Journal of Thermal Analysis, Vol. 37 (1991) 2239-2251

PHASE EQUILIBRIA IN THE TERNARY SYSTEM PbO-P_2O_5-$PbCl_2$ III. The partial system PbO–$Pb_5Cl_2O_4$–$Pb_{10}(PO_4)_6Cl_2$–$14PbO \cdot P_2O_5 \cdot 2PbCl_2$

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(Received April 3, 1990)

In the ternary system PbO-P_2O_5-$PbCl_2$, the partial system PbO–$Pb_5Cl_2O_4$–$Pb_{10}(PO_4)_6Cl_2$–$14PbO \cdot P_2O_5 \cdot 2PbCl_2$ has been examined by thermal, microscopic, X-ray, dilatometric and IR absorption analyses, and its phase diagram is reported. A new ternary compound with the formula $29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$ has been found to occur, which is formed peritectically in the system $Pb_5Cl_2O_4$–$Pb_{10}(PO_4)_6Cl_2$ making a pseudobinary section here. X-ray identification data on the newly discovered phase are presented.

Introduction

The partial system PbO–$Pb_5Cl_2O_4$–$Pb_{10}(PO_4)_6Cl_2$–$14PbO \cdot P_2O_5 \cdot 2PbCl_2$ forms the third subject of our study on the ternary system PbO–P_2O_5–$PbCl_2$, which has not been described in the literature so far.

The purpose of this study was to establish the phase diagram of this system. It has been presented in [1] and [2] over the composition range PbO–$14PbO \cdot P_2O_5 \cdot 2PbCl_2$–$Pb_{10}(PO_4)_6Cl_2$–$Pb_3(PO_4)_2$. New chemical compounds were not found to occur there. The binary system PbO–$PbCl_2$, tested and completed, was described in [3]. Over the composition range from 0 to 20 mol% (23.75 wt%) of PbO, only one lead oxychloride, with the formula $Pb_5Cl_2O_4$ (melting point 718°C), occurs in it. Together with PbO, this lead oxychloride forms a eutectic system with a eutectic composition e_1 of approx. 19.18 wt% (16 mol%) of $PbCl_2$ and a eutectic temperature of 710°C. X-ray identification data on $Pb_5Cl_2O_4$ were presented in [3] and it was found that this compound crystallizes in the tetragonal system with lattice constants

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$a=b=3.894$ Å and $c=13.070$ Å. Effects at 350, 420, 540 and 620°C during heating and cooling, were identified in thermal investigations and dilatometric ones during the heating of this oxychloride [4].

Experimental

The following reagents were used: PbO p.a., $PbCl_2$ p.a., and $NH_4H_2PO_4$ p.a.; and obtained in this laboratory (by synthesis in the solid phase): $Pb_5Cl_2O_4$, $Pb_3(PO_4)_2$, $Pb_{10}(PO_4)_6Cl_2$, $14PbO \cdot P_2O_5 \cdot 2PbCl_2$ (R) and $29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$ (S).

Before use, PbO p. a. was sintered at 750°C for 0.5 h then ground and sieved; $PbCl_2$ p.a. and $NH_4H_2PO_4$ p.a. were dried in a vacuum desiccator.

Table 1 presents the conditions of obtaining the other compounds used.

Table 1 The conditions of obtaining compounds in use

Obtained compound	Components used for syntesis	Temperature, °C of synthesis	Time, h	References
$Pb_5Cl_2O_4$	$PbO + PbCl_2$	650	0.5	[3]
$Pb_3(PO_4)_2$	$PbO + NH_4H_2PO_4$	250	2	
		500	2	[5]
		700	2	
$Pb_{10}(PO_4)_6Cl_2$	$Pb_3(PO_4)_2 + PbCl_2$	500	0.5	[6]
$14PbO \cdot P_2O_5 \cdot 2PbCl_2$	$PbO + Pb_3(PO_4)_2 + PbCl_2$	700	0.5	[2]
	$Pb_5Cl_2O_4 + Pb_{10}(PO_4)_6Cl_2$	700	0.5	
$29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$				
	$PbO + Pb_3(PO_4)_2 + PbCl_2$	600	0.5	

The phase purity of all compounds used was examined microscopically in reflected light for molten samples, and by X-ray for molten and sintered samples.

Samples with compositions on binary sections were generally prepared from the compounds prepared previously from the initial components, but from PbO, $PbCl_2$ and $Pb_3(PO_4)_2$ as well, while samples with compositions inside the ternary system were usually prepared from PbO, $PbCl_2$ and $Pb_3(PO_4)_2$.

