

Ion Conduction in the $\text{Ag}_2\text{HgI}_4\text{--Cu}_2\text{HgI}_4$ Systems Doped with Cd^{2+} , K^+ , and Na^+

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Ion conductivities of face centered cubic $\text{Ag}_2\text{HgI}_4\text{--Cu}_2\text{HgI}_4$ systems doped with Cd^{2+} , K^+ , and Na^+ were measured. In 67 mol% Ag_2HgI_4 solid solution doped with Cd^{2+} ions, the phase transition occurs at a lower temperature than in the parent compounds and the system shows higher conductivity. The increase in conductivity is discussed in terms of vacancies produced. K^+ doped Ag_2HgI_4 exhibits higher conductivity prior to the phase transition, which is attributed to lattice loosening. A decrease in conductivity is observed above 140°C. This is interpreted in terms of anion framework collapse. Na^+ doped Ag_2HgI_4 shows high conductivity for the high temperature phase because of the small size of Na^+ ions. The activation energy for ionic motion for all the samples is calculated from the graph of $\log(\sigma T)$ versus $1/T$. © 1996 Academic Press, Inc.

INTRODUCTION

Ag_2HgI_4 and Cu_2HgI_4 are materials with a well-known face centered cubic (fcc) anion structure (1). Investigations have been reported on the static or low frequency conductivity (2, 3), thermoelectric power (4), heat capacity, X-ray diffraction (5), and Raman scattering (6) of these materials. At elevated temperature Ag_2HgI_4 and Cu_2HgI_4 display high Ag^+ and Cu^+ ion mobility, respectively (7). Due to their special structural features, these compounds are excellent examples for fundamental studies in the field of superionic conductors. Kasper and Browell employed single crystal X-ray crystallography to obtain structures for the high temperature, α (8), and low temperature, β (9), phases of Ag_2HgI_4 and Cu_2HgI_4 . In the β phase the iodides form a fcc lattice with two silver or copper ions and one mercury ion occupying three of the four available tetrahedral sites, leaving one quarter of the tetrahedral sites empty. The two compounds differ in the relative position of the cations and empty sites. But above the phase transition, the cations disorder to partially occupy all of the tetrahedral sites and the two compounds become isostructural.

From the literature survey it appears that, even though a good understanding of the mechanism of ionic transport

in pure Ag_2HgI_4 and Cu_2HgI_4 has been obtained, the behavior of these compounds with guest ions in their lattices has not been reported. This paper therefore presents studies on doped Ag_2HgI_4 and Cu_2HgI_4 in order to understand the effect of cation substitution on the total conductivity and activation energy for conduction in this system. Studies in the doped system are motivated by the fact that many other systems, such as Ag_2SO_4 and Na_2SO_4 (10–12), have been reported to show higher conductivity when doped with lighter ions. In the present study we have selected isovalent ions of smaller and larger radius, K^+ and Na^+ , and a divalent Cd^{2+} ion as the guest ions to be incorporated into Ag_2HgI_4 and Cu_2HgI_4 .

EXPERIMENTAL

Materials

Ag_2HgI_4 and Cu_2HgI_4 were prepared from HgI_2 , AgNO_3 , and CuNO_3 obtained from E. Merck (India) Limited, with stated purity 99%, 99.8%, and 99.5%, respectively, by methods already reported (13). The X-ray diffraction patterns of these compounds corresponded to those of standard values.

The solid solutions and the doped compounds (Cd^{2+} , K^+ , and Na^+) were prepared by mixing respective iodomercurates in the requisite composition in an agate mortar and heating them at 200°C for 24 hr in a silica crucible. X-ray diffraction studies were carried out on the materials after the reactions were completed. The X-ray diffraction patterns were recorded by a Phillips PW 1710 diffractometer with $\text{CuK}\alpha$ radiation under the same conditions for every sample.

