

The ZSM-39 Zeolite Dodecasil-3C: A New Ferroic Material

David J. Finnie

Final Seminar

January 29, 1997

Ferroic materials possess two or more orientation states or domains that can be switched from one to another through application of a suitable external force.¹ Three types of ferroic materials are known: ferroelectrics, ferromagnets, and ferroelastics. Ferroelectric materials possess orientation states of spontaneous electrical polarization; switching of these states is accomplished by a suitably oriented electric field. Similarly, spontaneous magnetization in ferromagnetic materials can be switched by a magnetic field. In ferroelastic materials, the orientation states are defined by spontaneous strain and switching is accomplished by mechanical stress. Ferroic behavior is characterized by a hysteresis loop in a plot of ferroic property versus external force.

The key to understanding and hence engineering ferroic materials is the relationship between macroscopic ferroic properties and microscopic structure in terms of the crystal structure and domain boundaries. The central importance of this relationship is illustrated by the prototypical ceramic ferroic material, barium titanate, which is both ferroelectric^{2,3} and ferroelastic.⁴ The orientation states in BaTiO_3 arise during the phase transition from the high temperature cubic phase to the room temperature tetragonal phase. According to X-ray diffraction studies, the average position of each titanium atom lies at the center of an octahedron of oxygen atoms in the high temperature cubic phase. In the ambient temperature tetragonal phase, the average position of each titanium atom is displaced away from the center of the octahedron toward one oxygen, forming a short multiple bond with that oxygen and a much longer, weaker bond with the *trans* oxygen. The phase transition converts the high temperature cubic unit cell into an ambient temperature tetragonal unit cell having an elongated unique *c* axis and contracted *a* axes. In extremely small crystals, the entire crystal elongates in this manner.⁴ Normally, however, the shape change generates stresses which can be relieved by domain formation. Crystal defects cause different regions within a crystal to elongate in different directions, generating domains. Adjacent domains join most favorably at a plane of lowest strain,⁵ resulting in the formation of lamellar domains. These domain boundaries are designated 90° domains because the *c* axes on opposite sides of the domain boundary are nearly perpendicular.³ Ferroelastic domain switching is achieved by applying uniaxial stress to a BaTiO_3 crystal along the elongated *c* axis, producing an *a-c* axis switch.^{4,6}

Zeolites which contain organic guest molecules are attractive candidates for ferroic materials because of the possibility of tuning the ferroic properties by systematically changing the guest molecule. The all-silica ZSM-39 zeolite family, dodecasil-3C (D3C), exemplifies this type of tunable zeolite. By varying the size and composition of the organic molecule trapped in the D3C SiO_2 framework, the temperature of the D3C high temperature phase transition can be tuned over a 120 °C range from as low as 59 °C for cyclobutylamine-D3C to as high as 180 °C for piperidine-D3C.⁷ The availability of large crystals of pyridine dodecasil-3C (Py-D3C) has made possible investigation of the ferroic properties.

Optical photomicrographs of a polished thin section cut parallel to {100} obtained using cross-polarized light (Figure 1) show twin domains similar to those observed in BaTiO_3 , raising the possibility that the domains in Py-D3C might also be ferroic. These twin domains are classical transformation twins⁸ formed when the high temperature cubic phase transforms to the ambient temperature orthorhombic phase. The effect of this phase transformation on the unit cell of Py-D3C is conversion of the high temperature cubic unit cell into an ambient temperature orthorhombic unit cell having an elongated unique *c* axis and contracted *a* and *b* axes. The domains are oriented in six planes parallel to the cubic {110}. Similar to BaTiO_3 , the domain boundaries are 90° domain boundaries with the *c* axes on opposite sides of the domain boundary nearly perpendicular.

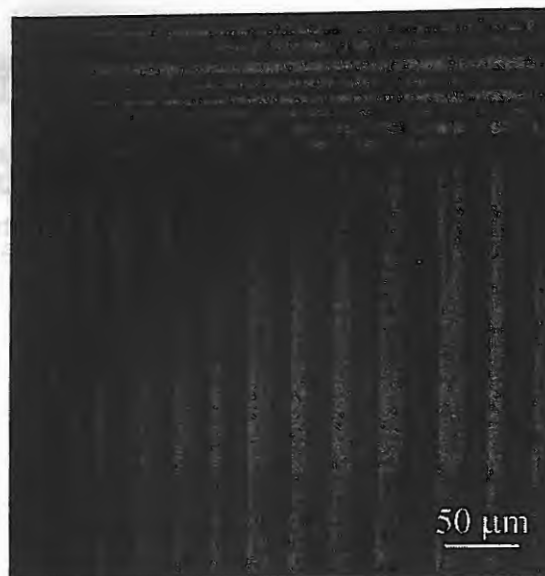


Figure 1. Optical photomicrograph of a thin section cut parallel to $\{100\}$.

