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The Structures of $BaCeO_3$, $BaPrO_3$ and $BaTbO_3$ by Neutron Diffraction: Lattice Parameter Relations and Ionic Radii in *O*-Perovskites

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The perovskites $BaCeO_3$, $BaPrO_3$ and $BaTbO_3$ containing tetravalent rare earth ions have been investigated by powder neutron diffraction. All three show distortions from cubic symmetry. $BaTbO_3$ is rhombohedral ($R\bar{3}c$) and $BaCeO_3$ and $BaPrO_3$ orthorhombic (*Pbnm*), but with $c/\sqrt{2} < a < b$. Atom positions have been determined from least-squares refinement of peak intensities, and $BaTbO_3$ has been shown to become a *G*-type antiferromagnet below 36°K. The rotations of octahedra necessary to produce the orthorhombic (*Pbnm*) structure are discussed and a relation between the lattice parameters and the metal oxygen distance has been derived. The influence of small distortions within the octahedra are considered, and the variability of ionic radii in the perovskite structure is discussed.

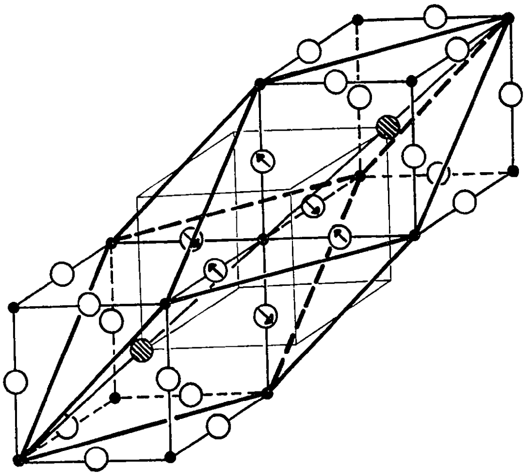
Introduction

The class of mixed metal ABO_3 oxides with perovskite-like structures is a large one, although few compounds have the ideal cubic unit cell (Goodenough & Longo, 1970; Galasso, 1969). For tolerance factors† less than unity two types of distortion commonly occur, both of which involve rotations of the BO_6 octahedra. The simple rhombohedral distortion is associated with a rotation about a trigonal axis (Fig. 1), lowering the symmetry to $R\bar{3}c$ (*e.g.* $LaAlO_3$). A further reduction of symmetry to $R3c$ may be observed when the A and B atoms are displaced along a trigonal axis (*e.g.* $BiFeO_3$). For larger deviations from the ideal ionic radius ratios the orthorhombic (*Pbnm*) $GdFeO_3$ structure is observed (see Fig. 2).

The cooperative tilting of the octahedra in these compounds can produce considerable oxygen-atom displacements from the ideal perovskite positions although the distortion of the unit cell may only be small, and line splittings in X-ray powder photographs have often been overlooked. For structures containing heavy A and B atoms, extra reflexions arising principally from oxygen displacements may be difficult to detect in X-ray work but are often observed with ease by neutron diffraction.

In this work we have determined the structures of $BaCeO_3$, $BaPrO_3$ and $BaTbO_3$ by neutron diffraction on powder samples. These compounds contain tetravalent rare earth cations and are all readily prepared at an oxygen pressure of 1 atmosphere. This may be contrasted with the more drastic preparative conditions necessary to form PrO_2 (MacChesney, Williams, Sherwood & Potter, 1964) and TbO_2 (MacChesney, Williams, Sherwood & Potter, 1966) and illustrates the stabilization of high formal oxidation states often observed in the perovskite structure. The magnetic behaviour of these high oxidation state rare earth ions as revealed by neutron diffraction is also of considerable interest.

Recently (Danelon Mastromonaco, Barbariol & Cocco, 1969), $BaCeO_3$ has been shown to have an orthorhombic cell ($a = 6.214$, $b = 6.236$, $c = 8.779$ Å) although earlier workers (Hoffmann, 1935; Smith & Welch, 1960) reported a simple cubic structure. $BaPrO_3$ and $BaTbO_3$ have previously been indexed as simple cubic ($a = 4.354$, Hoffmann, 1935; $a = 4.285$ Å, Paletta & Hoppe, 1966, respectively) although Nàray-Szabò



● Terbium ▨ Barium ○ Oxygen

Fig. 1. The rhombohedral structure of $BaTbO_3$. The relation of the primitive rhombohedral cell to the perovskite cube is shown, and the oxygen rotations about the trigonal axis are indicated for one BO_6 octahedron.

