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PHASE EQUILIBRIA IN THE BINARY SYSTEM PbO - $PbCl_2$

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The present paper forms part of a series of studies on the ternary system PbO - P_2O_5 - $PbCl_2$. The side binary system PbO - $PbCl_2$ has been investigated over the entire composition range and its phase diagram has been established. The components form three oxychlorides: $Pb_5Cl_2O_4$, $Pb_3Cl_2O_2$ and Pb_2Cl_2O. The examinations were carried out by means of thermal, microscopic, dilatometric, X-ray and IR absorption analyses. X-ray identification data for $Pb_5Cl_2O_4$ are presented.

The aim of this paper is to establish the phase equilibria in the binary system PbO - $PbCl_2$, a side system of the ternary system PbO - P_2O_5 - $PbCl_2$, which has not been described in the literature and which is a subject of the author's research.

The system PbO - $PbCl_2$ was examined by thermal and microscopic methods by Ruer [1] over the composition range 0-88 wt% of PbO. Ruer reported its phase diagram and found that PbO (melting point 835°) and $PbCl_2$ (melting point 499°) form three compounds in which the molar ratios of the initial components PbO and $PbCl_2$ are 4 : 1 ($4PbO\cdot PbCl_2$ – melting point 711°), 2 : 1 ($2PbO\cdot PbCl_2$ – melting point 693°) and 1 : 1 ($PbO\cdot PbCl_2$ – incongruent, melting point 524°).

The compound of $Pb_5Cl_2O_4$ with PbO forms a eutectic system with a eutectic composition of 18 wt% of $PbCl_2$ and a temperature of 703°. This compound forms solid solutions over the composition ranges from approx. 18 to 20 wt% and 34 to 36 wt% of $PbCl_2$. Ruer noticed a thermal effect over the composition range from approx. 24 to 30 wt% of $PbCl_2$ at 570° and in pure $Pb_5Cl_2O_4$ at 570°. However, he did not know what it should be attributed to. The compound $Pb_3Cl_2O_2$ reacts with $Pb_5Cl_2O_4$ to form a eutectic system with a eutectic composition of 36 wt% of $PbCl_2$ and a temperature of 691°. The third oxychloride, Pb_2Cl_2O, is formed peritectical-

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ly with a peritectic composition of 64 wt% of $PbCl_2$ and a temperature of 524°, and there appears a eutectic with a composition of 81 wt% of $PbCl_2$ and a temperature of 438° between Pb_2Cl_2O and $PbCl_2$.

Ruer excluded the possibility of other compounds being formed in this system. He did not provide the structure of any of the oxychlorides, but mentioned that $PbO \cdot PbCl_2$ is similar to the tetragonal mineral matlockite, PbFCl, while $2PbO \cdot PbCl_2$ corresponds to mendipite, a mineral forming orthorhombic crystals.

In 1934, Baroni [2] investigated the lead oxyhalides and confirmed that three compounds are formed in the system PbO - $PbCl_2$; however, their melting points and the compositions and temperatures of the eutectics occurring in this system were found to be slightly different from those reported by Ruer [1].

In 1934, Bannister [3] found no similarity of Pb_2Cl_2O with matlockite. He also provided lattice constants for mendipite, $4(Pb_3Cl_2O_4)$: a = 9.50 Å, b = 11.87 Å, and c = 5.87 Å

The possibilities of transformations of lead oxychlorides and oxybromides in the solid phase were examined in [4], and it was found that $PbO \cdot PbCl_2$ occurs in three polymorphic modifications: *L*, *M* and *N*. Modification *L* occurs up to 150°, modification *M* over the temperature range 150-325°, and modification *N* above 325°. Modifications *L* and *N* of $PbO \cdot PbCl_2$ are isomorphous with the corresponding modifications of $PbO \cdot PbBr_2$. Polymorphism was not observed for $2PbO \cdot PbCl_2$. Identification X-ray data were given for $2PbO \cdot PbCl_2$ and *N* $PbO \cdot PbCl_2$.

