Ionic transport in sodium phosphate glasses doped with chlorides of Co, Cd and Ag

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Several samples of sodium phosphate glasses doped with different concentrations of chlorides of cadmium and cobalt along with samples of undoped sodium phosphate glass have been prepared. Sodium phosphate glasses doped with varying amounts of AgCl have also been prepared to see the role of Ag⁺ ion in modifying the conductivity of sodium phosphate glass. These glasses have been characterized by elemental analysis, X-ray diffraction, IR spectra, differential scanning calorimetry, transference number measurements and electrical conductivity studies. All the glasses are found to be essentially ionic conductors. The undoped sodium phosphate glass has low σ value in comparison to the doped ones. The values of ionic conductivity in Na₂O-P₂O₅-CdCl₂ and Na₂O-P₂O₅-CoCl₂ glasses are maximum for 1% CdCl₂ and 5% CoCl₂ doped ones respectively. However, in the case of Na₂O-P₂O₅-AgCl glass the σ values go on increasing with the increasing concentrations of the dopant AgCl and the following sequence is observed.

$$\sigma(\text{-CdCl}_2) < \sigma(\text{-CoCl}_2) < \sigma(\text{-AgCl})$$

These results have been explained on the basis of changes in the structure of sodium phosphate glass matrix by the addition of different dopant cations, viz; Cd²⁺, Co²⁺ and Ag⁺.

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Glasses have acknowledged advantages over crystalline electrolytes including physical isotropy, the absence of grain boundaries, continuously variable composition and good workability. Furthermore, since room temperature conductivity can vary from as little as $10^{-15}$ to as high as $10^{-2}$ S cm⁻¹, the ion conducting glasses are suitable for a wide range of electrical and electrochemical applications. Among different class of ion conducting glasses, phosphate glasses are of potential interest because of diverse applications including solid state batteries, solid state lasers, water treatment, as hosts for nuclear wastes and as biomedical materials. Besides this they can be easily prepared at a lower temperature with strong glass forming character, simple composition and higher ionic conductivities in comparison with other glassy systems such as silicates and borates. Thus, they are the promising materials for the electrochemical research communities. The fast ionic conducting species identified in the phosphate glasses mainly include Ag⁺, Li⁺, Na⁺, Cu⁺, ionic conductions. Li⁺, Na⁺ and Ag⁺ ion conducting systems are the ones most studied with several possible uses. Sodium ion conducting phosphate glasses have been used as promising glassy electrolytes for the development of high energy density batteries particularly for sodium sulphur batteries. Sodium phosphate glasses which contain transition metals are technologically and biologically important materials with wide range of applications.

In the present paper, ion transport studies on some newly synthesized sodium phosphate glasses doped with various compositions of chlorides of transition metal ions (cadmium, cobalt and silver) have been reported. The role of transition metal ions (Cd²⁺, Co²⁺ and Ag⁺) 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 studies on these glasses.

**Experimental Procedure**

All the chemicals used in the preparation of glasses were of analytical reagent grade. Sodium phosphate glasses both undoped and doped with Cd/Co/or Ag chlorides were prepared by employing the melt quenching technique in the similar manner as described earlier. In the case of sodium phosphate glasses a mixture Na₂CO₃ with NH₄H₂PO₄ in 1:1 molar ratio was heated in a platinum dish in muffle furnace for the desired period of time (4 h) at a fixed temperature (800-900°C). The melt was then quenched over an ice cooled stainless steel plates to

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obtain glassy samples. For preparing metal (Cd, Co, Ag) chloride doped sodium phosphate glasses, appropriate amounts of metal chlorides were added to 1:1 molar mixture of Na$_2$CO$_3$ and NH$_4$H$_2$PO$_4$. The mixtures were first heated slowly in an oven to 150-200°C taking care that the material did not spurt out in the initial stages, when the frothing took place due to brisk evolution of ammonia, oxides of nitrogen and water vapour. When the frothing subsided, the platinum dishes were placed in the muffle furnace (pre heated to the desired temperature in the range 800-900°C) for a period of 4 h before quenching. Mixtures of both undoped and doped glasses were heated in the muffle furnace side by side in two platinum crucibles and their melts were quenched almost simultaneous so that similar condition of preparation could be maintained. After drying in an oven at 100°C, the glassy samples were stored in glass sample tubes kept in desiccators.

