

## PHASE EQUILIBRIA IN THE TERNARY SYSTEM

### PbO-P<sub>2</sub>O<sub>5</sub>-PbCl<sub>2</sub>

#### II. The partial system

### PbO-7PbO · PO<sub>2.5</sub> · PbCl<sub>2</sub>(R)-Pb<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>-Pb<sub>8</sub>P<sub>2</sub>O<sub>13</sub>

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Within the ternary system PbO-P<sub>2</sub>O<sub>5</sub>-PbCl<sub>2</sub>, the partial ternary system PbO-7PbO · PO<sub>2.5</sub> · PbCl<sub>2</sub>-Pb<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>-Pb<sub>8</sub>P<sub>2</sub>O<sub>13</sub> was investigated by thermal, microscopic, X-ray, dilatometric and IR absorption analyses, and its phase diagram was established. The occurrence of new chemical compounds was not discovered.

Investigation of the partial ternary system PbO-7PbO · PO<sub>2.5</sub> · PbCl<sub>2</sub>-Pb<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>-Pb<sub>8</sub>P<sub>2</sub>O<sub>13</sub> comprises part of the research on the ternary system PbO-P<sub>2</sub>O<sub>5</sub>-PbCl<sub>2</sub>.

The purpose of this work is to establish the phase diagram of this system. Its phase diagram over the composition range Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-Pb<sub>8</sub>P<sub>2</sub>O<sub>13</sub>-Pb<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub> was reported earlier [1]. The aim of the present paper is to establish the phase diagram of the system PbO-P<sub>2</sub>O<sub>5</sub>-PbCl<sub>2</sub> over the composition range PbO-7PbO · PO<sub>2.5</sub> · PbCl<sub>2</sub>-Pb<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>-Pb<sub>8</sub>P<sub>2</sub>O<sub>13</sub>.

In the examined part of this system, there are four compounds: lead monoxide - PbO, a ternary compound - 7PbO · PO<sub>2.5</sub> · PbCl<sub>2</sub>, lead chlorapatite - Pb<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>, and octaplumbic phosphate - Pb<sub>8</sub>P<sub>2</sub>O<sub>13</sub>.

PbO has been investigated by many authors. According to [2], it melts congruently at 898°. In [3], it was reported that PbO occurs in three crystallographic modifications:

- (1) tetragonal (red PbO), which occurs up to 488°, with lattice constants  $a = 3.94 \text{ \AA}$ ,  $c = 13.04 \text{ \AA}$ ,  $c/a = 3.309$ ;
- (2) orthorhombic (yellow PbO), over the temperature range 488-750°, with lattice constants  $a = 11.75 \text{ \AA}$ ,  $b = 11.58 \text{ \AA}$  and  $c = 7.30 \text{ \AA}$ ;

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(3) monoclinic (pink PbO), over 750°, with lattice constants  $a = 10.14 \text{ \AA}$ ,  $b = 5.70 \text{ \AA}$ ,  $c = 13.25 \text{ \AA}$  and  $\beta = 80^\circ 36'$ .

The melting point and the temperatures of the polymorphic transitions of this compound were confirmed in [4].

During phase investigations of the ternary system PbO-P<sub>2</sub>O<sub>5</sub>-PbF<sub>2</sub> [4] and of the binary system PbO-PbCl<sub>2</sub> [5], it was found that powdered PbO is a problematic compound in such experiments. Its crystallographic modifications undergo interconversion easily, even at as low as room temperature, for example during rubbing. This made the interpretation of X-ray and microscopic pictures difficult, especially for samples rich in PbO when this compound is a primarily evolved component.

The ternary compound 7PbO·PO<sub>2.5</sub>·PbCl<sub>2</sub> was described by Aurivillius [6], who defined its structure as tetragonal and gave its lattice constants as  $a = 0.39189$  [5] nm and  $c = 2.2797$  [5] nm. The melting point of this compound was not determined.

