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DILATOMETRIC EXAMINATIONS OF THE COMPOUNDS $14PbO \cdot P_2O_5 \cdot 2PbCl_2$ (R) AND $29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$ (S)

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The ternary compounds $14PbO \cdot P_2O_5 \cdot 2PbCl_2$ (R) and $29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$ (S), which are formed in the ternary system $PbO–P_2O_2–PbCl_2$, were examined by dilatometry. Numerous, previously undescribed thermal and dilatational effects were observed to occur in these compounds under the influence of temperature.

Keywords: dilatometry, system $PbO–P_2O_5–PbCl_2$

Introduction

The phase dependences in the ternary system $PbO–P_2O_5–PbCl_2$ have been studied [1–3]. The ternary compounds $14PbO \cdot P_2O_5 \cdot 2PbCl_2$ (called the R phase for simplification) and $29PbO \cdot 3P_2O_5 \cdot 6PbCl_2$ (called the S phase) occur in this system. Compound R crystallizes from the liquid phase; its structure has been examined by X-ray crystallography [4]. Compound S, which is formed in the solid phase, was previously unknown. It is formed in the binary system $Pb_5Cl_2O_4$–$Pb_{10}(PO_4)_6Cl_2$, which is one of the pseudobinary sections in the ternary system $PbO–P_2O_5–PbCl_2$, at a molar ratio of the initial components of 5:1 [3].

The melting points of these compounds have been determined as 780°C (R) [2] and 760°C (incongruent) (S) [3] and X-ray identification data for the S phase have been reported [3].

The present paper reports the results of dilatometric investigations on these compounds, which have not been described in the literature previously.

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Experimental

The compounds used in the examinations were obtained by sintering stoichiometric quantities of reactants in platinum crucibles, in air, at appropriate temperatures.

To synthesize compound R, PbO p.a., $Pb_3(PO_4)_2$, obtained in this laboratory and $PbCl_2$ p.a. were heated at 700°C for 0.5 h. Compound S was obtained either from a ternary mixture of PbO p.a., $Pb_3(PO_4)_2$ and $PbCl_2$ p.a. at 600°C for 0.5 h, or from the two components $Pb_5Cl_2O_4$ and $Pb_{10}(PO_4)_6Cl_2$ at 700°C for 0.5 h.

Lead orthophosphate $Pb_3(PO_4)_2$ was obtained from $NH_4H_2PO_2$ p.a. and PbO p.a. [5], lead oxychloride $Pb_5Cl_2O_4$ from PbO p.a. and $PbCl_2$ p.a. [6], and lead chlorapatite $Pb_{10}(PO_4)_6Cl_2$ from $Pb_3(PO_4)_2$ and $PbCl_2$ p.a. [7].

The phase purity of the compounds was tested microscopically (molten samples) and by X-ray means (molten and sintered samples).

Examinations were carried out with thermal microscopic, X-ray, dilatometric and IR absorption analyses.

Thermal analysis was performed during both the heating and the cooling of samples. A protective argon atmosphere or air, resistance furnaces constructed in this laboratory or a derivatograph (MOM, Hungary) and 10 g samples in platinum crucibles were used. The furnace was heated or cooled at a uniform rate and the temperature was taken with an electronic recorder (MOM, Hungary). The derivatograph was used only for thermal analysis during the heating of 0.5–1.5 g samples.

Dilatometric examinations during heating were performed in a dilatometer (type 802 BG) with programmed heating and computerized analysis of the results. Samples for dilatometric examinations were prepared in the form of 3×3×10 mm beams pressed under a pressure of 10 MPa with an admissible tolerance of the beam length of ±0.2 mm. Before pressing, the samples were powdered to obtain fractions of grain size < 80 μm, and 5 wt% of a 2.5 solution of methyl polymethacrylate in *n*-butyl acetate was then added.

Dilatometric analysis was performed with both previously molten samples and those obtained by synthesis in the solid phase. For comparison, dilatometric curves for both compounds under investigation are presented together in one figure for a molten and a sintered sample, and in the other figures individually with appropriate enlargement of different temperature ranges. The temperatures of deflections in curves were estimated by the tangent method.

X-ray examinations were carried out by the powder method in a Guinier camera, using CuK_α radiation. Microsections were made from molten samples and then observed in reflected light. IR absorption analysis was performed with samples in the form of pellets with potassium bromide in a Specol IR-75 spectrophotometer.

Results and discussion

In the course of thermal examinations during both heating and cooling, and dilatometric examinations during heating, numerous effects were observed for the ternary compounds $14PbO{\cdot}P_2O_5{\cdot}2PbCl_2$ (R) and $29PbO{\cdot}3P_2O_5{\cdot}6PbCl_2$ (S).

