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PHASE EQUILIBRIA IN TERNARY SYSTEM PbO - P_2O_5 - $PbCl_2$ Part I. Partial system $Pb_3(PO_4)_2$ - $Pb_8P_2O_{13}$ - $Pb_{10}(PO_4)_6Cl_2$

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In ternary system PbO - P_2O_5 - $PbCl_2$, the $Pb_3(PO_4)_2$ - $Pb_8P_2O_{13}$ - $Pb_{10}(PO_4)_6Cl_2$ partial ternary system has been examined by the thermal, microscopic, X-ray and dilatometric analyses, and its phase diagram provided. The components do not form any new chemical compounds.

The purpose of this paper is to establish the phase diagram of the $Pb_3(PO_4)_2$ - $Pb_8P_2O_{13}$ - $Pb_{10}(PO_4)_6Cl_2$ ternary system, which has not been systematically examined, so far. It is the first part of research on this ternary system and contains the partial ternary system over the composition range $Pb_3(PO_4)_2$ - $Pb_8P_2O_{13}$ - $Pb_{10}(PO_4)_6Cl_2$. The phase diagram of the first side system PbO - P_2O_5 has been previously known [1-3]. In the examined part of this system, there are four compounds: octaplumbic phosphate $Pb_8P_2O_{13}$ (melting point 860°), tetraplumbic phosphate $Pb_4P_2O_9$ (melting point 980°), lead oxyapatite $Pb_{10}(PO_4)_6O$ incongruent (melting point 967°), and lead orthophosphate $Pb_3(PO_4)_2$ (melting point 1014°). The second side system $Pb_3(PO_4)_2$ - $PbCl_2$ has been previously known [4, 5]. In this system, there is one compound - lead chlorapatite $Pb_{10}(PO_4)_6Cl_2$ (melting point 1156°).

Experimental

The following starting materials were used: lead oxide PbO p.a., ammonium dihydrophosphate $NH_4H_2PO_4$ p.a. and lead chloride $PbCl_2$ p.a. Lead oxide was sintered under air at 750° for 0.5h, then ground in an agate mortar and sieved. Ammonium dihydrophosphate was ground in an agate

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mortar and dried in a vacuum desiccator. Lead chloride was dried in a vacuum desiccator.

The other compounds were synthesized in this laboratory. Lead orthophosphate $Pb_3(PO_4)_2$ was obtained by mixing stoichiometric quantitites of lead oxide and ammonium dihydrophosphate and sintering as described in paper [6]. Lead phosphates $Pb_8P_2O_{13}$ and $Pb_4P_2O_9$, and lead oxyapatite $Pb_{10}(PO_4)_6O$ were synthesized by sintering stoichiometric quantities of lead oxide and lead orthophosphate as described in paper [3]. Lead chlorapatite $Pb_{10}(PO_4)_6Cl_2$ was synthesized by sintering stoichiometric quantities of lead orthophosphate and lead chloride as described in paper [7]. Phase purity of the compounds was controlled microscopically in reflected light in molten samples.

The examinations were carried out by the thermal, microscopic, X-ray and dilatometric methods as described in paper [5].

The thermal analysis (differential method) during cooling was performed in a resistance furnace with platinum winding under air. 10 g samples were fused in platinum crucibles. The temperature was read by means of

