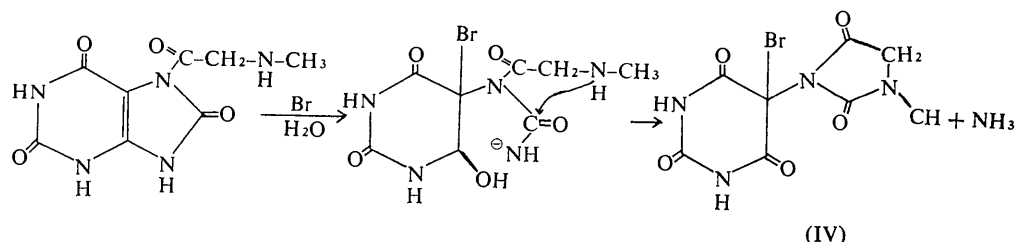


La bromation par l'eau de brome a fixé le brome sur la double liaison. Il y a eu oxydation, départ de NH₃ et cyclisation de la sarcosine pour former le composé (IV),



Références

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program*. USAEC Report ORNL TM 305.

L'auteur tient à remercier vivement M. Barbier pour la suggestion du problème, la synthèse des substances et pour l'intérêt qu'il a porté à ce travail. L'auteur est également reconnaissant à Monsieur B. Roques pour les fructueuses discussions d'ordre chimique.

BOLTON, W. (1963). *Acta Cryst.* **16**, 166.
 JEFFREY, G. A., GHOSE, S. & WARWICKER, J. O. (1961). *Acta Cryst.* **14**, 881.
 PASCARD-BILLY, C. & BARBIER, M. (1968). *Bull. Soc. chim. France*, p. 4470.
 DU PRÉ, S. & MENDEL, H. (1955). *Acta Cryst.* **8**, 311.

Acta Cryst. (1970). B26, 1425

Atomic Displacement Relationship to Rhombohedral Deformation in Some Perovskite-Type Compounds*

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(Received 19 June 1969)

In the rhombohedral, distorted perovskite-type compounds, PbZr_{0.9}Ti_{0.1}O₃, BiFeO₃, LiTaO₃, LiNbO₃, the oxygen octahedra are viewed as rotated around their threefold axes by an angle ω from the ideal perovskite position. A theoretical relationship is derived which relates the rotation angle ω to the rhombohedral cell angle α .

The crystal structures of ferroelectric BiFeO₃ and PbZr_{0.9}Ti_{0.1}O₃ have been reported recently (Michel, Moreau, Achenbach, Gerson & James, 1969 *a, b*). In these isomorphous perovskite-type compounds the rhombohedral unit-cell contains two formula units. The parameter a_R is the face diagonal of the unimolecular perovskite-like subcell, Fig. 1. The relations between the face-centered pseudocubic cell and the primitive rhombohedral cell are:

$$a_R = \frac{1}{2} a_f \sqrt{2(1 + \cos \alpha_f)},$$

$$\cos \alpha_R = \frac{1}{2} \frac{3 \cos \alpha_f + 1}{\cos \alpha_f + 1},$$

where a_f and α_f denote the pseudocubic parameters and the rhombohedral angle α_R is nearly 60°.

Fig. 2 shows the shift of the atoms from the ideal perovskite positions. The two cations are shifted in the same direction along [111]. The oxygen atoms rotate around the trigonal axis in the same type of oxygen shift as observed for LaAlO₃. The resulting space group is $R\bar{3}c$.

For the following discussion it is convenient to transform the rhombohedral cell into the corresponding hexagonal cell containing six formula units. The oxygen atoms are arranged in six equidistant planar layers normal to, and intersecting, the c axis $z = \frac{1}{12}(2n+1)$, where n is integral.

The atomic parameters of the ideal perovskite-like framework are [Fig. 3(a)]:

$$\begin{matrix} A & 0, 0, 0 \\ B & 0, 0, \frac{1}{4} \\ O & \frac{1}{6}, \frac{1}{3}, \frac{1}{12} \end{matrix}$$

* Supported by the U.S. Atomic Energy Commission.

