

Solid-state ionics: the phase diagram and high ionic conductivity of the system CuCl-TlCl

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The phase diagram of the CuCl-TlCl system has been determined by the use of differential thermal analysis, X-ray diffraction analysis and conductivity measurement. Two intermediate compounds, Tl_2CuCl_3 and $Tl_3Cu_2Cl_5$, have been identified. Tl_2CuCl_3 is stable up to $204^\circ C$ and above this temperature it disproportionates to TlCl and $Tl_3Cu_2Cl_5$. $Tl_3Cu_2Cl_5$ is stable between its incongruent melting point ($210^\circ C$) and $95^\circ C$. The electrical conductivity and the transport number measurements indicate that $Tl_3Cu_2Cl_5$ has a high copper ion conductivity of $2 \times 10^{-2} (\text{ohm cm})^{-1}$ at $100^\circ C$ and Tl_2CuCl_3 is a poor conductor.

1. Introduction

Many high silver ion conductivity solids have been found during the past decade. Recently, some high copper ion conductivity solids were reported by Takahashi *et al.* [1], Sammells *et al.* [2], Bonino and Lazzari [3] and Matsui and Wagner [4]. The copper ion conductivity solids would be of great practical use because of the lower cost and greater availability of Cu than Ag.

During research into high copper ion conductivity solids in our laboratory, a new compound having a high copper ion conductivity was found in the CuCl-TlCl system. The phase diagram of this system drawn by Sandonnini [5] showed only one intermediate compound Tl_2CuCl_3 (stable up to $210^\circ C$), which is a poor conductor. The phase diagram obtained by this study, however, showed another intermediate compound $Tl_3Cu_2Cl_5$, which has a high ionic conductivity. The present paper describes our phase diagram of the CuCl-TlCl system, which was obtained by using differential thermal analysis (DTA), X-ray diffraction analysis and electrical conductivity measurement. It also describes the electrical properties of the new compound $Tl_3Cu_2Cl_5$.

2. Experimental

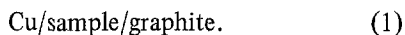
Copper (I) chloride was recrystallized from hydrochloric acid; it was dried under vacuum at $100^\circ C$

for 16 h and stored in a vacuum desiccator. The reagent grade TlCl was used without purification. The melting point of the TlCl used was in good agreement with the previously reported value ($412^\circ C$).

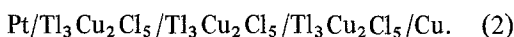
Weighing of CuCl and TlCl was followed by mixing and grinding. The mixture was then sealed in a Pyrex tube under vacuum and heated for about 18 h at $300^\circ C$; the resulting material was then allowed to cool to room temperature slowly. The samples thus obtained were used for DTA, X-ray diffraction analysis and conductivity measurement.

DTA was carried out for the sample sealed in a Vycor tube under vacuum; $\alpha\text{-Al}_2\text{O}_3$ powder sealed in the same size Vycor tube was used as the standard material. The rate of temperature change was $2^\circ C \text{ min}^{-1}$. In the composition range from 30 to 45 mol% CuCl, the transitions were studied at composition intervals of 1 mol%. In other composition ranges the intervals were 5-10 mol%. X-ray diffraction patterns of powdered samples were obtained with a diffractometer using $\text{CuK}\alpha$ radiation. The scanning speed was 1° min^{-1} . The electrical conductivity was measured on pellets with a 1000 Hz conductance bridge. A sample of about 0.6 g was pressed between two copper electrode layers under a pressure of 3000 bar cm^{-2} into a pellet of 13 mm in diameter. A mixture of powdered copper and the sample (2:1 weight ratio) was used as the electrodes. At the phase

transition temperature, the conductivity was measured after the sample had been maintained at this temperature for about 15 h. All the measurements were carried out in a nitrogen gas flow. The electronic conductivity was measured by means of polarization measurements on Cell 1, according to Wagner's method [6]



The ionic transport numbers in $\text{Tl}_3\text{Cu}_2\text{Cl}_5$ were measured by Tubandt's method [7] on a three-pellet arrangement clamped between a Pt cathode and a Cu anode



3. Results and discussion

3.1. Phase diagram

The phase diagram of the CuCl–TlCl system determined with DTA is shown in Fig. 1. This figure indicates that the CuCl–TlCl system contains two intermediate compounds, namely $\text{Tl}_3\text{Cu}_2\text{Cl}_5$ and Tl_2CuCl_3 , in the temperature range of 95–204°C. $\text{Tl}_3\text{Cu}_2\text{Cl}_5$ is stable between $95 \pm 3^\circ\text{C}$ and $210 \pm 3^\circ\text{C}$, which is its incongruent melting point, and it disproportionates to Tl_2CuCl_3 and CuCl below 95°C . The incongruent melting point of $\text{Tl}_3\text{Cu}_2\text{Cl}_5$ measured in this work had the same value as that of Tl_2CuCl_3 reported by Sandonnini [5]. Tl_2CuCl_3 shows a solid-state disproportionation reaction at