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† The tolerance factor is defined by:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

where r_A, r_B and r_O are the radii of the *A* and *B* metals and oxygen (see for example Goodenough & Longo, 1970).

(1947) reported a doubling of the unit cell for $BaPrO_3$ (a = 8·708Å).

Preparation and characterization of samples

Preparation

The starting materials were $BaCO_3$, CeO_2 and Tb_4O_7 (all 'Specpure': Johnson Matthey Chemicals Ltd.) and Pr_6O_{11} (99·9%, BDH Chemicals). The $BaCO_3$ was pre-dried by heating in CO_2 at 900°C, the CeO_2 was dried in oxygen at 900°C and the Tb_4O_7 and Pr_6O_{11} reduced to the sesquioxides by firing in vacuum at 1100°C. The $BaCO_3$-rare earth oxide mixtures were handled in a glove box filled with dry nitrogen since the oxides readily absorb water and carbon dioxide. The mixtures were fired twice at 1050°C for 48 hours in pure oxygen. The compounds thus prepared are white ($BaCeO_3$), dark brown ($BaPrO_3$) and yellow ($BaTbO_3$).

Analysis

The oxidizing powers of $BaCeO_3$ and $BaTbO_3$ were determined by oxidation of iodide in dilute HCl. The liberated iodine was titrated against standard sodium thiosulphate. The results obtained were $BaCeO_{3{\cdot}00\pm0{\cdot}01}$ and $BaTbO_{2{\cdot}96\pm0{\cdot}01}$. $BaPrO_3$ is too powerful an oxidizing agent to be easily determined in this way and the composition $BaPrO_{2{\cdot}990\pm0{\cdot}005}$ was found from the weight loss on reaction.

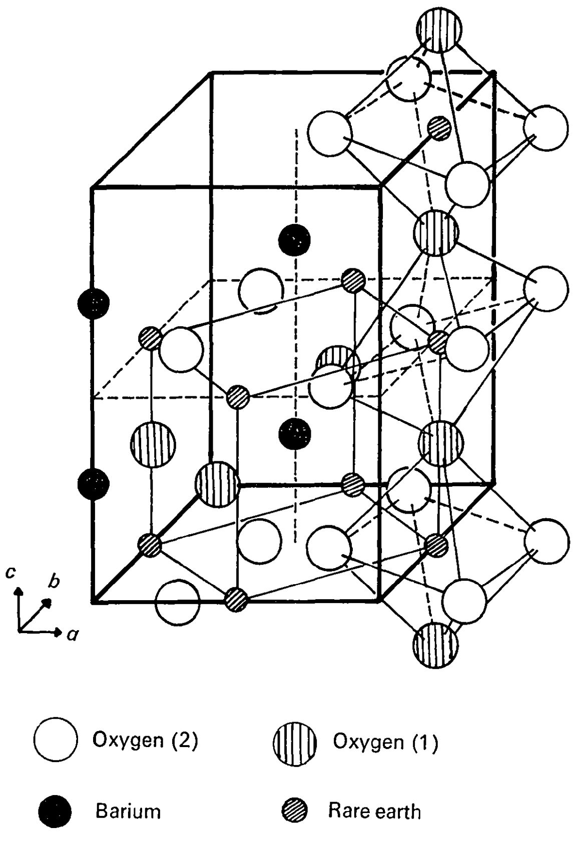

Fig..2 The orthorhombic ($GdFeO_3$) structure of $BaCeO_3$ and $BaPrO_3$. The tilting of the octahedra about the *b* and *c* axes may be observed.

X-rays

X-ray photographs of the three compounds were taken with a Debye–Scherrer camera (diameter 11·46 cm) using copper *Kα* radiation. For $BaTbO_3$ all the lines were indexed on the simple perovskite unit cell, although splittings were visible at high angle ($d < 1{\cdot}0$Å). These splittings, together with the appearance of extra lines in the neutron diffraction pattern (based on a doubled unit cell with *hkl* all odd) indicated a rhombohedral distortion.

