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PHASE EQUILIBRIA IN THE TERNARY SYSTEM $PbO–P_2O_5–PbCl_2$ IV. The partial system $Pb_5Cl_2O_4–Pb_3Cl_2O_2–Pb_{10}(PO_4)_6Cl_2$

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Abstract

In the ternary system $PbO–P_2O_5–PbCl_2$, the partial ternary system $Pb_5Cl_2O_4–Pb_3Cl_2O_2–Pb_{10}(PO_4)_6Cl_2$ was examined by thermal, microscopic, X-ray, dilatometric and IR absorption analyses and its phase diagram was provided.

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

Introduction

The present paper is the fourth part of research report on the ternary system $PbO–P_2O_5–PbCl_2$, which has not been described in the literature. The purpose of this study was to establish the phase diagram of the partial system $Pb_5Cl_2O_4–Pb_3Cl_2O_2–Pb_{10}(PO_4)_6Cl_2$. So far, the ternary system $PbO–P_2O_5–PbCl_2$ has been investigated over the composition range $PbO–Pb_5Cl_2O_4–Pb_{10}(PO_4)_6Cl_2$ [1–3]. These examinations resulted in its phase diagram and revealed the existence of a new, previously unknown chemical compound, for which X-ray identification data have been presented [3]. The binary system $PbO–PbCl_2$ which is a side system in the ternary system under investigation, was tested and the data completed [4]. Three lead oxychlorides are formed in it: $Pb_5Cl_2O_4$ (melting point 718°C), $Pb_3Cl_2O_2$ (melting point 695°C), and Pb_2Cl_2O (incongruent, melting point 525°C). Dilatometric examinations for lead oxychlorides [5] and for ternary compounds occurring in the ternary system under examination [6] were carried out as well. The investigations resulted in identification of many thermal and dilatation effects occurring in these compounds.

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Experimental

Compounds occurring in the partial ternary system under discussion were obtained in this laboratory from analytical grade PbO, $PbCl_2$ and $NH_4H_2PO_4$ by synthesis in the solid phase. Before use, lead monoxide PbO was homogenized by sintering at 750°C, while lead chloride $PbCl_2$ and ammonium dihydrogenphosphate $NH_4H_2PO_4$ were dried in a vacuum dessicator. The conditions of synthesis of compounds used in these examinations are shown in Table 1.

The synthesis was performed in platinum crucibles (with the exception of $Pb_3(PO_4)_2$ – for which corundum crucibles were used) in air. The phase purity of the compounds used was examined microscopically in reflected light in molten samples and by X-ray analysis in molten and sintered samples.

The following methods were used in the examinations: thermal analysis (differential method), X-ray phase analysis, microscopic analysis, dilatometric analysis and IR absorption analysis. Samples for the investigations were prepared from the previously obtained compounds, and from lead monoxide, dichloride and orthophosphate.

Thermal examinations, carried out with both heating and cooling of samples, served to draw liquidus and solidus curves in phase diagrams. Resistance furnaces constructed in this laboratory or a derivatograph (MOM, Hungary) and protective argon atmosphere or air were used.

For thermal analysis in a furnace, 10 g samples were placed in platinum crucibles. The furnace was heated or cooled steadily using an electronic recorder (MOM, Hungary) to measure temperature. A derivatograph was only used to perform thermal analysis with heating with 0.5–1.5 g samples.

During dilatometric examinations, phenomena which accompanied physical transitions and chemical reactions at elevated temperatures were observed by following the change in expansion of samples during heating. These examinations were performed in a dilatometer with programmed heating and computerized analysis of results (type 802 BG). Samples for dilatometric investigations were prepared in the form of pressed 3×3×10 mm beams.

Together with thermal examinations for all molten samples, microscopic analysis was carried out in reflected light with a metallographic microscope. The phase purities of the substances used and the phase structures of alloys under investigation could be determined with a high absolute accuracy by microscopic observations.

The phases in all the examined samples were identified by X-ray analysis which was performed by powder method in a Guinier's camera using CuK_α radiation.

