LEAD INDUSTRIES ASSOCIATION

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SUBJECT: REPRINT OF LEAD CERAMIC RESEARCH PAPER

To Members of the Lead Industries Association:

We are attaching a reprint from the Journal of the American Ceramic Society entitled, "Dilatometric and X-Ray Data for Lead Compounds."

As you will see, one of the authors of this paper is the LIA fellow at the Pennsylvania State University working under one of our ceramic research grants and the other author is his faculty supervisor. Information reported is the result of the first year of work by our fellow which comprises the academic year 1958-59. This fellowship is now entering its third year and additional papers are to be expected as a result of it. Printing of the paper in the Ceramic Society Journal has, of course, given it wide distribution throughout the ceramic industry and we have purchased a limited number of reprints to be used in answering inquiries and for personal distribution where we think it will be beneficial.

Members can obtain additional copies from us up to 25 free of charge and copies in quantity at our cost of 10¢ each, as long as our limited supply lasts.

Very truly yours,

Secretary.

[Reprinted from the Journal of The American Ceramic Society, Vol. 43, No. 9, September, 1960.]

Dilatometric and X-Ray Data for Lead Compounds, I

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Linear thermal-expansion data are presented for lead silicate, lead phosphate, lead borosilicate, and lead silicophosphate compounds. X-ray powder data for the compounds are given, and previous phase equilibria and X-ray data are discussed briefly.

I. Introduction

The influence of lead oxide on the thermal-expansion characteristics of glasses, glazes, and enamels has been extensively investigated and many data are available. For many types of lead glasses one already knows the expansion characteristics or can easily predict what changes in expansion will occur by raising or lowering the lead content.

In contrast, very few thermal-expansion data are available for crystalline lead compounds. The objective of this series of papers is to provide new expansion and X-ray data on synthetic lead compounds. It is anticipated that these data will be useful in cases where a crystalline lead-containing ceramic is prepared by nucleation and devitrification of high lead glasses or by sintering or reaction of crystalline compounds.

II. Literature

(1) Lead Silicates

Geller, Creamer, and Bunting[1] confirmed the existence of three lead silicate compounds in 1934 and McMurdie and Bunting[2] later studied their X-ray patterns. Other workers, in particular Krakau and Vakhrameev,[3] have postulated compounds of the composition $3PbO \cdot SiO_2$ and $3PbO \cdot 2SiO_2$, the latter corresponding to the natural mineral barysilite.

(2) Lead Phosphates

In 1912 Kroll[4] found five compounds in the binary system PbO–P_2O_5 in the range 0 to 40 mole % P_2O_5. Later, Andress and Fischer[5] described a metaphosphate and Schulz[6] studied a tetraphosphate ($3PbO \cdot 2P_2O_5$).

(3) Lead Borosilicate

Geller and Bunting[7] worked out phase relations in the system PbO–B_2O_3–SiO_2 and reported the existence of a compound $5PbO \cdot B_2O_3 \cdot SiO_2$. It was said to melt incongruently at 551°C. to form $2PbO \cdot SiO_2$ and liquid. Moore and Eitel[8] classified the ternary compound as an apatite after X-ray examination.

(4) Lead Silicophosphates

Paetsch and Dietzel[9] explored the ternary system and reported $5PbO \cdot P_2O_5 \cdot SiO_2$ as a distinct compound. A second

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The writers are, respectively, Lead Industries Association fellow and professor, Department of Ceramic Technology, College of Mineral Industries, The Pennsylvania State University.

[1] R. F. Geller, A. S. Creamer, and E. N. Bunting, "The System PbO-SiO$_2$," *J. Research Natl. Bur. Standards*, **13** [2] 237–44 (1934); RP 705; *Ceram. Abstr.*, **13** [11] 304 (1934).

[2] H. F. McMurdie and E. N. Bunting, "X-Ray Studies of Compounds in the System PbO-SiO$_2$," *J. Research Natl. Bur. Standards*, **23** [4] 533–47 (1939); RP 1251; *Ceram. Abstr.*, **19** [11] 33 (1940).

