

An investigation of ion transport properties in silver phosphate glassy systems doped with Fe, Mn and Zn chlorides

S S Das^{a*}, N P Singh^b, Vibha Srivastava^c & P K Srivastava^b

^aChemistry Department, D D U. Gorakhpur University, Gorakhpur 273 009, India

^bChemistry Department, U.P. Autonomous College, Varanasi, India

^cElectronic Materials Division, National Physical Laboratory, New Delhi 110 012, India

Received 3 September 2007; accepted 29 April 2008

The ion transport properties of silver phosphate glasses doped with different weight percent of chlorides of iron, manganese and zinc have been studied. The synthesized glasses have been characterized by X-ray, FTIR, differential scanning calorimetry, transference number measurements and electrical conductivity studies. Their amorphous nature, structure, glass transition temperature, transference number and ionic conductivity have been investigated. The variation of room temperature conductivity with dopant composition has been found to be controlled by the variation in the amount of dopant ions (Fe^{3+} , Mn^{2+} and Zn^{2+}) present in the glass samples and the trend is

$$\sigma(-\text{ZnCl}_2) > \sigma(-\text{MnCl}_2) > \sigma(-\text{FeCl}_3)$$

The $\text{Ag}_2\text{O}-\text{P}_2\text{O}_5-(10\%) \text{ZnCl}_2$ glass system yielded maximum while the system $\text{Ag}_2\text{O}-\text{P}_2\text{O}_5-(10\%) \text{FeCl}_3$ exhibited the lowest conductivity values respectively. The temperature variation of conductivity has been found to follow an Arrhenius relation.

The results of ion transport studies are in accordance with the variation of glass transition temperature and changes in the structure of $\text{Ag}_2\text{O}-\text{P}_2\text{O}_5$ glass by the addition of Fe, Mn and Zn ions as studied by infrared spectroscopy.

In recent years, there have been a lot of studies on fast ion conducting glasses¹⁻³. Among them ion conducting phosphate glasses are structurally more interesting and technologically important amorphous materials^{4,6} which have attracted greater attention of the researchers due to their ease of preparation at low temperatures, high thermal expansion, lower glass transition temperature and several possible electro-chemical applications^{7,8}.

Ion conducting phosphate glasses containing Li^+ , Na^+ , Ag^+ and Cu^+ ions possessing high ionic conduction are well known⁹. Among these silver ion conducting glasses are very useful from a fundamental and technical point of views². Their ease of preparation in different forms, interesting simple structure and high ionic conductivity make them suitable as solid electrolytes in electro-chemical applications such as solid state batteries and other electro-chemical devices^{7,9-11}.

The properties of the phosphate glasses can be modified and their chemical durability be increased by the addition of generally halides or oxides of the

alkali, alkaline earth and transition metals into the glassy network¹². Glasses doped with transition metal ions appear to be the most interesting due to their potential uses^{13,14}. Therefore, this work has been undertaken with the aim of arriving at a new class of solid glassy electrolytes with high value of ionic conductivity by doping appropriate amount of transition metals into the matrix of $\text{Ag}_2\text{O}-\text{P}_2\text{O}_5$.

Thus, the present study deals with the synthesis, characterization and an investigation of ion transport of a variety of silver phosphate glasses doped with different compositions (1, 5 and 10 wt%) of iron, manganese and zinc chlorides. The role of transition metal ions (Fe^{3+} , Mn^{2+} and Zn^{2+}) in ascertaining the ionic transference number and conductivity values has been studied. The results have been discussed on the basis of IR spectra and DSC studied on these glasses.

Experimental Procedure

The chemicals AgNO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, FeCl_3 , MnCl_2 and ZnCl_2 (Qualigens) were of analytical grade and used without any further purification. Silver phosphate glasses both doped and undoped were prepared by the melt quenching technique using a

*For correspondence (E-mail: ssdas2002@rediffmail.com)

muffle furnace. Details of the procedure adopted in the preparation of these glasses have been reported in an earlier paper¹⁴.

The prepared samples were analyzed by X-ray diffraction technique to ascertain their amorphous nature and the X-ray diffractogram of the powder samples were recorded on an automatic X-ray powder diffractometer.

The FTIR spectra of all the glassy samples were recorded on a Perkin Elmer PC FTIR spectrometer in the range 4000-400 cm^{-1} using KBr pellets.

The DSC experiments of all the synthesized glassy samples were carried out with the help of STA 409 PC (Netzsch, Germany) instrument.

The ionic transference numbers were obtained by Wagner's polarization technique¹⁵ in which a potentiostatic current across a sample pellet is measured as a function of time as described earlier¹⁶. The transference number, t_{ion} is then determined from the following equation

$$t_{ion} = \frac{I_T - I_e}{I_T} \quad \dots (1)$$

where I_T is the initial current and I_e is the residual current after polarization.

The electrical conductivities of all the samples of silver phosphate glasses were measured at room temperature with the help of Keithley 236 electrometer¹⁷ in which the resulting current was obtained with the help of an electrometer at 0.3 V. The electrical conductivity is then determined by using the following equation

$$\sigma = \frac{I d}{V A} \quad \dots (2)$$

where I is the current, d is thickness and A is the area of cross section of the sample pellet and V is the applied voltage.

The variation of conductivity with temperature was studied from room temperature (303 K) to 423 K for $\text{Ag}_2\text{O-P}_2\text{O}_5$, $\text{Ag}_2\text{O-P}_2\text{O}_5$ -(1%) FeCl_3 , $\text{Ag}_2\text{O-P}_2\text{O}_5$ -(5%) MnCl_2 and $\text{Ag}_2\text{O-P}_2\text{O}_5$ -(10%) ZnCl_2 glassy systems only whose conductivities were found to be the maximum at 303 K.

