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PHASE EQUILIBRIA IN THE TERNARY SYSTEM $PbO-P_2O_5-PbCl_2$
V. The partial system $Pb_3Cl_2O_2-PbCl_2-Pb_{10}(PO_4)_6Cl_2$

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Abstract

Phase dependencies in the ternary system $Pb_3Cl_2O_2-PbCl_2-Pb_{10}(PO_4)_6Cl_2$, which is a partial system of the ternary system $PbO-P_2O_5-PbCl_2$, have been investigated by thermal, X-ray phase, microscopic, dilatometric and IR absorption analyses. The phase diagram of the $Pb_3Cl_2O_2-PbCl_2-Pb_{10}(PO_4)_6Cl_2$ system has been provided. The components have been found not to form any new chemical compounds.

Keywords: dilatometry, IR, phase equilibria, phase diagram, ternary system $PbO-P_2O_5-PbCl_2$, thermal analysis, X-ray

Introduction

The author started examinations on phase equilibria in the ternary system $PbO-P_2O_5-PbCl_2$, which had not been previously described in the literature. They resulted the phase diagram of this system over the composition range $PbO-Pb_3Cl_2O_2-Pb_{10}(PO_4)_6Cl_2-Pb_3(PO_4)_2$ [1-4]. The occurrence of a new, previously unknown chemical compound was discovered [3], and its X-ray [3] and dilatometric data [5] were reported. Many previously unknown thermal and dilational effects, occurring in compounds which are formed in the system under investigation, were identified [5, 6]. The side binary system $PbO-PbCl_2$ was examined as well [7].

The purpose of the present work was to establish the phase diagram of the $PbO-P_2O_5-PbCl_2$ system over the composition range: $Pb_3Cl_2O_2-PbCl_2-Pb_{10}(PO_4)_6Cl_2$. Four compounds occur in the examined part of this system: lead oxychloride $Pb_3Cl_2O_2$ (T_2) (melting point 695°C), lead oxychloride Pb_2Cl_2O (T_3), (incongruent melting point 525°C), lead chloride $PbCl_2$ (melting point 501°C) and lead chloroapatite $Pb_{10}(PO_4)_6Cl_2$ (melting point 1156°C).

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Experimental

Analytically pure, commercial reagents, PbO, $PbCl_2$ and $NH_4H_2PO_4$ were used in the examinations. They were starting materials for the synthesis of the necessary compounds $Pb_3Cl_2O_2$, Pb_2Cl_2O, $Pb_3(PO_4)_2$ and $Pb_{10}(PO_4)_6Cl_2$, which were obtained in this laboratory by sintering stoichiometric quantities of the appropriate reagents at different temperatures. The phase purity of the compounds obtained was tested microscopically in reflected light (in molten samples) and by X-ray (in molten and sintered samples).

