INFLUENCE OF Cu(II) ON THE ELECTRONIC CONDUCTIVITY IN y-CuI

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Abstract—The hole conductivity of CuI is affected by the presence of Cu(II) ions arising from the synthesis process. By treating these ions as aliovalent impurities, the value of the hole migration energy is obtained.

INTRODUCTION

CuI is a mixed solid conductor, predominantly ionic at temperatures above 300°C, exhibiting an important hole electronic conductivity at lower temperatures [1-3].

When using this halide it is common practice to sinter it at 550°C. This thermal treatment should result in a "pure" Cul free from Cu²⁺ ions which are eliminated by the reaction[4]:

$$2CuI_2 = I_2(g) + 2CuI.$$
 (1)

Cu²⁺ ions appear when CuI is synthesized by the wet reaction between a sodium halide and a cupric salt.

In this paper, we report on the effect of the thermal treatment at different temperatures upon the electronic conduction in polycrystalline y-CuI (below 350°C). The results are explained treating the Cu² ions as aliovalent impurities.

EXPERIMENTAL

CuI was synthesized by the reaction between CuSO₄ and NaI both of pro analysi purity. The solid precipitate, carefully washed and dried at 120°C, was separated into two batches, which were treated at 400°C (batch 1) and 550°C (batch 2), under purified nitrogen for about 10 h. Pellets of 1 cm diameter and 0.3 cm thickness were prepared by pressing at about $1000 \, \text{kg} \, \text{cm}^{-2}$.

The electronic conductivity of these samples was measured by the Hebb-Wagner method, using the assembly (+) graphite/CuI/Cu (-), in which the graphite electrode works as the blocking electrode. Details on the furnace, measuring circuitry and temperature control are given elsewhere [5]. The working temperature was varied between 230 and 350°C, ie in the temperature range corresponding to the y-form of CuI. Before the measurements were carried out, the samples were allowed to equilibrate for several hours at each working temperature.

RESULTS

The conductivity data were obtained using the expression corresponding to hole conduction at potentials $E \gg RT/F$:

$$\ln I = \ln \left(\sigma_h^\circ ART / LF \right) + EF / RT \tag{2}$$

where I is the current, σ_{h}° is the hole conductivity of the sample in equilibrium with metallic copper, A is the cross-sectional area, L is the thickness of the solid electrolyte and E is the applied potential. T, R and Fhave their usual meanings.

The values of the experimental slopes of Equation (2) did not differ more than 3-4% from the theoretical ones.

These data are represented in Fig. 1 as $\log(\sigma_h T)$ vs 1/T for batches 1 and 2. The different behaviour is assigned to the presence of Cu(II) ions in the sample of batch 1.

Two other series of electronic conductivity measurements were carried out on samples of pure CuI previously exposed to an iodine atmosphere, as detailed in the following.

First, a CuI pellet obtained with the halide treated at 550°C was exposed to a 2.66×10^2 Pa iodine pressure for 24 h at ca 130°C. The pellet underwent a colour change from light grey-brown to grey, the latter remaining after separation of the iodine source. Prior to measurements, the sample was maintained at 420°C for ca 60 h. The electronic conductivity data obtained with the so-treated pellet were in satisfactory agreement with those corresponding to batch 1, and are included in Fig. 1.

Another series of conductivity determinations were made using a unique CuI pellet which was first exposed for 24 h to a 2.66×10^2 Pa iodine pressure at 420°C. Thereafter the electronic conductivity of the sample was measured after each one of the following sequence of annealing steps (the obtained data are represented in Fig. 2 by the indicated symbols):

(a) at 350°C for 24 h (open circles);

- (b) at 420°C for 60 h (squares);
- (c) at 450°C for 50 h (triangles);
- (d) at 450° C for 50 h (consec); (e) at 500° C for 50 h (crosses); (f) at 500° C for 15 h (diamonds).

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Fig. 1. Plot of log $(\sigma_h T)$ as a function of temperature. •, Batch 1; o, batch 2; \Box , batch 2 exposed to $I_2(g); \Delta$, data from Ref. 3.



Fig. 2. Plot of $\log(\sigma_k T)$ vs 1/T. A unique sample exposed to iodine after a sequence of annealing steps (see text).

In all cases the data obtained were very reproducible and showed no hysteresis when the measurements were performed going up and down with temperature. The hole concentration depends on the temperature because these defects arise from the ionization of cationic vacancies, according to the reaction:

$$V_{Cu}^{x} = V_{Cu}' + h^{*}$$
 (3)

DISCUSSION

The conductivity data obtained with CuI treated at 550°C are in good agreement with data reported in the literature[3] for pure CuI. It can be assumed that the only electronic carriers present are the intrinsic holes.

in which, according to the notation of Kroeger and Vinck[6], V_{Cu}^{x} represents a neutral vacant site in the cationic network; V_{Cu}' a negative charged vacancy and h a positive charged hole. The state of charge is referred to the crystalline lattice taken as neutral.