Results and Discussion

The amorphous nature of all the synthesized glasses was confirmed by X-ray diffraction studies.

The FTIR spectra of undoped, FeCl_3 , MnCl_2 and ZnCl_2 doped silver phosphate glasses are almost

similar with very slight shifts in the peak frequencies. Figure 1 show a typical IR spectra of the undoped and FeCl_3 doped $\text{Ag}_2\text{O-P}_2\text{O}_5$ glasses in the range 450-1500 cm^{-1} . Being almost similar the spectra of MnCl_2 and ZnCl_2 doped glasses have not been include in Fig. 1 for the sake of clarity. The corresponding band assignments of IR spectra of the doped and undoped glasses are listed in Table 1. The comparison of spectral bands suggests that all the characteristic IR bands found in the spectra of $\text{Ag}_2\text{O-P}_2\text{O}_5$ glass are also present in the doped ones with slight shift in their frequencies (5-50 cm^{-1}). The broad symmetric band appearing at 520 cm^{-1} in the case of undoped glass is attributed to deformation modes of PO_4^{3-} groups¹⁸. In 1%, 5% and 10% doped glasses this broad symmetric band splits into two weak bands ; one at 505-525 cm^{-1} and another one at 460-508 cm^{-1} respectively. The intensity of splitting increases with the increase in the dopant concentrations. These two weak bands could be assigned to the bending modes of δ (O = P-O) and δ (O-P-O) respectively¹⁹.

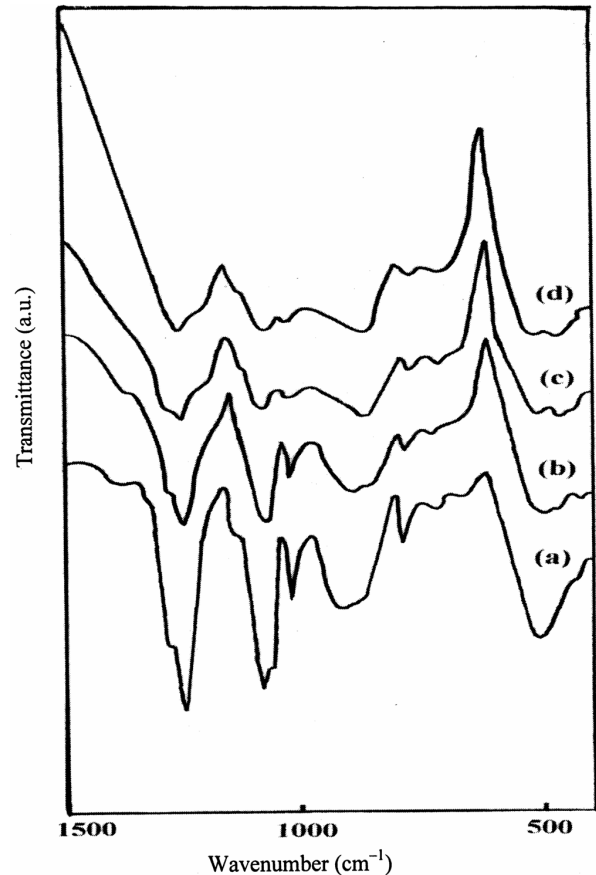


Fig. 1 – IR spectra of (a) undoped, (b) 1% FeCl_3 , (c) 5% FeCl_3 and (d) 10% FeCl_3 doped silver phosphate glasses in the range 450 – 1500 cm^{-1}

Table 1– Characteristic IR spectral band assignments for undoped and metal chloride doped silver phosphate glasses in the range 1500 – 450 cm^{-1}

Assignments	$\text{Ag}_2\text{O-P}_2\text{O}_5$	$\text{Ag}_2\text{O-P}_2\text{O}_5\text{-FeCl}_3$			$\text{Ag}_2\text{O-P}_2\text{O}_5\text{-MnCl}_2$			$\text{Ag}_2\text{O-P}_2\text{O}_5\text{-ZnCl}_2$		
		1%	5%	10%	1%	5%	10%	1%	5%	10%
PO_4^{3-} group	520 (br)	-	-	-	-	-	-	-	-	-
$\delta(\text{O-P-O})$	-	460 (vw)	461 (w)	478 (w)	499 (w)	507 (w)	508 (w)	468. (w)	469 (w)	469 (w)
$\delta(\text{O=P-O})$	518 (w)	507 (w)	512 (w)	514 (w)	512 (w)	518 (w)	525 (w)	504 (w)	507 (w)	527 (w)
$\nu_{\text{sym}}(\text{POP})$	719 (w)	731 (w)	707 (w)	710 (vw)	743 (w)	731 (w)	707 (w)	688 (w)	689 (w)	691 (w)
$\nu_{\text{sym}}(\text{POP})$	795 (w)	794 (vw)	795 (w)	796 (w)	794 (w)	794 (v)	792 (v)	750 (w)	759 (w)	761 (w)
$\nu_{\text{asy}}(\text{POP})$	925 (s)	905 (s)	875 (s)	880 (s)	871 (s)	905 (s)	876 (s)	905 (s)	878 (s)	882 (s)
$\nu(\text{P-O}^-)$	1035 (s)	1033 (s)	1034 (m)	1036 (m)	1033 (s)	1034 (s)	1035 (m)	1020 (m)	1021 (w)	1024 (m)
$\nu(\text{P-O}^-)$	1089 (s)	1088 (m,br)	1087 (m,br)	1087 (br)	1088 (br)	1088 (m,br)	1087 (m,br)	1071 (br)	1087 (m,br)	1090 (br)
$\nu_{\text{sym}}(\text{PO}_2)$	1147 (sh)	1146 (sh)	1134 (sh)	1134 (vw)	1139 (sh)	1135 (sh)	1134 (sh)	1123 (sh)	1189 (sh)	1189 (vw)
$\nu_{\text{asy}}(\text{PO}_2)$	1263 (vs)	1262 (vs)	1262 (s,br)	1263 (s,br)	1262(s,br)	1262 (s, br)	1266 (s,br)	1268 (vs)	1265 (vs)	1268 (vs)
$\nu(\text{P=O})$	1368 (w)	1371 (w)	-	-	1370 (w)	-	-	1372 (w)	-	-

s, strong ; m, medium; w, weak; br, broad; sh, shoulder; vs, very strong; vw,very weak .