Figure 1 presents DTA curves for compound R. Five exothermal effects can be observed at 410°, 485°, 555°, 610° and 700°C for a sintered sample, (Fig. 1a), and at 390°, 480°, 545°, 615° and 690°C for a molten one (Fig. 1b). No change in mass was observed and therefore the TG and DTG curves are not shown.

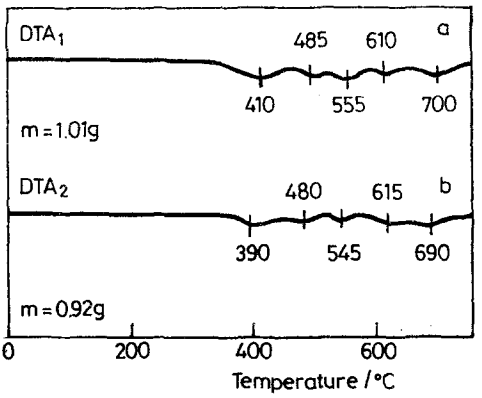

Fig. 1 DTA curves for $14PbO{\cdot}P_2O_5{\cdot}2PbCl_2$ (R) a) sintered, b) molten sample

Table 1 presents the results of dilatometric examinations of (a) a sintered sample of compound R and b) a molten sample of this compound.

Figure 2 shows dilatograms for a sintered (curve 1) and a molten (curve 2) sample of compound R. Figures 3 and 4 present dilatograms for a sintered and a molten compound, enlarged for different temperature ranges.

Figure 3a presents a dilatogram with a dilatometric curve for a sintered sample over the range of temperatures up to 300°C. One strong and three weak effects can be observed here at 96°C (max. — from methyl polymethacrylate [8]), 142° (min.), 214° (min.) and 260°C (min.). In the temperature range 150°–450°C (Fig. 3b), and effect can be observed at 236°C (min.), which leads to the conclusion that the effects at 214° and 260°C in Fig. 3a are the beginning and end of one effect with minimum at 236°C.

Figure 3c shows a dilatogram over the temperature range 250°–750°C. Effects are observed at 527° (max.), 610° (min.), 645° (min.) and 700°C (max.) Figure 3d shows a dilatogram over the temperature range 600°–740°C. Effects are observed at 604° (min.), 661° (min.), 697° (max.) and 712°C (max.).

Dilatograms of molten compound R are presented in Fig. 4. In the dilatometric curve over the temperature range 200°–500°C (Fig. 4a), the first deflection oc-

Table 1 The results of dilatometric investigations of a) a sintered, b) a molten sample of compound $14PbO{\cdot}P_2O_5{\cdot}2PbCl_2$ (R). Relative change of length (epsilon [%]) and linear thermal coefficient of expansion (alfa = 1.10^{-6}/deg).
The given errors correspond with the confidence probability P = 95% and were obtained while calculating instrumental correction. Compound: R. Sample: a) sintered, b) molten. Standard: Al_2O_3. Initial length [mm]: *a*) 10.1, *b*) 10.15. Heating rate: 10 deg·min^{-1}. Correction – sapphire

Temperatura /	*a*		*b*		*a* and *b*
°C	Epsilon / %	Alfa	Epsilon / %	Alfa	Measuring error / %
20	0.000	0.00	0.000	0.00	0.12
30	0.073	73.03	0.068	67.97	0.12
40	0.128	63.97	0.116	57.96	0.12
50	0.164	54.55	0.151	50.17	0.12
60	0.202	50.60	0.192	47.99	0.12
70	0.235	47.08	0.227	45.36	0.12
80	0.275	45.89	0.263	43.79	0.12
90	0.306	43.67	0.296	42.26	0.12
100	0.328	40.95	0.323	40.42	0.12
110	0.335	37.21	0.348	38.66	0.12
120	0.340	34.05	0.365	36.51	0.12
130	0.337	30.67	0.381	34.67	0.12
140	0.334	27.86	0.398	33.13	0.12
150	0.342	26.31	0.414	31.85	0.12
160	0.353	25.20	0.439	31.36	0.12
170	0.363	24.17	0.457	30.44	0.12
180	0.372	23.22	0.481	30.06	0.12
190	0.379	22.27	0.500	29.38	0.12
200	0.385	21.37	0.516	28.68	0.12
210	0.388	20.42	0.541	28.46	0.12
220	0.400	20.01	0.557	27.83	0.12
230	0.408	19.45	0.576	27.45	0.12
240	0.418	18.99	0.594	26.98	0.12
250	0.431	18.74	0.610	26.54	0.12
260	0.439	18.31	0.627	26.11	0.12
270	0.461	18.46	0.645	25.79	0.12
280	0.484	18.60	0.653	25.13	0.12
290	0.501	18.55	0.670	24.80	0.12
300	0.518	18.51	0.687	24.53	0.12
310	0.536	18.47	0.695	23.95	0.12
320	0.553	18.43	0.708	23.61	0.12
330	0.569	18.34	0.720	23.22	0.12
340	0.587	18.35	0.737	23.04	0.12
350	0.606	18.35	0.764	23.17	0.12
360	0.623	18.33	0.782	23.00	0.12

