

Phase Diagrams of the Copper(I) Bromide–Lead Bromide and Copper (I) Iodide–Lead Iodide Systems and the Ionic Conductivity of CuPb_3Br_7

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The phase diagrams of the systems CuBr-PbBr_2 and CuI-PbI_2 have been determined by the use of differential thermal analysis and X-ray diffraction analysis. A new compound CuPb_3Br_7 has been found in the CuBr-PbBr_2 system. This compound is stable between its incongruent melting point (300°C) and 160°C , and below 160°C disproportionates to CuBr and PbBr_2 . It has a relatively high ionic conductivity of $3 \times 10^{-2} (\text{ohm-cm})^{-1}$ at 200°C and a low activation energy for conduction of 22 kJ/mole. The transport number measurement with Tubandt's method shows that the copper ions must be considered as the only charge carriers. No intermediate compound has been found in the CuI-PbI_2 system.

1. Introduction

During the past decade, many high silver ion conductivity solids have been found in the silver iodide–inorganic iodides and –organic ammonium iodides systems (1). More recently, the double salts between copper(I) halides and organic ammonium halides (2–4) have been found to have high copper ion conductivity in the solid state. However, no inorganic compound having high copper ion conductivity has been found except in the high temperature modifications of copper(I) halides and Cu_2HgI_4 , and in KCu_4I_5 which is stable between 257 and 332°C (5). The crystal structure of the low temperature modification of copper(I) halides (γ phase), zincblende type, is the same as that of AgI (γ phase). Further, the high temperature modifications of CuI , CuBr , and AgI (α phase) have the average structure, in which the cations move freely through a large number of sites (6–7). This similarity of the crystal structure suggests that some double salts based on copper(I) halide may exhibit a high copper ion conductivity at relatively low temperatures.

The electrical conductivities of many systems of copper(I) halides–inorganic halides have been measured to develop new solid electrolytes in our laboratory. A new compound CuPb_3Br_7 was found to have relatively high conductivity in the temperature range from 160 to 300°C . In this paper, the phase diagrams of the CuBr-PbBr_2 and CuI-PbI_2 systems are presented and the electrical properties of the new compound CuPb_3Br_7 are described.

2. Experimental

2.1. Materials

Commercially available copper(I) bromide and copper(I) iodide were purified by recrystallization in the corresponding hydrohalogenic acid. The recrystallized copper(I) halides were completely dried *in vacuo* over P_2O_5 . Lead bromide (lead iodide) was prepared by mixing the aqueous solution of lead nitrate and hydrobromic acid (hydroiodic acid). The obtained PbBr_2 and PbI_2 were recrystallized in hot water. After being filtered,

the precipitate was dried *in vacuo* over P_2O_5 .

Appropriate quantities of copper(I) halide and lead halide were thoroughly ground together and the mixture was heated in a sealed evacuated Pyrex vessel for 17 hr at 300°C .

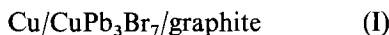
2.2 Differential Thermal Analysis

The phase diagrams were determined mainly with differential thermal analysis (DTA). A sample of about 0.5 g was sealed in a Vycor tube under vacuum to prevent oxidation by air; $\alpha\text{-Al}_2\text{O}_3$ powder sealed in the same size Vycor tube was used as the standard material. The heating and cooling rates were $2^\circ\text{C}/\text{min}$. In order to avoid any error due to supercooling, heating experiments were used to measure the transition temperatures.

2.3. Electrical Conductivity and Transport Number Measurements

A sample of about 1 g was stacked between two electrodes and pressed under a pressure of $3000\text{ kg}/\text{cm}^2$ into a pellet of 13-mm diameter. In order to reduce the contact resistance, a mixture of powdered copper (325 mesh) and the sample (2:1 weight ratio) was used as the electrodes. The total conductivity (ionic and electronic) was measured with a 1000-Hz conductance bridge in the temperature range from room temperature to 300°C . All the measurements were carried out in a nitrogen gas flow.

