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The crystal structure of $\text{Ba}(\text{Pb}_{0.8}, \text{Tl}_{0.2})_3$. By E. E. HAVINGA and J. H. N. VAN VUCHT, *Philips Research Laboratories, N. V. Philips' Gloeilampenfabrieken, Eindhoven, The Netherlands*

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$\text{Ba}(\text{Pb}_{0.8}, \text{Tl}_{0.2})_3$ has a hexagonal unit cell with $a = 7.342$, $c = 39.45 \text{ \AA}$ and $Z = 14$. The structure is built up from close-packed triangular AB_3 layers stacked in the *hhhchhc* mode.

Since the successful resolution of the structure of BaPb_3 by Sands, Wood & Ramsay (1964) this compound has become the prototype for intermetallic compounds AB_3 that can be described as being built up from *hhc*-stacked close-packed triangular (*T*) layers (Beck, 1968). On substitution of the barium or lead atoms other stacking modes are stabilized, some of which involve rather large stacking sequences (van Vucht, 1966). The fully hexagonal stacking mode (Ni_3Sn type) occurs when 50 per cent of the lead atoms are randomly replaced by thallium atoms. Calculations made by Havinga, van Vucht & Buschow (1969) showed that intermediate stacking modes might very likely be found in this system between the $\frac{2}{3}$ hexagonal and the fully hexagonal

phases. An experimental check indeed yielded a new phase upon a replacement of 15 to 30 per cent of the lead atoms. Indexing of the powder diffractogram of $\text{Ba}(\text{Pb}_{0.8}, \text{Tl}_{0.2})_3$ was possible on the basis of a hexagonal unit-cell 14 layers high. After rejection of all stacking modes more cubic than *hhc* on the grounds of their being very unlikely and considering interactions between layers separated by more than 7 intermediate layers to be negligible, three possible 7-layer stacking sequences seemed most suitable for a trial structure, *i.e.* *hhhhcc*, *hhhchhc* and *hhhchhc*. From these the second sequence is the counterpart of a stacking mode suggested for $(\text{Ni}_{0.11}, \text{Pt}_{0.89})_3\text{Ti}$ by van Vucht (1966) and confirmed by Sinha (1969). However, both the *hhhhcc* and *hhhchhc* modes do not appear among those calculated to be stable by Havinga *et al.* Thus the structure analysis of this compound might serve as a test case for the validity of the theoretical considerations.

The intermetallic compound was prepared by melting a mixture of the weighed components in an iron container which was closed by welding in an argon-arc furnace. The container was sealed in a silica envelope and then heated in air at 1200°C for one day and subsequently at 550°C for three days. The opening of the container, crushing of the sample and filling of a special X-ray sample holder, (which allowed the sample to be kept under an inert atmosphere during exposure), were carried out in a glove box filled with purified nitrogen. Exposures were made on a Philips wide-range X-ray diffractometer PW 1050/30 in combination with an AMR X-ray focusing monochromator using $\text{Cu } K\alpha$ radiation. Initially serious difficulties were encountered in preparing good X-ray specimens because of the strong inclination of the powder grains towards a preferred orientation of their hexagonal base-planes in the specimen surface. After numerous attempts we succeeded at last in obtaining specimens of better random orientation by sprinkling extra-fine powder loosely onto a slightly greased glass plate. For the calculations the diffractogram of the relatively small 0014 peak was chosen.

Intensities for all possible stacking modes giving rise to a 14-layered unit-cell (19 in all) were calculated from the parameters of an idealized close-packing of equal spheres. From the three possible 7-layered periods, the stacking modes *hhhhcc* and *hhhchhc* could be rejected immediately, since both gave rise to an index $R_I = \sum |I_o - I_c| / \sum I_o$ of 0.47 compared with 0.23 for the *hhhchhc* stacking. All 14-layered stacking modes yielded R_I values between 0.35 and 0.67. This indicates that the observed structure type is indeed the predicted one.