The examinations were carried out by means of thermal, microscopic, X-ray phase, dilatometric and IR absorption analyses [1–4].

Thermal analysis (differential method) was performed in protective argon atmosphere or in air, either in furnaces constructed in this laboratory, during

both cooling and heating, using 10 g samples (temperature read by an electronic recorder, MOM, Hungary), or in a derivatograph (MOM, Hungary, type 3247), only during heating, using 0.5–1.5 g samples. Dilatometric examinations during heating of PbO, $PbCl_2$, $Pb_3(PO_4)_2$ and $Pb_{10}(PO_4)_6Cl_2$ (10–20 g samples) were carried out in a Hungarian derivatograph (3247, MOM) with photographic recording, and for $Pb_5Cl_2O_4$, $14Pb \cdot P_2O_5 \cdot 2PbCl_2$ and $29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$ (beam 3×3×10 mm samples) in a dilatometer (802 BG, Germany) with programmed heating and computerized data analysis.

Microscopic observations of microsections were carried out on all molten samples in reflected light.

X-ray analysis was performed at room temperature by the powder method, using a focusing Guinier–de Wolff camera (radiation $\lambda(CuK_\alpha) =$ 1.5418 Å, quartz monochromator) and a DRON-2.0 diffractometer (radiation $\lambda(CuK_\alpha) = 1.5418$ Å, Ni-filter). The results of these investigations, which are mainly of a qualitative character here, were primarily used to identify the phases present in the preparations. This identification was performed on the basis of X-ray data, in accordance with the PDF1 data base. The positions of diffraction lines during indexing were calculated with the use of α-Al_2O_3 as internal standard. The indexing was performed with an automatic POWDER program [7], and the solution with the best fit was accepted [8].

IR absorption analysis was carried out in a Specord IR-75 spectrophotometer over the radiation range 400–4000 cm^{-1}, using pellet samples with potassium bromide.

Results and discussion

The partial ternary system PbO–$Pb_5Cl_2O_4$(T_1)–$Pb_{10}(PO_4)_6Cl_2$(ClA)–$14PbO \cdot P_2O_5 \cdot 2PbCl_2$(R) was examined by means of thermal, microscopic, X-ray, dilatometric and IR absorption analyses. The compositions of the samples in the system under investigation are indicated by points in Fig. 1. Their clearly visible concentration at the section $Pb_5Cl_2O_4$–$Pb_{10}(PO_4)_6Cl_2$ is caused by a new ternary compounds in this binary system, which was discovered during these investigations.

This new phase, which in an oxygen form can be assigned the formula $29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$, and is called S for simplification, melts incongruently at 760°C (Fig. 3).

The possibilities of formation of lead oxychlorides richer in PbO than T_1 [3], and of pseudobinary sections of these hypothetical oxychlorides with the ternary compound R, apatite or phosphates $Pb_8P_2O_{13}$ and $Pb_3(PO_4)_2$, were