[3] K. A. Krakau and N. A. Vakhrameev, "Diagram of Equilibrium of the System PbO-SiO$_2$," *Keram. i Steklo* (*Ceramics & Glass*), **8** [1] 42–43 (1932); *Ceram. Abstr.*, **11** [7] 430 (1932).

[4] (a) A. V. Kroll, "Thermische Untersuchung der Phosphate des Bleis und einige Erwagungen uber die Konstitutionsformeln derselben sowie ihrer Derivate in Form von Komplexsalzen, namentlich denen der Thomasschlacke," *Z. anorg. Chem.*, **78**, 95–133 (1912).

(b) A. V. Kroll, "Über Ultraphosphate: II, Thermische Untersuchung der glasigen Phosphate des Bleis," *ibid.*, **77**, 1–40 (1912).

[5] K. R. Andress and K. Fischer, "Polymere Metaphosphates: III, X-Ray Investigation of Kurrol's Potassium Metaphosphate and Studies on Lead Metaphosphate [$Pb(PO_3)_2$]$_\infty$," *Z. anorg. u. allgem. Chem.*, **273** [3–5] 193–99 (1953); *Ceram. Abstr.*, **1950**, February, p. 60b.

[6] I. Schulz, "Crystalline Tetraphosphates," *Z. anorg. u. allgem. Chem.*, **287** [1–2] 106–12 (1956); *Ceram. Abstr.*, **1956**, July, p. 194i.

[7] R. F. Geller and E. N. Bunting, "The System PbO–B$_2$O$_3$–SiO$_2$," *J. Research Natl. Bur. Standards*, **23** [2] 275–83 (1939); RP 1231; *Ceram. Abstr.*, **18** [11] 312 (1939).

[8] R. B. Moore and Wilhelm Eitel, "A Borosilicate of the Apatite Group," *Naturwissenschaften*, **44**, 250 (1957) (in English).

[9] H. H. Paetsch and Adolf Dietzel, "Untersuchungen über das System PbO-SiO$_2$-P$_2$O$_5$," (The System PbO-SiO$_2$-P$_2$O$_5$), *Glastech. Ber.*, **29** [9] 345–56 (1956).

Table I. Composition and Calcining and Firing Treatments for Lead Compounds

Composition	Weight per cent PbO	B_2O_3	SiO_2	P_2O_5	Calcinations Temp. (°C.)	Calcinations Time (hr.)	Firing of bars Temp. (°C.)	Firing of bars Time (hr.)
$PbO \cdot SiO_2$	78.81		21.19		750	24	750	6
$2PbO \cdot SiO_2$	88.14		11.86		725	24	725	6
$4PbO \cdot SiO_2$	93.71		6.29		700	36	700	6
$PbO \cdot P_2O_5$	61.12			38.88	550	12	550	6
$3PbO \cdot 2P_2O_5$	70.22			29.78	650	24	650	6
$2PbO \cdot P_2O_5$	75.89			24.11	800	24	800	6
$5PbO \cdot 2P_2O_5$	79.72			20.28	900	24	900	6
$3PbO \cdot P_2O_5$	82.50			17.50	950	24	970	6
$4PbO \cdot P_2O_5$	86.30			13.70	900	24	900	6
$8PbO \cdot P_2O_5$	92.15			7.85	800	24	800	6
$5PbO \cdot P_2O_5 \cdot SiO_2$	84.67		4.56	10.77	950	24	950	6
$5PbO \cdot B_2O_3 \cdot SiO_2$	89.56	5.59	4.85		500	24	500	6

phase, $16PbO \cdot P_2O_5 \cdot 2SiO_2$, was reported, but there is some doubt about its existence.

