

Electrical Conductivity Behavior of CdHgI₄ – CuI Mixed System

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Abstract

In this paper the electrical conductivity behaviour in CdHgI₄ - CuI mixed system were investigated. The mixed system were prepared by mixing CdHgI₄ with CuI in different mol% (10:90, 20:80, 30:70, 40:60 and 50:50 ratios). It was observed that the conductivity of 10:90 CdHgI₄ – CuI mixed system were higher than the other system. This increase in conductivity is due to the availability of additional vacancies created by addition of CdHgI₄ in CuI, but above 10mol% CdHgI₄ the conductivity of mixed system decreased due to the reduction in the mobility of Cu⁺ ion following vacancy interactions. Activation energy data also suggested the higher conductivity for 10:90 mol% mixed system.

Keywords: Electrical conductivity, Mixed system, Activation energy, X-ray diffraction

1. Introduction

CuI is a rather unique material in that both its ordered low temperature γ -phase and disordered high temperature fast ion conducting α -phase have anion face centred cubic (fcc) structures. In the γ -phase Cu⁺ ion sit on a fcc sub-lattice shifted by ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) from the Γ sub-lattice, forming the zinc blend structure with space group $F43m$. In the β -phase, which exists in the narrow temperature range between 642 and 680K, CuI has a hexagonal structure similar to wurtzite, with space group $p3m1$. At 680 K, it transforms back to a fcc Γ sub-lattice with Cu⁺ randomly distributed over the ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) sites, space group $Fm\bar{3}m$, the α -phase (Miyake, Hoshino & Takenaka, 1952, p19; Buhner & Halg, 1977, p701; Merrill, 1977, p1205; Hull & Keen, 1993, p129; Keen & Hull, 1994, p5868). The melting temperature is 873K. In all three crystalline phases Cu⁺ are tetrahedrally coordinated by I⁻. Tracer diffusion experiments (John, Anthony & Bruce, 1980, p377), show a low, yet significant, diffusion constant of order $10^{-7} \text{ cm}^2\text{s}^{-1}$ in the γ -phase, which rises by an order of magnitude to $10^{-6} \text{ cm}^2\text{s}^{-1}$ in the β -phase and then to $3 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ in the α -phase.

(Zheng-Johansson, 1992, p247) developed two body inter-atomic potentials for molecular dynamics simulations of CuI that satisfactorily reproduce the experimentally determined phonon density of states and diffusion constant in γ , β and α phases, as well as various thermodynamics parameter such as melting point. It is also suggested that the diffusion constants are extremely sensitive to the exact potential chosen. There is a strong evidence of cooperative diffusion in γ phase.

(Villian, Cabane, Roux, Roussel & Knouth, 1995, p229) investigated the electrical conduction of copper (I) iodide between 50 and 450°C by a measurements at different frequencies and four point d.c. experiments. The resistance and capacitance of the phase boundary copper/copper iodide depend exponentially on temperature. The interfacial resistance is practically negligible in α and β -phase, whereas the interfacial capacitance is very high.

(Keen & Hull, 1995, p5753) studied the structural behaviour of CuI between room temperature and its melting point ($T_m = 878\text{K}$) using neutron powder diffraction. Detailed measurements were made in the vicinity of two known structural phase transition γ - β and β - γ , which are observed at $643 \pm 2\text{ K}$ and $673 \pm 8\text{ K}$. Within the zinc trend structured γ -phase (space group $F\bar{4}3m$) increasing disorder of the Cu^+ ion sub-lattice is observed as the temperature approaches the γ - β transition in addition to a non-linear thermal expansion. The hexagonal β -phase (space group $P\bar{3}m1$) is observed as a single phase in the temperature range 645 - 668K but on first heating it is found to coexist with a rhombohedral phase. This transient phase observed in isolation for only a short time but it is sufficient to show that its structure was that of CuI-IV (space group $P\bar{3}m1$), which had only been observed earlier at elevated pressure. The high temperature phase of CuI has $Fm\bar{3}m$ symmetry with pressures, the Cu^+ ions distributed randomly over all the tetrahedral sites with the cubic-close I^- sublattice.

