RESEARCH ARTICLE | SEPTEMBER 05 2023

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https://doi.org/10.1063/5.0164669
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Superelastic-like nonlinear deformation hidden in ferroelectric ceramics

Cite as: J. Appl. Phys. 134, 094102 (2023); doi: 10.1063/5.0164669 Submitted: 30 June 2023 · Accepted: 15 August 2023 · Published Online: 5 September 2023



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ABSTRACT

The mechanical response of ferroelectric (piezoelectric) ceramics under high stress conditions has a crucial role from the perspective of engineering applications such as advanced actuator systems. In this study, we perform first-principles calculations to clarify the deformation behavior and (ideal) tensile strength for typical ferroelectric ceramics of PbTiO₃ (PTO) under high mechanical loading. We find the superelastic-like nonlinear deformation behavior in ferroelectric PTO. In addition, it has several inflection points and shows a large critical strain compared to the paraelectric phase. We conclude that the unique nonlinear deformation in PTO originates from attributable to the displace-ment of oxygen atoms due to the ferroelectric phase transition based on analyzing the interatomic distances of each atom and an integrated crystal orbital Hamiltonian population with respect to strain. Furthermore, we also calculate the piezoelectric coefficient for PTO and reveal that it shows the singular peak at inflection points of the stress–strain curve. Unveiling and engineering the hidden superelastic-like defor-mation in the ferroelectric phase may open promising paradigms for functional piezoelectric devices. *Published under an exclusive license by AIP Publishing*. https://doi.org/10.1063/5.0164669 compared to the paraelectric phase. We conclude that the unique nonlinear deformation in PTO originates from attributable to the displace-

I. INTRODUCTION

Ferroelectric (FE) ceramics, such as PbTiO₃ (PTO) and BaTiO₃, are characterized by spontaneous polarization arising from the displacement of cations and anions in a non-centrosymmetric crystal lattice at room temperature.¹⁻⁴ Ferroelectric ceramics show various electro-mechanical responses, including ferroelectricity and piezoelectricity. These properties make ferroelectrics help for various electromechanical devices, such as nonvolatile random access memory (FeRAM),^{5,6} transducers, sensors, and MEMS actuators.^{3,7–9}

The flexible ferroelectric ceramics, realized as a high-quality micrometer or nanometer scale thin film, now attracted attention to apply functional piezoelectric devices.^{10–13} The reversible deformation is allowed in ferroelectric ceramics because of fewer voids, defects, and dislocation; therefore, the deformation behavior at the ends under high stress and ideal strength is crucial in comprehending the fracture mechanism and designing devices and could be a helpful guide principle for evaluating the strength of macroscopic materials. In addition, recent studies show that a single interatomic bond governs the criteria for fracture initiation and unstable propagation of cracks at stress concentrations.^{14,15} However, observing the deformation behavior of ceramics under high pressure experimentally is still challenging due to its brittleness.

In this study, to clarify the mechanical response of ferroelectric ceramics under high stress condition, we perform firstprinciples calculations to evaluate the deformation behavior and (ideal) tensile strength for typical ferroelectric ceramics of PbTiO₃ (PTO). We find the superelastic-like nonlinear stress-strain curve for PTO in the FE phase, which diverged from conventional ceramics. This unique nonlinear deformation leads to increasing the ideal tensile strain. We conclude that the difference in the structure of the bonding network due to the minimal atomic displacement of about 0.2-0.4 Å in the FE phase produces nontrivial deformation and strength properties.

II. COMPUTATIONAL DETAILS

Figure 1 shows the crystal structure of PbTiO₃ in paraelectric (PE) and ferroelectric (FE) phases. PE and FE phases have a cubic crystal structure (space group $Pm\bar{3}m$) and a tetragonal crystal structure (space group P4mm), respectively. The optimized lattice constant of PbTiO₃ in the PE and FE phases, without strain, is obtained

ARTICLE pubs.aip.org/aip/jap Ferroelectric (FE) Paraelectric (PE) Pb Ti Ο z [001] y [010]

FIG. 1. Crystal structure of PbTiO₃ in paraelectric (PE) and ferroelectric (FE) phases. Gray, purple, and blue spheres indicate Pb, Ti, and O, respectively.

25

20

15

10

5

0 Ō

 $\sigma_{_{ZZ}}$ (GPa)

as (a = b = c = 3.885 Å) and (a = b = 3.860 Å, c = 4.033 Å), respectively; these values are equivalent to reported ones.^{16–19} A uniaxial tensile load is applied along the z direction to estimate the ideal tensile strength and piezoelectric properties. The uniaxial tensile strain is up to $\varepsilon_{zz}^{PE} = 0.35$ and $\varepsilon_{zz}^{FE} = 0.46$ for PE and FE phases, respectively. The in-plane lattice constant and atomic configuration under each uniaxial tensile strain are optimized to satisfy the maximum force of below 0.01 eV/Å based on the conjugate gradient algorithm.

x [100]

First-principles calculations based on the density functional theory^{20,21} were performed with the VASP code.^{22,23} A plane-wave basis was used to expand the wave function, and the kinetic cutoff energy was set to 600 eV. The effects of the nucleus and electrons were expressed by the projector-augmented wave (PAW) method.^{24,25} A $8 \times 8 \times 8$ k-point mesh with the Monkhorst-Pack scheme²⁶ was used for Brillouin zone sampling of the primitive cell. The local density approximation²⁷ was adopted for the exchange-correlation functional. We also consider the exchangecorrelation functional dependence of the stress-strain curve. For details, see the supplementary material.

