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POLYMORPHIC TRANSITIONS IN THE BINARY SYSTEM LEAD FLUORAPATITE [$Pb_{10}(PO_4)_6F_2$] – CALCIUM FLUORAPATITE [$Ca_{10}(PO_4)_6F_2$]

H. Podsiadlo

DEPARTMENT OF INORGANIC CHEMISTRY, ACADEMY OF ECONOMICS, 53345
WROCLAW, KOMANDORSKA 118/120, POLAND

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The phase diagram of the binary system lead fluorapatite [$Pb_{10}(PO_4)_6F_2$] – calcium fluorapatite [$Ca_{10}(PO_4)_6F_2$] was determined over the whole composition and temperature range. Special attention was paid to the polymorphic transitions of the initial compounds and their behaviour in the investigated system. The two apatites form continuous solid solutions. Examinations were performed by means of thermal, microscopic, X-ray and dilatometric analyses.

The aim of the present paper was to establish the full phase diagram of the binary system lead fluorapatite [$Pb_{10}(PO_4)_6F_2$] – calcium fluorapatite [$Ca_{10}(PO_4)_6F_2$]. The system was preexamined in [1] and it was discovered that the components form continuous solid solutions. Two previously unknown polymorphic transitions were then observed at 590° and 780° in lead fluorapatite. A polymorphic transition at 800° was earlier known in pure calcium fluorapatite, but the addition of different salts yielded a second (considerably weaker) polymorphic transition at 300°.

As a result of subsequent research on the chemistry of apatites, it was found that lead fluorapatite occurs in five polymorphic forms [2], with transitions at temperatures of 970, 720, 620 and 450°. On the other hand, the addition of small amounts (to 0.5 wt%) of Al_2O_3 to calcium fluorapatite yielded two polymorphic transitions: the previously known one (at 800°) and a new one (at 1060°) [3].

The significant difference in the ionic radii of calcium and lead ($r_{Ca^{2+}}$ = 1.00 Å and $r_{Pb^{2+}}$ = 1.19 Å) [4] suggested the possible occurrence of an im-

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miscibility gap in the solid phase of the system $Pb_{10}(PO_4)_6F_2$ - $Ca_{10}(PO_4)_6F_2$. Accordingly this system has been reexamined.

Experimental

The following reagents were used: PbO p.a., $PbCO_3$ p.a., $NH_4H_2PO_4$ p.a., $CaCO_3$ p.a., $CaHPO_4$ p.a. and H_2F_2 (40%) p.a.

$Ca_2P_2O_7$, $Ca_3(PO_4)_2$, CaF_2, $Ca_{10}(PO_4)_6F_2$, $Pb_3(PO_4)_2$, PbF_2 and $Pb_{10}(PO_4)_6F_2$ were synthesized in this laboratory.

Lead fluorapatite, $Pb_{10}(PO_4)_6F_2$, was prepared from stoichiometric quantities of lead orthophosphate, $Pb_3(PO_4)_2$, and lead fluoride, PbF_2, by sintering under argon at 850° for 0.5 h as described in [2]. The syntheses of lead orthophosphate, $Pb_3(PO_4)_2$, from lead monoxide, PbO p.a., and acid ammonium phosphate, $NH_4H_2PO_4$ p.a., were carried out by sintering stoichiometric quantities of the components in the air at 250, 500 and 700° for 2 h as described in [2]. Lead fluoride, PbF_2, was prepared from lead carbonate, $PbCO_3$ p.a., and 40% hydrofluoric acid, H_2F_2 p.a., as described in [5].

