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POLYMORPHIC TRANSITIONS IN THE BINARY SYSTEM LEAD CHLORAPATITE $Pb_{10}(PO_4)_6Cl_2$ - CALCIUM FLUORAPATITE $Ca_{10}(PO_4)_6F_2$

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Phase dependences in the binary system lead chlorapatite $Pb_{10}(PO_4)_6Cl_2$ - calcium fluorapatite $Ca_{10}(PO_4)_6F_2$ with special regard to polymorphic transitions of initial compounds have been examined. Phase diagram of this system over the full temperature and composition range has been provided and the occurrence of solid solutions discovered. The investigations have been carried out by the thermal, microscopic, X-ray and dilatometric analyses.

The aim of the present paper is to determine the influence of lead chlorapatite on polymorphic transitions of calcium fluorapatite.

Calcium fluorapatite is a compound popular in nature and because of its properties a subject of many investigations. It is a well known fact that polymorphic modifications of compounds often influence their various characteristics and the addition of even small quantities of certain substances can favour the intensity of polymorphic transitions. For that reason, the occurrence of polymorphic transitions of calcium fluorapatite has been taken into particular consideration. It seemed reasonable as systematic investigations on the polymorphic transitions of calcium fluorapatite have not been previously carried out.

It was found in this laboratory that calcium fluorapatite occurs in five polymorphic modifications: at 970, 750, 620 and 450° [1]. Four, previously unknown polymorphic transitions at 990, 810, 650 and 490° [2] were discovered in lead chlorapatite. During the investigations on the binary system lead fluorapatite - lead chlorapatite [3], favourable influence of lead chlorapatite on polymorphic transitions of fluorapatite was noticed. In

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paper [4] it was reported that the intensity of transitions in calcium fluorapatite grows under the influence of lead fluorapatite, which made the discovery of two new transitions of calcium fluorapatite at 620 and 520° possible.

It was decided to check the influence of lead chlorapatite on polymorphic transitions of calcium fluorapatite. Phase dependencies between calcium-lead fluor-chlorapatites have not been well known so far. Then, it was first necessary to carry out basic research on the phase structure of binary system of lead chlorapatite - calcium fluorapatite . The polymorphic transitions of initial compounds were studied on the basis of phase investigations.

Experimental

The following, pure for analysis reagents were used as initial materials: PbO, $PbCl_2$, $NH_4H_2PO_4$, $CaCO_3$, $CaHPO_4$, 40% H_2F_2; and produced in this laboratory: $Pb_3(PO_4)_2$, $Ca_3(PO_4)$, PbF_2, CaF_2, $Pb_{10}(PO_4)_6Cl_2$, $Ca_{10}(PO_4)_6F_2$. The reactions were performed in platinum crucibles under argon. The samples for measurements were prepared either from lead and calcium fluorapatites obtained earlier in this laboratory or from lead and calcium orthophosphates, lead chloride and calcium fluoride also produced in this laboratory.

The investigations were carried out by the thermal, microscopic, X-ray, and dilatometric analyses as described in papers [3] and [4].

Lead chlorapatite melts congruently at 1156° and above this temperature partly decomposes into orthophosphate and volatile lead chloride causing a change of chemical composition of samples. Lead salts react at higher temperatures with glass and ceramics which made the experiments much more difficult. To avoid the evaporation of lead chloride, the samples for thermal examinations were placed in platinum crucibles which were then sealed in quartz ampoules under reduced argon pressure. The crucible was provided with a cavity in its bottom which accomodated a suitable projection of the quartz ampoule to place the thermocouple. The synthesis, melting and thermal analysis during heating were performed in this way for all samples in the system under investigation.

Significant difference of melting points of the initial components (1156° for lead chlorapatite and 1710° for calcium fluorapatite) made the melting of samples over the entire system impossible. The elevation of melting point as the content of calcium fluorapatite increased, caused strong evaporation and losses of lead chloride. For that reason, in the system under investigation samples were fused only to 30 wt% of calcium fluorapatite, and others were sintered at adequate temperatures. The time and temperature of sintering depended on the composition of samples: mixtures obtained from apatites were sintered over the temperature range 1000-1150° for 0.5-1 h, and the ones obtained from lead and calcium fluorapatites; and lead chloride and calcium fluoride were sintered at 500-1160° for 0.5 h. Samples richer in calcium fluorapatite were sintered at higher temperatures for a longer time.