The electronic conductivity of CuPb_3Br_7 was measured by Wagner's polarization method (9). A dc voltage was applied to cell (I) with a copper anode and a graphite cathode,

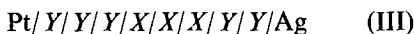


A constant current supplier was used and the resulting voltage was measured with a digital voltmeter with an internal resistance of $1000\text{ M}\Omega$.

The transport numbers of the ions in CuPb_3Br_7 were determined by Tubandt's method (10). Two types of cells



and



were used in this experiment, where X is CuPb_3Br_7 and Y is PbCl_2 . The $\text{CuBr}-3\text{PbBr}_2$ mixture and PbCl_2 were pressed under a pressure of $3000\text{ kg}/\text{cm}^2$ into a pellet 13 mm in diameter and 1–2 mm thick. The pellets were heated for several hours at 200°C , before being quenched to room temperature, and then their weights were measured. The electrolysis was performed after having maintained the cell for several hours at 200°C in a current of nitrogen. A direct current of a few hundred microamperes was passed through the cell for 10–20 hr, and the weight change of each part was measured. A silver coulometer was used to measure the total charge passed through the cell.

3. Results and Discussion

3.1. Phase Diagram

The phase diagram of the $\text{CuI}-\text{PbI}_2$ system, as determined with DTA, is shown in Fig. 1. An endothermic peak at $301 \pm 1^\circ\text{C}$ in the DTA curve was observed for all compositions between 10 and 90 mole % (m/o) CuI . In the composition range from 75 to 100 m/o CuI , two other endothermic peaks were found, which are due to the phase transitions of $\gamma\text{-CuI}$ to $\beta\text{-CuI}$ and $\beta\text{-CuI}$ to $\alpha\text{-CuI}$. The $\gamma \rightarrow \beta$ phase transition temperature of CuI ($365 \pm 2^\circ\text{C}$ for pure CuI) decreased slightly to $363 \pm 2^\circ\text{C}$ on incorporation of PbI_2 . The $\beta \rightarrow \alpha$ phase transition temperature

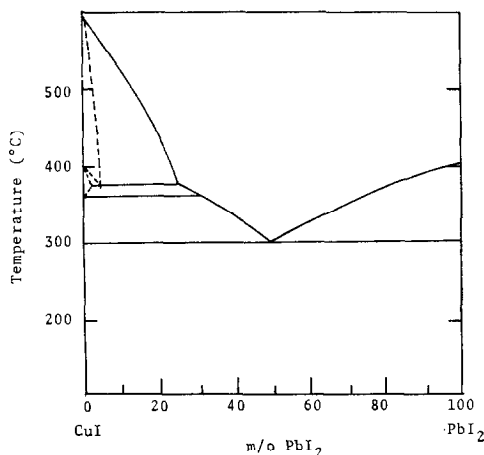


FIG. 1. Phase diagram of the $\text{CuI}-\text{PbI}_2$ system.

($400 \pm 2^\circ\text{C}$ for pure CuI) decreased to $369 \pm 2^\circ\text{C}$ on incorporation of 5 m/o PbI₂. Consequently, no intermediate compound was observed in this system and the phase diagram is a simple eutectic system similar to that of the CuCl-PbCl₂ system (8).

The phase diagram of the CuBr-PbBr₂ system is shown in Fig. 2. A broad endothermic peak was observed near 160°C in the DTA curves, and the maximum peak height was observed near the composition 25 m/o CuBr. This corresponds to the disproportionation temperature of CuPb₃Br₇ to CuBr and PbBr₂, which was confirmed by X-ray diffraction analysis. The more accurate disproportionation temperature was estimated to be $160 \pm 3^\circ\text{C}$ by the electrical conductivity measurement as described in the following section. For all samples containing 95 to 27.5 m/o CuBr, another endothermic peak was observed at $260 \pm 2^\circ\text{C}$, a temperature corresponding to the eutectic point. The eutectic point was observed at the composition 45 ± 2 m/o CuBr. The samples containing 25 to 5 m/o CuBr gave an endothermic peak at $300 \pm 2^\circ\text{C}$, which is due to the peritectic point. The peritectic composition was estimated to be 27.5 ± 2.5 m/o CuBr.