The *hhhchhc* structure was refined by allowing the (Pb, Tl) atoms to be displaced by an amount δ in the manner indicated in Fig. 1. The displacements are based on the geometrical considerations given by van Vucht (1966) and cause a clustering of the smaller atoms in hexagonally stacked layers, so giving more room to the larger atoms in the neighbouring layers. Fig. 2(a) shows that the agreement with the

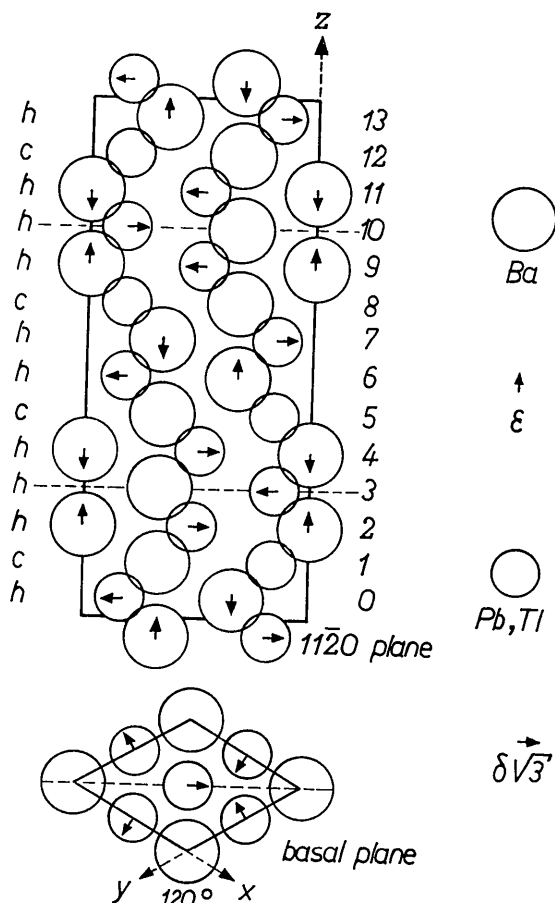


Fig. 1. Schematic drawing of the idealized filling of the unit cell of $\text{Ba}(\text{Pb}_{0.8}, \text{Tl}_{0.2})_3$ with the stress-relieving displacements discussed in the text.

SHORT COMMUNICATIONS

Table 1. X-ray data for $\text{Ba}(\text{Pb}_{0.8}\text{Tl}_{0.2})_3$ Cu $K\alpha$ radiation. Unobserved reflexions, calculated to be <3 (limit of observation), are not included.

