THE PARTIAL SYSTEM Pb$_3$(PO$_4$)$_2$–P$_2$O$_5$–PbCl$_2$

Halina Podsiadlo

Institute of Printing, Warsaw University of Technology, 00217 Warsaw, Konwiktorska 2, Poland

Abstract

The present research proved that no stable compounds are formed in the partial ternary system Pb$_3$(PO$_4$)$_2$–P$_2$O$_5$–PbCl$_2$ of the ternary system PbO–P$_2$O$_5$–PbCl$_2$. Reactions which may proceed in this partial system were considered theoretically. Examinations were performed by thermal, X-ray and chemical analyses.

Keywords: Pb$_3$(PO$_4$)$_2$–P$_2$O$_5$–PbCl$_2$

Introduction

During investigations of the ternary system PbO–P$_2$O$_5$–PbF$_2$ [1] no stable compounds were found to be formed over the composition range Pb$_3$(PO$_4$)$_2$–P$_2$O$_5$–PbF$_2$ since, at higher temperatures, lead phosphates richer in P$_2$O$_5$ than lead orthophosphate react with lead fluoride in the solid phase liberating volatile components. It involves changes in the chemical composition of the initial samples. On analogy with calcium phosphates [2, 3] and magnesium phosphates [4] it was assumed that the volatile product of the reaction is mainly POF$_3$. Thermogravimetric examinations showed that, for example, lead phosphate Pb$_5$P$_4$O$_{15}$ reacts with PbF$_2$ at around 600°C, and lead pyrophosphate Pb$_2$P$_2$O$_7$ at 400°C. Considering the liberation of highly toxic POF$_3$, further examinations of the partial system Pb$_3$(PO$_4$)$_2$–P$_2$O$_5$–PbF$_2$ were abandoned.

A similar procedure was used while investigating the partial system Pb$_3$(PO$_4$)$_2$–P$_2$O$_5$–PbCl$_2$. The subject of our study was the partial system of the ternary system PbO–P$_2$O$_5$–PbCl$_2$ [5–9]. The interaction of the phosphates Pb$_5$P$_4$O$_{15}$ and Pb$_2$P$_2$O$_7$ with lead chloride PbCl$_2$ and with lead chloroapatite Pb$_{10}$(PO$_4$)$_6$Cl$_2$ was examined at higher temperatures. Several chemical reactions which can proceed over this composition range were suggested as well.

Experimental

Analytical purity reagents (PbO, PbCl$_2$ and NH$_4$H$_2$PO$_4$) and those obtained in this laboratory by synthesis in the solid phase (Pb$_3$(PO$_4$)$_2$, Pb$_5$P$_4$O$_{15}$, Pb$_2$P$_2$O$_7$ and Pb$_{10}$(PO$_4$)$_6$Cl$_2$) were used as starting materials.

Lead monoxide PbO was sintered in air in corundum crucibles at 750°C for
0.5 h, then ground in an agate mortar and sieved to obtain fractions with parti-
cle-size <80 μm. Lead chloride $PbCl_2$ and ammonium dihydrogenphosphate
$NH_4H_2PO_4$ were dried in a vacuum desiccator in the presence of P_2O_5. Lead
phosphates $Pb_3(PO_4)_2$, $Pb_5P_4O_{15}$ and $Pb_2P_2O_7$ were obtained from stoichiomet-
ric amounts of PbO and $NH_4H_2PO_4$ by sintering in air in corundum crucibles at
250, 500 and 700°C for 2 h each time [10]. Lead chloroapatite $Pb_{10}(PO_4)_6Cl_2$
was obtained by sintering stoichiometric amounts of $Pb_3(PO_4)_2$ and $PbCl_2$ in
platinum crucibles under argon at 500°C for 0.5 h [11].

The purity of all components was checked by classical chemical analysis.
The phase purity of the used compounds was studied microscopically (except
$NH_4H_2PO_4$) in reflected light for samples melted in platinum crucibles, and by
X-ray diffraction for molten and sintered samples. The results showed that the
chemical compounds used had the intended compositions and did not contain
foreign phases.