The X-ray powder photographs of $BaCeO_3$ and $BaPrO_3$ also showed high-angle splittings and faint extra lines indicative of a doubled unit cell. An orthorhombic distortion was indicated by the presence of reflexions with *hkl* mixed in the neutron diffraction pattern.

A least-squares analysis of the high angle X-ray reflexions gave the lattice parameters in Table 1. The parameters reported by previous workers agree well with our results (Danelon Mastromonaco *et al.*, 1969; Palleta & Hoppe, 1966).

Table 1. *Lattice parameters*

$BaCeO_3$	$BaPrO_3$	$BaTbO_3$
$a = 6{\cdot}212 \pm 0{\cdot}001$ Å	$a = 6{\cdot}181 \pm 0{\cdot}001$ Å	$^*a = 8{\cdot}573 \pm 0{\cdot}001$ Å
$b = 6{\cdot}235 \pm 0{\cdot}001$	$b = 6{\cdot}214 \pm 0{\cdot}001$	$\alpha = 90°17' \pm 1'$
$c = 8{\cdot}781 \pm 0{\cdot}001$	$c = 8{\cdot}722 \pm 0{\cdot}001$	$^\dagger a = 6{\cdot}046 \pm 0{\cdot}001$
$c/\sqrt{2} = 6{\cdot}209$	$c/\sqrt{2} = 6{\cdot}167$	$\alpha = 60°22' \pm 1'$

* Face centered rhombohedral cell.
† Primitive rhombohedral cell.

Table 2. *Observed and calculated intensities for* $BaTbO_3$

hkl	I_{calc}	I_{obs}	$\sigma(I_{obs})$
200	42·7	43·3	2·1
220	37·7	35·6	1·6
311	14·2	14·6	1·0
222	59·4	62·5	1·5
400	145·4	145·6	2·1
331	7·2	6·2	1·0
420	34·4	34·6	1·3
422	35·0	34·5	1·1
333 511	4·9	4·9	0·9
440	129·1	129·2	1·6
531 600 442	43·4	42·2	1·5
620	16·1	13·6	1·1
533 622	38·4	36·2	1·9
444	51·4	49·4	1·5
711 551	18·2	17·2	2·0
642	31·4	30·5	1·2
731 553	15·3	17·0	1·7
800	25·6	29·2	1·8
733 820 644	18·3	18·1	1·4
822 660	28·7	32·2	1·6
751 555 662	26·6	25·6	1·9
840	74·8	77·0	1·8
911 753 842	34·9	37·0	1·9
664	11·5	11·0	1·1
931	12·5	10·2	1·5
844	57·5	56·0	1·4
933 771 755 10,0,0 860	21·1	20·8	1·6
10,2,0 862	38·0	39·7	1·7
951 753 10,2,2 666	7·0	8·2	1·5
10,4,0 864 973	17·4	16·3	2·1

Neutron diffraction measurements and refinements

Neutron diffraction measurements were made at room temperature on a powder diffractometer at the reactor PLUTO, A.E.R.E., Harwell. The samples were contained in thin-walled vanadium cans. The $BaTbO_3$ measurements were made at a wavelength of 1·105Å from the (311) planes of a copper monochromator with a take-off angle of 60°. The $BaCeO_3$ and $BaPrO_3$ were examined at a wavelength of 1·497Å from the (311) planes of a germanium monochromator with a take-off angle of 52°. Absorption and extinction effects were small and no corrections were necessary. The atom positions, scale factor and isotropic temperature factors of $BaTbO_3$ were refined from the observed intensities in space group $R\bar{3}c$ using a least-squares program to refine overlapping reflexions (written by P. J. Wiseman of this laboratory). The function minimized in this program is $\sum_i w_i(I_{obs}-I_{calc})^2$ where $w=1/\sigma^2$. All the 29 observed intensities were included in the refinement. The scattering lengths used were: $b_{Tb}=0·76\times10^{-12}$ cm., $b_O=0·577\times10^{-12}$ cm. (The Neutron Diffraction Commission, 1969), and $b_{Ba}=0·535\times10^{-12}$ cm. The barium value was calculated from the barium:fluorine ratio given by Cooper, Rouse & Willis (1968), but using a more recent fluorine value of $0·574\times10^{-12}$ cm. (Shull, 1971). The refinement converged after 4 cycles and the final R index (on intensities) was 0·037. The observed and calculated intensities are given in Table 2 and the atom positions in Table 4 (errors are quoted to σ). Refinement of the structure in the non-centrosymmetric space group $R3c$ did not improve the R index and atom displace-