<i>h</i>	<i>k</i>	<i>l</i>	$\sin^2 \theta (\times 10^3)$		I_{obs}	I_{calc}	
			Obs.	Calc.		$\delta=0$	$\delta=0.015$
1	0	0		14.7		{ 0.1	{ 0.6
1	0	1	14.9	15.1	5	{ 1.3	{ 11.0
1	0	2		16.1	9	1.7	11.2
1	0	7	33.4	33.4	3	4.2	0.5
1	1	0	44.0	44.1	3	4.0	2.8
2	0	0		58.8		{ 1.8	{ 1.9
2	0	1	59.0	59.2	32	{ 35.4	{ 34.5
2	0	2		60.1	47	49.7	46.9
2	0	3	62.3	62.2	3	2.0	1.5
2	0	4	64.7	64.9	3	5.8	5.0
2	0	5	68.4	68.3	9	14.2	13.6
2	0	6	72.3	72.5	94	82.2	78.6
0	0	14	74.7	74.8	91	88.3	88.2
2	0	7	77.4	77.5	171	193.9	187.4
2	0	8	83.1	83.2	50	68.9	65.9
1	0	14		89.5		{ 0.0	{ 0.2
2	0	9	89.5	89.7	6	{ 10.0	{ 9.6
2	0	10	97.4	97.0	19*	3.4	3.0
2	1	0		102.9		{ 0.0	{ 0.1
2	1	1	102.9	103.3	5	{ 0.3	{ 1.9
2	1	2		104.4		{ 0.4	{ 1.5
2	0	11	104.5	105.0	3	{ 1.0	{ 0.7
2	0	12	113.6	113.8	15	21.8	20.6
2	1	6	116.4	116.6	3	0.7	2.7
2	1	7	121.6	121.6	9	1.8	8.5
2	0	13	123.6	123.3	12	13.6	13.3
3	0	5	141.5	141.8	6	0.0	6.7
2	0	15	144.7	144.7	6	10.9	10.6
2	0	16	156.5	156.6	15	14.0	13.3
3	0	9	162.8	163.2	3	0.0	5.5
2	2	0	176.1	176.4	103	83.0	73.1
2	0	19	195.7	196.6	17*	3.4	3.3
2	0	20	211.6	211.5	15	19.1	18.2
2	0	21	227.5	227.2	52	44.1	42.6
4	0	0		235.2		{ 0.3	{ 0.4
4	0	1	235.0	235.6	6	{ 5.4	{ 5.3
4	0	2	236.5	236.5	6	7.8	6.5
2	0	22		243.6		{ 15.5	{ 14.8
4	0	5	244.0	244.7	27	{ 2.5	{ 2.1
4	0	6		248.9		{ 15.0	{ 12.3
2	2	14	251.0	251.2	91	{ 99.5	{ 87.6
4	0	7	254.0	253.9	35	37.5	32.0
4	0	8	259.0	259.6	9	14.1	11.6
2	0	23	260.5	260.8	3	2.2	2.2
3	0	19		270.1		{ 0.0	{ 2.7
2	1	21	270.0	271.3	20*	{ 0.6	{ 2.8
3	2	0		279.3		{ 0.0	{ 0.2
3	2	1	280.0	279.7	18	{ 0.1	{ 4.3
3	2	2		280.8		{ 0.1	{ 4.4
4	0	12	—	290.2	<3	5.6	4.8
1	0	27		293.0		{ 0.9	{ 0.3
3	2	6	293.0	293.2	7*	{ 0.2	{ 0.1
0	0	28		299.4		{ 12.8	{ 12.8
4	0	13	300.0	299.7	21	{ 3.8	{ 3.7
3	0	21		300.7		{ 0.0	{ 0.1
2	0	26		316.9		{ 5.1	{ 4.8
3	2	10	317.0	317.4	6	{ 0.0	{ 0.1
4	1	5		318.2		{ 0.0	{ 3.6
4	0	15	321.5	321.1	3	3.5	3.4
4	0	16		332.9		{ 4.7	{ 4.0
3	2	12	334.0	334.3	7	{ 0.1	{ 3.4
3	0	23		334.3		{ 0.0	{ 2.0
2	0	27	336.0	337.2	7	3.2	3.1

* Reflexions from a (Pb, Tl) solid solution contaminant.

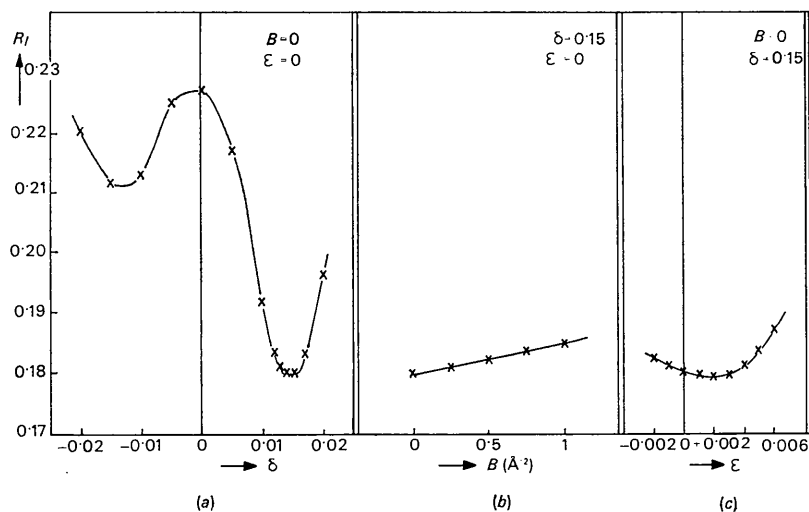


Fig. 2. (a) The effect on R_I of a displacement, δ , of (Pb, Tl) atoms in h -stacked layers (see also Fig. 1) (b) Effect of the introduction of a temperature factor on R_I . (c) Effect on R_I of a z -displacement, ϵ , of some Ba atoms in the manner indicated in Fig. 1.

observed intensities is improved significantly by the introduction of this parameter. The direction of the displacements giving rise to the best R_I index (0.18), see Table 1, agrees with the geometrical model.