The X-ray diffraction studies of all the samples of sodium phosphate glasses were done on an automatic X-ray powder diffractometer. IR spectral studies were carried on a Perkin-Elmer PC FTIR spectrometer in the range 4000-500 cm$^{-1}$ using KBr pellets. The DSC experiments were carried out using STA 409 PC (Netzsch, Germany) instrument which directly gave the $T_g$ values.

The ionic transference number was determined directly by Wagner’s polarization method$^{22}$ by employing the cell configuration $\text{Ag}^+/\text{glasses}/\text{C}^-$. In this method, silver paste (Elteck’s Co. India) was coated on one face of the sample pellet to act as the reversible electrode, whereas the other face of the pellet was coated with graphite paste as the irreversible electrode. A constant dc potential was applied across the sample pellets to polarize it first. The current was monitored as a function of time after the application of polarizing voltage and the experiments were performed in a similar manner as reported earlier$^{23}$.

The electrical conductivities were measured with the help of HIOKI 3532 50 LCR tester at different frequencies, viz: 1 kHz, 10 kHz, 50 kHz and 100 kHz at room temperature. In this method$^{24}$ a pellet of the sample under investigation was prepared with the help of a die and by giving a pressure of 5 ton by a hydraulic pressure. After measuring the thickness of the pellet with the help of screw gauge, silver epoxy was pasted on both of its sides. The pellet was allowed to dry completely before measuring electrical impedance with the help of the LCR tester. The variation of conductivity with temperature was studied from 30°C to 300°C for Na$_2$O-P$_2$O$_5$, Na$_2$O-P$_2$O$_5$-(1%) CdCl$_2$, Na$_2$O-P$_2$O$_5$-(5%) CdCl$_2$ and Na$_2$O-P$_2$O$_5$-(15%) AgCl glassy systems at a frequency of 100 kHz only. The temperature was monitored by a temperature monitor (model 806, Century Instruments, India) and measured by Chromel-Alumel thermocouple.

**Results and Discussion**

The results of X-ray diffraction studies of all the gassy samples show broad and diffused scattering which confirms the amorphous nature of all the samples.

The FTIR spectral studies of all the synthesized glasses almost yielded similar spectra. Figure 1 shows a typical spectra of Na$_2$O-P$_2$O$_5$ glassy system doped with 0%, 1%, 5%, 10% and 15% CoCl$_2$ in the frequency range 1500-450 cm$^{-1}$. The comparison of the spectral bands suggests that all the characteristic bands found in the spectra of the undoped Na$_2$O-P$_2$O$_5$ system are also present in the doped glasses with very slight shift (5-25 cm$^{-1}$) in their peak frequencies.