Table 3. *Observed and calculated intensities for* $BaCeO_3$ *and* $BaPrO_3$

$BaCeO_3$

hkl	I_{calc}	I_{obs}	$\sigma(I_{obs})$
200	8·66	9·17	0·15
220	9·86	8·91	0·14
310	3·37	3·19	0·13
311	24·17	23·85	0·24
222	45·44	44·88	0·33
320	1·09	0·35	0·22
321	3·82	3·73	0·20
400	65·67	66·45	0·28
410 322	1·41	1·19	0·10
331	10·17	10·05	0·14
420	8·83	9·31	0·14
421	2·34	2·24	0·11
422	22·84	23·57	0·18
430	0·29	0·26	0·16
510 431	1·79	1·89	0·11
333 511	5·76	5·44	0·14
520 432	1·09	0·88	0·12
521	1·51	1·28	0·13
440	47·15	46·68	0·30
522 411	0·74	0·54	0·19
530 531 600 442	38·54	38·70	0·49
532	4·43	4·50	0·23
620	5·33	4·59	0·21
621 540 443 541	2·28	1·72	0·37
533 622 630 542	27·95	27·69	0·47

$BaPrO_3$

hkl	I_{calc}	I_{obs}	$\sigma(I_{obs})$
200	2·87	2·67	0·16
220	3·03	2·74	0·14
310	0·95	0·87	0·17
311	8·36	8·42	0·16
222	18·80	18·69	0·19
321	0·93	1·15	0·17
400	24·69	25·24	0·21
331	3·66	3·63	0·14
420	3·04	3·45	0·14
422	6·68	7·15	0·16
510 431	0·53	0·49	0·10
333 511	2·01	1·84	0·10
440	18·33	18·20	0·22
530 531 600 442	13·69	13·21	0·30
532	1·35	0·99	0·14
620	1·76	1·61	0·14
533 622 630 542	11·94	11·24	0·30
444	6·20	6·30	0·18
710 543 711 551	5·07	5·42	0·24
720 641 721	1·67	0·77	0·40
642 722 544	5·95	5·38	0·21
730 731 533	4·22	4·11	0·24
800 810 740 652	3·29	2·69	0·23
733 820 644	2·55	2·17	0·23

ments from the special positions of $R\bar{3}c$ were not statistically significant.

The $BaCeO_3$ and $BaPrO_3$ intensity data were refined similarly in the orthorhombic space group *Pbnm*. The number of intensities collected (25 and 24 respectively) was insufficient to allow all the parameters to be varied and the temperature factors were fixed at the values obtained from the $BaTbO_3$ results. Refinement of the scale factor and the seven positional parameters was continued until the shifts were considerably less than the e.s.d.'s. The final *R* indices were 0·027 for $BaCeO_3$ and 0·050 for $BaPrO_3$. The observed and calculated intensities are given in Table 3 and the atom positions in Table 4. In Tables 2 and 3 the pseudo-cubic indices are given although the correct rhombohedral and orthorhombic indices were used in the refinement. Scattering lengths, $b_{\mathrm{Ce}} = 0{\cdot}479 \times 10^{-12}$ cm (Valentine & Willis, 1965) and $b_{\mathrm{Pr}} = 0{\cdot}44 \times 10^{-12}$ cm (Neutron Diffraction Commission, 1969) were used. Attempts to refine all parameters (constraining $B_{\mathrm{O}(1)} = B_{\mathrm{O}(2)}$: Fig. 2) led to atom positions which were essentially unchanged but gave spurious temperature factors with large standard deviations.

At low temperatures extra reflexions in the neutron diffraction pattern show that $BaTbO_3$ is a *G*-type antiferromagnet with a Néel temperature of 36°K. A more detailed account of this work, including a determination of the Tb^{4+} form factor will be published elsewhere. $BaPrO_3$ is not magnetically ordered at 4·2°K.

