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DILATOMETRIC EXAMINATIONS OF LEAD(II) OXYCHLORIDES

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The thermal properties of the lead(II) oxychlorides $Pb_5Cl_2O_4$, $Pb_3Cl_2O_2$ and Pb_2Cl_2O, formed in the binary system PbO–$PbCl_2$, were examined. During thermal and dilatometric analyses of these compounds, several thermal and dilatational effects not previously described in the literature were found to occur.

Introduction

Within study on the phase equilibria in the ternary system PbO–P_2O_5–$PbCl_2$, the side binary system PbO–$PbCl_2$ was examined [1]. Three lead oxychlorides are formed in this system, at molar ratios of the initial components of 4:1 ($Pb_5Cl_2O_4$ – melting point 718°C), 2:1 ($Pb_3Cl_2O_2$ – melting point 695°C) and 1:1 (Pb_2Cl_2O – incongruent, melting point 525°C).

Previous investigations of lead(II) compounds and the use of dilatometric analysis revealed several transitions in lead fluoride, PbF_2 [2], lead fluorapatite, $Pb_{10}(PO_4)_6F_2$ [3], lead chlorapatite, $Pb_{10}(PO_4)_6Cl_2$ [4], octaplumbic phoshate, $Pb_8P_2O_{13}$, tetraplumbic phosphate, $Pb_4P_2O_9$ [5], lead orthophosphate, $Pb_3(PO_4)_2$ [6], and lead oxyapatite, $Pb_{10}(PO_4)_6O$ [5].

In the early literature, such effects (thermal and dilatational) were considered to be proof of the occurrence of polymorphic transitions. However, scrupulous structural investigations were not carried out and these not precisely stated transitions were called polymorphic transitions of the second kind because they were thought to occur within the same structure.

Nowadays, such conclusions should be formed with greater care, if the structures of phases under investigation are not confirmed by qualifying.

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New thermal or dilatational effects not described in the literature are being found for different chemical compounds and they cannot be ignored in a description of their properties; when complemented with other, more specialized investigations, they can help to explain several difficult phenomena occurring in chemical compounds in the solid phase.

In 1960, for example, Argyle and Hummel [7] reported the results of X-ray and dilatometric examinations on lead phosphates. Numerous strong effect were observed at various temperatures in the dilatograms. Later studies by other authors [8–10] proved that these compounds exhibit good thermal and ferroelastic properties, which can be linked with their dilatational effects.

This paper will also present several interesting thermal and dilatational effects that occur in lead(II) oxychlorides, although the occurrence of new phases was no confirmed by X-ray methods. So far, such examinations have not been performed on lead oxychlorides. Only Ruer [11], examining phase dependences in the system PbO–$PbCl_2$, observed a thermal effect at 530°C in samples corresponding to the compound $Pb_5Cl_2O_4$. The authors of paper [12] found that Pb_2Cl_2O occurs in three polymorphic modifications: $L \overset{150°C}{\rightarrow} M \overset{325°C}{\rightarrow} N$, but X-ray identification data were reported only for modification N.

Experimental

The compounds used for the examinations were obtained in this laboratory from stoichiometric quantities of p.a. lead monoxide, and p.a. lead chloride, $PbCl_2$. They were synthesized in the solid phase by sintering in air, in platinum crucibles: $Pb_5Cl_2O_4$ at 650°C /0.5 h, $Pb_3Cl_2O_2$ at 600°C/ 0.5 h and Pb_2Cl_2O at 450°C/ 0.5 h.

The phase purity of the compounds under investigation was tested microscopically in molten samples and by X-ray examinations on both molten and sintered samples. Microscopic pictures did not show any foreign phases within the grains and no foreign lines were observed in the X-ray photographs.

The examinations carried out included thermal, microscopic, X-ray, dilatometric and IR absorption analyses.

Thermal analysis (differential method) was performed during both the cooling and the heating of samples previously obtained by synthesis or by only mixing the reactants. Resistance furnaces constructed in this laboratory

or a derivatograph (MOM, Hungary), platinum crucibles and an argon protective atmosphere or air were used. Microsections were made from molten samples and they were then observed microscopically in reflected light, X-ray examinations were carried out by the powder method in a Guinier camera using CuK_α radiation.

Dilatometric examinations were performed in a German dilatometer (type 802 BG), with programmed heating and computerized analysis of the results. Samples for these examinations were sieved to obtain fractions of grain size $<80\,\mu$m. 5 wt.% of a 2.5% solution of methyl polymethacrylate in *n*-butyl acetate was added to the powder and the mixture was homogenized. The samples were then pressed under a pressure of 10 MPa (at 20 MPa the samples delaminated) into 3×3×10 mm beams (the admissible tolerance of the beam length was ±0.2 mm).

The dilatometric curves for each compound under examination are presented together in one figure, for molten and then sintered samples, for comparison; each is then presented enlarged, individually, with different temperature ranges. The temperatures of deflections in the curves were estimated by the tangent method.

Results and discussion

Figure 1 presents DTA curves for $Pb_5Cl_2O_4$, curve (*a*) referring to the sintered and curve (*b*) to the previously molten sample.

No change in mass was observed during heating, and therefore the TG and DTG curves are not shown. The situation was similar with the oxychlorides $Pb_3Cl_2O_2$ and Pb_2Cl_2O.

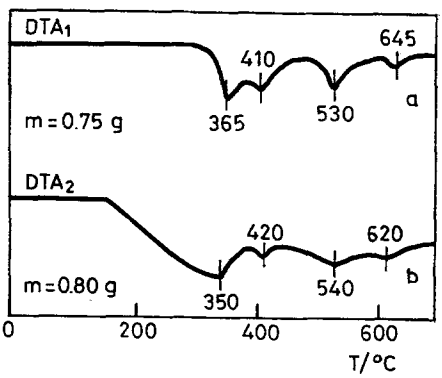

Fig. 1 DTA curves for $Pb_5Cl_2O_4$ *a*) sintered, *b*) molten sample

Table 1 The results of dilatometric investigation for the $Pb_5Cl_2O_4$ compound *a*) for sintered, *b*) for molten sample. Relative change of length (ε [%]) and linear thermal coefficient of expansion ($\alpha = 1.10^{-6}$/K). The given errors correspond with the confidence probability $P = 95\%$ and were obtained while calculating instrumental correction. Compound: $Pb_5Cl_2O_4$ sample: *a*) sintered, *b*) molten standard: Al_2O_3 initial length [mm]: *a*) 10.08, *b*) 10.1 heating rate: 10 deg/min correction sapphire

T /	*a*		*b*		*a* and *b*
°C	Epsilon/%	Alfa	Epsilon/%	Alfa	Measuring error/%
20	0.000	0.00	0.000	0.00	0.12
30	0.093	92.51	0.055	55.18	0.12
40	0.145	72.32	0.113	56.29	0.12
50	0.181	60.47	0.166	55.25	0.12
60	0.224	56.02	0.224	55.94	0.12
70	0.262	52.40	0.282	56.39	0.12
80	0.307	51.15	0.336	56.07	0.12
90	0.352	50.25	0.387	55.30	0.12
100	0.388	48.52	0.426	53.28	0.12
110	0.412	45.78	0.450	50.01	0.12
120	0.438	43.78	0.468	46.82	0.12
130	0.461	41.90	0.475	43.16	0.12
140	0.473	39.45	0.486	40.53	0.12
150	0.497	38.21	0.500	38.45	0.12
160	0.513	36.65	0.524	37.43	0.12
170	0.539	35.97	0.549	36.62	0.12
180	0.556	34.76	0.567	35.44	0.12
190	0.583	34.27	0.587	34.51	0.12
200	0.608	33.78	0.600	33.36	0.12
210	0.626	32.95	0.614	32.34	0.12
220	0.652	32.58	0.629	31.47	0.12
230	0.678	32.30	0.642	30.55	0.12
240	0.704	32.00	0.668	30.38	0.12
250	0.732	31.82	0.685	29.80	0.12
260	0.750	31.25	0.707	29.47	0.12
270	0.773	30.92	0.729	29.17	0.12
280	0.795	30.58	0.755	29.05	0.12
290	0.821	30.41	0.771	28.54	0.12
300	0.848	30.29	0.791	28.25	0.12
310	0.870	29.98	0.808	27.87	0.12
320	0.902	30.08	0.826	27.52	0.12
330	0.921	29.71	0.851	27.45	0.12
340	0.937	29.30	0.871	27.23	0.12

