

Electromechanical Properties of $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$ Perovskite Solid Solutions from First-Principles Calculations

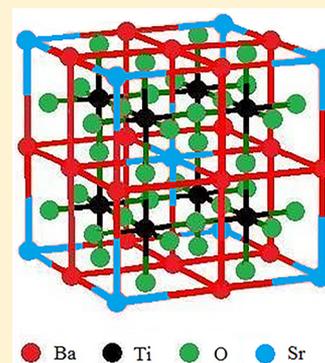
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ABSTRACT: An enhancement of the piezoelectric properties of lead-free materials, which allow conversion of mechanical energy into electricity, is a task of great importance and interest. Results of first-principles calculations of piezoelectric/electromechanical properties of the $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$ (BSTO) ferroelectric solid solution with a perovskite structure are presented and discussed. Calculations are performed within the linear combination of atomic orbitals (LCAO) approximation and periodic-boundary conditions, using the advanced hybrid functionals of density functional theory (DFT). A supercell model allows the investigation of multiple chemical compositions x . In particular, three BSTO solid solutions with $x = 0, 0.125, 0.25$ are considered within the experimental stability domain of the ferroelectric tetragonal phase of the solid solution ($x < 0.3$). The configurational disorder with $x = 0.25$ composition is also investigated explicitly considering the seven possible atomic configurations corresponding to this composition. It is predicted that Sr-doping of BaTiO_3 makes it mechanically harder and enhances its electromechanical/piezoelectric properties, which are important for relevant applications.



INTRODUCTION

In recent years, there has been an enormous interest in the efficient capture of environmental energy through the use of energy-harvesting devices that transform mechanical energy into electricity (refs 1 and 2 and references therein). In this respect, one of the most efficient methods of transformation is to utilize the piezoelectricity of nanoferroelectrics.^{3–5} In particular, ABO_3 -type perovskite ferroelectrics are used for many technological applications and therefore have been intensively studied for a long time.^{6–8} Lead-free BaTiO_3 (BTO) and SrTiO_3 (STO, an incipient ferroelectric) perovskites are among the most studied members of this class of materials.

The rapid progress of computational methods, on the one hand, and efficient parallel performance of modern computer architectures, on the other hand, nowadays allow us to calculate the elastic and piezoelectric properties of perovskites based on a very accurate *ab initio* (first-principles) approach. Indeed, several calculations of the piezoelectric properties of BTO crystals have recently been reported. In particular, Khalal et al.⁹ and Meng et al.¹⁰ studied the elastic and piezoelectric properties of BTO in the tetragonal phase whereas Mahmoud et al.¹¹ calculated the piezoelectric, dielectric, elastic, and photoelastic properties of BTO in its low-temperature rhombohedral phase.

From a structural point of view, both BTO and STO exhibit a cubic (paraelectric) phase at high temperature, where each Ti ion is octahedrally coordinated to six oxygen ions. This structure belongs to a centrosymmetric space group, $Pm\bar{3}m$

(SG 221), and therefore cannot reveal ferro and piezoelectricity, which are specific properties of noncentrosymmetric lattices. However, upon cooling, Ti ions are displaced along one of the cube main axes, which leads to a series of phase transitions. While STO undergoes a phase transition from the paraelectric cubic phase (SG 221) to another paraelectric tetragonal phase ($I4/mcm$, SG 140) at 105 K (ref 12), BTO undergoes three consecutive ferroelectric transitions: at 393 K, the crystalline symmetry reduces from cubic (SG 221) to tetragonal ($P4mm$, SG 99), then to orthorhombic ($Amm2$, SG 38) at 278 K and, last, to rhombohedral ($R3m$, SG 160) below 183 K (ref 11).