Table 1 (continued)

Temperatura /	*a*		*b*		*a* and *b*
°C	Epsilon / %	Alfa	Epsilon / %	Alfa	Measuring error / %
380	0.658	18.29	0.826	22.94	0.12
390	0.676	18.28	0.835	22.56	0.12
400	0.694	18.26	0.852	22.41	0.12
410	0.712	18.25	0.864	22.14	0.12
420	0.728	19.19	0.875	21.87	0.12
430	0.746	18.18	0.883	21.53	0.12
440	0.760	18.08	0.895	21.31	0.12
450	0.775	18.01	0.900	20.94	0.12
460	0.791	17.97	0.903	20.52	0.12
470	0.800	17.78	0.910	20.23	0.12
480	0.808	17.57	0.914	19.86	0.12
490	0.810	17.23	0.916	19.50	0.12
500	0.814	16.97	0.907	18.89	0.12
510	0.814	16.62	0.894	18.24	0.12
520	0.817	16.34	0.866	17.31	0.12
530	0.819	16.05	0.826	16.20	0.12
540	0.820	15.78	0.796	15.31	0.12
550	0.819	15.46	0.757	14.28	0.12
560	0.818	15.15	0.717	13.28	0.12
570	0.807	14.68	0.676	12.29	0.12
580	0.797	14.23	0.628	11.21	0.12
590	0.786	13.79	0.580	10.17	0.12
600	0.776	13.37	0.530	9.15	0.12
610	0.755	12.80	0.462	7.84	0.12
620	0.735	12.25	0.356	5.93	0.12
630	0.715	11.72	0.249	4.08	0.12
640	0.695	11.20	0.104	1.67	0.12
650	0.678	10.77	–0.061	–0.96	0.12
660	0.670	10.47	–0.263	–4.11	0.12
670	0.664	10.22	–0.533	–8.21	0.12
680	0.670	10.15	–0.938	–14.22	0.12
690	0.671	10.02	–1.430	–21.34	0.12
700	0.671	9.86	–2.056	–30.23	0.12
710	0.656	9.51	–2.882	–41.77	0.12
720	0.534	7.63	–3.962	–56.60	0.12

curs at 290°C (max.), the next at 341°C (min.) and a third at 364°C. In the temperature range 250°–750°C (Fig. 4b), three effects are noted at 504° (max.),

612° (max.) and 673°C (max.). In the temperature range from 504° to 673°C, the contraction of the sample $\Delta\varepsilon$ amounts to 1.4%.

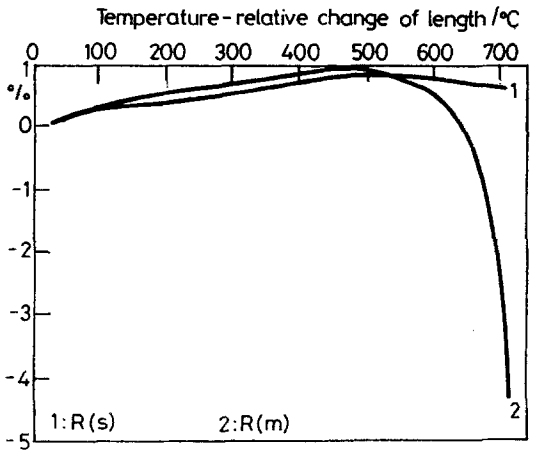

Fig. 2 Dilatograms for R 1 — sintered, 2 — molten sample

The temperatures of the effects obtained in the course of thermal analysis for compound R are slightly different from those obtained by dilatation.

Figure 5 presents DTA curves for the second ternary compound, with the formula $29PbO{\cdot}3P_2O_5{\cdot}6PbCl_2$, called S for simplification. Thermal analysis of this compound proved the occurrence of five exothermal effects; for a sintered sample at 380°, 500°, 570°, 615° and 680°C (Fig. 5a), and for a molten one at 370°, 495°, 565°, 605° and 675°C.

