The Art of Ceramics
The Blend of Art and Science in Technology
N. Claussen (Editor)

SYMMETRY AND ANTISYMMETRY IN ELECTROCERAMICS

Robert NEWNHAM and Eric CROSS
The Pennsylvania State University, University Park, PA, USA

Many types of symmetry are utilized in ceramic art and in ceramic science. In addition to the common mirror, rotation, inversion and translation symmetry elements observed in crystals and textured ceramics, artists and engineers often make use of the antisymmetry elements involved in color groups. We illustrate the application of color symmetry in controlling the vibration modes in ferroelectric and ferromagnetic ceramics prepared as spheres, hemispheres, and rings conforming to black-and-white Curie groups.

SYMMETRY IN ART AND SCIENCE

While visiting the city of Kütahya, one of the great centers for traditional ceramic tiles and porcelain products, we had the opportunity to view contemporary Turkish artwork. Islamic art has long been famous for its geometric patterns, but we were especially fascinated with the porcelains made by Kervan Chini, who incorporates many interesting symmetries into his pottery. The colorful dish shown in Fig. 1 contains a number of the symmetries and broken symmetries observed in electroceramic materials and devices: polar symmetry, chiral symmetry, symmetry of scale, quasisymmetry, the pseudosymmetry of incommensurate phases, and the antisymmetric elements of color symmetry groups.

Piezoelectric ceramics, pyroelectric glass ceramics, and certain functionally-graded ceramics have polar symmetry like that of a concave-shaped disk (Fig. 2a). Chiral symmetry is present in the porcelain dish as well (Fig. 2b). The leaf pattern of the flowers and the sleeping sheep near the edge are both arranged in a counterclockwise fashion leading to handedness. Chiral phenomena such as optical activity, acoustic activity, and the Faraday Effect are well known in crystal physics. Symmetry of scale is important in all classes of materials. The pattern in Fig. 1 violates the self-similarity principle introduced by Benoit Mandelbrot to describe fractal geometry. Beginning at the center, the porcelain dish shows 5-fold then 9-fold, 10-fold, and 19-fold rotational symmetry. Five-fold symmetry is characteristic of quasicrystals and the circle possesses a ∞-fold axis, one of Curie group symmetries found in textured polycrystalline ceramics. The change in symmetry with scale is illustrated in Fig. 2c.

The symmetry of scale is an important one in many electronic systems as component sizes become smaller and smaller. Current trends in multilayer capacitors are shown in Fig. 3 and 4. The lateral dimensions in MLC chips are now about 1 mm, approaching the limit for many of the pick-and-place machines used in assembling circuits. Layer thicknesses and grain sizes are also a concern. Ceramists are now testing $BaTiO_3$ MLCs with layers of 1 μm thickness which is pressing the limits of tape-casting technology. Particle sizes are in the 0.1 μm range which raises some fundamental questions regarding size effects in ferroelectrics. In large grain size, say 1 μm and larger, each grain contains many domains. The number of domains and the type of domain walls change as grain size drops below a micron. Eventually each grain becomes a single domain with profound changes in dielectric constant and switching behavior. In the nm range the ferroelectric phase transition becomes diffuse and the symmetry of $BaTiO_3$ appears pseudocubic. Size effects in primary ferroics are illustrated schematically in Fig. 5. Dielectric constants drop substantially for grain sizes less than 0.1 μm.

Returning to the porcelain plate in Fig. 1, the outer portions of plate provide an excellent illustration of pseudosymmetry or "almost" symmetry. In the central leaf pattern there are 10 leaves and between neighboring leaves are 10 flowers. Near the outside rim of the plate are red hearts which, at first glance, appear to be in register with the 10 leaves and with the 10 flowers, but such is not in the case. The artist has made a subtle change in symmetry with only 19 hearts instead of 20 (Fig. 2d). Many ferroelectric and ferrimagnetic oxides possess incommensurate structures in which the local polarization or magnetization vectors are out of register with the lattice periodicity (Fig. 6). These so-called incommensurate phases often exhibit unusual physical properties because of their abnormal symmetry.

