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SUBJECT: REPRINT ON LEAD CERAMIC RESEARCH PAPER.

To: Members of the Lead Industries Association, Inc.:

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

As you can see, this is the second in a series of papers on thermal-expansion properties of crystalline lead compounds. One of the authors of this paper is the LIA—Expanded Research Project fellow at The Pennsylvania State University, working under a ceramic research grant. The other author is his faculty supervisor and Chairman of the Dept. of Ceramic Technology.

Printing of this paper in the Ceramic Society Journal has, of course, given it wide distribution throughout the ceramic industry, and we have purchased only a limited number of reprints for distribution where we think it will be beneficial.

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Look Ahead with Lead

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Dilatometric and X-Ray Data for Lead Compounds, II

by J. F. ARGYLE and F. A. HUMMEL

College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania

Linear thermal-expansion data are presented for $PbAl_2O_4$, Pb_2GeO_4, $PbMoO_4$, $PbWO_4$, the perovskite-type structures Pb_2MgWO_6, Pb_2FeTaO_6, and $Pb_2Fe_2WO_9$, and the apatite-type structures $Pb_5(SiO_4)(VO_4)_2$, $Pb_5GeO_4(VO_4)_2$, and $Pb_5(GeO_4)(PO_4)_2$. X-ray powder data are given, and the behavior of the compounds is correlated with previous information from the literature.

I. Introduction

It was pointed out in Part I of this series[1] that more data on the thermal expansion behavior of crystalline lead compounds are necessary to predict better their behavior in complex ceramic systems composed of crystal mixtures or glass-crystal aggregates.

Data for ten compounds are presented in this paper, three of which have the perovskite type structure, three the apatite-type structure, and two the scheelite type structure.

II. Literature

(1) Perovskite-Type Compounds

Smolenskii, Agranovskaya, and Isupov[2] claimed that Pb_2MgWO_6 ($2PbO\cdot MgO\cdot WO_3$), Pb_2FeTaO_6 ($1PbO\cdot Fe_2O_3\cdot Ta_2O_5$), and $Pb_2Fe_2WO_9$ ($3PbO\cdot Fe_2O_3\cdot WO_3$) all had a perovskite type structure.

(2) Apatite-Type Compounds

Merker and Woodratschek[3] showed that $Pb_5(SiO_4)(VO_4)_2$ ($5PbO\cdot SiO_2\cdot V_2O_5$), $Pb_5(GeO_4)(VO_4)_2$ ($5PbO\cdot GeO_2\cdot V_2O_5$), and $Pb_5(GeO_4)(PO_4)_2$ ($5PbO\cdot GeO_2\cdot P_2O_5$) all had an apatite like structure. They gave the a and c parameters, c/a ratios, and congruent melting points as follows:

Compound	a (Å)	c (Å)	c/a	Congruent melting point (°C)
$5PbO\cdot SiO_2\cdot V_2O_5$	9.99	7.35	0.736	892
$5PbO\cdot GeO_2\cdot P_2O_5$	9.89	7.32	0.741	1003
$5PbO\cdot GeO_2\cdot V_2O_5$	10.06	7.37	0.733	913

(3) Lead Molybdate and Lead Tungstate

Jaeger and Germs[4] used heating curves and thermal analysis to determine melting points, inversions, and liquidus curves in the systems $PbO\text{-}WO_3$ and $PbO\text{-}MoO_3$. They claimed congruent melting for $PbMoO_4$ at 1065°C and for $PbWO_4$ at 1123°C. $PbWO_4$ was reported to undergo a reversible polymorphic transition at 877°C.

(4) Lead Aluminate and Lead Germanate

Geller and Bunting[5] worked in the system $PbO\text{-}Al_2O_3$ and suggested the existence of a compound $PbO\cdot Al_2O_3$. This compound breaks down rapidly at 1000°C to form beta Al_2O_3 and liquid. These investigators pointed out that this breakdown may be true incongruent melting or it may be a decomposition accelerated at 950° to 1000°C by the volatilization of PbO.

Schutz[6] claimed that $2PbO\text{-}GeO_2$ melted in an Al_2O_3 crucible formed a homogeneous glass. Merker and Woodratschek[7] showed that $2PbO\text{-}GeO_2$ melted in a platinum crucible rapidly crystallizes, and suggested that the glass obtained by Schutz[6] was probably stabilized by dissolved Al_2O_3 from the crucible.