Calcium orthophosphate, $Ca_3(PO_4)_2$, obtained from stoichiometric quantities of calcium pyrophosphate, $Ca_2P_2O_7$, and calcium carbonate, $CaCO_3$ p.a., by sintering this mixture at 1300° for 1 h, and calcium fluorapatite, $Ca_{10}(PO_4)_6F_2$. Calciumpurophosphate, $Ca_2P_2O_7$, used to synthesize calcium orthophosphate, was produced by sintering calcium fluoride CaF_2, prepared from calcium carbonate, $CaCO_3$ p.a., and 40% hydrofluoric acid, H_2F_2 p.a., as described in [6], were used to synthesize calcium hydrophosphate, $CaHPO_4$ p.a., in air at 900° for 1 h. Calcium fluorapatite was synthesized by sintering stoichiometric quantities of calcium orthophosphate and calcium fluoride under argon at 1100° for 1 h.

The investigations were carried out by means of thermal, microscopic, X-ray and dilatometric analyses, as described in [7]. The examined samples were prepared either from lead and calcium apatites or from lead and calcium orthophosphates and lead and calcium fluorides, all produced in this laboratory.

Thermal analysis (differential method) during heating was performed in a platinum winding furnace, under argon. Samples of 5-10 g were placed in platinum crucibles and then melted or sintered at appropriate temperatures in the furnace. The temperature was measured with a platinum thermocouple calibrated against the solidification points of potassium sulphate,

K_2SO_4 (1070°), and sodium chloride, NaCl (801°), and the polymorphic transition of K_2SO_4 (583°). The temperatures were read by means of an electronic recorder (MOM, Hungary). Thermal analysis during the heating of samples of 0.2 to 0.3 g was carried out with a derivatograph (MOM, Hungary), under argon. The microscopic analysis of all molten samples was performed with a metallographic microscope in reflected light. Powder X-ray analysis was carried out in a Guinier's camera, with an HZG-4 X-ray diffractometer and CuK_α radiation.

Dilatometric analysis during heating was performed with a derivatograph (MOM, Hungray). Samples of 15–20 g were carefully ground, pressed with the addition of ethanol into a cylindrical form, and then dried in vacuum at 200° for 1 h. The derivatograph was calibrated against the polymorphic transition of K_2SO_4 (583°). The conditions of the measurement were as follows: sensitivity TD – 1000 mg, heating rate – 10 deg/min. Reference material: Al_2O_3.

Lead fluorapatite melts congruently at 1098°, while the melting point of calcium fluorapatite, which also melts congruently, is 1710°. The significant difference between the melting points of the two compounds and the evaporation of lead fluorapatite at temperatures above 1400° make it impossible for all samples in the examined composition interval to melt. This is the reason why samples with a calcium fluorapatite content of over 40 wt% were only sintered over the temperature range from 1071° to 1150° for 0.5-1h The time and temperature of sintering depended on the composition of the sample; samples richer in calcium fluorapatite, prepared from the previously obtained apatites, were sintered at higher temperatures for the longest time; on the other hand, a shorter time and a lower temperature were used to sinter the samples poorer in calcium fluorapatite and prepared from the phosphates and fluorides of lead and calcium.

The phase purity of mixed calcium – lead fluorapatites for molten samples (to 40 wt%) of calcium fluorapatites was checked microscopically. The chemical analysis for fluorine, performed with a selective fluoride electrode and by distillation, for both molten and sintered samples, showed that the mixed calcium - lead fluorapatites were stoichiometric.

Samples containing 30, 50 and 70 wt% of calcium fluorapatite were placed in platinum tubes and sealed in quartz ampoules under reduced argon pressure to discover if there was an immiscibility gap in the examined system. The samples were then sintered at 800°, 600° and 400° for 120 h each, and investigated by the X-ray method.

Results and discussion

The phase diagram found for the binary system lead fluorapatite - calcium fluorapatite in this work is presented in Fig. 1. The behaviour of the polymorphic transitions of the initial components was checked on the basis of phase investigations.