All compounds under investigation underwent IR absorption analysis which was performed with potassium bromide pellets in a Specord IR-75 spectrophotometer.

Table 1 The conditions of preparation of the compounds used

Compound prepared	Reactant used for synthesis	Temperature of synthesis /°C	Time of synthesis /h	References
$Pb_5Cl_2O_4$	$PbO + PbCl_2$	650	0.5	[4]
$Pb_3Cl_2O_2$	$PbO + PbCl_2$	600	0.5	[4]
$Pb_3(PO_4)_2$	$PbO + NH_4H_2PO_4$	200	2	
		500	2	[7]
		700	2	
$Pb_{10}(PO_4)_6Cl_2$	$Pb_3(PO_4)_2 + PbCl_2$	500	0.5	[8]
$29PbO{\cdot}3P_2O_5{\cdot}6PbCl_2$	$Pb_5Cl_2O_4 + Pb_{10}(PO_4)_6Cl_2$	700	0.5	[3]
	$PbO + PbCl_2 + Pb_3(PO_4)_2$	600	0.5	[3]

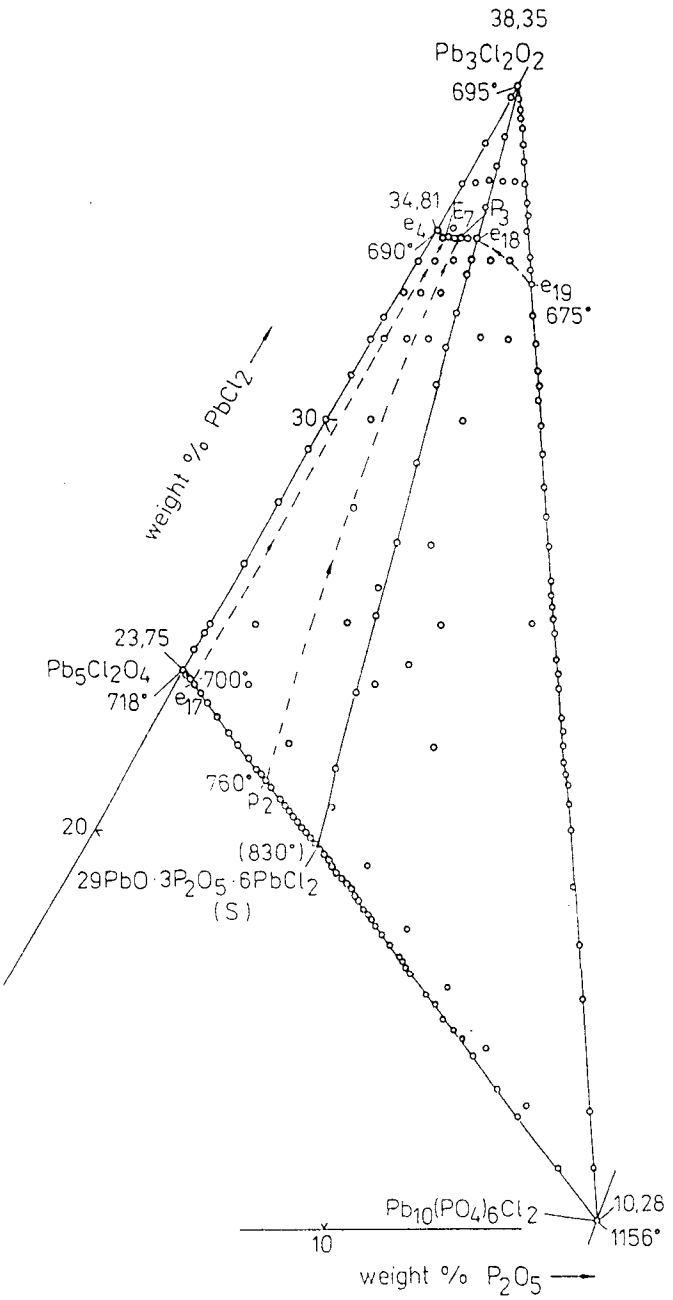

Fig. 1 Position of samples

Results and discussion

The phase diagram of the partial ternary system $Pb_5Cl_2O_4$–$Pb_3Cl_2O_2$–$Pb_{10}(PO_4)_6Cl_2$ was constructed on the basis of the results of thermal, microscopic, X-ray, dilatometric and IR absorption analysis.

