CHEMISTRY LETTERS, pp. 429-434, 1974. Published by the Chemical Society of Japan

CRYSTAL SYSTEMS AND LATTICE CONSTANTS OF PEROVSKITE-TYPE COMPOUNDS $BaThO_3$ AND $Ba_2(BaU)O_6$

Tetsurō NAKAMURA

Research Laboratory of Engineering Materials, Tokyo Institute of
Technology, Ookayama, Meguro-ku, Tokyo 152

$BaThO_3$ had an orthorhombic lattice (a=6.345Å,b=6.376Å,c=8.992Å) with four pseudomonoclinic perovskite units(a'=c'=4.498Å,b'=4.496Å,β=90°17'). $Ba_2(BaU)O_6$ was a tetragonal, ordered perovskite(a=b=6.286Å, c=8.972Å). Ahrens' radius of octahedral Ba^{2+} in $Ba_2(BaU)O_6$ was evaluated to be 1.16Å via a lattice parameter variation versus radius of M^{4+} ion in perovskites $BaMO_3$.

It is commonly anticipated from the torelance factor that the lattice of perovskite-type compound ABO_3 will distort from cubic symmetry [1)] for a large B ion. Th^{4+} is known as the largest tetravalent ion and U^{6+} the largest hexavalent ion.[2)] Therefore, the lattice distortion of perovskite-type compounds $BaThO_3$ and $Ba_2(BaU)O_6$ is of enormous interest. $BaThO_3$ was reported as having a cubic lattice (a=8.985Å) with eight perovskite units,[3)] and $Ba_2(BaU)O_6$ a pseudocubic, ordered perovskite (a=8.89Å) [4)] belonging to a family of distorted $(NH_4)_3FeF_6$ structure.[5)]

Polycrystalline samples were prepared from $BaCO_3$, ThO_2, and $(NH_4)_2U_2O_7$ with high purities(> 99.9 percent). Stoichiometric mixtures of the components were heated in an alumina boat at 1300°- 1350°C for one hour in air. The reacted mixtures were ground, pelletized, and reheated at 1400°C for 6 hours in air. $BaThO_3$ was white, $Ba_2(BaU)O_6$ orange. Powder patterns obtained by an X-ray powder diffractometer with Cu Kα radiation(λ=1.5405Å) indicated that the prepared samples were crystallized in the perovskite structures.

Strong superlattice lines were observed in the pattern of $Ba_2(BaU)O_6$, which were indexed as {111}, {311}, {331}, {333,511}, {531}, etc. by assuming the lattice with a doubled perovskite unit. Hence, the cations Ba^{2+} and U^{6+} are orderly arranged in the octahedral positions of $Ba_2(BaU)O_6$. The crystal system of $Ba_2(BaU)O_6$ was determined from line profiles of the {400}, {422}, {440}, {620}, {444}, and {800} diffraction pairs. The {400} and {440} of $Ba_2(BaU)O_6$ are asymmetrical doublets, as shown in Fig.1, with intensity ratios 1:2 and 2:1, respectively, whereas the {444} is a single line. The results denote that $Ba_2(BaU)O_6$ has a tetragonal lattice with c' > a' = b'. Line splittings of all the other reflections were consistent with the tetragonal symmetry. Lattice constants a'=b'= 8.890 ± 0.002 Å and c'= 8.972 ± 0.002 Å were obtained from the selected high-angle lines with a least squares method. This lattice, indexed by hkl in Table 1, is a face-centered, tetragonal one caused by the rock salt arrangement of the Ba^{2+} and U^{6+} ions in the octahedral