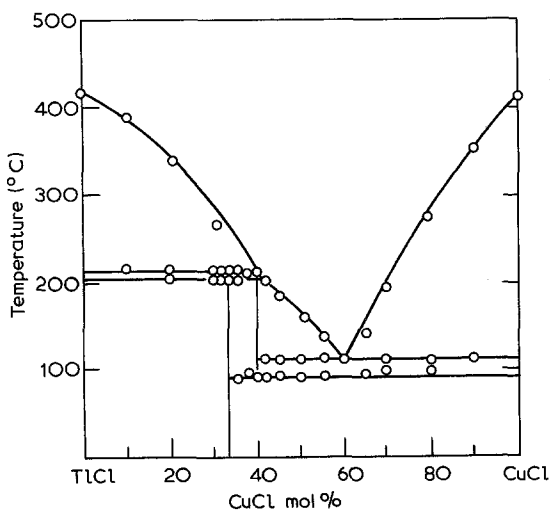


Fig. 1. Phase diagram of the CuCl–TlCl system.

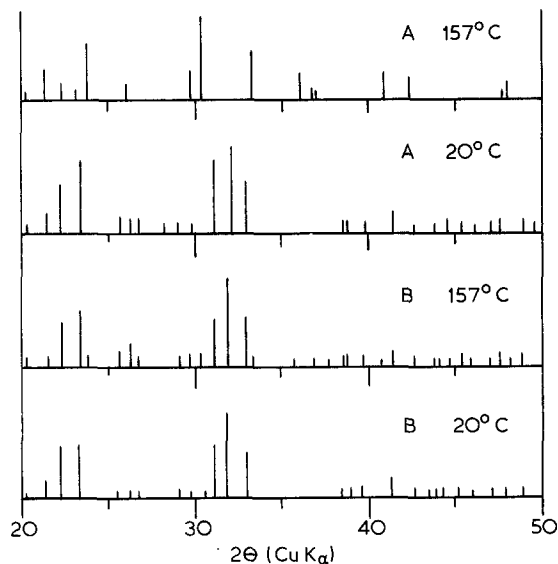


Fig. 2. X-ray diffraction patterns of CuCl 40 mol%–TlCl 60 mol% (A) and CuCl 33.3 mol%–TlCl 66.7 mol% (B) at 20 and 157°C .

$204 \pm 3^\circ\text{C}$. The endothermic peak due to this disproportionation reaction was not found on the DTA curve for the sample containing 40 mol% CuCl. A eutectic point is determined as $111 \pm 3^\circ\text{C}$ for $60 \pm 2\text{ mol \%}$ CuCl. The eutectic composition and temperature agreed with those of the earlier work. The endothermic peak at $111 \pm 3^\circ\text{C}$ in the heating DTA curves disappeared for the samples containing CuCl at 40 mol% or less. The liquidus lines were determined by the cooling DTA curves.

Powder X-ray diffraction analysis was carried out at room temperature and $157 \pm 5^\circ\text{C}$. The results for the samples containing 40 mol% CuCl and 33.3 mol% CuCl are shown in Fig. 2. At room temperature the sample containing 33.3 mol% CuCl does not give diffraction patterns corresponding to free CuCl and TlCl but corresponding to the intermediate compound Tl_2CuCl_3 . The diffraction patterns of 40 mol% CuCl indicate the existence of Tl_2CuCl_3 and free CuCl. The samples containing less than 33.3 mol% CuCl gave the patterns due to free TlCl. At $157 \pm 5^\circ\text{C}$, the sample containing 40 mol% does not give the patterns due to Tl_2CuCl_3 and CuCl, but due to a new phase, which can be considered to be $\text{Tl}_3\text{Cu}_2\text{Cl}_5$, as indicated on the phase diagram. The sample containing 33.3 mol% CuCl gives the patterns due to Tl_2CuCl_3 and a trace of $\text{Tl}_3\text{Cu}_2\text{Cl}_5$. The sample containing 35 mol% CuCl showed a mixed phase of Tl_2CuCl_3 and

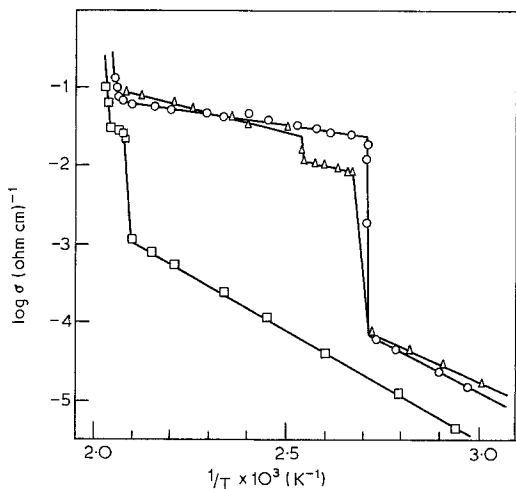
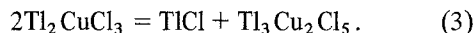


Fig. 3. Electrical conductivity (σ) of the system CuCl-TlCl: \circ 40 mol% CuCl; \triangle 42 mol% CuCl; \square 33.3 mol% CuCl.

