PIEZOELECTRICS

Giant piezoelectricity of Sm-doped Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ single crystals

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High-performance piezoelectrics benefit transducers and sensors in a variety of electromechanical applications. The materials with the highest piezoelectric charge coefficients (d_{33}) are relaxor-PbTiO₃ crystals, which were discovered two decades ago. We successfully grew Sm-doped Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (Sm-PMN-PT) single crystals with even higher d_{33} values ranging from 3400 to 4100 picocoulombs per newton, with variation below 20% over the as-grown crystal boule, exhibiting good property uniformity. We characterized the Sm-PMN-PT on the atomic scale with scanning transmission electron microscopy and made first-principles calculations to determine that the giant piezoelectric properties arise from the enhanced local structural heterogeneity introduced by Sm³⁺ dopants. Rare-earth doping is thus identified as a general strategy for introducing local structural heterogeneity in order to enhance the piezoelectricity of relaxor ferroelectric crystals.

he successful fabrication of relaxor ferroelectric solid-solution single crystals (relaxor-PT crystals), such as Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) and Pb(Zn_{1/3}Nb_{2/3})O₃-PbTiO₃ (PZN-PT), more than 20 years ago was a milestone achievement in ferroelectric research. These relaxor ferroelectric crystals possess very high piezoelectric coefficients d_{33} (1200 to 2500 pC N⁻¹) and minimal piezoelectric strain hysteresis (<5%), far outperforming mainstay piezoelectric materials [i.e., "soft" Pb(Zr,Ti)O₃ ceramics] whose d_{33} and strain hysteresis values are on the order of 500 to 700 pC N^{-1} and >30%, respectively (1-5). These unique features are attributed to the enhanced piezoelectricity of relaxor-PT crystals from the large intrinsic (lattice) contribution in domain-engineered configuration instead of the extrinsic domain wall motions observed in ceramic counterparts (6-12). Further enhancing the piezoelectricity to meet the ever-increasing demands of advanced piezoelectric devices is an active area, especially for high-frequency medical transducer arrays and ultralow field-driven actuators (13-16), for which high piezoelectric properties are strongly desired. However, despite these

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extensive efforts, progress toward improving piezoelectric responses in these devices over the past two decades has been slow.

According to the Landau phenomenological theory (6, 7, 17), a high intrinsic d_{33} can be achieved via increasing the dielectric permittivity $\varepsilon_{33}/\varepsilon_0$, which corresponds to a flat Gibbs free energy density profile with respect to polarization. Previous investigations showed that the free energy profile of ferroelectrics can be flattened by engineering the ferroelectric phase macroscopically (17-21) or the local structure microscopically (13, 22-27). Macroscopically, the free energy profile of a ferroelectric single domain can be flattened by designing a morphotropic phase boundary (MPB), at which energy barriers between two or more morphotropic phases are expected to be low (6-8, 18-20). Microscopically, the averaged free energy profile of a ferroelectric can be flattened by introducing local structural heterogeneity, due to the competition between the bulk energy and the interfacial energies associated with local polarization and strain discontinuities (12, 23). Many studies show that the high piezoelectricity of PMN-PT crystals benefits from both the MPB and nanoscale structural heterogeneity as a result of the unique feature of B-site cations (12, 25-27)-that is, the presence of Mg²⁺-Nb⁵⁺ ordered nanoscale regions (~ several nanometers) (28-30).

Li *et al.* reported further enhancement of local structural heterogeneity of PMN-PT polycrystalline ceramics by A-site modification, which increased the d_{33} to ~1500 pC N⁻¹ (23). The d_{33} for the Sm-doped PMN-PT ceramics is double the value of the best PMN-PT ceramics but still below those of PMN-PT single crystals. Implementing a similar approach in relaxor ferroelectric single crystals should synergize the enhanced local structural heterogeneity, the MPB, and the engineered domain structure via frustrative poling (i.e., the poling along a special nonpolar direction) (6, 7, 19, 31-34), leading to excellent dielectric and piezoelectric properties.

