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The Structures of Ba_5Pb_3, BaPb and $BaPb_3$*

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The structures of the compounds Ba_5Pb_3, BaPb, and $BaPb_3$ have been determined. Ba_5Pb_3 has the body-centered tetragonal $D8_l$ structure with $a = 9{\cdot}038 \pm 0{\cdot}010$, $c = 16{\cdot}843 \pm 0{\cdot}017$ Å; the space group is $I4/mcm$ and there are four formula units per unit cell. The room temperature modification of BaPb has the orthorhombic B_f structure with $a = 5{\cdot}29 \pm 0{\cdot}01$, $b = 12{\cdot}60 \pm 0{\cdot}02$, $c = 4{\cdot}78 \pm 0{\cdot}01$ Å; the space group is $Cmcm$ and there are four formula units per unit cell. $BaPb_3$ is rhombohedral with $a = 9{\cdot}565 \pm 0{\cdot}009$ Å, $\alpha = 44° 47' \pm 3'$; the space group is $R\bar{3}m$ and there are three formula units per primitive cell.

Introduction

The only determination of the entire barium–lead phase diagram of which we are aware is that of Grube & Dietrich (1938). Their diagram is based on thermal analysis and electrical resistivity measurements, and shows three compounds at or near the compositions Ba_2Pb, BaPb, and $BaPb_3$. BaPb has a high and a low temperature modification. For all of the phases but one, BaPb (*L*) (the low temperature form), electrical resistivity increases with increasing temperature.

Because of the interesting properties of the compounds in this system, and because we could find no reports of the structures of these compounds, we have carried out the investigation described below.

Experimental

Sample preparation

Samples of the various compounds were prepared by melting together, in an argon atmoshere, calculated, weighed amounts of Bram Chemical Company, >99·5% pure barium metal and remelted Baker Reagent Grade lead. In an argon-filled glove-box, the barium was scraped free of oxide, and the two metals were weighed and placed in a pure iron crucible. While still in an inert atmosphere, the crucible and its contents were assembled in the melting apparatus. When the lead melted, exothermic reaction took place. The melt was stirred, and a cooling curve was obtained. Our thermal analysis results agree with those of Grube & Dietrich (1938). Samples were removed from the apparatus and loaded into capillaries in the argon-filled box.

All of the compounds are brittle. Ba_5Pb_3 and $BaPb_3$ are silver colored, while BaPb is shiny black and fractures along well defined planes.

X-ray diffraction

The diffraction symmetries and probable space groups of the three compounds were obtained from oscillation and Weissenberg photographs made with Cu $K\alpha$ radiation. In each case the choice of the centrosymmetric space group was confirmed by the structure. The lattice constants of BaPb were obtained from a powder pattern made with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å); the lattice constants of Ba_5Pb_3 and $BaPb_3$ were obtained from uncalibrated precession photographs made with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). Intensity measurements were made visually on zero-level Weissenberg photographs, Cu $K\alpha$ radiation being used for the BaPb and Ba_5Pb_3 pictures and Mo $K\alpha$ radiation for the $BaPb_3$ pictures. After the Lorentz-polarization correction had been applied, the data were corrected for absorption by the method of Busing & Levy (1957) applied to the IBM 650 (Sands, 1958).

Least-squares refinements were carried out on an IBM 709 computer with the full matrix program of Busing & Levy (1959) and the weighting scheme of Hughes (1941). The scattering factors of Thomas & Umeda (1957) were used, uncorrected for anomalous dispersion. Unobserved reflections were included in the refinements with magnitude zero; these reflections are denoted in Table 1 by asterisks next to the minimum observable values. The standard deviations of the atomic parameters were computed by the method of Cruickshank (1949). The standard errors of the interatomic distances were computed by the method of Cruickshank & Robertson (1953).

