

Structural Aspects and ac Conductivity of the Solid Electrolyte $\text{Ag}_x\text{Cu}_{2-x}\text{HgI}_4$

A. MARY SUKESHINI AND K. HARIHARAN

Solid State Ionics Laboratory, Department of Physics, Indian Institute of Technology, Madras 600 036, India

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Lattice parameters of the solid electrolyte $\text{Ag}_x\text{Cu}_{2-x}\text{HgI}_4$ have been determined for the different values of x between 0 and 2. All compositions studied showed a tetragonal phase, except for a small range from $x = 1.14$ to $x = 1.30$. Compositions in this range had a cubic phase. The lattice parameters a and c of compositions outside this range increased steadily from 6.07 and 12.15 Å, respectively, for $x = 0$ (Cu_2HgI_4) to 6.29 and 12.55 Å for $x = 2$ (Ag_2HgI_4). Compositions in the region $1.14 \leq x \leq 1.3$ that had cubic phases were found to have lattice parameter a between 6.22 and 6.26 Å. The frequency-dependent conductivity of all compositions showed two distinct regions at low temperatures: a frequency-independent plateau region at lower frequencies (1 Hz to 10 kHz) and a power law variation, $A\omega^n$, at higher frequencies (10 to 65 kHz). At higher temperatures (>328 K) electrode polarization effects were seen at low frequencies and a frequency-independent plateau region at higher frequencies. The frequency-independent (i.e., dc) conductivity was on the order of 10^{-5} ($\Omega \text{ cm}^{-1}$) for compositions $1.14 \leq x \leq 1.3$. © 1992 Academic Press, Inc.

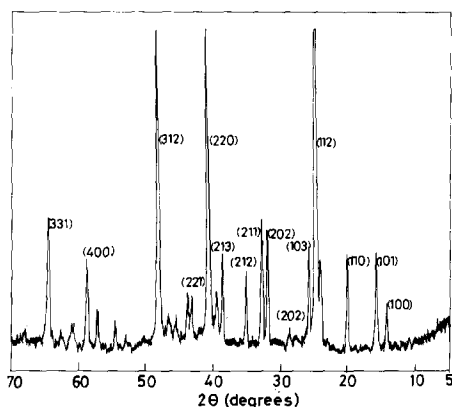
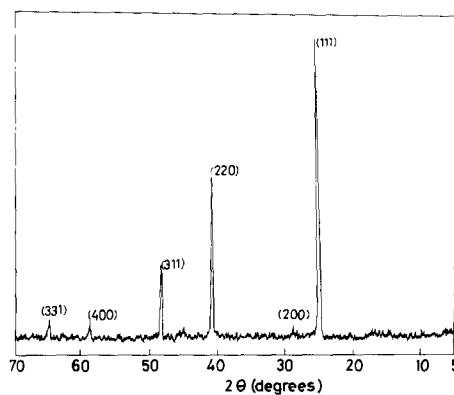
Introduction

α -AgI is a classic example of a solid electrolyte that has been extensively studied (1). A large number of highly cation-conducting solid electrolytes can be derived from AgI by partial substitution of the silver ions (2), iodide ions (3), or even both (4) by different kinds of ions. The compound Ag_2HgI_4 was one of the first examples of a solid electrolyte derived from AgI (5). The highly conducting α -phase or superionic phase is realized at temperatures $\geq 52^\circ\text{C}$, where silver ion conduction is facilitated by the cubic structure of the compound, the unit cell of which has three cations distributed at random over four tetrahedral sites (6). The copper analog, Cu_2HgI_4 , also has superionic conduction in the α -phase, i.e., at tempera-

tures $\geq 70^\circ\text{C}$. In our previous paper (7), we discussed the thermal properties (phase transition) and change in conductivity at the phase transition temperature of $\text{Ag}_x\text{Cu}_{2-x}\text{HgI}_4$, where $0 \leq x \leq 2$. This work concerns the structural aspects (lattice parameters) and frequency-dependent behavior of the conductivity of $\text{Ag}_x\text{Cu}_{2-x}\text{HgI}_4$.

Experimental

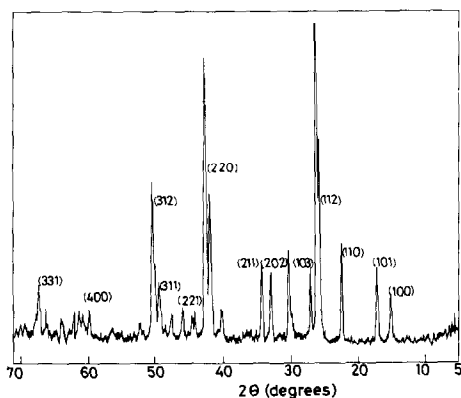
Details of the preparation of compounds and the pellet for conductivity study are presented elsewhere (7). The samples were characterized by powder X-ray diffraction with a Philips X-ray generator (Model PW 1130) using $\text{CuK}\alpha$ radiation. For the frequency-dependent conductivity study, a frequency response analyzer 1280 series

FIG. 1. X-ray diffractogram of Cu_2HgI_4 .FIG. 3. X-ray diffractogram of $\text{Ag}_{1.14}\text{Cu}_{0.86}\text{HgI}_4$.

was employed. The real and imaginary parts of complex impedance were recorded in the range 1 Hz to 65 kHz, from which the conductivity (real part) was calculated.