We developed a growth process for Smdoped PMN-PT single crystals in order to meet the requirements of advanced piezoelectric devices. The nominal selected composition was Sm_{0.01}Pb_{0.985}[(Mg_{1/3}Nb_{2/3})_{0.70}Ti_{0.30}]O₃ to maintain the rhombohedral/monoclinic phase and avoid the tetragonal side of the MPB region, which generally possesses inferior piezoelectric properties. We focused on [001]-oriented crystals, which simultaneously possess a large electrostrictive coefficient Q_{33} and ε_{33} , and thus are expected to have a high d_{33} , based on the relationship $d_{33} =$ $2P_{\rm S} \cdot Q_{33} \cdot \varepsilon_{33}$ (where $P_{\rm S}$ is the spontaneous polarization) (35).

We used a modified Bridgman approach to grow Sm-doped PMN-PT crystals (Fig. 1A) (36). The composition of the as-grown crystals varied along the growth direction as a result of the segregation of constituent elements in relaxor-PT solid solutions. We characterized the compositions of Sm-PMN-PT crystals by electron probe microanalysis (EPMA). We found that the segregation characteristics of Ti^{4+} and $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ were not affected by the Sm^{3+} dopant (table S1). Similar to the PMN-PT crystals, the concentration of Ti⁴⁺ increased during crystal growth while the concentration of $(Mg_{1/3}Nb_{2/3})^{4+}$ decreased. The concentration of Sm^{3+} [<0.87 mole percent (mol %)] was smaller than that of the nominal composition (i.e., 1 mol %), indicating that some of the Sm³⁺ was not incorporated into the crystal lattice during crystal growth. Of particular interest is that the concentration of Sm^{3+} decreased from the bottom to the top of the crystal boule, contrary to the trend observed for the Ti⁴⁺ content. This feature has an important impact on the phase and property variations of the asgrown Sm-PMN-PT crystals.

The $\varepsilon_{33}/\varepsilon_0$ and d_{33} values of our Sm-PMN-PT crystals exceed 11,000 and 3400 pC N⁻¹, respectively, and are much higher than those of an undoped PMN-30PT crystal (Fig. 1B and table S2). The electric field–induced strain of our Sm-PMN-PT crystals is approximately 0.30% at an electric field of 10 kV cm⁻¹, 90% higher than that of the PMN-30PT crystal (Fig. 1C). This displacement behavior demonstrates that our crystals can be used as actuators even at low electric fields.

In addition to the high piezoelectric and dielectric properties, the Sm-PMN-PT crystals exhibit improved uniformity of the $\varepsilon_{33}/\varepsilon_0$ and d_{33} along the crystal boule. This feature is important because compositional segregation leaves only about one-third of the undoped PMN-PT crystal boule grown by the Bridgman method having the properties required for certain medical transducer applications (3). The variations in the $\varepsilon_{33}/\varepsilon_0$ and d_{33} are below 10% and 20%, respectively, for our doped crystals. In contrast, the wide range of PT content (26 to 34%) in the undoped crystal boule resulted in a variation in $\varepsilon_{33}/\varepsilon_0$ of 3500 to 7500 and d_{33} of 1200 to 2500 pC N⁻¹ (37, 38). Such a large variation is a long-standing bottleneck for

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Fig. 1. Image and electromechanical properties of [001]-oriented Sm-doped PMN-PT crystals. (A) Image of as-grown Sm-PMN-PT crystal. The compositions of points A, B, C, and D are listed in table S1. (B) Dielectric and

piezoelectric coefficients of Sm-PMN-PT crystals versus those of PMN-30PT (patterned). (**C**) Electric field–induced strains for Sm-PMN-PT (sample B: 0.66 mol % Sm-doped PMN-30PT) and PMN-30PT crystals.



Fig. 2. Temperature-dependent dielectric behaviors of Sm-doped PMN-PT (sample B) and PMN-30PT crystals poled along the [001] direction. (A and B) Low- and high-temperature

properties of Sm-doped PMN-PT crystals, respectively. (C and D) Low- and high-temperature properties of PMN-30PT crystals, respectively.

