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Cu^+ ION CONDUCTIVITY OF $K_2Cu(CNS)_3$

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$K_2Cu(CNS)_3$ is found to be a Cu^+ ion conductor with a room temperature (30°C) conductivity of $\sim 5 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$. The phase structure of the CuCNS + KCNS system and data on temperature variation of the conductivity of $K_2Cu(CNS)_3$ is reported. The related compound $KAg(CNS)_2$ is found to be a Ag^+ ion conductor.

The solid electrolytes having highest recorded room temperature conductivities are Ag^+ ion conductors [1–3]. Although the Cu^+ ion is similar in size and coordination number to Ag^+, the number of known solids exhibiting high Cu^+ ion conductivity are quite few when compared to Ag^+ ion conductors. This is probably due to unavailability of a large number of cuprous salts to be used as the base substances. Almost all known Cu^+ ion solid conductors are based on cuprous halides [2]. Another stable cuprous salt that has escaped attention as a possible base substance for Cu^+ ion conducting solids is cuprous thiocyanate. In this note we report our observations on Cu^+ ion conductivity of $K_2Cu(CNS)_3$, which is found to have a room temperature (30°C) ionic conductivity of $\sim 5 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$.

$K_2Cu(CNS)_3$ was prepared by melting a homogeneous mixture of KCNS (analar and CuCNS in the molecular ratio 2:1 (CuCNS was prepared by method described by Vogel [4] using analar grade KCNS and $CuSO_4$). The product was powdered and dried in vacuum at 130°C (mp 138°C). Chemical analysis indicated that material has stoichiometric composition corresponding to the above formula. Samples for conductivity measurements were made by compacting the powder between copper electrodes in a glass tube (diameter ~0.6 cm, pellet length ~0.5 cm) at a pressure of 80 kbar. Ends of the tube were sealed with epoxy resin and ac conductivity (40 Hz) at different temperatures was determined using a conducting bridge operating at 40 Hz. The plot of log σ versus T^{-1} is indicated in fig. 1. The graph consists of two straight line portions 1 and 2 with activation energies 0.14 eV and 0.89 eV respectively, the transition temperature being 104°C. Polarization measurements [5] with blocking electrodes (carbon) showed that electronic conductivity is negligible. When dc currents were passed through pellets of the material pressed between copper electrodes, copper gets deposited on the cathode (deposited copper can be identified easily as it forms a loose layer on the anode). Absence of polarization, and absence of compositional and structural changes in the electrolyte during prolonged electrolysis indicated that the mobile ion is Cu^+. The phase diagram for the KCNS– CuCNS system obtained by differential thermal analysis on ~4 g of the material heated at a constant rate of 0.5°C min^{-1} is shown in fig. 2. It is seen that $K_2Cu(CNS)_3$ corresponds to a congruent melting point. Again it was noted that the maximum ionic conductivity in the solid state corresponds to this composition.

The phase diagram for the related system AgCNS–

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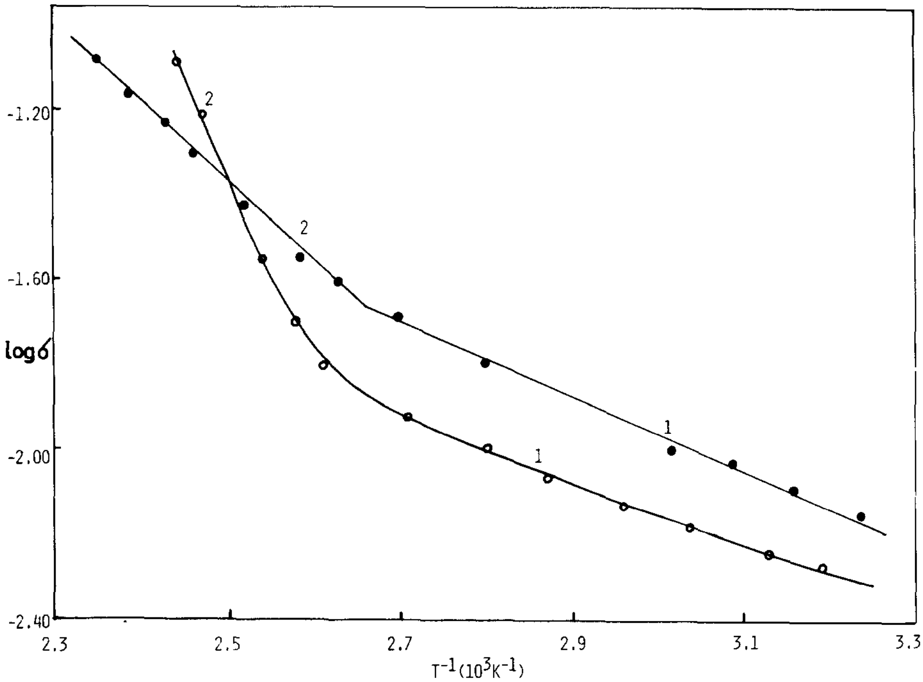

Fig. 1. Plot of log σ versus T^{-1} (σ in Ω^{-1} cm^{-1}). (○) $K_2Cu(SCN)_3$, (●) $KAg(SCN)_2$.