Pb<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub> is formed in the binary system Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-PbCl<sub>2</sub> [7, 8]. It melts congruently at 1156° and crystallizes in the hexagonal system with lattice constants  $a = 9.97 \text{ \AA}$ ,  $c = 7.32 \text{ \AA}$  and  $c/a = 7.734$  [9]. In paper [10], this compound was reported to show five polymorphic  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$ , with corresponding transition temperatures of 980, 810, 650 and 490°. In [11], thermal effect were observed at 1080°, which suggested the occurrence of one more polymorphic transition in this compound.

Pb<sub>8</sub>P<sub>2</sub>O<sub>13</sub> is formed in the system PbO-P<sub>2</sub>O<sub>5</sub> [2]. Its melting point is 896° and it has space group Cc, C2/c [12]. This compound was found [4] to occur in four polymorphic modifications,  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ , with transition temperatures 700, 580 and 420°, respectively.

## Experimental

The following commercial materials were used: PbO p.a., NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> p.a. and PbCl<sub>2</sub> p.a. while Pb<sub>8</sub>P<sub>2</sub>O<sub>13</sub>, Pb<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub> and 7PbO·PO<sub>2.5</sub>·PbCl<sub>2</sub> were synthesized in this laboratory.

PbO was sintered at 750° for 0.5 h, then ground and sieved. Lead orthophosphate, Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, one of the starting components for the synthesis of the other compounds, was obtained from stoichiometric quantities of PbO and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> as described in [13]. Pb<sub>8</sub>P<sub>2</sub>O<sub>13</sub> was obtained by sintering stoichiometric quantities of PbO and Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> as described in [4]. Pb<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub> was obtained from stoichiometric quantities of Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and PbCl<sub>2</sub> as described in [10]. 7PbO·PO<sub>2.5</sub>·PbCl<sub>2</sub>, denoted as *R* for





The dilatometric analysis during heating was performed in a dilatometer (type 802 BG, West Germany) as described in [15] for compound R, and in a derivatograph (type 3247, Hungary) as described in [4, 10, 13,14] for the other compounds.

Together with the thermal examinations, the microscopic analysis in reflected light of all molten samples was carried out with a metallographic microscope.

The X-ray investigations, which were of a qualitative character in this work and were intended to identify phases, were performed by the powder method with a Guinier camera and  $\text{CuK}\alpha$ -radiation.

All compounds under investigation were analysed by the IR absorption method. However, the results obtained were of little use for identification purposes, because the analysed substances did not show standard spectra and the obtained spectra were hardly legible.

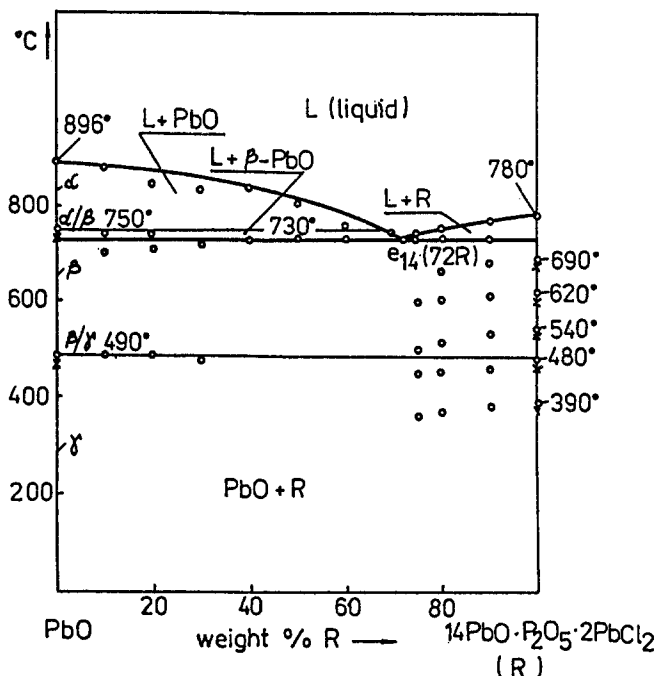


Fig. 3 Phase diagram of binary section  $\text{PbO}-14\text{PbO}\cdot\text{P}_2\text{O}_5\cdot 2\text{PbCl}_2$

**Results and discussion**

The partial ternary system  $PbO-R^*-Pb_{10}(PO_4)_6Cl_2-Pb_8P_2O_{13}$  was examined by means of thermal, microscopic, X-ray, dilatometric and IR absorption analyses (Fig. 1).