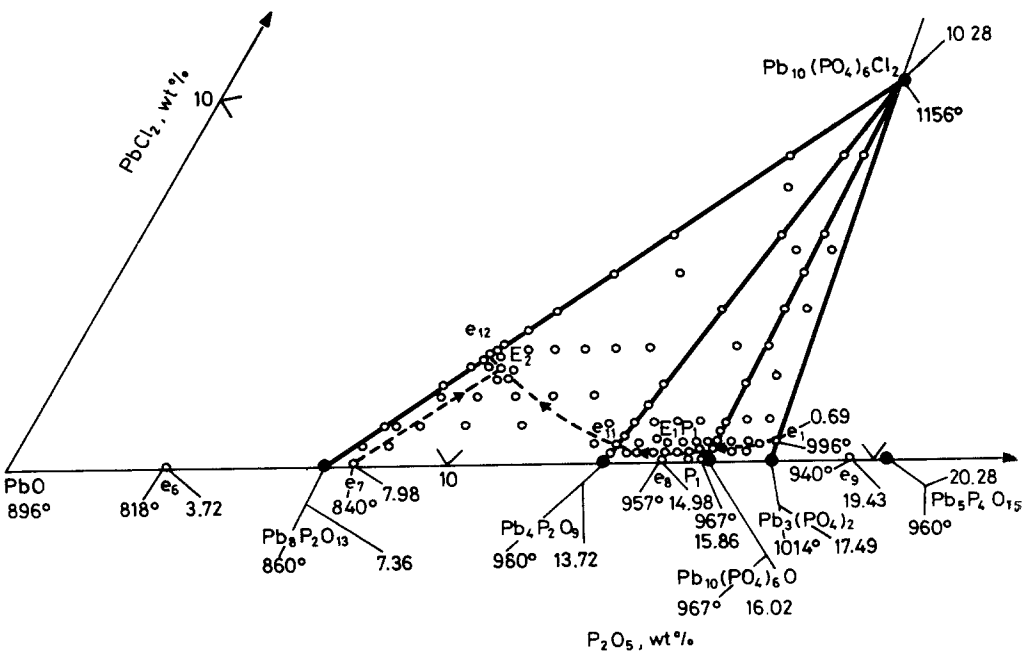

Fig. 1 Position of samples

calibrated thermocouple Pt-PtRh. An electronic recorder (MOM, Hungary) was used to measure temperature. The thermal analysis during heating for 0.2-0.3 g samples was performed in a derivatograph (MOM, Hungary) under air. A metallographic microscope was used for the microscopic analysis in reflected light of all molten samples. The X-ray examinations were carried out by the powder method with a Guinier camera and CuK_α radiation. The X-ray investigations were of qualitative character and were to identify phases. The dilatometric analysis during heating for 15-20g samples was performed in a derivatograph (MOM, Hungary) over the temperature range 20-1000°.

Results and discussion

Partial ternary system $Pb_3(PO_4)_2$ - $Pb_8P_2O_{13}$ - $Pb_{10}(PO_4)_6Cl_2$ has been examined by the thermal, microscopic, X-ray and dilatometric analyses. Figure 1 shows the position of samples in this system.

Figure 2 presents the phase diagram of the discussed partial ternary system with solidification isotherms. The major part of the system is occupied by the primary crystallization field of lead chlorapatite. The primary crystallization fields of phosphates and oxyapatite are much smaller. Lead

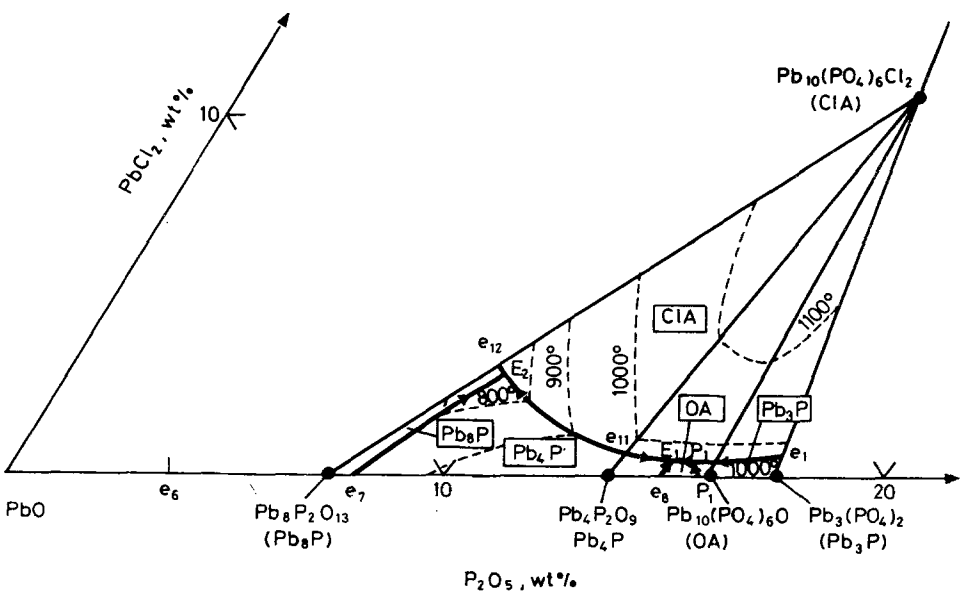

Fig. 2 Liquidus isothermal lines

chlorapatite $Pb_{10}(PO_4)_6Cl_2$ crystallizes primarily over the composition range $Pb_{10}(PO_4)_6Cl_2$ $e_1P_1E_1e_{11}E_2e_{12}$, lead orthophosphate $Pb_3(PO_4)_2$ over the range $e_8Pb_3(PO_4)_2p_1P_1$, lead oxyapatite $Pb_{10}(PO_4)_6O$ over $e_8E_1P_1p_1$, tetraplumbic phosphate $Pb_4P_2O_9$ over $e_7E_2e_{11}E_1e_8$, and octaplumbic phosphate $Pb_8P_2O_{13}$ over $Pb_8P_2O_{13}e_{12}E_2e_7$.