Table 1 continued

T /	a		b		a and b
°C	Epsilon/%	Alfa	Epsilon/%	Alfa	Measuring error/%
350	0.948	28.74	0.898	27.20	0.12
360	0.952	28.01	0.915	26.92	0.12
370	0.953	27.22	0.972	27.76	0.12
380	0.960	26.66	0.980	27.21	0.12
390	0.950	25.68	0.977	26.41	0.12
400	0.947	24.91	0.967	25.44	0.12
410	0.945	24.24	0.956	24.50	0.12
420	0.938	23.45	0.944	23.61	0.12
430	0.942	22.98	0.936	22.83	0.12
440	0.946	22.53	0.922	21.95	0.12
450	0.951	22.11	0.892	20.74	0.12
460	0.955	21.71	0.860	19.55	0.12
470	0.956	21.24	0.829	18.42	0.12
480	0.946	20.56	0.803	17.45	0.12
490	0.925	19.68	0.799	17.01	0.12
500	0.894	18.62	0.798	16.63	0.12
510	0.858	17.50	0.816	16.66	0.12
520	0.792	15.83	0.863	17.27	0.12
530	0.687	13.47	0.891	17.48	0.12
540	0.550	10.58	0.898	17.27	0.12
550	0.378	7.14	0.879	16.59	0.12
560	0.180	3.33	0.840	15.55	0.12
570	−0.054	− 0.98	0.796	14.47	0.12
580	−0.346	− 6.17	0.739	13.19	0.12
590	−0.666	−11.69	0.682	11.96	0.12
600	−1.068	−18.42	0.603	10.39	0.12
610	−1.482	−25.12	0.488	8.26	0.12
620	–	–	0.291	4.86	0.12
630	–	–	−0.120	− 1.98	0.12

Exothermic effects were observed at 365°, 410°, 560° and 645°C in the DTA curves for the sintered sample (Fig. 1a) and at 350°, 420°, 540° and 620°C for the molten sample (Fig. 1b). These effects were stronger for the sintered sample. The results of thermal examinations on 10 g samples during cooling and heating (in a resistance furnace constructed in this laboratory) were similar.

Table 1 presents the results of dilatometric examinations for (*a*) sintered and (*b*) molten samples of $Pb_5Cl_2O_4$. The dilatograms presented in Fig. 2 are analogous, curve (1) referring to the sintered, and curve (2) to the molten sample. It is generally known that the volumes of different substances vary with the temperature. However, in this case the variation is not linear, but occurs with several deflections, which can readily be observed after enlargement (Fig. 2b and 2c). As the two curves intersect several times, which makes interpretation of the dilatational effects difficult, the dilatograms presented below will be separated for a sintered sample of $Pb_5Cl_2O_4$ (Fig. 3) and a molten (Fig. 4) one, for different temperature ranges.

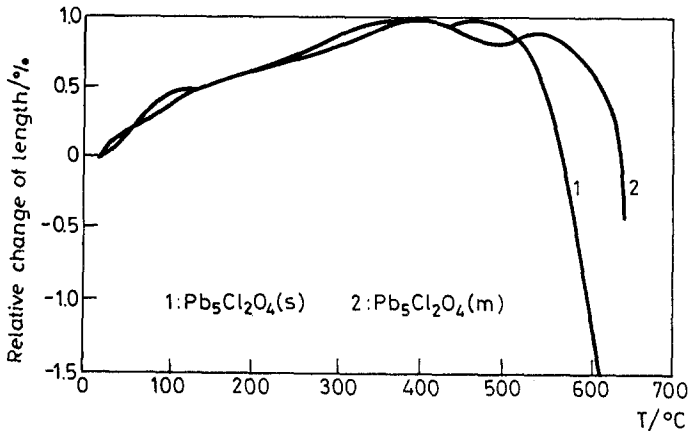

Fig. 2a Dilatograms for $Pb_5Cl_2O_4$ 1-sintered, 2-molten sample; general form,

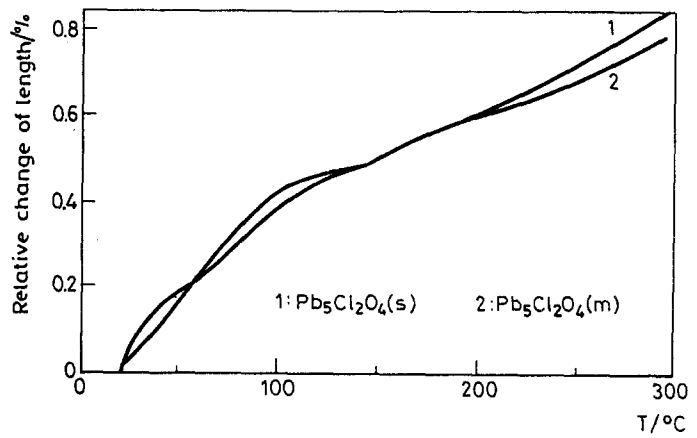

Fig. 2b Dilatograms for $Pb_5Cl_2O_4$ 1-sintered, 2-molten sample, over the temperature range 0°–300°C

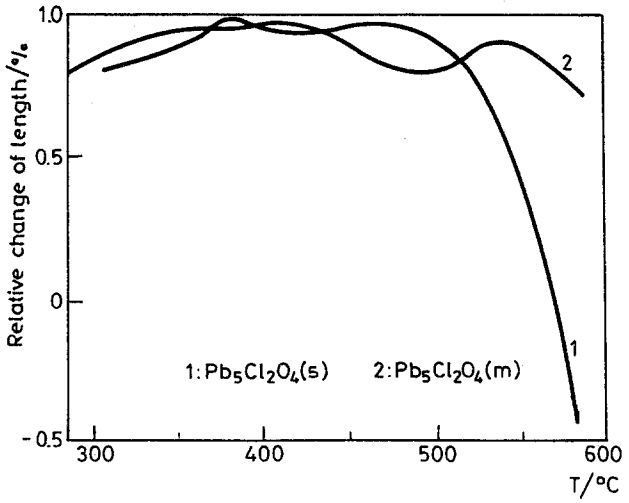

Fig. 2c Dilatograms for $Pb_5Cl_2O_4$ 1-sintered, 2-molten sample, over the temperature range 250°–600°C

Figure 3a shows the dilatogram of $Pb_5Cl_2O_4$ sintered in the temperature range 0°–300°C. The effect with a maximum at 100°C is due to the methyl polymethacrylate added to the samples before pressing. This effect occurred in all samples under investigation, at temperatures from 95° to 135°C, and will not be taken into consideration further.

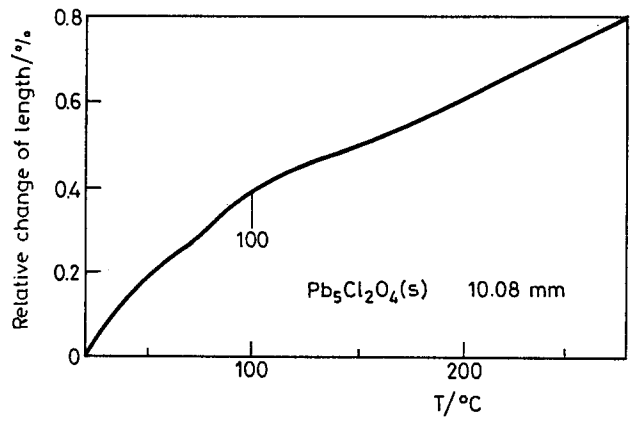

Fig. 3a Dilatogram for $Pb_5Cl_2O_4$ sintered (s) over the temperature ranges: 0°-300°C

Figure 3b presents the dilatogram of sintered $Pb_5Cl_2O_4$ for the temperature range 300°–500°C. The first deflection in the curve proceeds at approx. 345°C (maximum), the curve shows a minimum at 361°C and maximum at

379°C; it then goes down to a minimum at 421°C and up to a maximum at 460°C; there is next another minimum at 467°C, and another maximum at 475°C. The dilatogram for the temperature range 250°–550°C (Fig. 3c) presents a curve which changes its direction considerably at 335°C (maximum) and 417°C (maximum). Figure 3d shows the dilatogram for the temperature range 440°–620°C. An effect at 541°C can be noticed here with some difficulty. It starts at approx. 521°C (Fig. 3e).