Goni and Guillemin [5] reported identification X-ray data for the mendipite minerals from Langban and Brilon and discovered that they are similar.

In 1958, Gabrielson [6] examined the crystal structure of mendipite. He found that the mineral has the formula $Pb_3Cl_2O_2$, space group $P2_12_12_1$ and lattice constants a = 9.52 Å, b = 11.95 Å, and c = 5.87 Å, which are slightly different from those reported in [3].

It was found in [7] that the mineral blixite occurs in Langban, with a chemical formula close to $4(Pb_4Cl_2O_3)$. The chemical composition of this newly discovered oxychloride was reported. The results of chemical analysis suggested that the general formula of this mineral is probably $Pb_{16}Cl_8(O,OH)_{16-x}$, with $x = 2.6$. It was discovered to have an orthorhombic structure and lattice constants a = 5.832±0.003 Å, b = 5.694±0.005 Å, and c = 25.47±0.02 Å.

The magnetochemical properties of lead salts, among them Pb_2Cl_2O and $Pb_4Cl_2O_3$ were examined in [8] in 1960.

It was reported in [9] that what was considered to be the mineral lorettoite with the formula $Pb_7Cl_2O_6$ was in fact an oxychloride obtained artificially from PbO and $PbCl_2$ whereas the mineral chubutite can be assigned the chemical formula $Pb_8Cl_2O_7$.

According to [10] and [11], lorettoite has two crystallographic modifications. The α modification has an orthorhombic structure; it is pseudotetragonal, with space group F_{mmm} – D_h^{23}. It is isomorphous with α–$PbBr_2 \cdot 6PbO$, while the β modification of this oxychloride is not isomorphous with β–$PbBr_2 \cdot 6PbO$.

It was reported in [10] that, according to [11], a chemical compound $3PbCl_2 \cdot 2PbO$ with melting point 530° is formed by melting stoichiometric quantities of PbO and $PbCl_2$. The compound has an orthorhombic structure and lattice constants a = 15.7 Å, b = 5.82 Å, and c = 35.3 Å. $PbCl_2 \cdot 3PbO$ with a melting point of 710° can be obtained by the dehydration of $PbCl_2 \cdot 3PbO \cdot 3H_2O$ at 250° or by melting stoichiometric quantities of PbO and $PbCl_2$. It crystallizes in an orthorhombic system with lattice constants a = 5.58 Å, b = 5.62 Å and c = 13.6 Å.

The above-mentioned data demonstrated the necessity for reinvestigating the phase dependences in the system PbO - $PbCl_2$, especially because it is a side system in the ternary system PbO - P_2O_5 - $PbCl_2$, which is a subject of the author's further research.

Because of its properties, PbO has been the subject of many investigations. It was reported in [12] that it can occur in three crystallographic modifications. The low-temperature modification (red PbO) corresponds to the tetragonal structure (space group $P4/nmm/D_{4h}^7$) with lattice constants a = 3.96±0.07 Å and b = 5.03±0.4 Å. At 498° it changes into a yellow modification, thermodynamically stable over the temperature range 498-750°, which has a laminar, orthorhombic structure (space group Pbma (D_2^{11}) or Pca (C_{2h}^5)) with lattice constants a = 5.50±0.04 Å, b = 4.79±0.06 Å and c = 5.74±0.03 Å. Finally, the high temperature modification (pink PbO) observed over 750° forms a monoclinic cell (space group C_{2h}^2 sup 2 or C_2^2) with lattice constants [13] a = 7.8 Å, b = 5.7 Å and c = 7.2 Å and β = 58°. The melting point of PbO is 896° [13]. The melting point and the temperatures of the polymorphic transitions of PbO were confirmed in [14].

$PbCl_2$ is reported to crystallize in an orthorhombic system (space group D_{2h}^{16} – Pnma) and its lattice constants are a = 4.534 Å, b = 7.623 Å, and

c = 9.048 Å. The thermal and X-ray examinations carried out by Modestova [16] in 1960 showed that this compound, melting at 501°, occurs in two polymorphic modifications. It was observed that the polymorphic transition $\alpha \rightarrow \beta$ – $PbCl_2$ occurs at 422°, and weak additional lines appeared in X-ray photographs. The temperatures of the phase transitions of $PbCl_2$ were confirmed in [17].

