Fast ion transport in the new mixed system (CuI)$_x$·[(Ag$_2$O)$_2$·(V$_2$O$_5$)]$_{100-x}$ (40 $\leq$ x $\leq$ 80)

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The new mixed system (CuI)$_x$·[(Ag$_2$O)$_2$·V$_2$O$_5$)]$_{100-x}$ where x = 40, 45, 50, 55, 60, 65, 70, 75 and 80 mol % was investigated as a possible glassy fast ion conductor by preparing molten mixtures and quenching them to low temperatures. The analysis of their composition was carried out using differential scanning calorimetry (DSC) and powder X-ray diffraction (XRD) techniques. These studies have confirmed the formation of new substances. Formation of AgI in some samples was also revealed by XRD analysis and by the occurrence of a characteristic β → α phase transition temperature around 420 K identified through DSC experiments as well. Detailed temperature-dependent a.c. electrical conductivity studies were carried out on the new materials by a.c. impedance analysis in the frequency range 65.5 kHz–1 Hz and over the temperature range 293 to 398 K. It has been found that the highest electrical conductivity of 3.64 x 10^{-3} S cm^{-1} at 305 K due to the migration of Ag$^+$ ions and the lowest activation energy of 0.1 eV in the above temperature range of investigation could be realized for the composition 40CuI–40Ag$_2$O–20V$_2$O$_5$ in the mixed system.

1. Introduction

During the last two decades many highly conducting fast ion solids have been identified in view of their several promising features and applications in solid-state batteries, display panels, memory devices, sensors and biomedical devices. Significantly, glassy fast ion conductors are found to have special merits such as isotropic properties, tendency to form thin films, flexibility to control their properties over a wide range of temperatures and so on. A number of silver ion conducting glassy electrolytes have also been developed in recent years [1–5]. Glassy electrolytes containing Cu$^+$ ions as the mobile species have also been studied because Cu$^+$ ions have an electronic configuration similar to that of Ag$^+$ ions [6]. The present work concerns the result of our experimental investigations on the reciprocal role of Cu$^+$ ions in the matrix of [Ag$_2$O–V$_2$O$_5$] for various compositions in the new system (CuI)$_x$·[(Ag$_2$O)$_2$·(V$_2$O$_5$)]$_{100-x}$.

2. Experimental procedure

2.1. Sample preparation

Commercially available Analar grade chemicals of Ag$_2$O, V$_2$O$_5$, KI and CuSO$_4$·5H$_2$O were used as raw materials for the synthesis of various compositions. Cuprous iodide (CuI) was initially prepared as a precipitate from aqueous solutions of KI and CuSO$_4$·5H$_2$O followed by thorough washing with distilled water. Iodine liberated during the process was removed by treating the mixture with an aqueous solution of sodium thiosulphate. CuI thus obtained was dried at 373 K for several hours before use. Stoichiometric compositions of (CuI)$_x$·[(Ag$_2$O)$_2$·(V$_2$O$_5$)]$_{100-x}$ where x = 40, 45, 50, 55, 60, 65, 70, 75 and 80 mol % were prepared by mixing CuI, Ag$_2$O and V$_2$O$_5$ in appropriate amounts and grinding the mixture together before melting in quartz crucibles at 873 K for 3 h under a continuous flow of dry nitrogen gas. The molten mixture was quenched rapidly by pouring it on to a stainless steel plate kept in ice-water. The prepared samples were protected in darkened desiccators to avoid direct exposure to light.

2.2. Powder X-ray diffraction and DSC studies

The powder samples of various compositions obtained in the mixed system were characterized by X-ray diffraction (XRD) using a Philips X-ray generator unit model PW 1130 with a CuK_α radiation (λ = 0.154 18 nm) at room temperature. Differential scanning calorimetry (DSC) experiments were carried out on all the powder samples using a Perkin Elmer model DSC 7 differential scanning calorimeter along with a Perkin Elmer 3700 data station at a heating rate of 10 K min^{-1} over the temperature range 373–473 K.