In turn, the cationic vacancies may originate in two wavs:

(i) from Frenkel defect equilibrium,

$$Cu_{Cu}^{x} = Cu_{i}^{x} + V_{Cu}^{x}$$
(4)

ie a normal ion in the lattice goes to an interstitial site, leaving a vacant neutral site; and

(ii) from a small stoichiometric variation of a magnitude which in the present case is determined for the equilibration with metallic copper.

On the other hand, the conductivity data obtained with the CuI from batch 1 exhibit larger values and a lower slope in the Arrhenius-type plot. This may be interpreted as due to the presence of extrinsic holes resulting from the excess cupric ions, as indicated by the reaction:

$$\mathbf{Cu}_{\mathrm{Cu}}^{\star} = \mathbf{Cu}_{\mathrm{Cu}}^{\star} + h^{\star}. \tag{5}$$

A copper ion with a net positive charge in the lattice of CuI is, of course, equivalent to a cupric ion.

This type of behaviour is analogous to that observed in other cases in which the introduction of aliovalent impurities influences markedly the ionic or electronic conduction properties[7].

The relationship between conductivity and temperature arises from the dependence of temperature on the concentration and mobility factors in the general expression:

$$\sigma_h = q \mu_h[h^{\cdot}] \tag{6}$$

where q is the elementary charge, μ_h the hole mobility and [h] the hole concentration.

Thus, for the intrinsic hole conductivity (batch 2), in which both μ and [h] depends on temperature:

$$\sigma_{h,i}T = \text{constant} \times \exp \left(\frac{E_f + E_m}{RT}\right)$$
 (7)

where E_f is the defect formation energy and E_m the hole migration energy.

For batch 1, in turn, the concentration of extrinsic holes outnumbers that of the intrinsic ones and the only temperature-dependent factor will be that of the mobility:

$$\sigma_{h,e}T = \text{constant}' \times \exp{-\left(\frac{E_m}{RT}\right)}.$$
 (8)

From the data shown in Fig. 1, the following figures are obtained: $E_m = 17 \pm 2 \text{ kJ mol}^{-1}$ and $(E_f + E_m)^{-1} = 45 \pm 2 \text{ kJ mol}^{-1}$. The difference, $28 \pm 4 \text{ kJ mol}^{-1}$ corresponds to the hole formation energy. This value is in good agreement with the value of 28 kJ mol⁻¹ reported by Vine and Maurer[8].

On the other hand, taking into account that according to the reaction expressed by Equation (1), pure CuI free of Cu²⁺ is obtained with simultaneous evolution of iodine gas, application of an iodine pressure on purified CuI would have the reciprocal effect.

This may be expressed by the reaction:

$$Cul + \frac{1}{2}I_2(g) = Cu_{Cu}^x + h' + V'_{Cu} + 2I_1^x \qquad (9a)$$

$$CuI + \frac{1}{2}I_2(g) = Cu_{Cu} + V'_{Cu} + 2I_1^x.$$
(9b)

This behaviour was in fact observed, as demonstrated by the agreement between the data obtained with the CuI pellet exposed to iodine and those corresponding to batch 1 (Fig. 1).

As for the data obtained with the CuI pellet submitted to the annealing steps, it is to be noted that the points corresponding to steps (b), (c) and (d) agree very well with those corresponding to batch 1 in Fig. 1. whereas those of step (f) agree with those of batch 2 (pure CuI).

These facts indicate the existence of a state in which a certain amount of extrinsic defects are present for a long time, and the system behaves as if in equilibrium, as indicated by the agreement between the experimental and the theoretical slopes of Equation (2), together with the absence of hysteresis during the measurements. This should be unexpected, for the thermodynamically defined equilibrium state should be that of batch 2, ie pure CuI in contact with metallic copper. However, the system could be thought as in a nonequilibrium state, slowly evolving towards its true equilibrium position.

As for the points corresponding to annealing step (a), the intermediate slope they show may be explained by the assumption of an incomplete distribution of extrinsic defects in the pellet. Thus, a heterogeneous mixture of pure CuI and Cu²⁺-containing CuI is present. For this situation, the total conductivity of the two-phase mixture would be that of a series circuit of the two phases.

Step (b) should then be seen as yielding a homogeneous distribution of the concentration of extrinsic defects which thus attains the value corresponding to the electronic conductivity of batch 1.

From step (e) onwards, the heating eliminates iodine according to Equation (1), ie the hole concentration becomes progressively lower. The appearance of the "knee" may result from quenching of the remaining extrinsic defects, which still outnumber the intrinsic ones at that state. This type of behaviour has already been observed in a number of cases, for example in the introduction of extrinsic defects in CoO equilibrated with oxygen[9]. It may be said that the observed behaviour could be explained as a consequence of a kinetic inhibition for reaction (1), which proceeds readily only at temperatures higher than 400°C. In this context it is worthwhile to remember the total conductivity vs temperature curve of CuI[5, 10] in which the conductivity remains low from 200 to about 350°C, thereafter increasing rapidly until at ca 420°C a plateau of high conductivity (mainly ionic) is reached. Thus, the influence of the temperature upon the reequilibration process might involve some transport processes involving Cu⁺ ions. It is thus possible to accept the quenching of defects at temperatures below ca 350°C.

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