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Dependence of local atomic structure on piezoelectric properties of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ materials

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ABSTRACT

Lead zirconate titanate (PZT, $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$) is a piezoelectric ceramic which can be used for several applications such as actuators, sensors, and microelectronic devices. Depending on its composition, PZT can exhibit rhombohedral, orthorhombic (tetragonal) phases, with the piezoelectric charge constant (e_{ij}) key to evaluating its piezoelectric properties. In this study, (e_{ij}) was calculated using density functional perturbation theory (DFPT) based on first-principles methods. First, we reveal that the rhombohedral structure is stable for Zr-rich compositions. Second, extending the study to $\text{PbZr}_{0.56}\text{Ti}_{0.44}\text{O}_3$ and $\text{Pb}_{0.94}\text{Sr}_{0.06}\text{Zr}_{0.56}\text{Ti}_{0.44}\text{O}_3$ (PSZT), we evaluated the values of e_{ij} both theoretically and experimentally to investigate how they are affected by doping. The microscopic movements of individual atoms within the optimized crystal were analyzed to investigate the correlations between the structural characteristics and e_{ij} . The results show that the relative positions of Ti and Zr (B-site) atoms and the quadratic elongation in the PZT octahedron depend strongly on the piezoelectric charge constant e_{33} , which itself depends on the Ti content. The local atomic structural parameters described in this study can be used as a descriptor for the high-throughput screening of PZT materials.

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1. Introduction

Lead zirconate titanate (PZT, $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$) is a representative perovskite “ ABO_3 ” piezoelectric material whose properties can be enhanced by substituting various dopants to the A- or B-sites [1–5]. Due to its piezoelectric properties, it has been used as an important component in many actuators, sensors, and microelectronic devices [1–3]. It is known that PZT exists in the rhombohedral phase at $x = 0$ –0.44, and in an orthorhombic (tetragonal) phase at $x = 0.56$ –1.0, while a morphotropic phase boundary (MPB) region in which the rhombohedral and tetragonal phases coexist appears at $x = 0.44$ –0.56 [4–8]. In this MPB region, PZT shows significantly high piezoelectric properties [9].

Many attempts have been made to predict and calculate piezoelectric properties such as the piezoelectric charge constant (e_{ij} , d_{ij}), elastic compliance (s_{ij}), and elastic stiffness (c_{ij}). However, most of the previous studies have focused on the piezoelectric and structural characteristics based on the tetragonal or orthorhombic structures close to the MPB region [10–12]. For example, Sághi-Szabó et al. calculated e_{33} for $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ for the tetragonal structures [13]; Bellaiche and Vanderbilt also calculated e_{33} for tetragonal $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ using the virtual crystal approximation [14]. In addition, the piezoelectric properties of

Zr-rich compositions have been calculated for orthorhombic structures [15,16]. Rodriguez et al. calculated the structural parameters of orthorhombic $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ and PbZrO_3 (i.e. PZO ($x = 0$)) [11]. For rhombohedral structures, Cohen et al. calculated the elastic constant and Young’s modulus of $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ [17,18]; however, no studies have reported the dependence of the piezoelectric charge constant and of the structural characteristics on the rhombohedral PZT.

To address this issue, we performed first-principles calculations of the composition-dependent piezoelectric charge constant in rhombohedral PZT, which can also be obtained experimentally for Zr-rich compositions. Based on the calculated results, we investigated the relationship between the piezoelectric charge constant and the atomic structure. Also, the calculation results were verified through a comparison with the experimentally measured values for identical compositions.

2. Methodology

2.1. Theoretical calculation method for e_{ij} of PZT material

Theoretical calculations were performed using density functional theory (DFT) calculations. To ensure accurate atomic structure predictions, we adopted the

exchange-correlation potential as generalized gradient approximation (GGA) functions with the solid version of the Perdew–Burke–Ernzerhof functional (PBEsol) for $PbZr_{1-x}Ti_xO_3$ ($x = 0-0.5$) and 6 mol% Sr-doped PZT ($x = 0.44$). The plane wave kinetic energy cutoff was set to 520 eV and the k -points in the Brillouin zone were sampled by a $2 \times 2 \times 2$ mesh both for the structural optimization procedure and to calculate the piezoelectric charge constant. The equilibrium structure was obtained by optimizing the atomic positions, cell shape, and volume until the forces on the atoms were less than ± 2.5 meV/Å. The piezoelectric charge constant of the optimized structure was calculated using density functional perturbation theory (DFPT). All DFT-based calculations were implemented using the Vienna *ab-initio* simulation package (VASP) and MedeA-VASP software [19,20].