The presence of metal oxygen (M–O) bond (where M = Fe, Mn or Zn) can be confirmed by the appearance of bands in the region below 500 cm^{-1} assignable to $\nu(\text{M-O})$. In the IR spectra of doped silver phosphate glasses one such band is seen in the range $460\text{-}508 \text{ cm}^{-1}$, which may be attributed due to P–O–M linkages. Further, it is assumed that the stretching band corresponding to P–O–M linkage might be near 1100 cm^{-1} similar to P–O–Sn as proposed by Day *et al.*²⁰ in the case of Sn–P–O–F glasses, or it may be overlapped by the dominant P–O⁻ stretching band which is sufficiently broad enough to hide it. The formation of P–O–Pb and P–O–Al linkages due to Pb and Al dopings respectively have already been reported elsewhere^{10,21}.

The two absorption bands at 725 cm^{-1} and 785 cm^{-1} are assigned to the symmetric stretching modes of the P–O–P linkage, while the band at $\sim 900 \text{ cm}^{-1}$ is attributed to the asymmetric stretching mode of P–O–P group^{18,22}. In the present study the symmetric stretching bands are found in the range $688\text{-}744 \text{ cm}^{-1}$ and $750\text{-}796 \text{ cm}^{-1}$ respectively while the asymmetric one appears in the range $871\text{-}925 \text{ cm}^{-1}$. Thus, these three bands could be associated to the symmetric and asymmetric motions of the bridging oxygens in linear P–O–P bonds, $\nu(\text{POP})_{\text{sym}}$ and $\nu(\text{POP})_{\text{asy}}$ respectively which indicate the presence of linear metaphosphate chains in the glasses^{23,24}. The absorption bands near 1100 cm^{-1} and 1000 cm^{-1} have been assigned to P–O stretching modes^{18,23}. In the present investigation such bands have shifted in the range $1070\text{-}1090 \text{ cm}^{-1}$ and $1020\text{-}1036 \text{ cm}^{-1}$ respectively, exhibiting decrease in their intensity with increase in the dopant concentrations. The width of the band in the range $1020\text{-}1036 \text{ cm}^{-1}$ is

also found to increase alongwith a shift towards lower frequency with the increasing concentrations of dopant chlorides. Further, it has been reported that the shifting of P–O⁻ stretching band below 1100 cm^{-1} (in the range $1070\text{-}1090 \text{ cm}^{-1}$) indicates the existence of covalent bonds between silver ions and the non-bridging oxygen²⁵. The shifting of the absorption bands for (P–O⁻) stretching towards lower frequency side as well as their broadening could be attributed to the formation of P–O⁻–M⁺ linkages in phosphate tetrahedra of the glasses²³.

The strong intense band in the range $1260\text{-}1270 \text{ cm}^{-1}$ can be ascribed to asymmetric stretching mode of the two non-bridging oxygen bonded to phosphate atom, the O–P–O or $(\text{PO}_2)_{\text{asy}}$ units, in the phosphate tetrahedra^{26,27}. The weak band near 1190 cm^{-1} have been assigned to $\nu(\text{PO}_2)_{\text{sym}}$ ^{18,26}. In the present study presence of weak shoulders have been noticed in the range $1123\text{-}1190 \text{ cm}^{-1}$ which indicate the presence of symmetric stretching mode of two non-bridging oxygen atoms, $\nu(\text{PO}_2)_{\text{sym}}$. The intensity of these shoulders decrease with increasing dopant concentrations.

In the IR spectra of $\text{Ag}_2\text{O-P}_2\text{O}_5$ and all the glassy systems doped with 1% metal chlorides weak bands are observed at $\sim 1370 \text{ cm}^{-1}$ which probably arise due to the terminal double bonded oxygen atom, $\nu(\text{P=O})$. These bands could be due to the presence of a small fraction of Q³ tetrahedral units in the glassy network²³. However, on increasing the concentration of the dopant chlorides, the weak bands appearing at $\sim 1370 \text{ cm}^{-1}$ disappear completely indicating thereby total elimination of Q³ tetrahedral units present in (1%) metal chloride doped glassy systems.

The FTIR spectra (Fig. 2) of all the synthesized glasses (in the spectral range $4000\text{-}1500\text{ cm}^{-1}$) show intense broad bands in the region $3470\text{-}3490\text{ cm}^{-1}$ and less intense bands in the region $1660\text{-}1680\text{ cm}^{-1}$. The bands appearing at $\sim 3490\text{ cm}^{-1}$ are assigned to the antisymmetric and symmetric stretching frequency ν (OH) of physisorbed water molecules while the bands observed at $\sim 1680\text{ cm}^{-1}$ could be due to the δ (H_2O) in-plane bending vibration mode of physisorbed water molecules^{23,28}. It can be assumed that the hydroxyl group act as partial modifiers of the glass network²⁴. The intensity of these bands are maximum in undoped glass and then it decreases with the increasing dopant concentration. This clearly indicates that in the doped glasses less amount of physisorbed water is present as compared to that in the undoped glass. The presence of less amount of physisorbed water in the doped glasses could be due to an increase in cross-links with increasing dopant concentration.

