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An Explanation of the Structures of Hexagonal Barium Titanate and Titanium Dioxide

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The structure of hexagonal barium titanate is explained in terms of the semipolar nature of the Ti–O bond, and the Ti–O and Ba–O bond distances. The brookite and anatase forms of TiO_2 are explained by bond-angle considerations.

Introduction

Barium titanate ($BaTiO_3$) has two crystal structures: (*a*) the well known cubic perovskite structure and its ferroelectric derivatives (see Megaw, 1947; Forsbergh, 1949; Kay & Vousden, 1949); (*b*) a hexagonal phase whose structure has been determined by Burbank & Evans (1948) and which was first reported by Megaw (1946).† The latter transforms to the cubic phase only when heated to 1050° C., and so is probably the more stable (Frondel; see Burbank & Evans, 1948).

The perovskite structure is well understood. Given the ionic radii and the sign of the ion charges, it is the simplest atomic arrangement, and is assumed by many structures (see, for example, Wood, 1951). The TiO_6 octahedra share corners, so that the Ti–O–Ti bond angles are 180°. The hexagonal structure, however, is unique. Its distinctive feature is the *face sharing* of two-thirds of the octahedra. Burbank & Evans point out that such face sharing is unknown in other compounds of this type. The object of this note is to explain the hexagonal structure in terms of the semipolar nature of the Ti–O bond, and thereby to explain the structures of TiO_2.

The hexagonal structure of $BaTiO_3$

The structure may be visualized as follows. Three pairs of octahedra are arranged at 120° about a vertical axis, with shared faces horizontal and coplanar (Fig. 1). A barium atom is placed, at the centre of this configuration. Above and below the barium atoms are placed the other octahedra, which share corners with those already positioned. The remaining barium atoms occupy holes at the sides of these octahedra.

Explanation

We shall assume that the Ti–O bond is semipolar. The chemical properties of compounds with these bonds make this conclusion reasonably certain, whilst the homopolar character is about 50% on Pauling's scale (Pauling, 1945). Kaenzig (1951) has arrived at the same conclusion from an X-ray study of the thermal vibrations of $BaTiO_3$, whilst Megaw (1952) has argued that the semipolar character is responsible for the ferroelectricity.

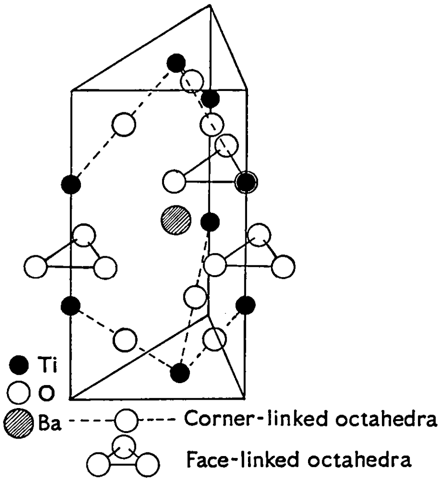

Fig. 1. Linkage of octahedra in hexagonal $BaTiO_3$. A number of the atoms are omitted for clarity.

Face sharing of octahedra is unexpected if the Ti–O bond is ionic, because of the resultant close approach of the titanium atoms (see Burbank & Evans, 1948). But if the bond is semipolar the titanium and barium charges will be about equal. Hence the Ti–Ti repulsion will not be outstanding, so that face sharing should not be inhibited.

A study of the bond distances shows why face sharing is *preferred*. In Table 1 the Ti–O and Ba–O bond distances in the cubic and hexagonal structures

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† Megaw reports a smaller cell than Burbank & Evans but her powder photograph contains a number of unindexed lines. If these correspond to the larger cell, as a comparison of the published photographs strongly suggests, the corresponding structures appear identical.

Table 1. *Comparison of* Ti–O *and* Ba–O *bond distances with ideal values*

	TiO (Å)	Ba–O (Å)
Ideal values	1·96	2·85
Cubic $BaTiO_3$	2·00	2·82
Hexagonal $BaTiO_3$	1·96	2·84, 2·94
	1·95	2·89, 2·96
	2·02	2·78

are compared with the ideal values, derived from the Goldschmidt radius sum (see Megaw, 1946).