In this study, we focus our attention on the tetragonal (room temperature) ferroelectric BTO phase, which is the most interesting for technological applications.⁶ An enhancement of the piezoelectric, ferroelectric, and dielectric properties of perovskites can be achieved by engineering a lattice strain.^{8,13} Partial replacement of atoms is one of the effective ways to produce lattice strain. Solid solutions near a morphotropic phase boundary, separating two crystal symmetries, are known to exhibit anomalously high piezoelectric and dielectric responses.¹⁴ BTO is commonly doped by various impurity atoms, in order to improve its dielectric and electromechanical properties. In particular, a series of experimental papers was devoted to $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$ (BSTO) solid solutions with a

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perovskite structure (refs 6, 7, and 15 and references therein) with a focus on dielectric properties. An artificial superlattice constructed from the two perovskites (e.g., BTO and STO) can also be applied to enhance piezoelectric and dielectric responses.^{16,17}

The aim of this paper is the study of the electromechanical/piezoelectric properties of the tetragonal BSTO solid solution by means of first-principles calculations. The elastic and piezoelectric constants are computed, which show that the Sr-doping of BTO enhances its electromechanical properties. The advantage of the $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$ solid solution, in contrast to BTO, is that the structural phase transition, which occurs in BTO at 5 °C, shifts to lower temperatures as x increases.¹⁸ As the result, there is no phase transition in BSTO in a wide temperature range around room temperature, which leads to a temperature-stable piezoelectric property that is important for practical applications.

■ COMPUTATIONAL DETAILS

First-principles calculations are performed with the CRYSTAL14 code for quantum-chemical ab initio simulations,^{19,20} which computes elastic and piezoelectric (direct and converse) tensors within a fully automated procedure. The PBE0 hybrid DFT-HF exchange-correlation functional²¹ is used, which already proved reliable for piezoelectric properties.^{11,12} Hay and Wadt effective small core pseudopotentials^{22–24} are used for Ba, Ti, and Sr atoms, with $5s^2$, $5p^6$, $6s^2$ valence electrons for Ba; $3s^2$, $3p^6$, $3d^2$, $4s^2$ for Ti; and $4s^2$, $4p^6$, $5s^2$ for Sr. The oxygen atoms are described by an all-electron basis set. The basis sets for Ba, Sr, and Ti are taken from ref 25, where these were optimized for BTO and STO crystals, while the basis set for oxygen is taken from ref 26. All basis sets are available on the CRYSTAL Web site.²⁷

In order to define an optimal set up for the calculations on the BSTO solid solution, we started from the calculation of the lattice constants, electronic properties, and elastic and piezoelectric constants for several phases of BTO and STO crystals and compared our results with both available experimental data and previous results of ab initio calculations (see below). Additionally, we performed calculations of lattice constants, band gap, bulk modulus, elastic, and piezoelectric constants for the tetragonal BTO phase. Calculations have been performed with three hybrid functionals (see ref 20). The first one is the PBE0 functional, which combines the PBE exchange functional with 25% of the Hartree–Fock (HF) exchange and the PBE correlation functional. In the second, the exchange part in the PBE0 functional was replaced by the WCGGA (Wu–Cohen) exchange functional²⁸ with the same HF fractions (25%). This functional is designated in this paper as the WC functional. Lastly, the third functional, B1WC, combines the WCGGA exchange functional with 16% HF and the PWGGA (Perdew–Wang) correlation functional.

Our computational setup has been calibrated in terms of accuracy and computational time. In particular, the five thresholds governing the truncation of infinite lattice sums in the two-electron integral evaluation have been set to 8, 8, 8, 8, 16, and a regular Monkhorst–Pack mesh of points in reciprocal space has been used, whose shrinking factor has been set to 12 and 6 for bulk and supercell calculations, respectively. These parameters ensure converged results.

A structural model for the BSTO solid solution has been built, which consists of a $2 \times 2 \times 2$ supercell of the tetragonal BTO primitive unit cell. Such the supercell consists of eight

primitive BTO unit cells, and hence, it contains 40 atoms. In the supercell calculations, we have studied $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$ solutions with different compositions (i.e. Sr/Ba ratio), where Ba atoms are progressively replaced by Sr atoms. Thus, the calculations are performed for artificial ordered BSTO superstructures. We have performed calculations for three different Sr concentrations: without substitution ($x = 0.0$; SC0); one Ba atom is replaced with one Sr atom ($x = 0.125$; SC1); two Ba atoms are replaced with two Sr atoms ($x = 0.25$; SC2). For the $x = 0.125$ composition, any of the eight Ba atoms in the cell could be substituted with a Sr atom. We replaced the Ba atom at the origin of the coordinate system—atom with coordinates (0, 0, 0)—to preserve as much symmetry as possible. For the $x = 0.25$ composition, two Ba atoms are replaced with two Sr atoms: the one at the origin and a second one. All seven possible configurations are here considered.