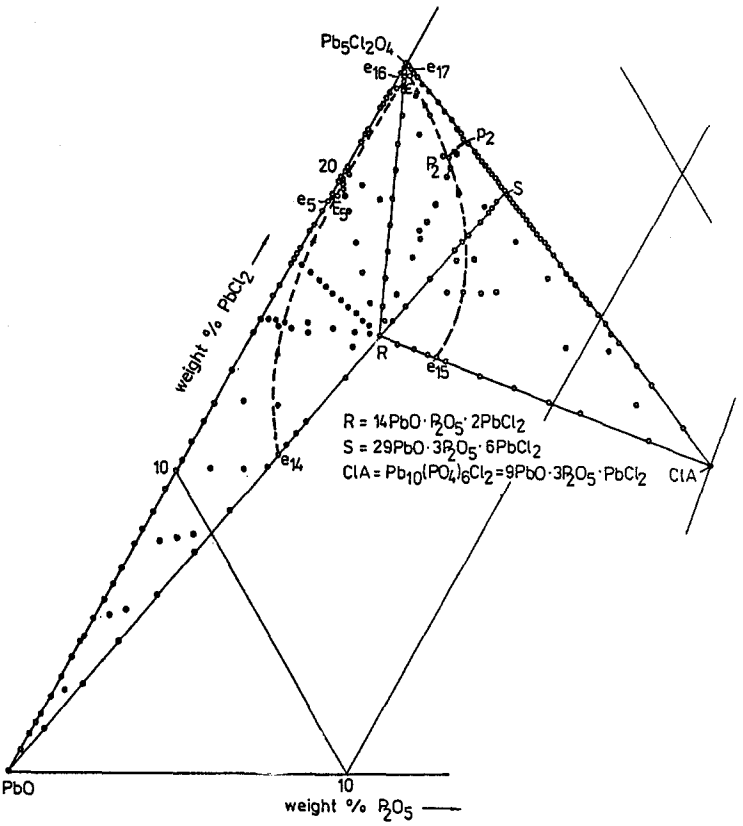

Fig. 1 Position of samples

tested during investigations of this partial system. For this purpose, compounds R, ClA, $Pb_8P_2O_{13}$ and $Pb_3(PO_4)_2$ were added to samples with compositions corresponding to hypothetical oxychlorides with the formulae $Pb_8Cl_2O_7$, $Pb_7Cl_2O_6$ and $Pb_6Cl_2O_5$, and the mixtures were then examined by thermal, microscopic and X-ray methods. The results of these examinations confirmed that only the compound $Pb_5Cl_2O_4$ is formed under these conditions in the PbO-$PbCl_2$ system over the composition range up to 20 mol%.

Figure 2 shows the phase diagram of the partial ternary system under discussion, with the solidification isotherms. The major part of the system is occupied by the primary crystallization field of the ternary compound R, a smaller one by the primary crystallization field of lead chlorapatite ClA, and a still smaller one by that of PbO. The primary crystallization fields of the oxychloride T_1 and of the ternary compound S occupy much smaller areas.

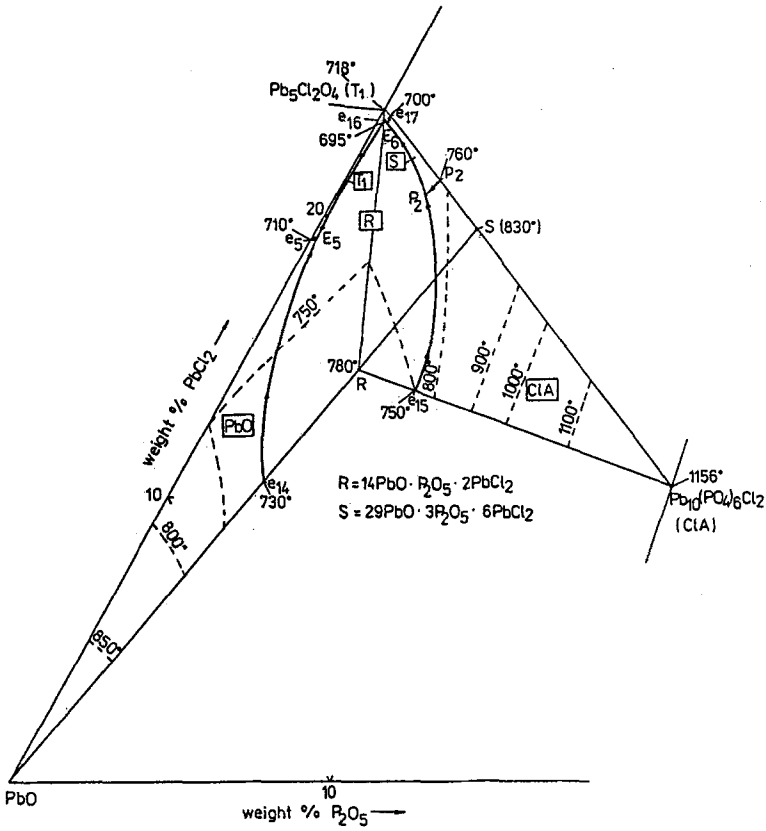

Fig. 2 Liquidus isothermal lines

In the part of the ternary system PbO–P_2O_5–$PbCl_2$ under investigation, PbO crystallizes primarily over the composition range $PbOe_5E_5e_{14}$, $Pb_5Cl_2O_4(T_1)$ does so over the range $T_1e_{17}E_6e_{16}E_5e_5$, the ternary compound S does so over $p_2P_2E_6e_{17}$, lead chlorapatite $Pb_{10}(PO_4)_6Cl_2$(ClA) does so over $ClAe_{15}P_2p_2$ and the ternary compound R does so over the composition range $Re_{14}E_5e_{16}E_6P_2e_{15}$.