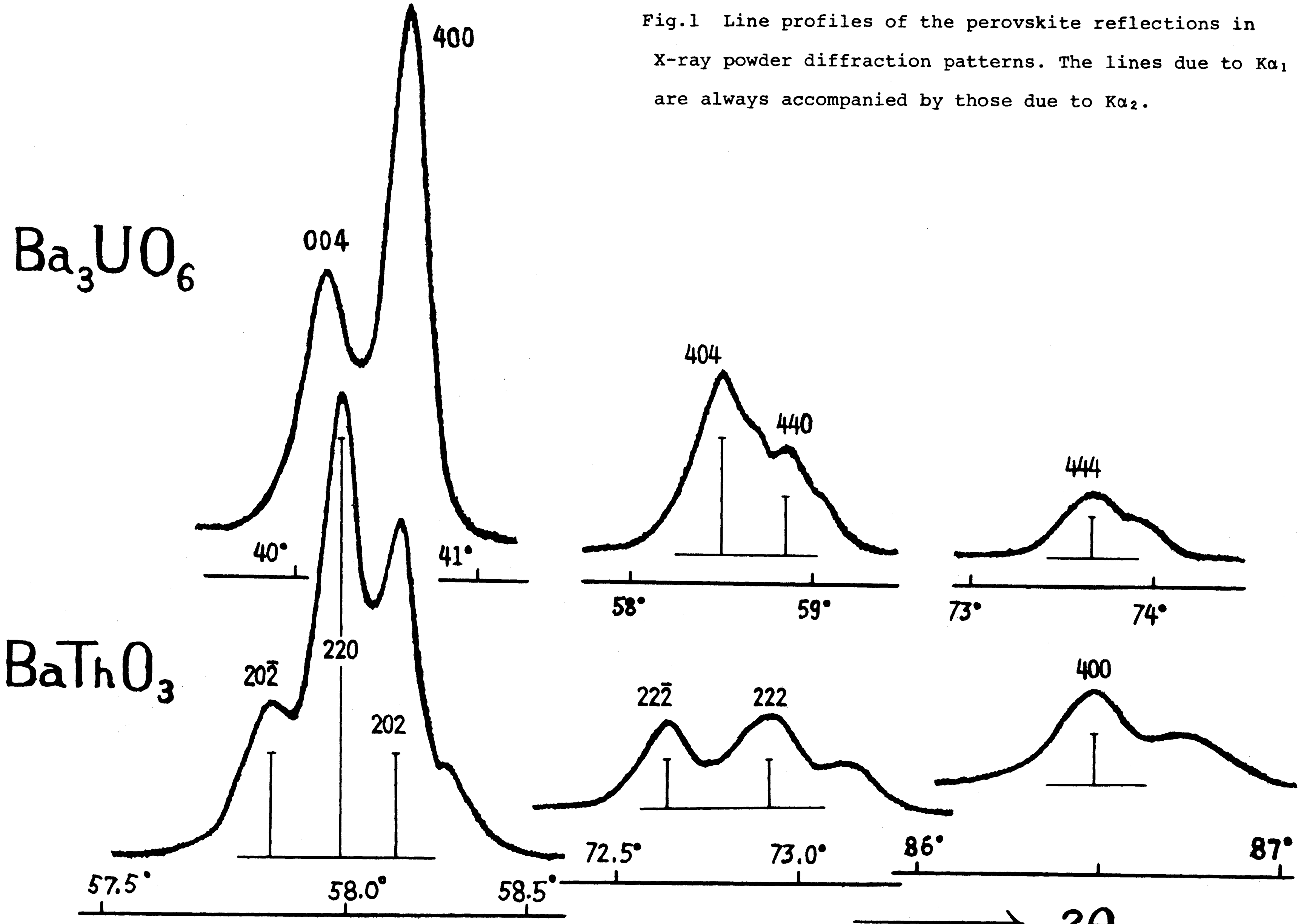


Fig.1 Line profiles of the perovskite reflections in X-ray powder diffraction patterns. The lines due to Kα_1 are always accompanied by those due to Kα_2.

positions. Hence, the lattice was reduced to a body-centered, tetragonal lattice (Bravais lattice) indexed by HKL in the Table 1, with lattice constants a = b = 6.286 ± 0.002 Å and c = 8.972 ± 0.002 Å. In the Table 1 are compared the calculated lattice spacings of $Ba_2(BaU)O_6$ with the observed ones.

Table 1 X-ray powder diffraction data for $Ba_2(BaU)O_6$.

H K L	h k l	$d_{calc.}$	$d_{obs.}$	$(I/I_0)_{obs.}$
101	111	5.148	5.16	10
002	002	4.486	4.48	6
110	200	4.445		
112	202	3.157	3.156	100
200	220	3.143		
103	113	2.701	2.687	9
211	311	2.683		
202	222	2.574	2.581	2
004	004	2.243	2.246	10
220	400	2.223	2.224	17
213	313	2.048	2.045	7
301	331	2.040		
114	204	2.003	2.006	7
222	402	1.992	1.991	
310	420	1.988		
204	224	1.826	1.827	37
312	422	1.817	1.818	
105	115	1.725	1.725	13
303	333	1.716	1.713	
321	511	1.711		
224	404	1.579	1.579	13
400	440	1.572	1.572	
215	315	1.513	1.506	8
323	513	1.506		
411	531	1.503		
116	206	1.417	1.417	6
332	602	1.407	1.406	10
420	620	1.406		
305	335	1.363	1.358	5
413	533	1.358		
404	444	1.287	1.287	6
430	710	1.257	1.257	6
500	701	1.257		
325	515	1.250	1.251	
431	711	1.245	1.245	
501	551	1.245		

$Ba_2(BaU)O_6$: tetragonal a = b = 6.286 Å, c = 8.972 Å (±0.002 Å) for HKL system.