■ RESULTS AND DISCUSSION

Before investigating the mechanical and piezoelectric response of BSTO solid solutions, we have calculated the elastic tensors for all of the four phases of BTO, the piezoelectric (direct and converse) tensors for the three ferroelectric phases of BTO, and the elastic constants for cubic STO. Structural and elastic properties as well as the band gaps of the cubic phases of BTO and STO are given in Table 1, where they are also compared

Table 1. Lattice Constant a , Band Gap E_g , Elastic Constants C_{ij} , and Bulk Modulus B for the Cubic Structures of BTO and STO

	this study	PBE0 ^c	expt
BTO, SG 221			
a , Å	3.993	3.98, ¹¹ 3.99 ²⁹	3.996 ³⁰
E_g^a , eV	3.97	4.0 ^{11,29}	3.2 ³¹
C_{11} , GPa	328.5		206; ²⁵ 255 ³²
C_{12} , GPa	120.5		140; ²⁵ 82 ³²
C_{44} , GPa	147.7		126; ²⁵ 108 ³²
B , GPa	189.8	194, ¹¹ 189 ²⁹	162, ^{11,29} 195 ¹¹
STO, SG 221			
a , Å	3.901	3.91 ³³	3.905 ³⁴
E_g^b , eV	4.16 (4.47)	3.9 (4.2) ³³	3.25 (3.75) ³⁵
C_{11} , GPa	367.6	370 ¹²	317.6 ³⁶
C_{12} , GPa	113.6	114 ¹²	102.5 ³⁶
C_{44} , GPa	134.2	133 ¹²	123.5 ³⁶
B , GPa	198.2	199; ¹² 195 ³³	179 ³⁷

^aThe experimental band gap energy³¹ for BTO corresponds to a temperature around 130 °C, i.e. above the phase transition temperature. ^bIndirect (direct) band gap. ^cPBE0—earlier calculated data.

with existing experimental data and with previous theoretical investigations performed with the same PBE0 functional. The cubic crystal system exhibits the simplest form of the symmetric elastic tensor, with only three independent constants (C_{11} , C_{12} , C_{44}). The agreement of our calculated values with previous theoretical investigations is remarkable, which confirms the accuracy of our computational setup. As expected, when comparing the calculated values for the elastic constants of these two high-temperature cubic phases with the experimental counterparts, they are found to be systematically larger, because thermal expansion was neglected in the calculations at this stage. Calculations for both cubic phases, BTO and STO, give indirect band gaps (Table 1). While for BTO the difference

between indirect and direct values of band gap is very small (~ 30 meV), for STO this discrepancy is calculated significantly larger (~ 0.3 eV). The experimental difference in the direct and indirect band gap energies for a cubic STO is 0.5 eV (ref 35), slightly larger than the calculated value. The absolute values of the calculated band gap energies are larger by $\sim 25\%$ than the experimental ones, which is much better than typical underestimate known for GGA-type functionals.²⁵

The results of our BTO calculations in the tetragonal phase are given in Table 2 (structural properties and band gap) and

Table 2. Structural Properties and Band Gap of BTO for Tetragonal Phase (SG 99)^a

	PBE0	WC	B1WC	expt
	lattice constants, Å			
$a = b$	3.971	3.950	3.962	3.992 ³⁰
c	4.131	4.032	4.050	4.036 ³⁰
c/a	1.040	1.021	1.022	1.011
	band gap, eV			
E_g^b	4.08	4.07	3.26	3.38 (3.27) ³¹

^aData are calculated using PBE0, Wu–Cohen (WC), and B1WC functionals. ^bExperimental values³¹ at room temperature for light polarized parallel (and perpendicular) to the ferroelectric c axis.