Electrical conductivity and structural correlation for MxHgI_4 type compounds were studied by (Dumitru & Tudor, 1994, p201). In this study they have explained structural modification of complex compound MxHgI_4 by the application of 5.30 Mpa to its powder. These modifications were confirmed by X-ray diffraction and by measurement of electrical conductivity.

Diffraction thermal analysis of compound Ag_2HgI_4 , Cu_2HgI_4 , Tl_2HgI_4 , PbHgI_4 and CdHgI_4 have been compared (Tudor, Lidia, Mirela & Anca, 1997, p21) and the results thus obtained lead to the idea of using DTA and electrical conductivity as methods for accessing the thermochromic transition in these compounds. [MxHgI_4 , where $M = \text{Ag}$, Cu , Tl , Pb and Cd , $x = 1, 2$].

Earlier workers have studied some mixed systems involving fast ionic conductors and suggested the role of fast conducting ions. Like (Rivolta, Bouino & Scrosoti, 1988, p557), investigated the system $\text{CuI-Ag}_3\text{AsO}_4$ and observed high silver ion conductivity. Others like (Viswanathan & Austin, 1992, p89), studied the fast ion transport in the mixed system $\text{CuI-Ag}_2\text{MoO}_4$.

Encouraged by these results we have tried to prepare CdHgI_4 , a solid electrolyte using solid state reaction method and measured electrical conductivity of the mixed system involving CdHgI_4 and CuI in various mole percents.

2. Experimental Details

2.1 Preparation of CdHgI_4 and CuI

Cadmium tetraiodomercurate was prepared from CdI_2 and HgI_2 obtained from BDH (India), with stated purity 99.5% and 99.2% respectively, by the conventional solid state reaction. Both CdI_2 and HgI_2 were mixed in the requisite composition in an agate mortar and were heated at 200°C for 48 hours in a silica crucible with intermittent grinding. The product so formed is yellowish in colour and X-ray diffraction of the powder sample has been done and it confirmed formation of the product.

CuI was prepared as a precipitate by gradually adding an aqueous solution of commercially available AnalaR grade chemicals of KI and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Iodine liberated during the process was removed by treating the precipitate with sodium thiosulphate solution. CuI thus obtained was washed several times with distilled water and then dried at 100°C for several hours before use.

Mixed system of CdHgI_4 -CuI were prepared by taking $10, 20, 30, 40$ and 50 mole% of CdHgI_4 and mixing with powdered CuI in an agate mortar and heating them at 200°C for 24 hours in a silica crucible.

2.2 Conductivity Measurement

In order to measure the electrical conductivity powdered samples were pressed into pellets of 4.54 cm^2 area with thickness of 0.1 cm at a pressure of about 4 tonnes with the help of a press. Pellets so formed were heated upto 200°C for 12 hours temperature in order to relieve strains and improve homogeneity.

The conductivity measurements were performed by means of two probe method. The pellet was 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 of 25 - 200°C using GenRad 1659 RLC Digibridge at a fixed frequency.

3. Results and Discussion

X-ray diffraction pattern and electrical conductivity measurements (Fig. 1 & 2) of $1:1$ molar mixture of CdI_2 and HgI_2 suggest the formation of tetragonal and fast conducting CdHgI_4 .

The temperature dependence of 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 the number of ions per unit volume, e the ionic charge, λ the distance between two jumps 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 experimental activation energy for ionic motion, which may include a defect formation enthalpy contribution (Secco & Usha, 1994, p213).

Fig.2, show plots of electrical conductivity of pure and mixed CdI₂ and HgI₂. It can be seen that the conductivity of the 1:1 molar mixture is much higher than pure CdI₂ and HgI₂. Higher conductivity of the mixture is due to the formation of CdHgI₄ which is a solid fast ion conductor. The formation of product was also suggested by X-ray powder diffraction of the 1:1 molar mixture.