Bruge[10] patented refractory compositions in the ternary system with the empirical formulas $(PbO)_{x+y} \cdot (SiO_2)_x \cdot (P_2O_5)_y$, where the ratio of y to x is 0.35 to 0.70. In this range he claims three compounds, $5PbO \cdot 3SiO_2 \cdot 2P_2O_5$, $3PbO \cdot 2SiO_2 \cdot P_2O_5$, and $11PbO \cdot 8SiO_2 \cdot 3P_2O_5$. All these compounds are claimed to have very high melting points, the 5:3:2 composition not melting at 1700°C., the 3:2:1 not melting at 1300°C., and the 11:8:3 not melting at 1400°C. It is likely that these are empirical formulas rather than true compounds in the usual chemical sense.

III. Experimental Procedures

Compositions were made from c.p. lead carbonate, silicic acid, boric acid, and diammonium hydrogen phosphate. After weighing, the batches were hand mixed in a glass mortar with acetone for 15 to 20 minutes and allowed to air-dry overnight. The batches were then heated gently in a Globar furnace to allow such components as diammonium hydrogen phosphate and boric acid to convert to the required oxide. The initial calcining temperatures were kept low enough (200°C. for 4 hours) to expel H_2O, NH_3, and CO_2 but to prevent the loss of components such as B_2O_3 or P_2O_5.

After low-temperature calcining, the batches were fired to temperatures sufficient to cause complete or partial reaction to occur (Table I). The mixtures were cooled, ground, remixed, and then fired until complete equilibrium was attained, as indicated by X-ray diffraction and petrographic examination.

After the final calcination, the batches were ground, mixed with a Carbowax solution, and forced through a 20 mesh sieve, after which they were pressed into 10- by 1- by 1-cm. bars at 1000 lb. per sq. in. The specimens were fired slowly to a point below the temperature of liquid formation for the particular compound and held until the bar was sintered to a relatively dense condition. Heat-treatments are shown in Table I.

The crystal size of each compound remained so small after calcination and final firing that the microscope was used only to determine that the phases were homogeneous. The growth of larger crystals suitable for determination of optical properties would require the use of temperatures above the fusion point of the congruently melting compounds. It was found that volatilization of constituents was not a serious problem when calcining and firing was done 25°C. or more below the fusion temperatures. Above the fusion temperatures, it was found that vaporization was appreciable, especially in the phosphates. Hallse and Cook[11] have recently provided quantitative data on the volatility of lead silicate melts.

Thermal-expansion runs were made in a fused silica vertical dilatometer, using a heating rate of 120°C. per hour. The expansions were measured by dial gauges which were accurate to $^1/_{10,000}$ in. At least two runs were made on each specimen.

X-ray diffraction patterns were obtained on a Norelco diffractometer using CuKα radiation. The specimens were ground to pass a 200-mesh sieve and packed into sample holders in such a way as to minimize the possibility of any preferred orientation of the crystal aggregate. The samples were run between 10° and 80° 2θ at 1° 2θ per minute. While the samples were being run, a scale factor of 4, a multiplier of 1, and a time constant of 4 were used, the strongest peak of the pattern being brought completely onto the recording chart by placing thin nickel foils in front of the counter tube when peak intensities required it.

IV. Experimental Results and Discussion

(1) Lead Silicates

The existence of the three compounds $PbO \cdot SiO_2$, $2PbO \cdot SiO_2$, and $4PbO \cdot SiO_2$ was verified, the data agreeing with that of Geller, Creamer, and Bunting.[1] Attempts were made to synthesize the two previously suggested compounds $3PbO \cdot SiO_2$ and $3PbO \cdot 2SiO_2$[3] by the usual solid-state methods and also by devitrification of a glass in the case of $3PbO \cdot 2SiO_2$. All the attempts failed, the X-ray diffraction patterns yielding a mixture of $4PbO \cdot SiO_2$ and $2PbO \cdot SiO_2$ in the case of the 3:1 composition and $2PbO \cdot SiO_2$ and $PbO \cdot SiO_2$ in the case of the 3:2 composition. These data show that these two compounds probably do not exist in the binary system PbO–SiO_2 under normal conditions of temperature and pressure.