Discussion

Ba_5Pb_3

Ba_5Pb_3 is body-centered tetragonal with

$$a = 9{\cdot}038 \pm 0{\cdot}010,\ c = 16{\cdot}843 \pm 0{\cdot}017 \text{ Å}.$$

There are four Ba_5Pb_3 groups per unit cell, resulting in a calculated density of 6·31 $g.cm^{-3}$. General *hkl* reflections were observed only when $h+k+l=2n$;

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Table 1. *Observed and calculated structure factors*

Asterisks denote unobserved reflections

Ba_5Pb_3									
h	k	l	F_o	F_c	H	k	l	F_o	F_c
0	2	2	*108	74	3	6	3	423	-244
0	4	4	166	137	3	7	4	260	152
0	6	6	178	227	3	8	5	*54	-49
0	8	8	305	318	3	9	6	187	-120
0	10	10	145	111	3	10	7	133	106
1	1	0	*54	-19	3	3	6	674	-659
1	2	1	*69	53	3	4	7	*62	-31
1	3	2	*185	46	3	5	8	63	124
1	4	3	580	-395	3	6	9	133	194
1	5	4	707	646	3	7	10	94	-89
1	6	5	215	-221	3	8	11	*31	40
1	7	6	254	-215	3	9	12	85	100
1	8	7	212	-247	4	4	0	907	790
1	9	8	*46	34	4	5	1	336	224
1	10	9	*23	3	4	6	2	145	74
1	1	2	305	-359	4	7	3	741	281
1	2	3	937	-904	4	8	4	257	-117
1	3	4	233	362	4	9	5	*46	-11
1	4	5	*54	-48	4	10	6	42	-37
1	5	6	*54	58	4	4	8	447	556
1	6	7	172	218	4	5	9	94	137
1	7	8	*46	63	4	6	10	115	151
1	8	9	48	-81	4	7	11	127	-127
1	9	10	200	-240	4	8	12	*23	-32
2	2	0	692	645	5	5	0	60	-94
2	3	1	314	-395	5	6	1	218	161
2	4	2	133	-149	5	7	2	145	88
2	5	3	599	575	5	8	3	187	-146
2	6	4	487	419	5	9	4	212	139
2	7	5	245	244	5	10	5	60	-76
2	8	6	*54	49	5	5	10	118	-106
2	9	7	145	-96	5	6	11	88	-103
2	10	8	172	110	5	7	12	142	151
2	2	4	236	270	6	6	0	550	503
2	3	5	293	350	6	7	1	212	-175
2	4	6	*54	12	6	8	2	*54	-23
2	5	7	*54	111	6	9	3	79	69
2	6	8	103	147	6	6	12	151	184
2	7	9	*46	-59	6	7	13	70	108
2	8	10	63	-84	7	7	0	67	23
2	9	11	51	63	7	8	1	63	-53
3	3	0	759	-429	7	9	2	118	-109
3	4	1	*108	41	8	8	0	269	276
3	5	2	466	-332					

BaPb (L)				
h	k	l	F_o	F_c
0	0	2	97	-100
0	0	4	67	55
0	0	6	26	-24
0	2	0	30	40
0	2	1	11	12
0	2	2	25	-30
0	2	3	10	-9
0	2	4	20	17
0	2	5	7	5
0	2	6	10	-8
0	4	0	90	-74
0	4	1	57	59
0	4	2	50	57
0	4	3	36	-38
0	4	4	30	-32
0	4	5	30	20
0	6	0	95	-53
0	6	1	42	41
0	6	2	34	44
0	6	3	28	-27
0	6	4	30	-26
0	6	5	24	14
0	8	0	8	1
0	8	1	66	-36
0	8	2	*12	0
0	8	3	33	25
0	8	4	*10	0
0	8	5	23	-13
0	10	0	8	9
0	10	1	71	-54
0	10	2	7	-8
0	10	3	59	38
0	10	4	5	5
0	12	0	13	10
0	12	1	5	-4
0	12	2	13	-9
0	12	3	5	3
0	12	4	7	6
0	14	0	22	16
0	14	1	20	26
0	14	2	19	-14
0	14	3	10	-19
0	16	0	5	6