Figure 2 shows the phase diagram of this system with solidification isotherms. The major part of the system is occupied, as in [1], by the primary crystallization field of lead chlorapatite. The primary crystallization fields of the other compounds are much smaller. In this partial ternary system,  $Pb_{10}(PO_4)_6Cl_2$  crystallizes primarily over the composition range  $Pb_{10}(PO_4)_6Cl_2$   $e_{12}E_{3e_{15}}$ ,  $Pb_8P_2O_{13}$  over the range  $Pb_8P_2O_{13}$   $e_6E_{4e_{13}}E_{3e_{12}}$ ,  $PbO$  over the range  $PbO$   $e_{14}E_{4e_6}$  and compound  $R$  over the range  $R$   $e_{15}E_{3e_{13}}E_{4e_{14}}$ .

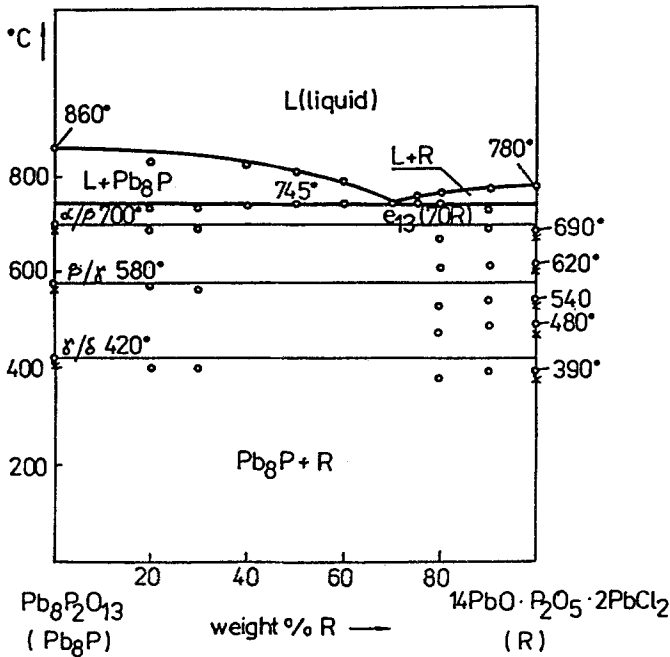


Fig. 4 Phase diagram of binary section  $Pb_8P_2O_{13}-14PbO \cdot P_2O_5 \cdot 2PbCl_2$

\*  $R = 14PbO \cdot P_2O_5 \cdot 2PbCl_2$

Three pseudobinary sections were found to occur in this partial ternary system: (1) PbO-R, (2)  $\text{Pb}_8\text{P}_2\text{O}_{13}$ -R and (3) R- $\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$ . They are all eutectic systems. Figure 3 shows the phase diagram of the first pseudobinary section, PbO-R. The components form a eutectic system with the eutectic  $e_{14}$  composition amounting to approximately 72 wt% of R at 730°.

As a result of these thermal examinations, it was found that compound R melts congruently at 780°. Well-visible exothermal effects were observed at 390, 480, 540, 620 and 690° in the cooling and heating curves obtained for this compound. Dilatometric investigations on both molten and sintered samples showed effects at 380, 460, 520, 610 and 680°[15]. At the same time, microscopic observations of microsections did not reveal foreign phases within grains, and lines from the starting components were not observed in the X-ray photographs.