0.20

0.15

0.05

0.00

0.20

0.15

0.10

0.05

0.00

Loss facto

Loss factor

the application of relaxor ferroelectric solidsolution crystals (3, 37, 38). The minimal property variation we observed in the Sm-PMN-PT crystals was because Ti^{4+} increased while Sm³⁺ decreased along the crystal growth direction. For rhombohedral/monoclinic Sm-PMN-PT crystals, the increase in Ti^{4+} shifts the composition toward the MPB, whereas the decrease in Sm^{3+} moves the composition away from the MPB because both Ti^{4+} and Sm^{3+} favor the tetragonal



Fig. 3. Atomic-resolution HAADF-STEM images for Sm-doped PMN-PT (sample B) and PMN-3OPT crystals recorded along the [010] crystallographic direction. (**A** and **B**) Normalized intensities of the A sublattice for Sm-PMN-PT and PMN-30PT, respectively. The color of the circles indicates the intensity of each atom column. (**C** and **D**) Atomic distances between A sublattice positions in Sm-PMN-PT and PMN-30PT crystals, respectively. The color of the lines represents the distance between A-site atom columns. Although the long-range averaged phase of Sm-PMN-PT inferred by XRD diffractions is a mixture of tetragonal *P*4mm and orthorhombic *A*mm2 phases, the local symmetry can be much lower than that of *P*4mm and *A*mm2 because of the presence of cation disordering. As expected, the symmetry of a specific lattice observed by STEM (C) is lower than that of either tetragonal *P*4mm or orthorhombic *A*mm2. (**E** and **F**) Unit cell *c/a* ratios for Sm-PMN-PT and PMN-30PT crystals, respectively. The color of the circles indicates the *c/a* ratio for each unit cell. phase (fig. S1). This unique characteristic guarantees that the composition of the whole Sm-PMN-PT crystal is in the proximity of the MPB, which we confirmed with x-ray diffraction (XRD) measurements (fig. S2). The minimal property variation in the doped crystal increases the usable portion of the crystal, reducing the cost of the final product.

We characterized the temperature-dependent dielectric properties of sample B (Fig. 1A) from 20 to 300 K (Fig. 2). We separated the $\epsilon_{33}/\epsilon_0\text{-versus-}$ T curves into stage I (20 to 200 K) and stage II (200 to 300 K). In stage I, we observed an increase in ϵ_{33}/ϵ_0 for both doped and undoped crystals with increasing temperature. This was accompanied by dielectric relaxation, the frequency dispersion of permittivity, and loss maxima. The increase in ϵ_{33}/ϵ_0 is not the result of a ferroelectric phase transition based on XRD measurements (8, 39) (fig. S3). The $\varepsilon_{33}/\varepsilon_0$ behavior is associated with switching or interface motions of the heterogeneous local polar regions whose polar directions are different from those of the longrange ferroelectric domains, as demonstrated by phase field simulations (12) and the relaxation behavior we observed. The dielectric enhancement in stage I for Sm-PMN-PT (~5500) is much larger than that of PMN-30PT (~2600) (Fig. 2, A and C) and indicates more heterogeneous local polar regions in our doped crystal. Both Sm-PMN-PT and PMN-30PT approach a ferroelectricferroelectric phase transition temperature (T_f) in stage II. Above this temperature, we observed that the crystals transformed from either rhombohedral (PMN-30PT) or mixed orthorhombic and tetragonal phases (doped PMN-PT) to a tetragonal phase from XRD measurements (fig. S3). We observed a much higher dielectric ramping rate in our doped sample, which we partially attributed to its lower $T_{\rm f}$ (Fig. 2, B and D). We expect an increase in ϵ_{33}/ϵ_0 to be more prominent when approaching the phase transition temperature for a ferroelectric, as described by Landau phenomenological theory (17). Previous analysis from phase field simulations of the heterogeneous ferroelectric system (23) leads us to believe that the larger volume fraction of heterogeneous polar regions may also explain the higher dielectric ramping rate. In addition, the lower Curie temperature of sample B (388 K) in contrast to PMN-30PT (410 K) indicates that the Sm³⁺ dopant occupies A-site in PMN-PT, because there is an empirical relationship showing that $T_{\rm C}$ will decrease about 25°C per mol % as rare earth cations go to the A-site of PMN-PT ceramics (40).