The Arrhenius plots of specific conductivity verses temperature for pure and 10:90, 20:80, 30:70, 40:60 and 50:50 mol% CdHgI₄-CuI mixture are given in Fig.3. It can be seen that the electrical conductivity for 10:90 mol% CdHgI₄-CuI mixed system is much higher in comparison to other compositions. In all, other compositions conductivity decreases with the increasing concentration of CdHgI₄. Electrical conductivity of the mixed system CdHgI₄-CuI for different compositions of CdHgI₄ at room temperature is shown in the Fig.4. The maximum conductivity is obtained for 10 mol% CdHgI₄ in the CdHgI₄-CuI mixed system.

The activation energy for ionic conductivity is tabulated in Table-1. The lowest activation energy value is obtained for the 10mol% CdHgI₄ suggesting the highest conductivity for 10:90 mol% CdHgI₄-CuI mixed system.

The partial replacement of the monovalent host ion by the divalent guest ion gives rise to additional vacancies in the host lattice in accordance with the electroneutrality requirement. It was reported that in the high temperature phase such extrinsic vacancies contribute mainly to the conductivity and ionic size is having insignificant effect following aliovalent dopant substitution in the host lattice (Hofer, Eysel & Alpen, 1981, p365).

With the availability of additional vacancies created by CdHgI₄ substitution, in the cubic phase of the host lattice CuI, the Cu⁺ ions move through the lattice with a high elementary hopping probability (Ganthiaer & Chamberland, 1979, p1579). The increasing vacancy concentrations due to partial replacement of Cu⁺ creates additional migration paths for Cu⁺, which in turn increases the conductivity. Upon further addition of CdHgI₄ over 10mol%, the mobility of the Cu⁺ ion was reduced following vacancy interactions such as cluster formation and also cationic sub-lattice ordering (Hofer, Eysel & Alpen, 1981, p365).

Another important feature observed in this system is erratic conductivity behaviour above 150°C (Fig.3). This drop in conductivity seems to results from the collapse of the iodide framework (Usha & Secco, 1985, p324). Ionic conductivity is mainly controlled by the valency of the cation. The self-trapping effect of the substituent divalent cation which is negligibly mobile could impede the pathways of Cu⁺. This will in turn decrease the mobility of Cu⁺ and hence, causes an inconsistent behaviour at the higher temperatures.

4. Conclusion

The conductivity is very high in 10:90 mol% CdHgI₄-CuI mixed systems as compared to other concentrations. It is found that this mixed system exhibits the highest conductivity of $3.031 \times 10^{-3} \text{ cm}^{-1}$ at 25°C. This increase in conductivity is due to the availability of additional vacancies created by addition of CdHgI₄ in CuI, but above 10mol% CdHgI₄ the conductivity of mixed system decreased due to the reduction in the mobility of Cu⁺ ion following vacancy interactions.

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Table 1. Activation energy values of all the compositions of the mixed system CdHgI_4 -CuI

Composition CdHgI_4 -CuI (mol%)	E_a (eV)
10:90	0.26
20:80	0.28
30:70	0.31
40:60	0.37
50:50	0.43