The results of dilatometric investigations of compound S are shown in Table 2, where *a*) refers to a sintered and *b*) to a molten sample.

Figure 6 shows dilatograms for a sintered (curve 1) and a molten (curve 2) sample of compound S.

Dilatograms of sintered compound S are presented in Fig. 7, where Fig. 7a refers to the range 0°–400°C, with effects at 98°C (max. from methyl polymethacrylate) and 300°C (min.), while Fig. 7b includes the range 300°–700°C. Here, deflections were observed in the dilatometric curve at 361° (max.), 464°C (min.), 553°C (max.) and 659°C (max.).

Figure 8 shows a dilatometric curve for a molten sample of compounds over the ranges of temperatures up to 700°C (Fig. 8a), 160°–360°C (Fig. 8b), 200°–450°C (Fig. 8c), 400°–600°C (Fig. 8d) and 300°–650°C (Fig. 8e). In Fig. 8a, the first deflection in the dilatometric curve, at 105°C, originates from methyl polymethacrylate, with subsequent deflections at 189° (min.), 216° (max.), 225° (min.), 260° (max.), 302° (min.) and 403°C (min.). This deflection changes into another at 516°C (min.), the curve then goes up linearly to 569°C

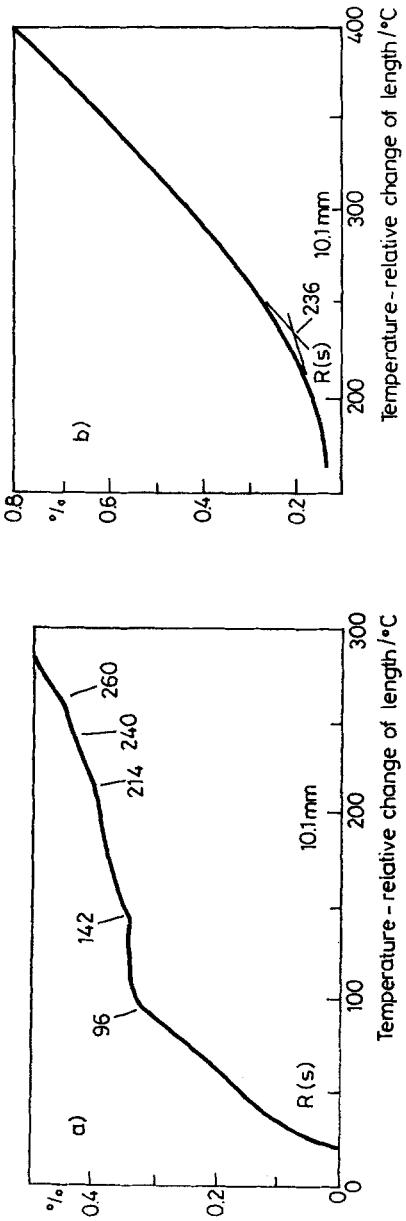

Fig. 3 Dilatogram for R sintered (s) over the temperature ranges: a) 0°–300°C, b) 150°–450°C, c) 250°–750°C, d) 600°–740°C

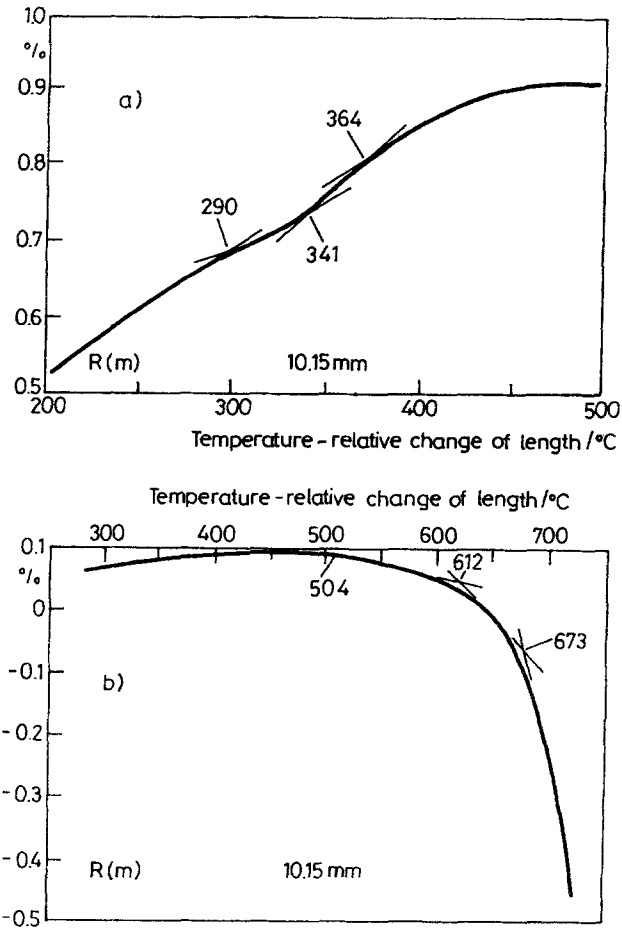

Fig. 4 Dilatogram for molten R(m) over the temperature ranges: a) 200°–500°C, b) 250°–750°C

(min.), and above this temperature irregularities begin again up to 585°C (max.) and the curve rises sharply.