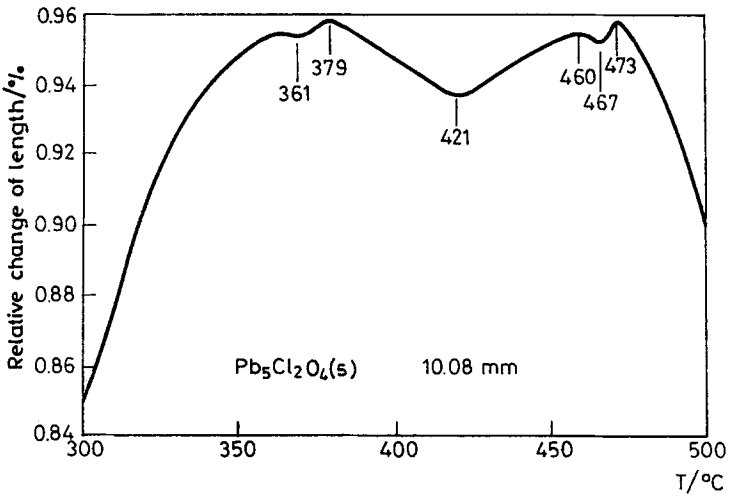

Fig. 3b Dilatogram for $Pb_5Cl_2O_4$ sintered (s) over the temperature ranges: 300–500°C,

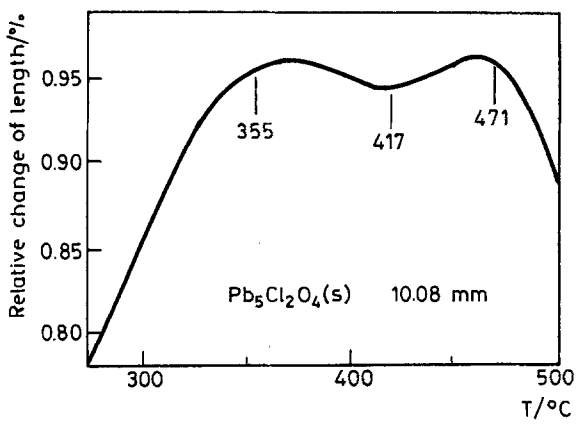

Fig. 3c Dilatogram for $Pb_5Cl_2O_4$ sintered (s) over the temperature ranges: 250–550°C

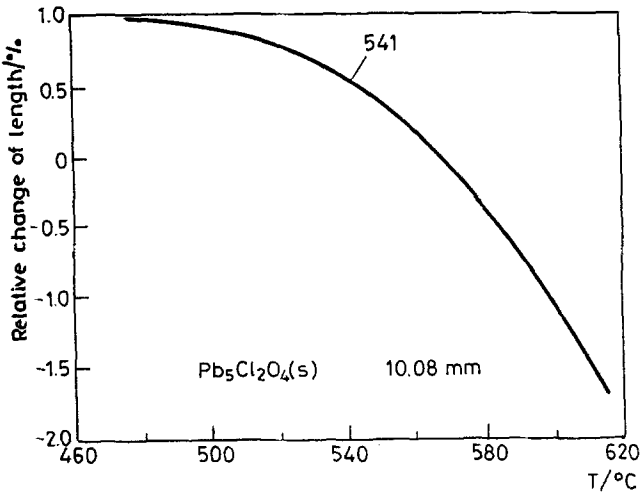

Fig. 3d Dilatogram for $Pb_5Cl_2O_4$ sintered (s) over the temperature ranges: 440°–620°C

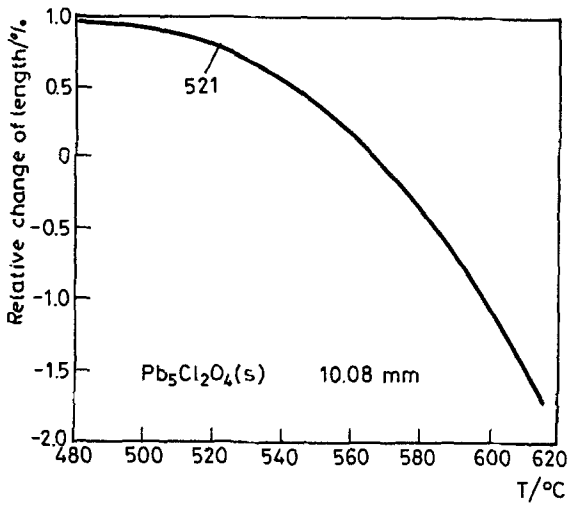

Fig. 3e Dilatogram for $Pb_5Cl_2O_4$ sintered (s) over the temperature ranges: 440°–620°C

Figure 4 shows dilatograms for the temperature ranges 250°–600°C (Fig. 4a), 340°–540°C (Fig. 4b), 500°–580°C (Fig. 4c) and 520°–640°C (Fig. 4d) for molten $Pb_5Cl_2O_4$. The dilatational effects were as follows: the first deflection (Fig. 4a) proceeds at 367°C (min.) and the second at 370°C (max.) then, after a minimum at 376°C, the curve goes up to 380°C (max.) and down almost linearly to 420°C, where another deflection occurs (min.);

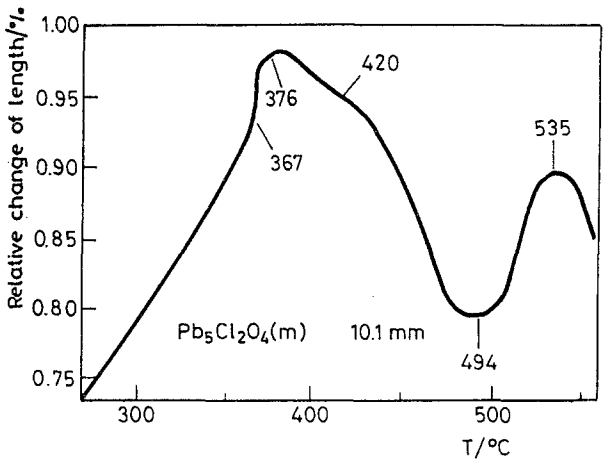

Fig. 4a Dilatogram for molten $Pb_5Cl_2O_4$ (m) over the temperature ranges: 250°–600°C

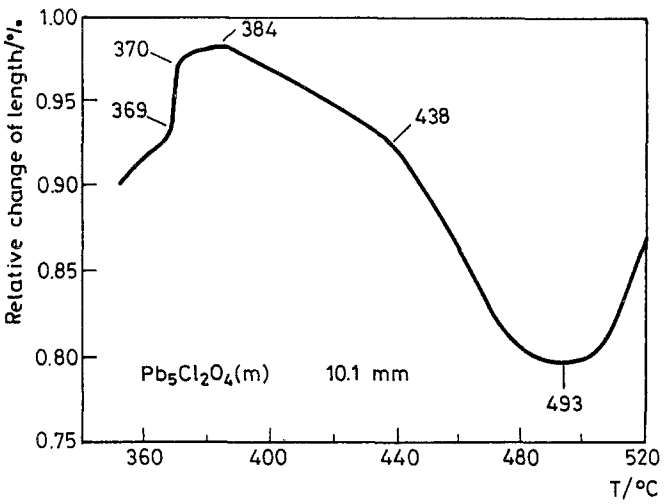

Fig. 4b Dilatogram for molten $Pb_5Cl_2O_4$ (m) over the temperature ranges: 340°–540°C

there is next a deflection (min.) and a sharp ($\Delta\varepsilon = 0.14\%$) slope down to a minimum at 494°C, after which a rise to a maximum at 535°C occurs. In the temperature range 340–540°C (Fig. 4b), the changes in direction of the curve are associated with the following temperatures: 368°C (min.), 370°C (max.), 384°C (max.), 438°C (max.) and 493°C (min.). In the dilatogram presented in Fig. 4c (500°–580°C), changes in direction of the curve are ob-

served at 505°C (min.), 528°C (max.), 539°C (max.), 541°C (min.) and 544°C (max.); and in that in Fig. 4d (520°–640°C) at 613°C (min.).