2.2. Calculation method of local atomic structure of PZT material

To investigate how the B-atom position affects the piezoelectric characteristics, we evaluated two structural parameters, the relative B-site atom position (δ) and the quadratic elongation (λ) within the perovskite oxygen octahedron. δ was calculated relative to the distance from the center of the oxygen octahedron in the $[111]$ direction for the optimized structures of each PZT composition as shown in Figure 1. For every B-site atom inside the octahedron, the initial B-site atom position was defined as the center of the oxygen octahedron, while the structurally optimized B-site atom position was defined as atoms moving in the $[111]$ direction. The unrelaxed (x_i, y_i, z_i) and the structurally optimized ($\alpha_i, \beta_i, \gamma_i$), coordinates, were used in the following equation to obtain δ .

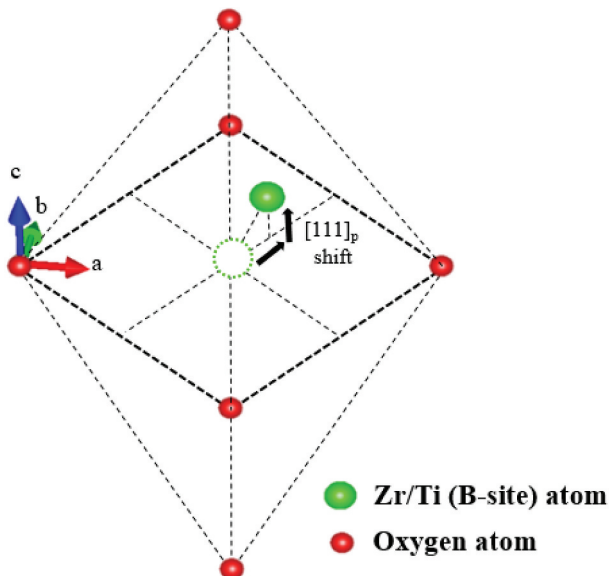


Figure 1. Diagram illustrating the direction of B-site atomic movement in an oxygen octahedron.

$$\delta = \sum_{i=1}^n \frac{\sqrt{(x_i - \alpha_i)^2 + (y_i - \beta_i)^2 + (z_i - \gamma_i)^2}}{n} \quad (1)$$

where n is the number of B-site atoms inside the supercell. So, the relative B-site atom position was taken as the average of the moving distances obtained for each composition. The quadratic elongation (λ), is a dimensionless quantity providing a quantitative measurement of the polyhedral distortion in a crystal independent of the polyhedral size [21,22]. It is defined as

$$\lambda = \sum_{i=1}^6 \frac{(l_i/l_0)^2}{6} \quad (2)$$

where l_i is the distance from the B-site atom to the i th oxygen atom and l_0 is the center-to-vertex distance of a regular polyhedron of the same volume.

3. Results and discussion

3.1. Crystal structure optimization

In Zr-rich regions, PZT has partial orthorhombic (tetragonal) and rhombohedral structures [6–8]. We selected $PbZrO_3$ (PZO, $x = 0$) to represent Zr-rich PZT. The total energy of PZO was used to evaluate the structural optimization procedure, with the aim to identify the most stable balance between orthorhombic and rhombohedral structures in Zr-rich compositions. The reference lattice parameters of the rhombohedral ($a = b = c = 5.79$ Å, $\alpha = 59.24^\circ$) and orthorhombic ($a = 5.84$ Å, $b = 11.72$ Å, $c = 8.13$ Å, $\alpha = 90^\circ$) structures of PZO were obtained according to previous experiments [18,23]. For the total energy comparison, we used a 40-atom supercell ($2 \times 2 \times 2$ unit cells) for the orthorhombic structure and a 10-atom supercell ($1 \times 1 \times 2$ unit cells) for the rhombohedral structure. Table 1 lists the lattice parameters for the rhombohedral and orthorhombic PZO crystal structures, which were obtained by atomic relaxation. The total energies calculated for the optimized orthorhombic and rhombohedral structures were 3.94×10^1 and -4.13×10^1 eV per unit cell, respectively, which shows that the energy of the rhombohedral structure is lower by 1.9 eV per unit (Table 2). The total energy calculations confirm that the rhombohedral structure is more stable than the orthorhombic structure in the Zr-rich PZT compositions.