$\text{Tl}_3\text{Cu}_2\text{Cl}_5$, while the 30 mol% CuCl sample indicated a mixed phase of TlCl and Tl_2CuCl_3 . From these results of the DTA and the X-ray investigations, the existence of two intermediate compounds Tl_2CuCl_3 and $\text{Tl}_3\text{Cu}_2\text{Cl}_5$ in the CuCl-TlCl system can be concluded.

3.2. Electrical conductivity

The electrical conductivity was measured for the samples containing 90–10 mol% CuCl in the temperature range between room temperature and 200°C. Fig. 3 shows the logarithm of the electrical conductivity *v.* the reciprocal of the absolute temperature curves for the samples containing 40 mol%, 42 mol% and 33.3 mol% CuCl. The curve for 40 mol% CuCl shows an abrupt conductivity change of about three orders of magnitude near 95°C and a conductivity knee at $212 \pm 2^\circ\text{C}$. The former temperature corresponds to the disproportionation temperature of $\text{Tl}_3\text{Cu}_2\text{Cl}_5$ and the latter to its incongruent melting point as shown in Fig. 1. From Fig. 3, the activation energy for conduction is calculated as 20 kJ mol^{-1} in the temperature range of 95–212°C. This value is as small as that of high ionic conductivity solids known so far [8]. In the case of 33.3 mol% CuCl, no conductivity knee was observed in the temperature range of 50–204°C, and an abrupt conductivity change appears near 205°C, which corresponds to the solid-state disproportionation reaction temperature



A conductivity knee at $212 \pm 2^\circ\text{C}$ is of the incongruent melt of $\text{Tl}_3\text{Cu}_2\text{Cl}_5$. The conductivity curve for 42 mol% CuCl shows the abrupt conductivity changes near 95°C and 111°C. The abrupt conductivity change was observed for all samples containing more than 40 mol% CuCl near 111°C, which corresponds to the eutectic temperature.

The dependence of conductivity on the content of CuCl at 105°C is shown in Fig. 4. This figure shows a maximum conductivity around 40 mol% CuCl, which suggests that an intermediate compound exists near the composition of 40 mol% CuCl at this temperature. These results verify the phase diagram determined with DTA and X-ray diffractometry.

The electronic contribution to the total electrical conductivity (a.c. conductivity) of the new compound $\text{Tl}_3\text{Cu}_2\text{Cl}_5$ was estimated by the help of Wagner's polarization method [6]. The value of the hole conductivity of about $10^{-11} (\text{ohm cm})^{-1}$ at 180°C was calculated from the current-voltage relation of Cell 1 using Wagner's theory. The value is comparable to that extrapolated from the high temperature results of pure CuCl [9]. It took many hours to obtain the steady-state hole current, so that the above hole conductivity value is not so accurate but indicates only the order of its magnitude. Consequently, the conduction in $\text{Tl}_3\text{Cu}_2\text{Cl}_5$ can be considered to be essentially ionic.

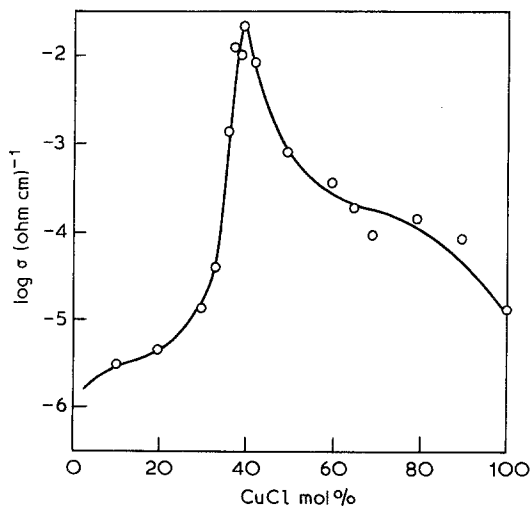


Fig. 4. Composition dependence of the electrical conductivity (σ) of the system CuCl-TlCl at 105°C.

Table 1. Transport number determination on Cell 2 at 110° C

	Change in weight (mg)
Pt cathode	+10.8
Tl ₃ Cu ₂ Cl ₅	
Tl ₃ Cu ₂ Cl ₅	-0.05
Tl ₃ Cu ₂ Cl ₅	-10.3
Cu anode	
Ag in coulometer	19.22
Cu equivalent	11.32

3.3. Transport number

Copper (I) chloride in equilibrium with copper is essentially a copper ion conductor at elevated temperatures [9], and thallium chloride is a predominant chloride ion conductor; the Cl⁻ ion transport number in TlCl is calculated to be 0.96 at 300° C from the results of the diffusion measurements of Cl⁻ and Tl⁺ [10]. Therefore, it is interesting to determine the kinds of ions which are predominant charge carriers in Tl₃Cu₂Cl₅. In this study, ionic transport number

was determined by Tubandt's method using Cell 2. A constant current of 75 μA was passed through Cell 2 for about 60 h at 110° C, and the weight change of each part of the cell was measured. A typical result is shown in Table 1. The result shows that the transport number of copper ion in Tl₃Cu₂Cl₅ must be considered to be nearly unity.

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