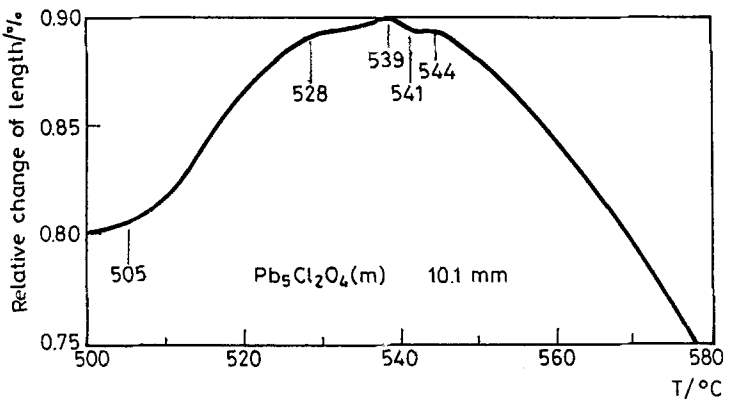

Fig. 4c Dilatogram for molten $Pb_5Cl_2O_4$ (m) over the temperature ranges: 500°–580°C

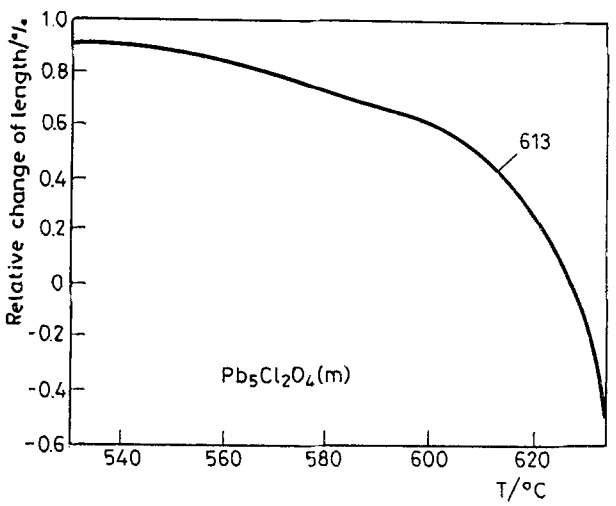

Fig. 4d Dilatogram for molten $Pb_5Cl_2O_4$ (m) over the temperature ranges: 520°–640°C

Figure 5 shows DTA curves for $Pb_3Cl_2O_2$. During the heating of this compound, exothermic effects were observed at 440°, 560° and 640°C for a sintered sample (Fig. 5a), and at 430°, 550° and 630°C for a molten sample (Fig. 5b).

Table 2 presents the results of dilatometric examinatios if this oxychloride which was (*a*) sintered and (*b*) melted.

Table 2 The results of dilatometric investigations for the $Pb_3Cl_2O_2$ compound *a*) for sintered (10.06 mm) *b*) for molten (10.22 mm) sample. The remaining values and experimental conditions as in Table 1.

T/	*a*		*b*		*a* and *b*
°C	Epsilon/%	Alfa	Epsilon/%	Alfa	Measuring error/%
20	0.000	0.00	0.000	0.00	0.12
30	0.068	67.54	0.092	92.30	0.12
40	0.111	55.50	0.155	77.61	0.12
50	0.146	48.62	0.199	66.41	0.12
60	0.191	47.87	0.243	60.83	0.12
70	0.246	49.21	0.297	59.41	0.12
80	0.293	48.82	0.351	58.48	0.12
90	0.336	48.00	0.395	56.48	0.12
100	0.371	46.43	0.432	54.02	0.12
110	0.387	43.05	0.473	52.56	0.12
120	0.394	39.40	0.501	50.06	0.12
130	0.394	35.80	0.517	46.97	0.12
140	0.400	33.37	0.531	44.25	0.12
150	0.404	31.10	0.548	42.18	0.12
160	0.411	29.37	0.559	39.93	0.12
170	0.420	28.00	0.577	38.49	0.12
180	0.425	26.57	0.589	36.82	0.12
190	0.432	25.42	0.606	35.63	0.12
200	0.431	23.92	0.622	34.58	0.12
210	0.437	22.99	0.639	33.64	0.12
220	0.443	22.15	0.659	32.94	0.12
230	0.451	21.49	0.682	32.49	0.12
240	0.462	20.98	0.709	32.22	0.12
250	0.476	20.69	0.735	31.97	0.12
260	0.480	20.02	0.767	31.95	0.12
270	0.483	19.32	0.789	31.54	0.12
280	0.489	18.79	0.815	31.36	0.12
290	0.496	18.38	0.833	30.87	0.12
300	0.508	18.14	0.861	30.76	0.12
310	0.531	18.31	0.896	30.88	0.12
320	0.560	18.67	0.931	31.04	0.12
330	0.595	19.20	0.960	30.97	0.12
340	0.630	19.70	0.996	31.11	0.12
350	0.660	19.99	1.034	31.33	0.12

Table 2 continued

T/	*a*		*b*		*a* and *b*
°C	Epsilon/%	Alfa	Epsilon/%	Alfa	Measuring error/%
360	0.697	20.49	1.069	31.43	0.12
370	0.724	20.68	1.103	31.53	0.12
380	0.745	20.68	1.132	31.43	0.12
390	0.750	20.26	1.150	31.08	0.12
400	0.755	19.87	1.149	30.23	0.12
410	0.756	19.39	1.152	29.54	0.12
420	0.756	18.89	1.155	28.88	0.12
430	0.764	18.63	1.136	27.70	0.12
440	0.771	18.36	1.074	25.58	0.12
450	0.779	18.13	0.945	21.98	0.12
460	0.778	17.68	0.736	16.74	0.12
470	0.777	17.26	0.318	7.06	0.12
480	0.766	16.64	–0.182	– 3.96	0.12
490	0.735	15.64	–0.621	–13.22	0.12
500	0.657	13.69	–1.024	–21.33	0.12
510	0.538	10.99	–1.369	–27.93	0.12
520	0.334	6.69	–1.676	–33.51	0.12
530	0.109	2.14	–1.916	–37.56	0.12
540	–0.143	– 2.74	–2.117	–40.72	0.12
550	–0.447	– 8.43	–2.299	–43.37	0.12
560	–0.828	–15.34	–2.463	–45.61	0.12
570	–1.303	–23.69	–2.629	–47.81	0.12
580	–1.760	–31.44	–2.812	–50.21	0.12
590	–2.616	–45.89	–3.011	–52.82	0.12
600	–	–	–3.212	–55.38	0.12
610	–	–	–3.433	–58.18	0.12
620	–	–	–3.661	–61.01	0.12
630	–	–	–3.968	–65.05	0.12
640	–	–	–4.505	–72.66	0.12

Figure 6 shows dilatograms for a sintered (curve 1) and a molten (curve 2) sample, while Figs 7 and 8 give dilatograms for sintered and molten $Pb_3Cl_2O_2$, respectively the temperature range up to 350°C (Fig. 7a), dilatational effects were observed in the dilatometric curve at 102°C (max. from methyl polymethacrylate), 198°C (min.), 238°C (min.), 270°C (min.) and 300°C (min.). Similar effects were observed in the temperature range