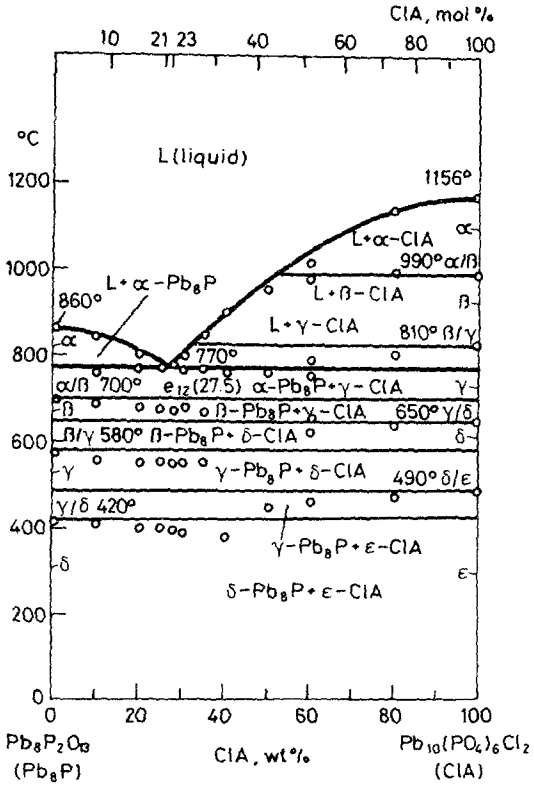

Fig. 3 Phase diagram of binary section $Pb_8P_2O_{13}$ - $Pb_{10}(PO_4)_6Cl_2$

Three pseudobinary sections were found to occur in the discussed partial ternary system: 1/ $Pb_8P_2O_{13}$ - $Pb_{10}(PO_4)_6Cl_2$, 2/ $Pb_4P_2O_9$ - $Pb_{10}(PO_4)_6Cl_2$, 3/ $Pb_{10}(PO_4)_6O$ - $Pb_{10}(PO_4)_6Cl_2$. The first and the second one are binary over the full temperature range, while the third section is binary in lower temperatures and ternary in higher ones.

The phase diagram of the first pseudobinary section $Pb_8P_2O_{13}$ - $Pb_{10}(PO_4)_6Cl_2$ is shown in Fig. 3. The components form an eutectic system of the eutectic e_{12} composition amounting to approx. 27.5 wt.% (21.24

mol%) chlorapatite at 770°. The polymorphic transitions of both initial components have been confirmed.

Figure 4 shows the phase diagram of the second pseudobinary section $Pb_4P_2O_9$ - $Pb_{10}(PO_4)_6Cl_2$. This system is also eutectic of the eutectic e_{11} composition equal to 5 wt% (1.97 mol%) of chlorapatite at 950°. The polymorphic transitions of both initial compounds have been confirmed.

The phase diagram of the third pseudobinary section $Pb_{10}(PO_4)_6O$ - $Pb_{10}(PO_4)_6Cl_2$ is presented in Fig. 5. This section is ternary above 960° (P_1)