Powder X-ray diffraction analyses were carried out at room temperature and 168°C . At room temperature, only the diffraction

patterns due to the mixture of CuBr and PbBr₂ were observed for all samples containing 95 to 5 m/o CuBr. At 168°C , the diffraction patterns due to free CuBr and PbBr₂ were not observed for the sample containing 25 m/o CuBr, but patterns due to a new compound were found as shown in Fig. 3. The samples containing 17.5 m/o or less and 30 m/o or more CuBr showed patterns due to free PbBr₂ and free CuBr at 168°C . From these results of the DTA and the X-ray investigations, it can be concluded that an intermediate compound CuPb₃Br₇, stable between 160 and 300°C , exists in the CuBr-PbBr₂ system.

3.2. Electrical Conductivity

The logarithm of the electrical conductivity vs the reciprocal of the absolute temperature curves for the CuBr-PbBr₂ system are shown as in Fig. 4. These curves show an abrupt conductivity change of three or four orders of magnitude near 160°C , a temperature corresponding to the disproportionation temperature of CuPb₃Br₇ shown in the CuBr-PbBr₂ phase diagram. Further, the conductivity curves show a knee at 290°C for the samples containing 25 and 20 m/o CuBr, and at 250°C for the sample containing 30 m/o CuBr. The conductivity knees at 290 and 250°C correspond to the eutectic and peritectic temperatures, respectively. From the data of Fig. 4, the activation energy can be calculated as 22 kJ/mole for CuPb₃Br₇, a value which corresponds to that of high ionic conductivity

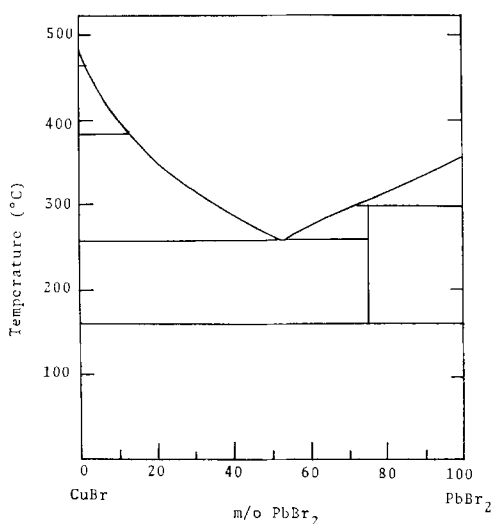


FIG. 2. Phase diagram of the CuBr-PbBr₂ system.

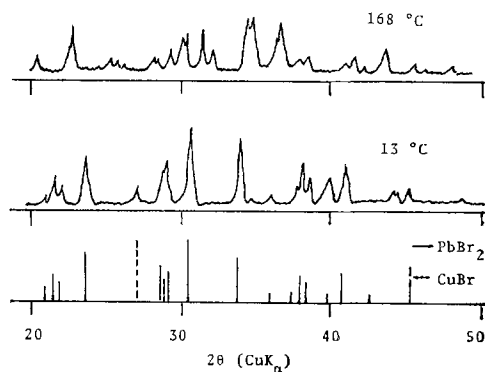


FIG. 3. X-ray diffraction patterns of CuBr-3PbBr₂ at 13 and 168°C .