Conductivity Measurements

Pellets for the conductivity measurements were prepared by pouring different molar mixtures into a stainless steel die at a pressure of 4 tonnes/cm² with the help of a hydraulic press. We observed a linear increase in conductivity with pelletizing pressure up to a pressure of 4 tonnes/cm² and after that it became almost constant. The

pellets had diameter 4.524 cm² and thickness 0.1 cm. All the samples were annealed at 200°C for 12 hours before measurements to eliminate any grain boundary effect. The electrical measurements were performed by a two probe method. The pellet was mounted on a stainless steel sample holder assembly between copper leads using two polished platinum electrodes. The copper leads were electrically insulated from the sample holder by Teflon sheets. The electrical conductivity of the samples were measured in the temperature range 30–200°C using a Gen Rad 1659 RLC digi bridge at a fixed frequency (1 KHz). 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,

$$\begin{aligned}\sigma &= ne^2\lambda^2\nu\gamma/kT \exp(-\Delta G^*/kT) \\ &= ne^2\lambda^2\nu\gamma/kT \exp(\Delta S^*/k - \Delta H^*/kT),\end{aligned}$$

where n is number of ions per unit volume, e the ionic charge, λ the distance between two jump positions, ν the jump frequency, γ the intersite geometric constant, k the Boltzmann constant, and ΔG^* , ΔS^* , and ΔH^* are activation free energy, entropy, and enthalpy terms. The equation can be written in a simpler form as

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

where $\sigma_0 = ne^2\lambda^2\nu\gamma/k \exp(\Delta S^*/k)$ and $\Delta H^* = E_a$; i.e., the activation enthalpy equals the experimental activation energy for ionic motion, which may include a defect formation enthalpy contribution (14).

The plots of specific conductivity vs temperature for pure Ag_2HgI_4 , 50:50 mol%, 33:67 mol%, and 67:33 mol% of $\text{Ag}_2\text{HgI}_4:\text{Cu}_2\text{HgI}_4$, and Cd^{2+} doped 67 mol% Ag_2HgI_4 are given in Fig. 1. Similar plots are given for pure and doped Ag_2HgI_4 in Fig. 2. The usual $\log(\sigma T)$ vs $1/T$ system of coordinates were used to present the data.

From Fig. 1 it may be seen that the conductivity values for the solid solution are intermediate between those obtained for the parent compounds, showing a sharp rise in conductivity at characteristic transition points in each case. The phase transition temperatures of the pure forms and various solid solutions of Ag_2HgI_4 and Cu_2HgI_4 are given in Table 1. The transition temperatures of each solid solution is intermediate between those observed for the parent compounds, except in the case of 67 mol% Ag_2HgI_4 , where a considerable decrease in transition temperature was observed. It undergoes a phase transition at 33°C, much lower than the parent compounds. The activation energy for ionic motion in the high temperature α phase of 67 mol%