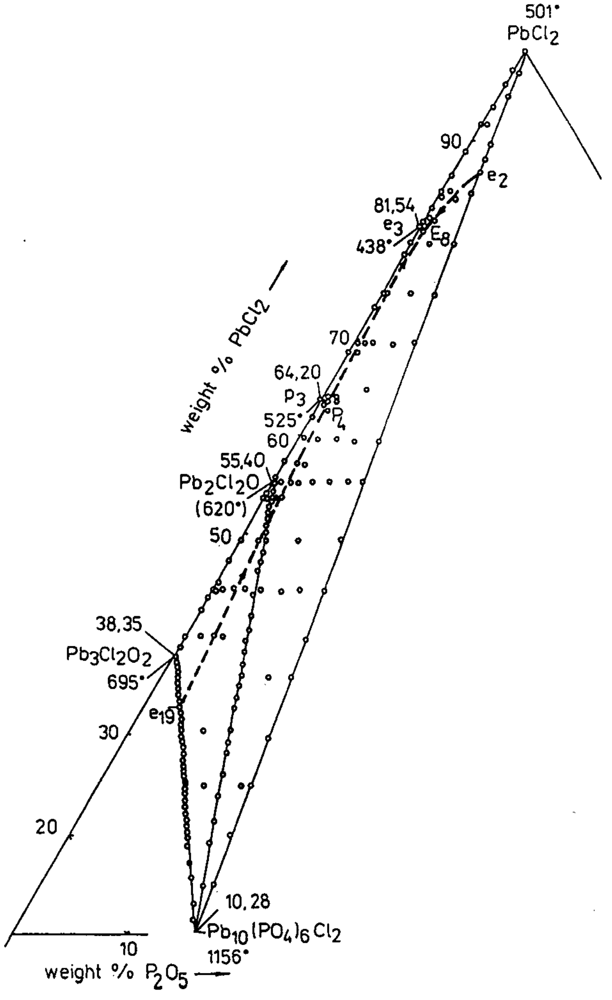

Fig. 1 Composition of samples

The examinations were carried out by thermal (differential method), microscopic, X-ray, dilatometric and IR absorption methods. Samples for the investigations were prepared from previously obtained the compounds as well as from lead monoxide, dichloride and orthophosphate.

Thermal analysis with cooling and heating was performed in resistance furnaces constructed in this laboratory – with 10 g samples using an electronic recorded (MOM, Hungary) and with a derivatograph (only heating) (MOM, Hungary) with 0.5–1.5 g samples.

The temperatures of phase transitions were established on the basis of cooling and heating curves which resulted the solidification isotherms, liquidus and

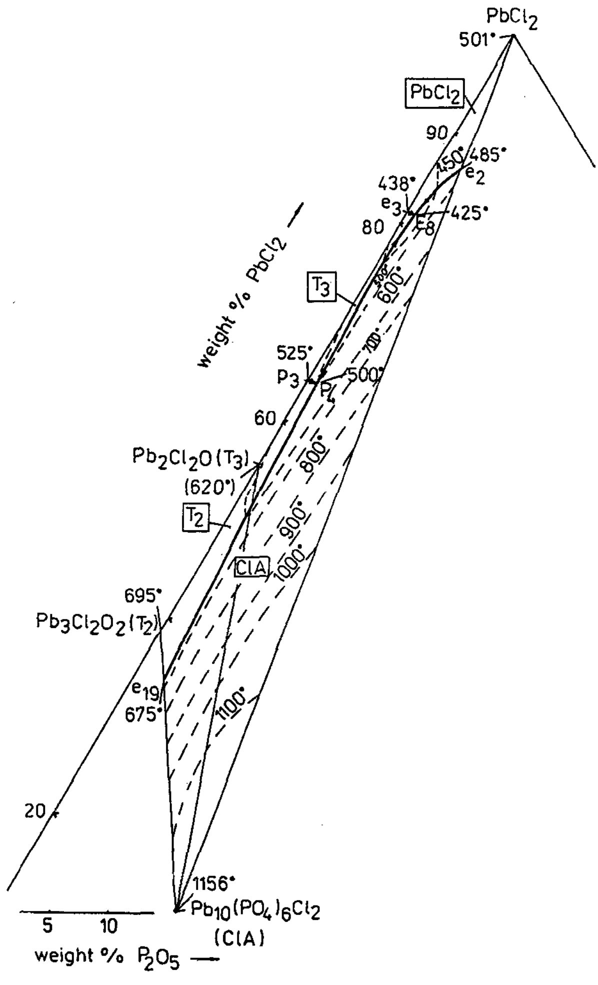

Fig. 2 Liquidus isothermal lines

solidus curves, and binary and ternary phase diagrams. Microsections were prepared from molten samples, observed microscopically in reflected light and then X-ray diffraction patterns were taken. These examinations provided the qualitative composition of the microsections and their phase structure.

Dilatometric analysis during heating was carried out in a dilatometer (type 802 BG) with programmed heating and computerized analysis of the results using samples pressed into 3×3×10 mm beams. X-ray examinations were performed by the powder method with a Guinier's camera using CuK_{α} radiation. IR absorption analysis was performed with a Specord IR-75 spectrophotometer with samples in the form of pellets with potassium bromide.

Results and discussion

The partial ternary system $Pb_3Cl_2O_2$–$PbCl_2$–$Pb_{10}(PO_4)_6Cl_2$ was examined by thermal, microscopic, X-ray, dilatometric and IR absorption methods. Figure 1 shows, marked by points the compositions of samples in the partial ternary system studied by thermal, microscopic and X-ray methods.