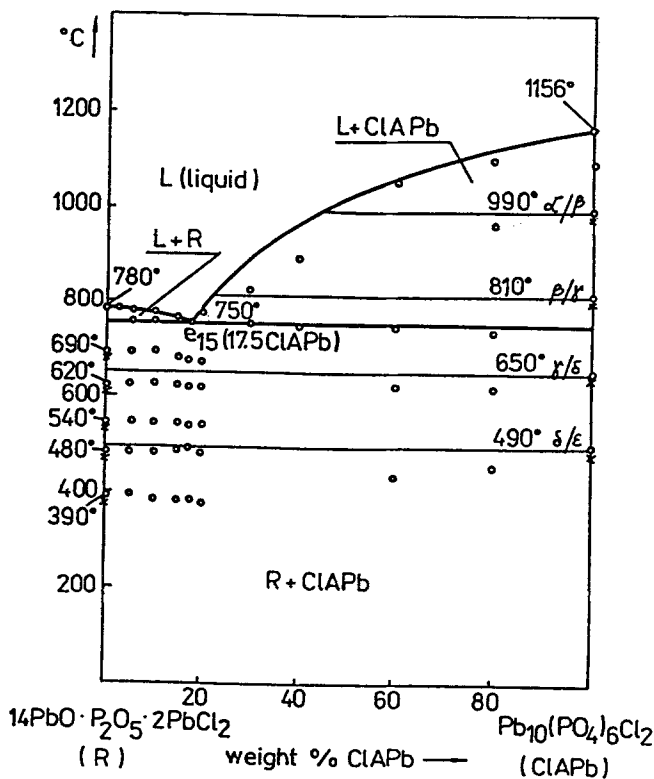


Fig. 5 Phase diagram of binary section  $14\text{PbO} \cdot \text{P}_2\text{O}_5 \cdot 2\text{PbCl}_2$ - $\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$

During the thermal examinations of the system PbO-R, PbO was not observed to influence the intensity of the thermal effects occurring in the pure compound R. They were well seen close to this system, and they then disappeared.

Figure 4 presents the phase diagram of the second pseudobinary section,  $\text{Pb}_8\text{P}_2\text{O}_{13}$ -R. This system is also a eutectic ones, with the eutectic  $e_{14}$  composition amounting to approximately 70 wt% of R at  $745^\circ$ . In examinations of this system, effects similar to those occurring in the pure compound were observed in the part richer in compound R.

Figure 5 shows the phase diagram of the third pseudobinary section, R- $\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$ . The components do not form new compounds but a simple eutectic system. The eutectic  $e_{15}$  composition amounts to approximately 17.5 wt% of chlorapatite, at  $750^\circ$ . As before, thermal effects at