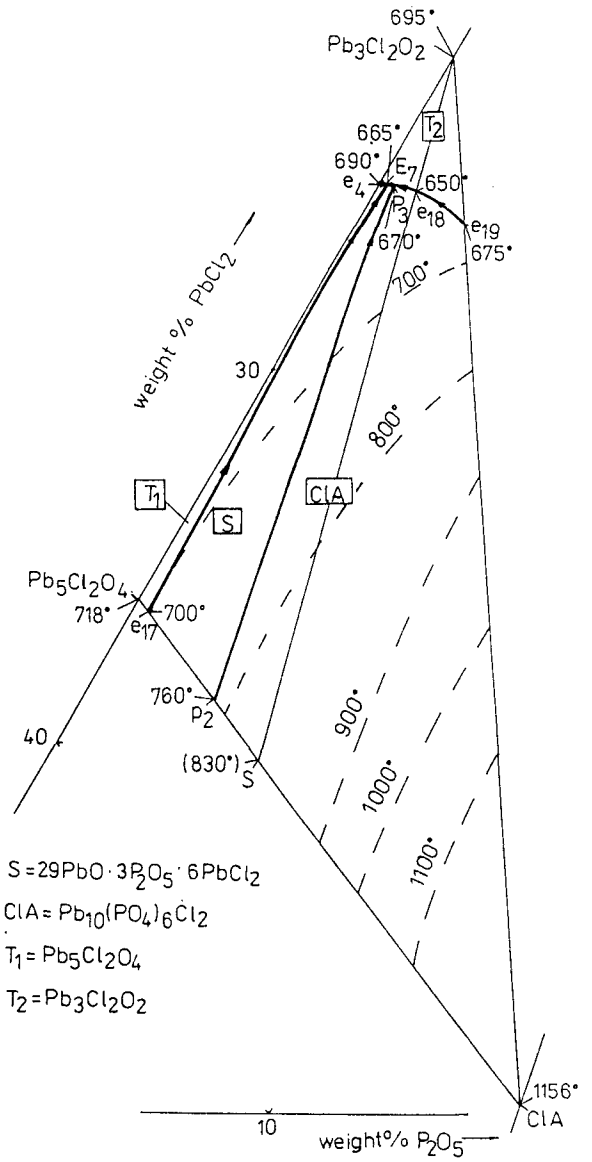

Fig. 2 Liquidus isothermal lines

Figure 1 shows the compositions of samples in the discussed partial system which were examined by thermal, microscopic and X-ray methods. Figure 2 presents the phase diagram of this system with solidification isotherms. The major part of the system is occupied by the primary crystallization field of lead chloroapatite and a smaller area is occupied by primary crystallization fields of the other compounds.

Over the composition range under discussion lead chloroapatite $Pb_{10}(PO_4)_6Cl_2$-ClA crystallizes primarily over the composition range: ClA$p_2P_3e_{18}e_{19}$, the S ternary compound over the range: $p_2e_{16}E_7P_3$, oxychloride $Pb_5Cl_2O_4$-T_1, over: $T_1e_{16}E_7e_4$ and oxychloride $Pb_3Cl_2O_2$-T_2 over the composition range: $T_2e_{18}e_{19}P_3E_7e_4$.

Two pseudobinary sections: 1) T_2-ClA and 2) S-T_2 were found to occur in the partial system T_1-T_2-ClA. The first one is a simple eutectic system, and the second section is binary only at lower and ternary at higher temperatures.

