FACTORS AFFECTING THE GENERAL SHAPE OF THE PHASE DIAGRAM AND COMPOUND FORMATION IN THE BINARY COPPER(I) HALIDE–ALKALI-METAL HALIDE SYSTEMS

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A set of phase diagrams for the systems CuX–AlkX (where *Alk*=Li, Na, K, Rb or Cs and *X*=Cl, Br or I) is given, basing on authors investigation and selected literature data. Sizes and valences of ions involved in Coulombic and polarization interactions were considered as main factors affecting phase equilibria. An increasing tendency for compound formation was noted in series Na→K→Rb→Cs, Na→Li and I→Br→Cl. The most strongly represented are compounds of the formulas $AlkCu_2X_3$ and Alk_2CuX_3.

Introduction

High ionic conductivities of some solid phases found in the systems involving copper(I) halides and alkali-metal halides [1–13] as well as possibility of their application as solid electrolytes make studies of phase equilibria in these systems interesting. However, polymorphism of the pure copper(I) halides [14–16] and their susceptibility to oxidation [17] are likely to make such investigations difficult. Therefore phase diagrams, even for the binary systems, are not always known or fully credible.

The ionic conductivity of some copper(I) compounds e.g. that of the high-temperature phase KCu_4I_5 is of the same order than that of well known silver compounds: $RbAg_4I_5$ and KAg_4I_5 but it drops on cooling over three orders of magnitude due to disproportionation into KI and CuI [11]. Unfortunately, the respective rubidium iodocuprate(I) is not formed. However, a lower cost of copper materials as compared with those of silver is stimulating in looking for similar compounds in the systems involving cuprous halides. Room temperature fast Cu^+ conductors were found in the system CuCl–RbCl [2–7, 18–20] as well as in ternary or quaternary systems with two or three different halide anions or alkali-metal cations [21–24].

In this work we present the main features of phase equilibria in the binary systems of cuprous halides with alkali-metal halides as well as factors influencing compound formation in these systems. This knowledge can be helpful in searching new phases (also in multi-component systems) which reveal high ionic conductivity and can be applied as solid electrolytes.

Polymorphism of the pure copper(I) halides

Temperature ranges of respective phases of copper(I) halides stable at normal pressure are given in Table 1 [25–27].

Table 1 Stability ranges of copper(I) halides modifications at normal pressure

	Temperature/K			
	γ-phase	β-phase	α-phase	references
CuCl	0–680	680–696	–	25
CuBr	0–657	657–741	741–759	26
CuI	0–643	643–679	679–866	27

Polymorphism of the pure cuprous halides often results in a complex form of phase diagrams for the binary and higher systems. At times, phases such as β-CuCl and α-CuBr are missing on reported phase diagrams because they are stable only in a narrow range of temperature. Existence of β-CuCl was indicated relatively late [14] and, even later, it was not always taken into consideration in establishing phase diagrams [4, 28, 29].

The pure cuprous halides are mixed ionic-electronic conductors at room temperature [16]. The γ-phases transform at a higher temperature into β-phases which display only the ionic conductivity [30]. α-CuBr [31] and α-CuI [32] are the so-called 'superionic phases', which exhibit exceptionally high values of ionic conductivity like the well-known α-AgI.

The three halides: CuCl, CuBr and CuI have the cubic zinc-blende structure in their room-temperature

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γ-phases and the hexagonal wurtzite structure in β-phases. β-CuBr and β-CuI transform to the cubic, but not isostructural, superionic α-phases [15]. β-CuCl melts before the structure transforms to the α-phase which only appears at high pressure [33].

