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Phase diagram for the CuBr–CsBr system

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Abstract

The phase diagram for the CuBr–CsBr system has been determined using differential scanning calorimetry and X-ray diffraction. The occurrence of three intermediate compounds has been shown: Cs_2CuBr_3, melting incongruently at 635 K; $CsCu_2Br_3$, melting congruently at 636 K and $CsCu_{19}Br_{20}$, melting incongruently at 624 K and decomposing in the solid state at 562 K. The coordinates of two eutectic points are 589 K, 48 mol% CsBr and 575 K, 21 mol% CsBr. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Phase diagram; DSC; X-ray diffraction; Cuprous bromide; Cesium bromide; Bromocuprates(I)

1. Introduction

Bradley and Greene [1,2] who in the late sixties discovered compounds with exceptionally high ionic conductivity at room temperature did not investigate systems involving cuprous bromide. The growing interest in such compounds resulted in many publications on silver and copper(I) ionic compounds during the following decade. In 1979, Takahashi et al. [3] quoted results of their earlier work (Ref. [8] in [3]) reporting the occurrence of a high Cu^+ conductivity compound $CsCu_9Br_{10}$, stable between 563 and 579 K where it melts incongruently. But it seems that until now a complete phase diagram of the CuBr–CsBr system has not been published.

Additional information concerning the CuBr–CsBr system comes from publications of Meyer [4] and Bazan et al. [5]. Meyer [4] determined the crystal structure of $CsCu_2Br_3$ single crystals obtained via a dry route by synproportionation:

$$CsCuBr_3 + Cu = CsCu_2Br_3$$

Recently Bazan et al. [5] measured the electrical conductivity of cuprous bromide and its mixtures with cesium bromide, containing up to 15 mol% CsBr.

In the present study, phase equilibria in the whole range of composition have been studied by the method of differential scanning calorimetry and X-ray diffraction in view to establish the phase equilibrium diagram for the system CuBr–CsBr.

2. Experimental

Cesium bromide (Aldrich Chemical, 99.999) was used after heating up to 700°C in a stream of hydrogen bromide, next removed by an argon flow.

Cuprous bromide (Riedel de Haën, 99%) was used after purification, which had been carried out in the

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following way: the salt was ground and wetted with a small quantity of sulfuric acid solution to form a paste, which was put on a sintered-glass filter. Sulfur dioxide was then being passed through the mixture. After that the mixture was washed by glacial acetic acid and anhydrous ethyl alcohol. The product was filtered and dried under vacuum and melted under argon atmosphere. Finally it was mixed with some copper powder and distilled twice in silica tubes at 600°C under vacuum.

Mixtures of salts of desired composition were prepared by weighing appropriate quantities of CuBr and CsBr on a Mettler Toledo AT 261 balance (±0.01 mg) and melting them in silica ampoules sealed under vacuum.

Samples for DSC experiments were homogenized in the ampoules next used for measurements. The bottoms of the ampoules were flattened by grinding. Their diameter was 6 mm and their height after sealing — between 12 and 14 mm. Compositions of mixtures were taken at intervals of 2–3 mol% or less. The total weight of a sample was 20–30 mg.

DSC was performed on a Mettler Toledo DSC 25 measuring cell with improved ceramic heat flow sensor, controlled with a TC15 TA interface and the