Results and Discussion

Figures 1 and 2 show the X-ray diffraction patterns for $x = 0$ and $x = 2$, respectively, i.e., Cu_2HgI_4 and Ag_2HgI_4 . By comparing the position and intensity of these X-ray peaks with the data reported in the literature (8), compound formation was confirmed. The X-ray patterns of $\text{Ag}_x\text{Cu}_{2-x}\text{HgI}_4$ for dif-

FIG. 2. X-ray diffractogram of Ag_2HgI_4 .

ferent values of x between 0 and 2 show similar patterns, with only a small shift in the d values of the X-ray lines in a systematic fashion from $x = 0$ to 2, except for a few compositions $x = 1.14$ to $x = 1.3$, whose patterns were distinctly different. These had fewer lines in comparison with the rest of the compositions. The X-ray peaks of these compositions seem to be a subset of the lines present in the X-ray pattern of other compositions. Figure 3 shows the X-ray diffraction pattern for $x = 1.14$. The patterns of composition $x = 1.2$ and $x = 1.3$ were similar. The lines were indexed assuming a cubic phase as suggested by the pattern. The lattice parameter a of the cubic unit cell of these compositions was around 6.20 \AA . Other compositions $x < 1.14$ and $x > 1.3$ showed a tetragonal phase. The lattice parameters a and c were, respectively, 6.07 and 12.15 \AA for $x = 0$, and 6.29 and 12.55 \AA for $x = 2$. These values compare well with the reported values (8). Figure 4 gives the plot of lattice parameter a vs composition. a increases as x goes from 0 to 0.6, remains almost constant over a range of compositions from $x = 0.6$ to 1.6, barring the range from 1.14 to 1.3, and once again increases further, reaching a value of 6.29 \AA for $x = 2$. The region $x = 1.14$ to 1.3, having a cubic phase, shows a slightly higher value

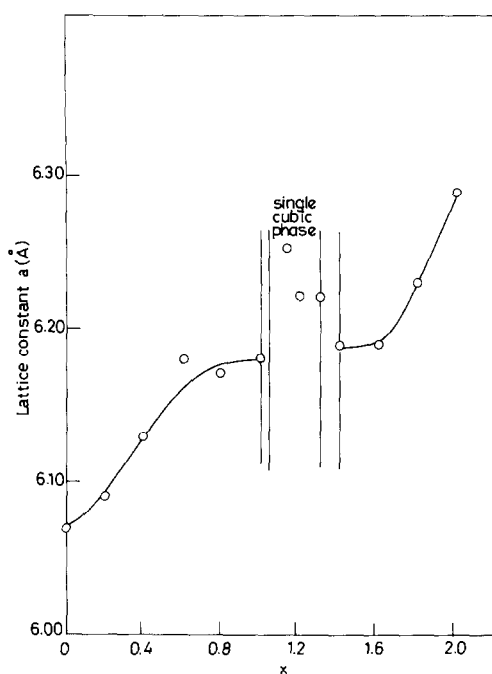


Fig. 4. Lattice parameter a as a function of x in $\text{Ag}_x\text{Cu}_{2-x}\text{HgI}_4$.

of the lattice constant a . Table I summarizes the results of X-ray diffraction.

From the results of X-ray diffraction, it is clear that as we approach the region $1.14 \leq x \leq 1.3$ from either end, superlattice lines of the tetragonal phase disappear, ascribing cubic symmetry to compositions in this region. The fundamental lines 110, 200, 220, 310, and 222 confirm a fcc unit cell for compositions in the region $1.14 \leq x \leq 1.3$. The positional disordering (in the α -phase) that can be observed on thermal activation of superionic compounds like AgI , CuI , Ag_2HgI_4 , and Cu_2HgI_4 is seen here by the substitution of ions of somewhat different size at room temperature.