The expansion curves (Fig. 1) are continuous in the cases of $PbO \cdot SiO_2$ and $2PbO \cdot SiO_2$, but the $4PbO \cdot SiO_2$ curve shows a discontinuity due to the reversible inversion of γ-$4PbO \cdot SiO_2$ to β-$4PbO \cdot SiO_2$. According to Geller, Creamer, and

[10] E. C. Bruge, "Lead Silicophosphate Compositions and Processes for Preparing Them," U. S. Pat. No. 2,703,300, Sept. 18, 1956, *Ceram. Abstr.*, 1957, January, p. 22g.

[11] R. L. Hallse and R. L. Cook, "Volatility Studies of Lead Silicate Melts," *J. Am. Ceram. Soc.*, 41 [9] 311-36 (1958).

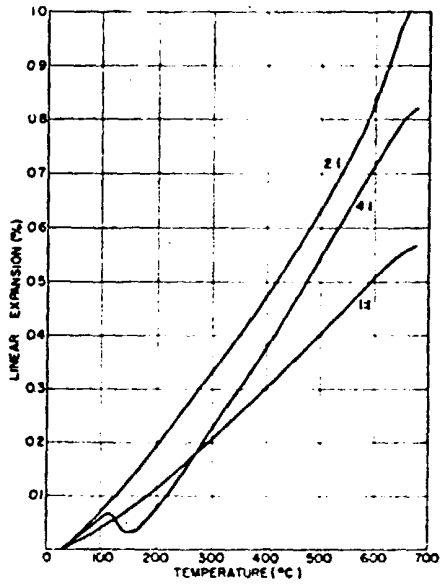

Fig. 1. Expansion vs. temperature for lead silicate compounds.

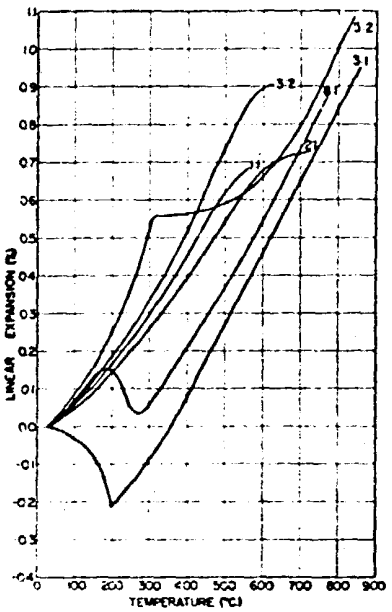

Fig. 2. Expansion vs. temperature for lead phosphate compounds.

Table II. X-Ray Diffraction Data for Lead Silicates

d (a.u.)	I/I₀	d (a.u.)	I/I₀	d (a.u.)	I/I₀
		PbO·SiO₂			
6.42	18	2.80	24	1.834	10
5.79	10	2.74	13	1.797	10
5.68	39	2.71	34	1.784	9
5.13	1	2.66	25	1.755	19
4.37	6	2.61	6	1.737	13
4.06	6	2.52	14	1.688	19
3.55	55	2.46	5	1.647	8
3.52	44	2.37	6	1.639	8
3.33	100	2.34	73	1.566	11
3.21	41	2.23	21	1.537	8
3.09	20	2.20	12	1.514	5
3.04	31	2.14	9	1.463	4
2.98	45	2.03	13	1.396	8
2.90	28	1.98	13	1.372	8
2.86	11	1.937	8	1.333	8
				1.284	8
		2PbO·SiO₂			
6.03	28	2.78	19	1.872	14
4.29	8	2.55	24	1.838	8
3.71	27	2.43	13	1.791	14
3.56	16	2.41	10	1.778	8
3.22	100	2.37	17	1.756	8
3.13	88	2.23	14	1.731	4
3.00	62	2.14	8	1.676	7
2.95	21	2.03	10	1.633	17
2.89	16	2.01	10	1.603	8
2.80	36	1.933	7		
		γ-4PbO·3SiO₂			
7.31	18	2.95	17	1.909	4
5.91	8	2.82	16	1.855	8
5.47	8	2.72	15	1.824	10
4.62	8	2.68	6	1.773	8
3.22	8	2.54	8	1.656	6
3.13	100	2.49	8	1.635	8
3.02	36	1.951	8		