Table 1. Theoretically optimized unit cell lattice parameters of $PbZrO_3$ with rhombohedral and orthorhombic structures [18,23].

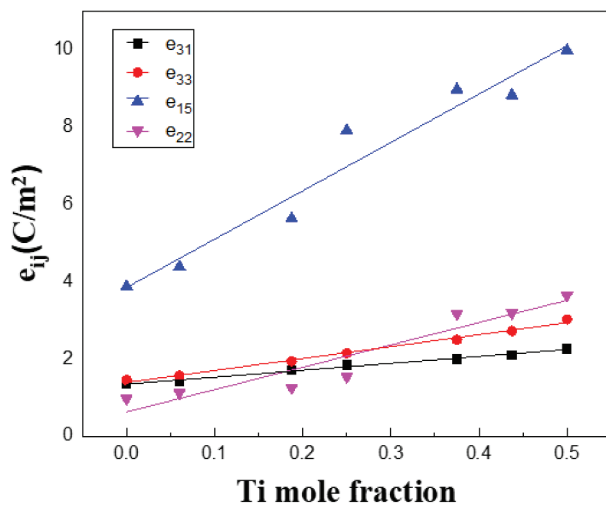
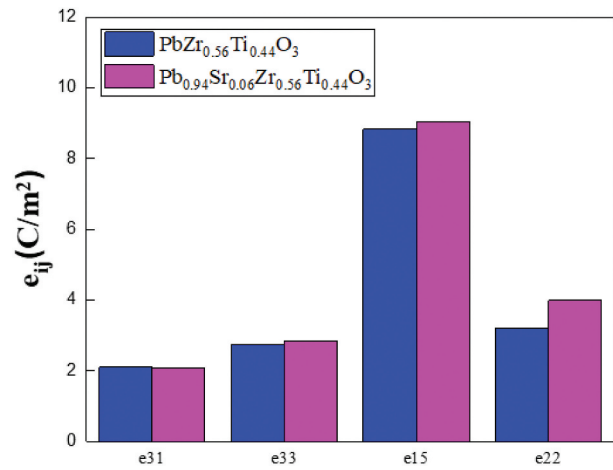
Lattice parameter	Phase	a (Å)	b (Å)	c (Å)	α (deg.)	V (Å ³)
Orthorhombic (tetragonal)		5.88	11.78	8.18	90	566.02
Rhombohedral		5.93	5.93	5.93	59.31	145.24

Table 2. Calculated total energies of $PbZrO_3$ material with orthorhombic and rhombohedral structures.

Phase	Total energy (eV)	Formula unit	eV/f.u
Orthorhombic (tetragonal)	-3.15×10^2	8	-3.94×10^1
Rhombohedral	-8.27×10^1	2	-4.13×10^1

3.2. Piezoelectric charge constants of PZT material

Based on the results presented in Section 3.1, the crystal structure of Zr-rich $PbZr_{1-x}Ti_xO_3$ compositions were determined to be rhombohedral. Having determined that the stable structure for Zr-rich composition is rhombohedral, now we first change the composition and then we introduce doping to see the influence on the piezoelectric charge constant (e_{ij}). The crystal structure optimization and piezoelectric charge constant (e_{ij}) calculations were conducted by substituting Ti for Zr ($PbZr_{1-x}Ti_xO_3$ ($x = 0-0.5$)) in a $2 \times 2 \times 4$ supercell. Figure 2 shows the influence of Ti content on the calculated piezoelectric charge constant. The predicted values of e_{33} and e_{31} increase with the Ti concentration, while e_{15} showed a significant increase at $x = 0.25$ and continued increasing up to $x = 0.5$. In addition, e_{22} almost doubled in value at $x = 0.375$, before gradually increasing up to $x = 0.5$. Overall, the calculated e_{ij} value increased as it approached the MPB region, which is consistent with the behavior of PZT reported in previous experiments [9]. To investigate the effect of Sr doping on e_{ij} , we substituted a single Sr atom on a single Pb atom in the composition of $x = 0.44$, which corresponds to MPB-region PZT. Figure 3 shows the calculated e_{ij} results for PZT and PSZT. We can see that Sr-doping increases e_{ij} with respect to bare PZT, as e_{33} , e_{15} , and e_{22} are increased by 4.03%, 2.38%, and 24.78%, respectively. It should be