The thermal analysis during heating and dilatometric analysis were performed under argon by means of a derivatograph (MOM, Hungary). Previously synthesized or fused samples of 0.5-1.5 g for the thermal analysis and of 10-20 g for the dilatometric analysis were used in these examinations. To check if there is full miscibility in the solid phase, the samples of the composition 25, 50 and 75 wt% of calcium fluorapatite were placed in platinum tubes and sealed in quartz ampoules under reduced argon pressure. They were sintered then at 900, 700 and 500° each time for 100 h and X-ray photographs were taken.

Results and discussion

The phase diagram of the lead chlorapatite-calcium fluorapatite system, prepared as a results of these examinations is presented in Fig. 1. The components form continuous solid solutions. The melting point of the mixed apatites grows at an uniform rate when calcium apatite is added; and it was observed thermally to 30% wt of calcium fluorapatite.

The determined changes of lattice constants in the system confirm the occurrence of continuous solid solutions, too. They change over the ranges: constant "a" from 9.99 to 9.39 Å, constant "c" from 7.34 to 6,89 Å, which is presented in Fig. 2.

Four polymorphic transitions at 990, 810, 650 and 490° were known in lead chlorapatite. The transitions examined by thermal and dilatometric methods occur over the entire system continuously, becoming proper transitions of calcium fluorapatite. It also confirms a complete miscibility of the two apatites over the whole temperature range.

One more previously unknown polymorphic transition at 1240° was found in calcium fluorapatite as the result of these thermal and dilatometric examinations. In the part of the system richer in lead chlorapatite it goes down to 1080° which suggests the occurrence of the fifth polymorphic transition at this temperature in lead chlorapatite. In the previous investigations [2-4] ef-

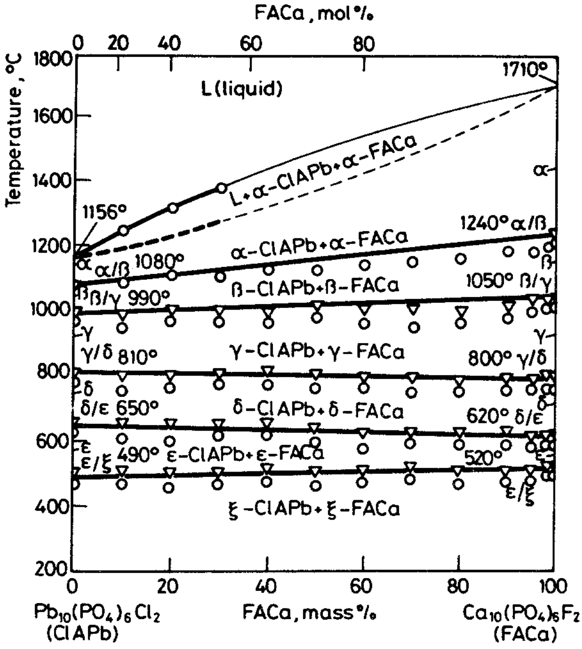

Fig. 1 Phase diagram of binary system $Pb_{10}(PO_4)_6Cl_2$-$Ca_{10}(PO_4)_6F_2$: o-thermal analysis (cooling), v-dilatometric analysis (heating)

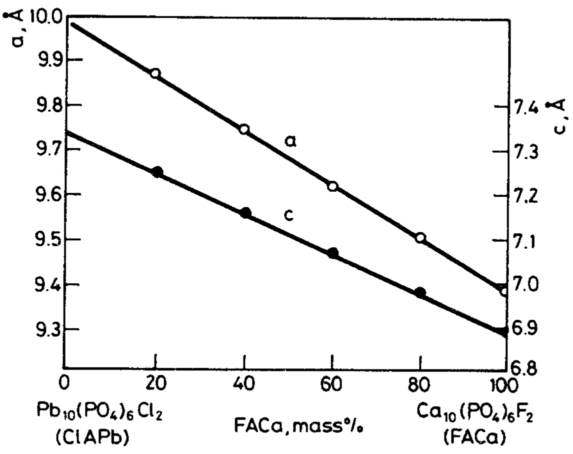

Fig. 2 The change of lattice parameters in the $Pb_{10}(PO_4)_6Cl_2$-$Ca_{10}(PO_4)_6F_2$ system

fects resulting from the thermal analysis during heating were weak, so they were ignored as not convincing. Now, the author became convinced of this transition.

