

RELAXOR-FERROELECTRICS

High piezoelectricity via enhanced disorder

Ultrahigh piezoelectricity in relaxor-ferroelectric ceramics is engineered by chemical and structural heterogeneities at the nanoscale.

Barbara Malic and Tadej Rojac

Materials that do not possess centrosymmetry exhibit piezoelectricity, meaning that they can be electrically polarized by a mechanical stress, or alternatively be strained by an electric field. Among existing piezoelectric materials, perovskite ABO_3 ferroelectrics have the highest piezoelectric response. For more than half a century, the most commercially widespread piezoelectric ceramics — that is, $Pb(Zr,Ti)O_3$ (PZT) — have been extensively used in sensors, transducers and actuators. What makes this class of polycrystalline materials unique is not only their high piezoelectricity, but their versatility for applications and ease of processing leading to their use in a huge range of products, from scanning probe microscopes to simple electric toothbrushes. Typically, though, they possess piezoelectric coefficients inferior to those in more expensive domain-engineered relaxor-ferroelectric single crystals¹. Now, writing in *Nature Materials*, Fei Li and colleagues² report the success of a strategy to induce high piezoelectric coefficients in polycrystalline relaxor-ferroelectrics by enhancing disorder at the nanoscale.

Exemplified by $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), relaxors are a class of related materials that in many aspects are different from ‘normal’ ferroelectrics. The essential structural characteristic of relaxors is compositional lattice-site disorder, which is the basis for their unique feature — that is, the existence of nanoscale polar regions³ (blue circles in Fig. 1), as opposed to ferroelectric domains in normal ferroelectrics (yellow region in Fig. 1). In a relaxor-ferroelectric solid solution, such as PMN- $PbTiO_3$ (PT), both ferroelectric domains and polar nanoregions can in principle coexist (Fig. 1).

The wide range of properties exhibited by lead-based perovskites has traditionally been achieved using compositional design. This leads to the so-called morphotropic phase boundary, a compositional point or region in the solid-solution series where typically two or more ferroelectric phases with different symmetries come together⁴. Phenomenologically speaking, the different

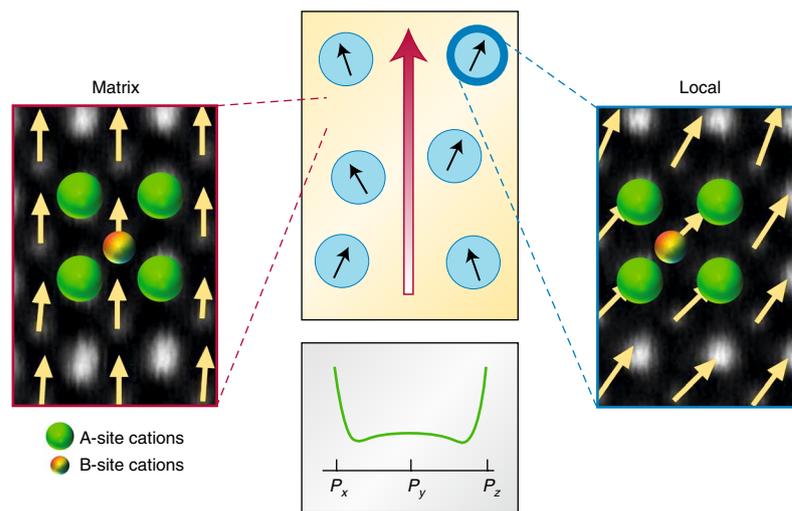


Fig. 1 | Schematic of the polar structure and atomic-resolution images of the Sm-doped PMN-PT relaxor-ferroelectric.