The ferroelastic properties of Py-D3C were investigated by subjecting thin samples to uniaxial compressive force and observing changes in the orientations of the domain boundaries using an optical microscope with crossed polarizers. Uniaxial compression of a sample cut parallel to $\{100\}$ resulted in only elastic behavior, but compression of a sample cut parallel to $\{111\}$ showed ferroelastic behavior (Figure 2). The orientation of the domains in the sample cut parallel to $\{111\}$ could be switched by an applied "horizontal" force from the "vertical" domain boundaries shown in Figure 2a to the "diagonal" domain boundaries shown in Figure 2b. Releasing the stress left the domain boundaries switched to this "diagonal" orientation. "Vertical" stress switched the domain boundaries in Figure 2b to the "vertical" orientation in Figure 2c. Figures 2d-f show a crystallographic interpretation of the switching.

A further understanding of the relationship between ferroic properties and crystal structure was impossible until the crystal structure was determined. Crystal structure determination proved to be impossible using standard X-ray diffractometers because the twinning produced diffraction patterns with overlapped reflections. The use of a CCD area detector for X-ray diffraction allowed the reflections to be separated into sets of reflections arising from individual twins. Thus, the crystal structure of an individual twin domain could be

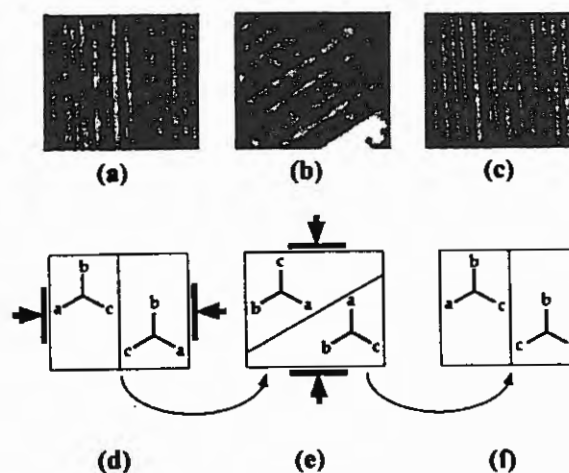


Figure 2. Ferroelastic switching in a sample cut parallel to $\{111\}$.

obtained. The crystal structure is most easily described as a pseudo-tetragonal distortion of an idealized cubic structure. The structure consists of 28-vertex $[5^{12}6^4]$ cages arranged at the point of a diamond lattice with an additional Si(3) silicon atom at the center of each adamantane cage in the diamond lattice. As the symmetry is lowered from idealized cubic to real pseudo-tetragonal, each cage is rotated and the connected Si(3) are counter-rotated (Figure 3). The greatest deviation from the idealized cubic structure is at the oxygen atoms connected to the Si(3) atoms. The elongation of the crystallographic c axis is due to bending of the Si(2)-O-Si(3) bond.

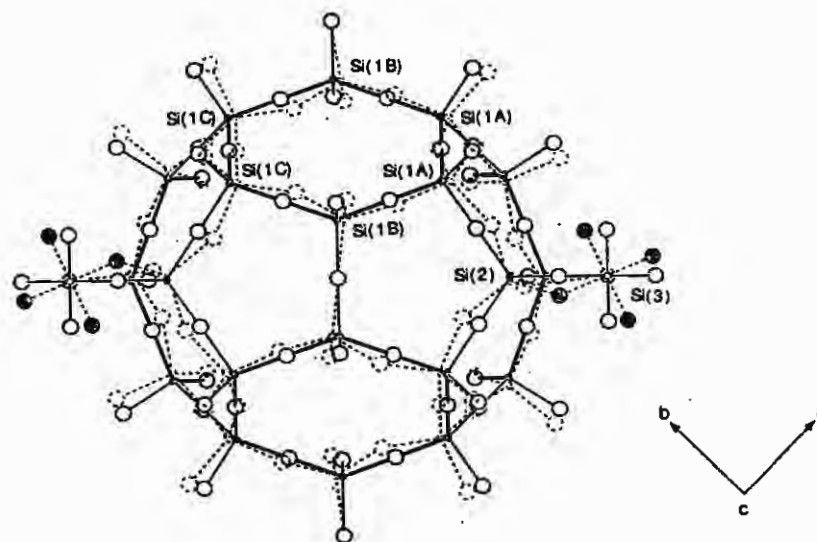


Figure 3. An overlay of the real pseudo-tetragonal structure (dashed lines) on top of the idealized cubic structure (solid lines). The oxygens connected to Si(3) are shaded.

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