Phase diagrams for the systems CuX–AlkX

In Fig. 1 we present a selection of phase diagrams [1, 4, 34–41] for the systems CuX–AlkX, where Alk=Li, Na, K, Rb, Cs and X=Cl, Br, I. For the respective cation or anion, values of Pauling's ionic radii are given.
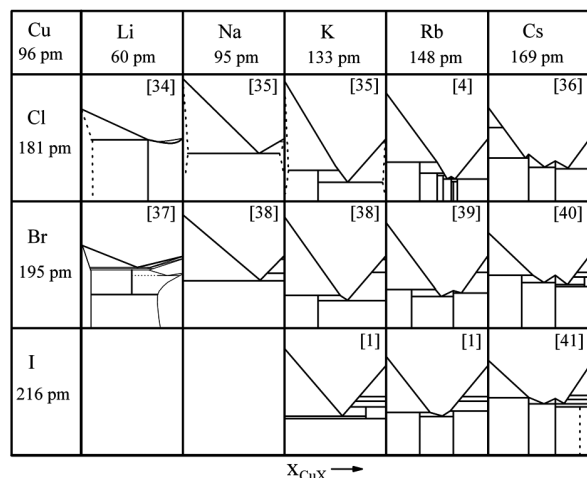
Fig. 1 Phase diagrams for the systems copper(I) halide–alkali-halide [1, 4, 34–41]; for the respective cation or anion values of Pauling's ionic radii are given

Phase equilibria in all the bromide systems as well as in the CuI–CsI system were investigated in our laboratory [37–41]. Phase diagrams for the systems CuBr–LiBr [37] and CuBr–RbBr [39] have been established for the first time [42]. Phase diagrams for the other systems [43–45] have been reinvestigated by us [38, 40, 41]. We intend to pursue our studies of the systems CuI–LiI and CuI–NaI for which, to our knowledge, phase diagrams have not been reported yet.

Our phase diagrams [37–41] have been determined mainly by differential scanning calorimetry (Mettler Toledo) but additional methods: X-ray diffraction and conductivity measurements were used as well. Samples for DSC were inserted into small silica ampoules and sealed under vacuum. Samples for studying the system CuBr–LiBr were prepared in a glove box.

Extended solid solutions based on copper(I) halide as well as on alkali-metal halide have been found in the systems involving lithium salts: CuCl–LiCl and CuBr–LiBr. They do not exceed 5 mol% in the CuCl–NaCl system and 4 mol% in the CuCl–KCl system.

As far as the stoichiometry of compounds is concerned, it appears from Fig. 1 that the general formula $AlkCu_2X_3$ is the most frequent. Such compounds have been found in all systems built of rubidium and cesium halides as well as in the CuCl–LiCl system.

Compounds of the formula $CsCu_2X_3$ melt congruently and their melting points increases in the order Cl→Br→I. Among rubidium compounds of the formula $RbCu_2X_3$ only $RbCu_2Br_3$ melts congruently. $RbCu_2I_3$ melts incongruently, $RbCu_2Cl_3$ decomposes in the solid state on heating [4]. The latter is not stable at room temperature either [4, 7]. However, a compound with formula $Rb_9Cu_{16}Cl_{25}$, melting congruently and having composition very close to $RbCu_2Cl_3$, has been found [4] in this system.

Comparing the relative heights of local maxima corresponding to the compounds of the formula $AlkCu_2X_3$ (Fig. 1) one can observe that they are the highest for the bromide compounds. On the other hand, comparing phase diagrams for the systems CuBr–RbBr and CuBr–CsBr (Fig. 2) one can see that the height of local maximum on the liquidus curve at x_{CuBr}=0.667 is lower in the CuBr–RbBr system. In view of that, the compound $RbCu_2Br_3$ may be considered as less stable than $CsCu_2Br_3$.
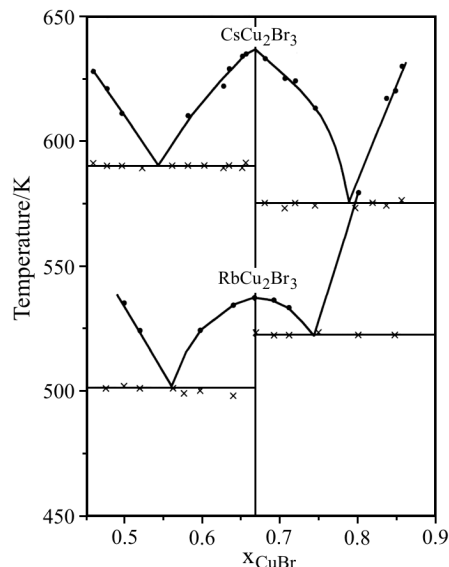
Fig. 2 Melting point and areas of crystallization for $RbCu_2Br_3$ and $CsCu_2Br_3$ [39, 40]