The dilatometric curve presented in Fig. 8b is very irregular with deflections at 200° (min.), 218° (max.), 222° (min.), 239° (min.), 260° (max.), 265° (min.), 280° (max.), 285° (min.), 295° (max.), 302° (min.), 315° (min.), 325° (max.), 330° (min.) and 340°C (max.).

In the temperature range 200°–450°C (Fig. 8c), deflections occur in the dilatometric curve at 213° (max.), 220° (min.), 244° (max.), 301° (min.), 345° (max.), 375° (max.) and 400°C (min.). Four effects may be noted here:

1/ 213°–244°C, min. 220°C
2/ 250°–345°C, min. 301°C
3/ 350°–375°C, min. 370°C

4/ 380°–450°C, min. 400°C

Figure 8d shows the temperature range 400°–600°C, where three effect can be observed with a slight volume contraction, with minima at 474°, 496° and 515°C, and two effects with a volume increase (of approx. 0.02%), with maxima at 572° and 586°C. These are recorded at:

1/ 470°–489°C, min. 474°C
2/ 490°–510°C, min. 496°C
3/ 512°–535°C, min. 515°C
4/ 570°–575°C, max. 572°C
5/ 577°–595°C, max. 586°C

Figure 8e shows the dilatometric curve for the temperature range 300°–650°C, with deflections at 400° (min.), 470° (max.), 475° (min.), 488°

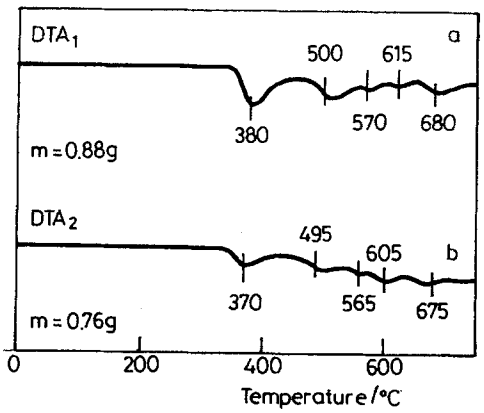

Fig. 5 DTA curves for $29PbO{\cdot}3P_2O_5{\cdot}6PbCl_2$ (S) a) sintered, b) molten sample

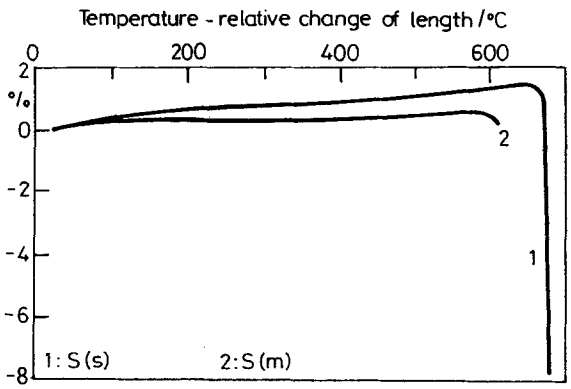

Fig. 6 Dilatograms for $29PbO{\cdot}3P_2O_5{\cdot}6PbCl_2$ (S) 1 — sintered, 2 — molten sample

Table 2 The results of dilatometric investigations of *a*) a sintered (10.1 mm), *b*) a molten (10.15 mm) sample of compound $29PbO{\cdot}3P_2O_5{\cdot}6PbCl_2$ (S). The experimental conditions are as given in Table 1.

