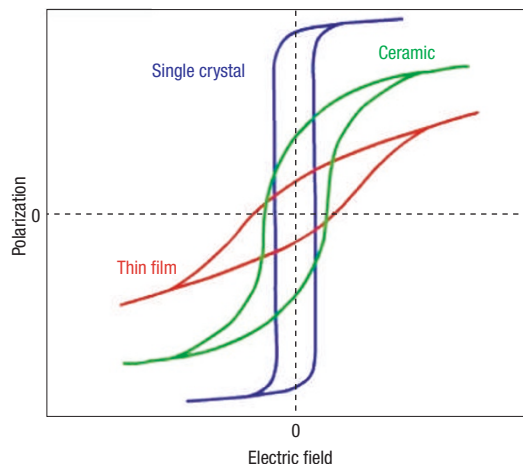**Figure 2** Hysteresis loops for ferroelectric single crystals. Polycrystalline ceramics and thin films show that the maximum achievable polarization is largest for single crystals and smallest for thin films.

ceramic $BaTiO_3$. Neutron diffraction measurements also indicate that there are no noticeable 90° reorientations during poling in tetragonal phase PZT[1]. 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[1,4].

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

1. Li, J. Y., Rogan, R. C., Üstündag, E. & Bhattacharya, K. *Nature Mater.* **4**, 776–781 (2005).
2. Megaw, H. D. *Proc. Phys. Soc.* **58**, 133–152 (1948).
3. Jeffe, B., Cook, W. R. & Jaffe, H. in *Piezoelectric Ceramics* (Academic, London and New York, 1971).
4. Berlincourt, D. & Krueger, H. H. A. *J. Appl. Phys.* **30**, 1804–1810 (1959).
5. Subbarao, E. C., McQuarrie, M. C. & Buessem, W. R. *J. Appl. Phys.* **28**, 1194–1200 (1957).

MATERIAL WITNESS
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 smartest 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 — β-C_3N_4 was for several years a promising candidate, and B_6O 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