Experimental

Phase investigations were performed by means of thermal, microscopic, X-ray, dilatometric and IR absorption analyses.

PbO p.a. and $PbCl_2$ p.a. were used as starting materials. PbO was sintered in air at 750° for 2 h, then ground in an agate mortar and sieved to obtain the fraction with grain size <50 µm. $PbCl_2$ was dried in a vacuum desiccator in the presence of P_2O_5. Samples for examination were obtained by mixing and grinding the starting components.

$Pb_5Cl_2O_4$, $Pb_3Cl_2O_2$ and Pb_2Cl_2O were obtained from stoichiometric quantities of PbO and $PbCl_2$ by sintering in platinum crucibles in air for 1 h at 650, 600 and 500°, respectively. The phase purity of the obtained compounds was examined microscopically (in molten samples), by X-ray techniques and by chemical analysis for chlorine.

Because of its properties, PbO proved to be a very difficult compound for phase investigations. Attempts to obtain pure, crystallochemical modifications of this compound by sintering for a long time at appropriate temperatures and then freezing were successful, which was manifested by the colour of the preparations, but even a delicate grinding of yellow PbO made it change into red PbO. This ready transition of one crystallochemical modification into another and the occurrence of mixtures of several modifications posed considerable difficulties in the X-ray phase analysis. Molten PbO crystallizes in the form of thin plates, sometimes with a large surface. According to the direction of their packing, different microscopic pictures were obtained for the same samples (rich in PbO, i.e. over the composition range from 0 to approx. 19 wt% of $PbCl_2$). The primary separation of PbO made the interpretation of the phase structure of the alloys difficult. An unfavourable reaction of this compound with the material of the crucibles and thermocouples was noticed for samples rich in PbO.

$PbCl_2$ evaporates at temperatures above 700°. For this reason, the thermal analysis during the cooling of samples which melt above 700° (over the composition range up to approx. 20 mol% of $PbCl_2$) was performed in platinum crucibles placed in silica ampoules sealed under reduced argon pressure. The bottom of the crucible had a depression to fit the corresponding hollow of the silica ampoule, allowing the insertion of a thermocouple. The thermal analysis of other samples (with a composition over 20 mol% of $PbCl_2$) was carried out in open platinum crucibles in air or argon.

The thermal analysis (differential method) during cooling was performed in a resistance furnance with a platinum winding in a protective atmosphere of argon or in air. 10 g samples were placed into platinum crucibles. The temperature was measured with a Pt-PtRh10 thermocouple (accuracy ±2 deg), calibrated for the melting points of K_2SO_4 (1070°) and NaCl (801°) and for the polymorphic transition of K_2SO_4 (583°). Temperatures were read by means of an electronic recorder (MOM, Hungary). To protect the main thermocouple from the unfavourable action of lead salts, especially PbO, a platinum tube with the thermocouple was put into the crucible with the sample.

The thermal analysis during heating of 0.5-1.5 g samples was performed in a derivatograph (MOM, Hungary) with photographic recording over the temperature range 20-1000°.

Dilatometric examinations of lead oxychlorides were carried out during heating in a German dilatometer, type 802-BG,with programmed heating and computerized data analysis. The results of these investigations are the subject of a different paper [18].

The microscopic analysis of molten samples was performed with a metallographic microscope in reflected light.

X-ray investigations were performed at room temperature by the powder method, using a Guinier - de Wolffe focusing camera [radiation $\lambda(\text{Cu-K}_\alpha)$ = 1.5418 Å], a quartz monochromator and a DRON-2.0 diffractometer [radiation λ (Cu-K_α) = 1.5418 Å], Ni filter. The positions of lines were determined by using α–Al_2O_3 as the internal standard. Indexing was performed with an automatic POWDER program [19], and the solution with the best figure of merit was accepted [20]. In this work, the X-ray analysis was mainly of a qualitative character and served to identify phases in all samples, both molten and sintered. The identification of phases present in the preparations was carried out on the basis of known X-ray data in accordance with the PDF 1 data base.

