A new positive mixed anion effect on fast Ag⁺ ion conductivity in Ag₂WO₄

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The electrical conductivity measurements have been made for pure and doped Ag₂WO₄ in the temperature range 293-478K using Gen Rad 1659 RLC digibridge. The sample with 10 mol % Ag₂MoO₄ shows the highest ionic conductivity at room temperature. A positive mixed anion effect is observed. The higher Ag⁺ ion conductivity is attributed to the free volume created by the substitution of a small sized isovalent guest ion.

Studies on fast ionic conductors are interested not only for their great variety of technological applications such as electrochemical power sources, optical devices, lasers, fuel cells and double layer capacitors but also from the fundamental necessity to understand the fast ionic behaviour and to explore the possibility to improve the properties of such compounds 1,2.

Although most of the glasses have very low conductivity at room temperature, there has been considerable interest recently in glasses with high conductivity, both ionic and electronic. Glasses with ionic conductivity in the range 10⁻¹ ohm⁻¹ cm⁻¹ at 25°C are mainly those containing mobile Ag⁺ ion. In this note, we report the mixed anion effect on the fast Ag⁺ ion conductivity of Ag₂WO₄ with MoO₄²⁻ as the guest ion.

Experimental

Ag₂MoO₄ and Ag₂WO₄ were prepared separately by mixing 0.5 M aqueous solution of AgNO₃ with boiling solution of 0.5 M Na₂MoO₄ / 0.5 M Na₂WO₄ with constant stirring. The white precipitate so obtained was filtered and washed with hot doubly distilled water repeatedly, dried thereby over porous plate in a thermostat at 60°C for two days.

The preparations were carried out in dark to avoid any photochemical reaction. The chemicals used were Analar grade obtained from E Merck (India) with a stated purity of 98% for AgNO₃, 98.4% for Na₂MoO₄ and 98% for Na₂WO₄.

X-ray diffraction studies were carried out for the materials using PHILIPS PW 1710 diffractometer with Cu-Kα radiation. The X-ray patterns of the compounds matched well with the standard values.

Conductivity measurements

Different solid solutions were prepared by mixing Ag₂MoO₄ and Ag₂WO₄ in requisite composition in an agate mortar and heating at 200°C for 24 h in a silica crucible with intermittent grinding. For carrying out the conductivity measurements, pellets were prepared by pouring the sample powder into a stainless steel die and pressed at a pressure of 4 ton with the help of a hydraulic press (spectra Lab. Model SL-89). These pellets had diameter of 4.524 cm and thickness 0.1 cm. All the samples were annealed at 200°C for 12 h before measurements to eliminate any grain boundary effect.

The electrical conductivity measurements were performed by means of a two probe method. The pellets were mounted on a stainless steel sample holder assembly between copper leads using two polished platinum electrodes. The electrical conductivity of the samples were measured in the temperature range 20-205°C using a Gen Rad 1659 RLC digibridge with the frequency range 100HZ - 10KHZ. The rate of heating was maintained at 1°C / min.

Results and discussion

The temperature dependence of the ionic conductivity is given by the Arrhenius expression,

\[ \sigma = \frac{n e^2 \lambda^2 V \gamma / kT \exp \left(- \frac{\Delta G^*}{kT} \right)}{\exp \left(\frac{\Delta S^*}{k}\right) - \exp \left(\frac{-\Delta H^*}{kT} \right)} \]

where \( n \) is the number of ions per unit volume, \( e \) the ionic charge, \( \lambda \) the intersite distance, \( \nu \) the jump
Fig. 1- The temperature dependence of electrical conductivity of Ag$_2$MoO$_4$ - Ag$_2$WO$_4$ system.

frequency, $\gamma$ the intersite geometric constant, $k$ the Boltzmann constant and $\Delta G^*$, $\Delta S^*$ are activation free energy, entropy and enthalpy terms respectively. The equation can be written as:

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

where

$$\sigma_0 = n e^2 \gamma^2 / kT \exp \left( \frac{\Delta S^*/k}{\Delta H^*} \right)$$

i.e., the activation enthalpy equals the experimental activation energy for ionic mobility, which may include a defect formation enthalpy contribution. On the basis of the above equation, heat mode plots of log ($\sigma T$) vs $10^3/T$ are given in Fig. 1 for pure Ag$_2$WO$_4$ and various molar ratios of Ag$_2$MoO$_4$ - Ag$_2$WO$_4$ viz. 10:90, 20:80; 30:70; 40:60; 50:50; 60:40; 70:30% and 80:20.