2.3. A.c. impedance and transport number measurements

The solid samples were ground and pressed with electrodes on both the faces under a pressure of $4000 \, kg \, cm^{-2}$ to form circular pellets for electrical conductivity measurements. The electrodes used for the conductivity measurements were prepared by mixing silver powder with the sample in the weight ratio 2:1. A.c. impedance studies were made on all the prepared samples using a Solartron model 1254 four-channel frequency response analyser and a Solartron model 1286 electrochemical interface in conjunction with a BBC model B^+ microcomputer over the frequency range 65.5 kHz to 1 Hz and in the temperature range 293 to 398 K. The transport number of these specimens was determined by constructing a galvanic cell. The cell was fabricated with a configuration (−) Ag + sample/sample/I_2(+) where a powder mixture of metallic silver and the sample in the weight ratio 2:1 was used as the anode. The cell was made in the form of a cylindrical pellet by pressing the above three components of the cell assembly together at a pelletizing pressure of $4000 \, kg \, cm^{-2}$. The open-circuit voltage of the galvanic cell was measured at room temperature in order to estimate the transport number of silver ions in the new materials.

3. Results and discussion
3.1. XRD and DSC results

Table I presents typical XRD data obtained for the composition $50CuI-33.33Ag_2O-16.66V_2O_5$ together with the ASTM data reported for γ-AgI, γ-CuI, Ag_2O and Ag. From Table I it is clear that the d spacings of the above composition are different from those of the starting materials. This observation indicates that new substances could be obtained while melting the solid mixtures of CuI, Ag_2O and V_2O_5 together. Table I also suggests that only a few traces of AgI may be present in the sample, in view of the fact that d spacings at 0.228 and 0.147 nm could be attributed to the presence of AgI traces alone. On the other hand, it was found that the XRD pattern for the composition $40CuI-40Ag_2O-20V_2O_5$ is featureless, indicating its glass-like structure.

Fig. 1 shows the DSC traces recorded for all the compositions $(CuI)_x \cdot [(Ag_2O)_2 \cdot (V_2O_5)]_{100-x}$ where $x = 40, 45, 50, 55, 60, 65, 70, 75,$ and 80 mol %. It is obvious that endothermic peaks would be exhibited

around 420 K by those compositions where AgI could have been formed. Interestingly, three compositions in the mixed system containing 40, 45 and 50 mol % of CuI (i.e. at $x = 40, 45$ and 50) have been found to show endothermic peaks at 424, 422 and 424 K, respectively. These transition temperature values are comparable to the characteristic $\beta \rightarrow \alpha$ phase transition temperature of pure AgI ($\simeq 420$ K). These results appear to suggest that AgI may probably be the major content in those three compositions in the mixed system. However, XRD studies have confirmed that only a few traces of AgI are present in the composition namely $50CuI-33.33Ag_2O-16.66V_2O_5$ and that $40CuI-40Ag_2O-20V_2O_5$ samples are glass-like. Therefore, it is reasonable to assume that the latter would exhibit the highest electrical conductivity at ambient temperatures. Detailed a.c. impedance data to be discussed in the following section will throw more light on these results.

3.2. A.c. impedance and transport number studies

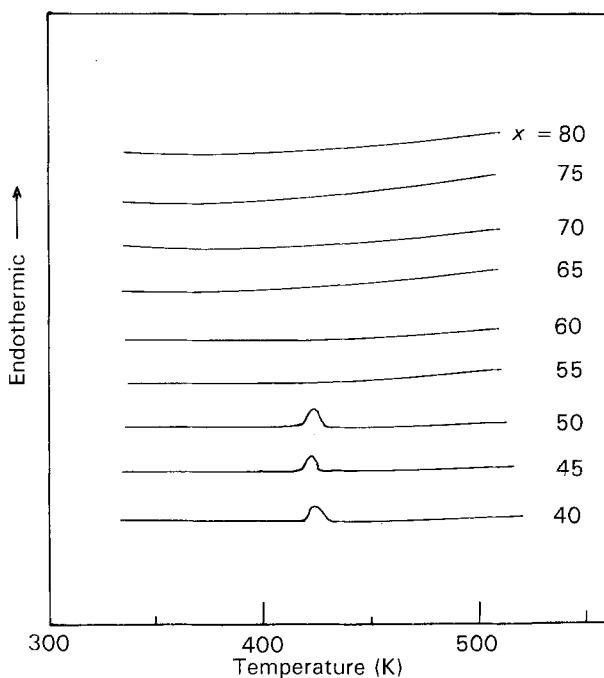Typical complex impedance plots obtained for the composition $65CuI-23.33Ag_2O-11.66V_2O_5$ for four