Table 3 (elastic and piezoelectric constants), along with available experimental values. As one can see, the PBE0 functional gives a better agreement with experimental data for the $a = b$ lattice constant, while the WC and B1WC functionals give a better agreement for the c constant and tetragonal ratio c/a .

The computations of BTO in the tetragonal phase predict an indirect band gap, which is very close for the PBE0 and WC functionals, 4.08 eV (cf. 4.1 eV in ref 29 and 4.2 eV in ref 11), are both larger than the experimental values³¹ (see Table 2). On the other hand, the band gap, calculated by means of the B1WC functional, is very close to experimental data. The same is true for the cubic phase of BTO and STO—the B1WC band gap is closer to the experiments than that for the PBE0

functional. Thus, the B1WC functional is well suited for the band gap calculations. Note also that the band gap likely depends more on the correlation part of the functional rather than on the exchange one. Note that the calculations for the tetragonal STO phase (SG 140) confirm the results of previous⁴¹ hybrid calculations on the direct nature of the band gap as lowest in energy (unlike the STO cubic phase). The PBE0 calculations show that the band gap increases by 11 meV in the STO tetragonal phase as compared to the cubic phase (cf. 12 meV in ref 41).

The elastic tensor for the tetragonal phase of BTO (SG 99) has six independent constants, whereas direct and converse piezoelectric tensors only have three independent components. The elastic and piezoelectric constants can be theoretically given as sums of purely electronic “clamped-ion” and nuclear (atomic) relaxation contributions. The results of the calculations for both the electronic contribution (“Clamped”) and the total values (“Total”), including nuclear relaxation, are presented separately in Table 3. Almost for all elastic constants (except for C_{12}) the electronic contribution is larger than the total one, since the nuclear relaxation contributions for the elastic constants are negative. If the atoms are not allowed to relax (“clamped-ion” case), the imposing of deformation shows more rigid material compared to the opposite case when atoms relax, and thus, the internal stress is reduced. As the result, we obtained larger elastic constants for the electronic term.

From Table 3, it is clearly seen that the origin of the piezoelectricity in BTO arises from the nuclear relaxation whereas the electronic “clamped-ion” contribution is rather small.

The calculated PBE0 bulk modulus for BTO in the tetragonal phase is 113 GPa. Previously calculated values (with the same functional) are 117 GPa (ref 11) and 112 GPa (ref 29). For both cubic and tetragonal phases, we obtained a good agreement with previous theoretical results and experimental data for the lattice constants and elastic properties. A rather large discrepancy is however observed between calculated and experimental values of the piezoelectric constants. Note, however, a broad dispersion of relevant

Table 3. Bulk Modulus (B) as Well as Elastic and Piezoelectric Constants of BTO for Tetragonal Phase (SG 99)

	PBE0 ^b		WC ^b		B1WC ^b		expt ^a
	total	clamped	total	clamped	total	clamped	
	elastic constants, GPa						
$C_{11} = C_{22}$	302.7	314.1	337.5	346.1	325.1	333.4	222; 275
C_{12}	120.8	118.1	127.8	126.9	124.4	122.8	134; 179
$C_{13} = C_{23}$	88.4	115.0	98.0	123.2	96.1	118.7	111; 152
C_{33}	118.6	309.3	166.4	346.9	159.8	333.8	151; 165
$C_{44} = C_{55}$	89.8	129.3	116.6	142.1	110.4	135.5	61.1; 54.4
C_{66}	141.2	141.2	149.5	149.5	142.8	142.8	134; 113
B	112.6	181.5	143.3	198.4	138.7	191.2	134; ¹¹ 141 ¹¹
	direct piezoelectric constants, C/m ²						
$e_{15} = e_{24}$	10.116	0.199	9.205	0.148	9.354	0.152	34.2 ³⁸
$e_{31} = e_{32}$	0.686	0.274	0.804	0.230	0.763	0.233	-0.7 ³⁸
e_{33}	3.293	-0.471	4.357	-0.399	4.213	-0.403	6.7 ³⁸
	converse piezoelectric constants, pC/N = pm/V						
$d_{15} = d_{24}$	112.674	1.536	78.935	1.041	84.699	1.120	392; ³⁹ 564 ⁴⁰
$d_{31} = d_{32}$	-6.062	1.296	-5.038	0.964	-5.296	1.013	-34.5; ³⁹ -33.4 ⁴⁰
d_{33}	36.811	-2.485	32.126	-1.835	32.733	-1.928	85.6; ³⁹ 90 ⁴⁰