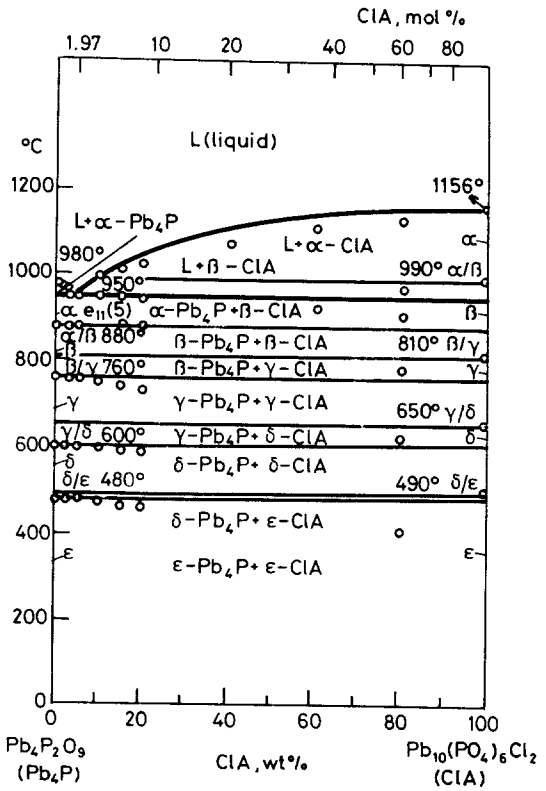

Fig. 4 Phase diagram of binary section $Pb_4P_2O_9$ - $Pb_{10}(PO_4)_6Cl_2$

and binary below it, which will be described further on. Lead oxyapatite $Pb_{10}(PO_4)_6O$ (Fig. 6) of the composition 16.02 wt.% (23.08 mol%) of P_2O_5 is formed incrongruently at 967° according to the equation: L_{P1} + $Pb_3(PO_4)_2$ = $Pb_{10}(PO_4)_6O$ and shows four polymorphic transitions at 890, 780, 640 and 430°. The addition of chlorapatite favours the intensity of oxyapatite polymorphic transitions.

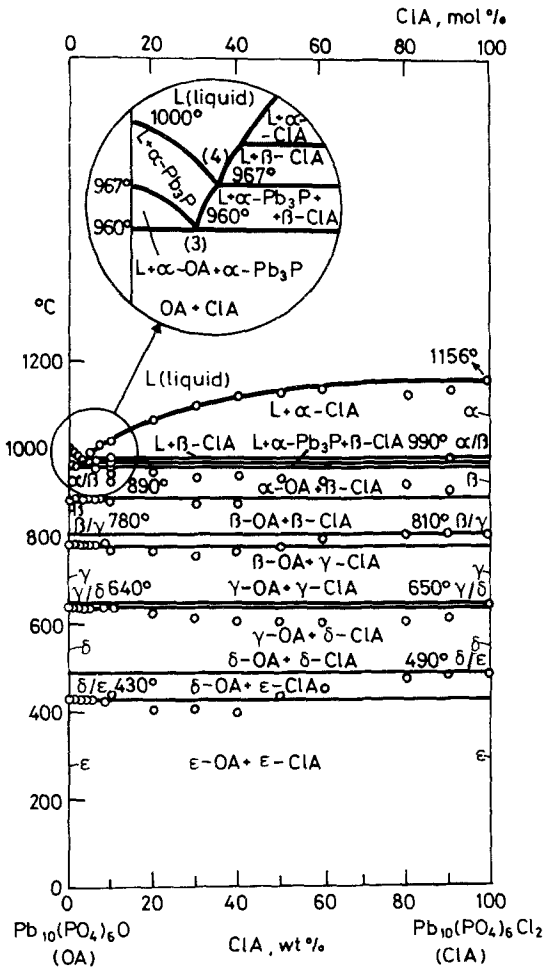

Fig. 5 Phase diagram of binary section $Pb_{10}(PO_4)_6O$ - $Pb_{10}(PO_4)_6Cl_2$

The above discussed pseudobinary sections divide the investigated partial ternary system into three more partial ternary systems (Fig. 6):

1/ $Pb_8P_2O_{13}$ - $Pb_{10}(PO_4)_6Cl_2$ - $Pb_4P_2O_9$,

2/ $Pb_4P_2O_9$ - $Pb_{10}(PO_4)_6Cl_2$ - $Pb_{10}(PO_4)_6O$,

3/ $Pb_{10}(PO_4)_6O$ - $Pb_{10}(PO_4)_6Cl_2$ - $Pb_3(PO_4)_2$.

Figure 6 shows the phase diagram of partial ternary system $Pb_3(PO_4)_2$ - $Pb_8P_2O_{13}$ - $Pb_{10}(PO_4)_6Cl_2$, and Fig. 7 its isothermal section at room temperature.