![Fig. 1 — FTIR spectra of (a) undoped (b) 1% CoCl$_2$ (c) 5% CoCl$_2$ (d) 10% CoCl$_2$ and (e) 15% CoCl$_2$ doped sodium phosphate glasses](attachment:fig1.png)
In IR spectra, the strong bands in the region 1260-1285 cm\(^{-1}\) may be attributed to asymmetric stretching modes of the two non-bridging oxygen atoms bonded to phosphorous atoms, the O–P–O or (PO\(_2\))\(_{asy}\) units, in the phosphate tetrahedra. The weak bands appearing around 1162-1190 cm\(^{-1}\) are assigned to the PO\(_3\) symmetric stretching mode, \(\nu\) (PO\(_3\))\(_{sym}\) of the two non bridging oxygens and their amplitudes decreases with the increasing dopant concentrations in all the cases. It is reported that the band at 1130 cm\(^{-1}\) is due to asymmetric stretching of PO\(_4\) group, \(\nu_{asy}\) (PO\(_2\)) modes. In the present IR investigation, such bands have been observed in the frequency range 1093-1099 cm\(^{-1}\) which confirms the presence of asymmetric stretching of PO\(_4\) group in all the glassy systems. The bands appearing in the range 1029-1000 cm\(^{-1}\) in all the spectra of synthesized glasses may be attributed to asymmetric stretching of P–O–P groups, \(\nu_{asy}\) (P–O–P) modes. It has also been reported that the absorption bands near 1100 and 1000 cm\(^{-1}\) are assigned to the ionic stretching modes of P–O–P groups. The bands in the range 1093-1099 cm\(^{-1}\) and 1029-1000 cm\(^{-1}\) ascribable to P–O– stretching mode exhibit decrease in their sharpness with increase in the dopant concentrations. The broadening as well as shifting of P–O– bands towards lower frequencies can be attributed to the formation of P–O–M\(^+\) (where M = Co or Cd) linkages in the PO\(_4\) tetrahedra. It is further reported that the three absorption bands at 878, 775 and 737 cm\(^{-1}\) associated with P–O–P linkages indicate the presence of linear metaphosphate. In the present study intense bands appearing around 875 cm\(^{-1}\) and weak bands at 775 cm\(^{-1}\) the spectra of all the synthesized glasses could be assigned to the asymmetric, \(\nu\) (POP)\(_{asy}\) and symmetric \(\nu\) (POP)\(_{sym}\) stretching modes of the two-bridging oxygen atoms bonded to phosphorous atoms in a phosphate tetrahedra indicating the existence of linear P–O–P linkages in all the phosphate glasses. The two weak bands appearing in the range 474-478 cm\(^{-1}\) and 525-535 cm\(^{-1}\) have been assigned to the bending vibrational modes of \(\delta\) (O–P–O) and \(\delta\) (O = P–O) respectively.

The FTIR spectral studies, thus reveal that the structure of all the phosphate glasses consist a network of PO\(_4\) tetrahedral units with three bridging (P–O–P) and one terminal double bonded non-bridging (P = O) oxygen atoms. When alkali oxide (Na\(_2\)O) is added into the PO\(_4\) network of phosphate glass, it results in conversion of three-dimensional network into linear phosphate chains with the cleavage of P–O–P linkages and creation of non-bridging oxygen atoms. Formation of P–O–Na\(^+\) bonds in the undoped sodium phosphate glass takes place which are replaced by P–O–M (where M = Cd\(^{2+}\)/Co\(^{2+}\)) bonds on the addition of Cd/or CoCl\(_2\) as dopants in the undoped glass.

The value of \(T_g\) for all the synthesized glasses as determined by DSC thermogram are given in Table 1. The \(T_g\) value of all the samples of sodium phosphate glasses doped with chlorides of Cd and Co increase with increasing concentrations of dopants Cd/or Co chlorides. However, the \(T_g\) values were found to decrease when the AgCl was taken as the dopant and the following sequence is observed.

\[
T_g(\text{CoCl}_2) > T_g(\text{CdCl}_2) > T_g(\text{AgCl})
\]

The increasing values of \(T_g\) with increasing concentrations of Cd/or Co chlorides in all the cases indicate an increase in the crosslink density of the glassy network which improves the chemical durability. However, incorporation of AgCl in Na\(_2\)O–P\(_2\)O\(_5\) system decreases the \(T_g\) values which suggest the loosening of the glass structure.

The total ionic transference number \(I_{\text{ion}}\) was evaluated by using the Eq. (1)

\[
I_{\text{ion}} = I_e - I_r
\]

where \(I_e\) is the residual current after polarization and \(I_r\) is the initial current. The \(\% I_i\) values of all the glassy samples are reported in Table 1. These values are found to lie in between 88.8-93.2. This shows that all these glasses are principally ionic conductors with negligible electronic conductivity in them. Electrical conductivities of all the glassy samples were calculated by using Eq. (2).

\[
\sigma = \frac{G}{A}
\]

where \(G\) is the conductance, \(l\) is thickness and \(A\) is the area of cross-section of the sample pellet.