The high reactivity of the samples under investigation (especially those rich in PbO), manifested by the strong corrosive action on the materials used, made experiments difficult and high-temperature X-ray investigations impossible.

The chemical analysis for chloride was performed by the Volhard method. The obtained results showed that the chloride content in the examined samples was as intended.

All compounds under investigation (initial, i.e. PbO and $PbCl_2$, and both known and hypothetical lead oxychlorides) underwent IR absorption analysis. The examinations were performed over the range from 400 to 4000 cm^{-1} with a Specord IR-75 spectrophotometer. However, the results obtained in this way were of little use for identification purposes because of both the lack of standard spectra of the analysed substances and the poor legibility of the obtained spectra.

As the samples were prone to overcooling, the grafting of samples with preliminarily precipitated crystals of similar composition was used.

In this work, special attention was paid to the possibility of other lead oxychlorides being formed at the molar ratio of the initial components: 7 : 1 ($Pb_8Cl_2O_7$), 6 : 1 ($Pb_7Cl_2O_6$), 5 : 1 ($Pb_6Cl_2O_5$), 3 : 1 ($Pb_4Cl_2O_3$), 3 : 2 ($Pb_5Cl_4O_3$), 2 : 3 ($Pb_5Cl_6O_2$), 1 : 2 (Pb_3Cl_4O) and 1 : 3 (Pb_4Cl_6O). To solve this problem, the samples of appropriate compositions were examined thoroughly and in every respect. Aurivillius wrote [21] that the $Pb_7Cl_2O_6$ which he investigated was not formed during the normal cooling of the appropriate mixture of PbO and $PbCl_2$ in a platinum crucible. It could only be obtained in porcelain crucibles.

For this reason, samples corresponding to hypothetical compounds were melted in platinum, porcelain and corundum crucibles, and microsections, X-ray photographs and thermograms were then made. They were also put into platinum crucibles, sintered at different temperatures in argon and air, and then refrigerated and examined by X-ray techniques.

Results and discussion

The binary system PbO - $PbCl_2$ was examined by thermal, dilatometric, microscopic, X-ray and IR absorption analysis. Figure 1 shows in a general form, without measurement points, a simplified phase diagram of this system, examined and completed within the author's research. The formation in this system of three lead oxychlorides was confirmed $Pb_5Cl_2O_4$ with a molar ratio of the initial components of 4 : 1, $Pb_3Cl_2O_2$ (2 : 1) and Pb_2Cl_2O (1 : 1).

$Pb_5Cl_2O_4$ melts congruently at $718\pm2^{\circ}$ and together with PbO forms a eutectic system with the e_1 eutectic composition amounting to approximately 19.18 wt% (16 mol%) of $PbCl_2$ at 710°. The thermal and dilatometric examinations demonstrated that this compound showed strong exothermal effects [18]. The most common temperatures of these effects were 620, 540, 410 and 350°.

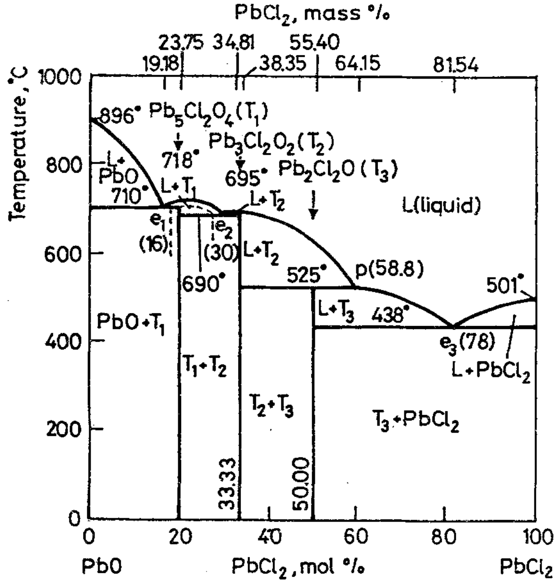

Fig. 1 Phase diagram of binary system PbO–PbCl$_2$ (general form)