The sketch shows a tetragonal ferroelectric domain (yellow) spontaneously polarized in the (001) pseudo-cubic direction (red arrow), embedding local polar nanoregions (blue circles). This hypothetical picture is consistent with the results that the authors obtained when using atomic-resolution dark-field imaging. The dark-field images adjacent to the schematics show the tetragonal domain (matrix) and a polar nanoregion (local) with different crystallographic symmetries (see arrows). Sm doping is expected to further enhance the local disorder otherwise inherent in PMN-PT, leading to a flatter thermodynamic energy landscape for polarization rotation under external fields. Such a landscape is illustrated for arbitrary polarization directions (P_i) below the schematic. Adapted from ref. ², Macmillan Publishers Ltd.

phases link via a flattened thermodynamic energy landscape (Fig. 1), allowing the spontaneous polarization to be easily rotated under external electric or stress fields⁵. A peak in the dielectric and piezoelectric properties around the morphotropic composition is the net result in both PZT⁴ and PMN-PT⁶. In addition, donor doping — that is, exchange of A and/or B-site cations with a higher valence state (for example, Nb^{5+} exchanging for Ti^{4+} and Zr^{4+} in PZT) — is often used in combination with morphotropic phase boundaries to increase piezoelectric properties. Donor doping in PZT is believed to create disorder due to a random defect distribution. The resulting energy landscape for ferroelectric and ferroelastic domain walls becomes flatter, making them mobile⁷.

Hypothetically, does the inherent disorder in PMN-PT, and the associated polar nanoregions, have any relationship with the piezoelectric response of this material? In a previous paper by Li and colleagues⁸, it was shown that in domain-engineered PMN-PT single crystals this might be the case. They suggested that polar nanoregions, effectively aligned in the ferroelectric matrix, might couple elastically and electrically to spontaneous polarization in the domains, facilitating polarization rotation. The interaction of polar nanoregions with polarization in the domains might thus in part explain the ultrahigh piezoelectricity in domain-engineered relaxor-ferroelectric crystals (piezoelectric coefficient $\sim 2,500$ pC N⁻¹ in $Pb(Zn_{1/3}Nb_{2/3})O_3$ -PT)¹.

Moreover, is it possible to further enhance disorder in PMN-PT to really boost the properties? Here, Li et al. show that this can be achieved by doping PMN-PT ceramics — that is, introducing chemical and structural heterogeneity on the local scale. By combining phase-field simulations with experiments, they show that doping with rare earths apparently enhances disorder in PMN-PT, further flattening the energy landscape for polarization rotation. The largest effect was observed with a samarium (Sm) donor dopant, resulting in spectacular piezoelectric coefficients of $\sim 1,500 \text{ pC N}^{-1}$, the highest ever reported in polycrystalline ceramics. The existence of polar nanoregions inside tetragonal ferroelectric domains with a different symmetry was confirmed in Sm-doped PMN-PT by atomic resolution electron microscopy (Fig. 1).

Common to all sciences is that discoveries always raise additional questions. What is so special about Sm that it gives rise to the largest effect among the many dopants tested? What is the defect structure of the material? How do the donor-dopant sites and the compensating defects (probably lead vacancies) distribute locally and how does this affect polarity at the nanoscale? To what extent does processing come into play when

considering the dopant distribution in the ceramic matrix? Some of these questions may be answered by first-principles atomistic computations combined with advanced experimental approaches — for example, atomic-resolution microscopy with in situ field biasing — which could provide a mechanistic background to further develop and apply this discovery.

The modelling studies performed by the authors suggest the possibility of manipulating interfaces, and thus interfacial energies, between normal ferroelectric phases to enhance piezoelectric response via nanoscale engineering. It would be interesting to see if superlattices could be one such case, and we could easily imagine and engineer a variety of nanocomposites with different levels of connectivity.

Although the maximum temperature up to which these materials can be utilized remains low (Curie temperature of $\sim 90 \text{ }^\circ\text{C}$), the authors show remarkable stability of piezoelectric response for temperatures almost up to this value. It is possible to imagine relaxor-ferroelectric ceramics with extremely high piezoelectric coefficients of $\sim 1,500 \text{ pC N}^{-1}$ replacing single crystals in piezoelectric devices, with the advantage of exhibiting comparable performance, but at a lower cost and with

up-scalable processing, yielding a variety of sizes and shapes. When completely understood and verified, it would be interesting to determine whether nanoscale-engineered enhancement of piezoelectric response could be transferred to other groups of ferroelectrics. Implementing this approach in lead-free piezoelectric ceramics, which in many applications are currently outperformed by lead-based ferroelectrics, could certainly aid the sustainability of these devices. □

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