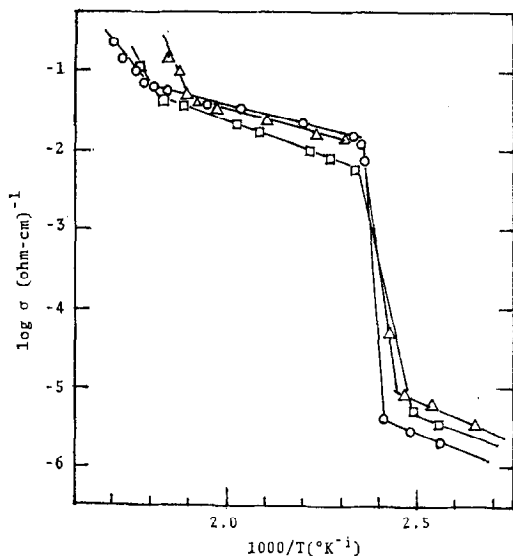


FIG. 4. Electrical conductivity (σ) of the system CuBr-PbBr_2 . \square , 20 m/o (mole percent) CuBr ; \circ , 25 m/o CuBr ; Δ , 30 m/o CuBr .

solids known so far (1). The dependence of conductivity on the content of CuBr at 200°C is shown in Fig. 5. This figure shows a maximum conductivity around 25 m/o CuBr and suggests that an intermediate compound may exist near the composition 25 m/o CuBr at 200°C . The conductivity re-

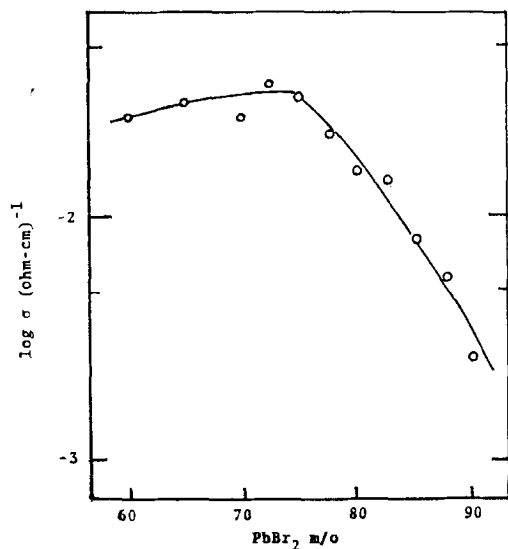


FIG. 5. Composition dependence of the electrical conductivity (σ) of the system CuBr-PbBr_2 at 200°C .

sults confirm the phase diagram as determined with DTA and X-ray diffractometry.

It is very important to decide the nature of the charge carriers for conduction in CuPb_3Br_7 . In this study, Wagner's polarization method was used to determine the electronic conductivity. Current density, I , vs cell voltage, E , curves for cell (I) give a quasi-exponential increase of the current as shown in Fig. 6. According to Wagner's theory, the current density for the contribution of positive hole conduction is given by

$$I = (RT/LF)\sigma_h^0 [\exp(EF/RT) - 1] \quad (1)$$

and if $EF/RT \gg 1$,

$$I = (RT/LF)\sigma_h^0 \exp(EF/RT) \quad (2)$$

where σ_h^0 is the hole conductivity which is in equilibrium with metallic copper, and L the thickness of the sample, and the other symbols have their usual meanings. The plots of $\log I$ vs E shown in Fig. 6 give virtually straight lines whose slopes are close the value of $F/2.3RT$. The temperature dependence of the electronic conductivity of CuPb_3Br_7 calculated from the I - E curves is shown in Fig. 7. The contribution of the electronic conductivity to the total conductivity of CuPb_3Br_7 is negligible.