^aRef 32 and references there. ^bData are calculated using PBE0, Wu–Cohen (WC), and B1WC functionals. Purely electronic (“Clamped”) contribution and total values of constants (“Total”), including nuclear relaxation contribution, are presented.

experimental data. Therefore, we focus mainly on the trends in electromechanical property changes rather than in absolute values. The results of our calculations show that the PBE0 functional provides a slightly better description of piezoelectric properties, and further, in tables, we present only the results of PBE0 calculations.

The calculated Mulliken atomic charges for BTO in cubic and tetragonal phases are presented in Table 4. Our computed

Table 4. Mulliken Atomic Charge (e) for Cubic (SG 221) and Tetragonal (SG 99) BTO Phases

	Ba	Ti	O1	O2	O3
SG 221	1.797	2.392	-1.396	-1.396	-1.396
SG 99	1.801	2.367	-1.361	-1.403	-1.403

charges coincide with those in ref 29, calculated for the cubic phase. These charges indicate a considerable covalent contribution to the Ti–O chemical bonds, and a small variation in charges of nonequivalent O ions in the tetragonal phase.

As mentioned above, to model the BSTO solid solution, we used 40 atom supercells. Any of the eight Ba atoms in such supercells could be replaced by Sr atoms. When no Ba atoms are substituted, the $x = 0$ chemical composition is called SC0. When only one Ba atom is replaced (SC1), the Sr atom is put at the origin of the coordinates, to maximize the residual point-symmetry. When two Ba atoms are replaced (SC2), the first Sr is placed at the origin, and the second Sr replaces one of the seven remaining Ba atoms. By default, we consider the second atom with fractional coordinates (0.5, 0.5, 0.5) in the supercell. We discuss below the effect of configurational disorder.

The results of our calculations for the elastic and piezoelectric properties of the BSTO solid solution for $x = 0, 0.125,$ and 0.25 are reported in Table 5, where they are compared with those of the BTO tetragonal bulk crystal (with five atoms in the unit cell). First of all, we notice that all elastic and most of piezoelectric constants of the $x = 0$ case (SC0) coincide with

Table 5. Elastic and Piezoelectric Constants, Calculated for Perfect Bulk Crystal BTO (SG 99) and Three Supercells^a

	bulk	SC0	SC1	SC2
elastic constants, GPa				
$C_{11} = C_{22}$	302.7	302.6	307.3	311.5
C_{12}	120.8	120.8	120.4	120.2
$C_{13} = C_{23}$	88.4	88.5	89.3	90.5
C_{33}	118.6	118.3	123.5	130.3
$C_{44} = C_{55}$	89.8	89.8	92.6	95.8
C_{66}	141.2	141.2	133.4	137.3
B	112.6	112.5	116.1	120.7
direct piezoelectric constants, C/m ²				
$e_{15} = e_{24}$	10.116	-2.101	-2.397	-2.717
$e_{31} = e_{32}$	0.686	0.679	0.740	0.839
e_{33}	3.293	3.294	3.719	4.270
converse piezoelectric constants, pC/N = pm/V				
$d_{15} = d_{24}$	112.674	-23.381	-25.895	-28.350
$d_{31} = d_{32}$	-6.062	-6.124	-6.522	-6.947
d_{33}	36.811	36.987	39.546	42.404

^a“Bulk”—perfect crystal, SC0—without substitution of atoms, SC1—one Ba atom (at the coordinate origin) is replaced with an Sr atom, SC2—two Ba atoms (at the coordinate origin and with fractional coordinates (0.5, 0.5, 0.5)) are replaced with two Sr atoms. B —bulk modulus.