Figure 2 presents the phase diagram of this system with solidification isotherms. The major part of this system is occupied by the primary crystallization field of lead chloroapatite $Pb_{10}(PO_4)_6Cl_2$-ClA, which in this partial ternary system crystallizes primarily over the composition range: ClA$e_{19}P_4E_8e_2$. Lead oxy-

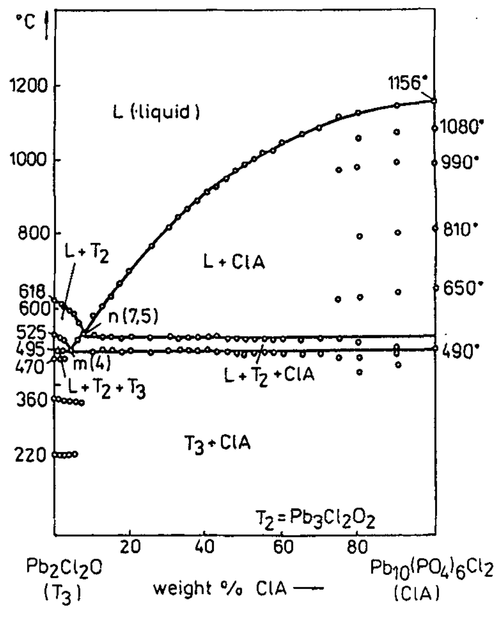

Fig. 3 Phase diagram of the binary section Pb_2Cl_2O–$Pb_{10}(PO_4)_6Cl_2$

chloride $Pb_3Cl_2O_2$ (T_2) crystallizes primarily over the composition range: $T_2e_{19}P_4p_3$, oxychloride Pb_2Cl_2O (T_3) over the range: $p_3P_4E_8e_3$ and lead chloride $PbCl_2$ over: $PbCl_2e_2E_8e_3$.

In the partial ternary system T_2PbCl_2–ClA, there is only one pseudobinary section T_3–ClA, the phase diagram of which is presented in Fig. 3. It is binary only at lower temperatures while at higher temperatures it is ternary, which will be explained later on. It results from the fact that the oxychloride T_3 with the composition 55.4 wt% (50 mol%) of $PbCl_2$ is formed incongruently at 525°C according to the reaction: $L_{p_3} + T_2 = T_3$ [7].