The author's X-ray examinations proved beyond any controversy that $Pb_5Cl_2O_4$ is a new phase in comparison with PbO and $Pb_3Cl_2O_2$. Careful examination of both X-ray and powder photographs and diffractograms showed that the content of this compound varies in the different samples over the composition range from e_1 to e_2. Table 1 presents X-ray identification data for $Pb_5Cl_2O_4$. It was discovered that they are different from the X-ray data of all known compounds from the PbO - $PbCl_2$ system [22].

Preliminary structural investigations showed that $Pb_5Cl_2O_4$ crystallizes in a tetragonal system. The lattice constants of an elementary cell of this compound were determined; they are $a = b = 3.89 \pm 0.01$ Å and $c = 13.07 \pm 0.01$ Å

Data from [1] confirmed that $Pb_5Cl_2O_4$ reacts with both PbO and $Pb_3Cl_2O_2$ to form solid solutions over the composition range from approximately 22 to approximately 32 wt% of $PbCl_2$.

$Pb_3Cl_2O_2$ melts congruently at 695±2° and reacts with $Pb_5Cl_2O_4$ to form a eutectic system with a eutectic composition of e_2 = 34.81 wt% (30 mol%)

of $PbCl_2$ and a temperature of 690°. The compound has an orthorhombic structure, which confirms data from [6].

Table 1 X-ray diffraction data for oxychloride $Pb_5Cl_2O_4$

2Θ exp (Cu–Kα)	d, exp	d, calc	h	k	l
13.54	6.54	6.53	0	0	2
23.83	3.73	3.73	1	0	1
27.35	3.26	3.26	0	0	4
30.80	2.903	2.903	1	0	3
32.63	2.744	2.753	1	1	0
41.52	2.175	2.170	1	0	5
		2.178	0	0	6
42.99	2.104	2.105	1	1	4
46.67	1.946	1.947	2	0	0
53.01	1.727	1.726	2	1	1
53.64	1.709	1.708	1	1	6
54.55	1.682	1.683	1	0	7
54.88	1.673	1.673	2	0	4
56.94	1.617	1.617	2	1	3

system:tetragonal; lattice parameters: $a=b=3.89\pm0.01$Å, $c=13.07\pm0.01$Å; volume of the unit cell: 198.2Å^3; lattice type: I

Thermal and dilatometric examinations showed that three thermal effects appear for this compound, at 625, 560 and 440° [18].

Pb_2Cl_2O melts incongruently at 525±2° and has a tetragonal structure [1]. The peritectic composition is approximately 64.15 wt% (58.79 mol%) of $PbCl_2$. The e_3 eutectic of the composition amounts to approximately 81.54 wt% (78 mol%) of $PbCl_2$ with a temperature of 438°, between $PbCl_2$ and $Pb_3Cl_2O_2$. Effects at 470, 360 and 220° were observed for this compound during thermal and dilatometric examinations [18]. These temperatures are different from those of polymorphic transitions attributed to this oxychloride in [14].

The melting point of particular oxychlorides and the eutectic temperatures are slightly different from those reported in [1] and [2].

$Pb_5Cl_2O_4$ and $Pb_3Cl_2O_2$, which are formed in the PbO-$PbCl_2$ binary system under investigation and which melt congruently, permit the division of this system into three smaller binary eutectic systems: (1) PbO-$Pb_5Cl_2O_4$, (2) $Pb_5Cl_2O_4$-$Pb_3Cl_2O_2$ and (3) $Pb_3Cl_2O_2$-$PbCl_2$. The division makes the discussed range less "dense", so the obtained results concerning the possibilities of new oxychlorides being formed can be presented more easily.