We may write the parameters of both BiFeO_3 and $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ as follows:

$$\begin{aligned} A & 0, 0, w \\ B & 0, 0, \frac{1}{4} + w' \\ O & \frac{1}{6} - u, \frac{1}{3} + v, \frac{1}{12} \end{aligned}$$

where w , w' , u , and v express the atomic shift from the ideal positions.

Fig. 3(b) describes the oxygen shifts from their ideal perovskite positions for different values of n . The heavy atom B lies at the center of an oxygen octahedron oriented with two opposite faces perpendicular to the c axis.

Table 1 gives the values of the lengths of different oxygen octahedron edges. The spread of the oxygen distances around the average value is very small. Therefore the oxygen positions can be considered as resulting from a rotation around the c axis from the ideal position of a rigid octahedron. The rotation of the octahedron is evaluated by an angle ω given by the relation:

$$\cos \omega = \frac{\vec{OM} \cdot \vec{OP}}{|\vec{OM}| |\vec{OP}|}$$

where O is the center of the octahedron and M is the projection onto the (0001) plane of the octahedral corners tilted from the ideal perovskite position P (Fig. 4). According to Megaw (1968), it is topologically possible to transform an octahedral framework continuously from the ideal perovskite configuration to the hexagonal close-packed configuration. This transformation may be realized by rotating the rigid BO_6 octahedron around the c axis as shown in Fig. 5. When ω attains the value of 30 degrees, the oxygen framework is then hexagonal close-packed, [Fig. 3(c)], the oxygen atom coordinates being $0, \frac{1}{3}, \frac{1}{12}$. In a note, Megaw (1968) considered oxygen octahedra in LiNbO_3 as rotated around their triad axis by an angle of 6.5° from the ideal hexagonal close-packed position and pointed out that with increasing temperature this struc-

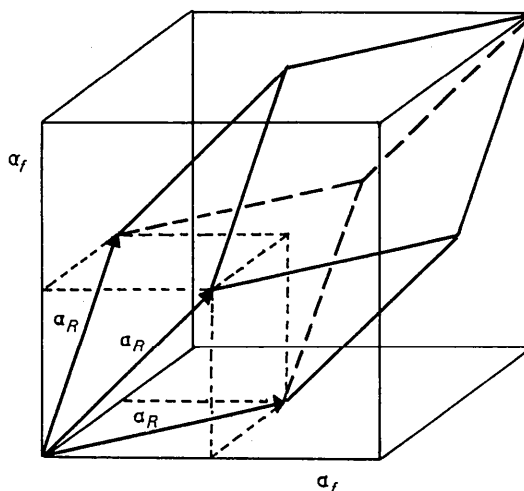


Fig. 1. Primitive rhombohedral cell derived from multiple pseudocubic cell.

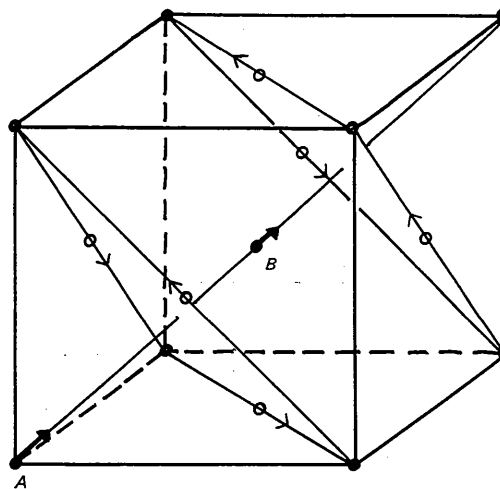


Fig. 2. Heavy atom shifts along the threefold axis [111]. The rotation of the oxygen octahedron around [111] is shown in the pseudocubic perovskite cell.