A slight amount of cubic ThO_2(fluorite structure) was detected in the pattern of $BaThO_3$. After the removal of the lines of ThO_2, very weak superlattice lines characteristic of the orthorhombic lattice of $CaTiO_3$ 6) and $GdFeO_3$ 7) (see Fig.2) were found in addition to the major lines which came from the perovskite structure. Similar results were reported for $BaCeO_3$, $BaPrO_3$ and $BaTbO_3$ in the previous paper.8) The major lines showed multiple splittings which were indexed with a monoclinic perovskite cell a'= c' > b' and β' > 90°. Line profiles of the {220}, {222} and {400} reflection pairs from the perovskite cell were shown in the Fig.1. The {200} and {400} were single lines in appearance. The {220} and {310} were triplets with intensity ratio approximately 1:4:1, and {222} was a symmetrical doublet. Cell dimensions of the perovskite unit, a'= c'= 4.498 ± 0.002 Å, b'= 4.496 ± 0.002 Å and β'= 90°17' ± 1', were calculated from the lines in the Fig.1, and refined by a least squares method using high-angle lines. By taking the superlattice lines into account, $BaThO_3$ is concluded to have an orthorhombic lattice (see Fig.2) with four pseudomonoclinic perovskite units. The orthorhombic lattice constants were obtained by transformations : $a = 2a' \cos(\frac{1}{2}\beta') = 6.345 \pm 0.002$ Å , $b = 2a' \sin(\frac{1}{2}\beta') = 6.376 \pm 0.002$ Å, and $c = 2c' = 8.992 \pm 0.002$ Å. According to the

Delaunay reduction,[9)] these constants belong to the simple orthorhombic lattice. In Table 2 are compared the calculated lattice spacings of $BaThO_3$ with the observed ones. Corresponding perovskite indices were indicated by {hkl} in the Table 2.

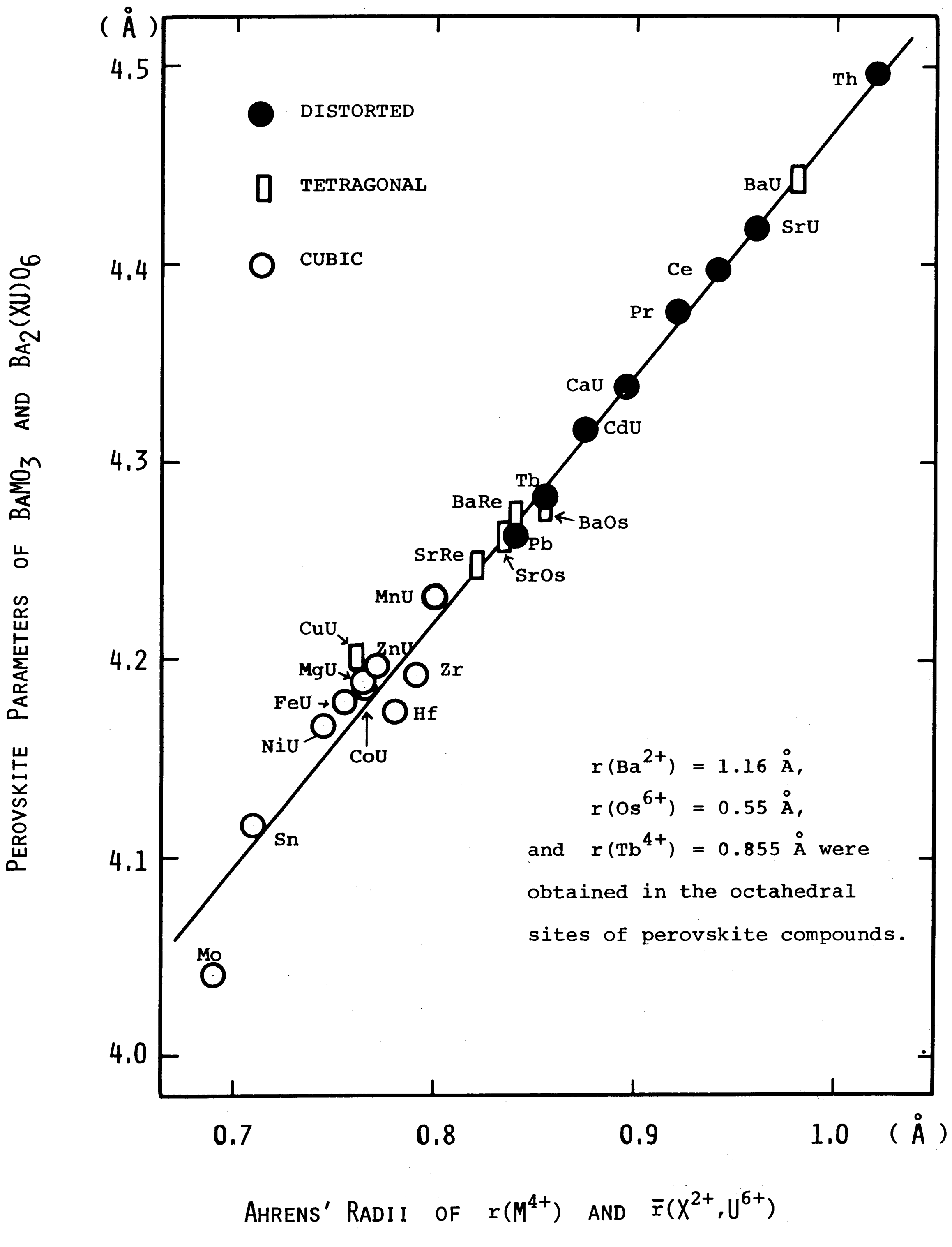
Table 2 X-ray powder diffraction data for $BaThO_3$.