From Fig. 2(b) it is seen that the introduction of a temperature factor is no improvement, indicating that the thermal motion is small. Finally we calculated the effect of the introduction of a z displacement, ϵ , of the Ba atoms in the hexagonally stacked layers adjacent to the cubic ones (see also Fig. 1). Fig. 2(c) shows that such a displacement improves the agreement slightly but not significantly.

The unit cell and its contents may be described as follows:

Space group $P6_3/mmc$ (No. 194)

$a = 7.342$, $c = 39.45$ Å, $Z = 14$

2 Ba in $2(d)$: $\pm(\frac{1}{3}, \frac{2}{3}, \frac{2}{3})$

4 Ba in $4(e)$: $(0, 0, \pm z; 0, 0, \frac{1}{2} \pm z)$ with $z = \frac{9}{28} - \epsilon$

8 Ba in $4(f)$: $\pm(\frac{1}{3}, \frac{2}{3}, z; \frac{2}{3}, \frac{1}{3}, \frac{1}{2} + z)$

with $z = \frac{1}{28} - \epsilon$,

$z = \frac{1}{28}$

6 (Pb_{0.8}, Tl_{0.2}) in $6(h)$: $\pm(x, 2x, \frac{1}{4}; 2x, x, \frac{3}{4}; x, \bar{x}, \frac{1}{4})$
with $x = \frac{1}{6} + \delta$

36 (Pb_{0.8}, Tl_{0.2}) in $12(k)$: $\pm(x, 2x, z; 2x, x, z;$
 $x, \bar{x}, z; x, 2x, \frac{1}{2} - z; 2x, x, \frac{1}{2} + z; \bar{x}, x, \frac{1}{2} + z)$ with
 $x = \frac{1}{6} - \delta$ and $z = \frac{9}{28}$
 $x = \frac{1}{6}$ and $z = \frac{1}{28}$,
 $x = \frac{5}{6} + \delta$ and $z = \frac{1}{28}$.

With idealized triangular layers ($\delta = 0$): $\sum |I_o - I_c| / \sum I_o = 0.23$.
Refined with clustering in the layers: $\sum |I_o - I_c| / \sum I_o = 0.18$
with $\delta = 0.015$.

The structure as described shows that the (Pb, Tl) atoms in the h layers are markedly clustered. The smallest (Pb, Tl)–(Pb, Tl) distance decreases from the value 3.67 Å, still

present in the c layers, to 3.34 Å, which is rather small compared with the distance for these atoms in a twelvefold coordination (3.48 Å). The Ba–(Pb, Tl) distances within a hexagonal layer are 3.68 Å, which is only slightly larger than in the cubic layer (3.67 Å). The distances of Ba to (Pb, Tl) atoms in neighbouring layers vary from 3.53 Å for (Pb, Tl) atoms in the c layers to 3.65 Å for the (Pb, Tl) atoms in the h layers. All are small compared with the sum of the metallic radii of both atoms (3.99 Å). The smallest calculated Ba–(Pb, Tl) distance of 3.53 Å can only be enlarged by allowing the barium atoms to be squeezed out of the close-packed planes in the z direction. The value of $\epsilon = 0.002$ at the minimum in the curve of Fig. 2(c) results in the distances from the Ba atoms in the h layers to the two sets of three (Pb, Tl) atoms in the two adjacent c and h layers respectively being equal (3.59 Å). However, our data do not allow the existence of such puckered layers to be established with any certainty.

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References

- BECK, P. A. (1968). *Advanc. X-ray Analysis*. In the press.
HAVINGA, E. E., VUCHT, J. H. N. VAN & BUSCHOW, K. H. J. (1969). Paper presented at the Third Bolton Landing Conference; see also *Philips Res. Repts.* **24**, 407.
SANDS, D. E., WOOD, D. H. & RAMSAY, W. J. (1964). *Acta Cryst.* **17**, 986.
SINHA, A. K. (1969). *Acta Cryst.* **B25**, 996.
VUCHT, J. H. N. VAN (1966). *J. Less-Common Metals*, **11**, 308.