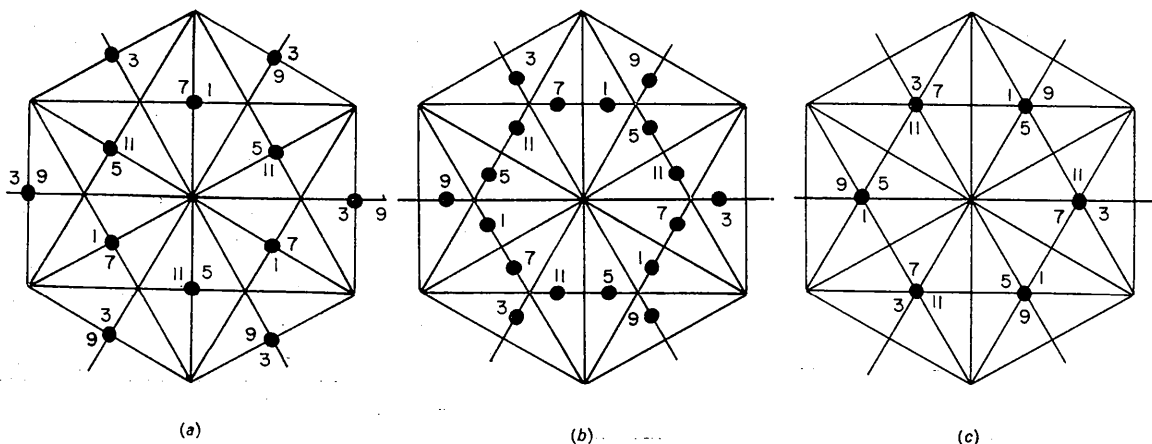


Fig. 3. Oxygen atomic positions, projected on (0001), $R\bar{3}c$, for different values of atomic parameters in the same unit-cell. Numbers correspond to the position expressed as $c/12$. (a) Oxygen framework in ideal perovskite. (b) Intermediate oxygen framework. (c) Ideal hexagonal close-packed oxygen framework.

ture could be looked upon as a highly distorted perovskite-type.

Table 1. Oxygen octahedra edge lengths in Å

PbZr _{0.9} Ti _{0.1} O ₃	BiFeO ₃	LiNbO ₃
3.04 Å	2.89 Å	2.879 Å
2.85	2.76	2.719
2.93	2.84	2.801
2.94	2.87	2.840

Thus, we can consider the oxygen array in PbZr_{0.9}Ti_{0.1}O₃ and BiFeO₃ as being in the early stage of a continuous transformation which is fully developed in LiNbO₃ and the isomorphous LiTaO₃.

In this isomorphous series, the different stages of the rotation of oxygen octahedra give rise to a variation of both the hexagonal cell parameter a and the rhombohedral angle α .

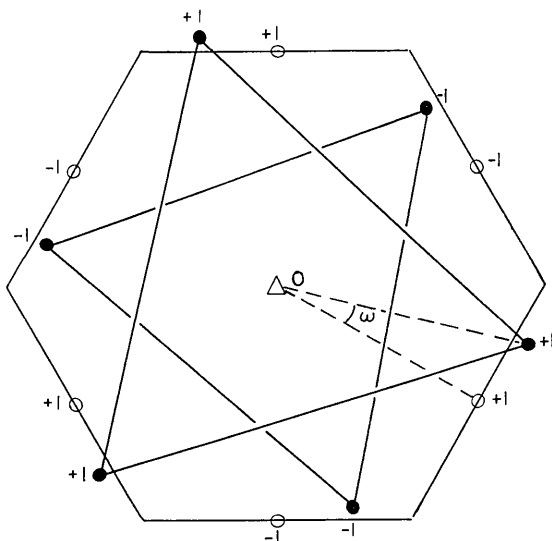


Fig. 4. Rotation, ω , and slight distortion of one oxygen octahedron centered at origin. ○ Oxygen atom position in ideal perovskite, ● shifted position of oxygen atom.