H K L	h k l	$d_{calc.}$	$d_{obs.}$	$(I/I_0)_{obs.}$
110	{100}	4.497	4.493	20
002		4.497		
111		4.022	4.022	1
020	{110}	3.188	3.178	100
112		3.180		
200		3.172		
121		2.715	2.708	2
013		2.713		
103		2.711		
211		2.708		
022	{111}	2.600	2.595	3
202		2.592		
113		2.494	2.495	2
220	{200}	2.248	2.245	47
004		2.248		
023		2.184	2.179	1
221		2.181		
203		2.179		
031		2.068	2.065	2
123		2.065		
213		2.062		
3ol		2.059		
130	{210}	2.015	2.010	17
222		2.011		
310		2.007		
132	{211}	1.839	1.834	66
024		1.837		
204		1.834		
312		1.833		
040	{220}	1.594	1.595	4
224		1.590	1.589	17
400		1.586	1.585	4
041		1.569	1.569	2
025		1.567		
205		1.565		
401		1.562		
042	{221}	1.502	1.501	5
134		1.501		
330		1.499		
006		1.499		
314		1.497		
402		1.496		
331		1.479	1.479	1
142		1.462	1.464	1
106		1.459		
016		1.459		
412		1.456		
240	{310}	1.424	1.425	5
332		1.422	1.422	21
116				
420		1.420	1.420	5
043		1.407	1.406	1
241		1.407		
225		1.405		
421		1.403		
403		1.402		
242	{311}	1.358	1.356	3
026		1.356		
206		1.355		
422		1.354		
044	{222}	1.300	1.301	3
404		1.296	1.295	3

a = 6.345 Å , b = 6.376 Å , c = 8.992 Å (± 0.002 Å)

In Fig.3 plotted the perovskite parameter $\bar{a}$, defined by the cube root of cell-volume of the perovskite unit, of perovskite-type compounds $BaMO_3$ (M = Ce, Pr, Tb,[8)] Pb,[10)] Zr, Hf, Sn, Mo [5)]) against ionic radius of M^{4+} ion, $r(M^{4+})$.[2)] The parameters $\bar{a}$ of 1:1 ordered perovskites $Ba_2(XU)O_6$ (X = Sr, Ca, Cd, Mn, Zn, Cu, Mg, Co, Fe, Ni)[4)] were also plotted against the mean radius

$\bar{r}(X,U) = \frac{1}{2}\left\{r(X^{2+}) + r(U^{6+})\right\}$ in the Fig.3. This figure denotes that the both compounds $BaMO_3$ and $Ba_2(XU)O_6$ fall on the same linear relationship. The parameter



$r(Ba^{2+}) = 1.16$ Å,
$r(Os^{6+}) = 0.55$ Å,
and $r(Tb^{4+}) = 0.855$ Å were obtained in the octahedral sites of perovskite compounds.