Three pseudobinary sections:

1) $Pb_5Cl_2O_4$-$Pb_{10}(PO_4)_6Cl_2$,

2) $14PbO \cdot P_2O_5 \cdot 2PbCl_2$–$Pb_5Cl_2O_4$ and

3) $14PbO \cdot P_2O_5 \cdot 2PbCl_2$–$29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$ were found to occur over the composition range PbO–T_1–ClA–R.

The phase diagram of the first pseudobinary section T_1–ClA is presented in Fig. 3. The oxychloride and chlorapatite form a pseudobinary section

where a new compound with the formula $29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$ occurs at a 5:1 molar ratio of the initial components (31.66 wt% of ClA).It melts incongruently at 760°C. In this system, the eutectic e_{17} is formed at a ClA content of 2.5 wt% at 700°C, and the peritectic p_2 at 20 wt% of ClA. For samples corresponding to the compound S, the end of melting (or the beginning of crystallization) was at 830°C.

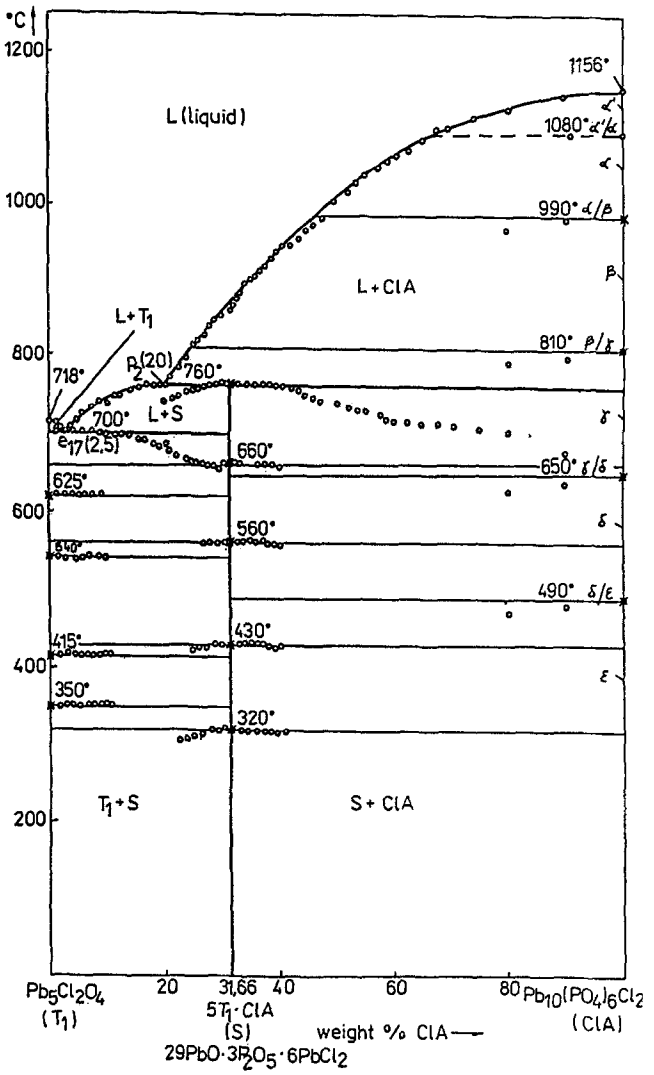

Fig. 3 Phase diagram of binary section $Pb_5Cl_2O_4$–$Pb_{10}(PO_4)_6Cl_2$

Thermal and dilatometric examinations [9] revealed that thermal and dilatation effects occur at 370, 495, 565, 605 and 675°C in this system. Microscopic and X-ray investigations proved that this compound was a homogeneous phase, so the observed effects were not caused by impurities. During the studies on the system T_1–ClA, it was discovered that these effects were clear in pure compound S and close to it, but they then disappeared. To explain these effects unambiguously, high-temperature X-ray examinations are necessary, which is very difficult with this group of compounds because of their high reactivity.