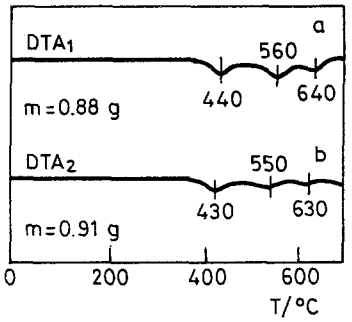

Fig. 5 DTA curves for $Pb_3Cl_2O_2$ *a*) sintered, *b*) molten sample

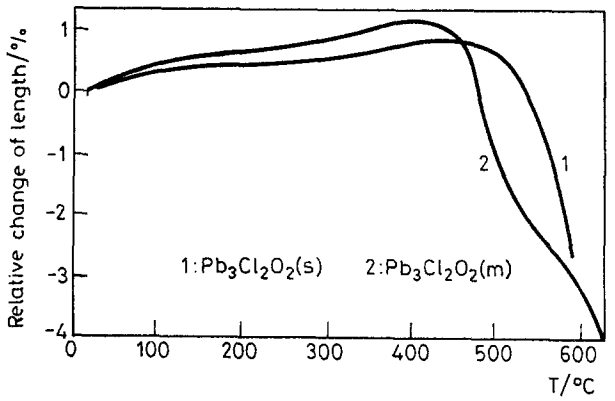

Fig. 6 Dilatograms for $Pb_3Cl_2O_2$ 1-sintered, 2-molten sample

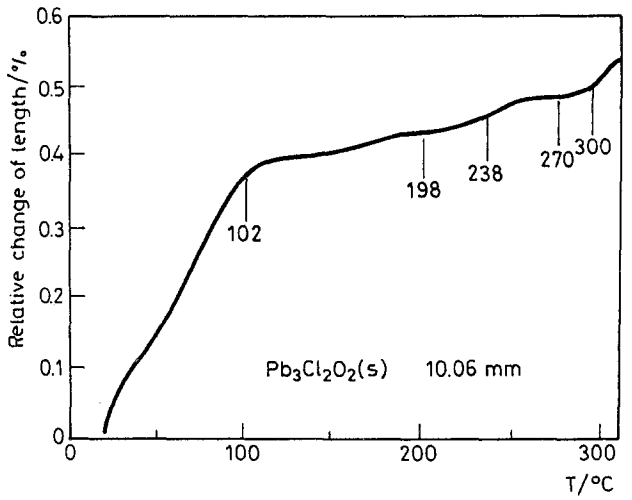

Fig. 7a Dilatogram for sintered $Pb_3Cl_2O_2$ (s) over the temperature ranges: 0°–350°C

180–400°C (Fig. 7b), at 197°C (min.), 239°C (min.), 270°C (min.) and 298°C (min.).

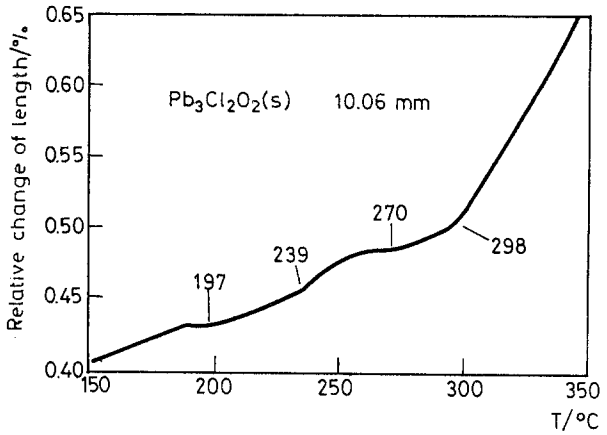

Fig. 7b Dilatogram for sintered $Pb_3Cl_2O_2$ (s) over the temperature ranges: 150°–400°C

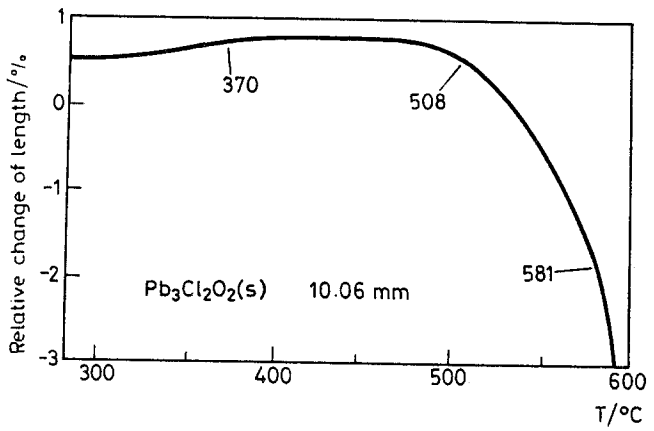

Fig. 7c Dilatogram for sintered $Pb_3Cl_2O_2$ (s) over the temperature ranges: 250°–600°C,

In the temperature range 250°–600°C (Fig. 7c), effects were seen at 370°C (max.), 508°C (max.) and 581°C (max.); and in the range 300°–500°C (Fig. 7d) there were effects at 377°C (max.), 421°C (min.) and 471°C (max.). The effect with minimum at 421°C in the temperature range from 377° to 471°C can readily be observed in this picture.

Figure 7e presents the dilatogram for the temperature range 440°–600°C, with effects at 504°C (min.), 564°C (min.) and 584°C (max.).

Table 3 The results of dilatometric investigations for the Pb_2Cl_2O compound *a*) for sintered (10.15 mm) *b*) for molten (10.13 mm) sample. The remaining values and experimental conditions as in Table 1.

T/	*a*		*b*		*a* and *b*
°C	Epsilon/%	Alfa	Epsilon/%	Alfa	Measuring error/%
20	0.000	0.00	0.000	0.00	0.12
30	0.097	96.74	0.072	71.80	0.12
40	0.160	80.03	0.147	73.69	0.12
50	0.212	70.67	0.206	68.74	0.12
60	0.268	66.98	0.270	67.46	0.12
70	0.322	64.39	0.334	66.73	0.12
80	0.377	62.85	0.390	64.98	0.12
90	0.421	60.12	0.436	62.24	0.12
100	0.466	58.21	0.472	58.98	0.12
110	0.504	55.98	0.495	54.95	0.12
120	0.532	53.15	0.501	50.11	0.12
130	0.543	49.36	0.502	45.63	0.12
140	0.550	45.80	0.507	42.22	0.12
150	0.547	42.05	0.518	39.87	0.12
160	0.530	37.82	0.529	37.78	0.12
170	0.503	33.51	0.532	35.47	0.12
180	0.477	29.81	0.535	33.45	0.12
190	0.461	27.12	0.540	31.78	0.12
200	0.459	25.53	0.535	29.72	0.12
210	0.464	24.40	0.535	28.17	0.12
220	0.474	23.69	0.543	27.13	0.12
230	0.498	23.69	0.550	26.18	0.12
240	0.524	23.82	0.557	25.33	0.12
250	0.551	23.95	0.565	24.55	0.12
260	0.578	24.10	0.572	23.84	0.12
270	0.597	23.87	0.573	22.92	0.12
280	0.612	23.53	0.578	22.22	0.12
290	0.629	33.30	0.576	21.32	0.12
300	0.637	22.74	0.574	20.49	0.12
310	0.654	22.56	0.580	20.01	0.12
320	0.681	22.71	0.582	19.41	0.12
330	0.706	22.78	0.588	18.98	0.12
340	0.729	22.77	0.595	18.60	0.12
350	0.743	22.52	0.603	18.28	0.12

Table 3 continued

T/	*a*		*b*		*a* and *b*
°C	Epsilon/%	Alfa	Epsilon/%	Alfa	Measuring error/%
360	0.751	22.09	0.608	17.88	0.12
370	0.750	21.42	0.609	17.41	0.12
380	0.720	20.00	0.602	16.72	0.12
390	0.669	18.09	0.589	15.91	0.12
400	0.596	15.68	0.565	14.87	0.12
410	0.481	12.32	0.516	13.24	0.12
420	0.328	8.20	0.457	11.42	0.12
430	0.154	3.75	0.389	9.49	0.12
440	–0.071	– 1.69	0.289	7.12	0.12
450	–0.369	– 8.58	0.161	3.74	0.12
460	–0.755	–17.16	–0.013	– 0.30	0.12
470	–1.343	–29.85	–0.234	– 5.21	0.12
480	–2.143	–46.59	–0.569	– 12.37	0.12
490	–3.426	–72.89	–1.101	– 23.42	0.12
500	–6.061	%–126.28	–2.131	– 44.39	0.12
510	–	–	–5.744	%–117.22	0.12

