

PHASE DIAGRAM FOR THE RbBr–CuBr SYSTEM

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Abstract

The phase diagram for the RbBr–CuBr system has been determined. In the system two intermediate compounds are formed: RbCu₂Br₃, melting congruently at 537 K and Rb₃CuBr₄, melting incongruently at 544 K. The coordinates of the two eutectic points are: 501 K, 54 mole% CuBr and 522 K, 74 mole% CuBr.

Keywords: copper(I) bromide, DSC, phase diagram, rubidium bromide

Introduction

To our knowledge, the phase diagram for the RbBr–CuBr system has not been reported. The only information [1] was that an intermediate compound RbCu₄Br₅, analogous to RbAg₄I₅, one of the best known solid electrolytes, has not been found.

On the other hand, a room temperature superionic conductor RbCu₃Cl₄ was found [2] in the homologous chloride system. Afterwards, the system RbCl–CuCl has been thoroughly investigated. Apart from RbCu₃Cl₄ [3, 4] other formulae for the superionic phase i.e. Rb₃Cu₇Cl₁₀ [1, 5–7], Rb₄Cu₉Cl₁₃ [8, 9], RbCu₂Cl₃ [10, 11] and Rb₉Cu₁₆Cl₂₅ [12] have been proposed within a range of compositions from 75 to 64 mole% CuCl.

As yet, the system RbCl–CuCl is the only one among the alkali metal halide–copper(I) halide binary systems with common anion components of which form a superionic conductor stable at room temperature. It seemed that searching for new phases in the system RbBr–CuBr could also be promising.

Experimental

The phase diagram for the RbBr–CuBr system has been determined by differential scanning calorimetry using DSC25 apparatus (Mettler Toledo) with TC15 TA Controller and STAR^e Software 4.0. The heating rates were 2 and 0.5 K min⁻¹ for the all samples. Mixtures of salts of desired composition were prepared by weighing appropriate quantities of CuBr and RbBr (± 0.01 mg) on AT 261 balance (Mettler Toledo). The accuracy of the temperature and the composition determination was 1 K and 0.1 mole%, respectively.

The compositions of the eutectic and peritectic points were determined by extrapolation (liquidus curves and Tamman triangle methods) with an accuracy of ± 0.5 mole%.

An additional method employed was X-ray diffraction. X-ray powder patterns were obtained with a DRON-3 type diffractometer at room temperature with $\text{CuK}\alpha$ radiation.

CuBr was obtained in a reaction of CuBr_2 with powdered copper in sealed evacuated silica tubes, heated up to 875 K. Then the product obtained was distilled twice under vacuum. The preparation technique was reported in details in [13].

Prior to use, RbBr (Aldrich Chem. Co., 99% pure) was purified first by heating up to 975 K in hydrogen bromide gas stream and then by vacuum distillation.

Mixtures of CuBr and RbBr for DSC measurements were prepared *in situ* in silica ampoules sealed under vacuum [14]. The total mass of a mixture was 20–30 mg. Succeeding compositions of samples differed by 2–3 mole% or less. In order to become well homogenous, the samples were kept at 870 K for about 5 h, then cooled to 470 K and annealed for about 30 days before measurements.

Results

The phase diagram for the RbBr–CuBr system, determined in this study, is shown in Fig. 1. Two intermediate compounds are formed in the system:

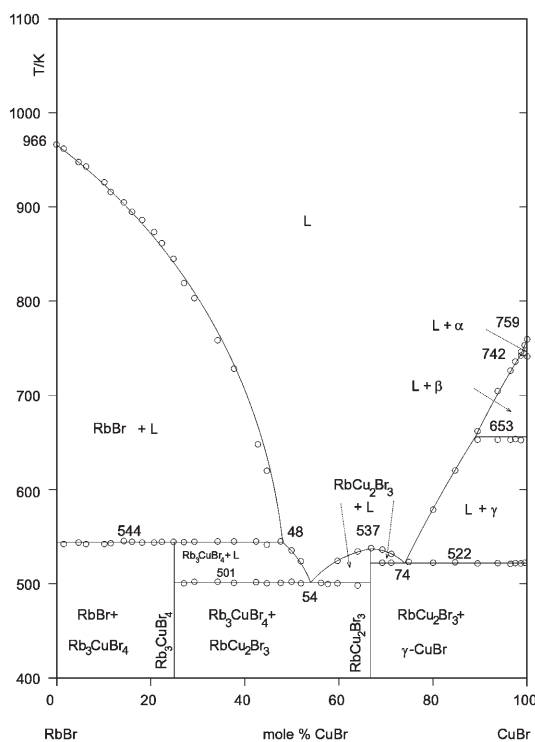


Fig. 1 Phase diagram for the RbBr–CuBr system

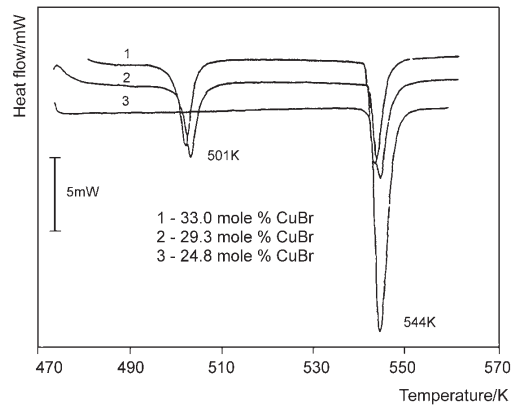


Fig. 2 DSC curves (1 and 2) showing two thermal effects (eutectic and peritectic) and (3) showing only one thermal effect (peritectic)

- RbCu_2Br_3 , melting congruently at 537 K (a maximum on the liquidus curve). The coordinates of the two eutectic points are 501 K, 54 mole% CuBr and 522 K, 74 mole% CuBr.
- Rb_3CuBr_4 , melting incongruently at 544 K, the peritectic point being at 49 mole% CuBr.

