

New solid electrolyte: $\text{CsCu}_4\text{Cl}_3\text{I}_2$

S. Geller, A. K. Ray, and H. Z. Fardi

Department of Electrical Engineering, University of Colorado, Boulder, Colorado 80309

K. Nag

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700032, India

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The solid electrolyte $\alpha\text{-CsCu}_4\text{Cl}_3\text{I}_2$ is thermodynamically stable above 431 K and to at least 505 K. It is isostructural with $\text{RbCu}_4\text{Cl}_3\text{I}_2$. At 431 K it has a conductivity of $0.76 \Omega^{-1}\text{cm}^{-1}$; at 419 K the conductivity is $0.72 \Omega^{-1}\text{cm}^{-1}$ and extrapolation to 298 K gives $0.29 \Omega^{-1}\text{cm}^{-1}$. When corrected for deviation of bulk from x-ray density, the expected values are 0.84, 0.80, and $0.35 \Omega^{-1}\text{cm}^{-1}$, respectively. Its activation enthalpy of motion is 0.112 eV. There are two first-order phase transitions: $\beta\text{-}\alpha$ at 431 K and $\gamma\text{-}\beta$ at 418 K; both are very sluggish. The α phase does not reconvert to the β phase; it returns to the γ phase below ~ 418 K. At 298 K the conductivity of the γ phase is $5.3 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$; at 425.5 K, the conductivity of the β phase is $0.11 \Omega^{-1}\text{cm}^{-1}$. The enthalpy of activation of motion of the β phase is 0.77 eV. The γ phase is orthorhombic with $a = 14.242$, $b = 24.984$, $c = 11.712 \text{ \AA}$, probable space groups $Cmca$ or $C2ca$, and 16 $\text{CsCu}_4\text{Cl}_3\text{I}_2$ in the unit cell.

This is the fifth of a series of papers from this laboratory on solid electrolytes which are Cu^+ ion conductors and have crystal structures related to that of $\alpha\text{-RbAg}_4\text{I}_5$.¹ The first of these² was devoted to the structure and electrical conductivity of the stoichiometric $\text{RbCu}_4\text{Cl}_3\text{I}_2$, followed by a paper³ on the structure and conductivity of the related ammonium compound which could not be obtained stoichiometrically; its formula is $\text{NH}_4\text{Cu}_4\text{Cl}_3(\text{I}_{1.9}\text{Cl}_{0.1})$, with narrow solid solution range about this formula. Further investigation of the stability and conductivity of the system $\text{RbCu}_4\text{Cl}_3(\text{I}_{2-x}\text{Cl}_x)$ $0 \leq x \leq 0.40$ has been carried out.^{4,5} It appears that cold-working of the stoichiometric $\text{RbCu}_4\text{Cl}_3\text{I}_2$ causes a transition, with concurrent slight decomposition to a new complex phase which is itself stable (perhaps not thermodynamically) in only a narrow temperature range ($0\text{--}35^\circ\text{C}$).⁴ The stoichiometric $\text{RbCu}_4\text{Cl}_3\text{I}_2$ is thermodynamically stable in only a narrow temperature range, $200 \pm 15^\circ\text{C}$. With just slight replacement of some I^- ions by Cl^- ions, the compounds become stable between at least 78 K and their preparation temperatures which depend on x . Replacement of I^- by a Cl^- ion causes a decrease in the conductivity (with increasing x) at a given temperature.⁵ The enthalpies of activation of motion of the Cu^+ ions increase with increasing x , indicating that the decrease in conductivity with increasing x is caused by the disorder introduced by replacement of iodide by chloride ions.⁵

Here we report results on a new solid electrolyte $\text{CsCu}_4\text{Cl}_3\text{I}_2$ which is thermodynamically stable above 431 K and is isostructural with $\text{RbCu}_4\text{Cl}_3\text{I}_2$. It has a

newness not simply because of the replacement of Rb^+ by Cs^+ , but mainly because it has two low-temperature phases one of which is surely not a "true"⁶ solid electrolyte.

The procedure for preparation of $\text{CsCu}_4\text{Cl}_3\text{I}_2$ was similar to that of the rubidium compounds.^{4,5} The preparation temperature was 225°C . When quenched to room temperature from 215°C after a five-hour anneal, the cubic phase is metastable for a time sufficiently long to obtain an x-ray powder diffraction photograph with sharp back-reflection lines. The lattice constant of the cubic phase at room temperature (296 K) is $10.158 \pm 0.001 \text{ \AA}$. The pure low-temperature phase was obtained by annealing in 0.05-atm dry N_2 at 110°C for 2 days.

An x-ray powder diffraction photograph was taken at 505 K with $\text{Cu K}\alpha$ radiation and a camera similar to that designed by Bond.⁷ In the course of the 10-h exposure, there was no indication of decomposition. Thus, unlike stoichiometric $\text{RbCu}_4\text{Cl}_3\text{I}_2$,⁴ $\text{CsCu}_4\text{Cl}_3\text{I}_2$ has a broad temperature stability range, and in particular $\alpha\text{-CsCu}_4\text{Cl}_3\text{I}_2$ is thermodynamically stable from 431 K to, at least, 505 K.