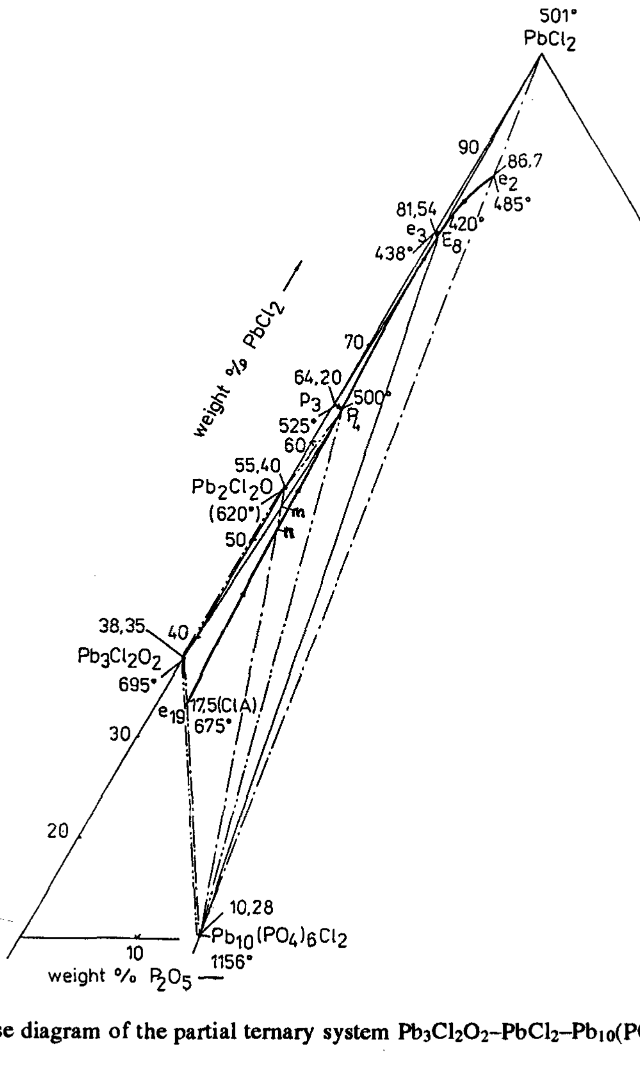

Fig. 4 Phase diagram of the partial ternary system $Pb_3Cl_2O_2$–$PbCl_2$–$Pb_{10}(PO_4)_6Cl_2$

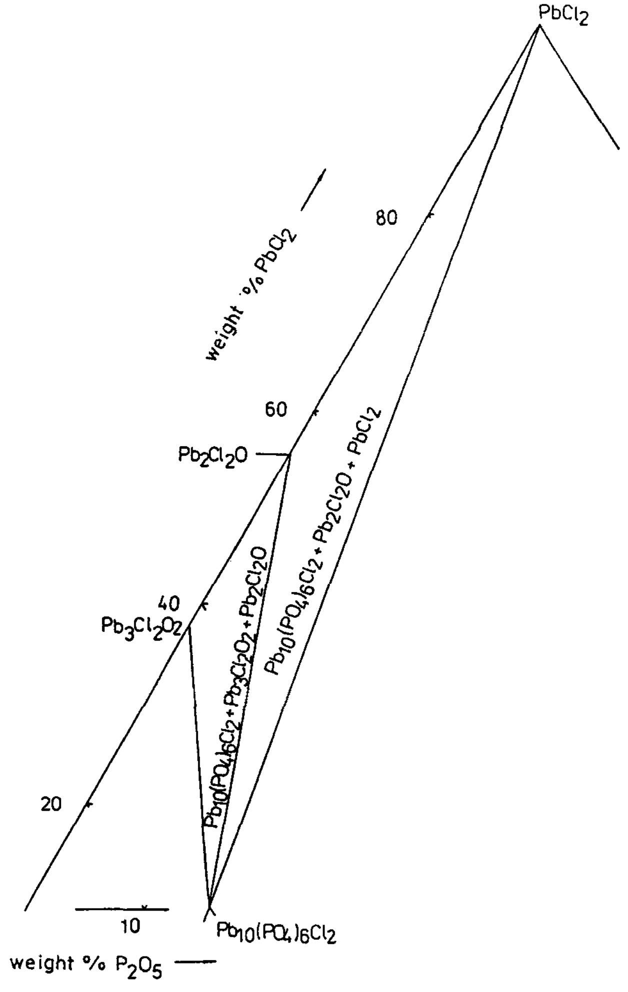

Fig. 5 Isothermal section at room temperature of the partial ternary system $Pb_3Cl_2O_2$–$PbCl_2$–$Pb_{10}(PO_4)_6Cl_2$

The T_3–ClA section divides the partial system under investigation into two smaller partial ternary systems: 1) T_2–T_3–ClA and 2) T_3–$PbCl_2$–ClA, which can be noticed easily in Fig. 4 showing the phase diagram of the ternary system T_2–$PbCl_2$–ClA. The phase dependencies are complex because of the proceeding peritectic reaction. The eutectic curve runs from point e_{19} to P_4 and oxychloride T_2 and chloroapatite ClA crystallize along it according to the reaction: $L = T_2 + ClA$. The peritectic curve runs from point p_3 to P_4 where the oxychloride T_3 is formed from liquid with composition p_3 and oxychloride T_2 according to the reaction: $p_3 + T_2 = T_3$. The curves converge at point P_4 where at 500°C the ternary peritectic reaction: $P_4 + T_2 = T_3 + ClA$ proceeds, which results in the reaction of liquid with composition P_4 and oxychloride T_2 forming