The FTIR spectral studies, thus reveal that the structure of all the phosphate glasses consist of Q^3 type PO_4 tetrahedral units with three bridging

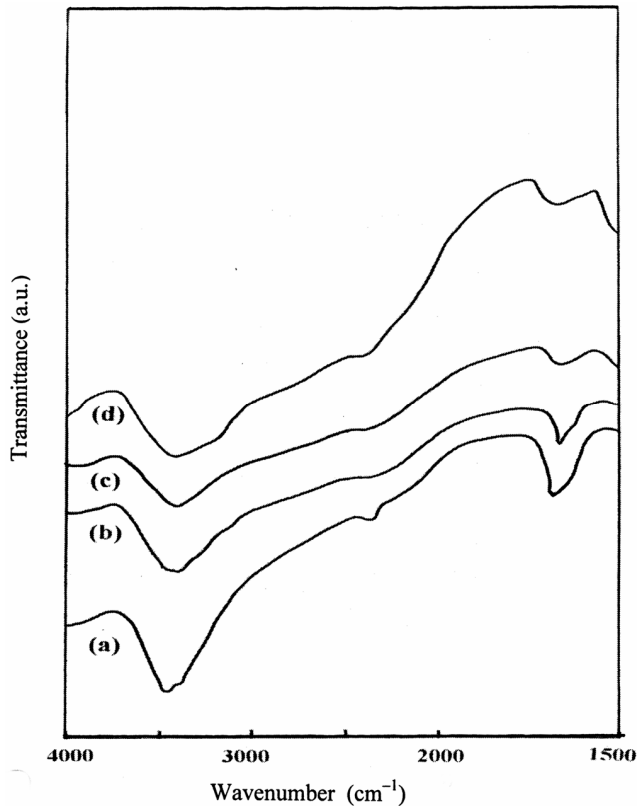


Fig. 2 – IR spectra of (a) undoped, (b) 1% FeCl_3 , (c) 5% FeCl_3 and (d) 10% FeCl_3 doped silver phosphate glasses in the range $4000\text{-}1500\text{ cm}^{-1}$

(P–O–P) and one terminal double bonded non-bridging (P=O) oxygen atoms as shown in Fig. 3. When Ag_2O is added into the PO_4 network of phosphate glass, it results in conversion of three-dimensional network into linear phosphate chains²⁹ with the cleavage of P–O–P linkages and creation of non-bridging oxygen atoms in the glass. Formation of P-O^- – Ag^+ bonds in the undoped silver phosphate glass (Q^2 type tetrahedra) takes place which are replaced by P–O–M bonds on the addition of dopant chlorides in the undoped glass^{18,23}. The metal ions M having higher field strength in comparison to Ag^+ ions, get attached to the negative ends of the P-O^- replacing Ag^+ ions. The bivalent Mn^{2+} , or Zn^{2+} , or trivalent Fe^{3+} will thus eventually lead to stronger binding force with the surrounding phosphate chains. As such significant extent of cross-linking exists with the increasing concentrations of dopant chlorides in all the glassy samples. The fraction of P-O^- – M^+ bond increases with the increase in dopant concentrations leading to higher cross-links in the glassy network. The doped metal ions serve as ionic cross-links between the non-bridging oxygens of different phosphate chains. The proposed schematic structure for metal chloride doped silver phosphate glass is shown in Fig. 4.

The glass transition temperature (T_g) values for all the glasses studied are given in Table 2. The T_g values increase with the increase in dopant concentrations and the following sequence is observed;

$$T_g(-\text{FeCl}_3) > T_g(-\text{MnCl}_2) > T_g(-\text{ZnCl}_2) > T_g(\text{Ag}_2\text{O} - \text{P}_2\text{O}_5)$$

The increase in glass transition temperature values reflect an increase of the cross – link strength of the glass network as Fe^{+3} , or Mn^{+2} , Zn^{+2} ions are introduced in the undoped silver phosphate glass. The increased cross – linking appears to be responsible for better chemical durability of the doped glasses. Thus, FeCl_3 doped silver phosphate glasses with maximum T_g values are the most durable ones out of all the other glasses.

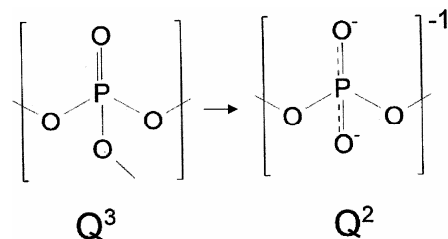


Fig. 3 – The Q^3 and Q^2 tetrahedral units in phosphate glasses

Table 2– Glass transition temperature (T_g), percent ionic transference number ($\% t_i$), conductivity (σ) and activation energy (E_a) values of silver phosphate glasses with Fe, Mn and Zn ions as dopants.

S. No.	Phosphate Glasses	Glass Transition Temperature (T_g) (K)	% Ionic Transference Number ($\% t_i$)	Conductivity (σ) S cm ⁻¹		Activation Energy (E_a) (eV)
				at 303 K	at 423 K	
1	Ag₂O – P₂O₅ (undoped)	467.6	88.9	1.95×10⁻⁷	1.28×10 ⁻⁵	0.63
2	Ag₂O – P₂O₅ – (1%) FeCl₃	481.8	90.8	5.24×10⁻⁷	4.53×10 ⁻⁵	0.58
3	– (5%) FeCl ₃	497.6	89.7	2.03×10 ⁻⁷		
4	– (10%) FeCl ₃	505.9	88.7	4.25×10 ⁻⁸		
5	Ag₂O – P₂O₅ – (1%) MnCl₂	476.1	90.4	2.14×10 ⁻⁷		
6	– (5%) MnCl₂	485.4	91.2	5.34×10⁻⁷	8.48×10 ⁻⁵	0.56
7	– (10%) MnCl ₂	494.6	90.3	2.17×10 ⁻⁷		
8	Ag₂O – P₂O₅ – (1%) ZnCl₂	470.3	94.2	9.23×10 ⁻⁶		
9	– (5%) ZnCl ₂	474.1	95.1	4.13×10 ⁻⁵		
10	– (10%) ZnCl₂	481.2	96.3	5.65×10⁻⁵	1.10×10 ⁻⁴	0.51

The total ionic transference number (t_i) values, as evaluated by using Eq. (1), are given in Table 2. The $\% t_i$ values of all the glassy samples range in between 88.9-96.3. These values indicate that the prepared glasses are mainly ionic conductors with negligible electronic conductivity³⁰.