The values of the conductivity of at different frequencies, viz; 1 kHz, 10 kHz, 50 kHz and 100 kHz at room temperature are given in Table 1. From Table 1, it is clear that as the frequency increases, the \(\sigma\) values of all the samples increase and are maximum at 100 kHz frequency. It is observed that the conductivity of undoped Na\(_2\)O–P\(_2\)O\(_5\) glass is less than that of Na\(_2\)O–P\(_2\)O\(_5\)–CdCl\(_2\), Na\(_2\)O–P\(_2\)O\(_5\)–CoCl\(_2\) and Na\(_2\)O–P\(_2\)O\(_5\)–AgCl glasses at all the frequencies. For
example the value of \( \sigma \) for the undoped \( \text{Na}_2\text{O}-\text{P}_2\text{O}_5 \) is \( 1.09 \times 10^{-7} \ \text{Scm}^{-1} \) and those of \( \text{Na}_2\text{O}-\text{P}_2\text{O}_5-(1\%) \text{CdCl}_2, \text{Na}_2\text{O}-\text{P}_2\text{O}_5-(1\%) \text{CoCl}_2, \) \( \text{Na}_2\text{O}-\text{P}_2\text{O}_5-(1\%) \text{AgCl} \) glasses are \( 1.99 \times 10^{-7}, 1.77 \times 10^{-7} \) and \( 2.22 \times 10^{-7} \ \text{Scm}^{-1} \) respectively at 100 kHz frequency. In case of cadmium chloride doped sodium phosphate glass, the \( \sigma \) value \( (1.99 \times 10^{-7} \text{ at } 100 \text{ kHz}) \) for 1% \text{CdCl}_2 doped glass is maximum. It then decreases with the increasing concentrations of \text{CdCl}_2. In case of \text{CoCl}_2 doped glass the \( \sigma \) value is maximum \( (2.19 \times 10^{-7} \text{ Scm}^{-1} \text{ at } 100 \text{ kHz}) \) for (5%) \text{CoCl}_2 doped one. Further, addition of \text{CoCl}_2 then leads to a decrease in the \( \sigma \) value. Whereas, in the case of \text{AgCl} doped sodium phosphate glasses, it is found that as the \text{AgCl} concentration increases from 1% to 15%, \( \sigma \) values increase to a large extent and for (15%) \text{AgCl} doped glass the value is maximum \( (\sigma = 1.41 \times 10^{-3} \text{ Scm}^{-1} \text{ at } 100 \text{ kHz}) \). The increase in conductivity with increasing frequency may be explained on the basis of presence of electrode-electrolyte polarization and grain boundary effects at low frequencies. However, at higher frequencies, the electrical signal gives excitation energy to the charge carriers which in turn increases the mobility of the charges carriers and decreases the relaxation time. Hence, an increase in conductivity is noticed with the increasing frequencies.

The explanation for higher conductivity in \text{Cd}/or \text{CoCl}_2 doped sodium phosphate glasses may be given in the following manner. The conductivity of undoped sodium phosphate glass at room temperature is \( \sim 10^{-7} \ \text{Scm}^{-1} \). Probably \text{Na}_2\text{O} is not able to provide sufficient \text{Na}^+ ions free to move in \text{Na}_2\text{O}-\text{P}_2\text{O}_5 \) glassy network. On doping the sodium phosphate glass with \text{Cd}/or \text{CoCl}_2 the conductivity increases. But the results (Table 1) suggest that the increase in conductivity in these glasses is not as high as expected. In these glasses the conductivity increases up to a certain concentration (for 1% \text{CdCl}_2 and 5% \text{CoCl}_2 doped ones) and then starts decreasing with increasing dopant concentrations. The increase in \( \sigma \) values with increasing dopant concentration can be explained by two factors; (i) an increase in the number of mobile ions and their mobility, and (ii) an increase in the glass network polarization, since the three-dimensional net of \text{PO}_4 tetrahetra gradually breaks into negatively charged P-O fragments.