Temperatura /	*a*		*b*		*a* and *b*
°C	Epsilon / %	Alfa	Epsilon / %	Alfa	Measuring error / %
20	0.000	0.00	0.000	0.00	0.12
30	0.066	66.30	0.062	61.88	0.12
40	0.118	59.17	0.125	62.60	0.12
50	0.160	53.27	0.168	56.12	0.12
60	0.198	49.38	0.203	50.77	0.12
70	0.235	46.90	0.238	47.59	0.12
80	0.277	46.22	0.273	45.48	0.12
90	0.316	45.20	0.300	42.90	0.12
100	0.348	43.48	0.324	40.49	0.12
110	0.374	41.51	0.330	36.70	0.12
120	0.392	39.17	0.327	32.72	0.12
130	0.406	36.91	0.324	29.47	0.12
140	0.425	35.44	0.307	25.56	0.12
150	0.443	34.05	0.289	22.27	0.12
160	0.465	33.21	0.276	19.72	0.12
170	0.490	32.69	0.264	17.59	0.12
180	0.505	31.56	0.254	15.90	0.12
190	0.525	30.86	0.250	14.70	0.12
200	0.543	30.19	0.238	13.21	0.12
210	0.559	29.43	0.245	12.89	0.12
220	0.585	29.24	0.244	12.18	0.12
230	0.602	28.66	0.250	11.90	0.12
240	0.619	28.13	0.260	1183	0.12
250	0.636	27.65	0.273	11.89	0.12
260	0.653	27.21	0.280	11.66	0.12
270	0.670	26.81	0.280	11.19	0.12
280	0.689	26.48	0.284	10.91	0.12
290	0.714	26.43	0.285	10.57	0.12
300	0.732	26.14	0.288	10.29	0.12
310	0.758	26.14	0.291	10.04	0.12
320	0.785	26.17	0.307	10.22	0.12
330	0.806	26.01	0.316	10.20	0.12
340	0.836	26.14	0.334	10.43	0.12
350	0.858	26.00	0.351	10.65	0.12
360	0.876	25.75	0.359	10.57	0.12
370	0.890	25.44	0.373	10.66	0.12
380	0.901	25.03	0.383	10.64	0.12
390	0.909	24.57	0.388	10.49	0.12

Table 2 (continued)

Temperatura /	*a*		*b*		*a* and *b*
°C	Epsilon / %	Alfa	Epsilon / %	Alfa	Measuring error / %
400	0.917	24.14	0.394	10.38	0.12
410	0.925	23.71	0.399	10.24	0.12
420	0.931	23.27	0.409	10.22	0.12
430	0.940	22.92	0.416	10.14	0.12
440	0.949	22.60	0.424	10.10	0.12
450	0.958	22.29	0.432	10.05	0.12
460	0.973	22.12	0.441	10.01	0.12
470	0.994	22.10	0.449	9.98	0.12
480	1.022	22.22	0.450	9.77	0.12
490	1.050	22.33	0.455	9.68	0.12
500	1.087	22.65	0.455	9.48	0.12
510	1.117	22.79	0.462	9.42	0.12
520	1.152	23.05	0.464	9.28	0.12
530	1.192	23.37	0.471	9.23	0.12
540	1.228	23.61	0.479	9.22	0.12
550	1.255	23.69	0.488	9.20	0.12
560	1.274	23.59	0.496	9.19	0.12
570	1.292	23.49	0.505	9.18	0.12
580	1.306	23.33	0.523	9.35	0.12
590	1.319	23.14	0.523	9.18	0.12
600	1.337	23.06	0.491	8.46	0.12
610	1.350	22.88	0.296	5.03	0.12
620	1.365	22.76	—	—	0.12
630	1.381	22.64	—	—	0.12
640	1.392	22.45	—	—	0.12
650	1.410	22.39	—	—	0.12
660	1.418	22.16	—	—	0.12
670	0.866	13.33	—	—	0.12

(max.), 495° (min.), 510° (max.), 515° (min.), 570° (min.), 572° (max.), 577° (min.) and 598°C (max.).

Conclusions

The above analysis of the thermal and dilatometric curves reveals that the ternary compounds R and exhibit strong effects during changes of temperature.