The electrical conductivities of all the glassy samples as calculated by using Eq.(2) are reported in Table 2. The conductivity of undoped Ag₂O-P₂O₅ glass (1.95×10⁻⁷ Scm⁻¹) is less than those of Ag₂O-P₂O₅-FeCl₃, Ag₂O-P₂O₅-MnCl₂ and Ag₂O-P₂O₅-ZnCl₂ glasses at all dopant concentrations except for the glass Ag₂O-P₂O₅-(10%) FeCl₃ for which the σ value is 4.25×10⁻⁸ Scm⁻¹. In case of iron chloride doped silver phosphate glass, the σ value for 1% FeCl₃ doped glass (5.24×10⁻⁷ Scm⁻¹) is maximum. It then decreases with the increasing concentration of FeCl₃. In case of MnCl₂ doped glasses, the σ value (5.34 × 10⁻⁷ Scm⁻¹) is maximum for (5%) MnCl₂ doped one. Further, addition of MnCl₂ then decreases the conductivity. But in the case of ZnCl₂ doped glasses the conductivity increases with the increasing concentration of ZnCl₂ and is maximum ($\sigma = 5.65 \times 10^{-5}$ Scm⁻¹) for the 10% ZnCl₂ doped one. The variation of conductivity (log σ) with concentration (wt%) of dopant chlorides is given in Fig. 5 which suggests that the trend is

$$\sigma (-ZnCl_2) > \sigma (-MnCl_2) > \sigma (-FeCl_3) > \sigma (-Ag_2O - P_2O_5) > \sigma (-10\% FeCl_3)$$

The increase in σ values of the doped glasses may be due to: (i) An increase in the number of mobile ions and of their mobilities, (ii) An increase in the

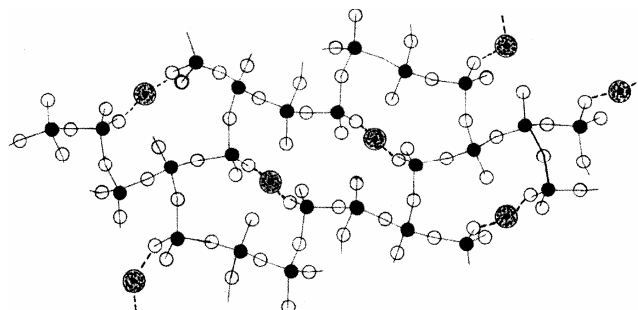


Fig. 4 – Schematic structure of metal chloride doped silver phosphate glass

glass network polarization. The σ value of undoped Ag₂O-P₂O₅ glass is 1.95×10⁻⁷ Scm⁻¹ at room temperature which is essentially due to the presence of mobile Ag⁺ ions in the glass matrix. In the doped silver phosphate glasses, FeCl₃ or MnCl₂ or ZnCl₂ upon dissociation yield Fe³⁺, Mn²⁺ or Zn²⁺ ions in the glassy network³¹. Since the mobilities of these cations are very less, their contribution towards an increase in conductivity will be very low³².

The other possibility for the increase in conductivity is that during glass preparation, the dopant chlorides may react with Ag₂O to form AgCl and metal oxide (MO) when Ag₂O, P₂O₅ and the metal chlorides are melted together. Therefore, in the doped glasses, AgCl thus formed, may dissociate to give additional free Ag⁺ ions having greater mobility than the dopant metal ions. The existence of P[≡]O¹⁻...Ag⁺ bonds in the undoped silver phosphate glass has been confirmed by FTIR studies³³. During glass formation when metal chlorides are added

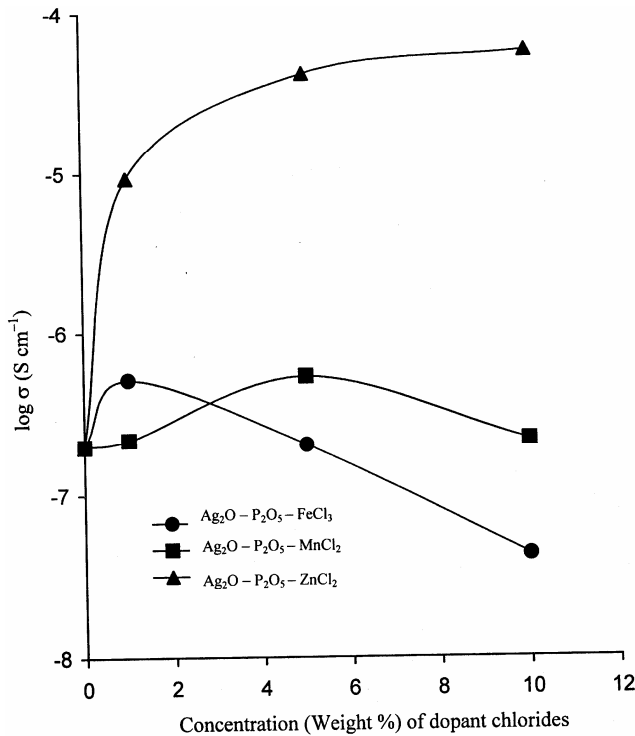


Fig.5 – Composition dependence of conductivity ($\log \sigma$) in $\text{Ag}_2\text{O-P}_2\text{O}_5\text{-FeCl}_3$, $\text{Ag}_2\text{O-P}_2\text{O}_5\text{-MnCl}_2$ and $\text{Ag}_2\text{O-P}_2\text{O}_5\text{-ZnCl}_2$ glassy systems

P–O–M bonds with a stronger covalent character³⁴ are formed between different chains of the silver phosphate glass. The Ag^+ ions of the main chain are replaced by the dopant cations and remain free in the glassy network. Therefore, these additional Ag^+ ions are mainly responsible for an increase in the conductivity values of the doped glasses.