As regards the increase in numbers of mobile ions is concerned, the first possibility is that \text{Cd}/or \text{CoCl}_2 upon dissociation may yield divalent \text{Cd}^{2+} or \text{Co}^{2+} ions in the glassy network but the mobility of these diveralent cations are very less, therefore, increase in conductivity due to the presence of \text{Cd}^{2+} or \text{Co}^{2+} ions will be very low. The second possibility for increase in \( \sigma \) values in these glasses is that during glass preparation, the dopant \text{Cd}/or \text{CoCl}_2 react with \text{Na}_2\text{O} to form \text{NaCl} and metal oxide.

\[
\text{Na}_2\text{O} + \text{MCl}_2 \rightarrow 2 \text{NaCl} + \text{MO}
\]

(where \( \text{M} = \text{Cd} \) or \text{Co} )

<table>
<thead>
<tr>
<th>S.No</th>
<th>Phosphate glasses</th>
<th>% Ionic transference number (% ( t_{\text{ion}} ))</th>
<th>Conductivity (( \sigma )) at room temperature (30°C) and at different frequencies (Scm(^{-1}))</th>
<th>Glass transition temperature ( (T_g) ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>\text{Na}_2\text{O}-\text{P}_2\text{O}_5 (undoped)</td>
<td>88.8</td>
<td>8.31 \times 10^{-9}</td>
<td>3.56 \times 10^{-8}</td>
</tr>
<tr>
<td>2</td>
<td>\text{Na}_2\text{O}-\text{P}_2\text{O}_5-(1%) \text{CdCl}_2</td>
<td>90.4</td>
<td>9.4 \times 10^{-8}</td>
<td>4.6 \times 10^{-8}</td>
</tr>
<tr>
<td>3</td>
<td>\text{Na}_2\text{O}-\text{P}_2\text{O}_5-(5%) \text{CdCl}_2</td>
<td>89.5</td>
<td>1.03 \times 10^{-8}</td>
<td>3.29 \times 10^{-8}</td>
</tr>
<tr>
<td>4</td>
<td>\text{Na}_2\text{O}-\text{P}_2\text{O}_5-(10%) \text{CdCl}_2</td>
<td>89.4</td>
<td>1.01 \times 10^{-8}</td>
<td>3.18 \times 10^{-8}</td>
</tr>
<tr>
<td>5</td>
<td>\text{Na}_2\text{O}-\text{P}_2\text{O}_5-(5%) \text{CoCl}_2</td>
<td>89.3</td>
<td>8.52 \times 10^{-9}</td>
<td>2.58 \times 10^{-8}</td>
</tr>
<tr>
<td>6</td>
<td>\text{Na}_2\text{O}-\text{P}_2\text{O}_5-(1%) \text{AgCl}</td>
<td>89.5</td>
<td>1.1 \times 10^{-8}</td>
<td>5.4 \times 10^{-8}</td>
</tr>
<tr>
<td>7</td>
<td>\text{Na}_2\text{O}-\text{P}_2\text{O}_5-(5%) \text{CoCl}_2</td>
<td>91.3</td>
<td>1.43 \times 10^{-8}</td>
<td>5.11 \times 10^{-8}</td>
</tr>
<tr>
<td>8</td>
<td>\text{Na}_2\text{O}-\text{P}_2\text{O}_5-(10%) \text{CoCl}_2</td>
<td>88.9</td>
<td>6.19 \times 10^{-9}</td>
<td>3.14 \times 10^{-8}</td>
</tr>
<tr>
<td>9</td>
<td>\text{Na}_2\text{O}-\text{P}_2\text{O}_5-(15%) \text{CoCl}_2</td>
<td>88.8</td>
<td>6.02 \times 10^{-9}</td>
<td>2.65 \times 10^{-8}</td>
</tr>
<tr>
<td>10</td>
<td>\text{Na}_2\text{O}-\text{P}_2\text{O}_5-(1%) \text{AgCl}</td>
<td>88.9</td>
<td>1.3 \times 10^{-8}</td>
<td>7.0 \times 10^{-8}</td>
</tr>
<tr>
<td>11</td>
<td>\text{Na}_2\text{O}-\text{P}_2\text{O}_5-(5%) \text{AgCl}</td>
<td>89.3</td>
<td>3.69 \times 10^{-7}</td>
<td>4.29 \times 10^{-7}</td>
</tr>
<tr>
<td>12</td>
<td>\text{Na}_2\text{O}-\text{P}_2\text{O}_5-(10%) \text{AgCl}</td>
<td>91.3</td>
<td>1.55 \times 10^{-4}</td>
<td>1.76 \times 10^{-4}</td>
</tr>
<tr>
<td>13</td>
<td>\text{Na}_2\text{O}-\text{P}_2\text{O}_5-(15%) \text{AgCl}</td>
<td>93.2</td>
<td>9.34 \times 10^{-4}</td>
<td>1.25 \times 10^{-3}</td>
</tr>
</tbody>
</table>
This leads to the formation of pseudo quaternary glassy system NaCl-Na2O-P2O5-MO. Probably it is the formation of NaCl in the glassy system that dissociates to provide mobile Na ions responsible for an increase in the conductivity of Cd/or CoCl2 doped Na2O-P2O5 glasses.