Examinations were performed by thermal analysis (differential method) dur-
ing both cooling and heating, thermogravimetric analysis during heating, X-ray
analysis (powder method using a Guinier's camera and CuK_α radiation), and by
classical chemical analysis.

Results and discussion

Figure 1 presents a fragment of the partial ternary system $Pb_3(PO_4)_2–P_2O_5–$
$PbCl_2$, with the compositions of the examined samples marked. They are at sec-
tions $Pb_5P_4O_{15}–PbCl_2$, $Pb_2P_2O_7–PbCl_2$, $Pb_5P_4O_{15}–Pb_{10}(PO_4)_6Cl_2$ and $Pb_2P_2O_7–$
$Pb_{10}(PO_4)_6Cl_2$. As a result of these investigations, the sections were found not
to be stable binary systems. Figure 2 shows the thermogravimetric curves of
a/ $Pb_5P_4O_{15}$, b/ equimolar mixture of $Pb_5P_4O_{15}$ and $PbCl_2$, c/ equimolar mix-
ture of $Pb_5P_4O_{15}$ and $Pb_{10}(PO_4)_6Cl_2$, d/ $Pb_2P_2O_7$, e/ equimolar mixture $Pb_2P_2O_7$
and $PbCl_2$ and f/ equimolar mixture of $Pb_2P_2O_7$ and $Pb_{10}(PO_4)_6Cl_2$.

Figure 2b shows that the decomposition reaction begins at around 450°C in
the solid phase and it is accompanied by a loss in mass amounting to about
2.5%. In the curve presented in Fig. 2c, a slight (approx. 0.5%) and uniform
mass loss can be noticed from about 150°C. In the mixture of $Pb_2P_2O_7$ and
$PbCl_2$ the reaction begins at around 400°C and the accompanying mass loss
amounts to approx. 6.5% (Fig. 2e). The reaction of pyrophosphate with chlo-
roapatite (Fig. 2f) starts at around 250°C and the total mass loss is 1%.

$POCl_3$ was assumed to be one of the decomposition products. In an attempt
to identify the products of the reaction of $Pb_2P_2O_7$ and $PbCl_2$, the gaseous prod-
ucts were passed through an aqueous solution, which was then analysed. The
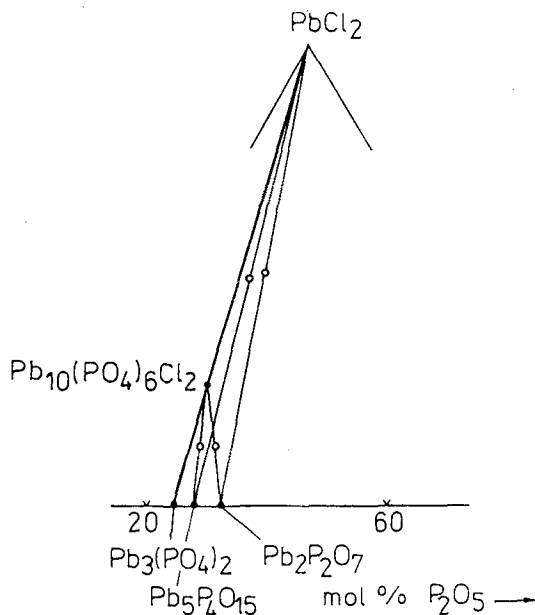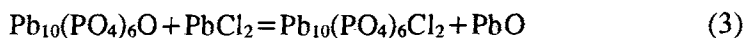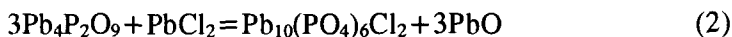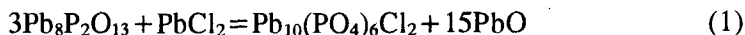results confirmed the above-mentioned hypothesis. X-ray diffractograms of the

Fig. 1 Position of samples

residual solid phase showed lines resulting from only lead pyrophosphate, or-thophosphate and chloroapatite.

