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CONTRIBUTION TO THE PHASE DIAGRAM OF THE SYSTEM $PbCl_2$–AgCl

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The side parts of the phase diagram of the binary system $PbCl_2$–AgCl were studied by using DTA. The only miscibility was found on the silver chloride side up to a concentration of 1.5 ± 0.5 mole% $PbCl_2$. No solid solution of AgCl in $PbCl_2$ was observed on the lead chloride side.

The phase diagram of the binary system PbCl–AgCl has been studied several times in the past [1–3]. A eutectic-type binary diagram was reported, with no compound formation. Recently, the eutectic composition and the courses of both branches of the liquidus curve were determined with more precision [5]. It is also known, that by means of the directed crystallization of the eutectic melt, a normal eutectic of lamellar type comes into being [6]. Up to the present time no attention has been paid to the subsolidus part of this diagram and to the regions of solid solutions, that is to the side parts. From a comparison with other systems of AgCl–$M^{II}Cl_2$, such as AgCl–$CdCl_2$ [7, 8] the existence of solid solutions may be expected on the AgCl side of the diagram.

The aim of the present paper is to complete the diagram of the binary system $PbCl_2$–AgCl on the side parts with a low concentration of one of the components. A better insight into the system results in a better understanding of the crystallization process and of the properties of directly solidified eutectic.

Experimental

Single-crystals of both chlorides of high purity without any cation or anion impurity (7N grade) served as starting materials. The single-crystals were grown by the Bridgeman method in the Institute of Physics of the Czechoslovak Academy of

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Sciences in Prague. The raw materials (analytical grade crystal powders) were zonerefined by 30-fold passage through the zone.

DTA measurements were performed in silica crucibles in a static helium atmosphere (He of extra high purity) in a specially developed apparatus constructed in the Institute of Crystallography of the Academy of Sciences of the USSR in Moscow [9]. A W5%Re–W20%Re thermocouple was used. The sample weight ranged from 0.5 to 2.2 g, the heating rate was 15–35 deg/min. ICTA standard materials were used for the thermocouple calibration [14]. A dosing equipment was constructed so that the weighed second component could be added to the crucible without having to open the whole apparatus.

Results and discussion

The results of the DTA measurements on the side parts are shown in Fig. 1. The melting points of the two components (496° and 455° for $PbCl_2$ and AgCl, respectively) and the melting point of the eutectic correspond to those in the literature [1–4]. No $\alpha \rightleftarrows \beta$ phase transition was found in the lead chloride, in accordance with our previous results [5]. The measurements showed that the AgCl melt did not indicate any supercooling whereas the $PbCl_2$ melt, did display supercooling the extent of this increasing with increasing cooling rate; it reached $\Delta T = 10$ deg at a cooling rate of 15 deg/min, and $\Delta T = 70$ deg at a cooling rate of

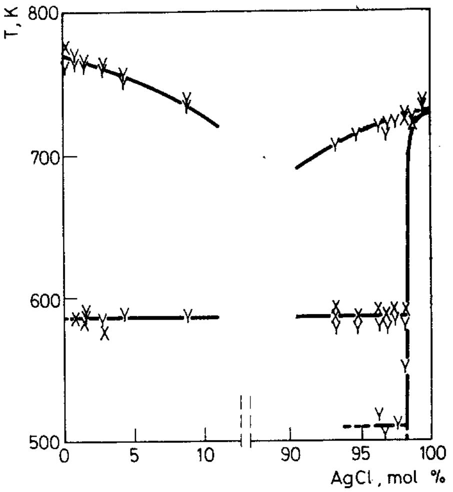

Fig. 1 Liquidus and solidus curves in the side parts of the phase diagram in the system $PbCl_2$–AgCl: (X) – experimental points from the DTA heating curves, (Y) – experimental points from the DTA cooling curves

100 deg/min. When small amounts of silver chloride were added, the eutectic effect on the side of the lead chloride appeared at a concentration of 0.8 mole% AgCl. This is evidence of the fact that the solid solution based on $PbCl_2$ (if it comes into existence at all) is limited to very small concentrations of AgCl, and the region of the miscibility of small amounts of silver chloride in lead chloride is very narrow and can be neglected from a practical point of view.