Results

From the experimental values of the atom positions some of the important interatomic distances and angles in the three compounds have been calculated (Table 5 and Figs. 1 and 2). The angles in the PrO_6 octahedron are similar to those in $BaCeO_3$ but the standard deviations are much larger (1·8°).

The rhombohedral perovskite: $BaTbO_3$

In $BaTbO_3$ the Tb–O distances are all equal (2·15Å) and the distortion of the octahedron is small. We would expect, therefore, a good correlation between the rotation of the octahedron from the ideal perovskite position about the trigonal axis, and the rhombohedral angle α. The angle of rotation ω may be calculated from the oxygen positions and is related to α as shown by Moreau, Michel, Gerson & James (1970):

$$\cos\alpha = \frac{4-\cos^2\omega}{4+2\cos^2\omega}$$

The value of ω calculated is 7°33′, giving $\alpha = 60°25'$, in excellent agreement with the value of $60°22' \pm 1'$ derived from the X-ray powder pattern. The magnitude of the rotation is similar to that found in $Pb(Zr_{0{\cdot}9}Ti_{0{\cdot}1})O_3$ where $\omega = 8°$ (Michel, Moreau, Achenbach, Gerson & James, 1969; Moreau, *et al.*, 1970). The agreement between the observed and calculated values is rather better in $BaTbO_3$ than in $Pb(Zr_{0{\cdot}9}Ti_{0{\cdot}1})O_3$ (where the discrepancy is 8′), presumably because the latter compound is more distorted, since the metal atoms are displaced along the $\langle 111 \rangle$ directions.

The orthorhombic perovskites: $BaCeO_3$ and $BaPrO_3$

The results for $BaCeO_3$ and $BaPrO_3$ are in accord with those obtained for other orthorhombic perovskites. The oxygen environment of the large A cation

Table 4. *Atom positions in* $BaTbO_3$, $BaCeO_3$ *and* $BaPrO_3$

(x,y,z are fractions of the unit cell edges, B is in Å².)

$BaTbO_3$ ($R\bar{3}c$)

		x	*y*	*z*	*B*
$2Tb^{4+}$	2(*b*)	0·0	0·0	0·0	0·24 ± 0·07
$2Ba^{2+}$	2(*a*)	0·25	0·25	0·25	0·75 ± 0·10
$6O^{2-}$	6(*c*)	−0·2876 ± 0·0006	0·7876 ± 0·0006	0·25	0·89 ± 0·06

$R(I) = 0{\cdot}037$ (29 intensities)

$BaCeO_3$ (*Pbnm*)

		x	*y*	*z*
$4Ba^{2+}$	4(*c*)	0·001 ± 0·001	0·023 ± 0·002	0·25
$4Ce^{4+}$	4(*b*)	0·0	0·5	0·0
$4O(1)^{2-}$	4(*c*)	0·071 ± 0·004	0·487 ± 0·004	0·25
$8O(2)^{2-}$	8(*d*)	−0·274 ± 0·004	0·278 ± 0·003	0·041 ± 0·002

$R(I) = 0{\cdot}027$ (25 intensities)

$BaPrO_3$ (*Pbnm*)

		x	*y*	*z*
$4Ba^{2+}$	4(*c*)	0·014 ± 0·009	0·023 ± 0·007	0·25
$4Pr^{4+}$	4(*b*)	0·0	0·5	0·0
$4O(1)^{2-}$	4(*c*)	0·071 ± 0·006	0·481 ± 0·010	0·25
$8O(2)^{2-}$	8(*d*)	−0·271 ± 0·005	0·271 ± 0·006	0·037 ± 0·003

$R(I) = 0{\cdot}050$ (24 intensities)

is considerably distorted but the BO_6 octahedra remain almost regular. The average praseodymium–oxygen distance is slightly smaller than the cerium–oxygen distance (2·22Å compared with 2·24Å) as expected. The formal coordination number of the A cation is twelve, though Marezio, Remeika & Dernier (1970) have shown that in the rare earth orthoferrites the lanthanide ion may be effectively only eight coordinate. However, in $BaCeO_3$ and $BaPrO_3$ twelve coordination is indicated by the absence of sharp discontinuities in the increasing barium–oxygen distances (Table 5). The average Ba–O distances increase from $BaTbO_3$ to $BaPrO_3$ and $BaCeO_3$ (3·03, 3·11 and 3·13Å, respectively) and are all larger than the value of 3·0Å (Shannon & Prewitt, 1969) expected for twelve-coordination (*cf.* discussion below). This may be understood if we consider the barium ion to be located on a site defined by rotations of rigid BO_6 octahedra (see below).