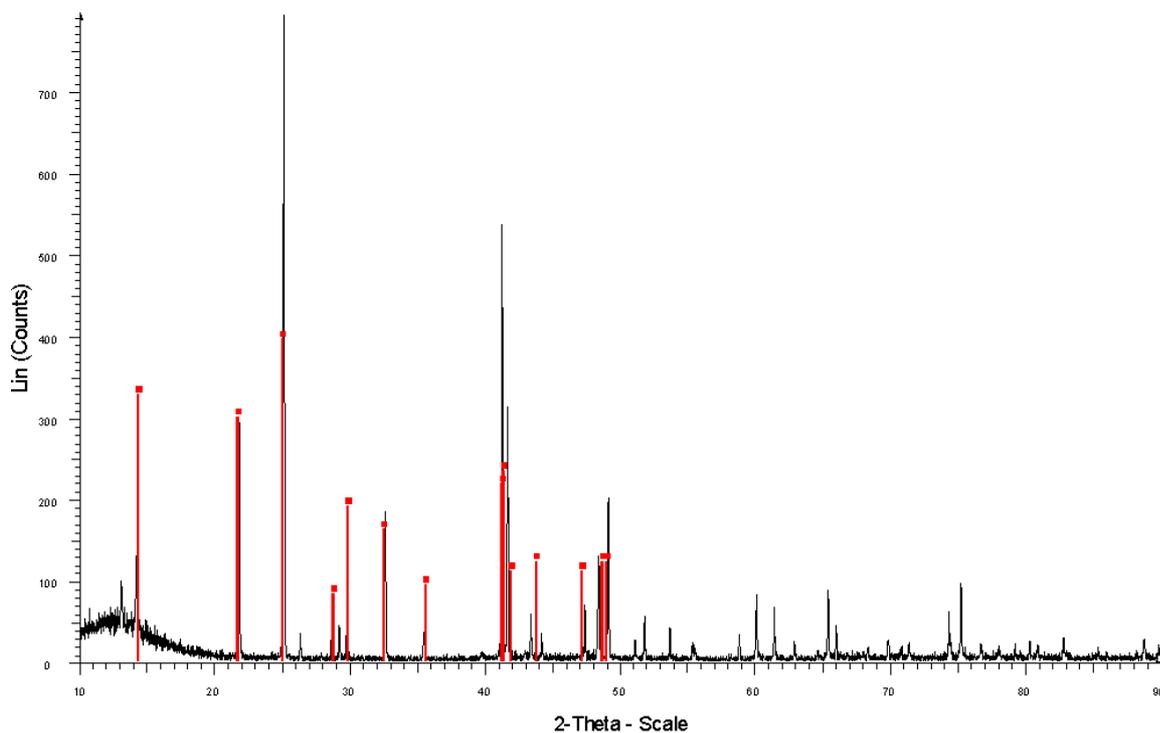


Figure 1. X-ray powder diffraction pattern of CdHgI₄

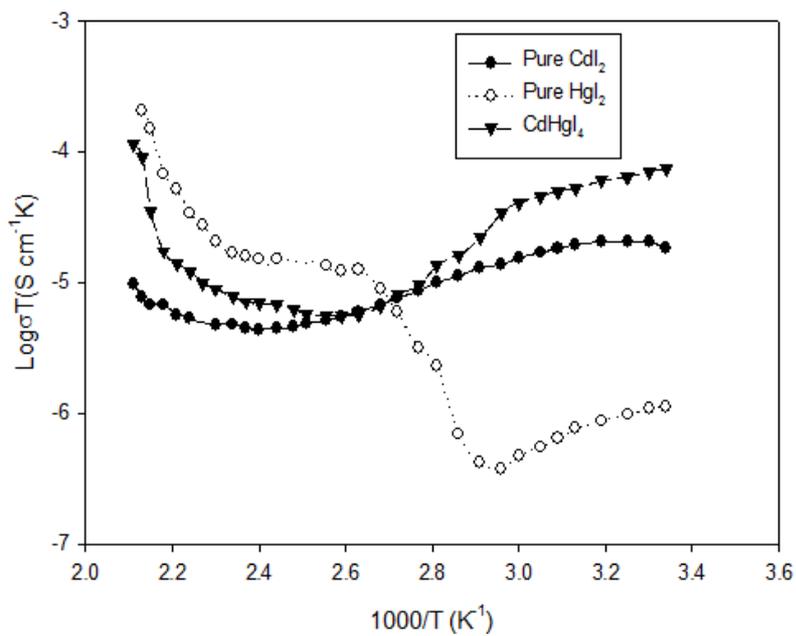


Figure 2. Electrical conductivity data of the CdHgI₄ with its parent compounds

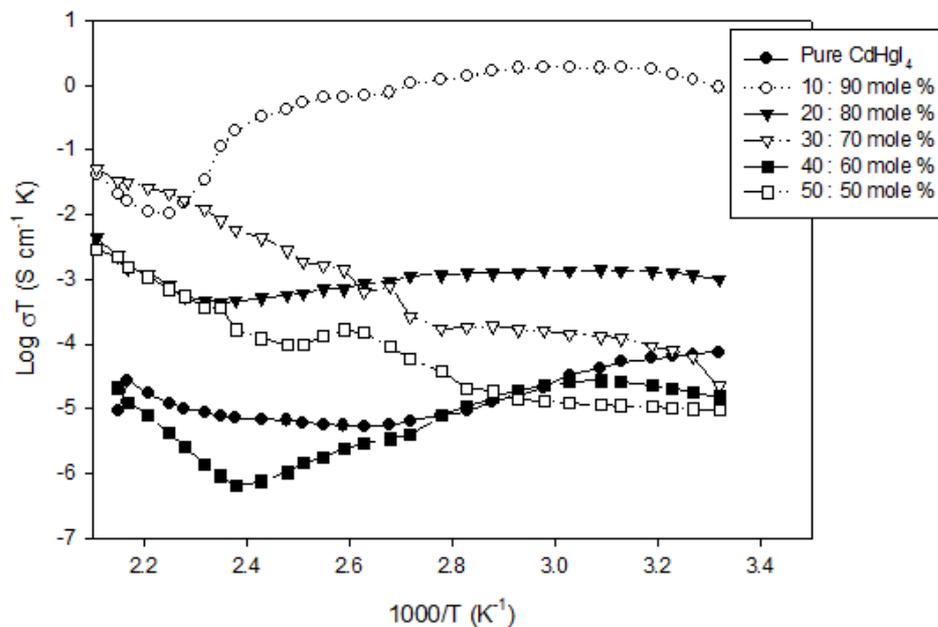