Further, the results show (Table 2) that as the concentration of dopant chloride increases from 1% in the case of FeCl_3 and 5% in the case of MnCl_2 , there is a decrease in σ values. In Mn/ZnCl_2 doped glasses in which both manganese and zinc are in divalent state^{28,35}, formation of P–O–Mn/or Zn bonds would take place between two different phosphate chains of silver phosphate glass. At lower concentration of MnCl_2 (1-5%) insignificant cross-linking retains the glass network structure of the $\text{Ag}_2\text{O-P}_2\text{O}_5$ glass and thereby, the mobility of the replaced Ag^+ ions remains unaffected which ultimately leads to a higher σ value, but above 5%, the conductivity decreases. It is reported that the addition of small amount of Mn^{2+} ions to the phosphate glass matrix in lead phosphate oxide glasses produces strong structural change and leads to an increase in the thermal diffusivity coefficient, but at higher concentrations of Mn^{2+} ions,

the magnitude of thermal diffusivity coefficient decreases because of the increased disorder of the glass structure²⁸. Since the diffusivity ultimately affects the mobility of the ions and hence the conductivity, therefore, higher σ values at lower concentrations (up to 5%) and lower values of σ at higher concentrations (above 5%) of the dopant MnCl_2 are in order.

In FeCl_3 doped glasses the formation of P–O–Fe bond is expected to occur between three different phosphate chains³⁶. Moreover, the presence of both Fe (II) and Fe (III) states are expected to play different structural roles and strong cross-linking of the phosphate chains both by Fe^{2+} and Fe^{3+} ions will occur³⁷. In $\text{Ag}_2\text{O-P}_2\text{O}_5$ -(1%) FeCl_3 glass, the cross-linking seems to be insignificant and therefore, the σ value of this glass is highest. But with the increasing concentration of FeCl_3 the σ value exhibits a sharp decreasing trend and out of all synthesized glasses it is lowest for $\text{Ag}_2\text{O-P}_2\text{O}_5$ -(10%) FeCl_3 system. The following reason could be given for this behaviour; The polarizing power strength of iron cations is higher than that of silver ions. This leads to the formation of higher amount of non-bridging oxygen ions at lower concentrations of the iron ions³⁸. As such the σ value for 1% FeCl_3 doped $\text{Ag}_2\text{O-P}_2\text{O}_5$ glass is high. On the other hand, a decrease in the conductivity upon doping with higher concentration of iron ions could possibly be explained by the blocking effect of the iron ions on the over all mobility of the silver ions³⁹. The large difference in size between the two ions (Ag and Fe) increases the stability and therefore, decreases the mobility due to strengthening of coulomb forces associated with the two ions⁴⁰. FTIR and DSC studies suggest that the cross-link density of FeCl_3 doped glasses are much higher as compared to MnCl_2 or ZnCl_2 doped ones. Further, the σ value of $\text{Ag}_2\text{O-P}_2\text{O}_5$ -(10%) FeCl_3 is the lowest. Due to maximum cross-linking in this glass (since its T_g value is the highest) the mobility of Ag^+ ions drastically reduces, and hence makes no contribution towards conductivity.

In the case of ZnCl_2 doped glasses, the σ values do not decrease with the increasing weight % of ZnCl_2 and $\text{Ag}_2\text{O-P}_2\text{O}_5$ -(10%) ZnCl_2 glass has the highest conductivity ($\sigma = 5.65 \times 10^{-5} \text{ Scm}^{-1}$). This could be explained in terms of partial opening of the three-dimensional network structure and shortening of the average chain length due to breaking of those oxygen bonds which form bridges between the corners of the

PO_4 tetrahedra³⁵. Because of this, the number of non-bridging oxygen atoms grows to a high concentration with the addition of more and more ZnCl_2 in silver phosphate glass matrix. The Zn^{+2} ions are bonded more ionically with more of their oxygen neighbours and depolymerize the phosphate chains⁴¹ more leading to a loosened structure. Therefore, the mobility of Ag^+ ions in ZnCl_2 doped glasses are maximum which eventually lead to high values of conductivity in them. The low T_g values (Table 2) in $\text{Ag}_2\text{O}-\text{P}_2\text{O}_5-\text{ZnCl}_2$ glassy systems support this explanation. The observed variation in σ values with increasing concentrations of dopant chlorides are consistent with the FTIR and DSC studies on these glasses³⁶.

The electrical conductivities (σ) of 1% FeCl_3 , 5% MnCl_2 and 10% ZnCl_2 doped silver phosphate glasses, which exhibited the maximum σ values at room temperature (303 K), were measured up to 423 K. Variation of $\log \sigma$ versus reciprocal temperature ($1000/T$) for these glasses along with the undoped one are given in Fig. 6 which suggest that the conductivity of all the glasses increases with increasing temperature. In the temperature range 363-403 K, the increase is linear in all the cases. On the other hand the increase in conductivity shows deviation from linearity below 363 K and above 403 K. At lower temperatures, the non-Arrhenius behaviour (below 363 K) is due to desorption of water molecules from the glassy samples⁴². The reason for the non-Arrhenius behaviour of the conductivity in glassy systems, at higher temperatures, have been given by many workers⁴²⁻⁴⁵. At higher temperatures, the number of charge carrier Ag^+ ions decreases due to the formation of dimers of mobile Ag^+ ions. But their mobility increases due to the formation of more non-bridging oxygen atoms which provide more opened up paths for Ag^+ ion conduction⁴². Since it is the charge carrier concentration that dominates the conductivity at higher temperatures⁴⁶, it may be inferred that the increase in the conductivity of all the glasses is less than expected above 403 K and becomes non-Arrhenius.