Because of the high toxicity of $POCl_3$, the number of preparations studied was kept to a minimum.

Earlier studies of the ternary system $PbO-P_2O_5-PbCl_2$ [5–9] have shown that stable compounds are formed over the composition range $PbO-Pb_3(PO_4)_2-PbCl_2$ while in the other part of this ternary system, no stable compounds are formed. In the partial system $PbO-Pb_3(PO_4)_2-PbCl_2$ lead phosphates poorer in P_2O_5, such as $Pb_8P_2O_{13}$, $Pb_4P_2O_9$ and $Pb_3(PO_4)_2$ or oxyapatite $Pb_{10}(PO_4)_6O$, react with lead chloride according to the following equations:

$$3Pb_8P_2O_{13} + PbCl_2 = Pb_{10}(PO_4)_6Cl_2 + 15PbO \qquad (1)$$

$$3Pb_4P_2O_9 + PbCl_2 = Pb_{10}(PO_4)_6Cl_2 + 3PbO \qquad (2)$$

$$Pb_{10}(PO_4)_6O + PbCl_2 = Pb_{10}(PO_4)_6Cl_2 + PbO \qquad (3)$$

$$3Pb_3(PO_4)_2 + PbCl_2 = Pb_{10}(PO_4)_6Cl_2 \qquad (4)$$

Phosphates richer in P_2O_5, such as $Pb_5P_4O_{15}$ or $Pb_2P_2O_7$, behave in a different way. Various products can be obtained according to the composition of the
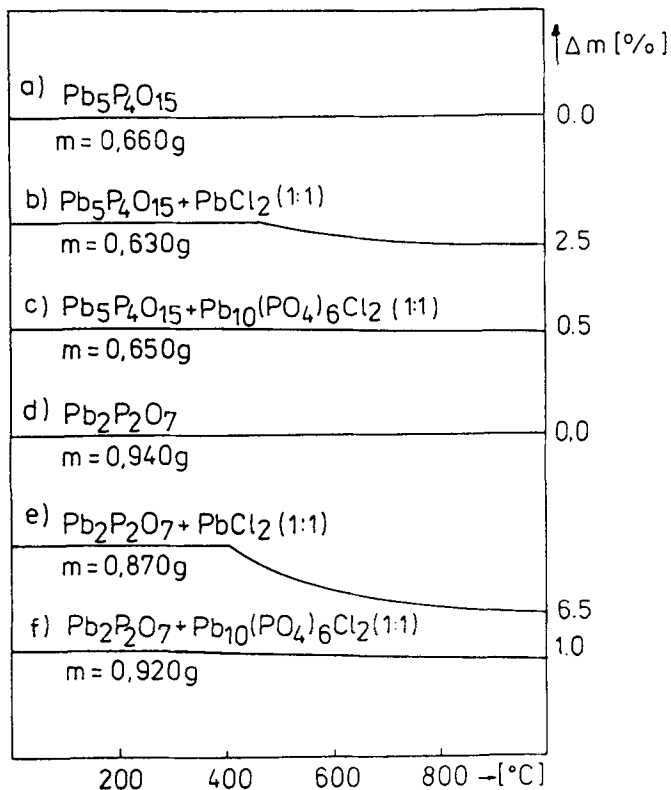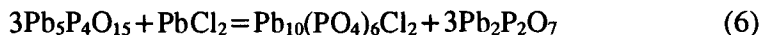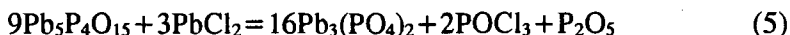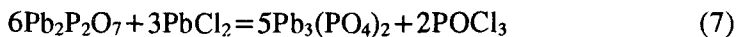
Fig. 2 TG curves for a) $Pb_5P_4O_{15}$, b) the mixture of $Pb_5P_4O_{15}$ and $PbCl_2$ made at the 1:1 molar ratio, c) the mixture of $Pb_5P_4O_{15}$ and $Pb_{10}(PO_4)_6Cl_2$ (1:1), d) $Pb_2P_2O_7$, e) the mixture of $Pb_2P_2O_7$ and $PbCl_2$ (1:1) and f) the mixture of $Pb_2P_2O_7$ and $Pb_{10}(PO_4)_6Cl_2$ (1:1)