Fig.3 Perovskite Parameters versus Ahrens' radii of octahedral ions for compounds $BaMO_3$ and $Ba_2(XU)O_6$.

$\bar{a}$ of $BaThO_3$ fitted well with the linear relationship in the Fig.3 for the Ahrens' value $r(Th^{4+}) = 1.02$ Å, but the $\bar{a}$ of $Ba_2(BaU)O_6$ did not. The Ahrens' value $r(Ba^{2+}) = 1.34$ Å was too large for the octahedral Ba^{2+} ion in $Ba_2(BaU)O_6$ and the radius $r(Ba^{2+}) = 1.16$ Å had to be chosen in order to fit the $\bar{a}$ of $Ba_2(BaU)O_6$ with the linear relationship.. The parameters $\bar{a}$ of tetragonal perovskites $Ba_2(SrOs)O_6$ and $Ba_2(SrRe)O_6$^11)^ were also compatible with the linear relationship for the Ahrens' radii of Sr^{2+}, Re^{6+} and newly obtained one $r(Os^{6+}) = 0.55$ Å. While for tetragonal perovskites $Ba_2(BaOs)O_6$ and $Ba_2(BaRe)O_6$,^11)^ the radius $r(Ba^{2+}) = 1.16$ Å again had to be employed for the octahedral Ba^{2+} ion in order to fit their parameters $\bar{a}$ with the linear relationship in the Fig.3. A large contraction ∼ 0.18 Å in the radius of octahedral Ba^{2+} ion in $Ba_2(BaZ)O_6$ (Z = U, Os, Re) relative to that in BaO (rock salt structure) is surprising. The anomalous contraction was also recognized by use of ionic radii after Shannon and Prewitt,12) although the relationship $\bar{a}$ vs. $r(M^{4+})$ was not linear in terms of their radii.

The author wishes to express his sincere gratitude to Okura Kazuchika Memorial Foundation for financial support.

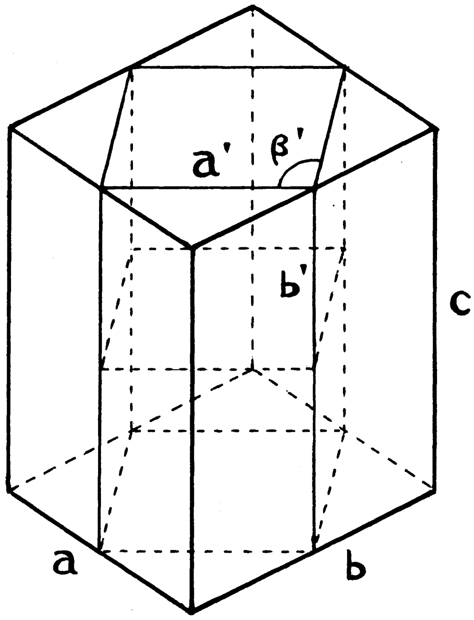


Fig.2 Orthorhombic cell with four pseudomonoclinic perovskite units.

References

1) R.S.Roth, J.Research NBS,RP,2736,58(1957).
2) L.H.Ahrens, Geochim. et Cosmochim.Acta,2,135(1952).
3) A.J.Smith and A.J.E.Welch, Acta Cryst.,13,653(1960).
4) A.W.Sleight and R.Ward, Inorg.Chem.,1,790(1962).
5) R.W.G.Wyckoff, "Crystal Structures," Interscience Pub.(1964),2nd ed.Vol.3.
6) H.F.Kay and P.C.Bailey, Acta Cryst.,10,219(1957).
7) P.Coppens and M.Eibschutz, Acta Cryst.,19,524(1965).
8) M.Yoshimura, T.Nakamura and T.Sata, Chem.Lett.,No.9,923(1973).
9) B.Delaunay, Z.Krist.,84,132(1933).
10) R.D.Shannon and P.E.Bierstedt, J.Am.Ceram.Soc.,53,635(1970).
11) A.W.Sleight, J.Longo and R.Ward, Inorg.Chem.,1,245(1962).
12) R.D.Shannon and C.T.Prewitt, Acta Cryst.,B25,925(1969).

(Received November 15, 1973)