In Fig. 8a for a molten sample, there is a weak effect with minimum at 316°C in the temperature range 220°–400°C but it is almost imperceptible in the range 250°–650°C (Fig. 8b), where the following effects were noted: 442°C (max.), 525°C (min.) and 627°C (max.). Thus, in the interval 442°–627°C an effect with minimum at 525°C occurs. This is confirmed by Fig. 8c,

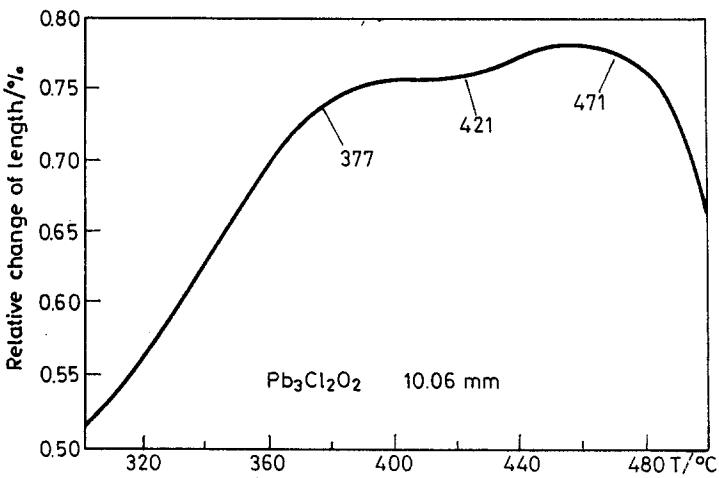

Fig. 7d Dilatogram for sintered $Pb_3Cl_2O_2$ (s) over the temperature ranges: 300°–500°C

where in the temperature range 500°–600°C, with $\Delta\varepsilon = -1.8\%$, the minimum is observed at 525°C in the dilatometric curve.

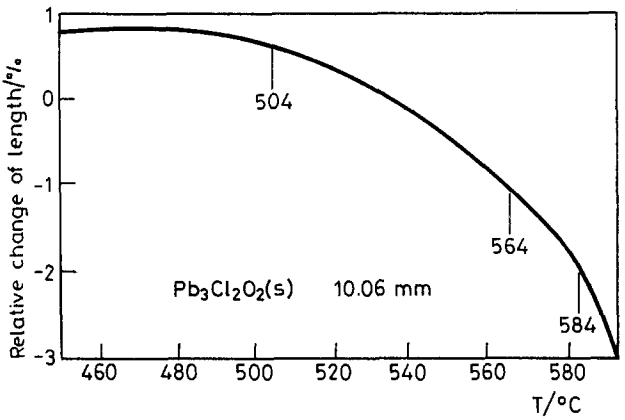

Fig. 7e Dilatogram for sintered $Pb_3Cl_2O_2$ (s) over the temperature ranges: 440°–600°C

Figure 9 presents the DTA curves for $PbCl_2O$, where three exothermal effects occur at 240°, 370° and 495°C for a sintered sample (Fig. 9a), and at 220°, 360° and 470°C for a molten one (Fig. 9b).

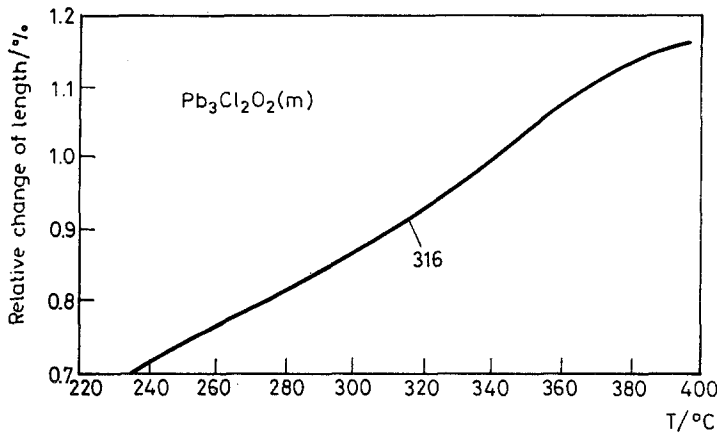

Fig. 8a Dilatogram for molten sample $Pb_3Cl_2O_2$ (m) over the temperature ranges: 220°–400°C

Table 3 shows the results of dilatometric examinations of Pb_2Cl_2O which was (*a*) sintered and (*b*) melted.

Figure 10 presents the dilatograms of the sintered (curve 1) and molten (curve 2) oxychloride. The two curves are shown together enlarged in

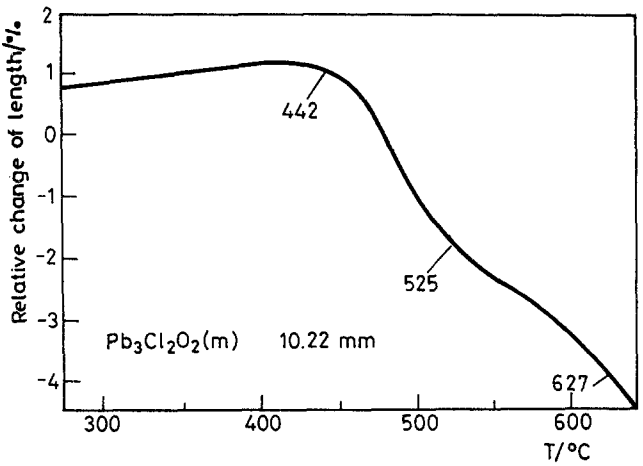

Fig. 8b Dilatogram for molten sample $Pb_3Cl_2O_2$ (m) over the temperature ranges: 250°–650°C

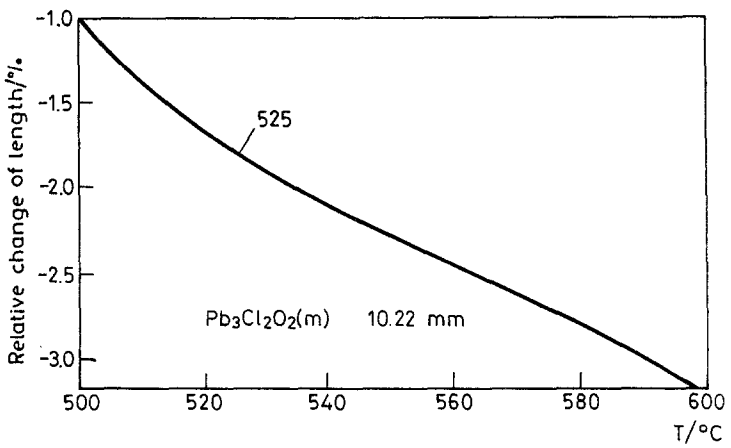

Fig. 8c Dilatogram for molten sample $Pb_3Cl_2O_2$ (m) over the temperature ranges: 500°–600°C

Fig. 10b and 10c. To make interpretation of the deflections easier, Figs 11 and 12 show dilatometric curves for sintered and molten samples of Pb_2Cl_2O separately.

In the temperature range up to 300°C (Fig. 11a), an effect beginning at 135°C was observed with maximum at 199°C; in the range 240°–420°C (Fig. 11b) there were two effects, at 304°C (max.) and 360°C (min.); in the range 300°–500°C (Fig. 11c) two effects, at 366°C (min.) and 449°C (min.); and in the temperature range 360°–520°C (Fig. 11d) effects at 420°C (min.) and 482°C (min.).