In the linear region, the conductivity of all the synthesized glasses follows the Arrhenius law behaviour and obeys the following Eq. (3):

$$\sigma = A \exp(-E_a/kT) \quad \dots (3)$$

where E_a is the activation energy, A is pre exponential factor and k is Boltzman constant. From this equation

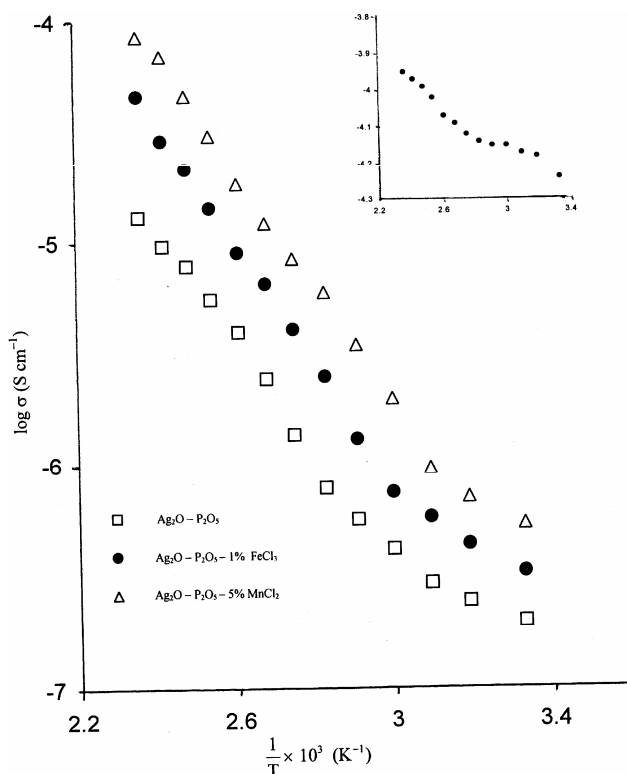


Fig. 6 – Variation of $\log \sigma$ versus $10^3/T$ for undoped, 10% ZnCl_2 , 5% MnCl_2 and 1% FeCl_3 doped silver phosphate glasses. The inset shows the plot of $\text{Ag}_2\text{O}-\text{P}_2\text{O}_5-(10\%) \text{ZnCl}_2$

the activation energy for conduction, E_a has been calculated (Table 2) which follow the trend

$$E_a(\text{undoped}) > E_a(1\% \text{FeCl}_3) > E_a(5\% \text{MnCl}_2) > E_a(10\% \text{ZnCl}_2)$$

However, the electrical conductivity values of these glasses follow the reverse sequence at all the temperature. The E_a value is found to be lowest (0.51 eV) for $\text{Ag}_2\text{O}-\text{P}_2\text{O}_5-(10\%) \text{ZnCl}_2$ glass which exhibits the highest conductivity $5.65 \times 10^{-5} \text{Scm}^{-1}$ at 423 K. The E_a value of $\text{Ag}_2\text{O}-\text{P}_2\text{O}_5$ glass is the highest. These results clearly indicate that upon doping loosening of the glassy network⁴⁷ occurs which facilitates the easy migration of mobile Ag^+ ions in the glass matrix.

At higher temperatures, the increase in conductivity is mainly due to an enhancement in the mobility⁴² of the free replaced Ag^+ ions, which could be explained with the help of Cluster Bypass model⁴⁸ in which the formation of non-bridging oxygen functional groups open up some of the partial pathways for the easy migration of mobile ions. FTIR studies on these glasses support the formation of non-bridging oxygen atoms in the glassy network³⁶.

Conclusions

In case of $\text{Ag}_2\text{O-P}_2\text{O}_5\text{-FeCl}_3$ and $\text{Ag}_2\text{O-P}_2\text{O}_5\text{-MnCl}_2$ glasses, the conductivity increases initially and then decreases with the increasing concentrations of dopants. The σ values for 1% FeCl_3 and 5% MnCl_2 doped silver phosphate glasses are maximum at room temperature. But in the case of $\text{Ag}_2\text{O-P}_2\text{O}_5\text{-ZnCl}_2$ glasses the σ values show an increasing trend with the increasing concentration of ZnCl_2 . In doped glasses the increase in conductivity could be due to the formation of more Ag^+ ions in the glass matrix during glass preparation. Formation of P–O–M bonds (where M = Fe, Mn or Zn) occur which increases the cross-link density with increasing concentrations of the dopant ions resulting in an enhanced T_g values of the glasses. The electrical conductivity variations upon changing the composition of the dopants are also consistent with the structural changes in the glass matrix. The higher concentrations of Fe, or Mn ions cause significant increase in the cross-link density and decrease of free volume, which leads to a tightened and close packed structure. Therefore, the movement of free Ag^+ ions is restricted and as a result the ionic conductivity decreases. However, the increase in σ values of $\text{Ag}_2\text{O-P}_2\text{O}_5\text{-ZnCl}_2$ glasses with increasing amount of ZnCl_2 have been explained in terms of partial opening of three-dimensional structure which increases the number of non-bridging oxygen atoms in silver phosphate glass matrix. At higher temperatures significant increase in conductivity is mainly due to the increase in the mobility of Ag^+ ions as a result of the formation of more non-bridging oxygen atom. The results have adequately been supported by the FTIR and DSC studies on these glasses.