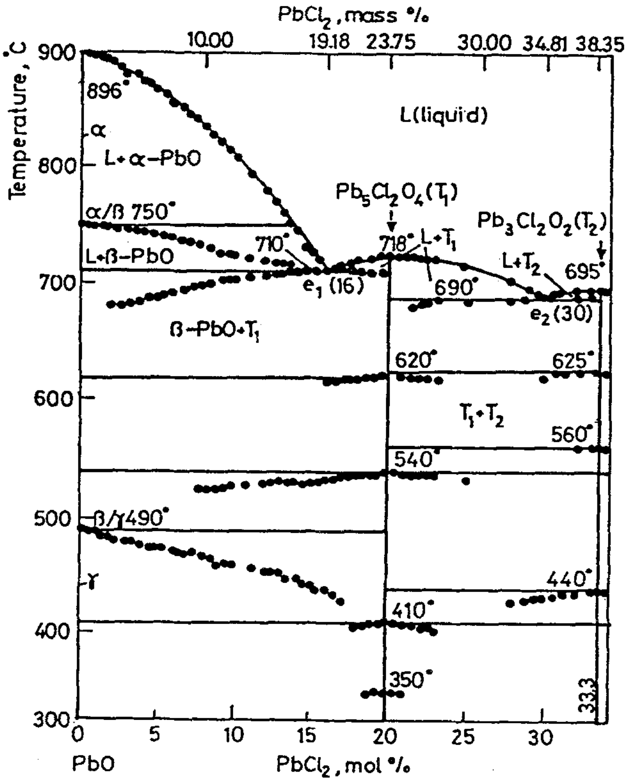

Fig. 2 Phase diagram of system PbO-$Pb_3Cl_2O_2$ (portion of system PbO-$PbCl_2$)

Figure 2 presents the phase diagram of the system PbO-$PbCl_2$ over the composition range up to 33.33 mol of $PbCl_2$ i.e. the system PbO-$Pb_3Cl_2O_2$. As reported in [7, 9], the lead oxychlorides $Pb_8Cl_2O_7$, $Pb_7Cl_2O_6$, $Pb_6Cl_2O_5$ and $Pb_4Cl_2O_3$ with compositions 15.11 wt% (12.5 mol%) of $PbCl_2$, 17.20 wt% (14.29 mol%) of $PbCl_2$, 19.95 wt% (16.67 mol%) of $PbCl_2$ and 29.35 wt% (25 mol%) of $PbCl_2$, respectively, can be formed over this composition range.

Figure 3 presents thermal curves of samples with $PbCl_2$ contents of (in mol%): (a) 10, (b) 12.5, (c) 13.5, (d) 14.29, (e) 15, (f) 16.67, (g) 18, (h) 23, (i) 25 and (j) 30. Change in mass was not observed during the heating, and therefore the TG and DTG curves are not shown in the thermograms. Ther-

