

PHASE EQUILIBRIA IN THE BINARY SYSTEM LEAD FLUORIDE [PbF₂]-CALCIUM FLUORIDE [CaF₂]

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Abstract

The phase diagram of the binary system lead fluoride [PbF₂]-calcium fluoride [CaF₂] was determined over the whole composition range. The investigations were carried out by means of thermal microscopic, X-ray and dilatometric analyses. It was concluded that the components did not form chemical compounds.

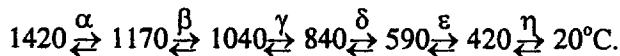
Keywords: phase equilibria, system lead fluoride-calcium fluoride

Introduction

The purpose of the present paper is to determine the phase diagram of the binary system lead fluoride [PbF₂]-calcium fluoride [CaF₂], which is a side system in the reversible system Ca₃(PO₄)₂-Pb₃(PO₄)₂-PbF₂-CaF₂. No examinations of the side system have been performed previously, but polymorphic transitions of the initial compounds have been known [1, 2].

It has been reported [1] that lead fluoride PbF₂, which melts congruently at 824°C, occurs in five polymorphic modifications: α, β, γ, δ and ε. The temperatures of the transitions are: 720, 560, 460 and 340°C. The transition proceeding at 340°C is a first-order transition because it proceeds together with a change in structure [3]. Below 340°C lead fluoride has a contunnite structure (orthorhombic modification), and above this temperature shows a fluorite structure (cubic modification). The lattice constants of both modifications reported in [4] are: a=3.891 Å, b=6.427 Å, c=7.627 Å – for the orthorhombic modification and a=5.927 Å – for the cubic modification. The other polymorphic transitions of PbF₂ are of a second-order character.

Calcium fluoride CaF₂ melts congruently at 1420°C [5] and has six polymorphic modifications [2]:



All transitions are second-order ones [2]. According to [6] the lattice constant of calcium fluoride is 5.464 Å.

Experimental

Lead fluoride PbF_2 and calcium fluoride CaF_2 obtained in this laboratory were used during the investigations. Lead fluoride PbF_2 was prepared by treating lead carbonate PbCO_3 (p.a.) with 40% hydrofluoric acid HF (p.a.). The reaction mixture was then evaporated to dryness three times in a water bath. After each evaporation the samples were ground thoroughly in an agate mortar and sieved. Lead fluoride obtained in this way was dried in vacuum (oil rotary pump) at about 200°C for 1 h.

Calcium fluoride CaF_2 was obtained in the same way from calcium carbonate CaCO_3 (p.a.) and 40% hydrofluoric acid HF (p.a.).

The phase purity of the fluorides 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. The results of chemical analysis for fluorine performed by using a fluoride ion-selective electrode following distillation showed that the fluorine content in the initial compounds was as expected.

Samples with varying proportions of the components were obtained by thorough mixing and grinding of the initial components in an agate mortar. Thermal analysis (differential method) during cooling was performed in a bell-type resistance furnace with platinum winding in an argon atmosphere, 5–10 g samples were placed in platinum crucibles, then melted or sintered at suitable temperatures. The temperature was measured with Pt-PtRh 10 thermocouple calibrated for the melting points of K_2SO_4 (1070°C) and of NaCl (801°C), and for the polymorphic transition of K_2SO_4 (583°C). Thermal analysis during heating of 0.2–0.3 g samples and dilatometric analysis during heating of 10–20 g samples were performed with a derivatograph (MOM, type 3427, Hungary) over the temperature range 20–1000°C in an argon atmosphere. X-ray examinations were carried out by the powder method in a Guinier's camera, using copper radiation. Microsections were made from molten samples and then they were observed by microscopy in reflected light.

Over 1200°C lead fluoride evaporates violently, causing the destruction of crucibles and thermocouples. Therefore the samples in the system under investigation were melted only up to 50 mol% of CaF_2 and those richer in calcium fluoride were sintered over the temperature range 900–1200°C for 0.5–1 h.

Results and discussion

The PbF_2 – CaF_2 system was investigated by means of thermal, dilatometric microscopic and X-ray analyses. Its phase diagram was determined and presented in Fig. 1.

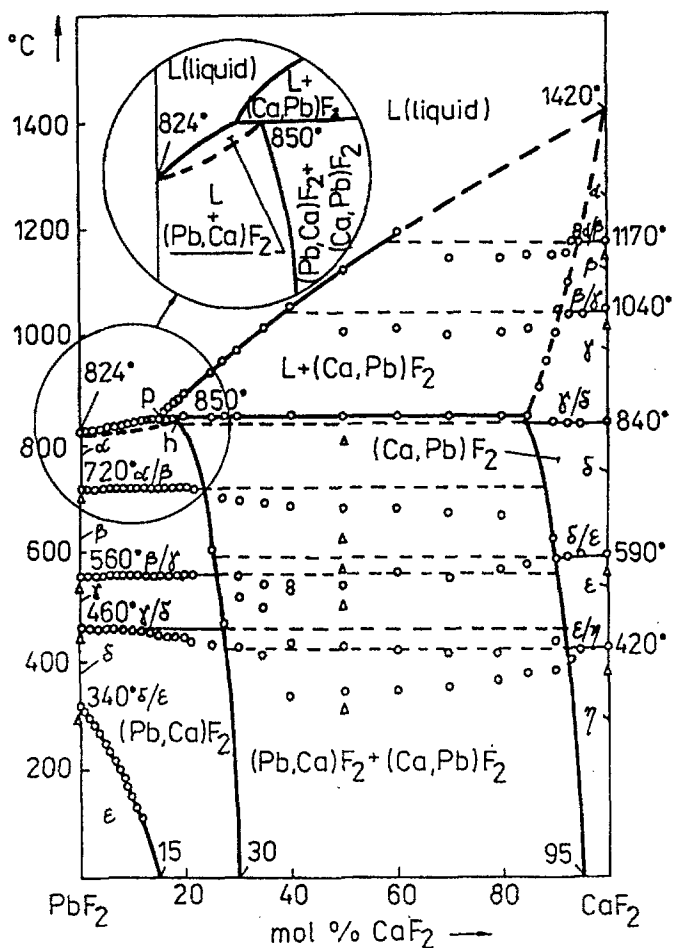
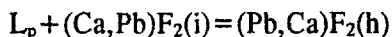


Fig. 1 Phase diagram of the binary system $\text{PbF}_2\text{-CaF}_2$: o-thermal analysis (cooling), Δ -dilatometric analysis (heating)

The components form a peritectic system with infinitely diluted solid solutions. At 850°C a peritectic reaction proceeds according to the equation:



The liquid with composition 'p' (approx. 15 mol% of CaF_2) reacts with solid solutions $(\text{Ca,Pb})\text{F}_2$ having composition 'i' (approx. 85 mol% of CaF_2) thus forming the solid solution $(\text{Pb,Ca})\text{F}_2$ with composition 'h' (20 mol% of CaF_2). Below the peritectic temperature there is a two-phase area, $(\text{Pb,Ca})\text{F}_2 + (\text{Ca,Pb})\text{F}_2$. At room temperature this area occurs over the composition range 20–95 mol% of CaF_2 . Under the influence of calcium fluoride, the temperature

of the α to β transition in PbF_2 is reduced and at room temperature it occurs over the composition range up to approx. 20 mol% of CaF_2 .

References

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