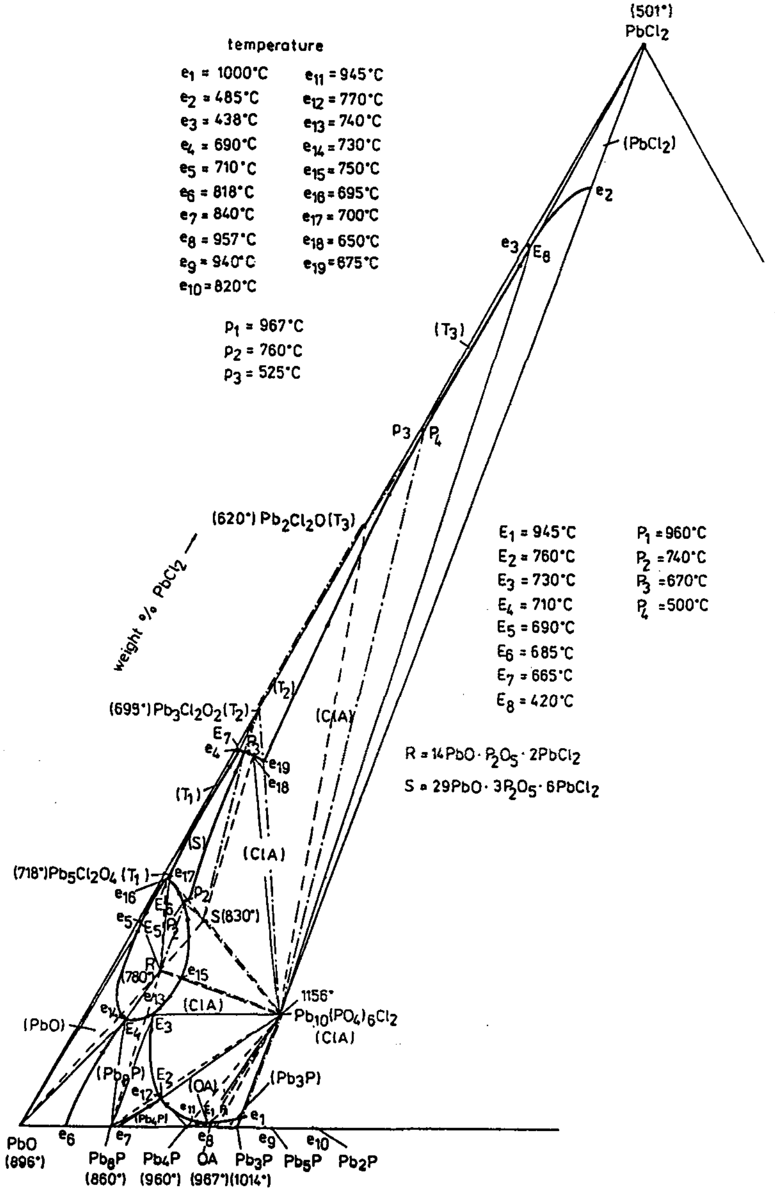

Fig. 6a Phase diagram of the ternary system $PbO–P_2O_5–PbCl_2$ general form

oxychloride T_3 and chloroapatite ClA. The composition of the ternary peritectic P_4 amounts to approx. 35.8 wt% of PbO, 0.5 wt% of P_2O_5 and 63.7 wt% of $PbCl_2$. The T_3–ClA section is binary below 500°C (P_4) and ternary above this temperature (Fig. 3). It cuts off the partial system T_2–T_3–ClA from the partial system T_3–$PbCl_2$–ClA. Figure 5 (isothermal section at room temperature) shows that three phases: T_2 + T_3 + ClA coexist in the partial system T_2–T_3–ClA.