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

[1] J. F. Argyle and F. A. Hummel, "Dilatometric and X-Ray Data for Lead Compounds, I," *J. Am. Ceram. Soc.*, 43 [9] 452-57 (1960).

[2] G. A. Smolenskii, A. I. Agranovskaya, and V. A. Isupov, "New Ferroelectrics of Complex Composition: III. Pb_2MgWO_6, $Pb_2Fe_2WO_9$, and Pb_2FeTaO_6," *Fiz. Tverd. Tela*, 1, 990-92 (1959).

[3] Ludwig Merker and Hans Woodratschek, "Compounds of Apatite Type Structure," *Fortschr. Mineral.*, 35, 15-16 (1957).

[4] F. M. Jaeger and H. C. Germs, "The Sulphate, Chromate, Molybdate and Tungstate Binary Systems of Lead," *Z. anorg. u. allgem. Chem.*, 119, 145-73 (1921).

[5] R. F. Geller and E. N. Bunting, "Report on the Systems Lead Oxide-Alumina and Lead Oxide-Alumina-Silica," *J. Research Natl. Bur. Standards*, 31 [5] 255-70 (1943); RP 1564; *Ceram. Abstr.*, 23 [3] 70 (1944).

[6] Wolfram Schutz, "Die kristallchemische Verwandtschaft zwischen Germanium und Silicium" (Crystal Chemical Relation Between Germanium and Silicon), *Z. physik. Chem.*, B31, 292-308 (1936); *Ceram. Abstr.*, 18 [1] 15 (1939).

[7] Ludwig Merker and Hans Woodratschek, "Einige Bemerkungen zum Bleiorthosilikat und -germanat und deren Glasigkeit" (Lead Orthosilicate and Germanate, and Their Glassy Character), *Glastech. Ber.*, 30 [11] 471-73 (1957).

Table I. Calcining and Firing Treatments for Lead Compounds

Compound	Calcination			Firing
	First (temp., °C)	Second (temp., °C)	Time (hr)	Period of burn (temp., °C)
$2PbO \cdot MgO \cdot WO_3$	800	800	24	900
$4PbO \cdot Fe_2O_3 \cdot Ta_2O_5$	800	800	24	900
$3PbO \cdot Fe_2O_3 \cdot WO_3$	600	700	24	700
$5PbO \cdot SiO_2 \cdot V_2O_5$	400	700	24	470
$5PbO \cdot GeO_2 \cdot V_2O_5$	400	700	24	480
$5PbO \cdot GeO_2 \cdot P_2O_5$	450	700	24	510
$PbO \cdot WO_3$	850	1000	24	1000
$PbO \cdot MoO_3$	850	1050	24	1050
$PbO \cdot Al_2O_3$	750	800	12	900
$2PbO \cdot GeO_2$	400	480	12	480

III. Experimental Procedures

All compositions were made from cp chemicals. After weighing, the batches were hand mixed in a glass mortar with acetone for 15 to 20 minutes, air dried, and then heated slowly in a Globar furnace to 300°C and held for 4 hours to expel volatiles. The batches were remixed, given a "first calcination" for 24 hours, cooled, remixed, and given a "second calcination," as shown in Table I.

After the second calcination, the batches were ground, mixed with a Carbowax solution, nodulized through a 20-mesh sieve, and pressed into 10- by 1- by 1-cm bars at 1000 psi. The specimens were fired slowly to the temperatures indicated in Table I and held for 6 hours until the bar was sintered to a relatively dense condition.

Note that several volatile oxides (PbO, WO_3, V_2O_5, P_2O_5, MoO_3, and GeO_2) were involved in the preparation of these compositions. By the use of repeated low-temperature calcining, repeated grinding and mixing, and carefully chosen final sintering temperatures for each composition, it is highly probable that losses due to volatilization were negligible.

Thermal expansion runs were made in a vertical fused silica dilatometer, using a heating rate of 120°C per hour. The expansions were measured by dial gages which were accurate to 1/10,000 in. At least two runs were made on each specimen. Any flattening of the expansion curve near its high-temperature extremity is probably due to deformation of the specimen under the weight of the fused silica transmission tube (about 55 g).