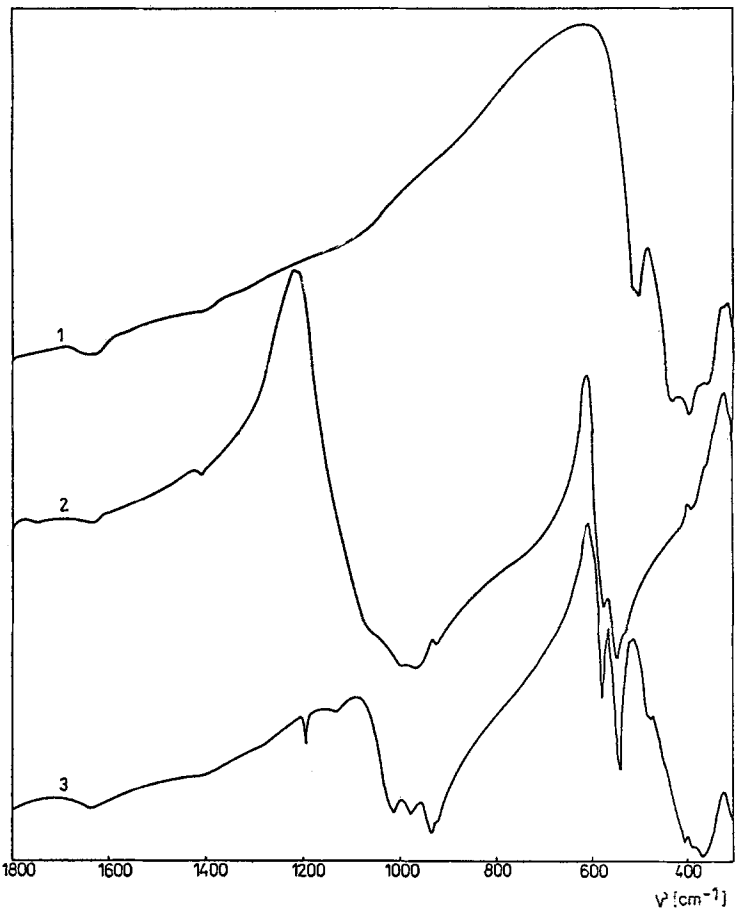

Fig. 4 IR spectra of T_1 (curve 1), ClA (curve 2) and S (curve 3)

X-ray examinations were performed on compound S in order to determine its structure. The same methods were used as for the X-ray structural ex-

Table 2 X-ray identification data for phase *S*

$2\Theta_{exp}$ (Cu–K$\bar{\alpha}$)	d_{exp}	d_{calc}	h	k	l
7.98	11.08	11.08	(0	1	1)
11.96	7.40	7.48	(0	1	2)
15.14	5.85	5.85	0	0	3
15.93	5.56	5.54	0	2	2
17.60	5.04	5.02	1	2	0
19.42	4.57	4.59	0	3	1
22.53	3.95	3.95	1	3	0
23.34	3.81	3.81	1	2	3
25.22	3.53	3.54	2	0	0
25.33	3.51	3.51	0	0	5
25.98	3.43	3.44	2	1	0
29.33	3.04	3.05	0	4	3
29.37	3.04	3.03	2	0	3
30.61	2.92	2.93	0	0	6
31.97		2.799 { 2.803	2	3	1
...		2.799	1	4	3
32.13	2.786	2.788	2	2	3
32.28	2.773	2.769	0	4	4
33.06		2.715	0	5	2
...		2.708	0	2	6
...		2.710 { 2.706	2	1	4
...		2.705	1	0	6
...		2.702	2	3	2
33.89	2.645	2.647	1	5	0
40.32		2.237 { 2.240	3	2	0
...		2.237	1	6	1
40.56		2.222	2	1	6
...		2.224 { 2.228	3	2	1
...		2.222	2	5	0
...		2.219	0	3	7
43.05		2.104	1	6	3
...		2.101 { 2.099	3	3	1
...		2.097	1	0	8
...		2.098	0	2	8

system: orthorhombic
lattice parameters: $a = 7.081 \pm 1$Å, $b = 14.27 \pm 1$Å, $c = 17.56 \pm 1$Å
volume of the unit cell: 1774.8 Å^3
lattice type: P

aminations of compound T_1 [3]. The X-ray data [10] on all the known compounds which can be formed in this reacting system indicated that compound S formed a new phase. In preparations with different compositions, its quantity changed at a uniform rate on addition of one of the initial components (T_1 or ClA). Table 2 shows X-ray identification data on phase S. It is probable that, phase S exhibits from a structural aspect, a deformation from the tetragonal to the orthorhombic system. Some diffraction lines can be recognized as doublets from this deformation. The constant $\vec{a}$ is almost twice as small as constant $\vec{b}$, which may suggest the occurrence of structural subunits along direction $\vec{b}$, with identity period equal to constant $\vec{a}$.

Several attempts to obtain monocrystals of compound S were unsuccessful, which is due to a large extent to its peritectic formation.

Figure 4 presents the IR spectra of the T_1 and ClA initial components and of phase S newly formed from them. However, as mentioned above, the results of examinations of new phases by IR absorption analysis do not result in interesting information because there are no standards of analysed substances and the obtained spectra are poorly resolved.