3.3. Transport Number

In order to determine what kind of ion is the predominant charge carrier in CuPb_3Br_7 , a

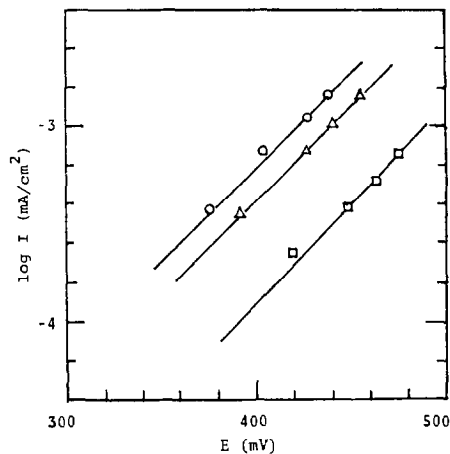
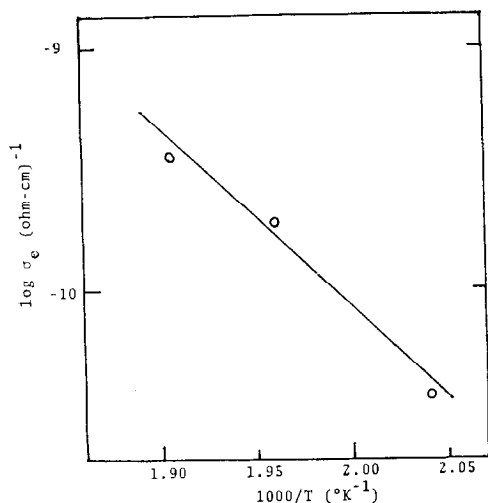


FIG. 6. $\log I$ vs E curves for cell (I). \circ , 252°C ; Δ , 237°C ; \square , 217°C .

FIG. 7. Electronic conductivity (σ_e) of CuPb₃Br₇.

Tubandt experiment was carried out using cells (II) and (III). In a preliminary experiment, the lead ion transport number was estimated using cell (II) with the lead electrodes. A constant current of 100 μ A was passed through cell (II) for about 30 hr at 200°C. A typical result is shown in Table I. The result shows that the transport number of lead ion must be considered to be nearly zero. This seems reasonable from the fact that, in general, the divalent cations cannot move through the crystal lattice as easily as the monovalent cations.

The transport numbers of Cu⁺ and Br⁻ were determined with the help of cell (III), the construction of which was the same as that used by Tubandt (10) to determine the

TABLE I
TRANSPORT NUMBER DETERMINATION ON CELL (II)

	Change in mass (mg)
Pb anode } X ₁	-10.83
X ₂	+0.46
X ₃	+9.23
Pb cathode }	
Ag in coulometer	16.72
Cu equivalent	9.85
Pb equivalent	16.06

TABLE II

TRANSPORT NUMBER DETERMINATION ON CELL (III)

	Change in mass (mg)
Pt cathode } Y ₁	+11.13
Y ₂	
Y ₃	
X ₁	-0.09
X ₂	
X ₃	
Y ₄	-14.10
Y ₅	
Ag anode }	
Ag in coulometer	24.00
Cu equivalent	13.91
Transport number of Cu ⁺	1.0

transport number of Ag⁺ and Cl⁻ in the solid solution AgCl-PbCl₂. A constant current of 100 μ A was passed through cell (III) at 215°C for about 50 hr; a typical result is shown in Table II. Though the weight loss at the anode was not equal to the weight gain at the cathode, the transport number of Cu⁺ calculated from the change in weight at the anode side was 1.0. From the above two experimental results, it can be concluded that the copper ions must be the predominant charge carrier in CuPb₃Br₇.

4. Conclusion

From the phase diagram study and the conductivity measurements, a new compound CuPb₃Br₇, which has the relatively high copper ion conductivity, has been found between 160 and 300°C. The conductivity of 0.03 (ohm-cm)⁻¹ at 200°C is the highest value of any inorganic copper ion conductor known at this temperature.

Though the crystal structure of this compound cannot be determined by use of powder X-ray diffraction analysis, the low activation energy for conduction (22 kJ/mole) and the high copper ion conductivity suggest that the copper ions may be statistically distributed in the lattice, giving an average structure.

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