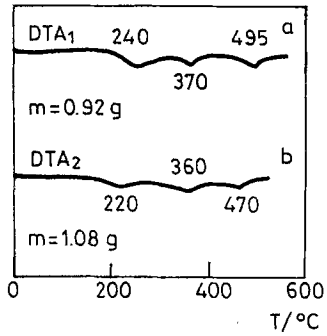

Fig. 9 DTA curves for Pb_2Cl_2O *a*) sintered, *b*) molten sample

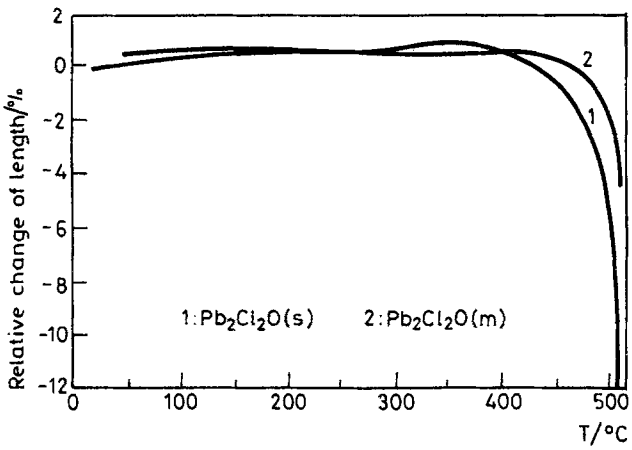

Fig. 10a Dilatograms for Pb_2Cl_2O 1-sintered, 2-molten sample; general form,

Figure 12 presents the dilatogram for molten Pb_2Cl_2O in the temperature range up to 300°C (Fig. 12a), with three effects, one with maximum at 102°C, the second proceeding in the temperature range 170–260°C with minimum at 210°C, and the third, weak one with minimum at 270°C. Effects at 173°C (max.), 204°C (min.) and 275°C (min.) can be observed in the dilatometric curve for the range of temperatures 100°–350°C (Fig. 12b). In the temperature range 240°–400°C (Fig. 12c), effects were observed at 265°C (max.), 318°C (min.) and 367°C (max.). Figure 12d presents the dilatogram for the range of temperatures 250°–550°C and the effect with maximum at 470°C. In the range 340°–500°C (Fig. 12e), three effects can be noted, at 403°, 446° and 470°C (all with minimum). The occurrence of several strong effects results from the above presented analysis of the thermal and dilatometric curves

obtained for lead(II) oxychlorides. Their temperatures differ a little for molten and sintered samples. No logical dependences of these differences were observed, i.e. in some cases the temperatures of the effects in the curves for sintered samples were higher, and in some cases lower than those for molten samples.

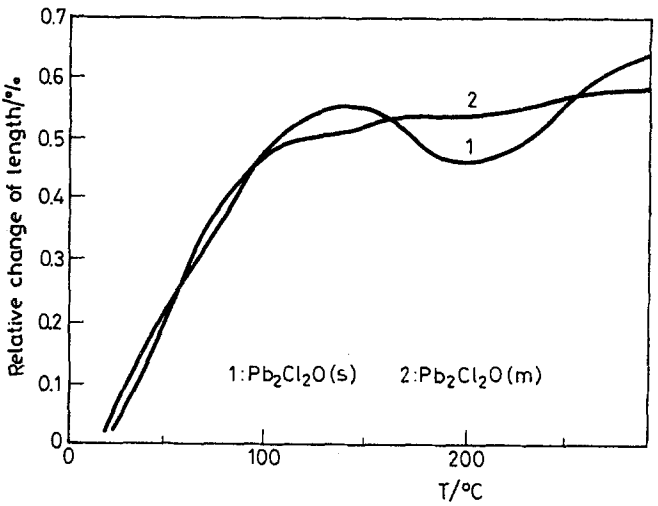

Fig. 10b Dilatograms for Pb_2Cl_2O 1-sintered, 2-molten sample; over the temperature range 0°–300°C,

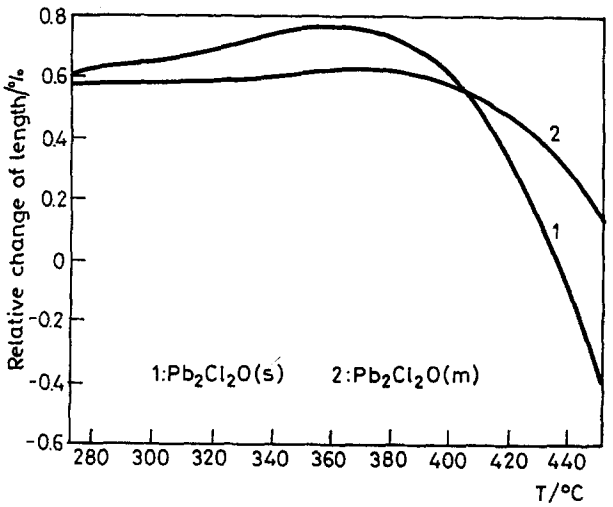

Fig. 10c Dilatograms for Pb_2Cl_2O 1-sintered, 2-molten sample; over the temperature range 260°–460°C

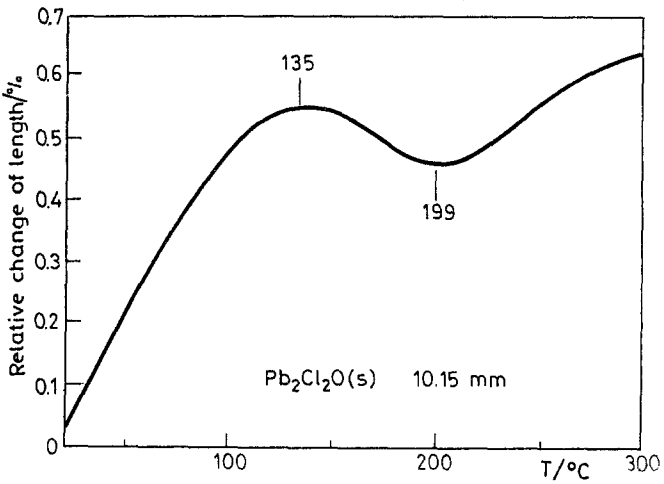

Fig. 11a Dilatogram for sintered sample Pb_2Cl_2O (s) over the temperature ranges: 0°–300°C

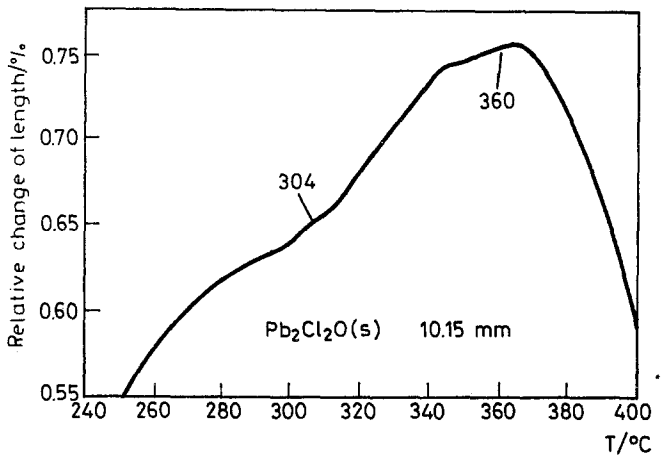

Fig. 11b Dilatogram for sintered sample Pb_2Cl_2O (s) over the temperature ranges: 240°–420°C

Conclusions

To summarize the results obtained for the group of compounds under investigation, and taking into consideration the most common temperatures of these effects, it can be concluded that they occur:

in $Pb_5Cl_2O_4$ at 350°, 420°, 540° and 620°C,

in $Pb_2Cl_2O_2$ at 430°, 550° and 630°C,

in Pb_2Cl_2O at 220°, 360° and 470°C.