III. RESULTS AND DISCUSSION

A. Mechanical properties of PbTiO₃

Let us first discuss the tensile deformation of ferroelectric ceramics PbTiO₃. Figure 2 shows the stress-strain curve of PbTiO₃ in PE and FE phases. The stress-strain curve for the PE phase (gray squares) exhibits a convex upward function with increasing tensile strain, consistent with the behavior of conventional ceramics,²⁸⁻³⁰ and the critical tensile strain is approximately 0.25. On the other hand, we find an unconventional nonlinear stressstrain curve in the FE phase (red circles), and the critical tensile strain is approximately 0.44, which is around 1.8 times larger than the PE phase. The nonlinear stress-strain curve in the FE phase forms an S-shaped curve with several inflection points. Such S-shaped nonlinear behavior is commonly observed in soft materials with superelasiticity such as polymer or rubber,^{31,32} although the stress level of PbTiO₃ is much higher than that of soft materials. These results indicate that the FE phase transition can change the deformation properties dramatically, even from ceramics to superelastic-like ceramics.

To discuss the change in mechanical properties in detail, we gasso estimate Young's modulus. The estimated value of Young's $\frac{1}{2}$ also estimate Young's modulus. The estimated value of Found 1 modulus for PE and FE phases is 259 and 53 GPa, respectively. By Structural parameters, Young's modulus *E*, ideal tensile strength $\sigma_{\rm IS}$, and critical tensile strain $\varepsilon_{\rm IS}$ for PbTiO₃ in PE and FE phases



0.2

0.3

0.1

0.5

FE

PF

0.4

TABLE I. Structural parameter of PbTiO₃ of PE and FE phases, Young's modulus *E*, ideal tensile strength σ_{IS} , critical tensile strain ε_{IS} , and displacement of oxygen atoms along with *z* direction δd_z .

	a, c (Å)	E (GPa)	$\sigma_{ m IS}~(m GPa)$	$arepsilon_{ ext{IS}}$	δd_z (Å)
PE	a = c = 3.885	259	23.6	0.25	0
FE	a = 3.860, c = 4.033	53	11.6	0.44	0.4

are listed in Table I. Unconventional mechanical responses are realized in the FE phase in PbTiO₃ compared with the PE phase or other well-known ceramics.^{28,33} The ideal tensile strain $\varepsilon_{\rm IS}$ in the FE phase is about 75% increase, and PbTiO₃ ceramic will spontaneously increase its fracture toughness through the PE to FE phase transition with no other ceramics. Ferroelectric phase transition in PTO, the relative atomic displacement of about 0.4 Å in an oxygen atom, may lead to superelastic-like nonlinear deformation in ceramics.

B. Origin of superelastic-like nonlinear deformation nonlinear deformation in the FE phase

Next, let us investigate the origin of superelastic-like nonlinear deformation of PbTiO₃ in the FE phase. To discuss the effect of the relative atomic displacement in nonlinear deformation, we analyze the charge density of PbTiO₃ in PE and FE phases. Figures 3(a), 3(b), 3(d), and 3(e) show the contour plot for the charge density in PE and FE phases without tensile strain. The PE phase shows

isotropic charge density distribution based on cubic symmetry; it leads to an isotropic bonding network between Ti–O atoms. On the other hand, the FE phase shows an anisotropic charge density distribution in the (001) direction due to the breaking symmetry, indicating anisotropic bonding between Pb–O and Ti–O. This anisotropic bonding originates from hybridization of Pb 6s-O 2p and Ti 3d-O 2p orbitals and is the driving force to stabilize the FE phase.²

We illustrate the bonding network based on the above analysis [Figs. 3(c) and 3(f)]. The monotonically stress-strain curve of the PE phase (Fig. 2) can be understood to be caused by the isotropic bonding of the PE phase. On the other hand, the FE phase is composed of truss-like bonding, which is similar to the polymer, 31,32 and thus, it could be an origin of a nonlinear stress-strain curve. Hereafter, we only focus on the FE phase.

Next, let us consider the deformation mechanism based on the bond length and chemical bonding. The stability of chemical bonding was analyzed using the integrated crystal orbital Hamiltonian population (ICOHP)^{34–36} implemented in the LOBSTER code.³⁷ Figure 4 shows tensile strain dependence of the bond length and ICOHP.