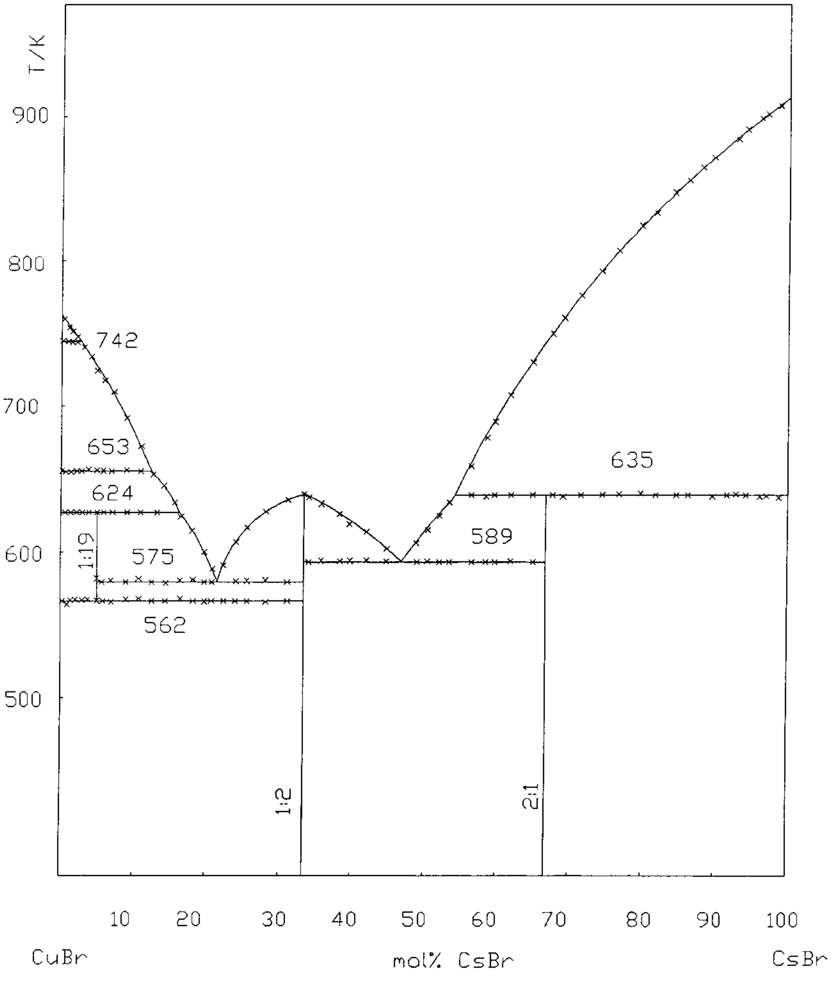

Fig. 1. Phase diagram for the CuBr–CsBr system.

STAR^e 4.0 software. The heating rates used in this work were 2 and 0.5 K min^{-1}.

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

3. Results and discussion

The phase diagram of the CuBr–CsBr system, determined in this study using DSC and X-ray diffraction is shown in Fig. 1. Three intermediate compounds: Cs_2CuBr_3, $CsCu_2Br_3$ and $CsCu_{19}Br_{20}$ and seven invariances: two eutectics, two peritectics, two polymorphic transitions and one eutectoid have been found in the system.

In binary systems with a common anion, involving cesium salts, the occurrence of intermediate compounds is not surprising, in view of the large cation Cs^+. The second cation, a smaller one, can thus easily coordinate the anions around it. This may lead to formation of a new compound.

Compounds of the general formula M_2CuX_3 (where X = Cl, Br or I), melting incongruently, are present in nearly all known systems of cuprous halides with halides of monovalent cations where a tendency for the formation of compounds occurs [6]. Cs_2CuBr_3, discovered in this work, melts incongruently at 635 K. Thermal events, corresponding to the respective peritectic reaction, were observed for all the mixtures with compositions above 54 mol% CsBr (liquidus) and below 100 mol% CsBr. The latter proves that the limiting solid solution of CuBr in CsBr is negligible. The formula Cs_2CuBr_3 has been established on the basis of three reasons:

> the heat of the peritectic reaction being the largest for a mixture having the molar ratio CsBr–CuBr equal to 2:1,

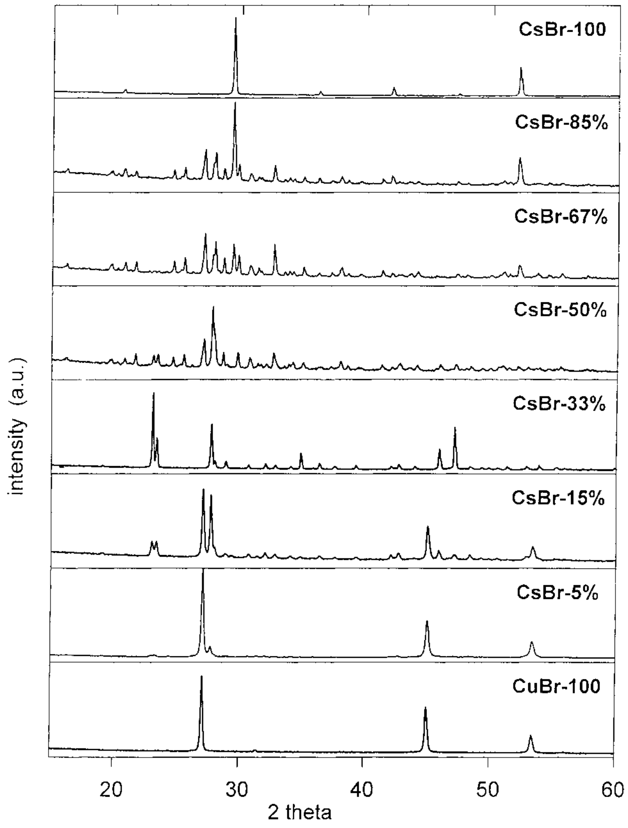

Fig. 2. X-ray diffraction patterns.