To provide evidence of the role that Sm^{3+} plays in PMN-PT crystals, we performed aberrationcorrected scanning transmission electron microscopy (STEM). We measured sample thicknesses between 9 and 12 nm using position-averaged electron diffraction (*41*). We calculated the standard deviation of the A sublattice intensities from five images obtained from high-angle annular dark field (HAADF) imaging (Fig. 3, A and B, and fig. S4). The standard deviation of the A sublattice intensities is ±5.4% for Sm-PMN-PT. In contrast, the standard deviation of the A

sublattice intensities for undoped PMN-30PT is ±3.2% of the mean. The intensity of an atom column in HAADF-STEM is strongly dependent on the atomic number (Z) and the distortion of the corresponding sublattice. Thus, the substitution of Pb^{2+} (Z = 82) by Sm³⁺ (Z = 62) along with the related A sublattice distortion and lead vacancies $(V_{Pb})''$, required to maintain charge neutrality) create enhanced intensity variations in Sm-PMN-PT. For comparison, the standard deviations of B sublattice intensities for Sm-PMN-PT and undoped PMN-30PT are ±9.3% and ±8.7%, respectively (fig. S5). The B sublattice has three cations $(Mg^{2+}, Ti^{4+}, and Nb^{5+})$, which increase the intensity variations. The relatively small change in the sublattice intensity standard deviation for the B sublattice between the doped and undoped samples provides evidence that the Sm³⁺ substitutes primarily in the A sublattice.

To investigate the impact of Sm³⁺ doping on the local structures of PMN-30PT, we calculated the distances between A-site cations on a perunit cell basis by STEM (42, 43) (Fig. 3, C and D, and fig. S4B). Although the effective lattice parameters for both doped and undoped PMN-PT samples remain similar at approximately 402 pm, the standard deviation of these values is significantly larger for Sm-doped PMN-PT. The fluctuation in the A sublattice parameter $\sigma_{A\text{-}A}$ is 5.8 pm for PMN-PT and 8.1 pm for Sm-PMN-PT. We calculated the local c/a ratio at the A sublattice positions (Fig. 3, E and F), which measures local tetragonality by determining the ratio of the $a_1 + a_2$ distances to the $c_1 + c_2$ distances (Fig. 3E). The c/a ratios for Sm-PMN-PT (SD ~ ± 0.023) are more varied than those for PMN-30PT (SD ~ ± 0.012) (fig. S4C). The smaller deviation in the c/a ratios for PMN-30PT is consistent with the expected average rhombohedral structure (8). The local fluctuations for the Sm-PMN-PT require enhanced local tetragonality, consistent with higher local structural heterogeneity.

We conducted first-principles calculations to understand the local structural heterogeneity we observed and to explore the impact on the local structure from Sm^{3+} and V_{Pb}'' . We used a 0.75PMN-0.25PT (PMN-25PT) composition that allowed for a supercell size feasible for density functional theory (DFT) calculations and was only a few percent lower in PT content than our single crystal (28 to 32%). We captured the local structural characteristics of a $2 \times 2 \times 2$ supercell with 40 atoms (36, 44-46) (Fig. 4A). As a result of the limited number of atoms in our simulations, our calculations have a much higher dopant/vacancy concentration (12.5 mol % in the supercell) (Fig. 4, B and C) than the asgrown crystals (<1 mol %). As a result, we focused on the relative variations in structure between the undoped and doped crystals. We calculated the lattice parameters and spontaneous polarizations of the supercell for PMN-25PT, Sm-PMN-25PT, and V_{Pb} "-PMN-25PT (Fig. 4, D and E). For undoped PMN-25PT, the lattice parameters of the $2 \times 2 \times 2$ supercell are calculated to be a = 8.06 Å, b = 7.92 Å, and c = 8.13 Å, with