X-ray diffraction patterns were obtained on a Norelco diffractometer using Cu $K\alpha$ 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° per minute, this rate being adequate to give patterns suitable for qualitative identification purposes. The strongest peak of each pattern was fully accommodated on the recording chart by placing thin nickel foils in front of the counter tube when peak intensities required it. High-temperature X-ray patterns were obtained with a platinum-wound furnace mounted on a Norelco diffractometer. A finely ground specimen was packed into a Pt depression slide and sintered in place for several hours at a temperature about 50°C higher than the temperature subsequently used to obtain the diffraction pattern. This procedure was used to prevent any effect of sintering on the positions or intensities of the X-ray reflections at elevated temperatures.

IV. Experimental Results and Discussion

(1) Perovskite-Type Structures

The linear thermal expansion curves of $2PbO \cdot MgO \cdot WO_3$, $3PbO \cdot Fe_2O_3 \cdot WO_3$, and $4PbO \cdot Fe_2O_3 \cdot Ta_2O_5$ are shown in Fig. 1. $3PbO \cdot Fe_2O_3 \cdot WO_3$ and $4PbO \cdot Fe_2O_3 \cdot Ta_2O_5$ have continuous expansion curves, but $2PbO \cdot MgO \cdot WO_3$ shows a discontinuity, with a marked negative expansion beginning at about 40°C. Smolenskii, Agranovskaya, and Isupov[1] claimed that $2PbO \cdot MgO \cdot WO_3$ undergoes an antiferroelectric transition at 38°C, which corresponds to the temperature below which this compound shows a marked negative expansion.

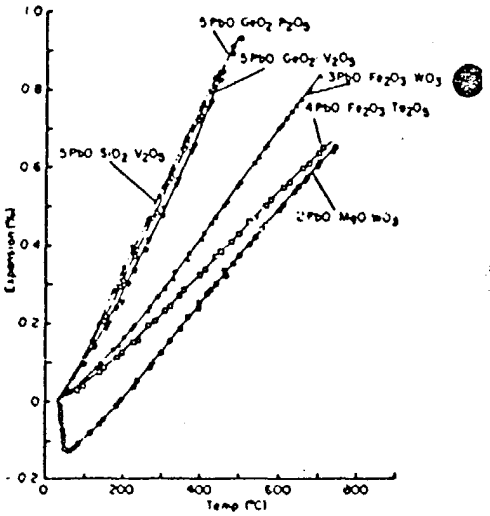

Fig. 1. Linear thermal expansion of perovskites and apatites.

The X-ray diffraction data for these three compounds are shown in Table II.

(2) Apatite-Type Structures

The linear thermal expansion characteristics of $5PbO \cdot GeO_2 \cdot P_2O_5$, $5PbO \cdot SiO_2 \cdot V_2O_5$, and $5PbO \cdot GeO_2 \cdot V_2O_5$ are

Table II. X-Ray Diffraction Data for Compounds with Perovskite-Type Structure

$3PbO \cdot Fe_2O_3 \cdot WO_3$		$4PbO \cdot Fe_2O_3 \cdot Ta_2O_5$		$2PbO \cdot MgO \cdot WO_3$	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
				4.62	36
3.99	15	4.02	9	4.00	6
				3.26	2
3.01	5	3.03	9		
2.81	100	2.84	100	2.83	100
2.61	3	2.64	4	2.55	3
				2.42	7
2.36	13	2.32	9	2.32	18
				2.15	4
				2.01	15
1.990	31	2.00	27	1.989	14
1.841	2	1.843	3	1.838	4
1.778	3			1.781	2
				1.716	2
1.626	35	1.637	31	1.637	21
				1.631	18
1.570	1	1.600	3		
		1.526	1		
1.408	15	1.417	11	1.410	10
				1.358	1
				1.274	5
1.250	10	1.268	9	1.259	4
1.150	3	1.158	2	1.155	6