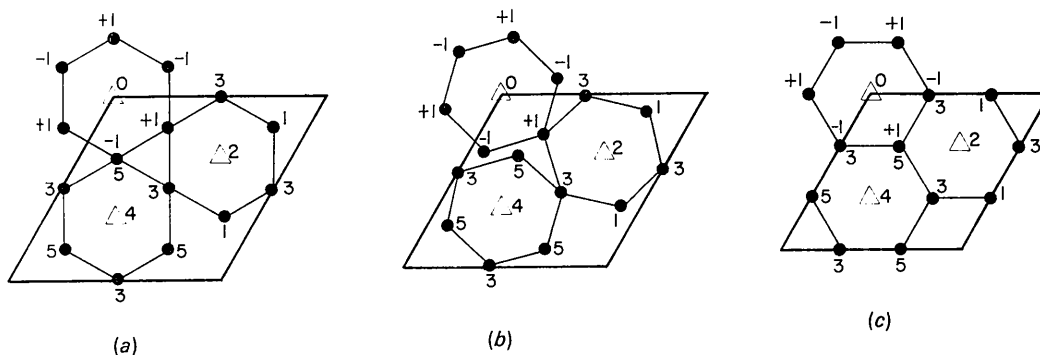


Fig. 5. Variation of cell dimensions related to the rotation, ω , of regular octahedra. Oxygen atomic positions projected onto (0001) for one half of cell; (a) Perovskite-like framework. (b) Intermediate oxygen framework. (c) Ideal hexagonal close-packed oxygen framework.

We derive, for the first time, a theoretical relationship between the angles ω and α .

For any value of the tilt angle ω , the rigid octahedron is a regular hexagon in projection with a constant edge length, l . The hexagonal cell parameter a depends only on the rotation of the octahedra (Fig. 5). Thus for the ideal perovskite configuration: $a = 2l\sqrt{3} = a_p$. For the intermediate configurations corresponding to oxygen shifts from this idealized system, Fig. 3(b) and 5(b):

$$a_{(\omega)} = 2l \cos\left(\frac{\pi}{6} - \omega\right) + 2l \cos\left(\frac{\pi}{6} + \omega\right)$$

$$a_{(\omega)} = 2l\sqrt{3} \cos \omega = a_p \cos \omega. \quad (1)$$

For the hexagonal close-packed configuration:

$$a_H = a_p \sqrt{\frac{3}{2}}.$$

During the continuous transformation in the ideal perovskite from the octahedral framework ($\omega = 0$) to the hexagonal close-packed framework ($\omega = \pi/6$), the hexagonal cell-parameter a decreases while c remains constant. The general relation between the axial ratio c/a of the hexagonal cell and the angle α of the corresponding rhombohedral cell is:

$$\left(\frac{c}{a}\right)^2 = \frac{9}{4 \sin^2\left(\frac{\alpha}{2}\right)} - 3 \text{ or } \cos \alpha = 1 - \frac{9}{6 + 2\left(\frac{c}{a}\right)^2}. \quad (2)$$

Therefore for the oxygen configuration in the ideal perovskite, $\alpha_p = \pi/6$ and $c/a = \sqrt{6}$, whereas for the hexagonal close-packed configuration, $\alpha_H = 53^\circ 50'$ and $c/a_H = \sqrt{8}$. From equation (1) one can calculate the ratio $c/a = \sqrt{6}/\cos \omega$ which when combined with equation (2) gives α as a function of ω :

$$\alpha = \arccos \frac{4 - \cos^2 \omega}{4 + 2 \cos^2 \omega}. \quad (3)$$

This angular relationship is independent of the cell parameters and therefore can be applied to any