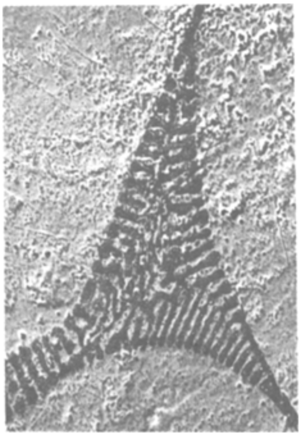

Fig. 2 Scanning electron micrograph of $PbCl_2+8$ mole% AgCl, magnification 600 ×. White: lead chloride; black: silver chloride. The lamellar growth of eutectic can be seen

Figure 2 shows a scanning electron micrograph of lead chloride containing 8 mole% AgCl, at a magnification of 600 ×. The eutectic structure (black and white lamellar strips) fills the space between three blocks of lead chloride (white). Examinations of sets of samples revealed only the eutectic and the excessive component.

On the side of silver chloride, the eutectic effect did not appear after the addition of 0.6 and 1.3 mole% $PbCl_2$. It was found at the composition containing 1.8 mole% $PbCl_2$. It is evident that on the silver chloride side the region of solid solutions exists up to a concentration of 1.5 ± 0.5 mole% $PbCl_2$. The liquidus curve declines after the addition of this amount of lead chloride.

In the concentration range 1.9–3.8 mole% $PbCl_2$, one more effect was found at 230–240°, the origin of which has not yet been clarified.

In Fig. 3, the liquidus and solidus curves of the whole system $PbCl_2$–AgCl are presented. Points marked (●) are calculated values from [5], and (X) and (Y) are experimental data. The eutectic was analysed and was found to contain 40.68 mole% $PbCl_2$. Evaluation of the peak areas from the DTA measurements of the samples with concentrations near the eutectic one [13] gave a eutectic concentration of 40.47 mole% $PbCl_2$.

The existence of the solid solution based on silver chloride does not seem to very surprising, as heterovalent solid solutions of AgCl with chlorides of other divalent metals are already known. The best examined system is AgCl–$CdCl_2$, where the region of solid solution reaches a concentration of 20 mole% [7] or 30 mole% $CdCl_2$ [8]. The density measurements indicated that the solution of $CdCl_2$ in AgCl comes into existence with the simultaneous appearance of vacancies in the cation sublattice. The same mechanism can be expected in the system AgCl–$PbCl_2$. Since the ionic radius of Pb^{2+} (1.20 Å) is larger than that of Cd^{2+} (0.97 Å) [12], the solid solution region must be considerably smaller in the system $PbCl_2$–AgCl. From the liquidus curves in the part near the AgCl side, the distribution coefficient of $PbCl_2$ can be determined. Our value of 0.4 ± 0.1 is in good agreement with that found for Pb^{2+} in AgCl earlier [11].

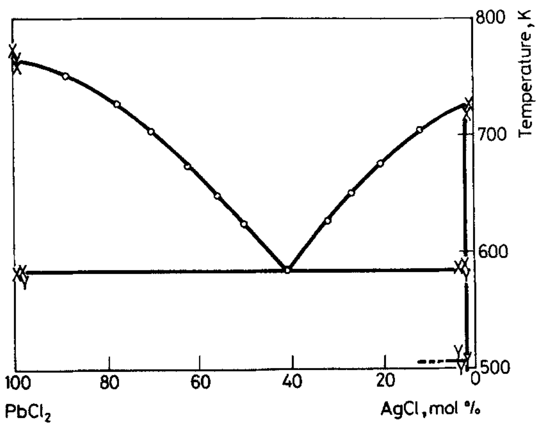

Fig. 3 The phase diagram of the system $PbCl_2$–AgCl: (●) – calculated values from [5], (*X*) – experimental values from the DTA heating curves, (*Y*) – experimental values from the DTA cooling curves

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Zusammenfassung — Mittels DTA wurden die Randzonen des Phasendiagrammes des binären Systemes $PbCl_2$–AgCl untersucht. Mischbarkeit konnte lediglich auf der Silberchloridseite bis zu einer Konzentration von 1.5±0.5 mol% mol% $PbCl_2$ festgestellt werden. Auf der Bleichloridseite konnten keinerlei Mischkristalle zwischen AgCl und $PbCl_2$ beobachtet werden.

Резюме — Методом ДТА изучены боковые части фазовой диаграммы двойной системы $PbCl_2$–AgCl. Только на стороне хлорида серебра была найдена совместимость с хлоридом свинца до концентрации 1,5±0,5 мольных %. На стороне хлорида свинца не наблюдалось образования твердого раствора хлорида серебра в хлориде свинца.