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PHASE EQUILIBRIA IN THE BINARY SYSTEM LEAD FLUORIDE [PbF_2]–CADMIUM FLUORIDE [CdF_2]

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Abstract

Phase dependences in the binary system lead fluoride [PbF_2]–cadmium fluoride [CdF_2] were examined and the phase diagram of this system was established. The occurrence of solid continuous solutions with a minimum melting point of 750°C and a CdF_2 content of 35 mol% was confirmed. Thermal, dilatometric, microscopic and X-ray analytical methods were used during the investigations.

Keywords: binary system PbF_2–CdF_2, dilatometry, phase diagram, phase equilibria, polymorphic transitions, thermal analysis, X-ray

Introduction

The purpose of the present paper was to determine the phase diagram of the binary system PbF_2–CdF_2 and to examine the polymorphic transitions in this system. The system PbF_2–CdF_2 has been investigated by several authors. Its phase diagram was published in [1, 2].

The authors of paper [1] examined the system PbF_2–CdF_2 at higher temperatures (above 600°C) and found that the components from continuous solid solutions with a minimum melting point of 745°C and a CdF_2 content of 30 mol%. Polymorphic transitions of the components were not taken into consideration.

As earlier papers reported, lead fluoride PbF_2 occurs in two polymorphic modifications [3]. Below 340°C there is an orthorhombic modification with a contunnite structure, and above this temperature a cubic modification with a fluorite structure. According to [4], the lattice constants are a=3.891 Å b=6.427 Å and c=7.627 Å for the orthorhombic modification and a=5.927 Å for the cubic one.

O'Horo and White [2] found that, at above 500°C, the components form solid solutions with a minimum melting point of 720°C and a CdF_2 content of

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40 mol%. They took into consideration the occurrence of PbF_2 in two crystallographic modifications: low-temperature orthorhombic, α, and high-temperature cubic, β. The α→β transition proceeds without hindrance as the temperature increases, the β→α transition proceeds with difficulty during normal cooling, and β phase is very stable at room temperature. It was observed that the polymorphic transition occurring in pure PbF_2 at 375°C in the system PbF_2–CdF_2 reduces under the influence of CdF_2 to approximately 30 mol% of CdF_2 and then stabilizes to CdF_2 at 330°C.

Paper [5] reports investigations on the obtaining and the structure of mixed solutions $Cd_{1-x}Pb_xF_2$. It was discovered that the transition of the orthorhombic modification into the cubic one in PbF_2 proceeds at 337°C. At room temperature, a mixture of both modifications of PbF_2 occurs, which made the obtaining of pure, cubic, mixed crystals of cadmium–lead fluorides difficult. These could be obtained only by refrigerating the regular phase.

Raman's investigations of mixed cadmium and lead fluorides [6] also revealed irregularities.

The authors of paper [7] examined the electrical properties of solid solutions in the system PbF_2–CdF_2 and observed anomalies at a CdF_2 content of 35–40 mol%. These were attributed to the minimum melting point of the solid solutions in the phase diagram.

Thermal, dilatometric, microscopic and X-ray examinations of PbF_2 [8] showed that this compound melts congruently at 824°C and occurs in five polymorphic modifications: α, β, γ, δ and ε. The transitions proceed at 720, 560, 460 and 340°C, respectively. The transition at 340°C (represented by δ→ε here) is a first-order transition and proceeds with change from a regular structure into an orthorhombic one, while the other transitions are second-order ones, with no change in structure.

CdF_2, which melts congruently at 1076°C, has a cubic fluorite structure with a lattice constant according to [9] of a=5.39 Å. It was discovered in [10] that CdF_2 has five polymorphic modifications, at 990, 860, 730 and 550°C. All of them are second-order transitions.

Paper [11] reports that, under high pressure, CdF_2 exhibits a high-pressure orthorhombic modification, isomorphous with an orthorhombic modification of PbF_2.

In the light of those data, reinvestigation of the phase dependences in the system PbF_2–CdF_2 seemed necessary.