**Figure 2.** Effect of Ti molar ratio on the DFPT-calculated piezoelectric charge constants (e_{ij}) of $PbZr_{1-x}Ti_xO_3$ (PZT) with a rhombohedral structure.**Figure 3.** Calculated piezoelectric charge constants (e_{ij}) of $PbZr_{0.56}Ti_{0.44}O_3$ (PZT 56/44) and $Pb_{0.94}Sr_{0.06}Zr_{0.56}Ti_{0.44}O_3$ (PSZT 6/56/44) in rhombohedral structure.

noted that e_{31} showed no significant change, which indicates that e_{31} is not notably influenced by Sr doping.

3.3. Relationship between local atomic structure and e_{ij} in PZT

Spontaneous polarization in PZT is known to stem from B-site atoms being shifted slightly off-center of the oxygen octahedron. The B-site atom position (δ) and the quadratic elongation (λ) of the oxygen octahedron were calculated to determine the correlation between the piezoelectric constant and the structural distortion of the oxygen octahedron. Table 3 shows the structural parameters δ and λ of $PbZr_{1-x}Ti_xO_3$ calculated varying the Ti molar fraction. Each value was calculated according to equation (1), (2) as presented in Section 2.2, respectively. These two structural parameters and the e_{33} value were normalized for the $PbZr_{1-x}Ti_xO_3$ ($x = 0.5$) composition, and the comparative values are shown in Figures 4 and 5. Figure 4 compares the dependence of $1/\delta$ and e_{33} on the Ti molar fraction. The correlation coefficients (R^2) of the linear regressions, calculated as 0.91 and 0.99, respectively, confirm a very good agreement with a linear fit.

Figure 5 shows normalized inverse of quadratic elongation ($1/\lambda$) and e_{33} as a function of Ti molar fraction. Also, in this case, the linear regression validates a linear relation between $1/\lambda$ and e_{33} , and Ti molar

Table 3. Structural parameters of $PbZr_{1-x}Ti_xO_3$ which are calculated according to Ti mole fraction.

x	$1/\delta$ (Å)	$1/\lambda$
0.06	4.61	1.56
0.1875	4.75	1.94
0.25	4.83	2.15
0.375	5.16	2.50
0.4375	5.37	2.72
0.5	5.67	3.03

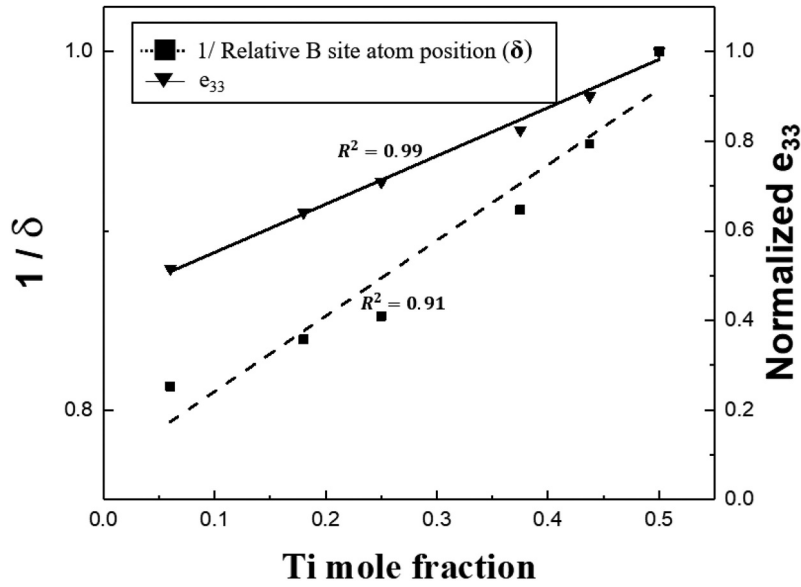


Figure 4. Calculated inverse of the relative b site atom position($1/\delta$) and piezoelectric charge constant(e_{33}) of $PbZr_{1-x}Ti_xO_3$ as a function of the Ti molar ratio. Both quantities are normalized with respect to the value at $x = 0.5$ (i.e. max = 1.0).