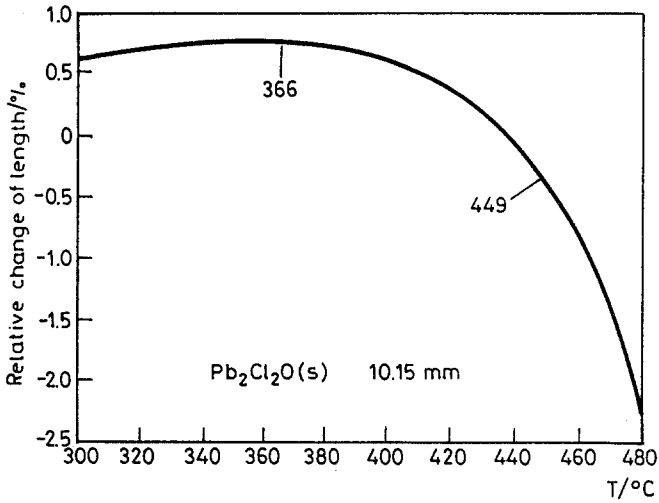

Fig. 11c Dilatogram for sintered sample Pb_2Cl_2O (s) over the temperature ranges: 300°–500°C

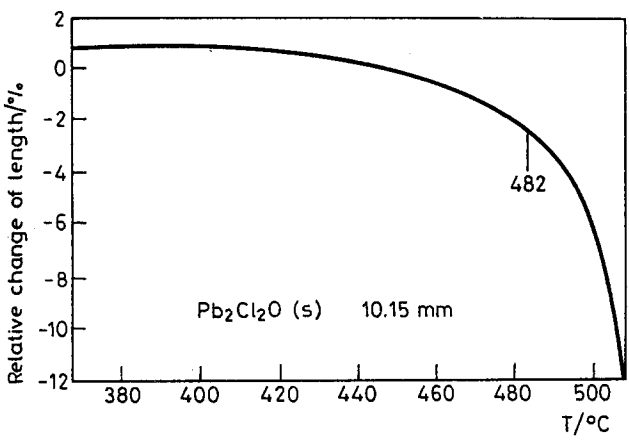

Fig. 11d Dilatogram for sintered sample Pb_2Cl_2O (s) over the temperature ranges: 360°–520°C

It is not possible to explain precisely the causes of the occurrence of the abovedescribed thermal and dilatational effects, and structural examinations are therefore absolutely necessary. However, the presented results might be of considerable importance if we take into consideration the search for materials with ferroelastic properties [8–10].

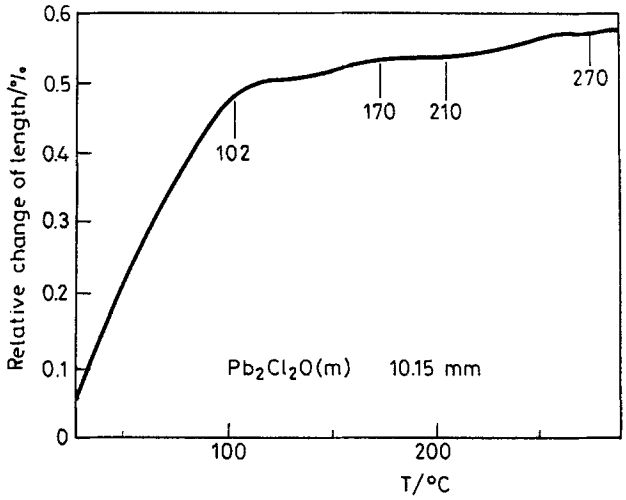

Fig. 12a Dilatogram for molten sample Pb_2Cl_2O (m) over the temperature ranges: 0°–300°C,

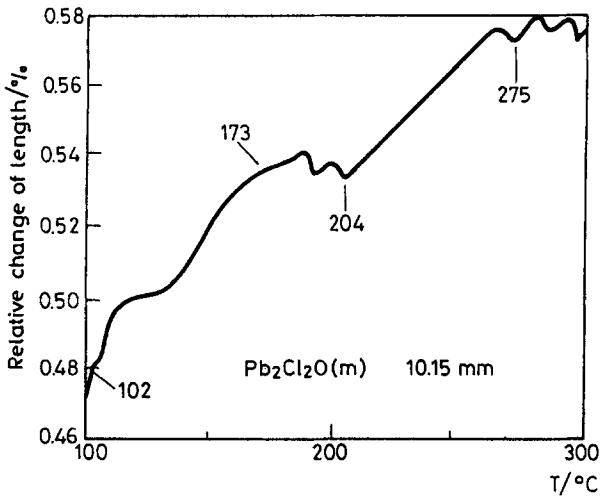

Fig. 12b Dilatogram for molten sample Pb_2Cl_2O (m) over the temperature ranges: 100°–300°C

At the present stage, the results obtained during these investigations are an important complement of phase dependences observed in the solid phase in the system PbO–$PbCl_2$ [1].

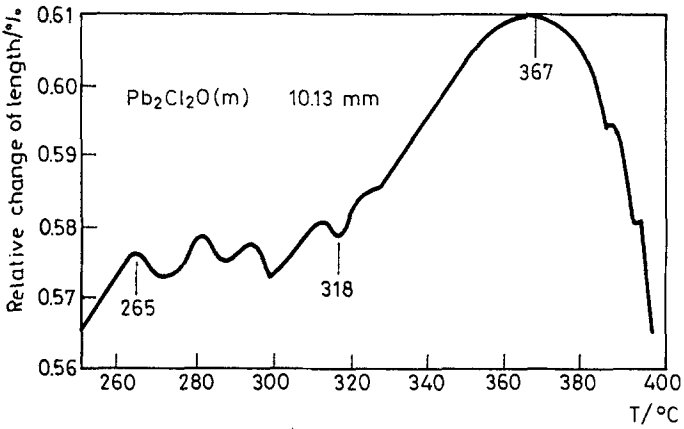

Fig. 12c Dilatogram for molten sample Pb_2Cl_2O (m) over the temperature ranges: 240°–400°C

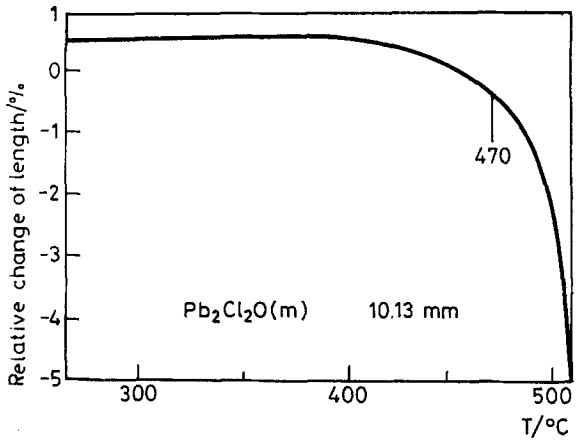

Fig. 12d Dilatogram for molten sample Pb_2Cl_2O (m) over the temperature ranges: 250°–550°C

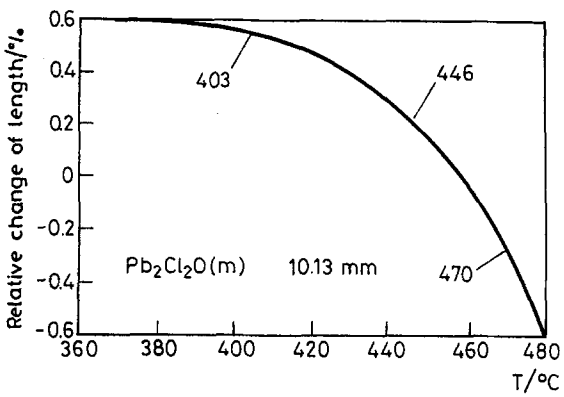

Fig. 12e Dilatogram for molten sample Pb_2Cl_2O (m) over the temperature ranges: 340°–500°C

* * *

The author would like to thank Dr. M. Szafran for his help during dilatometric examinations.

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Zusammenfassung — Es wurden die thermischen Eigenschaften der im binären System PbO–$PbCl_2$ gebildeten Blei(II)-oxychloride $Pb_5Cl_2O_4$, $Pb_3Cl_2O_2$ und Pb_2Cl_2O untersucht. Während der thermischen und dilatometrischen Untersuchungen konnten zahlreiche bislang in der Fachliteratur nicht beschriebene thermische und dilatometrische Effekte gefunden werden.