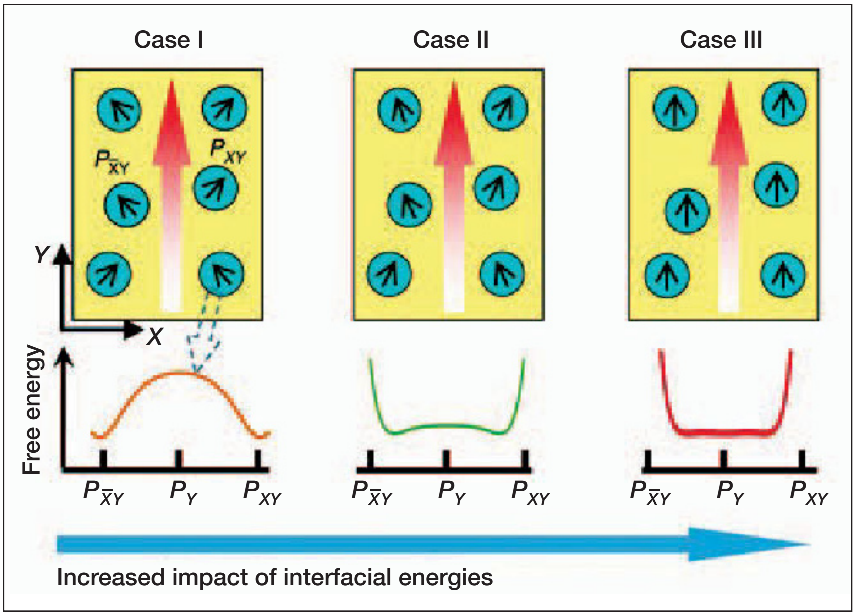
Energy profile flattened to enhance piezoelectricity in ceramics

Ceramic materials that generate charge under mechanical stress and vice versa are of great importance for various applications, such as underwater acoustics and medical ultrasonics used for imaging, diagnostics, and therapy. This effect, piezoelectricity, has been studied for over a century. However, improvements in piezoelectric properties of ceramics have slowed in recent years.

A new approach developed by a collaborative team of researchers from the United States, China, and Australia has revealed ceramics with record-high piezoelectric performance. Fei Li, a research associate at The Pennsylvania State University and lead author of the published study, describes their design strategy as "introducing local structural heterogeneity to add interfacial energies, such as electrostatic and elastic energy associated with the interfaces," to enhance piezoelectric properties. In their publication in a recent issue of *Nature Materials* (doi:10.1038/s41563-018-0034-4), the research team reports the highest-known piezoelectric coefficients, which quantify the polarization generated under stress, in polycrystalline ceramics (1510 pC N^{-1}), a threefold improvement over commercial ceramic piezoelectrics.

Barbara Malič, head of the Electronic Ceramics Department at the Jožef Stefan Institute in Slovenia and an expert in piezoelectric ceramics, says that these piezoelectric coefficients are "comparable to the values obtained in domain engineered single crystals … [But] in contrast to [single] crystals, ceramics are processed in a broad range of sizes and shapes, and they could be a cost-effective replacement for single crystals in piezoelectric devices with similar performance."

To find this ultrahigh piezoelectricity, the researchers began with phase-field simulations to calculate the polarization properties of piezoelectric materials with heterogeneous polar regions (see Figure). The polar regions add interfacial energy due to competition between the local regions maintaining their preferred polarization or aligning with that of the bulk. The additional interfacial energy flattens the thermodynamic free-energy profile of the ceramic, meaning it lowers the energetic barrier to polarization rotation. Because piezoelectric coefficients are related to the curvature of the free energy, a flatter profile means enhanced piezoelectric properties.



Top row: Schematic representation of bulk piezoelectric material (yellow) with local polar regions (cyan). The impact of the interfacial energy increases from case I to case III, which leads to alignment of polar regions with bulk polarization. Bottom row: The systems with a larger impact of the interfacial energy (cases II and III) have a flatter free-energy profile with respect to polarization, thus enhancing the piezoelectric properties. Credit: *Nature Materials*.

To experimentally create this structural heterogeneity on the nanoscale, the researchers screened the effects of various rare-earth dopants, ultimately choosing samarium (Sm), which had the largest influence. By adding small amounts of Sm to a solid solution of lead magnesium niobate and lead titanate (PMN-PT), the researchers were able to engineer local structural heterogeneity into the ceramic and further enhance its piezoelectric properties. It is "intriguing that doping with one rare earth, samarium, results in an extremely high piezoelectric coefficient … Why samarium [is superior to the other rare earths tested] still remains to be explained," Malič says.

Though this study focused only on the PMN-PT family of ceramics, the researchers showed that their approach of introducing additional interfacial energy terms to enhance piezoelectric properties can be applied to other materials systems, such as lead zirconium titanate (PZT) superlattices. But the generalization of the research team's approach does not end there. Introducing local heterogeneity may also enhance ferroic properties (such as ferromagnetism and ferroelasticity) that are also defined by the curvature of the free-energy landscape.

Abby Goldman