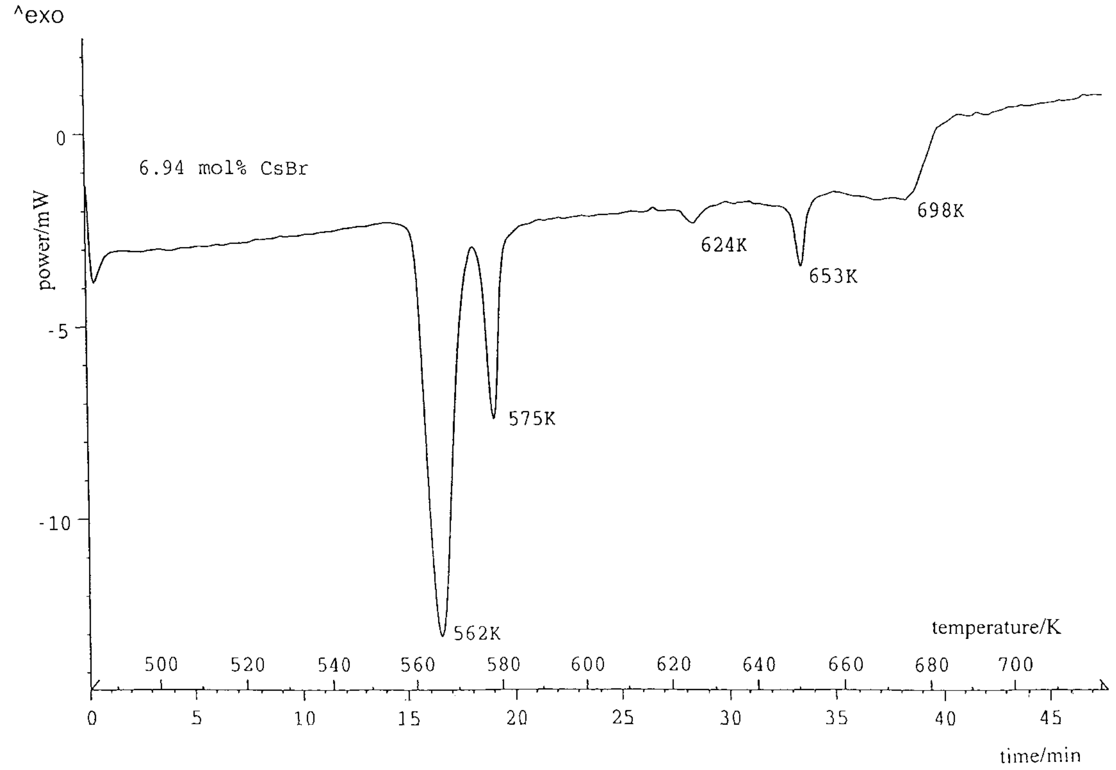

Fig. 3. DSC curve for a mixture containing 6.94 mol% CsBr.

the eutectic reaction at 589 K observed for samples having composition up to 66.67 mol% CsBr (Fig. 1),

X-ray diffraction pattern for Cs_2CuBr_3 different than that for $CsCu_2Br_3$ and CsBr (Fig. 2).

All compounds of the formula MCu_2X_3 (where X = Cl, Br or I), found until now in the systems involving rubidium and cesium halides, melt congruently. The melting point of $CsCu_2Br_3$, determined in this work, is 636 K. Coordinates of the eutectic points, situated on both sides of the clear maximum on the liquidus curve, are 589 K, 48 mol% CsBr and 575 K, 21 mol% CsBr. X-ray diffraction pattern for this compound is shown in Fig. 2. Details on the crystal structure of the $CsCu_2X_3$ compounds have been given by Meyer [4].

Both types of halogenocuprates(I): M_2CuX_3 and MCu_2X_3 are orthorhombic. Anions with stoichiometry CuX_3^{2-} form infinite chains of vertex-linked tetrahedra, and those with stoichiometry $Cu_2X_3^-$ form bands or double chains, composed of edge-sharing tetrahedra [4,7]. The lack of chains of face-sharing tetrahedra does not permit to expect a high ionic conductivity of Cs_2CuBr_3 and $CsCu_2Br_3$.

The third intermediate compound found in the system CuBr–CsBr, i.e. $CsCu_{19}Br_{20}$, melts incongruently at 624 K and decomposes in the solid state at 562 K (Fig. 1). The formula $CsCu_{19}Br_{20}$ was concluded from the fact that the eutectic reaction at 575 K starts at a composition very close to 5 mol% CsBr. The limits of temperature where the compound is stable coincide fairly well with changes of slope in the Arrhenius plot for conductivity obtained by Bazan et al. [5].

The intermediate compound $CsCu_9Br_{10}$ proposed by Takahashi et al. [3] has not been found. Nevertheless, the lower temperature limits for the stability of the compound found in this work (562 K) is almost identical (563 K) as theirs [3]. Instead, the incongruent melting point given by us (624 K) is 45 K higher form their one [3]. The latter lies not far from our value for the eutectic reaction at 575 K. The example of a DSC curve (Fig. 3) presented for 6.94 mol% CsBr shows five successive thermal effects found for this sample.

$CsCu_{19}Br_{20}$ being not stable at room temperature, X-ray diffraction patterns for samples containing 5 or 15 mol% CsBr (Fig. 2) show a γ-CuBr + $CsCu_2Br_3$ mixture. The same results at room temperature are obtained for samples first annealed during a week at 592 K and then quenched with liquid nitrogen.

The temperatures of the polymorphic transitions of cuprous bromide do not exhibit any change on the addition of cesium bromide. Values obtained are: 742 K for α/β and 653 K for β/γ transition. Respective invariances for the CuBr–CsBr mixtures are observed up to pure CuBr. So, the limiting solid solutions of CsBr in α-, β- and γ-CuBr may be considered negligible.

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