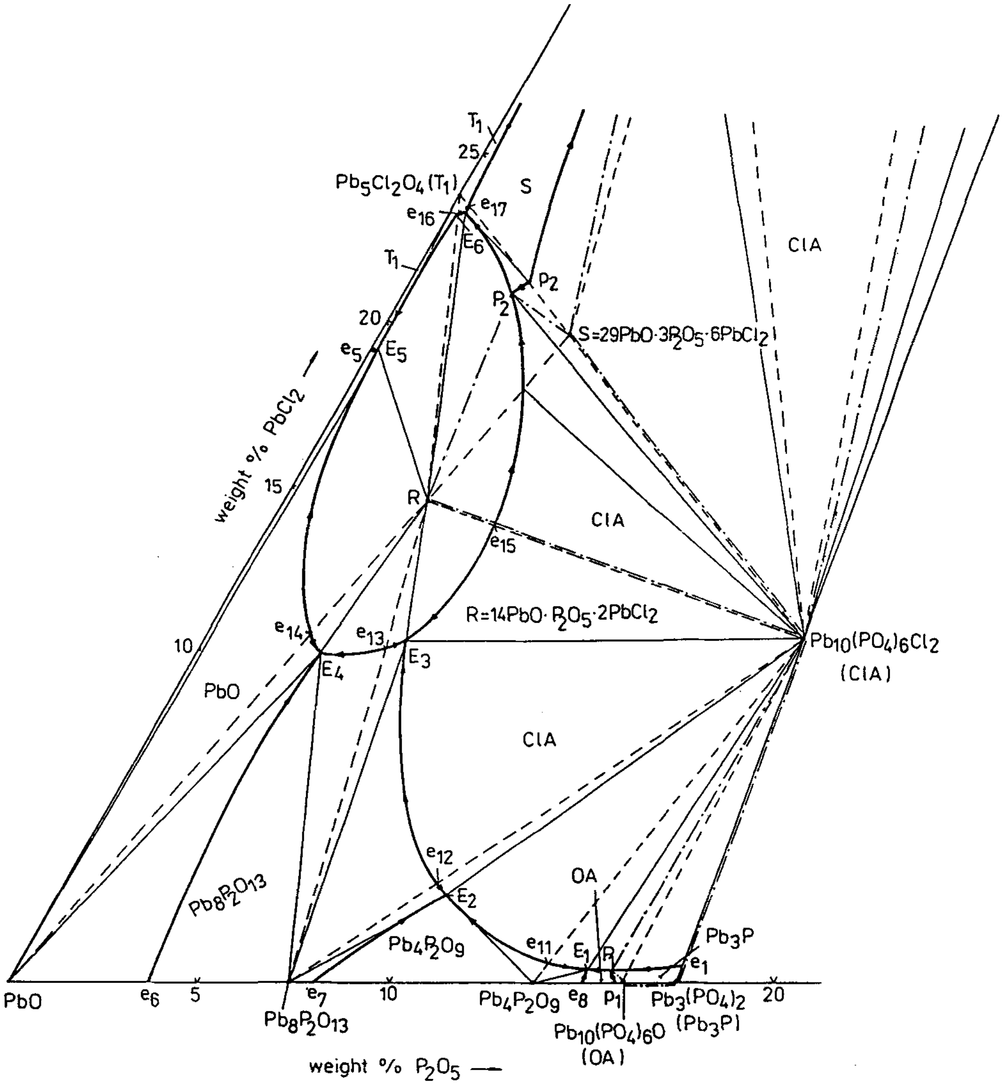

Fig. 6b Phase diagram of the ternary system $PbO–P_2O_5–PbCl_2$ fragment

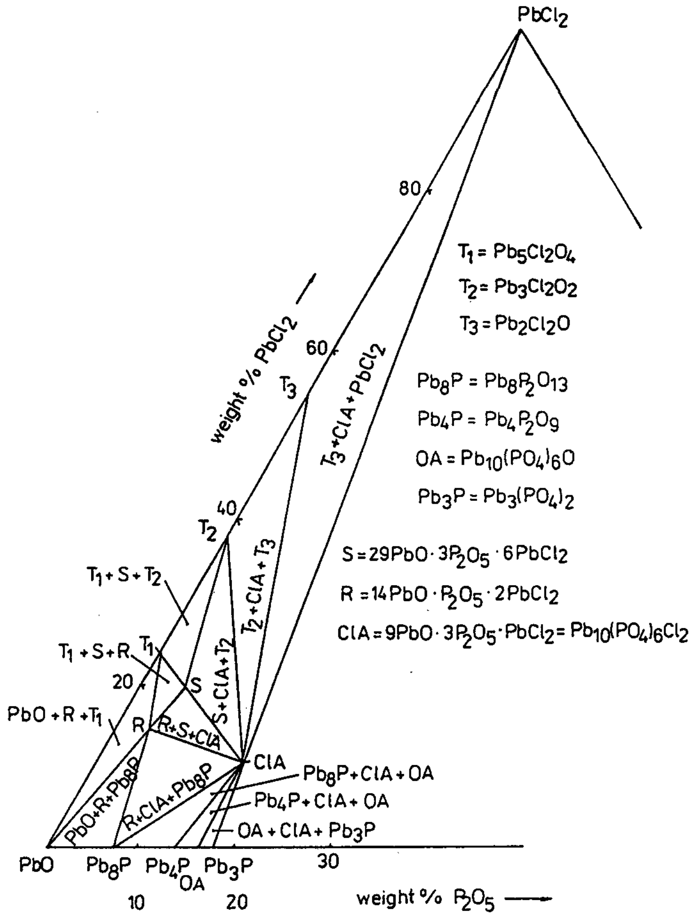

Fig. 7 Isothermal section at room temperature of the ternary system $PbO–P_2O_5–PbCl_2$

In the partial system T_3–$PbCl_2$–ClA, the eutectic curve runs from point e_2 to E_8 and lead chloride and chloroapatite crystallize along it according to the reaction: $L = PbCl_2 + ClA$. Along the eutectic curve e_3E_8 lead chloride and oxychloride crystallize: $L = PbCl_2 + T_3$. The eutectic curve runs from point P_4 to E_8 and oxychloride T_3 and chloroapatite crystallize along it according to the reaction: $L = T_3 + ClA$. The curves converge at point E_8 forming the ternary eutectic $E_8 = T_3 + PbCl_2 + ClA$, the composition of which is approx. 8.5 wt% of PbO, 0.3 wt% of P_2O_5 and 81.2 wt% of $PbCl_2$ and the temperature of 420°C. There are three phases: $T_3 + PbCl_2 + ClA$ (Fig. 5) in this ternary system at room temperature.

Conclusions

The present paper describes the phase dependencies in the partial ternary system T_2–$PbCl_2$–ClA. It is the last part in the series of papers on phase equilibria in the ternary system PbO–P_2O_5–$PbCl_2$ over the composition range $Pb_3(PO_4)_2$–PbO–$PbCl_2$.