Experimental

PbF_2 and CdF_2 obtained in this laboratory were used during the examinations. These compounds were synthesized by treating the appropriate carbonates ($PbCO_3$ p.a. and $CdCO_3$ p.a.) with 40% hydrofluoric acid (H_2F_2 p.a.), followed by triple evaporation in a water bath. After each evaporation the samples were ground thoroughly in an agate mortar and sieved. The fluorides obtained in this way were dried in vacuum (oil rotary pump) at approx. 200°C for 1 h.

The phase purity of the compounds was checked microscopically in reflected light with samples melted in platinum crucibles in an argon atmosphere. The molten samples were colourless and did not show any foreign phases on the edges of the grains. Chemical analysis for fluorine, performed with a fluorine-selective electrode and distillation, that the initial compounds obtained were stoichiometric.

Thermal and dilatometric examinations were performed in an argon atmosphere because the fluorides decompose in air at higher temperatures, and oxides, especially CdO, can be formed.

Thermal analysis (differential method) during cooling was performed in a belt-type resistance furnace with a platinum winding. 5–10 g samples were placed in platinum crucibles. The temperature was measured with Pt–PtRh10 thermocouple calibrated for the melting points of K_2SO_4 (1070°C) and NaCl (801°C) and for the polymorphic transition of K_2SO_4 (583°C). Dilatometric analysis during the heating of 10–20 g samples was carried out in a MOM Hungarian derivatograph (type 3427). X-ray examinations were performed by the powder method in a Guinier camera, using copper radiation. During microscopic investigations of molten samples, microsections were observed microscopically in reflected light.

In order to examine solid solutions in the system PbF_2–CdF_2 molten samples with CdF_2 contents of 20, 50 and 80 mol% were placed in platinum tubes and

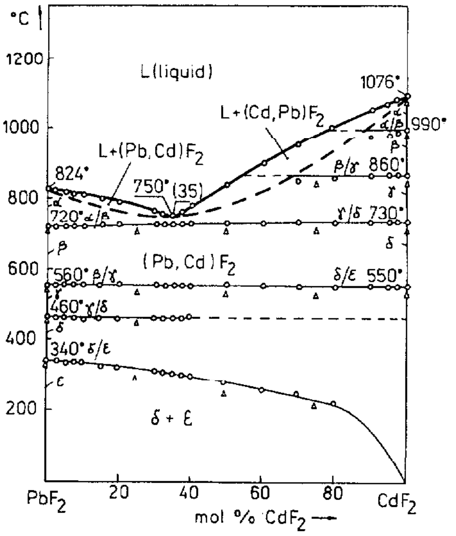

Fig. 1 Phase diagram of binary system PbF_2–CdF_2: o – thermal analysis (cooling), ▵ – dilatometric analysis (heating)

sealed in quartz ampoules under reduced argon pressure. They were then sintered at 650, 450 and 250°C for 200 h each and refrigerated, after which X-ray photographs were taken and microscopic observations were made.

Results and discussion

The system PbF_2–CdF_2 was examined by thermal, dilatometric, microscopic and X-ray analysis. It was confirmed that the components form solid continuous solutions with a minimum melting point of 750°C and CdF_2 content of 35 mol%. The temperature and composition at the minimum are a little different from those reported in [1, 2]. Figure 1 presents the phase diagram of this system completed with the polymorphic transitions.

The transitions of PbF_2 proceeding at 720 and 500°C run across the whole system to CdF_2, confirming the occurrence of solid solutions and analogous polymorphic transitions in CdF_2 at 730 and 550°C. The transitions of CdF_2 at 860 and 990°C run above the melting point of PbF_2. Thermal effects resulting from the polymorphic transition of PbF_2 at 460°C were observed to 40 mol% CdF_2. The transition of PbF_2 at 340°C was observed thermally up to 80 mol% CdF_2. The X-ray investigations revealed that, in spite of the long sintering of samples at 250°C; both modifications of PbF_2 (orthorhombic and cubic) were observed over the whole composition range. A cubic modification of mixed cadmium–lead fluorides could be obtained by the refrigeration of samples from temperatures higher than 340°C.

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