The strain limits on switching

The ability to change their dimensions in an applied electric field makes ferroelectric materials important for piezoelectric applications. The crystal symmetry and related strains of these materials are a strong influence on their switching behaviour.

WENWU CAO
Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania, 16802, USA.
e-mail: cao@math.psu.edu

One of the most interesting and useful features of ferroelectric materials is the strong coupling of polarization with elastic strain, which makes these materials the best piezoelectrics. Ferroelectric ceramics such as Pb(Zr,Ti)O₃ (PZT) are widely used for sensors and actuators as they can efficiently convert mechanical energy into electrical energy and vice versa. In order to use ferroelectric materials, they must be ‘poled’ by subjecting them to a large electric field, which causes some of the domains to switch so that the electric dipoles will be aligned. There are two distinctively different groups of domains. Domains with antiparallel polarization are labelled 180° domains, whereas others are referred to as non-180° domains. The formation of the domains is determined by the crystal symmetry of the material. The 180° domains have the same strain, and hence are easy to switch. However, the coupling of the polarization to the elastic strain limits the achievable remnant polarization (polarization at zero field) due to the more difficult switching of non-180° domains. On page 776 of this issue, Li and colleagues present a neat theoretical description of the relationship between crystallographic symmetry and the ability of a ferroelectric ceramic to switch. Their model is based on the compatibility of the elastic strain across the grain boundaries and explains why non-180° domains can switch in some ceramics but not in others.

The first type of strain limitation on switching is provided by the transformation strain. If this strain anisotropy is high, the crystal cannot achieve a single domain state through reorientation of non-180° domains because the reorientation may crack the crystal. This is clearly the case for PbTiO₃, although this material has exactly the same tetragonal crystal structure as BaTiO₃ both above and below the Curie point, it is not possible to totally align the polarization in PbTiO₃ even in its single-crystal form, whereas perfect dipole alignment can be easily achieved in BaTiO₃ single crystals. The reason is that at room temperature the unit cell $c/a$ ratio of BaTiO₃ is only 1.01 whereas the $c/a$ ratio of PbTiO₃ is 1.06 (refs 2,3). Figure 1 illustrates the global shape change and the local strain generated through a 90° domain reorientation.

The second type of strain restriction on switching occurs in ceramics, and is caused by intergranular interactions. Each ceramic material consists of many grains (small single crystals) that each contain a number of domains oriented along the crystallographically allowed directions. As the domains in one grain attempt to switch, they are constrained by the differently oriented neighbouring grains. As discussed above, non-180° domain reorientations will change the shape of the grain, and may be allowed only if there are enough variants in the ferroelectric phase, and enough domains in each grain, to allow for a cooperative adjustment so that no strain mismatch is produced at the grain boundaries. This requires a high symmetry of the paraelectric phase, whereas the symmetry of the ferroelectric phase needs to be sufficiently low to produce enough allowable domain states at the paraelectric to ferroelectric phase transition. Li and colleagues show that even if the compatibility is maintained on average, there should be no non-180° domain reorientations in tetragonal and rhombohedral ceramics such as BaTiO₃ and PZT (except at the morphotrophic phase boundary composition, for which the tetragonal and rhombohedral phases co-exist).

There have been many previous theoretical and experimental studies on the domain reorientation problem in ceramic BaTiO₃. On the basis of thermal expansion measurements, it has been estimated¹ that 90° domain reorientation in ceramic BaTiO₃ should be less than 15%. Other work⁴ concluded from dimensional changes before and after poling that only about 12% of 90° domain switching occurred in
ceramic BaTiO$_3$. Neutron diffraction measurements also indicate that there are no noticeable 90° reorientations during poling in tetragonal phase PZT. This means that one cannot use ceramics in the same way as the single-crystal form to make devices based on their large reorientation strain.

The third type of strain restriction on switching occurs in ferroelectric thin films. Because a thin film is always attached to a substrate and the substrate does not show dimensional changes in an applied electric field, strain accommodation at the interface cannot occur. This imposed strain from the substrate interface further limits the poling ability of the ferroelectric materials. The general features of the hysteresis loops are illustrated in Fig. 2. Strain limitations cause substantial back switching in ceramics and thin films, as is shown by the large difference between high-field and remnant polarization. Such strain limitations become less stringent if there are more switchable domain states available so that global accommodation can allow some non-180° domain switching. At the morphotropic-phase-boundary composition of PZT, the tetragonal and rhombohedral phases have the same energy so there will be a total of 14 domain states available. This explains why significant non-180° domain switching has been found in these PZT ceramics from direct strain measurements as well as from neutron diffraction experiments.

Strain limitation on attainable polarization in ceramic ferroelectric thin films has been a technical hurdle for their application in memory devices. To overcome these limitations, as stated by Li et al., we must use systems that either contain a large number of domain states or make oriented films (preferably epitaxial films) that can break the uniform orientational distribution of domains to provide a larger polarization along a desired direction.

**REFERENCES**


**NEWS & VIEWS**

Call yourself hard?

Those girls can flirt and other queer things can do. It's not, these days, a very acceptable mnemonic for remembering Friedrich Mohs' ordering of minerals according to hardness (talc, gypsum, calcite, fluorite, apatite, orthoclase, quartz, topaz, corundum and diamond). But there's no doubt that diamond still ranks highest — 10 on Mohs' ten-point scale.

Knocking diamond off its pedestal has become something of an obsession. The usual justification for this quest is that superhard materials are industrially important for cutting and abrasion, and that even diamond is not perfect in this regard — it can dissolve iron and so is of little use for shaping one of the most widespread industrial materials, steel.

That shortcoming is accommodated by cubic boron nitride — General Electric's Borazon — which ranks second to diamond in hardness and is mass-produced at high pressure and temperature. A material that rivals these two in hardness while being cheaper to make would be a boon to industry and technology, but it is hard to sustain the notion that many of the candidate superhard materials explored so far would indeed be manufacturable at less expense than is required to squeeze graphite.

One has to suspect that the real driver behind attempts to better diamond is the desire to come top: it is the same motivation that impels searches for the strongest, lightest or smallest materials. Most materials engineers acknowledge that, save for a few niche applications, the most useful materials tend to be not those that excel in one particular capacity but those that find the best compromise of several, often competing, properties.

"Superhard" is in any case open to interpretation (V. Brazhkin et al. Nature Mater. 3, 576; 2004): high Young's or bulk modulus (resistance to elastic deformation) has a different mechanistic origin from high hardness (resistance to plastic deformation). But because the two are often correlated, the search for superhardness tends to embrace materials with potentially high moduli. That's why, in addition to exploring materials made from light elements that form short, strong covalent bonds — [C, N]$_4$ was for several years a promising candidate, and B$_4$O has comparable hardness to cubic boron nitride — there is also interest in materials with a high density of valence electrons, which makes them resist elastic compression (R. B. Kaner et al. Science 308, 1268; 2005).

Now, however, it seems that diamond has been superseded, albeit by simply a variant of its standard crystalline form. Natalia Dubrovinskaia at the University of Bayreuth in Germany and her co-workers report a material they call aggregated diamond nanorods, with a bulk modulus of 491 GPa, compared with diamond's 442 GPa. A standard measurement of microhardness using a diamond tip did not work because the diamond caused no indentation (N. Dubrovinskaia et al. Appl. Phys. Lett. 87, 083106; 2005). The preparation conditions are more extreme than those needed to make synthetic diamond, however. So this, like most record-breakers, doesn't come without cost.

Philip Ball