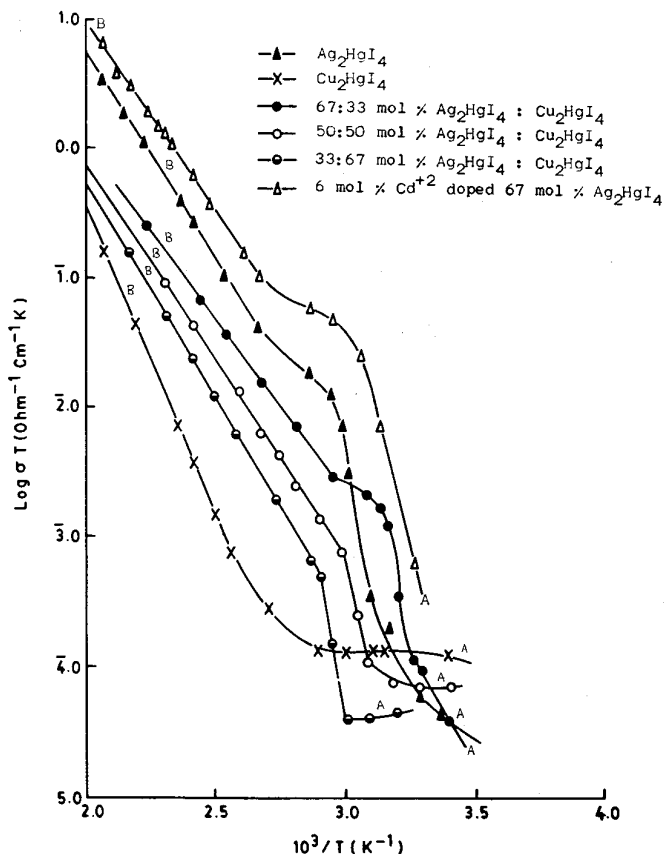


FIG. 1. Temperature dependence of the electrical conductivity of pure and doped $\text{Ag}_2\text{HgI}_4\text{-Cu}_2\text{HgI}_4$ systems.

Ag_2HgI_4 shows a decrease, but in the case of the low temperature β phase it is slightly larger than in the parent compounds.

The data for the temperature dependence of the conductivity of 6 mol% Cd^{2+} doped 67 mol% Ag_2HgI_4 solid solution are presented in Fig. 1. Higher conductivity is observed in the doped samples than in the undoped counterparts. Cd^{2+} was selected as the dopant with the expectation that it would preferentially replace Cu^+ in the lattice because the size of Cd^{2+} is close to that of Cu^+ compared to that of Ag^+ [10], viz. $r_{\text{Cd}^{2+}} = 109$ pm, $r_{\text{Cu}^+} = 91$ pm, $r_{\text{Ag}^+} = 129$ pm for CN = 6 [15]. The presence of Cd^{2+} on Cu^+ sites in the lattice would generate Cu^+ vacancies in accordance with the electroneutrality requirement. Vacancies would permit greater mobility of Cu^+ ions and therefore enhance the ionic conductivity.

Values of the activation energy for ionic conductivity are tabulated in Table 1. The Cd^{2+} doped sample has a low activation energy in the high temperature phase. The dopant ions produce a far greater number of defects than are produced by thermal excitation. Hence the number of defects in the high temperature phase can be considered

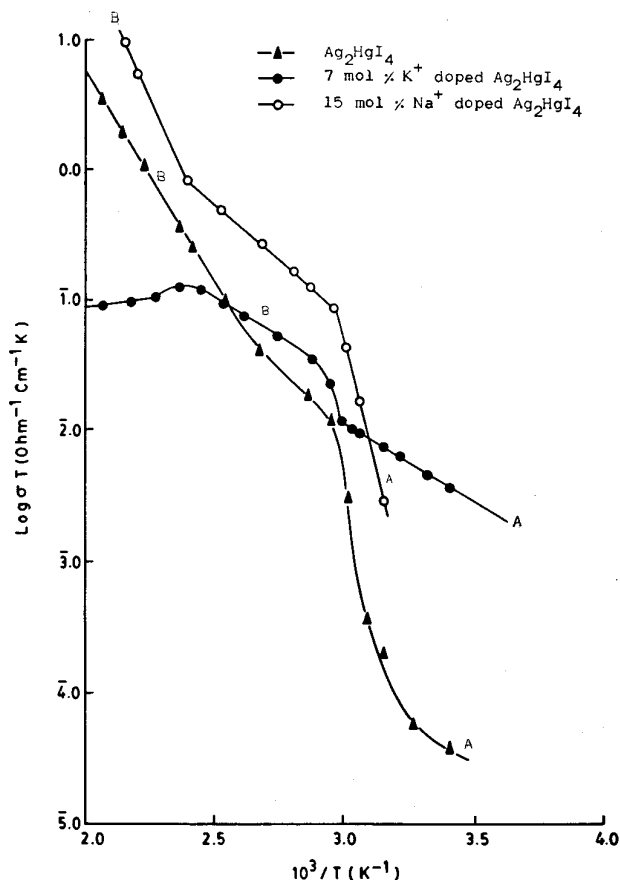


FIG. 2. Temperature dependence of the electrical conductivity of K^+ and Na^+ doped Ag_2HgI_4 .

approximately constant and the E_a will correspond to the enthalpy of migration of ions in this region (16).