Curve a of Fig. 5 shows the plot of the real part of conductivity as a function of frequency for $x = 0$ at 288 K, a temperature in the β -phase, and at 379 K, a temperature in the α -phase. In the β -phase we see two

regions: a frequency-independent plateau region at low to intermediate frequencies and a strong dispersion at high frequencies. The low-temperature high-frequency behavior of conductivity conforms to the universal response (9)

$$\sigma(\omega) = \sigma(0) + A\omega^n, \quad (1)$$

where $\sigma(0)$ is the dc limit of conductivity, A is a temperature-dependent parameter, and the frequency exponent n takes values between 0 and 1. The power law variation of conductivity at low temperature-high frequency is a universal phenomenon observed in systems with a non-Debye type of dielectric relaxation and is said to be due to many body effects (9). Several models have been developed with different nonexponential response functions to account for the power law variation in conductivity (11). The conductivity in the α -phase also shows two regions, but now the electrode effects are seen at lower frequencies and a frequency-independent plateau region is seen at high frequencies. Region I arises due to the interface (electrode-electrolyte) impedance as a

TABLE I
LATTICE PARAMETERS a AND c OF $\text{Ag}_x\text{Cu}_{2-x}\text{HgI}_4$

Composition x	Lattice parameters (Å)	
	a	c
0.0	6.07	12.15
0.2	6.09	12.22
0.4	6.13	12.24
0.6	6.18	12.33
0.8	6.17	12.36
1.0	6.18	12.40
1.14	6.26 ^a	
1.2	6.22 ^a	
1.3	6.22 ^a	
1.4	6.19	12.42
1.6	6.19	12.44
1.8	6.23	12.46
2.0	6.29	12.55

^a Cubic phase.

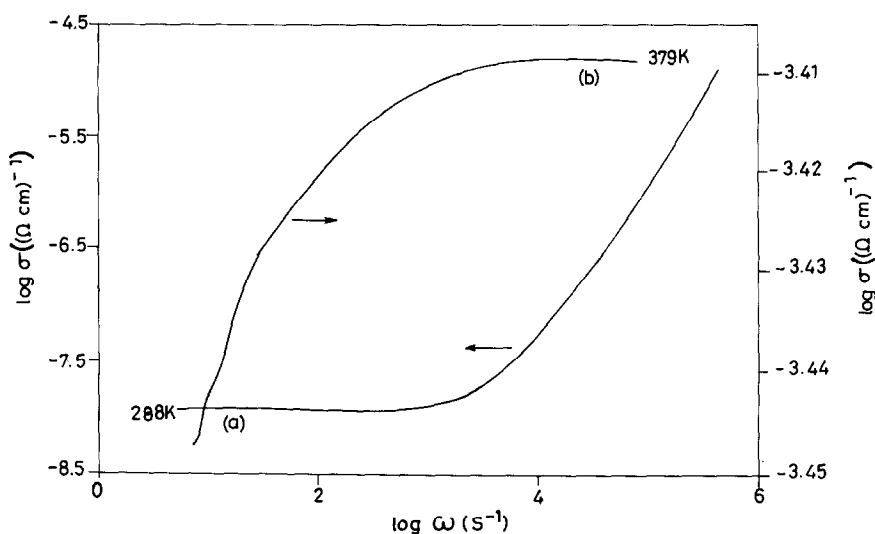


FIG. 5. Conductivity spectra of Cu_2HgI_4 .

result of ion diffusion in the screened region near the electrode surface (10). The behavior of all compositions is similar. The compositions $x = 1.14$ (designated eutectoid of the $\text{Cu}_2\text{HgI}_4\text{-Ag}_2\text{HgI}_4$ system (8)) had the highest frequency-independent region. It was seen earlier that this composition was characterized by a cubic phase at room temperature. This structural feature, where the unit cell has three cations distributed at random over four tetrahedral sites, is responsible for the higher conductivity ($10^{-5} \Omega^{-1} \text{cm}^{-1}$).

Conclusion

The X-ray diffractograms of solid solutions $\text{Ag}_x\text{Cu}_{2-x}\text{HgI}_4$ showed a single tetragonal phase for all values of x between 0 and 2, except compositions in the region $1.14 \leq x \leq 1.3$, where the disappearance of superlattice lines ascribes a cubic phase, clearly suggesting an order-disorder transition setting in from either end ($x = 0$, $x = 2$). Outside the disordered region expansion of the tetragonal unit cell was observed as an increase in the lattice parameters a and c ,

respectively, from $x = 6.07$ and 12.15 \AA for $x = 0$ to 6.29 and 12.55 \AA for $x = 2$ as a consequence of the progressive substitution of ions of different size which introduces a certain amount of positional disorder. The frequency-dependent conductivity of all compositions at temperatures in the β -phase showed a power law variation at higher frequencies conforming to the universal response, a characteristic feature in disordered materials due to many body effects. A frequency-independent plateau region was seen at lower frequencies. At temperatures in the α -phase, the dispersion at higher frequencies was not seen due to the shifting of the relaxation to still higher frequencies ($>65 \text{ kHz}$) at higher temperatures.

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