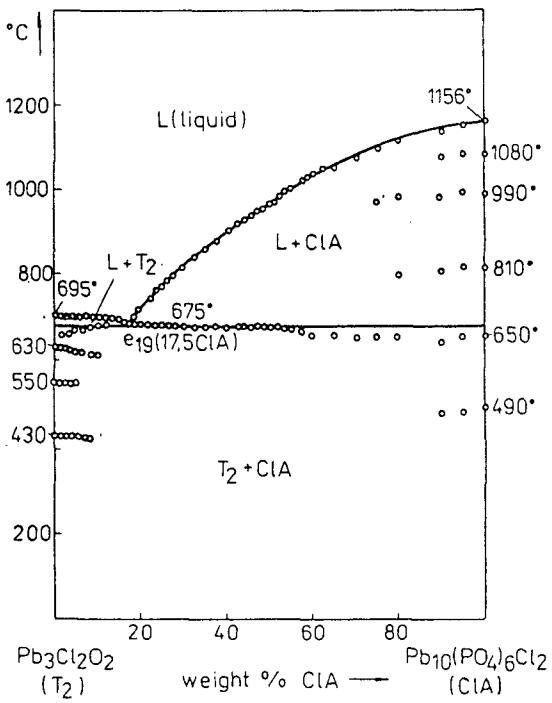

Fig. 3 Phase diagram of the binary section $Pb_3Cl_2O_2$–$Pb_{10}(PO_4)_6Cl_2$

The phase diagram of the first pseudobinary section $Pb_3Cl_2O_2$–$Pb_{10}(PO_4)_6Cl_2$ is shown in Fig. 3. The components form an eutectic system where the eutectic e_{19} contains about 17.5 wt% of chloroapatite and the eutectic temperature is 665°C. The occurrence of some previously described [5, 8] ther-

mal effects in both compounds was confirmed during the investigation of this system.

Figure 4 shows the phase diagram of the second pseudobinary section S-T_2. The ternary compound $29PbO{\cdot}3P_2O_5{\cdot}6PbCl_2$ (S) containing 31.66 wt% of chloroapatite is formed incongruently at 760°C according to the reaction: $Lp_2+ClA=S$ in the binary system $Pb_5Cl_2O_4$–$Pb_{10}(PO_4)_6Cl_2$ [3]. Therefore, above 665°C (P_3) this section is ternary, and below this temperature it is binary, which will be described later. The occurrence of thermal effects in both compounds, which have been described in [5, 6], was confirmed during the examinations of the S-T_2 system. Figure 5 shows the phase diagram of the ternary system T_1-T_2-ClA, and Fig. 6 its isothermal section at room temperature.

The two pseudobinary sections divide the partial ternary system under investigation into two smaller partial ternary systems: 1) T_1-T_2-S and 2) T_2-S-ClA. Phase dependencies which are highly complex because of a peritectic reaction will be described below.

An eutectic curve runs from point e_{18} (across e_{19} point) to P_3 and lead chloroapatite and oxychloride T_2 crystallize along it according to the equation: $e_{18}=T_2+ClA$. From point p_2 to P_3, a peritectic curve runs, where a peritectic reaction forming the ternary compound S takes place according to the reaction: $p_2+ClA=S$. The two curves converge at point P_3 with the approximate composition of 64.85 wt% of PbO, 0.4 wt% of P_2O_5, 64.85 wt% of $PbCl_2$ and at 665°C a peritectic ternary reaction takes place according to the equation: $P_3+ClA=S+T_2$. A liquid with the composition P_3 reacts with chloroapatite which results in formation of the ternary compound S and oxychloride T_2. Below 665°C, the S-T_2 section is binary and above this temperature it is ternary