The range of composition between 25 and 40 mol% CuX is a second area where chemical compounds are formed. The most strongly represented are compounds of the formula Alk_2CuX_3: K_2CuCl_3, K_2CuBr_3, Rb_2CuCl_3, Rb_2CuI_3 and Cs_2CuBr_3. They are absent in the systems CuCl–CsCl, CuBr–RbBr, CuI–KI and CuI–CsI. Instead, the following compounds appear: Rb_3CuBr_4, $Cs_3Cu_2Cl_5$ and $Cs_3Cu_2I_5$. With the exception

of $Cs_3Cu_2Cl_5$, all compounds in this group melt incongruently. Their peritectic temperatures increase in the order $Cl{\rightarrow}Br{\rightarrow}I$, as the anions become more polarisable and probably the bonding becomes less ionic.

Two 1:1 compounds have been found: $LiCuBr_2$, stable only in a higher temperature [37] and $RbCuCl_2$, melting incongruently [4].

Factors affecting phase equilibria in the systems CuX–AlkX

It seems that sizes and valences of ions [46–49] may be considered as main factors affecting phase equilibria in these systems in view of Coulombic and polarization interactions [50]. Other factors which may be taken in consideration in ionic systems are for instance: ionization energy or electronegativity [51].

Ionic radius

A transition from eutectic behavior to an increasing tendency for compound formation was observed in series $Na{\rightarrow}K{\rightarrow}Rb{\rightarrow}Cs$, i.e. with increasing alkali-metal ionic radius (except lithium). A number of compounds in the system are rising as well as the number of compounds melting congruently.

Also, an increasing tendency for compound formation was noted in passing from I to Cl in the systems with the same pair of cations. This last could be indicated by the following observations:

- an intermediate compound forming in the CuI–KI system is not stable at room temperature, whereas intermediate compounds forming in the systems CuCl–KCl and CuBr–KBr are stable at room temperature
- no intermediate compound melts congruently in the CuI–RbI system, whereas we find such compound in the CuCl–RbCl system as well as in the CuBr–RbBr system
- two congruently melting compounds are in the CuCl–CsCl system, whereas only one congruently melting compound is in the CuBr–CsBr system and in the CuI–CsI system as well

It should be noted that formation of many compounds in the CuCl–RbCl system stands out against these trends. The system was widely studied, because some phases exhibit high values of ionic conductivity at room temperature. Although the phase equilibrium diagram for the CuCl–RbCl system was reported a number of times [4, 36, 52, 53] still different suggestions appear [7], concerning formulas of intermediate compounds and temperature ranges where they are stable.

Ionic potential

The ratio of the cation valence Z_i and of the cation radius r_i:

$$\Phi_i = \frac{Z_i}{r_i}$$

called the ionic potential Φ_i of the cation i [54] was used in discussion of many series of binary salt systems with common anion [55–61]. Generally the bigger the difference of the ionic potentials for two cations, the higher the tendency for compound formation. It should be noted, however, that anions are not considered in this approach. Nevertheless, it is valid for the systems discussed here (Table 2).