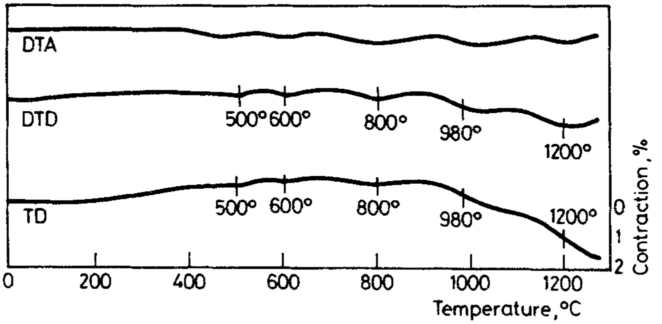

Fig. 3 Dilatogram of sintering lead-calcium fluor-chlorapatite $Pb_2Ca_8(PO_4)_6(Cl_{0.4}F_{1.6})$

Figure 3 shows, as an instance, one dilatogram of a mixed calcium-lead fluor-chlorine apatite $Pb_2Ca_8(PO_4)_6(Cl_{0.4}F_{1.6})$ of a composition 20% mol (40.2 wt%) $Pb_{10}(PO_4)_6Cl_2$ and 80% mol (59.8 wt%) $Ca_{10}(PO_4)_6F_2$ (10 g, 20 mm). The apatite was produced from lead and calcium orthophosphates, and lead chloride and calcium fluoride at 1000° for 0.5 h. On differential dilatometric curve there are five minima which correspond to five polymorphic transitions of the mixed apatite. The first modification is fairly weak, it starts at approx. 450° and finishes at approx. 520° with a minimum at approx. 500°. The second transition occurs over the temperature range from 580 to 650° with a minimum at approx. 600°; the third one over the range 760 - 820° with a minimum at approx. 800°; the fourth over 940 - 1030° with a minimum at approx. 980°; and the fifth over 1150-1220° with a minimum at approx. 1200°. The first transition is accompanied by a small change of volume while larger changes of volume are characteristic for the other ones. All transitions are accompanied by a contraction of volume during heating. The dilatometric TD curve shows five deflections and confirms the occurrence of five transitions proceeding with a contraction of volume during heating. The first transition is weak while the other ones much stronger. The DTA curve shows five endothermic effects which confirms the occurrence of five transitions. The total contraction of the sample was approx. 1.7%. In comparison with similar sample from research [4], the effects occurring here are stronger and more visible. The dilatograms for other samples were similar.

The results of dilatometric method were confirmed by the thermal analysis of heating and cooling. During cooling the transitions occurred over the temperature ranges 420-500° (peak at 460°), 540-600° (580°), 720-790° (750°), 900-1010° (960°), and 1030-1200° (1100°). The temperatures of transitions peaks on curves changed over the ranges 440-480, 560-600, 730-800, 950-1000, and 1090-1160°. All thermal effects during cooling were exothermal and weak. All polymorphic transitions are reversible. The microscopic investigations in reflected light performed for molten samples proved that the formed crystals of mixed apatites show many crackings. It confirmed the occurrence of polymorphic transitions accompanied by the change of volume cooling.

The X-ray investigations of samples sintered at lower and lower temperatures for a long time showed that continuous solid solutions occur in the solid phase of the system under examination.

Conclusions

The dilatometric and thermal investigations showed that mixed calcium-lead fluorchlorine apatites occur in six polymorphic modifications: $\alpha, \beta, \gamma, \delta, \varepsilon$ and ξ.

The occurrence of polymorphic transitions in lead chlorapatite, which were previously known from the investigations in this laboratory [2], was confirmed and one more polymorphic transition of this compound at 1080° was discovered. It was found that lead chlorapatite accelerated polymorphic transitions of calcium fluorapatite much stronger than lead fluorapatite, which resulted in discovering one more polymorphic transition of this compound at 1240°.

Research on polymorphic transitions of calcium fluorapatite and the influence of various additions on the will be continued.

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Zusammenfassung — Es wurde die Phasenabhängigkeit im binären System Bleichlorapatit $Pb_{10}(PO_4)_6Cl_2$ - Calciumfluorapatit $Ca_{10}(PO_4)_6F_2$ im besonderen Hinblick auf polymorphe Übergänge der Ausgangsverbindungen untersucht. Das Phasendiagramm dieses Systemes wurde im gesamten Temperatur- und Konzentrationsbereich erstellt und die Existenz von Mischkristallen entdeckt. Die Untersuchungen wurden mittels Thermo-, mikroskopischer, röntgenographischer und dilatometrischer Analyse durchgeführt.