Fig. 4. First-principles calculations for Sm-doped PMN-PT. (A) The 2 × 2 × 2 supercell of PMN-25PT that is used for calculations. (B) Schematic of the supercell used to study the impact of Sm^{3+} on lattice parameters and polarizations. (C) Schematic of the supercell used to study the impact of lead vacancy on lattice parameters and polarizations. (D) Lattice parameters for PMN-25PT, Sm-doped PMN-25PT, and PMN-25PT with lead vacancy. (E) Spontaneous polarizations for PMN-25PT, Sm-doped PMN-25PT, and PMN-25PT with lead vacancy. P_x , P_y , and P_z are the polarizations along x, y, and z directions, respectively; |P| is the magnitude of spontaneous polarization.

polarizations of $P_x = 0.26 \text{ Cm}^{-2}$, $P_y = 0.02 \text{ Cm}^{-2}$, and $P_z = 0.35 \text{ Cm}^{-2}$. We found that undoped PMN-25PT had triclinic symmetry with a polar vector 8° away from the [101] direction. The small size of the supercell does not allow us to reproduce the rhombohedral symmetry of PMN-25PT obtained by x-ray powder diffraction. By doping the A-site with Sm³⁺, the structure of PMN-25PT approaches a tetragonal phase with only a 0.003 Å difference between the a and blattice parameters. The calculations are consistent with Sm³⁺ doping inducing more local tetragonal regions in PMN-PT (Fig. 3). However, our calculations for the lead vacancy show that both the lattice parameters and spontaneous polarizations exhibit substantial decreases (Fig. 4, D and E). In contrast to Sm³⁺, the spontaneous polarization (|P|) drops by about half after introducing $V_{\rm Pb}''$ into the supercell, because lead vacancies are known to induce random fields that oppose dipole ordering (47). This behavior also explains the lower Curie temperature we observed for Sm-doped PMN-PT (Fig. 2), as lower Curie temperature corresponds to a smaller |P|in perovskite or perovskite-like ferroelectrics (fig. S6). We computed the crystal structures of the other two rare earths (La³⁺, Nd³⁺) with ionic sizes sufficiently large that they do not partition into the B-sites (48, 49). We found that the A-site dopant with a smaller ionic radius is more likely to settle into the tetragonal crystal structure (fig. S7) and thus induce a higher level of local structure heterogeneity of PMN-25PT. This result

may share some clues for the design of highperformance piezoelectric crystals by tailoring the microstructure from the atomic scale.

The introduction of Sm³⁺ dopants on the A sites of the PMN-PT crystal created disruptions in the long-range ferroelectric domains. We also incorporated the domain engineering and morphotropic phase boundary of ferroelectric crystals. These contributed to extremely high d_{33} (3400 to 4100 pC $N^{\text{--1}}$) and large ϵ_{33}/ϵ_0 (~12,000) in [001]-oriented Sm-PMN-PT crystals. These crystals have great potential for numerous roomtemperature piezoelectric applications, especially for high-frequency medical imaging transducers and low field-driven actuators. By using A-site rare earth dopants, we offset the macroscopic phase variation along the crystal growth direction induced by the segregation of B-site cations and circumvented the long-standing issue of nonuniform solid-solution single crystals grown by the Bridgman method. This strategy enlarged the usable portion of the as-grown crystals and should reduce the cost of the final products. This in turn improves reliability for piezoelectric devices requiring large crystal wafers with minimal variation in properties, providing commercialization opportunities for high-performance piezoelectric applications.

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SUPPLEMENTARY MATERIALS

science.sciencemag.org/content/364/6437/264/suppl/DC1 Materials and Methods Figs, S1 to S9 Tables S1 and S2 References (50-57)

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Giant piezoelectricity of Sm-doped Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ single crystals

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Samarium supersensors

Piezoelectric materials produce electric charge in response to changes in stress and are thus good sensor materials. One challenge has been growing single-crystal piezoelectrics with uniform properties. As of now, much of the crystal is discarded because of compositional variations. Li *et al.* synthesized single crystals of samarium-doped Pb(Mg 1/3Nb2/3)O3-PbTiO3 that have uniform and extremely high piezoelectric properties (see the Perspective by Hlinka). These crystals are ideal for a variety of sensing applications and could reduce cost by eliminating waste. *Science*, this issue p. 264; see also p. 228

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