Further, the results show (Table 1) that as the concentration of dopant chloride increases (from 1% in the case of CdCl2 and from 5% in the case of CoCl2), the σ values start decreasing. This may be explained due to the formation of cross-links (strain) in the glass structure. FTIR studies suggest that in the undoped sodium phosphate glass P —— O —— Na+ bond exist33,36. When Cd/or CoCl2 are added in it, few Na+ ions get replaced by Cd/or Co during glass formation and P —— O —— M+ bonds (where M =Cd2+ or Co2+) with a stronger covalent character41 are formed between two chains of the sodium phosphate glass. These replaced Na+ ions alongwith Cl ions remain free in the glassy network, and are responsible for an increase in σ values of the doped glasses. In the doped glass formation of P —— O —— M+ bonds between two chains of undoped sodium phosphate is considered to occur because of bivalent metal cations (Cd2+ or Co2+) and this leads to an increase in the cross-links of the glassy network. Furthermore, the existence of short covalent M—O bonds may lead to a lower mobility of the charge carriers. Thus, these bonds confer to Cd2+ or Co2+, a partial network forming character26. At lower concentrations of the dopant chlorides (1% CdCl2 and 5% CoCl2), the number of cross-links in the network of sodium phosphate glass is less due to which the mobility of the free replaced Na+ ions is more and hence σ value is high. But as the concentration of Cd/or CoCl2 increases, the number of cross-links in the glassy network increases and the mobile Na+ ions get trapped, become immobile and thereby make no contribution to an increase in the conductivity. The increase in the cross-links in the glassy network will eventually result in an increase in the glass transition temperature of the doped glasses. The higher values of Tg (Table 1) in Cd/or CoCl2 doped sodium phosphate glasses supports this explanation.