An x-ray powder diffractometer pattern taken with Cu K radiation of the low-temperature (γ) phase has been indexed on an orthorhombic unit cell with $a = 12.242$, $b = 24.984$, $c = 11.712 \text{ \AA}$, all $\pm 0.005 \text{ \AA}$. The volume of the unit cell is 4167 \AA^3 which is 3.98 times the volume of the cubic unit cell at room temperature. Thus the cell contains 16 $\text{CsCu}_4\text{Cl}_3\text{I}_2$. The possible space groups are $CmCa$ (D_{2h}^{18}) or $C2ca$ (C_{2v}^{17}). The x-ray densities of the cubic and orthorhombic phases at 296 K are 4.735 and 4.764

g cm^{-3} , respectively; the slightly lower value of the former must be associated with the disorder of the Cu^+ ions. Further details of the structural relationships will be published later. However, it should be mentioned here that the γ phase appears to be isostructural with the phase obtained by the cold-working of stoichiometric $\text{RbCu}_4\text{Cl}_3\text{I}_2$.⁴

The method of preparation of the cell for conductivity measurement is described in detail in Ref. 5. There are, however, two modifications: The electrode material is 50 wt. % Ag (2- μm powder), 50 wt. % $\text{RbCu}_4\text{Cl}_3(\text{I}_{1.9}\text{Cl}_{0.1})$; to obtain a bulk density of 94% of the x-ray density, it was necessary to change the pressurizing procedure. First, the electrode material was put into the die and pressurized at 60 kg cm^{-2} . Then the electrolyte was added and smoothed with the piston, after which the electrode material was added and smoothed. The die was heated slowly to 75 °C and held at this temperature for 5 min. Then the cell was pressurized at 770 kg cm^{-2} , while continuing the heating at 75 °C for 10 min; pressure was then reduced to zero gauge. Temperature was increased slowly to 80 °C and held for 10 min after which the temperature was reduced to ambient over a period of 2 h.

The apparatus used for the conductivity measurements is described in Ref. 2; Refs. 5 and 8 contain some additional details.

In Fig. 1, $\log_{10}(\sigma T)$ is plotted versus $1000/T$ for $\text{CsCu}_4\text{Cl}_3\text{I}_2$. At 296 K, the conductivity of the γ phase is $5.3 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. The γ - β and β - α transitions occur at 418 and 431 K, respectively; that is, the β phase exists only over a 13-K temperature range. The total enthalpy of activation in the β -phase region is 0.77 eV.

Both transitions are very sluggish. The γ - β transition began at 418 K, but the conductivity increased very slowly at this temperature. Therefore the temperature was increased in small increments to 425.5 K over a period of 10 h to attain complete conversion of the γ to β phase. (For clarity, not all the points are plotted.) At 425.5 K, the conductivity of the β phase is $0.11 \Omega^{-1} \text{cm}^{-1}$. After conversion was complete, conductivities reached constancy in 15 min or less at each temperature until 432.9 K was reached. Here the conductivity increased relatively rapidly. The temperature was then reduced to 431.2 K and the conductivity continued to increase. We estimate the total transition time to be 8–10 h under these conditions. When the conductivity attained constancy, measurements were taken at 432.9 and 434.8 K ($1000/T = 2.31$ and 2.30 , respectively). Then the temperature was reduced⁹ incrementally and conductivities measured (Fig. 1). In the α phase, equilibration is rapid; this is a feature common to true solid electrolytes. Deviation from the straight line began at about 387 K indicating reconversion to the γ phase (see below). After the measurement at 373.1 K

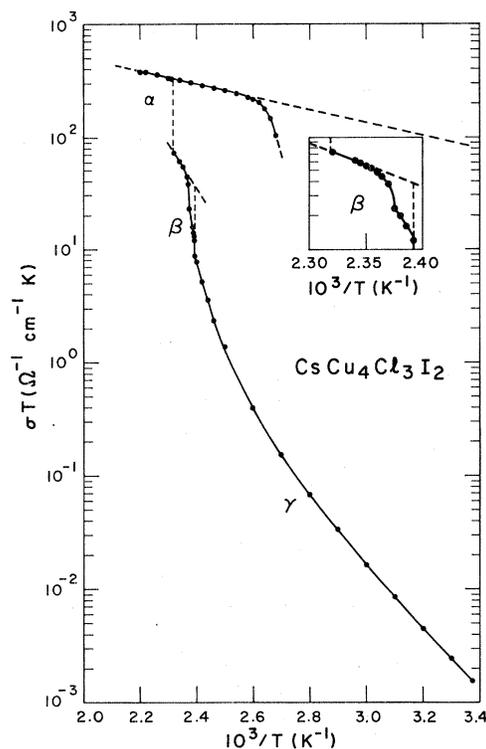


FIG. 1. \log_{10} of the conductivity multiplied by temperature vs reciprocal temperature.

($1000/T = 2.68$), the cell was reheated to 438.6 K.