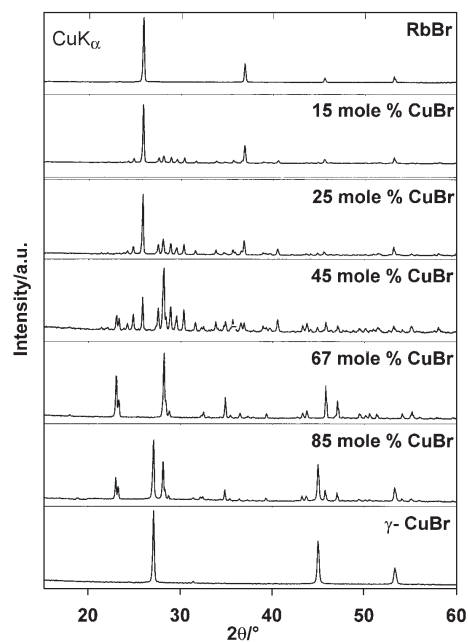


Fig. 3 X-ray diffraction patterns of pure components (RbBr, γ -CuBr) and of some RbBr+CuBr mixtures

The formula Rb_3CuBr_4 is assumed because the 25 mole% CuBr sample:

- displays the maximal thermal effect of the peritectic reaction at 544 K (Tamman triangle method),
- is the lower composition limit of appearance of the thermal effect of the eutectic reaction at 501 K (Fig. 2).

Both compounds are stable at room temperature as it is proved by X-ray diffraction patterns obtained for pure components (RbBr, γ -CuBr) and for samples containing 85.0, 66.7, 45.0, 25.0 and 15.0 mole% CuBr (Fig. 3).

Limiting solid solution of CuBr in RbBr as well as those of RbBr in α -, β - or γ -CuBr may be considered negligible. Respective invariances are observed for all compositions approaching the pure components. The temperatures of the polymorphic transitions of cuprous bromide do not exhibit any changes on the addition of rubidium bromide. The temperatures of the polymorphic transitions α/β and β/γ are: 742 and 653 K, respectively.

Discussion

The phase diagram for the RbBr–CuBr system, with the two compounds, appears to be unexpectedly simple as compared with that for the RbCl–CuCl system. The phase diagram for the latter system still does not seem well established. A variety of compounds has been reported, i.e. Rb_2CuCl_3 [7, 15–21], $\text{Rb}_3\text{Cu}_2\text{Cl}_5$ [17, 20, 21], RbCuCl_2 [7], $\text{Rb}_{11}\text{Cu}_{14}\text{Cl}_{25}$ [7], $\text{Rb}_2\text{Cu}_3\text{Cl}_5$ [3, 15, 17–21], $\text{Rb}_3\text{Cu}_5\text{Cl}_8$ [22], $\text{Rb}_9\text{Cu}_{16}\text{Cl}_{25}$ [7, 12], RbCu_2Cl_3 [7, 10, 11], $\text{Rb}_4\text{Cu}_9\text{Cl}_{13}$ [8, 9], $\text{Rb}_3\text{Cu}_7\text{Cl}_{10}$ [1, 5–7, 20] and RbCu_3Cl_4 [3, 4].

The compound Rb_3CuBr_4 has an unusual stoichiometry, not found in the other alkali metal halide–copper(I) halide systems where the most common formula for a compound richest in alkali metal halide is M_2CuX_3 [23]. Such a compound was found neither in the RbBr–CuBr system nor in the CsCl–CuCl or KI–CuI ones, all of them showing nearly the same value for $(r_{\text{Cu}^+} \cdot r_{\text{M}^+}) : r_{\text{X}^-} = 0.200 \pm 0.002 \text{ \AA}^{-1}$, where r_{Cu^+} , r_{M^+} and r_{X^-} are the Shannon's ionic radii [24].

The formula Rb_3CuBr_4 would suggest a formation of CuBr_4^{3-} species. To our knowledge, however, no mononuclear anions CuX_4^{3-} have been proved to exist in the solid state although the copper coordination number of four is that most commonly exhibited in halogenocuprates(I) [25].

Compounds of the formula MCu_2X_3 (where $X = \text{Cl, Br, I}$), have been found until now in all the systems built of rubidium and cesium halides. Three of them: CsCu_2Cl_3 [18, 26], CsCu_2Br_3 [14] and RbCu_2Br_3 [this work] melt congruently. Apparently, in the bromide systems compounds of this type are the most stable.

On the other hand, comparing phase diagrams for the systems RbBr–CuBr (Fig. 1) and CsBr–CuBr [14] one can observe that the relative height of a local maximum on the liquidus curve at 66.7 mole% CuBr is somewhat lower in the first system. Accordingly, the compound RbCu_2Br_3 may be considered a little less stable than CsCu_2Br_3 .

Structural data on MCu_2X_3 halogenocuprates(I) reveal that anions of the type $Cu_2X_3^-$ form bands or double chains, composed of edge-sharing tetrahedra [25]. $CsCu_2Cl_3$ [27, 28] and $CsCu_2Br_3$ [28] are orthorhombic. Our X-ray powder diffraction patterns for $RbCu_2Br_3$ and $CsCu_2Br_3$ resemble each other, which may be an indication of similar type of structure of these compounds.

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