Table 2 Differences of ionic potentials for cation Cu^+ and alkali-metal cation

	Li^+	Na^+	K^+	Rb^+	Cs^+
$\phi_{Cu}-\phi_{Alk}$	−0.0062	−0.0001	0.0029	0.0036	0.0045

The difference of ionic potentials for Cu^+ and Na^+ is minimal and no compound was found in respective halide systems. If the difference of ionic potentials increases, intermediate compounds appear.

Coulombic interactions

To discuss the problem of compound formation in ionic binary systems, Coulombic interactions of the cation 1 and the cation 2 with the common anion were being compared, using the following ratio [62]:

$$\frac{Z_{cation\,1}Z_{anion}}{(r_{cation\,1}+r_{anion})^2} : \frac{Z_{cation\,2}Z_{anion}}{(r_{cation\,2}+r_{anion})^2}$$

which for the binary systems of cuprous halides with alkali halides simplifies to the expression presented below:

$$K = \frac{(r_{Cu}+r_{anion})^2}{(r_{Alk}+r_{anion})^2}$$

Values of ratio K, comparing Coulombic interactions between cation Alk^+ with anion and cation Cu^+ with anion are given in Table 3.

Table 3 Values of ratio K, comparing Coulombic interactions between cation Alk^+ with anion and cation Cu^+ with anion

	Li^+	Na^+	K^+	Rb^+	Cs^+
Cl^-	1.32	1.01	0.78	0.71	0.63
Br^-	1.30	1.01	0.79	0.72	0.64
I^-	1.28	1.01	0.80	0.73	0.66

It appears from the Table 3 that the tendency to compound formation increases when the value of the ratio K becomes more and more different from 1.0, that is in order: Na→K→Rb→Cs and Na→Li. The value of the ratio K changes negligibly when the anion is changed.

Polarization interactions

A more sensitive indicator for the compound formation in such systems is the factor δ, defined as follows [63]:

$$\delta = \frac{Z_{Alk}}{(r_{Alk}+r_{anion})^2} : \frac{Z_{Cu}}{(r_{Cu}+r_{anion})^2}$$

Approximately, it may be considered as a measure of a difference of the polarization power of two cations, interacting with a common anion [64]. When the absolute value of δ increases, the tendency to compound formation increases too [65–68]. In this case the influence of the anion on compound formation is much more clear (Table 4).

Table 4 Values of factor δ, comparing the difference of polarization interactions of cation Cu^+ and cation Alk^+ with the common anion

	Li^+	Na^+	K^+	Rb^+	Cs^+
Cl^-	4.18	0.09	−2.89	−3.79	−4.87
Br^-	3.57	0.08	−2.51	−3.31	−4.26
I^-	2.85	0.07	−2.06	−2.72	−3.53

It should be noted that generally, the systems involving lithium salts do not satisfy above tendencies exactly. Actually, the tendency to compound formation in lithium systems is not so strong. In contrast, a tendency to form solid solutions with cuprous salts is obvious. This may arise from the fact, that the effective ionic radius of Cu is closer to that of Li and the polarizing power of the two cations is closer to each other as well.

Conclusions

An increasing tendency for compound formation is observed in series Na→K→Rb→Cs, i.e. with increasing alkali-metal ionic radius (except lithium).

In the systems involving lithium halide extended solid solutions appear, probably because of the fact that the effective ionic radius of Cu^+ is closer to that of Li^+. This may cause similar polarization interactions of both cations with the common anion and decrease tendency to compound formation.

Seven halogenocuprates(I) of the type $AlkCu_2X_3$ have been reported. Bromocuprates(I) $RbCu_2Br_3$ and $CsCu_2Br_3$ may be considered as more stable than re-

spective chloro- and iodocuprates(I) of the same type. Among compounds more rich in alkali-metal halide the most common are those having the formula Alk_2CuX_3.

Melting points or peritectic temperatures of halogenocuprates(I) of the same type increase in the order Cl→Br→I i.e. with the increasing size and polarizability of the anion.

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