The phase diagram of the binary system lead fluorapatite $[\text{Pb}_{10}(\text{PO}_{4})_6\text{F}_2]$ – calcium fluorapatite $[\text{Ca}_{10}(\text{PO}_{4})_6\text{F}_2]$ 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 $[\text{Pb}_{10}(\text{PO}_{4})_6\text{F}_2]$ – calcium fluorapatite $[\text{Ca}_{10}(\text{PO}_{4})_6\text{F}_2]$. 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$_2$O$_3$ 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 ($r_{\text{Ca}^{2+}} = 1.00$ Å and $r_{\text{Pb}^{2+}} = 1.19$ Å) [4] suggested the possible occurrence of an im-
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. Calcium pyrophosphate, 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,