However, in the case of Na2O-P2O5-AgCl glassy systems, the conductivity increases enormously with the increasing concentration of the dopant AgCl. The increase in conductivity with increasing concentration of AgCl is essentially due to Ag+ ions which comes from dissociation of the dopants AgCl during glass preparation. The dopant AgCl will not increase the cross-link density by interconnecting two linear chains of sodium phosphate glass because Ag+ is a monovalent cation and also the Ag+ ions are not able to replace Na+ ions from the main chains of the sodium phosphate glass since the electrode potential42 of Ag+ is lower than Na+. Therefore, the free Ag+ ions along with Cl− ions remain as such into the interstices of the glassy network of the sodium phosphate glass causing loosening of the glass structure43. The loosened glassy structure provides more openings/channels for Ag+ ionic conductivity44. As such, the increase in conductivity with increasing amount of AgCl may simply be due to the dopant salt expanding the glassy network resulting in a more opened up structure suitable for the ionic conduction of Ag+ ions45. The more loosened glassy network facilitates the movement of free Ag+ ions to a large extent and hence Na2O-P2O5-AgCl glasses have very high σ values in comparison to Cd/or CoCl2 doped sodium phosphate glasses. Loosening of the glassy structure with increasing AgCl concentration in these glasses is confirmed by a decrease in their Tg values (Table 1) when the amount of dopant (AgCl) increases from 1% to 15%. The Tg values of Na2O-P2O5-AgCl glasses are much lower in comparison to Na2O-P2O5 and Na2O-P2O5-Cd/or CoCl2 glassy systems.

The conductivities of sodium phosphate glasses doped with 1% CdCl2, 5% CoCl2 and 15% AgCl (which yielded maximum σ values at room temperature) alongwith the undoped Na2O-P2O5 glass were measured in the temperature range 30 to 300°C at 100 kHz frequency. The temperature dependence of the conductivities as shown from Fig. 2 represents the variation of log σ versus reciprocal temperature (1000/T) for different glassy systems. Their conductivities at room temperature 30°C and at 300°C are reported in Table 2. As seen in Fig. 2, the conductivity of all the glassy systems sharply increases with increase in temperature and then shows a shallow dip in the temperature range ∼40 to ∼80°C. After this, further increase in temperature increase the conductivity linearly, which follow the Arrhenius law behaviour.

\[ \sigma = A \exp(-E_a kT) \]  

(3)

where \(E_a\) is the activation energy, \(A\) is pre-exponential factor and \(k\) is Boltzman constant.

The initial sharp increase in σ values in all the cases may be due to presence of water molecules due to hygroscopic nature of the glassy samples. Probably
this adsorbed water provides H\textsuperscript{+} and OH\textsuperscript{−} ions that increase the conductivity very sharply. However, with the increasing temperature the number of these H\textsuperscript{+} and OH\textsuperscript{−} ions are reduced due to desorption and the conductivity shows a decreasing trend (in the temperature range \(\sim 40-80^\circ C\)) till all the water goes off. At higher temperatures the increase in \(\sigma\) values is mainly due to an enhancement in the mobility\textsuperscript{44} of the free replaced Na\textsuperscript{+} ions (in Cd/or CoCl\textsubscript{2} doped glasses) and Ag\textsuperscript{+} ions (in AgCl doped ones). The dopants do have a role in the ionic mobility and activation energy. The \(E_a\) values, as calculated from the linear regions of curves (Fig. 2), are reported in Table 2. The \(E_a\) value of the undoped Na\textsubscript{2}O-P\textsubscript{2}O\textsubscript{5} glass is highest (0.62 eV) and then the \(E_a\) values of the doped glassy systems decreases as the dopant cations are changed from Cd\textsuperscript{2+} to Co \textsuperscript{2+} to Ag\textsuperscript{+}. The \(E_a\) value is the lowest for AgCl doped glassy system. These results indicate the loosening of the glassy network\textsuperscript{46} on the addition of dopant salts. The loosening of the network in Na\textsubscript{2}O-P\textsubscript{2}O\textsubscript{5}-(1%)CdCl\textsubscript{2}, Na\textsubscript{2}O-P\textsubscript{2}O\textsubscript{5}-(5%)CoCl\textsubscript{2} and Na\textsubscript{2}O-P\textsubscript{2}O\textsubscript{5}-(15%) AgCl glassy systems causes a decrease in the activation energy for conduction which would facilitate the easy migration of the mobile Na\textsuperscript{+} (in case of Cd/or CoCl\textsubscript{2} doped ones) or Ag\textsuperscript{+} ions (in AgCl doped glasses). Due to this reason the Na\textsubscript{2}O-P\textsubscript{2}O\textsubscript{5}-(15%) AgCl glass with the lowest \(E_a\) value exhibit the maximum conductivity.