$BaPb_3$														
h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	6	*40	1	2	0	26	67	66	4	0	28	83	52
0	0	9	366	366	2	0	29	*46	-27	5	0	-22	72	-59
0	0	12	*52	0	2	0	32	84	35	5	0	-19	61	56
0	0	15	*51	2	3	0	-30	*68	-42	5	0	-16	*71	-23
0	0	18	351	245	3	0	-27	*55	-20	5	0	-13	100	-77
0	0	21	*44	2	3	0	-24	67	43	5	0	-10	80	69
0	0	24	*48	3	3	0	-21	56	-60	5	0	-7	*36	-22
0	0	27	137	149	3	0	-18	*45	-27	5	0	-4	50	-87
0	0	30	*45	4	3	0	-15	76	62	5	0	-1	75	68
0	0	33	*103	4	3	0	-12	78	-74	5	0	2	*56	-16
0	0	36	82	-83	3	0	-9	*42	-34	5	0	5	104	-84
1	0	-32	*59	-1	3	0	-6	84	74	5	0	8	37	53
1	0	-29	*55	10	3	0	-3	60	-75	5	0	11	*47	-8
1	0	-26	*59	-45	3	0	0	67	-40	5	0	14	80	-69
1	0	-23	*54	0	3	0	3	78	68	5	0	17	*51	32
1	0	-20	*50	16	3	0	6	56	-60	5	0	20	*54	-1
1	0	-17	75	-58	3	0	9	55	-42	5	0	23	73	-50
1	0	-14	*41	1	3	0	12	63	47	6	0	-18	86	90
1	0	-11	*36	22	3	0	15	42	-37	6	0	-15	*54	15
1	0	-8	74	-63	3	0	18	45	-38	6	0	-12	*42	27
1	0	7	45	19	3	0	21	*48	26	6	0	-9	65	119
1	0	10	67	-33	3	0	24	*52	-20	6	0	-6	*40	15
1	0	13	106	-25	3	0	27	*45	-31	6	0	-3	*40	33
2	0	-31	126	89	3	0	30	*48	12	6	0	0	122	131
2	0	-28	89	60	4	0	-26	65	53	6	0	3	*49	12
2	0	-25	51	-37	4	0	-23	147	105	6	0	6	*64	34
2	0	-22	196	151	4	0	-20	*50	-25	6	0	9	137	120
2	0	-19	135	97	4	0	-17	82	81	6	0	12	*52	9
2	0	-16	69	-63	4	0	-14	148	153	6	0	15	*54	31
2	0	-13	243	229	4	0	-11	42	-40	6	0	18	102	92
2	0	-10	137	139	4	0	-8	116	108	7	0	-8	55	-78
2	0	-7	92	-90	4	0	-5	152	191	7	0	-5	*44	19
2	0	-4	216	300	4	0	-2	58	-49	7	0	-2	*44	30
2	0	-1	223	166	4	0	1	150	121	7	0	1	82	-77
2	0	2	97	-98	4	0	4	207	193	7	0	4	*54	12
2	0	5	274	295	4	0	7	*40	-47	7	0	7	*63	30
2	0	8	173	146	4	0	10	102	108	7	0	10	91	-65
2	0	11	110	-78	4	0	13	160	155	8	0	-4	59	66
2	0	14	307	222	4	0	16	*46	-35	8	0	-1	*48	27
2	0	17	184	103	4	0	19	117	80	8	0	2	*48	17
2	0	20	63	-50	4	0	22	159	107	8	0	5	84	67
2	0	23	155	144	4	0	25	*55	-20					

$0kl$ reflections were observed only when $l=2n$. The space groups suggested by these extinction conditions and the diffraction symmetry are $I4cm$, $I4c2$, and $I4/mcm$. The choice of the centrosymmetric $I4/mcm$ was confirmed by the structure. This compound has the $D8_l$ structure reported for Cr_5B_3 (Bertaut & Blum, 1953) and the T_2 forms of Nb_5Si_3 and Ta_5Si_3 (Parthé, Nowotny & Schmid, 1955; Parthé, Lux & Nowotny, 1955). The composition of this phase was in fact established only when this structure was deduced from the Patterson projection along [111].