From Fig. 1 it can be seen that all the doped samples show a remarkable increase in conductivity particularly in low temperature range. The small dopant concentrations (10 mol% of Ag$_2$MoO$_4$) into the host lattice resulted in an increase in conductivity. A similar enhancement effect was anticipated for further additions of dopant concentrations in the host lattice of Ag$_2$MoO$_4$ , but could not be observed. Instead, an increase in dopant concentration decreased the conductivity monotonically which is also evident from the plots of log $\sigma T$ versus mol % of the added Ag$_2$MoO$_4$ depicted in Fig. 2.

Fig. 2- The variation of log ($\sigma T$) with mol % of Ag$_2$MoO$_4$ in Ag$_2$WO$_4$.

The incorporated anion, MoO$_4^{2-}$ into the host lattice of Ag$_2$WO$_4$ occupy a comparatively less available space because of its small size, thereby making the extra space available for the mobile Ag$^+$ ions. This ensures the easy movement of cations which in turn facilitate the increase in conductivity. However, by the introduction of a 'wrong' size ion in the host lattice, there may be a distortion in the lattice, which hinders the free rotation of the ions and can decrease the conductivity. But in this case, the lattice stays undistorted which was revealed by the X-ray studies. The XRD patterns of all the samples show lines corresponding to Ag$_2$WO$_4$.

With the availability of additional vacancies created by MoO$_4^{2-}$ substitution in the host lattice, the Ag$^+$ ions move through the lattice with a high elementary hopping probability. The increasing vacancy concentration due to the substitution of MoO$_4^{2-}$ creates additional migration paths for Ag$^+$ ions, which in turn increase the conductivity. Upon further addition beyond 10 mol% Ag$_2$MoO$_4$, the mobility of Ag$^+$ ion was reduced which may be due to vacancy interactions such as cluster formation and also cationic sublattice ordering.
As for the activation energies, two different linear regions are identified in the plots of $\log \sigma T$ vs $10^3/T$. Region I is associated with higher activation energies and may be considered as the extrinsic region. Whereas region II is associated with lower activation energies and may be considered as the intrinsic region.

The activation energy values for ionic conductivity are presented in Table 1. The MoO$_4^2-$ doped samples have a low activation energy in the high temperature phase between 373-478 K. The dopant ions produce a far greater number of defects than the defects produced by thermal excitation. Hence, the number of defects in the high temperature phase can be considered approximately constant and the activation energy ($E_a$) would correspond to the enthalpy of migration of ions in this region\(^5\). The higher activation energy values at the lower temperatures than at the higher temperatures and monotonic rise in both temperatures as seen from Fig.3 strongly suggest a number of contributing factors. However, the significant feature is the relatively constant $E_a$ value 50 ± 4 kJ mol\(^{-1}\) in the high temperature for 10 to 50 mol % Ag$_2$MoO$_4$ common with other binary systems\(^9,10\). This constant value of $E_a$ strongly supports a common conductivity mechanism as in a similar structure of mixed cation or mixed anion composition.

### Table 1: Ionic conductivity activation energy values for pure and doped Ag$_2$WO$_4$

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Temperature range</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Ag$_2$WO$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>46</td>
</tr>
<tr>
<td>Ag$_2$MoO$_4$: Ag$_2$WO$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:90</td>
<td>A</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>49</td>
</tr>
<tr>
<td>20:80</td>
<td>A</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>51</td>
</tr>
<tr>
<td>30:70</td>
<td>A</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>52</td>
</tr>
<tr>
<td>40:60</td>
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<td>78</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>54</td>
</tr>
<tr>
<td>50:50</td>
<td>A</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>55</td>
</tr>
<tr>
<td>60:40</td>
<td>A</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>81</td>
</tr>
<tr>
<td>80:20</td>
<td>A</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>82</td>
</tr>
</tbody>
</table>

A = 20-80°C
B = 125-205°C

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References