The increase in conductivity with increase in temperature which is mainly due to enhancement of the mobility of ions could also be explained with the help of Cluster Bypass model\textsuperscript{47} as reported earlier\textsuperscript{44} in which the formation of non-bridging oxygen functional groups open up some of the partial pathways for the migration of ions at higher temperatures. This leads to an increase in the mobility of ions with increasing temperature. Formation of non-bridging oxygen which lead to depolymerization of glassy network has been confirmed by IR spectral studies\textsuperscript{11} on these glasses.

**Table 2 — Conductivity (\(\sigma\)) and activation energy (\(E_a\)) of undoped and Cd/Co or Ag chloride doped sodium phosphate glasses**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Phosphate glasses</th>
<th>Conductivity ((\sigma)) (Scm\textsuperscript{-1}) at room temp. (30°C)</th>
<th>Conductivity ((\sigma)) (Scm\textsuperscript{-1}) at 300°C</th>
<th>Activation energy ((E_a)) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na\textsubscript{2}O-P\textsubscript{2}O\textsubscript{5} (undoped)</td>
<td>1.09×10\textsuperscript{-7}</td>
<td>1.56×10\textsuperscript{-3}</td>
<td>0.061</td>
</tr>
<tr>
<td>2</td>
<td>Na\textsubscript{2}O-P\textsubscript{2}O\textsubscript{5}-(1%)CdCl\textsubscript{2}</td>
<td>1.99×10\textsuperscript{-7}</td>
<td>3.51×10\textsuperscript{-3}</td>
<td>0.034</td>
</tr>
<tr>
<td>3</td>
<td>Na\textsubscript{2}O-P\textsubscript{2}O\textsubscript{5}-(5%)CoCl\textsubscript{2}</td>
<td>2.19×10\textsuperscript{-7}</td>
<td>4.46×10\textsuperscript{-3}</td>
<td>0.032</td>
</tr>
<tr>
<td>4</td>
<td>Na\textsubscript{2}O-P\textsubscript{2}O\textsubscript{5}-(15%)AgCl</td>
<td>1.41×10\textsuperscript{-3}</td>
<td>5.38×10\textsuperscript{-2}</td>
<td>0.027</td>
</tr>
</tbody>
</table>

Conclusions

On the basis of the ion transport studies reported above, it can be concluded that all the synthesized glasses are principally ionic conductors with negligible electronic conductivity in them. It is observed that the conductivity of all the glassy samples increases with the increasing frequencies and vary differently with the dopant concentrations when the cations of the dopant chlorides are changed. It has been found that \(\sigma\) value for 1% CdCl\textsubscript{2} doped glass is maximum. It then decreases with the increasing...
concentrations of CdCl$_2$. In case of CoCl$_2$ doped glasses, the $\sigma$ value is maximum for (5%) CoCl$_2$ doped one. Further, addition of CoCl$_2$ then leads to decrease in the $\sigma$ values. Whereas, in the case of AgCl doped sodium phosphate glasses, $\sigma$ values increase to large extent with increasing concentrations of AgCl and for (15%) AgCl doped sodium phosphate glass the $\sigma$ value is maximum. The doped glasses also exhibit lower activation energies in comparison to the undoped sodium phosphate glass indicating the loosening of the glassy network on the addition of the dopant chlorides which facilitates easy migration of mobile ions responsible for higher conductivities in the doped glasses. The increase in conductivity with increasing temperature could be attributed to an increase in the mobility of Na$^+$ or Ag$^+$ ions because of the formation of more non-bridging oxygens at higher temperatures. These results have been supported by the FTIR and DSC studies on these glasses.

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