Figure 5 shows the phase diagram of the second pseudobinary section R–T_1. The components form a simple eutectic system with the eutectic e_{16} com-

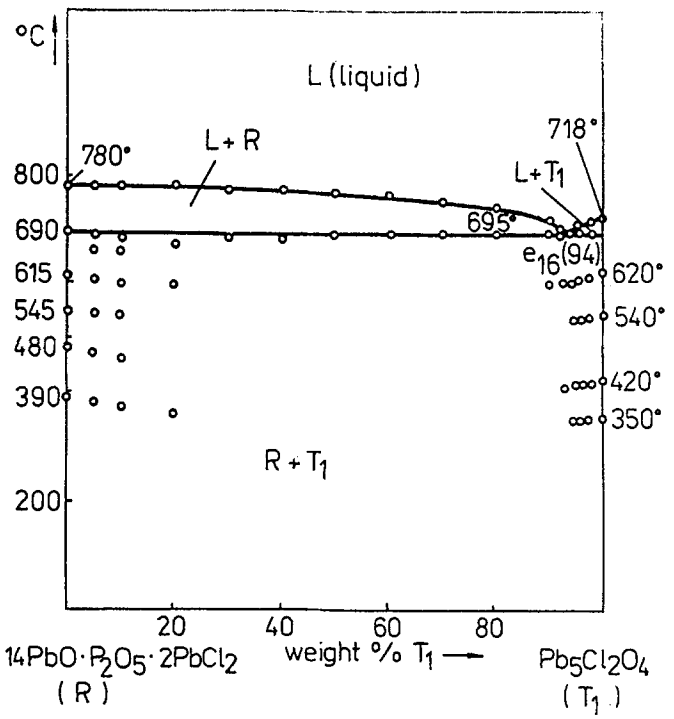

Fig. 5 Phase diagram of binary section $14PbO \cdot P_2O_5 \cdot 2PbCl_2$–$Pb_5Cl_2O_4$

position amounting to approx. 94 wt% of T_1 at 695°C. During the examination of this system, the occurrence of the thermal and dilatometric effects described above was confirmed during the heating and cooling of both compounds.

Figure 6 shows the phase diagram of the pseudobinary section R–S, which is the third and last one in the composition range under discussion. The components do not form any new chemical compounds.

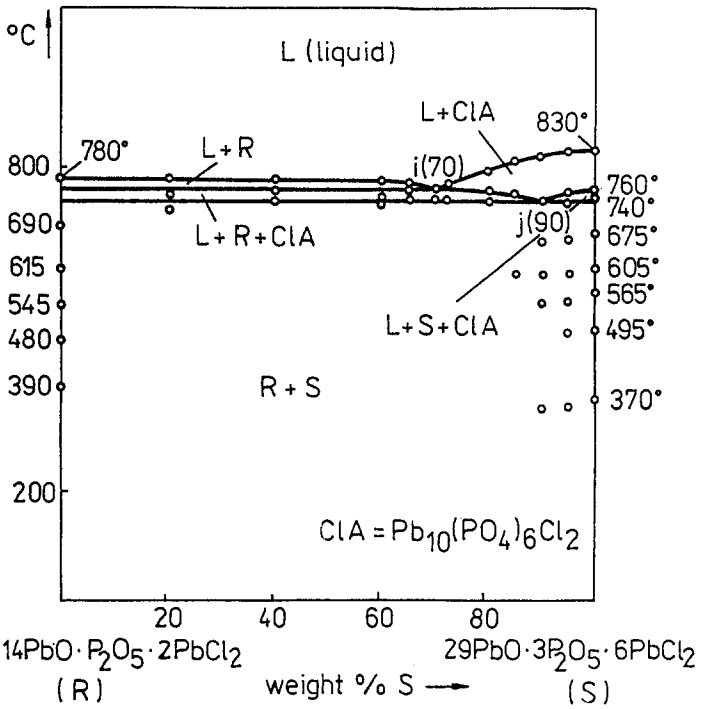

Fig. 6. Phase diagram of binary section $14PbO \cdot P_2O_5 \cdot 2PbCl_2$–$29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$

As mentioned previously, compound S is formed peritectically (Fig. 3) at a ClA content of 31.66 wt% (16.67 mol%) at 760°, according to the reaction: $L_{P_2} + 9PbO \cdot 3P_2O_5 \cdot PbCl_2$ (ClA) = $29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$ (S). For this reason, above 740°C (P_2) the R–S section is ternary and below this temperature it is binary, which will be discussed below.