Table 5. *Interatomic distances* (Å) *and angles*(°)

Numbers in parentheses give the number of atoms at that distance.

	$BaCeO_3$	$BaPrO_3$	$BaTbO_3$
M^{4+}–O(1)	2·24±0·02 (2)	2·23±0·06 (2)	2·154±0·004 (6)
M^{4+}–O(2)	2·22±0·02 (2)	2·22±0·03 (2)	
	2·26±0·02 (2)	2·22±0·03 (2)	
Ba–O(1)	2·67±0·05 (1)	2·58±0·09 (1)	2·807±0·004 (3)
	2·93±0·05 (1)	2·87±0·09 (1)	3·031±0·004 (6)
	3·37±0·05 (1)	3·39±0·09 (1)	3·264±0·004 (3)
	3·60±0·05 (1)	3·63±0·09 (1)	
Ba–O(2)	2·77±0·05 (2)	2·86±0·07 (2)	
	2·96±0·05 (2)	2·99±0·07 (2)	
	3·17±0·05 (2)	3·11±0·07 (2)	
	3·59±0·05 (2)	3·48±0·07 (2)	

O —–Tb–O	89·44±0·07
O(1)–Ce–O(2)	89·6±0·8
O(1)–Ce–O(2)	88·3±0·8
O(2)–Ce–O(2)	88·6±0·8

Distortions and interatomatic distances in *O*-perovskites

Lattice parameter relationships

It has not previously been pointed out that relationships between cell parameters and the rotations of the octahedra may be obtained for the orthorhombic as well as for the rhombohedral perovskites. The ideal $GdFeO_3$ structure may be generated from the simple cubic structure by cooperative rotations of regular octahedra about the orthorhombic ⟨010⟩ and ⟨001⟩ directions. If the angles of rotation are θ and φ respectively and l is the B–O distance the orthorhombic lattice parameters become:

$$a=2\sqrt{2}l\cos\theta\cos\varphi,\ b=2\sqrt{2}l\cos\varphi,\ c=4l\cos\varphi$$

giving (i) $a\le c/\sqrt{2}<b$ as is generally observed, where $a=c/\sqrt{2}$ for zero rotation about ⟨001⟩, and (ii) $l=bc/4a$. It is also possible to express the oxygen positional parameters in terms of l, θ and φ.

Several series of orthorhombic perovskites (including an extensive set of rare earth oxides $LnBO_3$) with different A cations but the same B cation have been prepared. In each series, relation (ii) gives consistent values for the average B–O distances, showing that the small distortions of the BO_6 octahedra which do occur, and which vary with the degree of orthorhombic distortion (*e.g.* $LnFeO_3$), in most cases do not significantly effect calculated values of l. Also, although atom positions have been determined for only a few $GdFeO_3$-type structures, predicted and experimental values for most of these are in very good agreement: for example $CaTiO_3$, predicted and experimental 1·93Å (Kay & Bailey, 1957), and all the orthoferrites from $GdFeO_3$ to $LuFeO_3$, predicted and experimental 2·01Å (Marezio *et al.*, 1970)