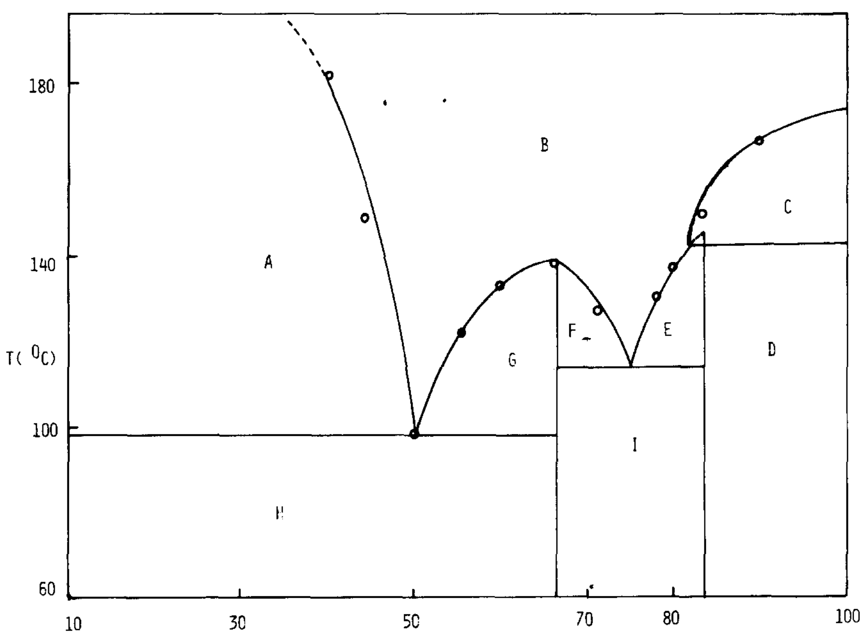

Fig. 2. Phase diagram for the CuCNS–KCNS system: A – solid CuCNS + liquid (KCNS in CuSCN), B – liquid, C – solid KCNS + liquid (CuCNS in KCNS), D – solid KCNS + solid $K_5Cu(CNS)_5$, E – solid $K_5Cu(CNS)_6$ + liquid (CuCNS in KCNS), F – solid $K_2Cu(CNS)_3$ + liquid (CuCNS in KCNS), G – solid $K_2Cu(CNS)_3$ + liquid (KCNS in CuCNS), H – solid CuCNS + solid $K_2Cu(CNS)_3$, I – solid $K_2Cu(CNS)_3$ + solid $K_5Cu(CNS)_6$.

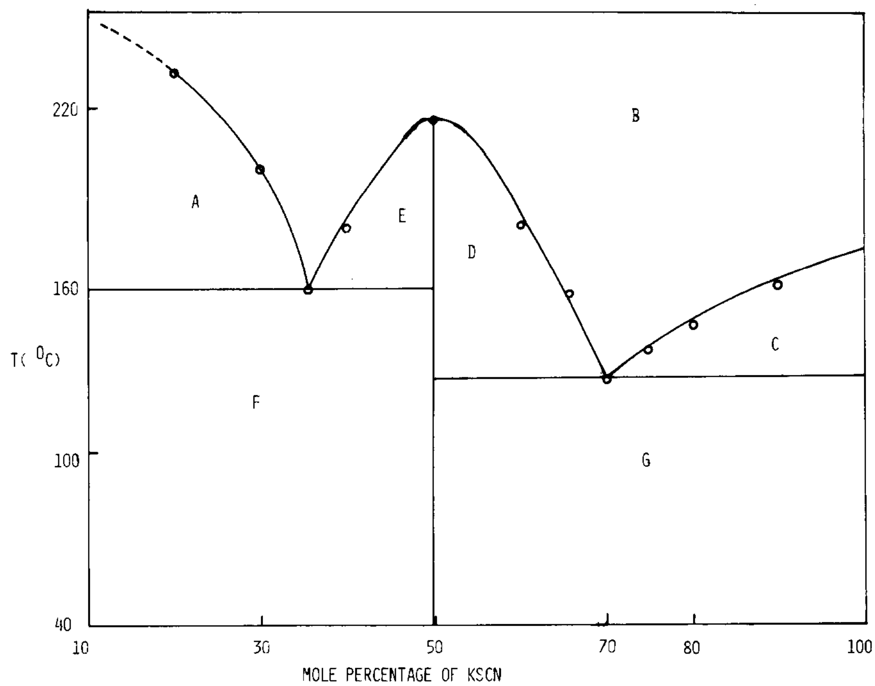

Fig. 3. Phase diagram for the AgCNS–KCNS system: A – solid AgCNS + liquid (KCNS in AgCNS), B – liquid, C – solid KCNS + liquid (AgCNS in KCNS), D – solid $KAg(CNS)_2$ + liquid (AgCNS in KCNS), E – solid $KAg(CNS)_2$ + liquid (KCNS in AgCNS), F – solid AgCNS + solid $KAg(CNS)_2$, G – solid KCNS + solid $KAg(CNS)_2$.

KCNS is shown in fig. 3. Here the congruent melting point and maximum conductivity in the solid state corresponds to the composition $KAg(CNS)_2$ (mp 145°C). The plot of log σ versus T^{-1} is indicated in fig. 1. Again the graph consists of two straight line portions 1 and 2 of activation energies 0.18 eV and 0.37 eV respectively. However, in contrast to the copper compound, the room temperature conductivity of this material is lower than most of the familiar Ag^+ ion conductors.

We did not have facilities to elucidate the crystal structure of these materials. Ionic conduction is most probably of the molten sublattice type with an order–disorder phase transition involving a change in activation energies [6] at 104°C in $K_2Cu(CNS)_3$ and 101°C in $KAg(CNS)_2$.

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