preparations. Theoretical considerations concerning this problem will be presented later on based on the results of studies on the system $Ca_3(PO_4)_2-P_2O_5-CaF_2$ [12]. Figure 3 shows how the composition of samples in the system $Pb_3(PO_4)_2-P_2O_5-PbCl_2$ can change. Hence, from the phosphate $Pb_5P_4O_{15}$ and lead chloride $PbCl_2$, $Pb_3(PO_4)_2$ or $Pb_{10}(PO_4)_6Cl_2$ and $Pb_2P_2O_7$ or their mixtures can be obtained according to the reactions:

$$9Pb_5P_4O_{15} + 3PbCl_2 = 16Pb_3(PO_4)_2 + 2POCl_3 + P_2O_5 \qquad (5)$$

$$3Pb_5P_4O_{15} + PbCl_2 = Pb_{10}(PO_4)_6Cl_2 + 3Pb_2P_2O_7 \qquad (6)$$

From lead pyrophosphate $Pb_2P_2O_7$ and lead chloride $PbCl_2$, lead orthophosphate $Pb_3(PO_4)_2$ or lead chloroapatite $Pb_{10}(PO_4)_6Cl_2$ or their mixtures can be obtained according to the reactions:

$$6Pb_2P_2O_7 + 3PbCl_2 = 5Pb_3(PO_4)_2 + 2POCl_3 \qquad (7)$$

$$18Pb_2P_2O_7 + 14PbCl_2 = 5Pb_{10}(PO_4)_6Cl_2 + 6POCl_3 \qquad (8)$$

Lead pyrophosphate or lead chloroapatite or their mixtures can be obtained from lead metaphosphate PbP_2O_6 according to the reactions:

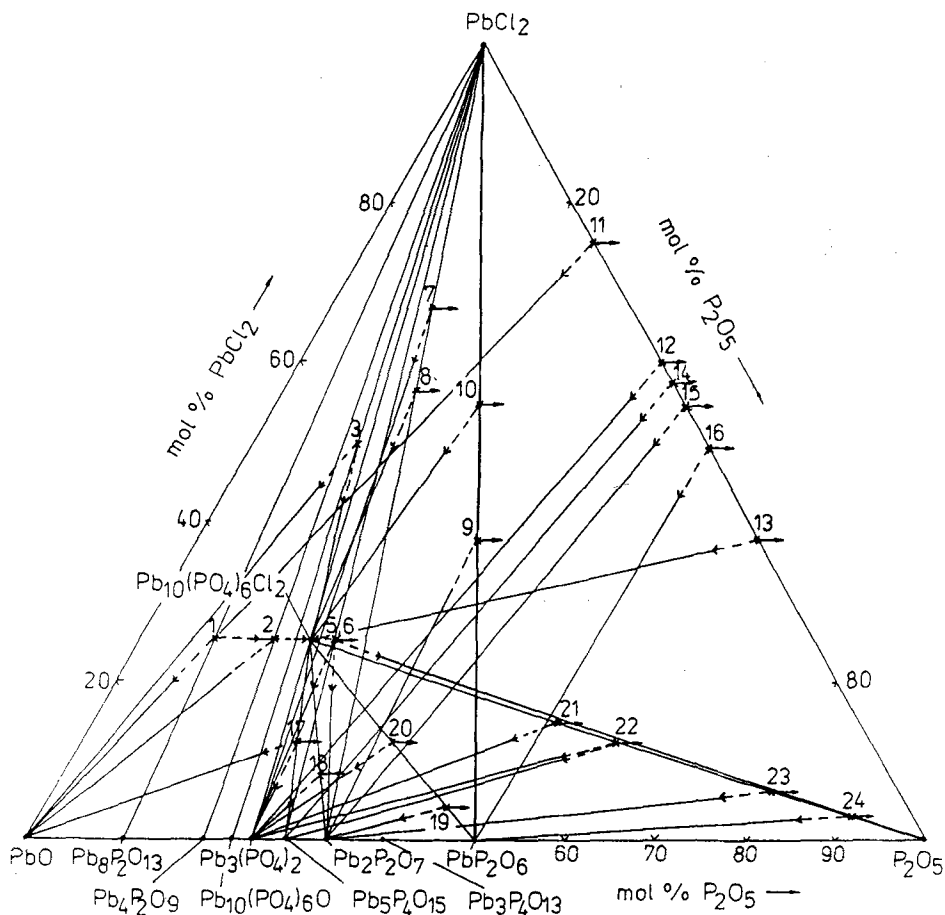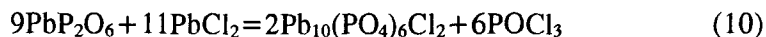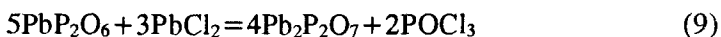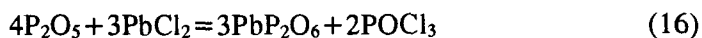$$5PbP_2O_6 + 3PbCl_2 = 4Pb_2P_2O_7 + 2POCl_3 \qquad (9)$$