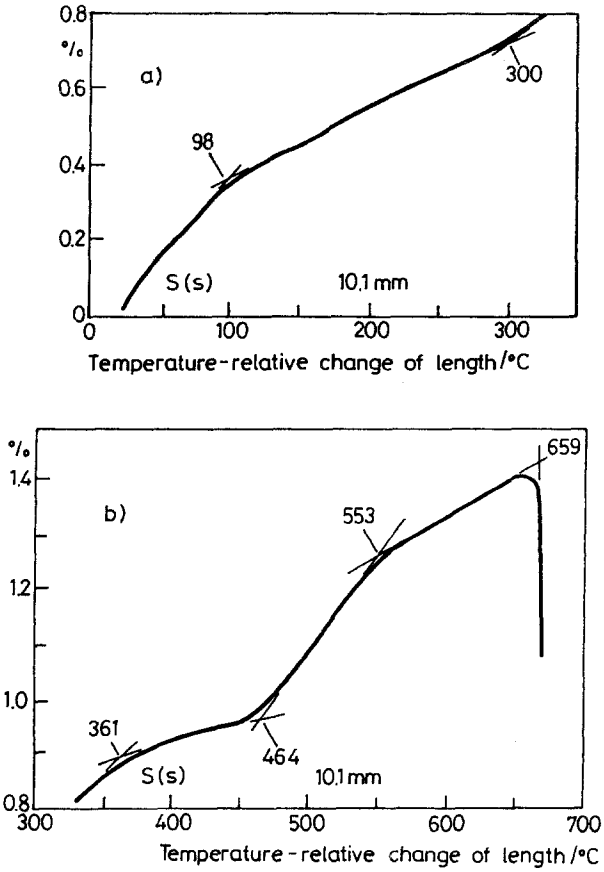

Fig. 7 Dilatogram for sintered S (s) over the temperature ranges: a) 0°–400°C, b) 300°–700°C

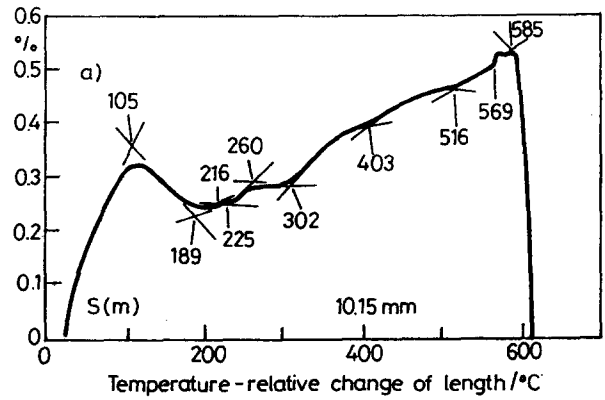

Fig. 8a Dilatogram for molten sample S (m) over the temperature ranges: a) 0°–700°C