Bunting[3] a reversible β to α inversion occurs at 720°C. This inversion cannot be easily demonstrated by thermal expansion methods since the inversion temperature is only 5°C. below the incongruent melting point of $4PbO \cdot SiO_2$.

Although the X-ray diffraction data (Table II) agree reasonably well with that of McMurdie and Bunting,[3] certain minor variations are apparent, especially with regard to d spacings. A significant variation occurs in the case of $4PbO \cdot SiO_2$, where the relative intensities of the two strongest lines are reversed.

(2) Lead Phosphates

The existence of the five compounds claimed by Kroll[4] and the two claimed by Andress and Fischer[5] and Schulz[6] was verified. Thus, in the binary system PbO–P_2O_5 there exist seven compounds, namely, 1:1, 3:2, 2:1, 5:2, 3:1, 4:1, and 8:1.

Some difficulty was encountered in preparing these compounds and obtaining reliable X-ray diffraction patterns. Although the starting materials reacted readily, complete equilibrium was not always attained, mixed phases being common. This difficulty was circumvented by pressing pellets 1 cm. in diameter and approximately 1 cm. long under a pressure of 1000 lb. per sq. in. Specimens were ground and remixed after initial calcination and partial reaction and then pressed into pellets. The pellets were fired to temperatures where complete reaction occurred, as determined by checking with X-ray methods until the patterns obtained gave no further change on prolonged heating.

The thermal expansion curves are shown in Fig. 2 for each compound except the 4:1. It was impossible to fire a pressed bar of this compound for thermal-expansion purposes, since the large volume change on passing through the inversion at 256°C. always shattered the bar to a powder. Kroll[4] showed that the 4:1 and 3:1 compounds had reversible inversions at 256° and 177°C., respectively. These data were confirmed in these experiments, but the thermal behavior shown in Fig. 2 also indicates inversions or discontinuities in the 5:2 and 8:1 compounds.

Differential thermal analysis data on these two compounds showed no peaks corresponding to the discontinuities in the thermal-expansion curves. Inasmuch as great care was taken to assure compound compositions of exact stoichiometric ratio and to avoid mixtures of phases and nonequilibrium conditions, there is at present no explanation for these anomalies.

The X-ray diffraction data for the seven compounds are given in Table III. The patterns of the 1:1, 3:1, 5:2, and

Table III. X-Ray Diffraction Data for Lead Phosphates

d(a.u.)	I/I_0	d(a.u.)	I/I_0	d(a.u.)	I/I_0
		$PbO \cdot P_2O_5$			
8.67	8	2.98	37	1.899	8
7.63	33	2.85	18	1.845	9
7.25	68	2.80	12	1.821	12
6.61	7	2.78	16	1.771	7
5.91	58	2.72	25	1.737	17
5.07	25	2.69	18	1.692	10
4.80	9	2.67	30	1.670	12
4.72	28	2.63	27	1.631	6
4.58	10	2.54	7	1.608	11
4.35	100	2.49	23	1.519	8
3.90	70	2.42	16	1.480	7
3.82	37	2.34	15	1.447	6
3.71	37	2.29	13	1.427	4
3.53	55	2.28	8	1.395	4
3.41	52	2.18	18	1.359	8
3.35	45	2.13	30	1.334	5
3.30	25	2.09	23	1.298	6
3.24	56	2.04	23	1.265	6
3.22	85	1.958	23	1.242	6
3.05	36	1.922	14		
		$3PbO \cdot 2P_2O_5$			
7.56	43	2.72	37	1.848	9
6.61	8	2.68	19	1.771	16
5.87	4	2.67	29	1.737	11
5.57	29	2.62	4	1.649	10
4.85	5	2.49	23	1.670	14
4.72	29	2.44	4	1.620	5
4.56	17	2.34	21	1.631	4
3.85	13	2.28	18	1.616	5
3.79	13	2.27	10	1.608	5
3.68	35	2.20	6	1.542	6
3.52	100	2.18	8	1.517	8
3.41	34	2.13	35	1.480	10
3.34	16	2.08	21	1.398	3
3.22	54	2.04	12	1.359	9
3.21	100	2.05	13	1.346	6
3.05	42	1.965	13	1.332	4
2.90	36	1.926	25	1.221	4
2.77	21	1.850	11		