$$9PbP_2O_6 + 11PbCl_2 = 2Pb_{10}(PO_4)_6Cl_2 + 6POCl_3 \qquad (10)$$

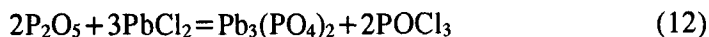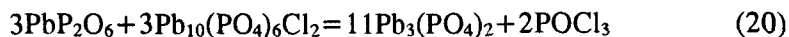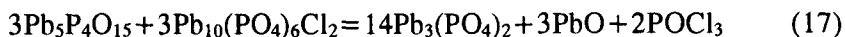**Fig. 3** Reactions in system $PbO-P_2O_5-PbCl_2$ (numbers in the figure correspond to the numbers of reactions, x means the beginning of reaction, arrows ——> mean the direction of reaction, and ⇢ mean $POCl_3$ release)

P_2O_5 can react with $PbCl_2$ as well, and depending on the ratio of the reacting substances, the following approximate equations are possible:

$$P_2O_5 + 3PbCl_2 = 3PbO + 2POCl_3 \qquad (11)$$

$$2P_2O_5 + 3PbCl_2 = Pb_3(PO_4)_2 + 2POCl_3 \qquad (12)$$

$$6P_2O_5 + 10PbCl_2 = Pb_{10}(PO_4)_6Cl_2 + 6POCl_3 \qquad (13)$$

$$11P_2O_5 + 15PbCl_2 = 3Pb_5P_4O_{15} + 10POCl_3 \qquad (14)$$

$$5P_2O_5 + 6PbCl_2 = 3Pb_2P_2O_7 + 4POCl_3 \qquad (15)$$

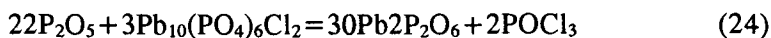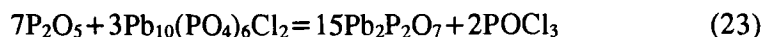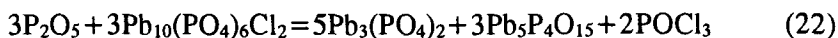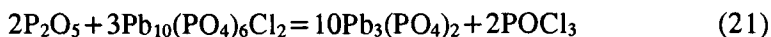$$4P_2O_5 + 3PbCl_2 = 3PbP_2O_6 + 2POCl_3 \qquad (16)$$
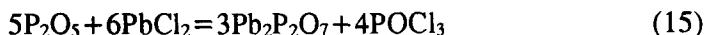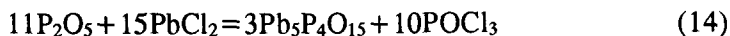
These chemical equations are not accurate since, according to the conditions of the reaction, some side processes causing deviations in composition can occur.