We can see that the Pb–O_I bond mainly contributes to deformation [Fig. 4(a)]. In addition, the bond length of Pb–O_I is rapidly increased at $\varepsilon_{zz} \sim 0.1$ because the deformation mechanism changes from truss deformation type to bond length loading type around $\varepsilon_{zz} \sim 0.1$ (see supplemental material). This change in the deformation mechanism of PbTiO₃ can also be explained in terms of



FIG. 3. Contour plot for charge density of PbTiO₃ on Pb–O, Ti–O plane for [(a) and (b)] PE and [(d) and (e)] FE phases. The charge density was obtained without tensile strain. Chemical bonding network for PE (c) and FE (f) phases. Red dotted line in (f) corresponds to Pb–O₁ bonding in Fig. 4.

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FIG. 4. Tensile strain dependence of (a) bond length Δd and (b) $-\Delta$ (ICOHP). Inset shows the side view of FE phase and chemical bonding. Red, blue, cyan, and green lines represent Pb-O1, Ti-O1, Ti-O1, and Pb-O1 chemical bonds, respectively.

chemical bonding. Figure 4(b) shows that only $-\Delta$ (ICOHP) in Pb-O_I bond decreases to the unstable bond in response to strain. This suggests that chemically unstable bonds preferentially contribute to deformation.

C. Piezoelectric properties in the FE phase

Finally, let us discuss the piezoelectric properties under high stress condition. Figure 5 shows the stress dependence of polarization P and piezoelectric strain coefficient d_{zz} of PbTiO₃. Here, polarization P is calculated using the Berry phase theory of modern theory of polarization.^{38,39} The d_{zz} without strain and stress in PbTiO₃ is about 0.1×10^{-9} C/N, comparable to well-known ferro-electric materials.^{40–42} On the other hand, the d_{zz} is maximized at $\sigma_{zz} \sim 1.6$ GPa, which is six times larger than d_{zz} without mechanical loading $(d_{zz}^{\text{max}} \sim 0.6 \times 10^{-9} \text{ C/N})$. The mechanical loading in PbTiO₃ leads to several benefits for piezoelectric devices application; one is the increasing piezoelectric coefficient, and another one is the tunable piezoelectric performance that can be provided in the specified piezoelectric material.

To discuss the origin of the striking peak of d_{zz} , we consider the polarization and nonlinear deformation in PbTiO₃. The piezoelectric strain coefficient d_{ij} can be evaluated by the following



FIG. 5. Stress dependence of polarization and piezoelectric strain coefficient for PbTiO₃.

equation: $d_{ij} = \partial P / \partial \sigma_{ij}$, that is, d_{ij} can be understood as a slope of P. The polarization rapidly increases around $\sigma_{zz} \sim 1.6$ GPa (red solid circle in Fig. 5); above we discussed, $\sigma_{zz} \sim 1.6$ GPa corresponds to the stationary point. The slope of the stress-strain curve would be close to zero near the region where the deformation mechanism is changed from truss-type to chemical bonding type. Therefore, the unique superelastic-like nonlinear deformation in PbTiO₃ can tune its electro-mechanical response and even give rise to colossal piezoelectric properties. Moreover, the piezoelectric R response with such sharp peaks represents a characteristic behavior get that deviates from the framework of the Landau–Ginzburg– Devonshire (LGD) theory⁴³ based on linear approximations.

In summary, to investigate the mechanical responses of ferroelectric ceramics under high stress condition, we performed firstprinciples calculations for PTO in PE and FE phases. The superelastic-like nonlinear stress-strain curve was obtained in the FE phase, which diverged from conventional ceramics. The ferroelectric phase transition dramatically changes its stiffness; that is, the ideal tensile strain ε_{IS} in the FE phase is about a 75% increase. We concluded that the unique nonlinear deformation originates from the truss-like bonding network due to the ferroelectric phase transition. In addition, we found that the switching point for the chemical bonding network deforming corresponds to the inflection points in the stress-strain curve.

We also evaluated the piezoelectric properties in the FE phase. The striking peak of the piezoelectric constant appears around 1.6 GPa, which is the inflection point of the stress-strain curve. In high-quality PTO, such as achieved in flexible ferroelectric ceramics, the unique piezoelectric response under tensile strain reported in this study would be experimentally observed. Further analysis of the distinctive piezoelectric response based on superelastic-like nonlinear deformations would lead to the extension of the LGD theory. These results will help us to unveil the hidden deformation mode in ceramics, and strain engineering may open promising paradigms for functional piezoelectric devices.

SUPPLEMENTARY MATERIAL

See the supplementary material for the details of the exchange-correlation functional dependence of lattice constants and elastic constants and the deformation mechanism of PbTiO₃.

ACKNOWLEDGMENTS

This work was partly supported by JSPS KAKENHI under Grant Nos. JP20H05653, JP22K14587, and JP23H00159 and JST FOREST Program (No. JPMJFR222H). The crystal structure was drawn by VESTA.44

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Susumu Minami: Investigation (equal); Validation (equal); Visualization (equal); Writing - original draft (lead); Writing review & editing (equal). Tomohiro Nakayama: Investigation (equal); Validation (equal); Visualization (equal). Takahiro Shimada: Conceptualization (lead); Project administration (equal); Supervision (lead); Validation (equal); Writing - original draft (equal); Writing - review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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