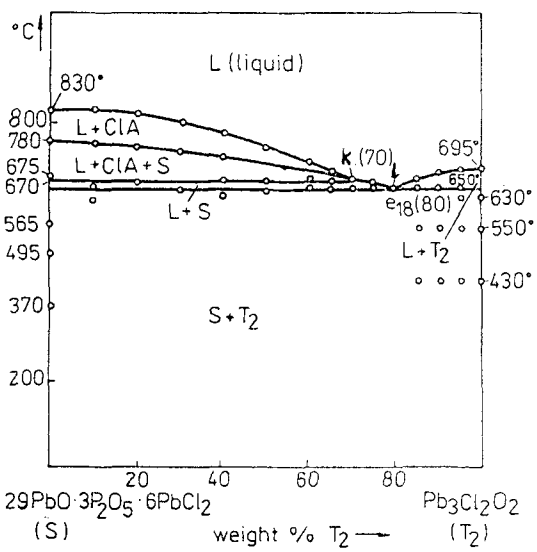

Fig. 4 Phase diagram of the binary section $29PbO{\cdot}3P_2O_5{\cdot}6PbCl_2$–$Pb_3Cl_2O_2$

(Fig. 4). This section cuts off the partial ternary system T_2-S-ClA from the second partial system T_1-T_2-S. Three phases: $S+T_2+$ClA coexist in the partial ternary system T_2-S-ClA, which can be easily noticed in the isothermal section at room temperature presented in Fig. 5.

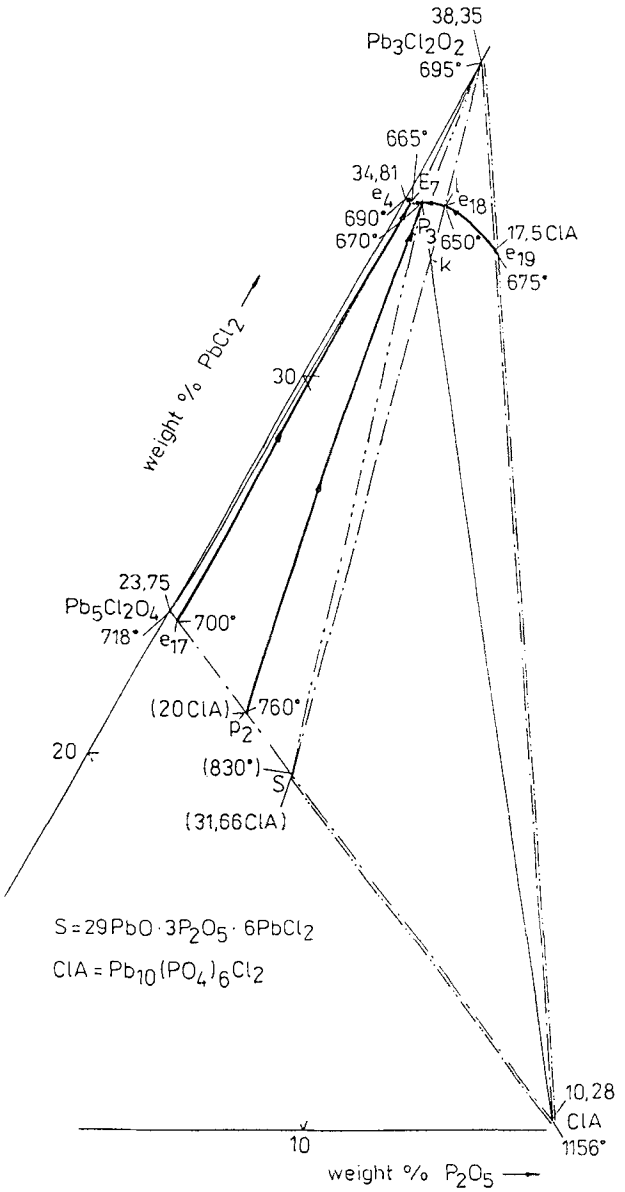

Fig. 5 Phase diagram of partial ternary system $Pb_5Cl_2O_4$–$Pb_3Cl_2O_2$–$Pb_{10}(PO_4)_6Cl_2$