(Table III concluded on following page)

Table III (concluded)

d(a.u.)	I/I₀	d(a.u.)	I/I₀	d(a.u.)	I/I₀
		$2PbO \cdot P_2O_5$			
6.37	4	3.35	20	2.32	4
5.79	3	3.18	100	2.21	4
4.90	3	3.10	13	2.20	10
4.75	4	3.07	9	2.12	18
4.46	13	2.96	4	1.907	5
4.10	6	2.90	6	1.856	6
3.72	6	2.71	7	1.743	4
3.47	23	2.54	5	1.676	4
3.38	12	2.46	3	1.583	6
				1.280	5
		$5PbO \cdot 2P_2O_5$			
5.87	8	3.07	100	1.881	27
4.00	16	3.00	25	1.811	7
4.46	11	2.78	27	1.781	5
4.35	19	2.72	63	1.710	7
4.29	7	2.60	33	1.667	9
4.17	27	2.53	5	1.647	5
4.00	21	2.49	5	1.627	13
3.87	64	2.18	33	1.563	12
3.79	20	2.14	13	1.514	7
3.52	46	2.07	49	1.496	6
3.46	11	2.04	39	1.425	9
3.33	77	2.01	12	1.391	7
3.27	77	1.977	52	1.377	13
3.20	56	1.945	5	1.336	5
3.16	49	1.922	13		
		$3PbO \cdot P_2O_5$			
6.71	2.3	2.73	4.6	1.734	1.3
4.72	2.3	2.47	9.0	1.687	1.2
4.08	3.1	2.23	100	1.598	2.7
3.49	7.5	2.08	1.6	1.577	1.4
3.12	12.5	2.05	3.4	1.549	10.0
3.05	6.1	1.866	7.1	1.348	7.1
2.84	1.4	1.752	1.8		
		$4PbO \cdot P_2O_5$			
6.37	10	3.39	66	1.945	27
5.64	15	3.08	91	1.914	21
5.01	15	2.90	87	1.884	27
4.77	34	2.88	100	1.853	12
4.60	7	2.82	29	1.834	23
4.33	44	2.77	47	1.784	22
4.13	40	2.53	7	1.768	16
3.87	15	2.49	7	1.664	9
3.72	7	2.29	12	1.598	10
3.68	7	2.25	6	1.588	9
3.58	19	2.20	7	1.542	28
3.48	66	2.16	7	1.519	7
3.39	25	2.12	7	1.508	6
3.34	26	2.08	7	1.490	12
3.27	34	2.06	44	1.410	7
3.19	26	2.01	9	1.399	6
3.12	99	1.972	18	1.361	9
3.05	37	1.961	34	1.298	30
		$8PbO \cdot P_2O_5$			
7.14	18	2.89	4	1.687	22
6.81	4	2.84	100	1.623	4
4.82	8	2.68	14	1.593	4
4.72	4	2.56	32	1.556	9
4.57	4	2.15	4	1.534	9
4.42	4	2.03	4	1.526	9
3.48	4	1.985	4	1.421	9
3.13	54	1.909	22	1.278	9
3.05	57	1.841	10		
2.95	4	1.704	13		