The above pseudobinary sections divide the partial ternary system under investigation into three smaller partial ternary systems: 1)PbO–T_1–R, 2)T_1–R–S and 3) S–R–ClA. Figure 7 presents the phase diagram of the partial ter-

nary system PbO–T_1–ClA–R, and Fig. 8 shows its isothermal section at room temperature.

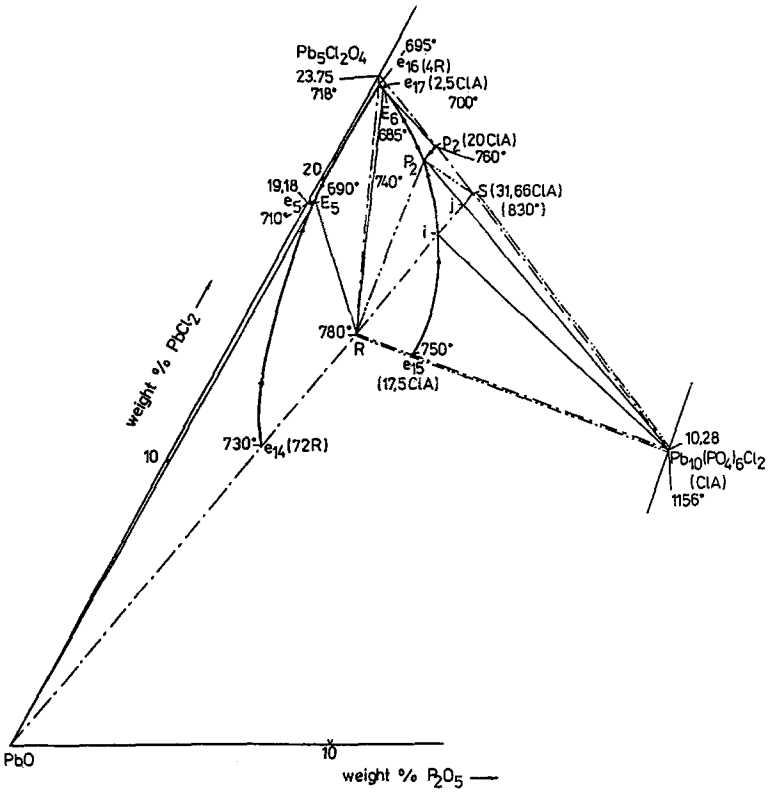

Fig. 7 Phase diagram of partial ternery system PbO–$Pb_5Cl_2O_4$–$Pb_{10}(PO_4)_6Cl_2$–$14PbO \cdot P_2O_5 \cdot 2PbCl_2$ (— · · — · · — peritectic reaction)

The partial ternary system PbO–T_1–R is a eutectic system with ternary eutectic E_5 of composition approx. 80.60 wt% of PbO, 0.15 wt% of P_2O_5 and 19.25 wt% of $PbCl_2$ and a temperature of 690°C. PbO and the ternary compound R crystallize along the eutectic curve $e_{14}E_5$:L = PbO + R. The eutectic curve runs from point e_5 to E_5, and PbO and oxychloride crystallize along it: L = PbO + T_1. Oxychloride and compound R crystallize along the eutectic curve $e_{16}E_5$:L = T_1 + R. The three curves converge at point E_5, where the ternary eutectic reaction takes place according to the equation E_5 = PbO + T_1 + R. Three phases coexist at room temperature in the partial ternary system PbO-T_1-R: PbO + T_1 + R. This can easily be seen in Fig. 8,

which presents the isothermal section of the system PbO-T_1-ClA-R at room temperature.

The second partial system T_1–R–S and the third one R–S–ClA are more complex because of the ternary peritectic reaction taking place at 740°C. Along the eutectic curve $e_{15}P_2$ (across point *i*), lead chlorapatite and compound R crystallize according to the equation: $e_{15} = R + ClA$, and along the peritectic curve p_2P_2 compound S is formed in the peritectic reaction according to the equation: $p_2 + ClA = S$. The two curves converge at point P_2 at a composition of approx. 76.50 wt% of PbO, 2.85 wt% of P_2O_5 and 20.65 wt% $PbCl_2$, where the peritectic ternary reaction takes place according to the equation $P_2 + ClA = S + R$ at 740°C. The liquid with composition P_2 reacts with chlorapatite, and both ternary compounds S and R are formed as a result of this reaction. Below 740°C, the S–R section is binary, while above this