FERROIC CRYSTALS AND ANTISYMMETRY ELEMENTS

The symmetry elements discussed thus far are purely spatial transformations such as mirror planes, rotation axes, and inversion centers. Spatial symmetry elements are all that are required for the usual crystallographic and limiting point groups, but additional symmetries occur in ferroic electroceramics. These additional symmetries can be described by color symmetry. The ceramic dish from Turkey possesses decagonal color symmetry in which the flower rotates by 36° and changes color (Fig. 2e). In this paper we discuss color groups and the antisymmetry elements found in ferroic ceramics with complex domain patterns. The 10′ antisymmetry element in Fig. 2e belongs to this type of color group.

More than a century ago, the basic relationships between symmetry and physical properties were established by Neumann and the brothers Curie, and systematized in Woldemar Voigt's monumental "Lehrbuch der Kristallphysik." (Voigt,1928) Using Neumann's Principle, the symmetry restrictions for piezoelectricity, magnetostriction, and other linear and nonlinear tensor properties have been enumerated, and have led to the development of many types of sensors, actuators, and transducers. For single crystals, the properties are governed by the 32 crystallographic point groups, and for textured polycrystalline materials, we use the seven limiting groups first described by Pierre Curie. In 1974 we extended these symmetry arguments to ferroic crystals, laying out the symmetry changes involved in the phase transformations leading to the hysteretic phenomena created by domain wall motion (Newnham, 1974). There are, for example, 15 symmetry changes consistent with pure ferroelastoelectric behavior in which adjacent domains differ only in the orientation of third rank polar tensor properties. A "pure" ferroelastoelectric does not exhibit any other primary or secondary ferroic behavior (Newnham and Cross, 1974).

In crystals with long range magnetic order, the addition of a time reversal operator leads to the generation of the 90 magnetic point groups used to describe ferromagnetic, ferrimagnetic, and antiferromagnetic substances (Birss, 1964). Introduction of the antisymmetric spin reversal operator makes it possible to apply Neumann's Principle to magnetic crystals and classify the symmetry restrictions for magnetic properties such as magnetoelectricity, pyromagnetism and piezomagnetism. All three of these cross-coupled phenomena are axial tensor properties and since spin reversal corresponds to the reversal of an axial vector, all three properties are strongly influenced by the antisymmetry operator.

In this paper we introduce antisymmetry elements for other types of ferroic materials with movable domain walls. Ferroelectricity, ferroelasticity, and the six types of secondary ferroics are also controlled by tensorial antisymmetry operators (Table 1). For a ferroelectric, polarization - a polar vector - is the key operator, since ferroelectricity is defined by polarization reorientation between symmetry related states. For a ferroelastic, the key operator is strain - a second rank polar tensor - since ferroelasticity is defined by strain reorientation between symmetry related states. For a ferrobielastic secondary ferroic, the key operator is a fourth rank tensor, etc.

The procedure will adopt for introducing these antisymmetry elements is as follows. Each operator is combined with the spatial symmetry elements of the 32 crystallographic point groups or to the seven Curie groups to generate a family of antisymmetric groups analogous to the 90 magnetic point groups. Having determined the relevant symmetries, Neumann's Principle is then applied to determine the polar and axial property matrices, enabling one to predict the useful symmetries that will optimize the material for a given

FIGURE 1 - A ceramic dish made by Kervan Chini which illustrates many types of unusual symmetry.

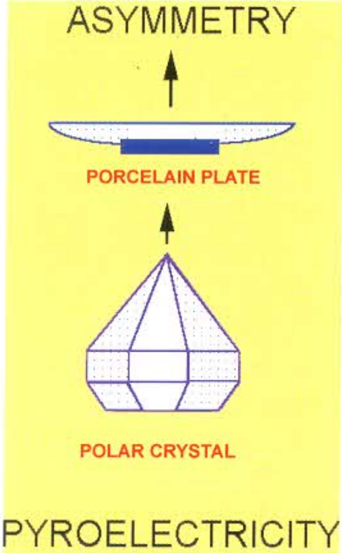

FIGURE 2a - Polarity.