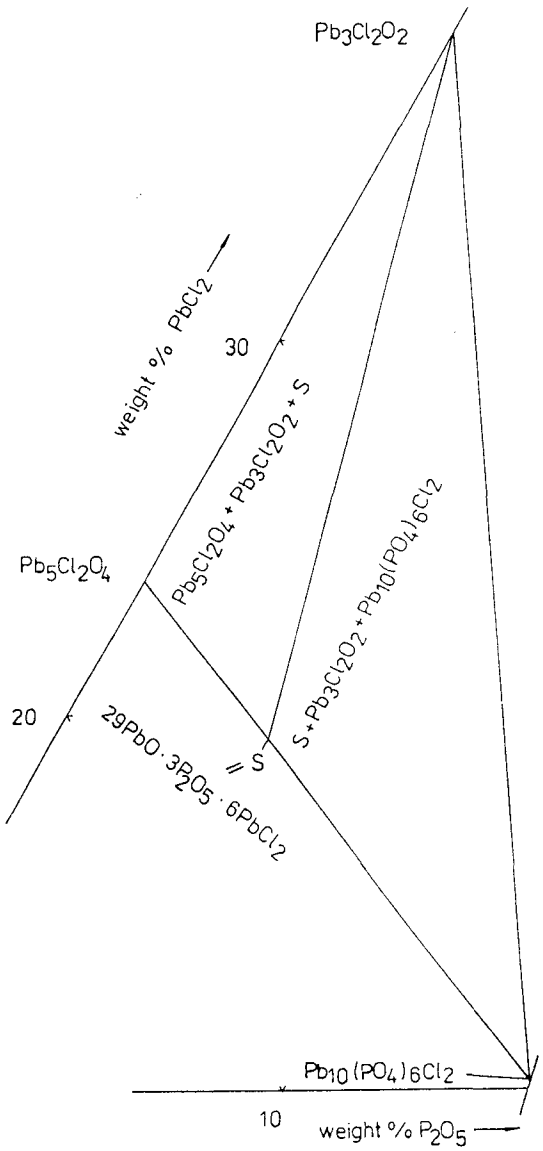

Fig. 6 Isothermal section at room temperature

In the partial system T_1-T_2-S, an eutectic curve runs from point e_{16} to E_7 and, oxychloride T_1 and the ternary compound S : $L=T_1+S$ crystallize along it. Along the eutectic curve e_4E_7, both oxychlorides: $L=T_1+T_2$ crystallize. The crystallization of oxychloride T_2 and the compounds S : $L=T_2+S$ occurs along an eutectic curve which runs from point P_3 to E_7. All three curves converge at

point E_7 forming a ternary eutectic: $E_7 = T_1 + T_2 + S$. This ternary eutectic contains about 65 wt% of PbO, 0.2 wt% of P_2O_5, 34.8 wt% of $PbCl_2$ at 660°C. Three phases $T_1 + S + T_2$ coexist in this partial ternary system at room temperature which can be seen in Fig. 6.

Conclusions

The phase diagram of the partial ternary system T_1-T_2-ClA was established based on the described examinations. Phase dependencies occurring here are interesting, although the components do not form any new chemical compounds.

References

1 H. Podsiadło, J. Thermal Anal., 36 (1990) 1369.
2 H. Podsiadło, J. Thermal Anal., 37 (1991) 139.
3 H. Podsiadło, J. Thermal Anal., 37 (1991) 2239.
4 H. Podsiadło, J. Thermal Anal., 37 (1991) 613.
5 H. Podsiadło, J. Thermal Anal., 37 (1991) 2649.
6 H. Podsiadło, J. Thermal Anal., 39 (1993) 161.
7 J. Berak, H. Dąbrowiecka, Polish J. Chem., 54 (1980) 137.
8 J. Berak, H. Dąbrowiecka, Polish J. Chem., 56 (1982) 1165.

Zusammenfassung — Im ternären System PbO–P_2O_5–$PbCl_2$ wurde mittels thermischer, mikroskopischer, röntgenographischer, dilatometrischer und IR-Absorptionsanalyse das partielle ternäre System $Pb_5Cl_2O_4$–$Pb_3Cl_2O_2$–$Pb_{10}(PO_4)_6Cl_2$ untersucht und das Phasendiagramm entwickelt.