The atoms occupy the following positions of space group $I4/mcm$:

4 Ba(1) in 4(c):
  body-centering $+(0, 0, 0; 0, 0, \frac{1}{2})$,
16 Ba(2) in 16 l):
  body-centering $\pm(x, \frac{1}{2}+x, \pm z; \frac{1}{2}+x, -x, \pm z)$,
  with $x=0{\cdot}33$, $z=0{\cdot}15$,
4 Pb(1) in 4(a):
  body-centering $\pm(0, 0, \frac{1}{4})$,
8 Pb(2) in 8(h):
  body-centering $\pm(x, \frac{1}{2}+x, 0; \frac{1}{2}+x, -x, 0)$
  with $x=0{\cdot}12$.

The 87 structure factors which were used in computing the Patterson projection were also used in confirming and refining the structure. These data are given in Table 1. The final reliability factor for the 67 observed reflections was 0·226. The refined atomic parameters are listed in Table 2, and the interatomic distances are given in Table 3.

Each Ba(1) atom is at a position of $4/m$ (C_4) symmetry. Its coordination polyhedron consists of two square antiprisms sharing a pinacoid. The vertices of the shared face are occupied by four Pb(2) atoms, and the other eight vertices, which form a square prism, are occupied by Ba(2) atoms. The polyhedron is pyramidally terminated by two Pb(1) atoms at 4·21 Å.

Table 2. *Atomic parameters*

Ba_5Pb_3

Atom	x	y	z	B (Å^2)
Ba(1)	0	0	0	2·9
Ba(2)	0·3323 ± 0·0010	0·8323 ± 0·0010	0·1505 ± 0·0013	2·1
Pb(1)	0	0	¼	2·9
Pb(2)	0·1194 ± 0·0010	0·6194 ± 0·0010	0	2·2

BaPb(L)

Atom	x	y	z	B (Å^2)
Ba	0	0·1266 ± 0·0008	¼	2·7
Pb	0	0·4198 ± 0·0003	¼	2·6

$BaPb_3$

Atom	x	y	z	B (Å^2)
Ba(1)	0	0	0	4·2
Ba(2)	0	0	0·2177 ± 0·0013	1·6
Pb(1)	½	0	0	1·4
Pb(2)	0·1866 ± 0·0013	− 0·1866 ± 0·0013	0·1102 ± 0·0004	1·8

Each Ba(2) atom is at a position of m (C_s) symmetry. Its neighbors include a pentagon of three Pb(2) atoms and two non-adjacent Ba(1) atoms. Directly above the Ba(1) atoms are the two Pb(1) atoms of a Pb(1)–Ba(2)–Pb(1) triangle of neighbors. A second Ba(2) neighbor touches the two adjacent Pb(2) atoms.

Each Pb(1) atom is at a position of 422 (D_4) symmetry. Its eight Ba(2) neighbors form a square antiprism. Along the axis of the antiprism are two Ba(1) atoms at 4·21 Å.

Each Pb(2) atom is at a position of $mm2$ (C_{2v}) symmetry. Its coordination polyhedron is like that of Pb in BaPb, consisting of two octahedra sharing a face. In this case, however, the vertices of the shared face are occupied by one Pb(2) and two Ba(1) atoms instead of by two Pb atoms and one Ba atom. The other six vertices, forming a trigonal prism, are occupied by Ba(2) atoms.