Acknowledgements

The authors are thankful to Prof. K D S Yadav, Head, Department of Chemistry, DDU Gorakhpur University, Gorakhpur and Prof. Suresh Chandra, Department of Physics, BHU, Varanasi, for providing necessary laboratory facilities and help in carrying out the present work. Thanks are also due to Prof. N B Singh, Former Head, Department of Chemistry DDU Gorakhpur University, Gorakhpur, for fruitful discussion. One of the authors (VS) thanks the Council of Scientific and Industrial Research, New Delhi, for the award of Research Associateship.

References

- Ingram M D, *Curr Opin Solid State Mater Sci*, 2 (1977) 399.

- Angell C A, *Ann Rev Phys Chem*, 43 (1992) 693.
- Dalvi Anshuman & Shahi K, *Solid State Ionics*, 159 (2003) 369.
- Brow R K, *J Non-Cryst Solids*, 263 (2000) 1.
- Abid M, Et-Tabirou M & Taibi M, *Mater Sci Eng*, B 97 (2003) 20.
- Hall A, Adams St & Swenson J, *Ionics*, 10 (2004) 396.
- Das S S, Baranwal B P, Gupta C P & Singh P, *J Power Sources*, 114 (2003) 346.
- Bausa L E, Jaque F, Sole J G & Duran A, *J Mater Sci*, 23 (6) (1988) 1922.
- Ingram M D, *Phys Chem Glasses*, 28 (1987) 251.
- Selvaraj U & Rao K J, *J Non – Cryst Solids*, 104 (1998) 300.
- Agrawal R C, Verma M L & Gupta R K, *Solid State Ionics*, 171 (2004) 199.
- Brow R K, *J Am Ceram Soc*, 76 (1993) 913.
- Murawski L, Barczynski R J & Samatowicz D, *Solid State Ionics*, 157 (2003) 293.
- Das S S & Srivastava V, *J Thermal Anal Calor*, 87 2 (2007) 363.
- Wagner J B & Wagner C, *J Chem Phys*, 26 (1957) 1597.
- Das S S, Gupta C P & Srivastava Vibha, *Ionics*, 11 (2005) 423.
- Mogus – Milankovic A, Santic B, Day D E & Ray C S, *J Non-Cryst Solids*, 283 (2001) 119.
- Shih P Y, Yung S W & Chin T S, *J Non-Cryst Solids*, 224 (1999) 211.
- Abid M, Et-Tabirou M & Taibi M, *Mater Sci Engg*, B 97 (2003) 20.
- Hu X J & Day D E, *Phys Chem Glasses*, 31 (1990) 183.
- Chakraborty S & Paul A, *J Mater Sci Lett*, 8 (1989) 1358.
- Liu H S & Chen T S & Yung S W, *Mater Chem Phys*, 50 (1997) 1.
- Das S S, Singh Punita & Agnihotry S A, *J Non-Cryst Solids*, 351 (2005) 3730.
- Tsai P P & Greenblatt M, *J Non-Cryst Solids*, 103 (1988) 101.
- Bartholomew R F, *J Non-Cryst Solids*, 7 (1972) 221.
- Brow R K, Tallant D R, Myers S T & Phifer C C, *J Non-Cryst Solids*, 191 (1995) 45.
- Meyer K, *J Non-Cryst Solids*, 209 (1997) 227.
- Bratu I, Ardelean I, Barbu A, Mih V, Maniu D & Botezan G, *J Mol Struct*, 482 (1999) 689.
- Moustafa Y M & El - Egili K, *J Non-Cryst Solids*, 240 (1998) 144.
- Sidhu K S, Sekhon S S & Chandra S, *Phys Chem Glasses*, 33 (1992) 212.
- Roling B & Ingram M D, *Phys Rev B*, 57 (1998) 14192.
- Chandra S, *Superionic Solids, Principles & Applications*, (North- Holland, Amsterdam), 1981.
- Yung H, Shih P Y, Liu H S & Chin T S, *J Am Ceram Soc*, 80 (1997) 2213.
- Pires R, Abrahams I, Nunes T G & Hawkes G E, *J Non-Cryst Solids*, 337 (2004) 1.
- Chaudhry M Ashraf & Bilal Shakeel, *Mater Chem Phys*, 41 (1995) 299.
- Das S S & Srivastava Vibha, *Prog Crystal Growth & Charact Mater*, 52 (2006) 125.
- Marasinghe G K, Karabulut M, Ray C S, Day D E, Shumsky M G, Yelon W B, Booth C H, Allen P G & Shuh D K, *J Non-Cryst Solids*, 222 (1997) 144.

- 38 Bahgate A A, El – Samanoudy M M & Sabry A I, *J Phys Chem Solids*, 60 (1999) 1921.
- 39 El-Desoky M M, *J Phys Chem Solids*, 59 (1998) 1659.
- 40 Wakabayashi H, *J Non-Cryst Solids*, 203 (1996) 274.
- 41 Mercier C, Palavit G, Montagne L & Follet-Houttemane C, *C R Chin*, 5 (2002) 693.
- 42 Kumar A, Shaju K M & Chandra S, *Can J Phys*, 73 (1995) 369.
- 43 Kincs J & Martin S W, *Phys Rev Lett*, 76 (1) (1996) 70.
- 44 Ribes M, Taillades G & Pradel A, *Solid State Ionics*, 105 (1998) 159.
- 45 Malki M, Micoulaut M, Chaimbault F & Vaills Y, *Phys Rev Lett*, 96 (2006) 145504.
- 46 Souquet J L & Perera W G, *Solid State Ionics*, 40 (1990) 595.
- 47 Julien C & Nazri G A, in *Solid State Batteries Materials Design and Optimization* (Kluwer Academic Publishers), 1994.
- 48 Ingram M D, Mackenzie M A, Muller W & Torge M, *Solid State Ionics*, 28 (1988) 677.