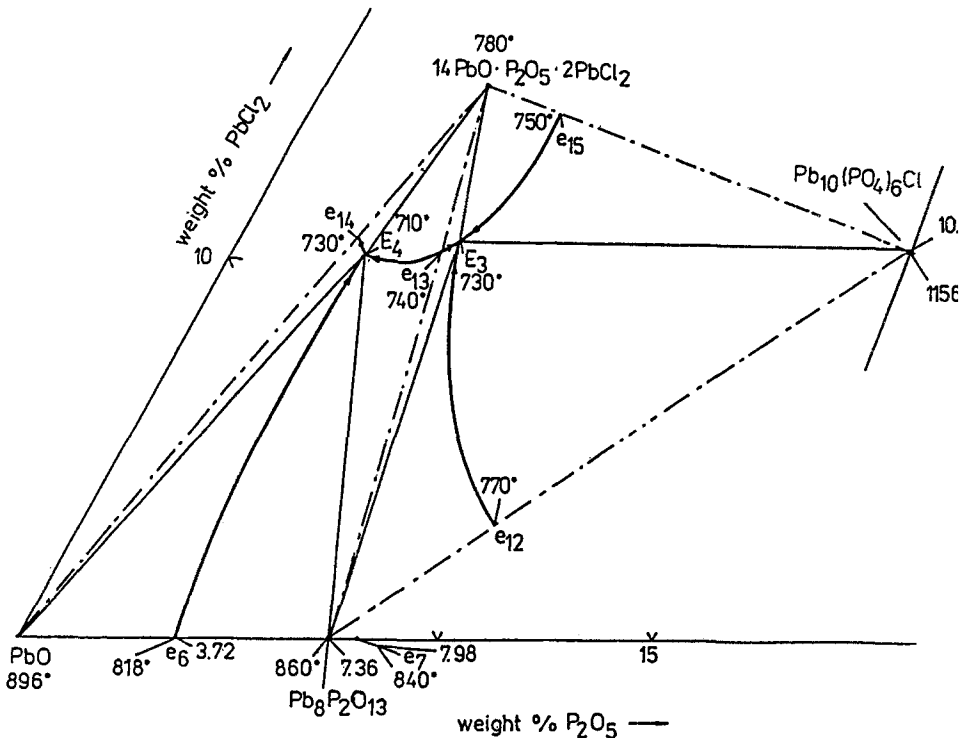


Fig. 6 Phase diagram of partial ternary system  
 $\text{PbO}\text{-}14\text{PbO}\cdot\text{P}_2\text{O}_5\cdot 2\text{PbCl}_2\text{-Pb}_{10}(\text{PO}_4)_6\text{Cl}_2\text{-Pb}_8\text{P}_2\text{O}_{13}$



the appropriate temperatures were observed in the part of the system richer in compound *R*.

The above pseudobinary sections divide the investigated partial ternary system into two smaller partial ternary systems: (1)  $\text{PbO-R-Pb}_8\text{P}_2\text{O}_{13}$  and (2)  $\text{Pb}_8\text{P}_2\text{O}_{13}\text{-R-Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$ ; this is well seen in Fig. 6, which presents the phase diagram of the partial ternary system  $\text{PbO-R-Pb}_{10}(\text{PO}_4)_6\text{Cl}_2\text{-Pb}_8\text{P}_2\text{O}_{13}$ .