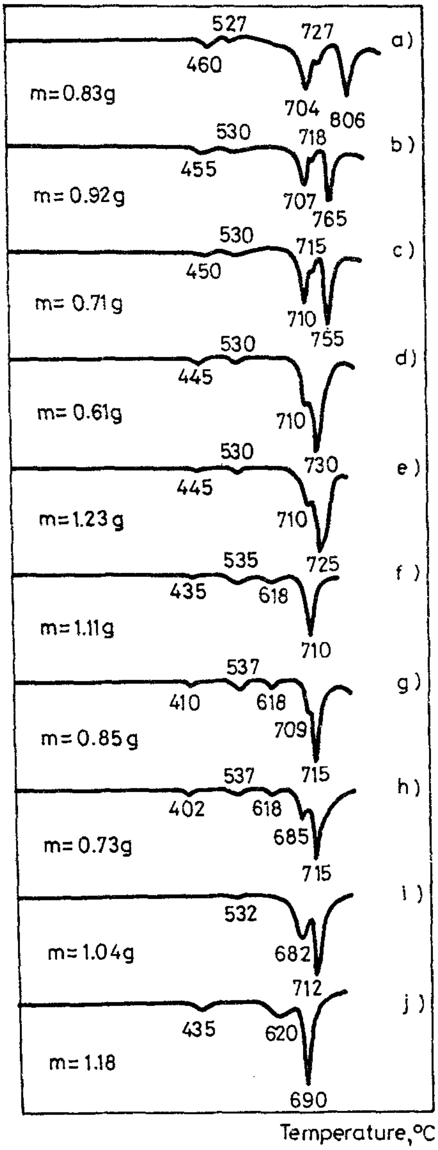

Fig. 3 DTA curves of samples from partial system PbO-$Pb_3Cl_2O_2$ a) 10, b) 12.5, c) 13.5, d) 14.29, e) 15, f) 16.67, g) 18, h) 23, i) 25, j) 30 mol% $PbCl_2$

mal effects in the curves arise mainly from crystallization and from eutectics e_1 and e_2. Effects with temperatures similar to those occurring in pure $Pb_5Cl_2O_4$ and $Pb_3Cl_2O_2$ [18] were observed as well. Microscopic observations of samples from this range did not show other phases, and no additional lines which could originate from compounds other than PbO, $Pb_5Cl_2O_4$ and $Pb_3Cl_2O_2$ were present in the X-ray photograps.

Figure 4 shows the phase diagram of the system PbO-$PbCl_2$ over the composition range from 33.33 to 100 mol% of $PbCl_2$, i.e. the $Pb_3Cl_2O_2$-$PbCl_2$ system. The possibility of formation of the following oxychlorides was observed: $Pb_5Cl_4O_3$ with the composition 45.38 wt% (40 mol%) of $PbCl_2$, Pb_3Cl_4O with the composition 71.39 wt% (66.67 mol%) of $PbCl_2$, Pb_4Cl_6O with the composition 78.89 wt% (75 mol%) of $PbCl_2$ and Pb_5Cl_8O with the composition 83.29 wt% (80 mol%) of $PbCl_2$. Figure 5 presents thermoanalytical curves of samples with the compositions: (a) 35, (b) 40, (c) 45, (d) 60, (e) 66.67, (f) 70, (g) 75, (h) 80 and (i) 85 mol% of $PbCl_2$. Thermal effects occurring in the curves correspond to temperatures of crystallization, the decomposition of Pb_2Cl_2O, the temperature of the eutectic e_3, and the temperatures observed for pure $Pb_5Cl_2O_4$ and $Pb_3Cl_2O_2$ [18]. Microscopic and X-ray photograps did not show any other phases.

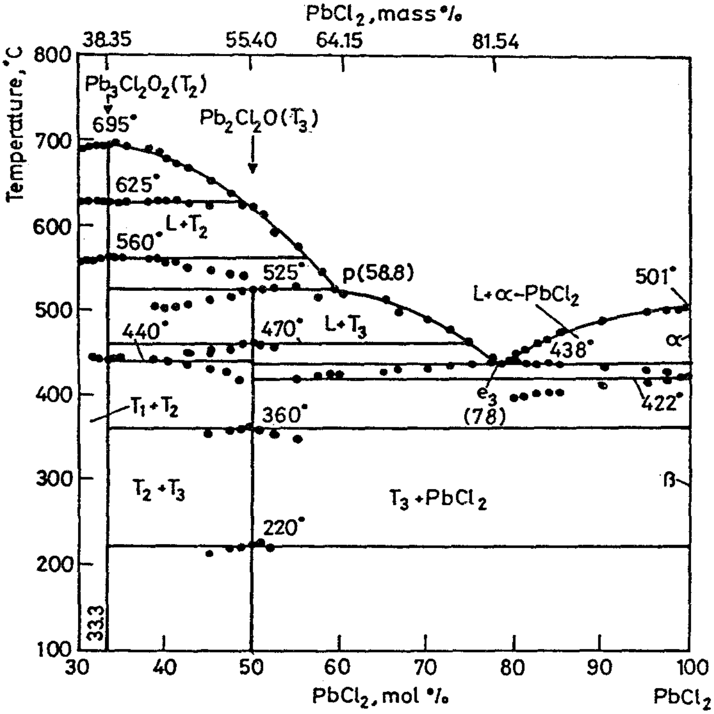

Fig. 4 Phase diagram of system $Pb_3Cl_2O_2$-$PbCl_2$ (portion of system PbO-$PbCl_2$)