BaPb(L)

BaPb(L) (the low temperature modification) is orthorhombic with

$$a=5\cdot29\pm0\cdot01,\ b=12\cdot60\pm0\cdot02,\ c=4\cdot78\pm0\cdot01\ \text{Å}\,.$$

There are four BaPb groups per unit cell, resulting in a calculated density of 7·18 g.cm^{-3}. General hkl reflections were observed only when $h+k=2n$; $h0l$ reflections were observed only when $l=2n$. The suggested space groups are $Cmc2_1$ and $Cmcm$. The axial ratios, probable space group, and composition are suggestive of the B_f structure of CrB (Kiessling, 1949) and of CaSn and CaGe (Eckerlin, Meyer & Wölfel, 1955)*, and this structure was ultimately confirmed. Both the Ba and Pb atoms are in the 4(c) positions of space group $Cmcm$: C-centering $\pm(0, y, \frac{1}{4})$ (*International Tables for X-ray Crystallography*, 1952), with $y_{Ba}=0\cdot127$, $y_{Pb}=0\cdot420$.

The confirmation and refinement of the structure were carried out with 43 $0kl$ reflections from a crystal with nearly rectangular cross section of dimensions 0·06 × 0·24 mm. The final reliability index, $R=$

Table 3. *Interatomic distances*

Ba_5Pb_3

Atom	Neighbors	Distances
4 Ba(1)	8 Ba(2)	4·21 ± 0·02
	2 Pb(1)	4·211 ± 0·004
	4 Pb(2)	3·605 ± 0·007
16 Ba(2)	2 Ba(1)	4·21 ± 0·02
	1 Ba(2)	3·96 ± 0·04
	1 Ba(2)	4·29 ± 0·03
	2 Ba(2)	4·52 ± 0·04
	4 Ba(2)	4·76 ± 0·01
	2 Pb(1)	3·76 ± 0·01
	1 Pb(2)	3·72 ± 0·02
	2 Pb(2)	3·65 ± 0·01
4 Pb(1)	2 Ba(1)	4·211 ± 0·004
	8 Ba(2)	3·76 ± 0·01
8 Pb(2)	2 Ba(1)	3·605 ± 0·007
	2 Ba(2)	3·72 ± 0·02
	4 Ba(2)	3·65 ± 0·02
	1 Pb(2)	3·05 ± 0·03

BaPb (L)

Atom	Neighbors	Distances
Ba	2 Ba	3·99 ± 0·02
	1 Pb	3·69 ± 0·01
	2 Pb	3·71 ± 0·01
	4 Pb	3·61 ± 0·01
Pb	1 Ba	3·69 ± 0·01
	2 Ba	3·71 ± 0·01
	4 Ba	3·61 ± 0·01
	2 Pb	3·13 ± 0·01

$BaPb_3$

Atom	Neighbors	Distances
Ba(1)	6 Pb(1)	3·643 ± 0·003
	6 Pb(2)	3·689 ± 0·014
Ba(2)	3 Pb(1)	3·65 ± 0·03
	3 Pb(2)	3·64 ± 0·03
	6 Pb(2)	3·655 ± 0·003
Pb(1)	2 Ba(1)	3·643 ± 0·003
	2 Ba(2)	3·65 ± 0·03
	4 Pb(1)	3·643 ± 0·003
	4 Pb(2)	3·47 ± 0·01
Pb(2)	1 Ba(1)	3·689 ± 0·014
	1 Ba(2)	3·64 ± 0·03
	2 Ba(2)	3·655 ± 0·003
	2 Pb(1)	3·47 ± 0·01
	2 Pb(2)	3·10 ± 0·02
	2 Pb(2)	3·21 ± 0·03

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* These authors chose the *Amma* representation.

$\Sigma|F_o-F_c|/\Sigma F_o$ was 0·224; before the absorption correction, R was 0·56. The observed and calculated structure factors are listed in Table 1. Table 2 lists the atomic parameters, and the interatomic distances are given in Table 3.