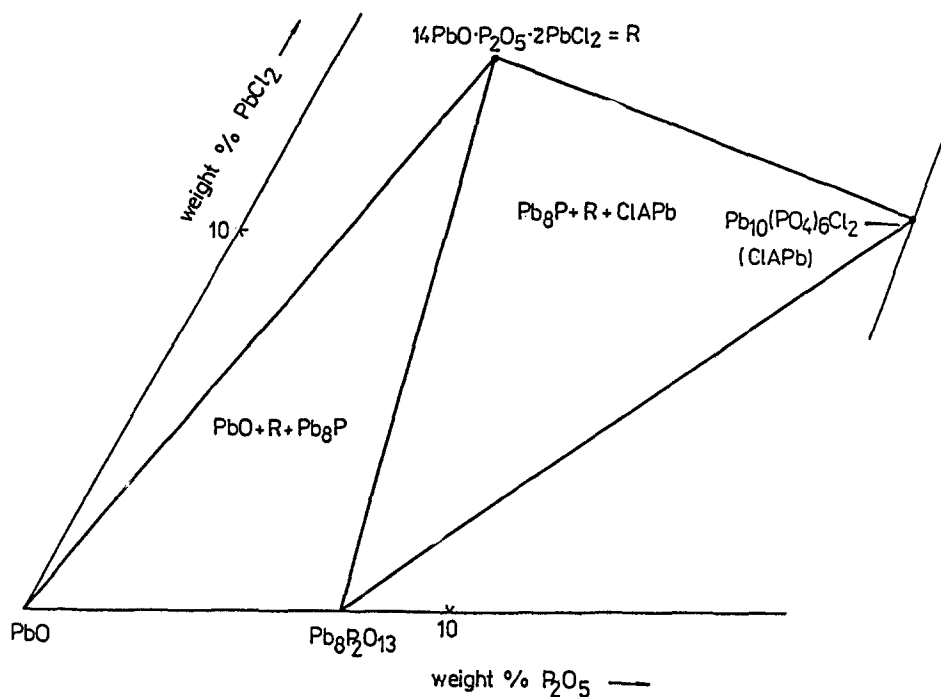


Fig. 7 Isothermal section at room temperature

The partial ternary system  $\text{PbO-R-Pb}_8\text{P}_2\text{O}_{13}$  is a eutectic system. Lead monoxide and octaplumbic phosphate crystallize along the eutectic curve  $e_6E_4$ :  $\text{L} = \text{PbO} + \text{Pb}_8\text{P}_2\text{O}_{13}$ . A eutectic curve runs from point  $e_{14}$  to  $E_4$ , and octaplumbic phosphate and compound *R* crystallize along it:  $\text{L} = \text{PbO} + \text{R}$ . The third eutectic curve runs from point  $e_{13}$  to  $E_4$ , and octaplumbic phosphate and compound *R* crystallize along it:  $\text{L} = \text{Pb}_8\text{P}_2\text{O}_{13} + \text{R}$ . The three curves converge at point  $E_4$ , forming the ter-

nary eutectic  $E_4 = \text{PbO} + \text{R} + \text{Pb}_8\text{P}_2\text{O}_{13}$ . The composition of this eutectic amount to approximately 86.85 wt% of PbO, 3.15 wt% of  $\text{P}_2\text{O}_5$  and 10 wt% of  $\text{PbCl}_2$ , at  $710^\circ$ . Figure 7 shows that in the isothermal section at room temperature, three phases coexist in the system ( $\text{PbO} + \text{R} + \text{Pb}_8\text{P}_2\text{O}_{13}$ ).

The second partial system,  $\text{Pb}_8\text{P}_2\text{O}_{13}$ -R- $\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$ , is also a eutectic system (Fig. 6). Octaplumbic phosphate and lead chlorapatite crystallize along the eutectic curve  $e_{12}E_3$ :  $L = \text{Pb}_8\text{P}_2\text{O}_{13} + \text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$ . A eutectic curve runs from point  $e_{13}$  to  $E_3$ , and octaplumbic phosphate and compound R crystallize along it:  $L = \text{Pb}_8\text{P}_2\text{O}_{13} + \text{R}$ . Compound R and chlorapatite crystallize along the eutectic curve  $e_{15}E_3$ :  $L = \text{R} + \text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$ . A ternary eutectic reaction proceeds at  $730^\circ$  at point  $E_3$ , where all three curves converge, with  $E_3 = \text{Pb}_8\text{P}_2\text{O}_{13} + \text{R} + \text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$ . The ternary eutectic composition amounts to approximately 84.5 wt% of PbO, 5.15 wt% of  $\text{P}_2\text{O}_5$  and 10.35 wt% of  $\text{PbCl}_2$ . Three phases coexist in this system at room temperature ( $\text{Pb}_8\text{P}_2\text{O}_{13} + \text{R} + \text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$ ), which is shown in Fig. 7.

Examinations of the system  $\text{PbO}$ - $\text{P}_2\text{O}_5$ - $\text{PbCl}_2$  are being continued.

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**Zusammenfassung** — Mittels thermischen, mikroskopischen, röntgenografischen, dilatometrischen und IR-Absorptionsuntersuchungen wurde innerhalb des ternären Systems  $\text{PbO} - \text{P}_2\text{O}_5 - \text{PbCl}_2$  das partielle ternäre System  $\text{PbO} - 7\text{PbO} \cdot \text{PO}_{2.5}\text{PbCl}_2 - \text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2 - \text{Pb}_8\text{P}_2\text{O}_{13}$  untersucht und dessen Phasendiagramm erstellt. Die Existenz neuer chemischer Verbindungen konnte nicht festgestellt werden.