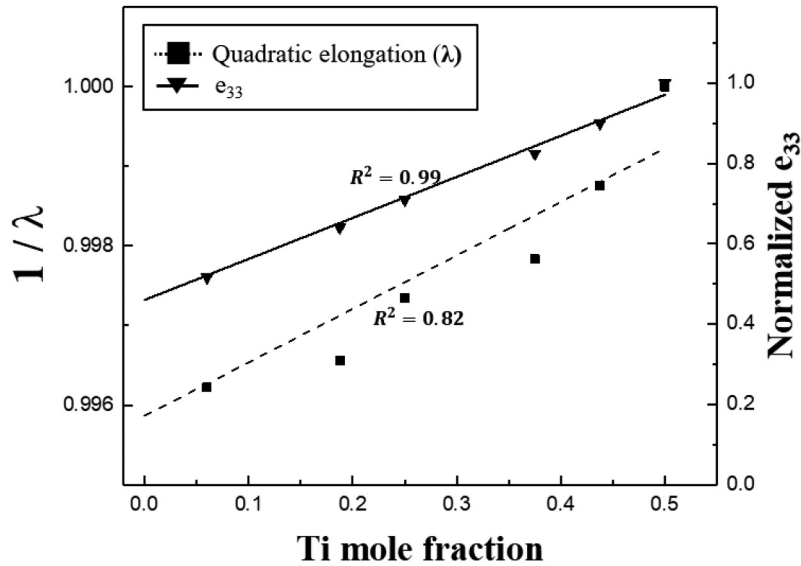


Figure 5. Calculated inverse of the quadratic elongation and piezoelectric charge constant(e_{33}) of $PbZr_{1-x}Ti_xO_3$ as a function of the Ti molar ratio. Both quantities are normalized with respect to the value at $x = 0.5$ (i.e. max = 1.0).

fraction with R^2 coefficients of 0.99 and 0.82, respectively. This means that the λ value decreases as the Ti content increases, which can be attributed to the smaller ionic radius of Ti atoms relative to Zr atoms. This is also consistent with the decrease in the δ value [24,25].

These results show that $1/\delta$ and e_{33} have a linear dependence on the Ti molar fraction, demonstrating the strong effect of Ti content on the piezoelectric properties of the material.

3.4. Experimental verification of PZT ceramics

For experimental validation of DFPT calculation, the specimens were synthesized using a conventional solid-state reaction process. The composition of PZT and PSZT are given as follows: $PbZr_{0.56}Ti_{0.44}O_3$ (PZT),

$Pb_{0.94}Sr_{0.06}Zr_{0.56}Ti_{0.44}O_3$ (PSZT). The raw materials such as PbO, ZrO₂, TiO₂, and SrO for the given composition were weighted by the molar ratio, and the powders were ball milled. And the mixed powders were calcined at 900°C for 3 h and sintered at 1300°C for 3 h in a sealed alumina crucible containing atmosphere powder, which has the same composition with specimens. The specimens were poled in a silicone oil bath at 120°C by applying an electric field of 2kV/mm for 30 min. The piezoelectric charge constant (e_{33}) was determined according to the method of resonance and antiresonance frequencies by using an impedance analyzer (HP 4194A, Agilent) based on the Institute of Electrical and Electronics Engineers (IEEE) standards [21], and the piezoelectric charge constant (d_{33}) was measured using d_{33} -meter (PM-300, Piezotest).

The relationship between d_{33} and e_{33} is expressed as follows:

$$d_{33} = 2e_{31}s_{13}^E + e_{33}s_{33}^E \quad (3)$$

$$e_{33} = 2d_{31}c_{13}^E + d_{33}c_{33}^E \quad (4)$$

where s_{ij}^E is the elastic compliance and c_{ij}^E is the elastic stiffness. Accordingly, e_{33} and d_{33} represent the strain- and stress-related electric charges, respectively, and the relationship between d_{33} and e_{33} can be compared with similar trend.

Table 4 compares the DFPT calculation and the experimental results for $PbZr_{0.56}Ti_{0.44}O_3$ (PZT,56/44). Each value was normalized respect to the value of PZT ($x = 0.44$). The e_{33} values of PZT (56/44) obtained experimentally and DFPT calculations were 8.72 and 2.72 (C/m²), respectively, and the corresponding d_{33} obtained from the experimental measurement was 156 (pC/N). In the case of $Pb_{0.94}Sr_{0.06}Zr_{0.56}Ti_{0.44}O_3$ (PSZT,6/56/44), the experimental and calculated values were 14.6 and 2.83 (C/m²), respectively, and the d_{33} value was 346 (pC/N). Introducing A-site Sr doping, the calculated e_{33} increased from 2.72 (C/m²) to 2.83 (C/m²) by 0.11 (C/m²), with an increase 4%. In the case of the experimental value though, e_{33} increased by 5.88 (C/m²) from 8.72 (C/m²) to 14.6 (C/m²) with an increase around 67%.