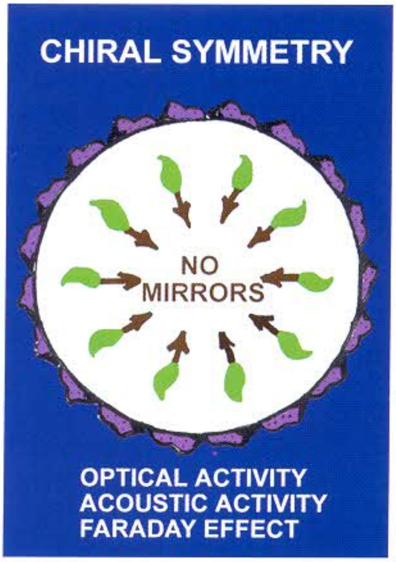

FIGURE 2b - Handedness.

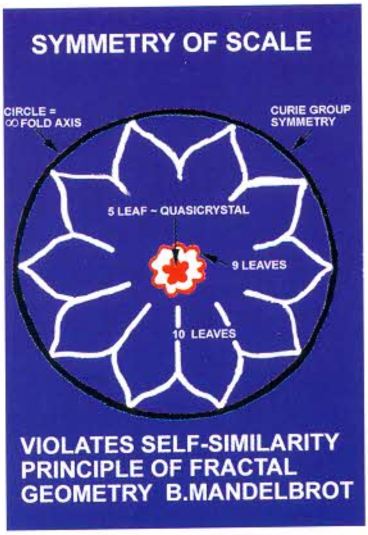

FIGURE 2c - Size effects.

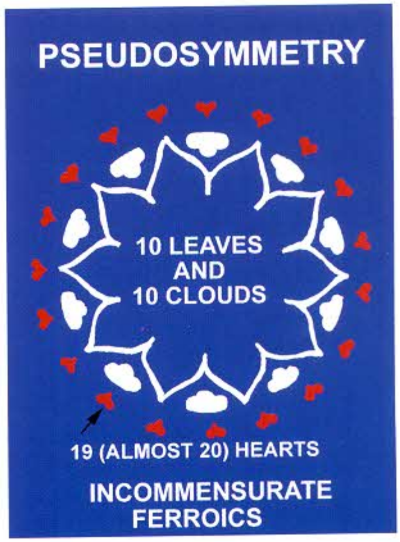

FIGURE 2d - Aperiodicity.

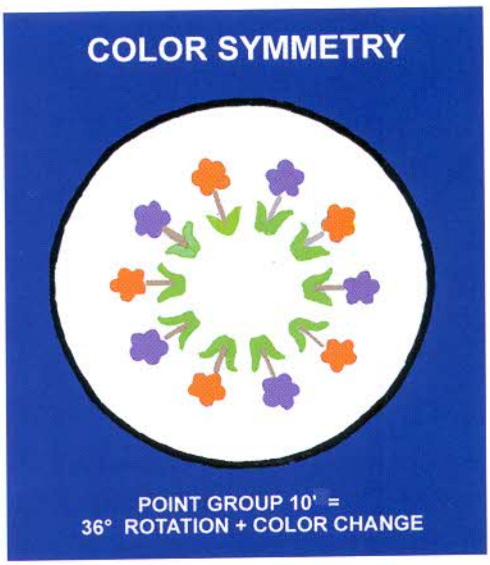

FIGURE 2e - Color patterns.