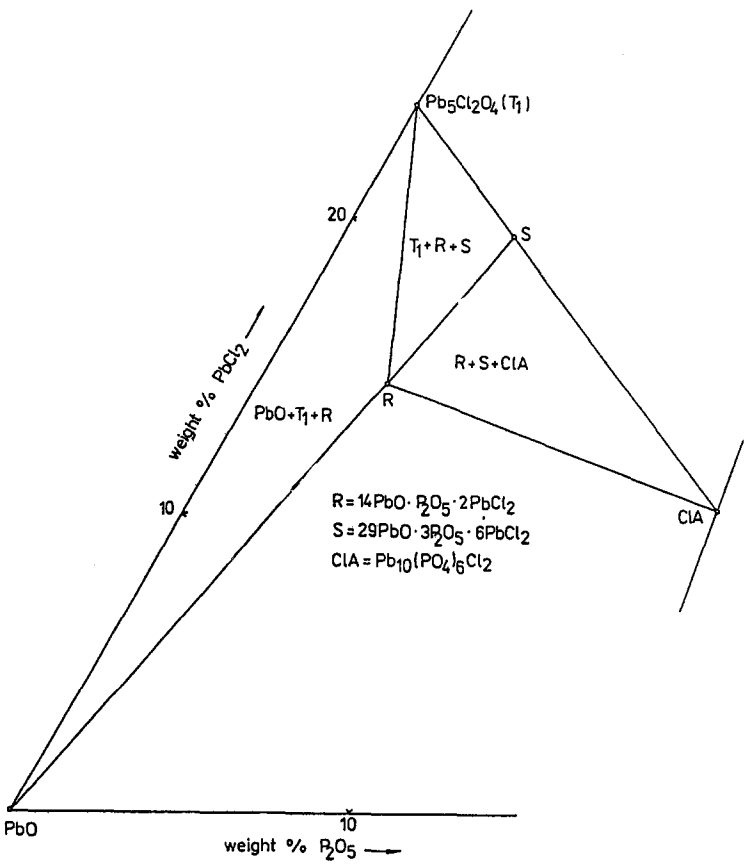

Fig. 8 Isothermal section at room temperature

temperature it is ternary (Fig. 6) and it cuts off the partial system R-S-ClA from the second partial system T_1–R–S. Three phases, R + S + ClA (Fig. 8), coexist at room temperature in the partial ternary system R–S–ClA.

The eutectic curve runs from point P_2 to E_6 in the partial system T_1–R–S, and ternary compounds crystallize along it: L = R + S. Oxychloride T_1 and ternary compound S crystallize along the eutectic curve which runs from point e_{17} to E_6: L = T_1 + S. Oxychloride T_1 and compound R crystallize along the eutectic curve $e_{16}E_6$: L = T_1 + R. The eutectic ternary reaction $E_6 = T_1 + R + S$ takes place at point E_6, were all three curves converge at 685°C. The composition of the ternary eutectic E_6 is approx. 76.40 wt% of PbO, 0.35 wt% of P_2O_5 and 23.25 wt% of $PbCl_2$. Three phases coexist in this partial ternary system at room temperature: $T_1 + R + S$.

Conclusions

The investigation of the partial ternary system PbO–$Pb_5Cl_2O_4$–$Pb_{10}(PO_4)_6Cl_2$–$14PbO \cdot P_2O_5 \cdot 2PbCl_2$ resulted in the establishment of its phase diagram and in the discovery of a new chemical compound $29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$, for which X-ray identification data are presented.

* * *

The author is deeply grateful to Dr. Janusz Matuszewski for his help during the X-ray examinations.

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Zusammenfassung — Im ternären System PbO-P_2O_5-$PbCl_2$ wurde mittels thermischer, mikroskopischer, röntgenografischer, dilatometrischer und IR-Absorptionsanalyse das Teilsystem PbO-$Pb_5Cl_2O_4$-$Pb_{10}(PO_4)_6Cl_2$-$14PbO \cdot P_2O_5 \cdot 2PbCl_2$ untersucht und sein Phasendiagramm erstellt. Es wurde die Existenz einer neuen ternären Verbindung mit der Formel $29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$ gefunden, die peritektisch im System $Pb_5Cl_2O_4$-$Pb_{10}(PO_4)_6Cl_2$ geformt wird und dort einen pseudobinären Bereich bildet. Zur Identifizierung werden hier die Röntgenangaben der neu entdeckten Phase veröffentlicht.