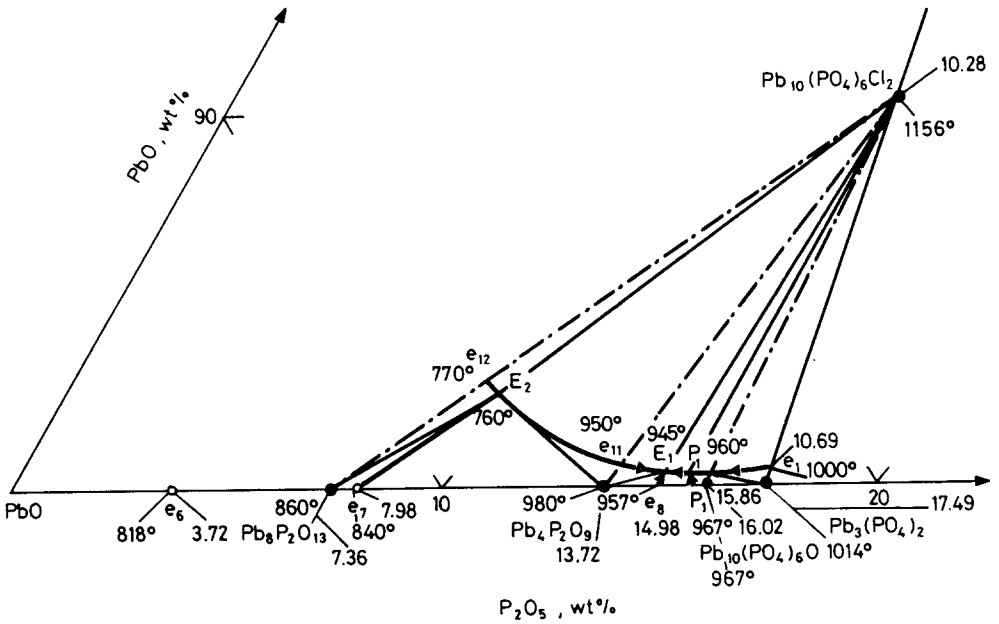

Fig. 6 Phase diagram of system $Pb_3(PO_4)_2$ - $Pb_8P_2O_{13}$ - $Pb_{10}(PO_4)_6Cl_2$

Partial ternary system $Pb_8P_2O_{13}$ - $Pb_{10}(PO_4)_6Cl_2$ - $Pb_4P_2O_9$ (Fig. 6) is an eutectic system. Octa- and tetraplumbic phosphates crystallize along the e_7E_2 eutectic curve: $L = Pb_8P_2O_{13} + Pb_4P_2O_9$. An eutectic curve runs from point e_{12} to E_2 and, octaplumbic phosphate and lead chlorapatite crystallize along it: $L = Pb_8P_2O_{13} + Pb_{10}(PO_4)_6Cl_2$. The third eutectic curve runs from point e_{11} to E_2 and tetraplumbic phosphate and lead chlorapatite crystallize along it: $L = Pb_4P_2O_9 + Pb_{10}(PO_4)_6Cl_2$. The three curves converge at point E_2 forming ternary eutectic $E_2 = Pb_8P_2O_{13} + Pb_4P_2O_9 + Pb_{10}(PO_4)_6Cl_2$. The ternary eutectic composition amounts to approx. 87.4 wt.% of PbO, 10 wt.% of P_2O_5 and 2.60 wt.% of $PbCl_2$ at 760°. Figure 7 shows that at the isothermal section at room temperature, three phases coexist in the system ($Pb_8P_2O_{13} + Pb_4P_2O_9 + Pb_{10}(PO_4)_6Cl_2$.)

The second partial system $Pb_4P_2O_9$ - $Pb_{10}(PO_4)_6Cl_2$ - $Pb_{10}(PO_4)_6O$ and the third one $Pb_{10}(PO_4)_6O$ - $Pb_{10}(PO_4)_6Cl_2$ - $Pb_3(PO_4)_2$ are more complex which results from the proceeding of a peritectic reaction. Lead orthophosphate and lead chlorapatite crystallize along the e_1P_1 eutectic curve according to the equation $e_1 = Pb_3(PO_4)_2 + Pb_{10}(PO_4)_6Cl_2$ and lead oxyapatite is formed in a peritectic reaction according to the equation: $p_1 + Pb_3(PO_4)_2 =$