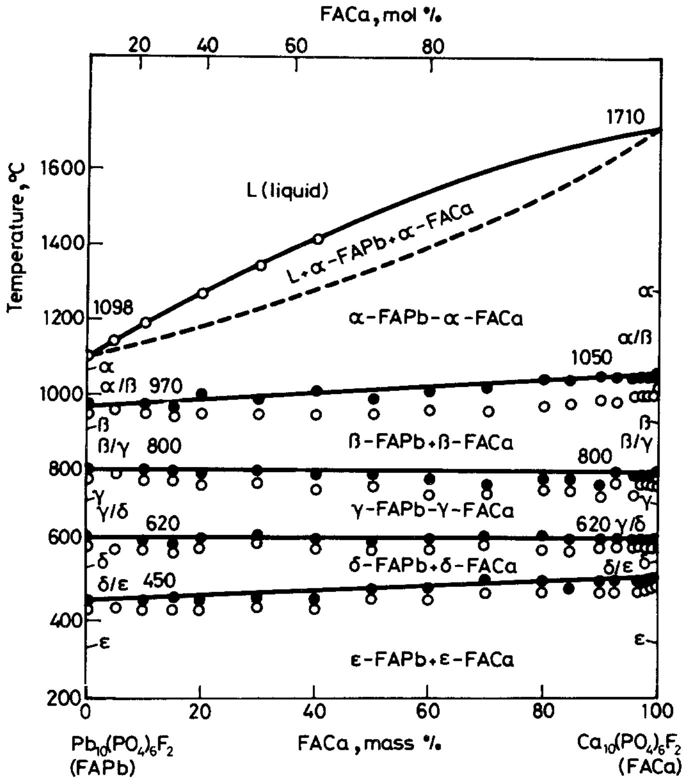

Fig. 1 Phase diagram of binary system $Pb_{10}(PO_4)_6F_2$ – $Ca_{10}(PO_4)_6F_2$ o – thermal analysis (cooling) ● – dilatometric analysis (heating)

The components do not yield new components, but only continuous solid solutions.

The melting point of the mixed apatites rises at a uniform rate as calcium apatite is added; it was observed thermally up to 40 wt% of calcium fluorapatite.

The lattice constants determined for the two apatites by Kreidler and Hummel [8] were confirmed in these investigations. For lead fluorapatite: a = 9.75 Å, c = 7.30 Å, c/a = 0.749, and for calcium fluorapatite: a = 9.38 Å, c = 6.89 Å, c/a = 0.734.

The change in the lattice constants in the examined system was calculated and is presented in Fig. 2. It was discovered that it has a continuous character, which confirms the occurrence of continuous solid solutions.

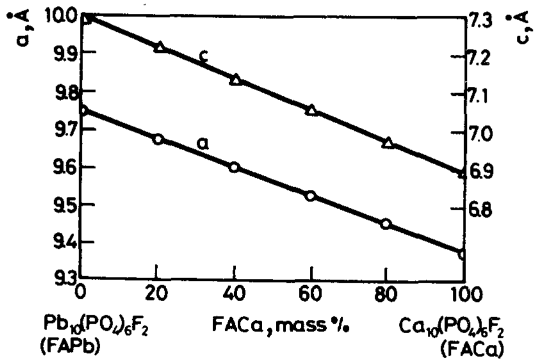

Fig. 2 Changes in lattice parameters in the $Pb_{10}(PO_4)_6F_2$ – $Ca_{10}(PO_4)_6F_2$ system

Lead fluorapatite appears in four polymorphic transitions at 970, 800, 620 and 450°. They were observed over the whole composition range by means of thermal and dilatometric analyses. It also confirms the complete miscibility of the two apatites and suggests the occurrence of the appropriate transitions in calcium fluorapatite.