Until 403 K was reached the conductivity decreased rapidly as the energy input activated the further conversion to the γ phase. The conductivity increased as the temperature increased from 403 to 438.6 K and conductivities were then measured at 0.02 increments of $1000/T$ until the temperature of 458.7 K was reached.⁹

The enthalpy of activation of motion for the α phase is 0.112 eV. At 419 K, the transition temperature of AgI to the true solid electrolyte phase, the conductivity of α - $\text{CsCu}_4\text{Cl}_3\text{I}_2$ is $0.72 \Omega^{-1} \text{cm}^{-1}$; extrapolation to 298 K gives a conductivity of $0.29 \Omega^{-1} \text{cm}^{-1}$.

In a previous experiment on $\text{CsCu}_4\text{Cl}_3\text{I}_2$ the cell was cooled to 368 K then reheated to 426.2 K ($1000/T = 2.346$) which is inside the β -phase temperature region. The σT product at this temperature stabilized at the value 115 for 14 h. At this temperature σT for the β phase is 56 and for the α phase, 310. The interpretation of this observation is as follows: At 368 K, only the α and γ phases could be present. (When the cell was reheated to 426.2 K the conductivity dropped at first as in the experiment described earlier, but, in both cases, not all the way back to that of the γ phase.) The γ phase transformed to the β phase, but the α phase did not;

this is the only way to account for the observation. Therefore the α phase does not transform to the β phase; one may say that the $\alpha \rightarrow \beta$ transition is "infinitely sluggish." There are undoubtedly more examples of high-temperature phases which cannot be made to transform to low-temperature phases via annealing only; one of these is $\alpha\text{-Ag}_8\text{W}_4\text{O}_{16}$.¹⁰

In the same experiment, the bulk density of the electrolyte was only 89% of the x-ray density. At 419 K, the conductivity was $0.65 \Omega^{-1}\text{cm}^{-1}$ as compared with $0.72 \Omega^{-1}\text{cm}^{-1}$ for the specimen with bulk density 94% of the x-ray density. If the relation between conductivity and bulk density were linear, the correct conductivity at 419 K should be close to $0.80 \Omega^{-1}\text{cm}^{-1}$; the value expected at 298 K is $0.35 \Omega^{-1}\text{cm}^{-1}$.

It should be emphasized that both the $\gamma\text{-}\beta$ and $\beta\text{-}\alpha$ transitions are first order as indicated by the evidence presented earlier. The space groups $Cmca$ and $C2ca$ are not subgroups of any hexagonal group. We suspect that the β phase is hexagonal; the α phase is pseudo-hexagonal.

The curve representing the $\log_{10}(\sigma T)$ vs $1000/T$ data (Fig. 1) of the γ phase is markedly nonlinear, the negative slope increasing with increasing temperature. However, it is possible to account rather closely for this behavior by two intersecting straight lines in the region $417 > T > 296$ K. The relation is best represented by

$$\sigma T = 8.77 \times 10^6 \exp(-0.577/kT) + 2.43 \times 10^{19} \exp(-1.538/kT) \quad (1)$$

A plot of σ vs $1000/T$ gives prefactors that are about three orders of magnitude less and enthalpies of activation that are about 10% less.

Contrasted with the results, for example, for NaCl,¹¹ the prefactors are very high, entirely because the conductivity of NaCl may be as much as ten orders of magnitude lower than that of $\gamma\text{-CsCu}_4\text{Cl}_3\text{I}_2$ in the same temperature region. Nevertheless, it seems reasonable to interpret Eq. (1) in a manner analogous

to the interpretation of the NaCl data,¹² namely, that in the lower-temperature region there are some ions that are *relatively* easily mobile, while in the higher-temperature region, additional ions are being thermally excited into mobile states. Actually it is probable that even in the lower-temperature region part of the enthalpy is a formation enthalpy, but if we call it only an enthalpy of motion, h_m , then the formation enthalpy,¹² h_f , in the higher temperature region is 1.92 eV, because $\frac{1}{2}h_f + h_m = 1.54$ eV.

The σT -vs- T^{-1} behavior of $\gamma\text{-CsCu}_4\text{Cl}_3\text{I}_2$ is similar to that of $\beta\text{-PyAg}_5\text{I}_6$ (Ref. 13) implying that in the $\gamma\text{-CsCu}_4\text{Cl}_3\text{I}_2$ crystal structure there are "built-in" sites into which the Cu^+ ions can move.

Note added in proof. An additional phase transition has been found at 476 K by differential thermal analysis. However, there is no indication of deviation from the cubic structure in the x-ray diffraction powder photograph taken at 505 K. Since finding this transition, attempts to obtain reproducible conductivities at temperatures exceeding 455 K have not been successful; the difficulties are experimental and work to solve this problem is continuing. Under the circumstances the phases should be renamed: α between 476 K and the melting point, 567 K; the present α , β , and γ become β , γ , and δ , respectively.

At this time, we can only speculate on the nature of these phases. There is a finite probability that the (new) β phase is actually rhombohedral with rhombohedral angle differing unresolvably (by the *photographic* technique utilized) from 90° , and the (new) α phase is the cubic one. Our intention is to solve all the crystal structure problems, but this will take some time.

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