$= Pb_{10}(PO_4)_6O$ along the p_1P_1 peritectic curves. Both curves converge at point P_1 of the composition 84.6 wt.% of PbO, 15.1 wt.% of P_2O_5 and 0.3 wt.% of $PbCl_2$, and at 960° a ternary peritectic reaction proceeds according to the equation: $L_{P1} + Pb_3(PO_4)_2 = Pb_{10}(PO_4)_6O + Pb_{10}(PO_4)_6Cl_2$. The liquid of the P_1 composition reacts with lead orthophosphate and both apatites are formed as the result of this reaction. Section $Pb_{10}(PO_4)_6O$ - $Pb_{10}(PO_4)_6Cl_2$ is binary below 960° and ternary above it (Fig. 5). It is well presented in Fig. 7 that three phases ($Pb_3(PO_4)_2 + Pb_{10}(PO_4)_6Cl_2 + Pb_{10}(PO_4)_6O$) coexist at room temperature in this system. The section cuts off the third partial ternary system from the second one. In the second partial ternary system $Pb_4P_2O_9$ - $Pb_{10}(PO_4)_6Cl_2$ - $Pb_{10}(PO_4)_6O$ both apatites: $L = Pb_{10}(PO_4)_6O + Pb_{10}(PO_4)_6Cl_2$ crystallize along an eutectic curve which runs from point P_1 to E_1. Tetraplumbic phosphate and lead chlorapatite crystallize along an eutectic curve which runs from point e_8 to E_1: $L = Pb_4P_2O_9 + Pb_{10}(PO_4)_6Cl_2$. All curves converge at point E_1 forming ternary eutectic $E_1 = Pb_4P_2O_9 + Pb_{10}(PO_4)_6O + Pb_{10}(PO_4)_6Cl_2$. The ternary eutectic composition amounts to approx. 85 wt.% of PbO, 14.8 wt.% of P_2O_5 and 0.2 wt.% of $PbCl_2$ at 945°. It is well presented in Fig. 7 that three phases: $Pb_4P_2O_9 + Pb_{10}(PO_4)_6O + Pb_{10}(PO_4)_6Cl_2$, coexist at room temperature in this system.

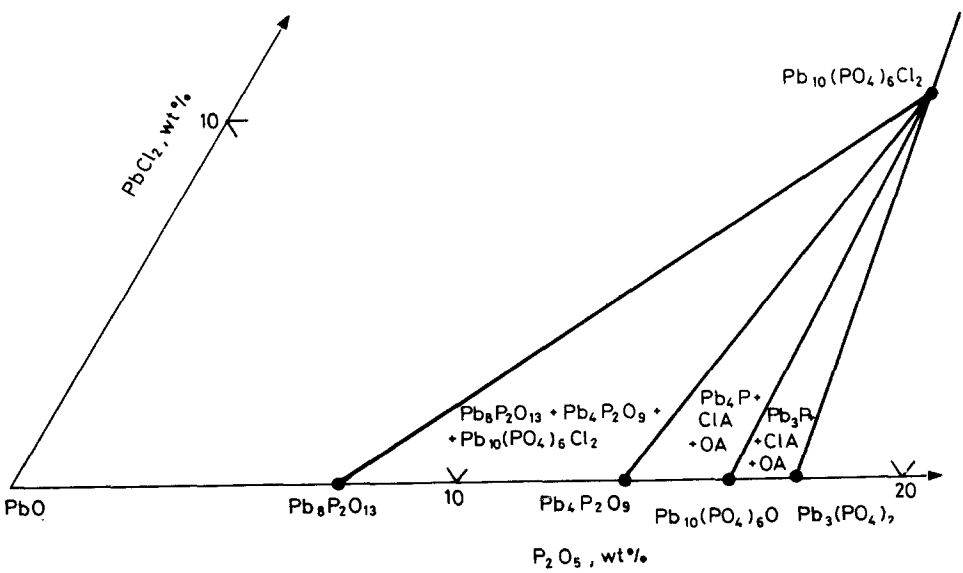

Fig. 7 Isothermal section at room temperature

Further examinations of the PbO - P_2O_5 - $PbCl_2$ ternary system are being continued.

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Zusammenfassung — Mittels Thermo-, mikroskopischer, röntgenographischer und dilatometrischer Analyse wurde im ternären System PbO - P_2O_5 - $PbCl_2$ das ternäre Teilsystem $Pb_3(PO_4)_2$ - $Pb_8P_2O_{13}$ - $Pb_{10}(PO_4)_6Cl_2$ untersucht und ein Phasendiagramm erstellt. Die Komponenten bilden keinerlei neue chemische Verbindungen.