Both types of atoms occupy positions of $mm2$ (C_{2v}) symmetry. The coordination polyhedron of a Ba atom can be regarded as a ditetragonal pyramid with a nonplanar base. The apex is occupied by a Pb atom, and the eight basal vertices are occupied by six Pb and two Ba atoms. The nearest neighbors of a Pb atom form two octahedra which share a face. The vertices of the shared face are occupied by two Pb atoms and one Ba atom. The other six vertices, which form a trigonal prism, are occupied by Ba atoms.

$BaPb_3$

$BaPb_3$ is rhombohedral with

$$a=9\cdot565\pm0\cdot009\ \text{Å},\quad \alpha=44^\circ\,47'\pm3';$$

the dimensions of the triply primitive hexagonal cell are

$$a=7\cdot287\pm0\cdot005,\quad c=25\cdot77\pm0\cdot03\ \text{Å}\,.$$

The space group is $R\bar{3}m$, and there are 9 $BaPb_3$ formula units per hexagonal unit cell. The calculated density is 9·57 g.cm^{-3}.

The structure was deduced from the observations that $00l$ reflections (hexagonal setting) were present only for $l=9n$ while $10l$ reflections were weak or missing unless $l=9n+1$. The positions of space group $R\bar{3}m$ which fit these conditions are:

3 Ba(1) in 3(a):
$(0,0,0;\ \frac{2}{3},\frac{1}{3},\frac{1}{3};\ \frac{1}{3},\frac{2}{3},\frac{2}{3})$,
6 Ba(2) in 6(c):
$(0,0,0;\ \frac{2}{3},\frac{1}{3},\frac{1}{3};\ \frac{1}{3},\frac{2}{3},\frac{2}{3})\pm(0,0,z)$, with $z=\frac{2}{9}$.
9 Pb(1) in 9(e):
$(0,0,0;\ \frac{2}{3},\frac{1}{3},\frac{1}{3};\ \frac{1}{3},\frac{2}{3},\frac{2}{3})+(\frac{1}{2},0,0;\ 0,\frac{1}{2},0;\ \frac{1}{2},\frac{1}{2},0)$,
18 Pb(2) in 18(h):
$(0,0,0;\ \frac{2}{3},\frac{1}{3},\frac{1}{3};\ \frac{1}{3},\frac{2}{3},\frac{2}{3})\pm(x,\bar{x},z;\ x,2x,z;\ 2\bar{x},\bar{x},z)$, with $x=\frac{1}{6}$, $z=\frac{1}{9}$.

The 125 $h0l$ reflections which were used in confirming and refining this structure are listed in Table 1. The final reliability index for the 78 observed reflections was 0·223. The refined parameters are given in Table 2, and Table 3 lists the interatomic distances.

Each Ba(1) atom is at a position of $\bar{3}m$ (D_{3d}) symmetry. Its neighbors consist of six Pb(1) atoms forming a regular hexagon and six Pb(2) atoms at the vertices of a trigonal antiprism.

Each Ba(2) atom is at a position of $3m$ (C_{3v}) symmetry. It is surrounded by a regular hexagon of six Pb(2) atoms and a trigonal prism with three Pb(1) atoms occupying the vertices of one base and three Pb(2) atoms occupying the vertices of the other base.

Each Pb(1) atom is at a position of $2/m$ (C_{2h}) symmetry. Its neighbors consist of four Pb(1) and two Ba(1) atoms forming a regular hexagon plus four Pb(2) and two Ba(2) atoms at the vertices of a trigonal antiprism.

Each Pb(2) atom is at a position of m (C_s) symmetry. It is surrounded by a tetrahedron whose vertices are occupied by one Ba(1), one Ba(2) and two Pb(2) atoms. It is also surrounded by a hexagon consisting of two adjacent Pb(2) atoms at 3·21 Å, two nonadjacent Ba(2) atoms at 3·655 Å, and two adjacent Pb(2) atoms at 4·08 Å.

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