Cubic $BaTiO_3$ is unstable because of the large radius of the barium ion. Table 1 shows that the Ba–O bond lengths are too small, and that the Ti–O lengths are too large (Megaw, 1946). This instability is thought to be closely related to the ferroelectricity (see, for example, Megaw, 1947, 1952; Kay & Vousden, 1949). The bond distances in the hexagonal structure, however, are appreciably closer to the ideal values. (Ba–O distances slightly greater than the ionic radius sum are not objectionable because of the ionic character of the bond*.)

The face sharing can therefore be explained simply by the more favourable bond distances it permits. This hexagonal structure is unusual, on this explanation, only because the necessary bond-length ratios rarely obtain.

The structures of TiO_2

TiO_2 has three structural modifications, namely, rutile, brookite and anatase. Their cohesive energies are similar, all three being found in nature. The first structure is assumed by a large number of compounds but the last two are unique.

The structures have similar bond distances, and differ only in the linking of the octahedra. Whereas in rutile there is only one shared edge (the other linkages being through corners), there are two shared edges in brookite and three in anatase. The distinctive feature of the Ti–O bonding in these compounds is thus the tendency to edge sharing.

This tendency can be explained by bond-angle considerations. A simple calculation shows that the change from corner to edge-sharing alters the Ti–O–Ti bond angle from 145–180° to about 95°. The latter value is the more stable if the Ti–O bond has an appreciable homopolar character, as the optimum value is then slightly less than the tetrahedral angle of 109° (Hall & Lennard Jones, 1951; Megaw, 1952). We conclude, therefore, that the cohesive energy increase resulting from this bond-angle change is sufficient to stabilize the brookite and anatase structures, in spite of the accompanying increase in the Ti–Ti repulsion (see below).

O–O *distances*

These are appreciably shorter for contacts across the shared faces and edges, being close to 2·5 Å as compared with the O^{-2} radius sum of 2·68 Å. A semipolar bond character will, however, reduce the electrostatic repulsion between the oxygens to about a quarter of that for O^{-2} ions. The *possibility* of shorter distances is therefore quite reasonable.

Shorter distances will be *preferred* in hexagonal $BaTiO_3$ because they equalize the distances to the central barium atom (Fig. 1).* Their occurrence in TiO_2 is probably due to the Ti–Ti repulsion, as suggested by Pauling (1945). This distorts the octahedra by increasing the Ti–Ti distance, and correspondingly reduces the O–O distance in the shared face or edge. Pauling assumes a Ti^{+4} ion, but the repulsion will still be important if the bond is semipolar (unlike the situation in hexagonal $BaTiO_3$) since the ratio of the Ti and O charges will be about the same for semipolar and ionic bonding, and there are no other ions to offset its effect.

References

Burbank, R. D. & Evans, H. T. (1948). *Acta Cryst.* **1**, 330.

Forsbergh, P. (1949). *Phys. Rev.* **76**, 1187.

Hall, G. G. & Lennard Jones, J. E. (1951). *Proc. Roy. Soc.* A, **205**, 30.

Kaenzig, W. (1951). *Helv. phys. Acta*, **24**, 175.

Kay, H. F. & Vousden, P. (1949). *Phil. Mag.* **40**, 1019.

Megaw, H. D. (1946). *Proc. Phys. Soc.* **58**, 153.

Megaw, H. D. (1947). *Proc. Roy. Soc.* A, **189**, 261.

Megaw, H. D. (1952). *Acta Cryst.* **5**, 739.

Pauling, L. (1945). *The Nature of the Chemical Bond.* Ithaca: Cornell University Press.

Wood, E. A. (1951). *Acta Cryst.* **4**, 353.

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* The short distance of 2·78 Å corresponds to only one-twelfth of the distances, and so does not seriously affect the argument. It may be remarked that the experimental error is greatest for this distance (0·06 Å), the average error being about 0·02 Å.

* Fig. 1 shows that the contraction increases the Ba–O distances in the horizontal plane. It decreases the distances in the near vertical directions, by the associated increase in the (vertical) Ti–Ti distances. (The Ti–O distances remain constant under the contraction.) If the octahedra were undistorted, these Ba–O distances would differ by up to ±10% from the ideal values.