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PHASE EQUILIBRIA IN THE CuBr–TlBr SYSTEM

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Abstract

The phase diagram for the CuBr-TlBr system was investigated using the differential thermal analysis completed by the X-ray powder diffraction data. Three intermediate phases were found: Tl_2CuBr_3 (stable from room temperature up to 234°C where decomposes in the solid state), $Tl_3Cu_2Br_5$ (stable between 168°C and its incongruent melting point 262°C) and a nonstoichiometric δ phase (centered about 75 mol% CuBr and stable above about 240°C).

Keywords: DTA, intermediate phases of Tl_2CuBr_3, phase diagram, X-ray

Introduction

Investigations of phase equilibria in the systems involving copper(I) halides may be useful to develop new solid electrolytes.

The copper(I) halides themselves have interesting electrical properties [1–4]. At room temperature the γ phases, with the zinc blende structure, are good conductors, mostly electronic. As the temperature arises, the contribution of the ionic conductivity increases. The hexagonal β phases are already entirely ionic conductors. The high temperature cubic α phase (in the case of CuCl such a phase appears only under a high pressure) are superionic conductors.

Superionic phases are formed also in the copper(I) halide–metal halide systems e.g. CuCl–RbCl [5], CuCl–NH_4Cl [4], CuBr-CsBr [7], CuI–KI [8], CuI–CsI [7].

In the system CuCl–TlCl [9] and CuI–TlI [10] three intermediate compounds: Tl_2CuCl_3, Tl_2CuI_3 and $Tl_3Cu_2Cl_5$ have been found. The last one is a good ionic conductor [9]. That is why it was interesting to examine phase equilibria in the CuBr–TlBr system which had not been studied before.

Experimental

CuBr was obtained by the reaction of $CuBr_2$ with powdered copper in sealed evacuated silica tubes heated slowly up to 600°C. Then the product was distilled

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two or three times under vacuum. Details of the preparation were reported elsewhere [11].

TlBr was precipitated by combining aqueous solutions of $TlNO_3$ and HBr. Thus obtained TlBr was filtered, dried at 120°C and finally heated slowly up to melting in an argon flow.

Phase equilibria in the CuBr–TlBr system were examined by DTA experiments and X-ray diffraction.

Differential thermal analysis was performed with an apparatus of the type Q-1500 D (system Paulik, Paulik and Erdey) calibrated against the melting point of metals: indium, tin, cadmium, zinc and the melting point of lead chloride. Mixtures of desired compositions for DTA measurements were prepared *in situ* from CuBr and TlBr, accurately weighed and placed in evacuated and sealed silica ampoules. The total weight of a sample was within 1 g. Compositions were examined at intervals of about 5 mol% CuBr. Prior to measurements the samples were homogenized at 500°C.

The heating rate was 10, 5 or 2.5 deg·min^{-1}. The cooling rate was generally lower, dropping below 1 deg·min^{-1} at a lower temperature where the furnace was not longer controlled. To avoid supercooling effects, the bottom of the DTA peaks from the heating experiments were taken as the transition temperatures. The apparatus did not assure a good reproducibility of DTA curves. That is why we assume the precision of the temperature determination to be of ±10°C.

X-ray powder patterns were obtained with a DRON diffractometer at room temperature with CuK_α radiation.

Results and discussion

The results obtained from DTA and X-ray diffraction experiments allowed the phase diagram to be roughly constructed (Fig. 1).

The lowest temperature of three phase equilibria in the CuBr–TlBr system is 168°C. Corresponding thermal effects appear on the DTA curves from nearly pure CuBr up to 33.33 mol% CuBr. This indicates the composition of an intermediate compound: Tl_2CuBr_3.

The existence of a new compound Tl_2CuBr_3 is confirmed by X-ray powder diffraction analysis. X-ray patterns for the pure components and for the samples containing 15.64, 33.33 and 66.66 mol% CuBr are shown in Fig. 2. The sample containing 33.33 mol% CuBr does not give diffraction patterns corresponding to free TlBr and γ-CuBr but corresponding to the intermediate compound Tl_2CuBr_3. The samples containing 15.64 mol% CuBr or 66.66 mol% CuBr produce patterns due to free TlBr and Tl_2CuBr_3 or due to free γ-CuBr and Tl_2CuBr_3, respectively.