those computed for the bulk BTO phase. However, this is not the case for the piezoelectric constants $e_{15} = e_{24}$ and $d_{15} = d_{24}$, which show a large discrepancy. Unlike these two calculations, which are expected to provide exactly the same results for a low-temperature stable phase, this is not guaranteed when a high-temperature phase is studied at 0 K (as performed in the standard DFT calculations). Indeed, in this case, a mechanical lattice instability occurs (related to presence of the vibrational modes with imaginary frequencies in the k -point other than the Γ in the phonon Brillouin zone) when the fourth strain component (according to Voigt's notation) is applied to the lattice, which is a shear strain involving lattice angle deformations and a drastic symmetry reduction (from eight to two operations). This analysis is confirmed by purely electronic “clamped-ion” calculations without nuclear relaxation, which provide the same piezoelectric constants both for the unit cell (bulk) and the supercell (SC0) calculations.

Let us now analyze the effect of an increased concentration of Sr-doping on the elastic and piezoelectric properties of the BSTO solid solution as a function of concentration x (Table 5). The main elastic constants of the system increase as a function of Sr concentration, which makes the system more rigid. Interestingly, a clear systematic (almost linear) increase of the piezoelectric response is also observed. Indeed, the absolute values of all piezoelectric constants increase with the Sr content. An enhancement of the piezoelectric response by 13–30% is documented for the $x = 0.25$ composition. The considerable effect of the substitution of Ba with Sr atoms on the electronic polarization properties is also observed in the atomic charges. The Mulliken atomic charges of Sr atoms are $1.88 e$, compared to $1.80 e$ for Ba atoms in the unperturbed BTO, which corresponds to a more ionic bonding. At the same time, the atomic charges of Ba and Ti atoms in the solid solution are practically unchanged.

We studied the limited Sr concentration range of $x = 0–0.25$ because, as known from experimental data,^{18,42,43} at room temperature and around $x \approx 0.3$, the BSTO solid solution undergoes the ferroelectric to paraelectric transition, from the tetragonal to cubic phase. For higher Sr concentrations, the solid solution thus exhibits a cubic symmetry without piezoelectric properties.

When studying the solid solution, one has to take into account the configurational disorder of the system. For a given structural model (here, a supercell containing 40 atoms), many independent structural configurations could exist for a given chemical composition. For the $x = 0.25$ composition, two of the eight Ba atoms are substituted with Sr atoms. The first Ba atom, which was replaced by Sr atom, was located at the origin of the coordinates. In Table 6, we report selected structural, elastic, and piezoelectric features of the seven possible configurations obtained by substituting, one at a time, the other seven Ba atoms by Sr. Our supercell contains two pairs of symmetry-related Ba atoms: (0.5, 0, 0.5)–(0, 0.5, 0.5) (marked with an asterisk in Table 6) and (0.5, 0, 0)–(0, 0.5, 0) (marked with two asterisks). If one of them is replaced with a Sr atom, the equivalence is lost in both pairs, and the symmetry of the system reduces from tetragonal down to orthorhombic. For example, when atoms (0, 0, 0) and (0.5, 0.5, 0.5) are replaced, the symmetry is still tetragonal, which implies that $a = b \neq c$ and that there are equivalent elements in the elastic and piezoelectric tensors, but when atoms (0, 0, 0) and (0.5, 0, 0.5) are replaced, the symmetry becomes orthorhombic with $a \neq b$

Table 6. Lattice Constants and Selected Elastic and Piezoelectric Constants of the BSTO Solid Solution for the $x = 0.25$ Chemical Composition, As Calculated for All Possible Atomic Configurations