Table III. X-Ray Diffraction Data for Compounds with Apatite-Type Structure

$3PbO \cdot GeO_2$, PbS		$3PbO \cdot GeO_2$, V_2O_5		$2PbO \cdot SiO_2$, V_2O_5	
d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
8.51	5	8.67	4		
		6.37	8		
				5.34	8
4.90	3				
		4.44	3		
4.25	20	4.33	32	4.31	34
				4.19	5
4.08	28	4.12	30	4.11	35
3.66	8	3.68	15	3.68	6
				3.47	3
3.36	28	3.39	30	3.38	31
3.22	34	3.29	42	3.27	43
		3.19	18		
		3.13	37	3.10	11
				3.04	5
2.92	100	2.99	100	2.98	100
		2.97	99	2.96	92
		2.91	55	2.88	55
2.84	47	2.85	67	2.82	5
2.77	4	2.76	3		
		2.39	4	2.37	3
2.25	4	2.24	11	2.23	5
2.19	9	2.21	9	2.20	9
2.14	5	2.18	8	2.16	8
				2.11	5
2.04	20	2.08	20	2.06	31
1.990	13	2.02	13	2.01	15
		2.01	6	1.9865	6
1.961	7	1.9820	28	1.9801	22
1.915	20	1.9529	22	1.914	22
		1.9413	13		
1.892	14	1.877	27	1.894	18
1.856	10			1.865	25
1.845	20	1.845	18	1.838	8
1.831	10	1.749	11		
1.681	3	1.682	6		
1.661	4	1.650	5		
		1.639	6	1.634	8
1.613	5			1.623	9
1.615	5	1.618	9	1.613	9
1.583	5	1.583	9	1.580	2
		1.578	6		
		1.568	4	1.568	5
1.549	5	1.554	16	1.551	12
1.542	10	1.543	9	1.544	9
1.530	9	1.530	13	1.519	12

shown in Fig. 1. All the curves are continuous and the three compounds have almost identical linear thermal expansions. During the final firing of these bar specimens it was noted that the edges became slightly rounded above about 500°C; the firing therefore was halted at this temperature since good sintering had already produced a suitable expansion specimen. Under the optical microscope only the apatite phase was observed in these specimens, making it highly likely that the rounding process was due to loss of oxide components from the specimen surface. Differential thermal analysis runs were made on small portions of the bar specimens, giving melting temperatures of 875°C ($5PbO \cdot SiO_2 \cdot V_2O_5$), 995°C ($5PbO \cdot GeO_2 \cdot P_2O_5$), and 985°C ($5PbO \cdot GeO_2 \cdot V_2O_5$); each temperature was 7° to 8° below those reported by Merker and Wondratschek.[3]

The X-ray diffraction data for these compounds are shown in Table III.

(3) Lead Tungstate and Lead Molybdate

The linear thermal-expansion curves of $PbWO_4$ and $PbMoO_4$ are shown in Fig. 2. Jaeger and Germs[4] claimed that $PbWO_4$ has a reversible inversion at 877°C, but the present expansion curve does not show an inflection at this point and a DTA run showed no heat effect.

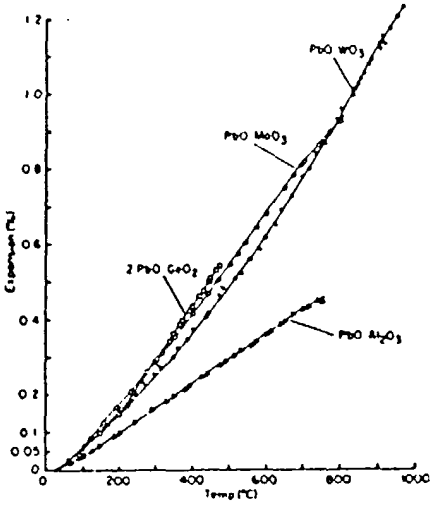

Fig. 2. Linear thermal expansion of scheelite-type compounds, $PbO \cdot Al_2O_3$ and $2PbO \cdot GeO_2$.

X-ray diffraction data were then obtained between room temperature and 925° C as shown in Table IV. It is interesting to note that both $PbWO_4$ and $PbMoO_4$ after relatively rapid cooling to room temperature (or near room temperature) do not give patterns which agree with the original room-temperature patterns (which are in essential agreement with ASTM data[5] for the two compounds). If, however, the specimen is left overnight, very close agreement with the original pattern is obtained. These data indicate a probable *rearrangement* of the heavy metal atoms in these compounds at high temperatures and a very pronounced dependence on time in returning to the room temperature configuration.[6] The line splitting observed in $PbMoO_4$ at high temperatures may indicate a transition from the tetragonal scheelite structure to one of lower symmetry.