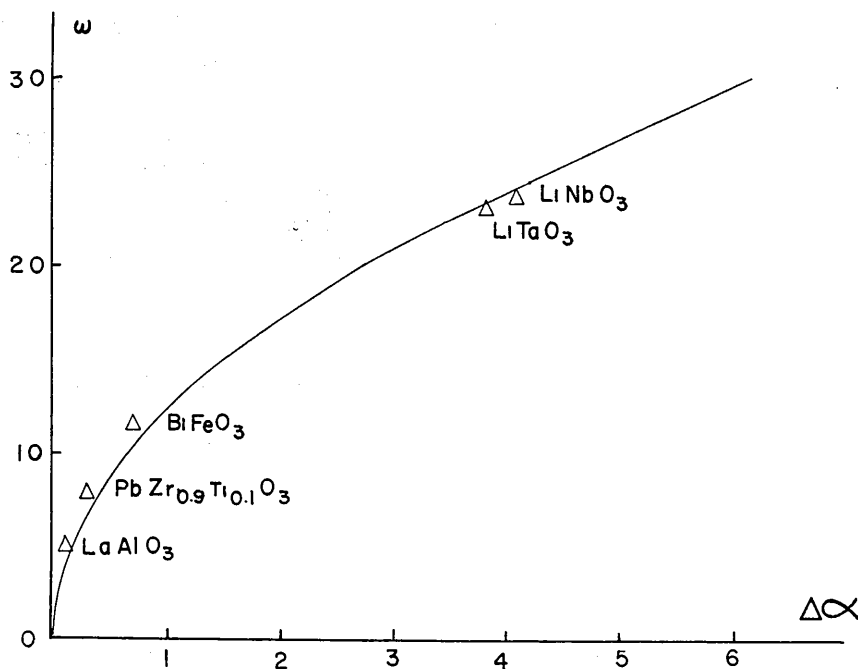


Fig. 6. Plot of ω vs. $\Delta\alpha$. Solid line, theoretical; Δ , experimental values.

rhombohedral compounds with this type of deformation.

The ratio $\kappa = \Delta\alpha / \Delta\alpha_M = (\alpha_p - \alpha) / (\alpha_p - \alpha_H)$, where $\Delta\alpha_M$ represents the maximum change in rhombohedral angle, increases from 0 for the octahedral framework of the ideal perovskite ($\omega = 0$), to 1 when this framework becomes hexagonal close-packed ($\omega = \omega_M = \pi/6$). κ can be expressed in reduced coordinates by the following equation:

$$\kappa = \frac{\Delta\alpha}{\Delta\alpha_M} = \frac{1}{\alpha_p - \alpha_H} \left[\frac{\pi}{3} - \arccos \left\{ \frac{7 - \cos \left(\frac{\pi}{3} \cdot \frac{\omega}{\omega_M} \right)}{10 + 2 \cos \left(\frac{\pi}{3} \cdot \frac{\omega}{\omega_M} \right)} \right\} \right] \quad (4)$$

$\kappa \rightarrow 0$ and $\omega/\omega_M \rightarrow 0$ as the oxygen array approaches that of the ideal perovskite-like configuration. Conversely, as the oxygen array approaches that found in the hexagonal close-packed arrangement, $\kappa \rightarrow 1$ and $\omega/\omega_M \rightarrow 1$.

Table 2 lists the different values of ω and $\Delta\alpha$ for the compounds LaAlO_3 , $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$, BiFeO_3 , LiTaO_3 , and LiNbO_3 .

Table 2. Octahedral tilt angle ω and corresponding rhombohedral angle difference $\Delta\alpha$

	ω	$\Delta\alpha = \alpha_p - \alpha$
LaAlO_3	5° 40'	6'
$\text{Pb}(\text{Zr}_{0.9}\text{Ti}_{0.1})\text{O}_3$	8	18
BiFeO_3	11 40	42
LiTaO_3	23	3° 50
LiNbO_3	23 30	4 08

The theoretical curve as derived from relation (4) is plotted in Fig. 6.

The experimental values reported from the preceding series are in good agreement with this relationship. The spread of the observed values around the theoretical curve can be attributed to experimental error and also to the fact that the oxygen octahedra are not regular but slightly distorted.

References

- MEGAW, H. D. (1968). *Acta Cryst.* A24, 583.
 MICHEL, C., MOREAU, J. M., ACHENBACH, G. D., GERSON, R. & JAMES, W. J. (1969a). *Solid State Comm.* 7, 701, 86S.
 MICHEL, C., MOREAU, J. M., ACHENBACH, G. D., GERSON, R. & JAMES, W. J. (1969b). *Solid State Comm.* 7, 865.