Figure 1 DSC traces of the mixed system $(CuI)_x \cdot [(Ag_2O)_2 \cdot (V_2O_5)]_{100-x} (40 \leq x \leq 80)$.

TABLE I Powder X-ray diffraction data obtained for $50CuI-33.33Ag_2O-16.66V_2O_5$ and ASTM data for γ-AgI, γ-CuI, Ag_2O and Ag

$50CuI-33.33 Ag_2O-16.66V_2O_5$ (present study)		γ-AgI		γ-CuI		Ag_2O		Ag	
d(nm)	I/I_0(%)	d(nm)	I/I_0(%)	d(nm)	I/I_0(%)	d(nm)	I/I_0(%)	d(nm)	I/I_0(%)
0.228	100	0.375	100	0.349	100	0.335	4	0.236	100
0.223	74	0.231	60	0.303	12	0.273	100	0.204	40
0.147	65	0.197	30	0.214	55	0.237	35	0.145	25
		0.162	6	0.182	30	0.167	18	0.123	26
		0.149	8	0.125	12	0.143	12	0.094	15
						0.137	6	0.092	12
								0.083	13

different temperatures, namely 324, 360, 380 and 400 K, are shown in Fig. 2. At 324 and 360 K the impedance plots are found to contain a portion of a semicircle corresponding to the combination of the geometric capacity (C_g) and the bulk resistance (R_b) of the specimen. In contrast, it may be pointed out that the impedance plots observed at both 380 and 400 K are just spikes intersecting the Z' (i.e. real part of the impedance) axis at values corresponding to R_b at these temperatures. Another interesting observation is that the R_b value decreases as the temperature is increased. From the values of bulk resistance evaluated from the impedance plots obtained during the present investigation, electrical conductivity (σ) values were estimated using the general relationship

$$\sigma = t/R_b A \qquad (1)$$

where t denotes the thickness of the sample pellet and A its area of cross-section.

In Fig. 3 variations of log σT as a function of reciprocal absolute temperature for different compositions in the mixed system in the temperature range 293–398 K are shown. From Fig. 3 it is evident that in this temperature range, all the compositions obey the Arrhenius relation

$$\sigma T = \sigma_0 \exp(-E_a/kT) \qquad (2)$$

where σ_0 is the pre-exponential factor, E_a the activation energy for the conduction process and k the Boltzmann constant. Usually, the activation energy for the conduction phenomenon represents an energy barrier for ions migrating from site to site within the solid. The values of activation energy have been evaluated from the slopes of these plots drawn by the least-squares method and they vary from 0.1 to 0.35 eV.
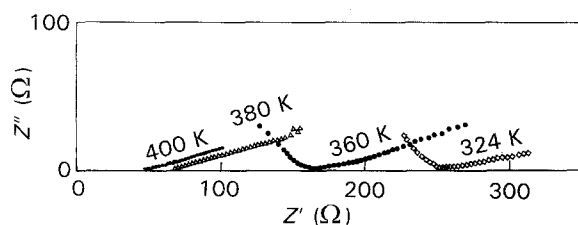
Table II presents the summary of DSC and electrical conductivity results together with the best-fit conductivity plots. It is interesting that the most highly conducting composition has been found to be 40CuI–40Ag$_2$O–20V$_2$O$_5$, which exhibits the highest electrical conductivity of 3.67×10^{-3} S cm^{-1} at 305 K and the lowest activation energy of 0.1 eV too. The highest conductivity observed in this case may be attributed to the glass-like structure as revealed by XRD studies.