The formula M_2CuY_3 (where M=K, Rb, Cs, NH_4, Tl and Y=Cl, Br, I) is the most characteristic for compounds formed in the system of copper(I) halide

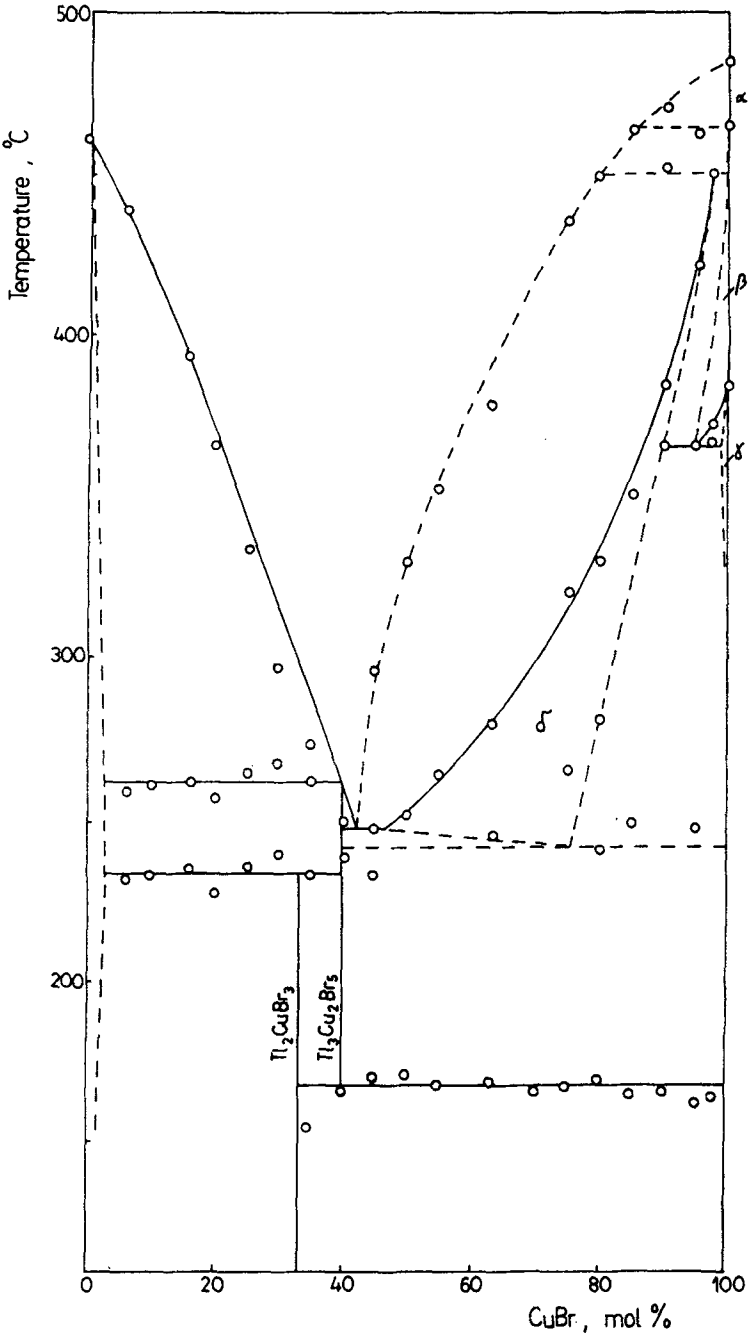

Fig. 1 Phase diagram of the CuBr–TlBr system

with halides involving monovalent cations [12]. All these M_2CuY_3 compounds found up to now are orthorhombic [13–18]. Tl_2CuBr_3 is probably isostructural with Tl_2CuCl_3 [9] since the respective diffraction patterns are very similar.

In the CuBr–TlBr system Tl_2CuBr_3 is the only intermediate compound which is stable at room temperature. Heating up to 234°C results in a solid state reaction. The Tl_2CuBr_3 decomposes for TlBr (or a limiting solid solution of CuBr in TlBr) and a new intermediate compound, probably $Tl_3Cu_2Br_5$. Such a formula was found for a compound in the system CuCl–TlCl [9], CuCl–CsCl [19] and probably in the system CuCl–RbCl [7, 20].