It can be observed from Fig. 2 that the 7 mol% K^+ doped sample undergoes a phase transition at about 60°C . It possesses higher conductivity than the pure Ag_2HgI_4 prior to the phase transition. The introduction of the comparatively larger K^+ ion, viz. $r_{\text{K}^+} = 152$ pm and $r_{\text{Ag}^+} = 129$ pm for CN = 6 (15), in the Ag_2HgI_4 lattice leads to an increase in the concentration of activated mobile ions effected by "lattice loosening," and the facility of ion movement provided by free volume causes higher conductivity of the K^+ doped sample (14).

Another important feature observed in the K^+ doped Ag_2HgI_4 is erratic conductivity behavior in the post-transition region. After the phase transition, the conductivity rises smoothly up to 140°C and thereafter shows a decreasing trend. The drop in the conductivity may be due to the collapse of the iodide framework above 140°C . But on cooling the higher conductivity is regained. The argument of lattice collapse and subsequent recovery on cooling implies restructuring of that sublattice. Such decrease in con-

TABLE 1
Ionic Conductivity Activation Energy Values of Pure and Doped $\text{Ag}_2\text{HgI}_4\text{-Cu}_2\text{HgI}_4$ System

Compounds	Phase transition temperature ($^\circ\text{C}$)	Temperature region	Activation energy (kJ/mol)
Pure Ag_2HgI_4	52	A	27
		B	63
Pure Cu_2HgI_4	70	A	25
		B	91
33 mol% Ag_2HgI_4	59	A	27
		B	59
50 mol% Ag_2HgI_4	55	A	31
		B	65
67 mol% Ag_2HgI_4	33	A	65
		B	51
6 mol% Cd^{2+} doped 67 mol% Ag_2HgI_4	54	A	153
		B	57
7 mol% K^+ doped Ag_2HgI_4	60	A	22
		B	25
15 mol% Na^+ doped Ag_2HgI_4	65	A	172
		B	31

Note. (A) Pre-transition; (B) post-transition.

ductivity has been reported for Na_2SO_4 (17) and K_2SO_4 (18) as well.

Figure 2 shows the electrical conductivity of the 15 mol% Na^+ doped Ag_2HgI_4 sample. The enhanced conductivity predicted for Na^+ incorporation in Ag_2HgI_4 is observed. There is no distortion in the lattice in this case, as is clear from the X-ray studies. In the mixed cation compounds it would generally be the case that the smaller cations are the more mobile ions (19). The partial replacement of the Ag^+ ions by smaller Na^+ ions, viz. $r_{\text{Ag}^+} = 129$ pm, $r_{\text{Na}^+} = 116$ pm for CN = 6 (15) in the Ag_2HgI_4 lattice, facilitates higher mobility of Na^+ ions and hence causes higher conductivity of the doped sample. The ionic conductivity and the activation energy for conduction show strong dependence on the concentration of Na^+ ion in the host lattice and it confirms the argument of Na^+ ion predominance in the conduction process.

The conductivity data reported in this study show that doped sample exhibit very high Na^+ ion conductivity in the high temperature phase analogous to the system of compound referred to as NASICON (20). The proposed model of a highly mobile Na^+ ion in a fixed HgI_4^{2-} sublattice in $(\text{AgNa})_2\text{HgI}_4$ compound parallels the accepted model of highly mobile Ag^+ ions in a fixed network of I^- in AgI compounds (21).

CONCLUSION

The picture that emerges from the above discussion is that a closely related structure of relatively open periodic

I^- ion polyhedra exists in the high temperature phase of Ag_2HgI_4 and Cu_2HgI_4 . The open I^- framework facilitates the motion of the cations. The superionic conductivity can be affected by the contraction or expansion of the sublattice within the structural limits effected by the guest cations of different ionic radii relative to the host ions and by the presence of vacancies on cation lattice sites.

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