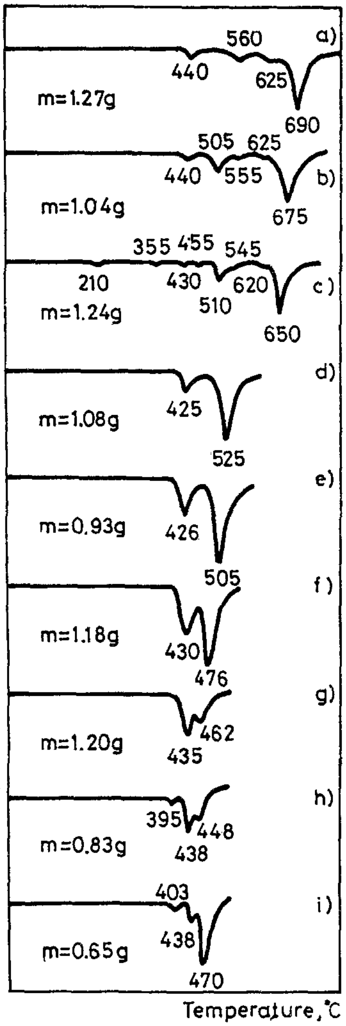

Fig. 5 DTA curves of samples from partial system $Pb_3Cl_2O_2$-$PbCl_2$ a) 35, b) 40, c) 45, d) 60, e) 66.67, f) 70, g) 75, h)80, i) 85 mol% $PbCl_2$)

Conclusion

Under the conditions of these measurements, it was discovered that only $P_5Cl_2O_4$, $Pb_3Cl_2O_2$ and Pb_2Cl_2O are formed in the binary system PbO-$PbCl_2$.

The system PbO-$PbCl_2$ is a side system in the tenary sytem PbO-P_2O_5-$PbCl_2$, wich is a subject of the author's research [23–25]. During research on phase equilibria of the partial ternary system PbO-$Pb_5Cl_2O_4$-$Pb_{10}(PO_4)_6Cl_2$-$Pb_8P_2O_{13}$ [24, 25], we tried to obtain $Pb_8Cl_2O_7$, $Pb_7Cl_2O_6$ and $Pb_6Cl_2O_5$ by adding small quantities of lead orthophosphate $Pb_3(PO_4)_2$ or lead chloropatite $Pb_{10}(PO_4)_6Cl_2$. The results of these investigations (thermal, microscopic and X-ray analyses) did not confirm the possibility of such lead oxychlorides being formed. The possibility of formation of different lead oxychlorides in this binary system was considered theoretically by using a morphological classification in [26]. It was concluded, as mentioned by Ruer [1] that only oxychlorides with the general formula $nPbO \cdot 1PbCl_2$ can be formed. The use of this classification suggested that, besides $Pb_5Cl_2O_4$, $Pb_3Cl_2O_2$ and $PbCl_2O$ the formation of $Pb_8Cl_2O_7$, $Pb_7Cl_2O_6$, $Pb_6Cl_2O_5$ or $Pb_4Cl_2O_3$ could be expected. However, this was impossible under the conditions of this research.

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Zusammenfassung — Vorliegende Arbeit ist Teil einer Untersuchungsreihe des ternären Systemes PbO - P_2O_5 - $PbCl_2$. Dabei wurde das binäre Untersystem PbO - $PbCl_2$ im gesamten Konzentrationsbereich untersucht und ein Phasendiagramm erstellt. Die Komponenten bilden die drei Oxidchloride $Pb_5Cl_2O_4$, $Pb_3Cl_2O_2$ und Pb_2Cl_2O. Die Untersuchungen wurden mittels mikroskopischer, dilatometrischer, röntgenographischer, IR- und Thermoanalyse durchgeführt. Die röntgenographischen Angaben für $Pb_5Cl_2O_4$ werden gegeben.