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Displacement of Oxygen in $BaTiO_3$

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ATTEMPTS to explain the ferroelectric character of $BaTiO_3$ in terms of ionic displacements[1–7] have usually concentrated attention on the Ti ion. Megaw[1] has pointed out that if one assumes the Goldschmidt ionic radii, the Ba ions at the corners of the unit cell are slightly too large to fit into a close-packed perovskite structure; consequently the lattice is expanded and the Ti ions, at the body centers, are free to move through small distances. In such a model each oxygen ion, at a face center, is squeezed between four Ba ions, but is free to move at right angles to the plane of Ba ions, toward the Ti ions. Devonshire[5] has estimated the forces on the Ti and O ions following Born's treatment, with the result that the Ti ion is definitely bound to its symmetrical position, but the force restoring an oxygen ion to its symmetrical position is much smaller, and of uncertain sign. It therefore appears that any theory of $BaTiO_3$ based on this model must consider displacement of the oxygen ions as being at least as effective a cause of polarization as is Ti displacement.

A model in which ionic polarization arises chiefly from the oxygen ions is capable of explaining in a very simple way the observed three phase transitions, and predicts the correct magnitude of the transverse electrostriction in the tetragonal phase. Each unit cell contains three oxygen ions, O_x, O_y, O_z, which are free to move in the x-, y-, and z-directions respectively. Starting with cubic $BaTiO_3$ above 120°C, and cooling the crystal, the effect of the mismatch in ionic size as the lattice contracts is first to squeeze one of the oxygens, say O_z, out of its plane of Ba ions. This results in a spontaneous polarization and a deformation of the crystal, the symmetry becoming tetragonal. Contraction in the directions at right angles to the polarization occurs, since the Ba ions, which were pressing against the O_z ion, can now come together by a small amount proportional to the square of the O_z displacement z. A simple geometrical argument based on hard spheres in contact gives for the transverse contraction $-\Delta a/a = (z/a)^2$, where "a" is the lattice constant. The polarization P_{0z} due to displacement of O_z is $2eza^{-3}$, so that the transverse contraction becomes

$$-\Delta a/a = (a^4/4e^2)P_{0z}^2 = 3.8\times 10^{-12}P_{0z}^2.$$

Experimentally,[8] $-\Delta a/a$ is found to be accurately proportional to the square of the total polarization, with a coefficient of 1.2×10^{-12}. Thus, if P_{0z} represents 56 percent of the total polarization, the transverse electrostriction is given correctly.

The displacement of O_z relieves the instability of the lattice to a certain extent; as we further cool the crystal, a second group of oxygens, say the O_y, get squeezed out of their symmetrical positions, and the polarization now has equal components in the z and y directions, the crystal distorting to orthorhombic symmetry. On further cooling, the O_x ions are squeezed out of place, resulting in a net polarization directed toward the diagonal of the original cube, and the symmetry becomes rhombohedral. All of these changes of phase and polarization direction are observed experimentally.[8]

Certain obvious refinements of this model would change the above numerical estimates, but it is clear that we get a qualitative understanding of two of the most puzzling features of $BaTiO_3$, namely the existence of three phase transitions with shifts of the direction of spontaneous polarization, and the very large electromechanical coupling.

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