DSC results have also been found to be in conformity with these observations, due to the fact that an endothermic peak at 424 K has been observed for the most highly conducting composition. However, the occurrence of a high electrical conductivity value of 3.67×10^{-3} S cm^{-1}, which is an order of magnitude higher than that of pure AgI, may be explained as follows: when a molten mixture of 40CuI–40Ag$_2$O–20V$_2$O$_5$ is quenched to low temperatures, probably a new compound other than AgI is formed. As a result of its glassy nature this might exhibit the
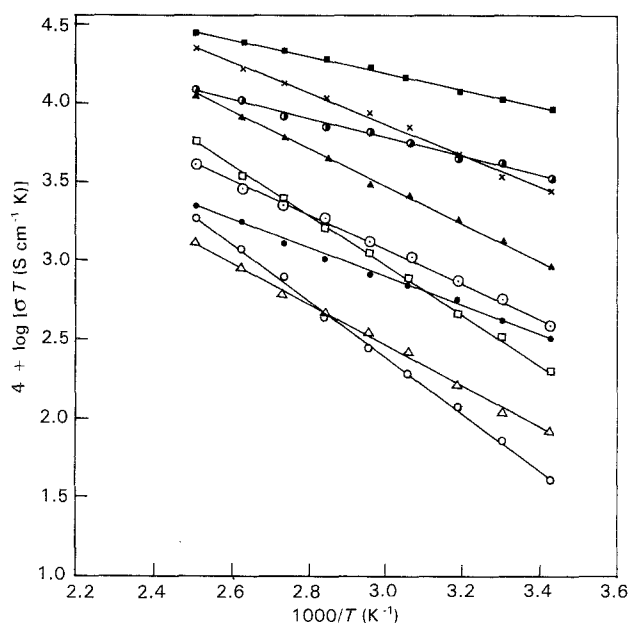

Figure 3 Plots of log σT versus $10^3/T$ for various compositions in the system $(CuI)_x \cdot [(Ag_2O)_2 \cdot (V_2O_5)]_{100-x}$ ($40 \leq x \leq 80$): $x = (\blacksquare)$ 40, ($\times$) 45, ($\circleddash$) 50, ($\blacktriangle$) 55, ($\bullet$) 60, ($\bigcirc$) 65, ($\triangle$) 70, ($\square$) 75, ($\bigcirc$) 80.

Figure 2 Complex impedance plots obtained for the composition 65CuI–23.33Ag$_2$O–16.66V$_2$O$_5$ at temperatures 324, 360, 380 and 400 K.

TABLE II DSC data and conductivity results for the new system CuI–Ag$_2$O–V$_2$O$_5$

Composition	DSC peak positions (K)	$\sigma_{305\,K}$ (S cm^{-1})	Activation energy, E_a (eV)	Conductivity equation logσ T = logσ_0- $(E_a/k)(10^3/T)$
80CuI–13.33Ag$_2$O–6.67V$_2$O$_5$	–	3.4×10^{-5}	0.35	$3.71 - 1.77(10^3/T)$
75CuI–16.66Ag$_2$O–8.33V$_2$O$_5$	–	1.22×10^{-4}	0.31	$3.67 - 1.57(10^3/T)$
70CuI–20Ag$_2$O–10V$_2$O$_5$	–	4.32×10^{-5}	0.25	$2.31 - 1.28(10^3/T)$
65CuI–23.33Ag$_2$O–11.66V$_2$O$_5$	–	1.89×10^{-4}	0.22	$2.39 - 1.11(10^3/T)$
60CuI–26.66Ag$_2$O–13.33V$_2$O$_5$	–	1.46×10^{-4}	0.18	$1.6 - 0.9(10^3/T)$
55CuI–30Ag$_2$O–15V$_2$O$_5$	–	6.9×10^{-4}	0.24	$3.04 - 1.19(10^3/T)$
50CuI–33.33Ag$_2$O–16.66V$_2$O$_5$	424	1.39×10^{-3}	0.12	$1.56 - 0.59(10^3/T)$
45CuI–36.66Ag$_2$O–18.33V$_2$O$_5$	422	1.2×10^{-3}	0.19	$2.78 - 0.97(10^3/T)$
40CuI–40Ag$_2$O–20V$_2$O$_5$	424	3.67×10^{-3}	0.10	$1.75 - 0.52(10^3/T)$