To explain this large discrepancy between the calculated and the experimental data, several reasons can be taken into account. First and foremost, experimentally, in the MPB region, the tetragonal and the rhombohedral phases coexist, while DFPT calculations were carried out using only in the rhombohedral structure for practical reasons. Second, the rhombohedral phase has a higher lattice energy barrier than tetragonal [26]. Therefore, the change induced on the lattice by Sr doping is smaller than in the tetragonal phase, and the spontaneous polarization is less pronounced, accordingly. In addition, in the actual experiment, the movement of atoms and the domain wall movement becomes easier because of the PbO loss in incomplete sintering and A-site voids due to Sr doping. As a result, E_c decreases and the piezoelectric constant increases. Therefore, we can assume that the

calculated value of the piezoelectric constant is lower than the experimental value because of the discrepancies in the microstructural features that are necessarily oversimplified in the computational model with respect to the actual phenomenon. Despite these quantitative differences, the experimental and the computational results definitely follow the same qualitative trend and provide useful insights to the understanding of the microscopic piezoelectric properties of PZT.

In addition, when calculating $1/\delta$ as a function of Sr doping, it increased by 0.24 (Å) from 5.07 (Å) to 5.31 (Å), an increase of about 5%. In this case, the increase in e_{33} was 4%, indicating that the $1/\delta$ and e_{33} increase proportionally. Therefore, in PZT-based perovskite piezoelectric materials, the piezoelectric properties can be predicted using the B-site atom position alone, without needing to consider the doping site. In addition, the change in piezoelectric properties following the changes in the relative B-site atom position and quadratic elongation indicates that the B-site atom position plays a key role in determining the piezoelectric properties of PZT.

Consequently, the linear correlation between each parameter proves that the relative B-site atom position and quadratic elongation of the rhombohedral PZT oxygen octahedron can be used as parameters to obtain accurate predictions of the piezoelectric properties without needing to resort to high-cost calculation methods such as DFPT.

4. Conclusion

The piezoelectric charge constants for rhombohedral PZT and PSZT were calculated using DFPT. We found that the rhombohedral structure is more stable than the orthorhombic in the Zr-rich region and that the piezoelectric charge constant (e_{ij}) increases as the composition approaches the MPB region ($x = 0.44$). In the MPB region, the values of e_{33} , e_{15} , e_{22} all increased in response to Sr doping; on the contrary, no significant changes were detected for e_{31} . The calculated values of e_{33} for PZT ($x = 0.44$) and PSZT were verified experimentally using the conventional solid-state method, with the calculated e_{33} and experimental e_{33} values exhibiting similar increases in response to Sr doping. The relative B-site atom position(δ) and the quadratic elongation(λ) in the oxygen octahedron exhibited close correlations with the piezoelectric charge constant, irrespective of the doping site. Therefore, our analyses indicate that the value of e_{ij} for various compositions of rhombohedral-phase PZT can be predicted using the relative B-site atom position and quadratic elongation after structural optimization as opposed to high-cost DFPT tensor calculations. Therefore, the relative B-site atom position and quadratic elongation can be utilized as descriptors in high-

Table 4. Normalized data of DFPT calculation and experimental results for $PbZr_{0.56}Ti_{0.44}O_3$ (PZT,56/44) and $Pb_{0.94}Sr_{0.06}Zr_{0.56}Ti_{0.44}O_3$ (PSZT,6/56/44) composition.

Method	Value	PZT(56/44)	PSZT(6/56/44)
DFPT	e_{33} (C/m ²)	2.72	2.83
	Normalized e_{33}	1.00	1.04
	$1/\delta$ (Å)	5.07	5.31
	Normalized $1/\delta$	1.00	1.05
Experiment	e_{33} (C/m ²)	8.72	14.6
	Normalized e_{33}	1.00	1.67
	d_{33} (pC/N)	156	346
	Normalized d_{33}	1.00	2.22

* Each result was normalized with respect to the value at PZT(56/44)

throughput screening (HTS) to identify new perovskite piezoelectric materials.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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