However, when the orthorhombic distortion is small, the calculated values of l appear to be low and this is borne out by a comparison of the calculated and experimental values for $LaFeO_3$ (Marezio & Dernier, 1971) and $PrFeO_3$ (Marezio *et al.*, 1970) as well as $BaCeO_3$ and $BaPrO_3$: $LaFeO_3$; l(calc.) = 1·97Å, l(exptl.) = 2·01Å, $PrFeO_3$ (1·98Å, 2·01Å), $BaCeO_3$ (2·20Å, 2·24Å) and $BaPrO_3$ (2·19Å, 2·22Å). The discrepancy appears to be a consequence of small angular distortions in the oxygen(2) plane which would be expected to increase a and reduce b. The O(2)–M–O(2) angles are 88·6 and 91·4° in $BaCeO_3$, 89·1 and 90·1° in $BaPrO_3$, 88·7 and 91·3° in $LaFeO_3$ and 89·3 and 90·7° in $PrFeO_3$. In contrast, in the orthoferrites mentioned above which are well behaved, the angles are closer to 90° though it is uncertain whether this is connected with the increased cell distortion. In any case, in both $BaCeO_3$ and $BaPrO_3$ $c/\sqrt{2}$ is less than a (*cf.* apparently also $SrZrO_3$ and $SmAlO_3$, Goodenough & Longo, 1970). For small orthorhombic distortions, therefore, this order of cell parameters is not necessarily associated with Jahn-Teller effects (Goodenough & Longo). Deviations from 90° of the O(1)–B–O(2) angles are also observed but appear to have a smaller effect on the cell parameters.

Variations in metal–oxygen distances

Metal-oxygen distances have not been determined experimentally for the majority of perovskites which are distorted though lattice parameters are often accurately known. Our knowledge of trends of B–O or A–O distances is thus limited. Relation (ii) however, allows comparisons to be extended to a large number of *O*-perovskites.

In the cubic perovskites a decrease in the B–O distance is observed when the size of the A cation is reduced. For example,

$BaTiO_3$	2·00Å	$RbUO_3$	2·164Å
$SrTiO_3$	1·95Å	KUO_3	2·145Å

As the size of the A cation is further decreased, significant distortions occur, and the B–O distances appear to reach limiting values (for example the rare

Table 6. *Limiting B–O distances in orthorhombic ABO_3 perovskites* (Å)

Derived oxygen radii are given in parentheses.

Sc^{3+}	2·08 (1·35)								
Ti^{3+}	2·02 (1·35)	Ti^{4+}	1·93 (1·325)	Zr^{4+}	2·06 (1·35)	Hf^{4+}	2·055 (1·34)	Ce^{4+}	2·20 (1·40)
V^{3+}	2·01 (1·37)	V^{4+}	1·90 (1·33)						
Cr^{3+}	1·98 (1·365)	Cr^{4+}	1·88 (1·33)	Mo^{4+}	1·99 (1·34)				
Fe^{3+}	2·01 (1·365)			Ru^{4+}	1·98 (1·36)				
		Al^{3+}	1·90 (1·37)	Sn^{4+}	2·02 (1·34)	Pa^{5+}	2·14		
		Ga^{3+}	1·98 (1·36)	Pb^{4+}	2·12 (1·34)	U^{5+}	2·11 (1·35)		
		In^{3+}	2·12 (1·33)						

earth orthoferrites). In a qualitative sense, this may be viewed as a change from AO_3 packing with B cations in octahedral holes to the packing of BO_6 octahedra with A cations in twelve coordinate sites.

Some limiting B–O distances for orthorhombic perovskites calculated by relation (ii) are given in Table 6. From these distances oxygen radii (given in parentheses in Table 6) have been derived by subtraction of the 'effective' cationic radii for six-coordination (Shannon & Prewitt, 1969). The oxygen radii are consistently smaller than that normally associated with six-coordinate oxygen (1·40Å, Shannon & Prewitt). Similarly, metal–oxygen distances for the twelve-coordinate A cation can also be significantly smaller than the sum of the 'effective' ionic radii. For example, in cubic $BaTiO_3$ the experimental value is 2·84Å, compared with a calculated sum of 3·00Å, and in $SrTiO_3$ the Sr–O distance is 0·08Å smaller than expected.

Shannon and Prewitt suggest that the short metal-oxygen distances observed in the perovskite structure arise from anion–anion repulsions. The deduced oxygen radii in Table 6 are, on the other hand, similar to the 'effective' ionic radius for two-coordinate oxygen (1·35Å), in line with the fact that the two B cation nearest neighbours are always significantly closer than the four nearest neighbour A cations. However, although the Shannon–Prewitt classification successfully correlates a wide range of metal–oxygen distances by simply taking into account the coordination number of the ions concerned, in view of the inevitable simplicity of the model it is to be expected that some variability in 'effective' ionic radii will occur, even within the same structure. In the present case it seems likely that the short metal-oxygen distances stem from the high lattice energy of the perovskite structure.

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