The two compounds have the *same* space group as $CaWO_4$ ($C_{4h}^6 - I4_1/a$) and similar lattice parameters as follows:

	a_0	c_0	Footnote reference
$CaWO_4$	5.242	11.372	(8)
$PbMoO_4$	5.435	12.11	(8)
	5.41	12.08	(9)
$PbWO_4$	5.4610	12.046	(8)
	5.44	12.01	(9)

Araki[10] has shown that the Pb ions are asymmetrically surrounded by oxygens in $PbMoO_4$, similar to other lead com-

[5] *ASTM Data Files*. American Society for Testing and Materials, Philadelphia, Pa.

[6] L. G. Sillén and Anna Lisa Nylander, "Oxygen Positions in Tungstates and Molybdates with Scheelite Structure," *Arkiv. Kemi, Mineral. Geol.*, 17A [14] 1–27 (1943).

[10] Takaharu Araki, "Crystal Structure of Wulfenite, $PbMoO_4$," *Mem. Coll. Sci. Univ. Kyoto, Ser. B*, 24, 155–60 (1957) (in English).

Table IV. X-Ray Diffraction Data for $PbWO_4$ and $PbMoO_4$

$PbWO_4$

Room temp		270°C (heating)		920°C		800°C (cooling)		725°C (cooling)		Room temp (after cooling)	
d (A)	*I/I*$_0$	*d* (A)	*I/I*$_0$	*d* (A)	*I/I*$_0$	*d* (A)	*I/I*$_0$	*d* (A)	*I/I*$_0$	*d* (A)	*I/I*$_0$
3.24	100	3.256	100	3.29	100	3.28	80	3.258	56	3.24	100
3.01	29	3.005	54	3.00	73	3.08	10	3.05	10	3.01	26
2.72	58	2.73	100	2.73	91	2.74	100	2.74	100	2.72	67
2.39	2	2.40	7	2.41	6	2.41	7	2.41	4	2.39	6
2.37	2										
2.18	1										
2.02	33	2.04	51	2.05	48	2.04	93	2.04	32	2.02	11
1.959	15	1.941	47							1.959	2
		1.811	47	1.817	25	1.821	14	1.807	4		
1.781	34									1.781	44
1.656	22	1.672	37	1.675	35	1.678	10	1.672	16	1.656	74
1.623	15	1.639	29	1.647	40	1.645	18	1.642	27	1.623	13
				1.347	19						
1.503	3									1.503	31
1.365	4	1.375	12			1.377	4			1.365	4
				1.347	19	1.342	4	1.344	4		
1.318	9	1.326	29	1.321	29	1.326	4	1.326	25	1.318	31
1.298	10									1.298	6
1.259	5	1.269	54							1.259	4
1.247	3	1.255	19	1.256	8	1.256	4			1.247	11
1.221	4									1.221	40
		1.207	21								
1.187	5			1.180	8	1.183	6			1.187	13
						1.175	12	1.172	13		

$PbMoO_4$

Room temp		270°C (heating)		900°C		800°C (cooling)		750°C for 2 hr (cooling)		300°C for 2 hr (cooling)	
d (A)	*I/I*$_0$	*d* (A)	*I/I*$_0$	*d* (A)	*I/I*$_0$	*d* (A)	*I/I*$_0$	*d* (A)	*I/I*$_0$	*d* (A)	*I/I*$_0$
4.95	15	4.98	15	5.10	6	5.01	3	5.04	13	4.98	20
				5.01	27	4.98	19	4.98	19		
3.23	100	3.25	100	3.31	70	3.29	100	3.28	80	3.24	100
				3.29	54						
3.02	20	3.05	20	3.12	100	3.11	53	3.09	28	3.03	42
						3.10	64				
2.71	19	2.74	19	2.75	53	2.75	27	2.74	19	2.71	21
2.37	7	2.40	7	2.41	9	2.40	11	2.40	12	2.38	24
2.21	4	2.24	4	2.28	5			2.28	8	2.21	6
										2.11	3
2.08	3	2.10	3	2.11	2	2.11	34	2.11	41	2.09	46
								2.10	37	2.08	40
2.02	24	2.04	24	2.06	58	2.05	63	2.05	80	2.02	38
1.947	8	1.947	8	1.941	21	1.941	16	1.945	100	1.922	38
								1.937	92		
1.784	13	1.814	13	1.829	26	1.821	25	1.821	18	1.787	51
				1.811	9	1.811	9				
1.653	17	1.668	17	1.672	11	1.672	9	1.670	20	1.653	50
1.621	11	1.617	11	1.645	12	1.645	7	1.642	7	1.623	5
1.512	4	1.580	4	1.556	17					1.514	3
				1.375	9						