best electrical properties among the various compositions. In addition, the extent of the electronic contribution to the total electrical conductivity of the most highly conducting composition has also been identified by measuring the open-circuit voltage of a galvanic cell having the same composition as the electrolytic phase. The measured open-circuit voltage values for the galvanic cells constructed using two compositions, namely $40CuI-40Ag_2O-20V_2O_5$ and $50CuI-33.33Ag_2O-16.66V_2O_5$, were found to be 644 and 641 mV, respectively, at room temperature. These observations clearly suggest that the silver ion transport numbers in the above compositions are 0.94 and 0.93, respectively, thus confirming that the appreciably high conductivity observed in the present investigation is due to the migration of Ag^+ ions alone.

Superionic glasses which are pure silver ion conductors have been reported by various workers to exhibit typical electrical conductivity values of the order of 10^{-2} to 10^{-4} S cm^{-1} at 298 K [1, 7]. For instance, the composition $50AgI-30Ag_2O-20V_2O_5$ has been reported to show a room-temperature electrical conductivity of 1.3×10^{-3} S cm^{-1} [1]. However, during the present investigation we have observed that the most highly conducting composition, $40CuI-40Ag_2O-20V_2O_5$, has an electrical conductivity value of 3.67×10^{-3} S cm^{-1} at 305 K, which is comparable to the value reported earlier. One of the significant observations in the present investigation on the $CuI-Ag_2O-V_2O_5$ system is that very high silver ionic conductivity values could be achieved as a result of the reciprocal role of Cu^+ ions in the matrix of $[Ag_2O-V_2O_5]$.

3.3. Reasons for the formation of Ag^+ ion conductors in the system $CuI-Ag_2O-V_2O_5$

The formation of high-conductivity silver ion conductors in the present study may be explained on the basis of the hard and soft acids and bases (HSAB) principle proposed by Pearson [8]. The HSAB rule states that soft acids prefer to bind to soft or polarizable bases and that hard acids would prefer to bind to hard or non-polarizable bases as a result of various degrees of ionic and covalent bonding. It is therefore possible that silver iodide is formed during the ion exchange reaction between cuprous iodide and the silver oxy-salt, $[(Ag_2O)_2 \cdot (V_2O_5)]$. The above exchange reaction is favoured because of the effect of softness of the Lewis acids Ag^+ and Cu^+ ions and I^- base. Usually, the acid–base combination will result in the formation of a complex ion or in an electrically neutral compound. Silver iodide may be assumed as a Lewis acid–base combination. Hence, AgI will be formed while CuI is melted together with $[(Ag_2O)_2 \cdot (V_2O_5)]$ in accordance with the HSAB principle. AgI formation has been reported to be possible in a report on the $CuI-Ag_3AsO_4$ system by Rivolta et al. [9]. Malugani et al. [10] have also observed the formation of silver halides in the case of $xMX_2 \cdot (1 - x)AgPO_3$ with $M^{2+} = Pb^{2+}$, Hg^{2+} and $X^- = I^-$, Br^-, Cl^-. From the above discussion it is clear that Ag^+ ionic solids are formed during the present investigation.

4. Conclusion

The present investigation concerning the structural and electrical characterization of the mixed system $(CuI)_x \cdot [(Ag_2O)_2 \cdot (V_2O_5)]_{100-x} (40 \leq x \leq 80)$ has indicated the formation of chemically stable silver-ion conducting fast ionic solids with an appreciably high electrical conductivity of the order of 10^{-3} S cm^{-1} at ambient temperatures. The most highly conducting composition in the above system has been identified to be $40CuI-40Ag_2O-20V_2O_5$, having an electrical conductivity of 3.67×10^{-3} S cm^{-1} at 305 K. The formation of fast ion conducting solids has been explained on the basis of the hard and soft acids and bases principle.

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