Figure 6 presents the phase diagram of the whole system and Fig. 7 the isothermal section at room temperature. In the examined part of the PbO–P_2O_5–$PbCl_2$ system, there are seven binary compounds: $Pb_5Cl_2O_4$, $Pb_3Cl_2O_2$, Pb_2Cl_2O, $Pb_8P_2O_{13}$, $Pb_4P_2O_9$, $Pb_{10}(PO_4)_6O$, $Pb_3(PO_4)_2$, and three ternary compounds: $Pb_{10}(PO_4)_6Cl_2$ = ClA, $14PbO \cdot P_2O_5 \cdot 2PbCl_2$ = R and $29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$ = S. Two of these compounds (ClA and R) crystallize from the liquid phase and the third (S) one is formed in the solid phase. This least compound, which is formed in the binary system $Pb_5Cl_2O_4$–$Pb_{10}(PO_4)_6Cl_2$, has not been known before.

All these compounds form with lead oxide and chloride 11 pseudobinary sections which divide the system into smaller partial eutectic and peritectic systems. It is well represented in Fig. 7. The regions of occurrence of the particular compounds in the system have been established. Their fields of primary crystallization are separated from one another by eutectic and peritectic curves (Fig. 6).

References

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Zusammenfassung — Mittels thermischer, röntgenographischer, mikroskopischer, dilatometrischer und IR-Absorptionsanalyse wurden Phasenabhängigkeiten im ternären System $Pb_3Cl_2O_2$–$PbCl_2$–$Pb_{10}(PO_4)_6Cl_2$ als Teilsystem des ternären Systemes PbO–Pb_2O_5–$PbCl_2$ untersucht. Das Phasendiagramm für das System $Pb_3Cl_2O_2$–$PbCl_2$–$Pb_{10}(PO_4)_6Cl_2$ wurde entwickelt. Man fand, daß die Komponenten keinerlei neue chemische Verbindungen bilden.