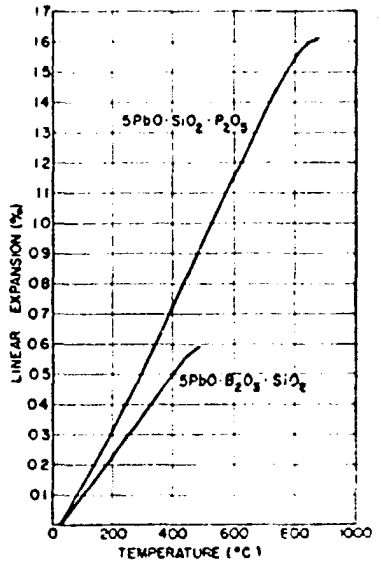

Fig. 3. Expansion vs. temperature for $5PbO \cdot B_2O_3 \cdot SiO_2$ and $5PbO \cdot SiO_2 \cdot P_2O_5$.

4:1 compounds were very complicated, containing a large number of peaks. In general, the compounds with a higher lead content gave somewhat simpler patterns, but this was not due solely to the increasing absorption of X rays as the lead content increased, as shown by the fact that the 2:1 and 3:1 compounds had a simpler pattern than the 4:1 compound.

It is obvious that there was one extremely strong reflection for the 3:1 compound and in the data given in Table III it seems that all other peaks were of relatively low intensity. To bring the 2.25-a.u. line completely onto the strip chart, a time constant of 16 and several nickel foils had to be used. If the standard conditions previously described were used (scale factor of 4, multiplier of 1, and time constant of 4), the second strongest 3.12-a.u. peak would have an intensity of 55 against 440 for the 2.25-a.u. line.

(3) Lead Silicophosphate and Lead Borosilicate

The thermal-expansion behavior and X-ray diffraction data for the 5:1:1 compounds are shown in Fig. 3 and Table IV, respectively. The thermal expansion of the borosilicate is considerably less than that of the silicophosphate over the same temperature range.

V. Summary and Conclusions

(1) Aggregate thermal-expansion data on lead silicate, lead phosphate, lead borosilicate, and lead silicophosphate compounds show that the per cent expansions range from about 0.6 to about 1.4 in the interval from room temperature to 700°C.

(2) The existence of several lead compounds has been substantiated and X-ray diffraction data which can be used for their identification have been provided.

Acknowledgment

The writers are grateful for the financial assistance of the Lead Industries Association which made possible the accumulation and publishing of these data on lead compounds.

Table IV. X-Ray Diffraction Data for Lead Silicophosphate and Lead Borosilicate

d (a.u.)	I/I_0	d (a.u.)	I/I_0	d (a.u.)	I/I_0
		$5PbO \cdot B_2O_3 \cdot SiO_2$			
6.61	4	3.11	17	2.09	10
6.03	4	3.05	5	2.01	15
4.83	5	2.98	11	1.949	15
4.35	4	2.94	6	1.913	15
4.21	39	2.78	78	1.855	15
4.00	53	2.55	100	1.828	10
3.87	4	2.79	30	1.814	25
3.71	4	2.55	7	1.791	15
3.56	16	2.37	5	1.556	4
3.43	4	2.32	5	1.508	6
3.29	39	2.24	4	1.495	4
3.22	6	2.20	6	1.409	5
3.16	47	2.14	10	1.318	3
		$5PbO \cdot P_2O_5 \cdot SiO_2$			
4.90	4	2.24	4	1.838	24
4.25	23	2.18	6	1.560	5
4.08	29	2.12	5	1.537	10
3.88	6	2.04	18	1.523	8
3.36	22	1.981	14	1.370	4
3.21	27	1.941	17	1.331	5
2.93	100	1.844	12	1.302	6
2.86	33	1.836	6	1.295	3
				1.277	6

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