characterizations

From the XRD results, all samples have been found to be amorphous. The glass transition temperature (T_g) was determined from DTA curve.

Electrical characterizations

The conductivities of all glasses obeyed the Arrhenius law namely $(\sigma T) = (\sigma T)_0 e^{\frac{-E_a}{kT}}$.

Table 1: Properties of Ag₂O : B₂O₃ : SiO₂ glass system

| n | y | Composition | T _g °C | σ (ohm × cm ⁻¹) | logσ | E _a (eV) |
|---|------|---|-------------------|-----------------------------|---------|---------------------|
| 3 | 0.73 | 25Ag ₂ O:55B ₂ O ₃ :20SiO ₂ | 443.6 | 9.96 × 10 ⁻⁴ | -3.001 | 0.34 |
| | 0.76 | 25Ag ₂ O:57B ₂ O ₃ :18SiO ₂ | 428.3 | 2.19 × 10 ⁻⁴ | -3.658 | 0.42 |
| | 0.8 | 25Ag ₂ O:60B ₂ O ₃ :15SiO ₂ | 456.7 | 1.52 × 10 ⁻³ | -2.8176 | 0.33 |
| | 0.86 | 25Ag ₂ O:65B ₂ O ₃ :10SiO ₂ | 440.2 | 2.39 × 10 ⁻³ | -2.619 | 0.36 |

The table 1 shows the glass transition temperature (T_g), conductivity (σ), activation energy (E_a) values of the Ag₂O:B₂O₃:SiO₂ glass system.

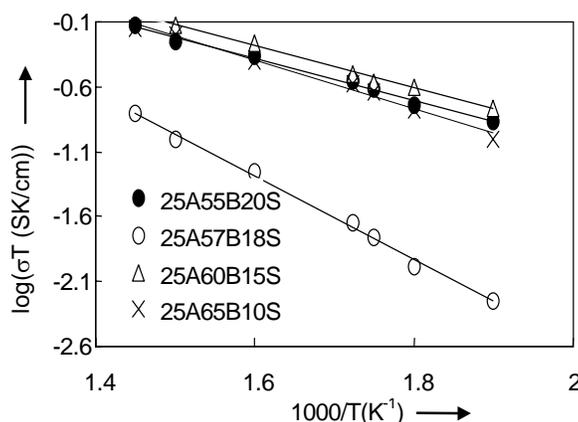


Fig. 1: Plot of log (σT) Vs 1000/T

The log (σT) Vs 1000/T plot for different compositions are shown in Fig. 1, which depicts a linear behavior. It can be seen from these curves that each series, characterized by a specific value of n. The result for the composition (25Ag₂O : 60B₂O₃ : 15SiO₂) gives the highest conductivity (σ) of the order of 1.52 × 10⁻³ S at 450°C.

These results go in line with the mixed former effect and can be explained microscopically using Anderson's and start's model⁴. According to the model the activation energy can be considered as –

$$E = E_S + \Delta E_B \quad \dots(1)$$

Where; E_S and ΔE_B are the network strain energy and the binding energy respectively. Martin⁵ has reported that the strain and binding energies are equivalent to the migration energy E_M and the coulombic force E_C respectively. In the case of oxide glasses the equation of the activation energy can be written as -

$$E_S = \Delta E_M = 4\pi Gr(r - r_D)^2 \quad \dots(2)$$

$$\Delta E_B = \Delta E_C = \frac{ZZ_0 e^2}{r + r_0} - \frac{ZZ_0 e^2}{\frac{\lambda}{2}} \quad \dots(3)$$

Where G , r_D , r and r_0 are the shear modulus, interstitial window radius, radius of cation and the radius of the oxygen respectively. Z and Z_0 are valences of the cation and oxygen ion respectively, e - electronic charge and λ is the jump distance.

According to Anderson and Stuart⁴ the addition of network former changes r_D . This follows because the former ions are considered to replace the boron substitutionally. As large amounts of network former ion are substituted for boron atoms, the average interionic bond distance becomes larger or smaller than the boron atom. In the present case, the Si-O distance of SiO_2 in the tetrahedral coordination is (1.6 Å) which is greater than the B-O distance (1.5 Å) in the trigonal coordination of B_2O_3 . Also the ionic radius of silica Si^{4+} (0.42 Å) is more than the ionic radius B^{3+} (0.20 Å). The substitution of boron by silica increases the interionic distance and consequently r_D increases, as silica is slightly larger in size than boron in turn, ΔE_M decreases. In order to understand the minimum in the activation energy it can be considered that the coulombic energy term ΔE_C increases with the addition of mixed former SiO_2 . In equation (3) all the parameters are constant for the present system except λ . Thus for an increase in ΔE_C , the jump distance λ is expected to increase with the addition of SiO_2 . It is quite reasonable to note that with the addition of SiO_2 , the average interionic bond distance increases. Thus for a decrease in ΔE_M and an increase in ΔE_C with the addition of mixed former explains the minimum activation energy and maximum conductivity.

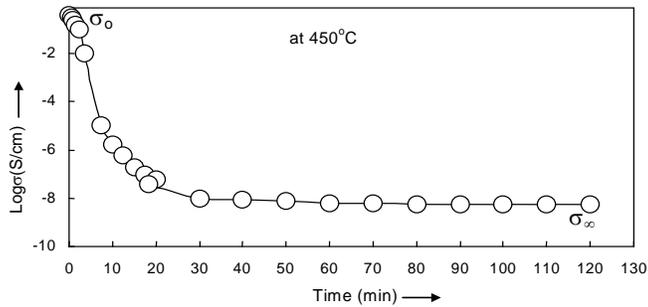


Fig. 2: Transport number of optimized sample

Fig. 2; Shows the dc conductivity variation with time to determine the transport number of the optimized sample ($25Ag_2O : 60B_2O_3 : 15SiO_2$) at $450^\circ C$ is found to be equal to unity. Hence the ionic conductivity is due to mobile Ag^+ carrier. It confirms that the present class of material belongs to solid electrolyte.

CONCLUSION

The present studies show that the conductivity of $Ag_2O : B_2O_3 : SiO_2$ glass system enhances with increase in temperature due to mixed former effect. 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, 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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