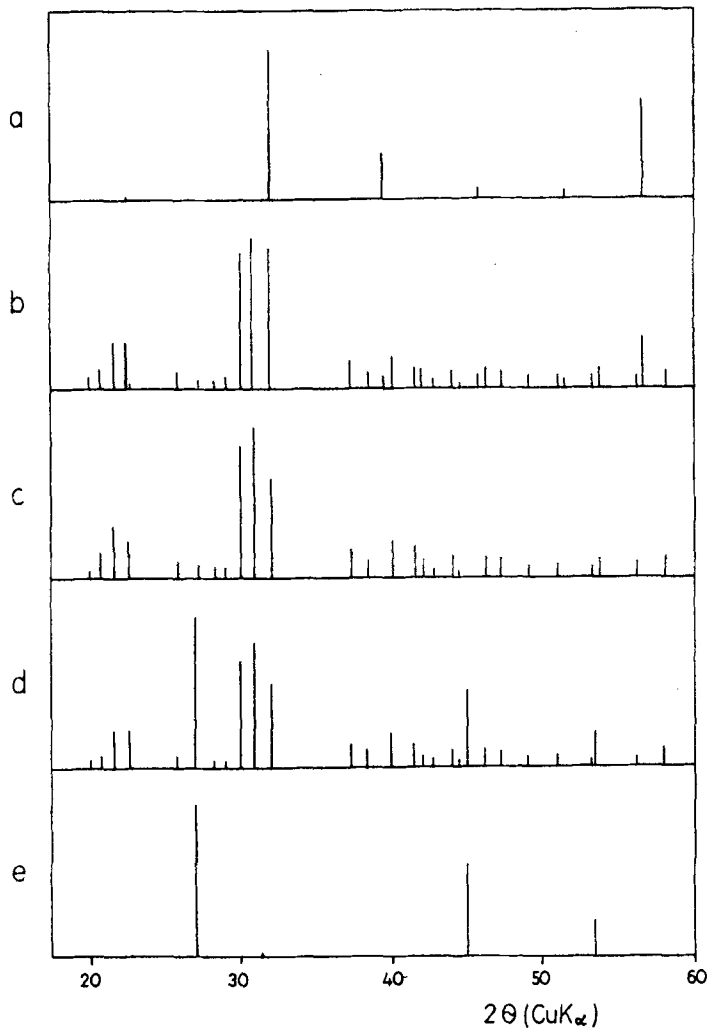

Fig. 2 X-ray diffraction patterns of TlBr (a), CuBr 15.64 mol%–TlBr 84.36 mol% (b), CuBr 33.33 mol%–TlBr 66.66 mol% (c), CuBr 66.66 mol%–TlBr 33.33 mol% (d) and γ-CuBr (e) at room temperature

$Tl_3Cu_2Br_5$ melts incongruently at 262°C. When cooled, like $Tl_3Cu_2Cl_5$, it decomposes for solid products Tl_2CuBr_3 and γ-CuBr at 168°C.

The eutectic point was estimated at 248°C and 42 mol% CuBr. Eutectic invariance corresponds to the equilibrium of the liquid with two solid phases: $M_3Cu_2Br_5$ and another but nonstoichiometric intermediate phase, δ.

The curve of the composition of the solid phase δ being in equilibrium with the liquid has been drawn (Fig. 1) on the basis of important thermal effects observed upon heating as well as upon cooling. It extends from about 47 mol% CuBr at the eutectic temperature to 97.5 mol% CuBr at 450°C. Other δ phase boundaries have been drawn approximately. The bottom limit of existence of the δ phase is probably at 240°C, near the composition of 75 mol% CuBr.

The melting point of CuBr as well as the temperatures of the polymorphic transitions α/β and β/γ agree with the values obtained previously [11]. When TlBr is added to CuBr the temperature of the β/γ transition changes from 384 to 365°C. Solid solutions of TlBr in β-CuBr may be expected up to about 5 mol% TlBr. The solubility of TlBr in γ-CuBr is lower than 2.5 mol% TlBr. The solubility of TlBr in α-CuBr is unknown. Apparently the transition liquid+α=β takes place at the same temperature (465°C) as the α/β transition in the pure solid CuBr. This part of the phase diagram together with the liquidus curve, however, require further investigations.

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Zusammenfassung — Mittels Differentialthermoanalyse und Röntgen-Pulverdiffraktionsangaben wurde das Phasendiagramm für das System CuBr-TlBr untersucht. Es wurden drei intermediäre Phasen gefunden; Tl_2CuBr_3 (stabil von Raumtemperatur bis 234°C, wo es sich im Festzustand zersetzt), $Tl_3Cu_2Br_5$ (stabil von 168°C bis zum kongruenten Schmelzpunkt bei 262°C) und eine nichtstöchiometrische Phase (bei 75Mol% CuBr und stabil oberhalb 240°C).