Figure 3 shows, as an instance, the dilatogram of a sample with composition 20 mol% (39.9 wt%) of $Pb_{10}(PO_4)_6F_2$ and 80 mol% (60.1 wt%) of $Ca_{10}(PO_4)_6F_2$. The samples were produced from lead and calcium orthophosphates and fluorides by sintering under argon at 1050° for 0.5 h. The first transition is slightly visible; it starts at approx. 400° and finishes at approx. 520°, with a minimum at approx. 440°. The second transition occurs over the temperature range from 590° to 650°, with a minimum at approx. 620°; the third one over the temperature range from 750° to 820°, with a minimum at 810°; and the fourth one over the range from 950° to 1020°, with a minimum at approx. 990°. The first transition is accompanied by a slight change in volume; the others proceed with larger changes in volume. All transitions are accompanied by a volume contraction during heating. The dilatometric TD curve exhibits four deflections and confirms the occurrence of four transitions proceeding with volume contraction during heating. The first deflection is weak; the others are much stronger. The differential DTA curve shows four weak endothermic effects, which confirms the occurrence of four transitions. The total contraction of the sample was approx. 1.4%. The dilatograms for other samples from the examined system were similar.

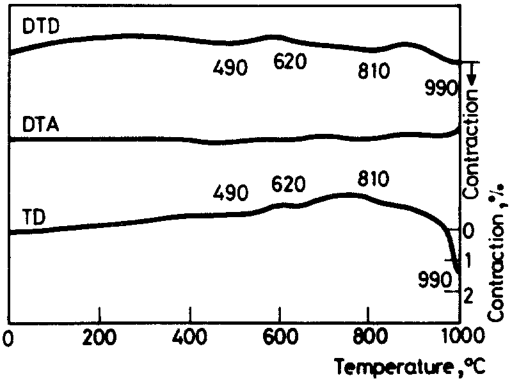

Fig. 3 Dilatogram of sintering lead – calcium fluorapatite $Ca_8Pb_2(PO_4)_6F_2$

The results of dilatometry were confirmed by thermal analysis involving heating and cooling. During cooling, the transitions occurred over the temperature ranges 400-500° (peak at 430°), 580-600° (590°), 700-780° (760°), and 940-1000° (980°). The temperatures of transitions (peaks in curves) covered the ranges 420-500°, 550-600°, 750-820° and 950-1020°. All thermal effects during cooling were exothermic and weak. All polymorphic transitions are reversible and are of second-phase character, without change in crystal structure.

X-ray investigations on samples sintered at lower and lower temperatures for a long time showed that there is full miscibility in the system under investigation.

Microscopic observations on molten samples confirmed the presence of solid solutions in the system. The crystals displayed many crackings, which proves that mixed apatites exhibit polymorphic transitions accompanied by a change in volume during cooling.

Conclusions

The dilatometric and thermal investigations showed that mixed calcium-lead fluorapatites, similarly to the initial apatites, occur in five polymorphic modifications: α, β, γ, δ and ε.

The occurrence of lead fluorapatite in five polymorphic modifications was confirmed. It was discovered that this compound accelerates polymorphic transitions of calcium fluorapatite. The occurrence of polymorphic transitions at 800° and 1060° in calcium fluorapatite, earlier reported in [3], was confirmed. Two new transitions in this compound, at 520° and 620°, were discovered. It was found that the polymorphic transition of calcium fluorapatite at 300°, described in [1], was caused by a wrong synthesis of this compound and misinterpretation of the dilatograms.

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Zusammenfassug — Im gesamten Konzentrations- und Temperaturbereich wurde das Phasendiagramm des binären Systemes Bleifluorapatit $Pb_{10}(PO_4)_6F_2$ – Calciumapatit $Ca_{10}(PO_4)_6F_2$ aufgestellt. Besonderes Augenmerk wurde polymorphen Übergängen der Ausgangsverbindungen und ihrem Verhalten im untersuchten System geschenkt. Es konnte festgestellt werden, daß beide Apatite kontinuierliche Mischkristallphasen bilden. Die Untersuchungen basieren auf Thermo-, Röntgendiffraktions-, mikroskopischer und dilatometrischer Analyse.