800°C for 1 hr	
d	*I/I*$_0$
3.29	100
3.13	33
3.10	33

pounds, such as the oxide, for example. Introduction of lead into the structure not only expands the lattice (especially in the *c* direction) but also brings about a change in the local environment of the lead ion and in the symmetry of the structure at high temperature relative to room temperature.

The high temperature diffraction patterns of $PbWO_4$ and $PbMoO_4$ were obtained by running at 1° per minute, and at some temperatures the specimens may not have been fully equilibrated to the extent needed for good thermal expansion data. The high temperature X-ray data therefore were not used for the calculation of *a* and *c* expansion coefficients or for comparison with the linear dilatometric data.

(4) Lead Germanate and Lead Aluminate

The linear thermal expansion characteristics of $2PbO \cdot GeO_2$ and $PbO \cdot Al_2O_3$ are shown in Fig. 2.

The X-ray diffraction data for $2PbO \cdot GeO_2$ and $PbO \cdot Al_2O_3$ are shown in Table V. The data for $PbO \cdot Al_2O_3$ are in good agreement with the previous work of Geller and Bunting.[8]

V. Summary and Conclusions

(1) Aggregate thermal expansion data on $2PbO \cdot MgO \cdot WO_4$, $3PbO \cdot Fe_2O_3 \cdot WO_3$, $4PbO \cdot Fe_2O_3 \cdot Ta_2O_5$, $5PbO \cdot SeO_2 \cdot V_2O_5$, $5PbO \cdot GeO_2 \cdot V_2O_5$, $5PbO \cdot GeO_2 \cdot P_2O_5$, $PbO \cdot WO_3$, $PbO \cdot MoO_3$,

Table V. X-Ray Diffraction Data for $2PbO \cdot GeO_2$ and $PbO \cdot Al_2O_3$

d (A)	I/I_0	d (A)	I/I_0
	$2PbO \cdot GeO_2$		
[illegible]	[illegible]	[illegible]	[illegible]

(continued next column)

Table V (concluded)

d (A)	I/I_0	d (A)	I/I_0
	$2PbO \cdot GeO_2$		
2.01	14	1.307	6
1.989	10	1.275	7
	$PbO \cdot Al_2O_3$		
4.02	24	1.626	5
4.45	23	1.615	4
4.13	16	1.565	9
4.08	28	1.561	12
3.12	45	1.549	9
3.07	100	1.533	6
2.83	19	1.517	5
2.54	13	1.490	6
2.51	13	1.461	8
2.39	4	1.441	1
2.31	5	1.425	1
2.23	24	1.412	1
2.18	11	1.397	3
2.15	5	1.344	9
2.12	8	1.329	3
2.03	8	1.308	5
1.988	12	1.302	2
1.932	13	1.298	2
1.910	14	1.294	2
1.797	5	1.249	1
1.701	11	1.244	4
1.675	4	1.230	4
1.664	3	1.212	5
1.650	9	1.192	3

2PbO·GeO$_2$ and PbO·Al$_2$O$_3$ show that the expansions range from about 0.3 to 1.0% in the interval from room temperature to 500°C.

(2) X-ray diffraction patterns have been provided which can be used to identify the foregoing compounds, and some observations on the high temperature structural changes in PbMoO$_4$ and PbWO$_4$ have been made which emphasize the need for detailed X-ray studies of these compounds.

Acknowledgment

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