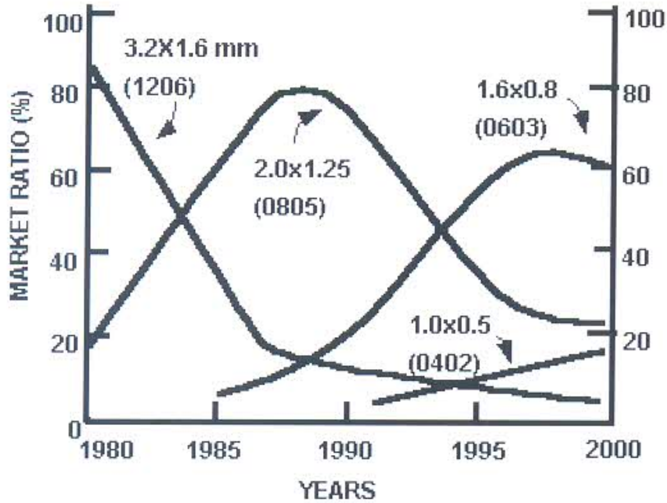

FIGURE 3 - The sizes of ceramic capacitors have decreased steadily with time while the market continues to grow exponentially following Moore's Law.

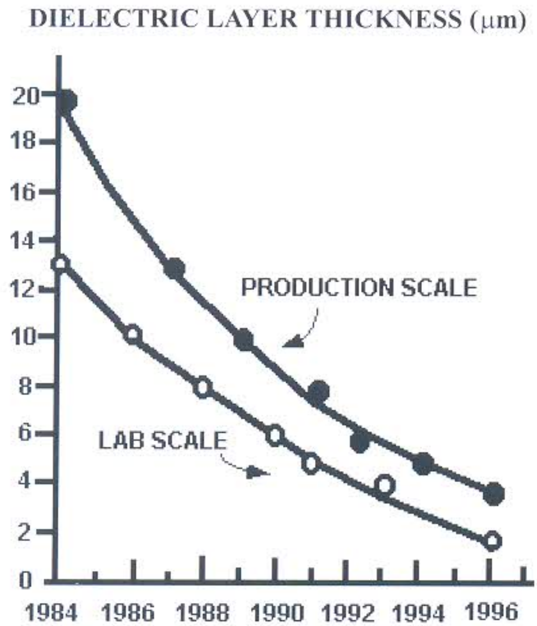

FIGURE 4 - Layer thicknesses in multilayer capacitors are now nearing one micron with grain sizes around 0.2 μm.

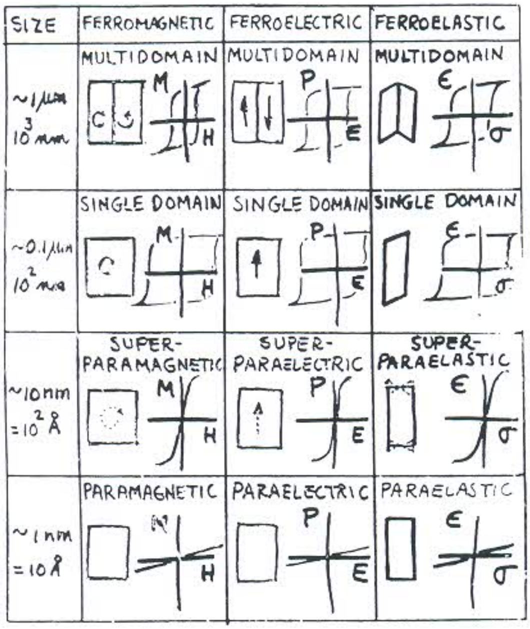

FIGURE 5 - Profound changes in properties take place in ferroic ceramics when the grain sizes drop below the micron range.

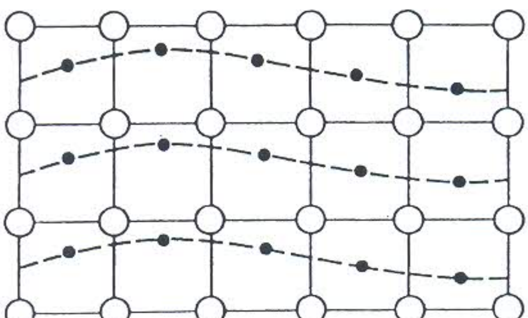

FIGURE 6 - Formation of incommensurate phase as a result of the "freezing" of a displacement wave with a length incommensurate with the unit-cell parameter.