Figure 3. Variation of log σT with $(1/T)$ for different compositions in mixed system $CdHgI_4$ - CuI

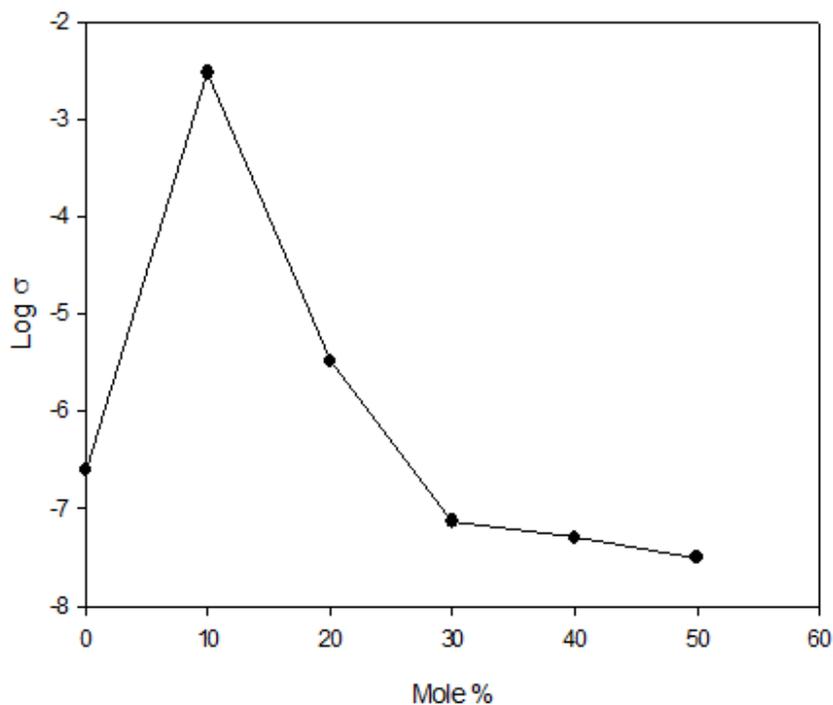


Figure 4. Electrical conductivity in the mixed system $CdHgI_4$ - CuI versus compositions of $CdHgI_4$ at room temperature