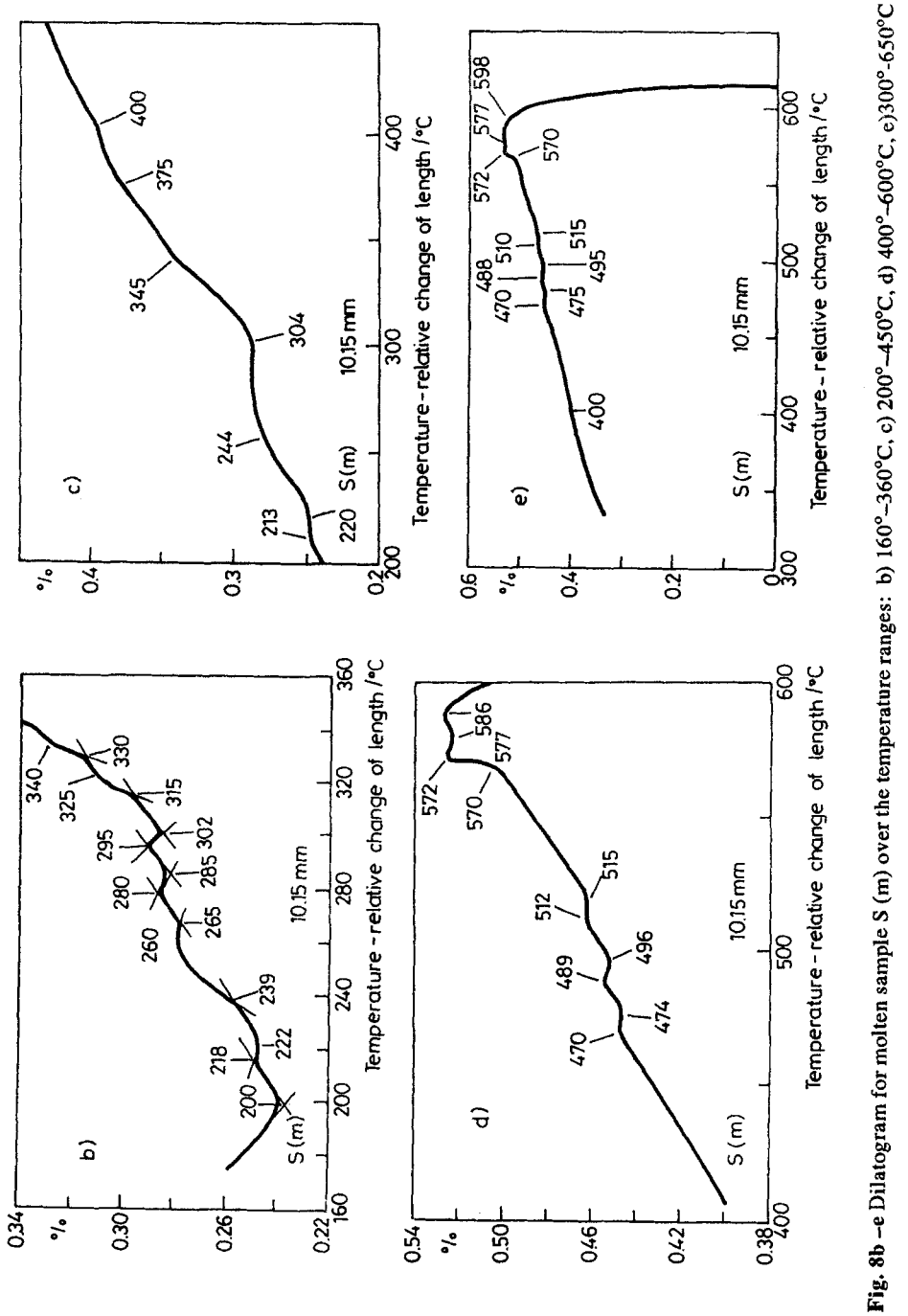

Fig. 8b –e Dilatogram for molten sample S (m) over the temperature ranges: b) 160°–360°C, c) 200°–450°C, d) 400°–600°C, e)300°-650°C

The temperatures of the effects observed during the thermal analysis (Fig. 1) of compound R differ a little from those of the dillatational effect (Figs 2–4). The situation is similar for compound S (Fig. 5 and Figs 6–8). The temperatures of the thermal dilatational effects observed for a molten and a sintered sample of the same compound are also different. However, no dependences of these differences were found, i.e. the temperatures of the effects are sometimes higher and sometimes lower for sintered samples than for molten samples.

The thermal and dilatational effects for the two compounds are quantitatively the same and they occur at similar temperatures. This may result from the similar structures of these compounds [3, 4]. It is evident from phase examinations of the ternary compounds PbP–R–$Pb_{10}(PO_4)_6Cl$–$Pb_8P_pO_{13}$ [2] and PbO–$Pb_5Cl_2O_4$–$Pb_{10}(PO_4)_6Cl_2$–R [3] that lead monoxide PbO forms a pseudobinary system PbO–S with compounds S, whereas with compound R congruent melting occurs. For the formulae of these ternary compounds, the following dependence can be written:

$$S + 13\ PbO = 3\ R$$

$$29\ PbO \cdot 3\ P_2O_5 \cdot 6\ PbCl_2 + 13\ PbO = 42\ PbO \cdot 3\ P_2O_5 \cdot 6\ PbCl_2 =$$

$$= 3\ (14\ PbO \cdot P_2O_5 \cdot 2\ PbCl_2)$$

When everything is taken into consideration, the occurrence of analogous thermal and dilatational effects for the two compounds seems natural.

The most common temperatures of the effects of these ternary compounds are as follows

– for compound R: 390°, 480°, 545°, 615° and 690°C
– for compound S: 370°, 495°, 565°, 605° and 675°C.

The results of these investigations provide an important complement to the phase dependences in the solid phase for the ternary compounds R and S formed in the ternary system PbO–P_2O_5–$PbCl_2$. It is not yet possible to explain the causes of the above effects, because this requires detailed structural examinations. However, they can not be ignored, for they might help to explain phenomena proceeding in the solid phase.

References

1 H. Podsiadlo, J. Thermal Anal., 36 (1990) 1369.
2 H. Podsiadlo, J. Thermal Anal., 37 (1991) 139.
3 H. Podsiadlo, J. Thermal Anal., 37 (1991) 2239.
4 B. Aurivillius, Chemica Scripta, 22 (1983) 5.
5 J. Berak and H. Dabrowiecka, Polish J. Chem., 54 (1980) 137.
6 H. Podsiadlo, J. Thermal Anal., 37 (1991) 613.

7 J. Berak and H. Podsiadlo, Polish J. Chem., 56 (1982) 1165.
8 H. Podsiadlo, J. Thermal Anal., 37 (1991) 2649.

Zusammenfassung–Mittels Dilatometrie wurden die im ternären System $PbO–P_2O_5–PbCl_2$ gebildeten ternären Verbindungen $14PbO·P_2O_5·2PbCl_2$ (R) und $29PbO·3P_2O_5·6PbCl_2$ (S) untersucht. Unter dem Einfluß von Wärme konnten an diesen Verbindungen zahlreiche, vorher noch nicht beschriebene Effekte beobachtet werden.