Similar approximate chemical equations were derived for reactions of phosphates with chloroapatite:

$$3Pb_5P_4O_{15} + 3Pb_{10}(PO_4)_6Cl_2 = 14Pb_3(PO_4)_2 + 3PbO + 2POCl_3 \qquad (17)$$

$$6Pb_2P_2O_7 + 3Pb_{10}(PO_4)_6Cl_2 = 14Pb_3(PO_4)_2 + 2POCl_3 \qquad (18)$$

$$14PbP_2O_6 + 3Pb_{10}(PO_4)_6Cl_2 = 22Pb_2P_2O_7 + 2POCl_3 \qquad (19)$$

$$3PbP_2O_6 + 3Pb_{10}(PO_4)_6Cl_2 = 11Pb_3(PO_4)_2 + 2POCl_3 \qquad (20)$$

and for reactions of P_2O_5 with chloroapatite:

$$2P_2O_5 + 3Pb_{10}(PO_4)_6Cl_2 = 10Pb_3(PO_4)_2 + 2POCl_3 \qquad (21)$$

$$3P_2O_5 + 3Pb_{10}(PO_4)_6Cl_2 = 5Pb_3(PO_4)_2 + 3Pb_5P_4O_{15} + 2POCl_3 \qquad (22)$$

$$7P_2O_5 + 3Pb_{10}(PO_4)_6Cl_2 = 15Pb_2P_2O_7 + 2POCl_3 \qquad (23)$$

$$22P_2O_5 + 3Pb_{10}(PO_4)_6Cl_2 = 30Pb2P_2O_6 + 2POCl_3 \qquad (24)$$

Reactions (5–24) could be checked experimentally by the simultaneous analysis of the products. However, complex safety measures would be needed because of the toxicity of $POCl_3$. For this reason, and because such examinations are of no technical importance in the partial system $Pb_3(PO_4)_2-P_2O_5-$

$PbCl_2$, further experiments were abandoned. However, the equations suggested to describe the probable chemical reactions may be helpful in similar investigations.

References

1 J. Berak and H. Dąbrowiecka, Polish J. Chem., 58 (1984) 401.
2 A. Montel, Ann. Chim., Paris, 3 (1956) 313.
3 J. Berak, Roczniki Chem., 35 (1961) 23; 35 (1961) 69; 36 (1962) 403.
4 J. Berak and I. Tomczak, Roczniki Chem., 39 (1965) 519; 39 (1965) 1761.
5 H. Podsiadło, J. Thermal Anal., 36 (1990) 1369.
6 H. Podsiadło, J. Thermal Anal., 37 (1991) 613.
7 H. Podsiadło, J. Thermal Anal., 37 (1991) 2239.
8 H. Podsiadło, J. Thermal Anal., 45 (1995) 471.
9 H. Podsiadło, J. Thermal Anal., 42 (1994) 991.
10 J. Berak and H. Dąbrowiecka, Polish J. Chem., 54 (1980) 137.
11 J. Berak and H. Dąbrowiecka, Polish J. Chem. 56 (1982) 1165.
12 J. Berak, Przem. Chem., 41 (1962) 74.2659

Zusammenfassung — Vorliegende Arbeit zeigt, daß in dem partiellen ternären System $Pb_3(PO_4)_2–P_2O_5–PbCl_2$ des ternären Systemes $PbO–P_2O_5–PbCl_2$ keine stabilen Verbindungen gebildet werden. Reaktionen, die in diesem partiellen System ablaufen können, wurden für rein theoretisch befunden. Die Untersuchung erfolgte durch thermische, Röntgen- und chemische Analyse.