SC2 (replacement of 2 Ba atoms: with coordinates (0, 0, 0) and another one) ⁴²							
	xyz	xy0	0yz*	x0z*	0y0**	x00**	00z
lattice constants, Å							
<i>a</i>	7.909	7.913	7.907	7.910	7.9080	7.9079	7.910
<i>b</i>	= <i>a</i>	= <i>a</i>	7.910	7.907	7.9079	7.9080	= <i>a</i>
<i>c</i>	8.136	8.128	8.142	8.142	8.142	8.142	8.132
elastic constants, GPa							
<i>C</i> ₁₁	311.5	312.7	313.326	311.932	312.079	313.315	313.0
<i>C</i> ₁₂	120.2	121.7	119.068	119.063	119.794	119.785	119.7
<i>C</i> ₁₃	90.5	89.4	89.334	91.345	90.326	90.776	90.2
<i>C</i> ₂₂	= <i>C</i> ₁₁	= <i>C</i> ₁₁	311.901	313.295	313.319	312.006	= <i>C</i> ₁₁
<i>C</i> ₂₃	= <i>C</i> ₁₃	= <i>C</i> ₁₃	91.266	89.299	90.876	90.220	= <i>C</i> ₁₃
<i>C</i> ₃₃	130.3	134.6	130.935	130.956	129.911	129.679	135.6
direct piezoelectric constants, C/m ²							
<i>e</i> ₃₁	0.839	0.802	0.811	0.836	0.793	0.759	0.817
<i>e</i> ₃₂	= <i>e</i> ₃₁	= <i>e</i> ₃₁	0.838	0.812	0.755	0.798	= <i>e</i> ₃₁
<i>e</i> ₃₃	4.270	4.190	4.206	4.205	4.124	4.131	4.199
converse piezoelectric constants, pC/N = pm/V							
<i>d</i> ₃₁	-6.947	-6.278	-6.599	-6.943	-6.731	-7.009	-6.313
<i>d</i> ₃₂	= <i>d</i> ₃₁	= <i>d</i> ₃₁	-6.923	-6.580	-7.002	-6.734	= <i>d</i> ₃₁
<i>d</i> ₃₃	42.404	39.469	41.451	41.439	41.323	41.444	39.356

⁴²Second Ba atoms, which are replaced with Sr atoms, are specified in the title of the columns (the first is atom at the coordinate origin). Designations of atoms: xyz—atom with fractional coordinates (0.5, 0.5, 0.5), xy0—with coordinates (0.5, 0.5, 0), etc.

≠ *c* and without equivalence among elastic and piezoelectric constants.

The results, reported in Table 6, clearly demonstrate that in this case, the configurational disorder is only marginally affecting the average properties of the solid solution. The elastic constants are almost independent of the particular selected configuration with differences among configurations being less than 4%. Most piezoelectric coefficients also show a little dispersion as the function of different atomic configurations. Here it is necessary to mention that the differences of the electronic energies for these configurations are so small (<0.006 eV) that no reliable conclusion could be drawn about relative configuration stabilities. More detailed analysis based on the Gibbs free energies would be necessary, which is beyond the scope of the present study.

Note, in conclusion, that it was predicted⁴⁴ for the ordered BSTO structure that it is thermodynamically unstable with respect to the heterophase mixture BTO and STO, i.e. spinodal decomposition of the solid solution should occur (ordered solid solutions were discussed in refs 45 and 46). As a consequence, at relative small concentration of Sr, clusters of STO could arise in a predominantly BTO matrix. However, this process could be very slow due to a very slow diffusion rate of cations in solid solution, especially at room temperature.

CONCLUSIONS

We performed the first theoretical study of the electromechanical/piezoelectric properties of the tetragonal (room temperature) Ba_(1-x)Sr_xTiO₃ solid solution by means of first-principles calculations based on advanced hybrid functionals of density functional theory. The supercell model was used for calculation of electromechanical properties of perovskite solid solutions. Three compositions ($x = 0$, $x = 0.125$, and $x = 0.25$) have been considered within the range where the solid solution is experimentally known to exhibit a ferroelectric behavior.

The present calculations clearly predict that the BaTiO₃ perovskite becomes mechanically harder when Ba atoms are progressively substituted with Sr atoms. Interestingly, a significant and almost linear enhancement of the piezoelectric properties of BaTiO₃ is predicted upon substitution of Ba with Sr atoms. Indeed, the *e*₃₃ direct piezoelectric coefficient is found to increase by ~30% for $x = 0.25$. Our calculations revealed that the nuclear relaxation rather than the electronic term contributes mainly to the BTO and BSTO piezoelectricity. On the other hand, the configurational disorder marginally affects the computed mechanical and piezoelectric properties of the BSTO solid solution. The study of other dopants, e.g. Ca, would be of interest.

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Notes

The authors declare no competing financial interest.

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