

## A lead-free high- $T_C$ ferroelectric $\text{BaTi}_2\text{O}_5$ : A first-principles study

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Previous experimental indications of ferroelectricity with Curie temperature ( $T_C$ ) of 747 K in  $\text{BaTi}_2\text{O}_5$  are confirmed through assessment of its structural stability and estimation of its spontaneous polarization using first-principles density functional theory calculations. The present work establishes that the polarization is observed along  $b$  axis only and determines its structural origin with calculations of the Born effective charges. We find its piezoelectric response is comparable to that of  $\text{PbTiO}_3$ , which with its high  $T_C$  and nonperovskite structure should open up possibilities for new lead-free ferroelectric materials. © 2004 American Institute of Physics.  
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The technologically most important piezoelectric material is  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  (PZT). It is used extensively in sensor-actuator applications. In recent years, a significant effort has been being directed toward the design of a new ferroelectric or a piezoelectric material that is lead-free, as the toxicity of Pb poses serious environmental problems. Some of the possibilities include chemical substitution of different elements for A- and B-site cations in the well-known perovskite ferroelectric oxides, such as  $\text{BaTiO}_3$  ( $T_C=403$  K). However, since the host material does not have a Curie temperature ( $T_C$ ) comparable to that of  $\text{PbTiO}_3$  ( $T_C=760$  K), it has proven difficult to find a system with a higher  $T_C$ . For practical applications this is desirable for  $T$ -independent properties at room temperature. Recently, another avenue was pursued by considering a solution with different proportion of the two binary oxides BaO and  $\text{TiO}_2$ . Whereas the perovskite  $\text{BaTiO}_3$ , for example, is a 1:1 solution, other proportions allow exploration of materials with nonperovskite structures, while maintaining the basic octahedral structure of  $\text{TiO}_2$ . Naturally, the linkage between the oxygen octahedra is altered. Here we explore a solution of BaO and  $\text{TiO}_2$  in 1:2 proportion, namely  $\text{BaTi}_2\text{O}_5$ . While  $\text{BaTi}_2\text{O}_5$  has been noted previously as a part of the BaO– $\text{TiO}_2$  phase diagram,<sup>1,2</sup> only recently was it probed experimentally for its potential as a high-temperature ferroelectric material.<sup>3–6</sup>

$\text{BaTi}_2\text{O}_5$  was first synthesized by Statton.<sup>7</sup> It was believed to be a stable compound<sup>2</sup> but it was suggested to be metastable.<sup>1</sup> The crystal structure of  $\text{BaTi}_2\text{O}_5$  was analyzed by Harrison<sup>8</sup> with the Weissenberg camera method using a single crystal prepared by cooling a melt of composition  $\text{BaCO}_3:\text{TiO}_2=37.3:62.7$  in molar ratio.<sup>2</sup>  $\text{BaTi}_2\text{O}_5$  was found to have a monoclinic cell [ $a=16.892(13)$  Å,  $b=3.930(1)$  Å,  $c=9.410(4)$  Å,  $\beta=103^\circ$ ] with the space

group  $C2/m$ . The  $R$  value of this analysis was about 20%. Tillmanns<sup>9</sup> synthesized a single crystal of  $\text{BaTi}_2\text{O}_5$  by rapid solidification from a melt with a composition of  $\text{BaCO}_3:\text{TiO}_2=40:60$  in molar ratio, and the crystal structure was refined using the data collected with a four-cycle x-ray diffractometer. This resulted in a much better fit as evidenced by the  $R2$  and  $R1$  values of 3.1% and 2.6%, respectively.

Recently, some of the authors synthesized  $\text{BaTi}_2\text{O}_5$  single crystal (of rectangular shape with size of about  $2 \times 1 \times 1$  mm) by a floating zone method and characterized its dielectric properties.<sup>3,4</sup> Dielectric permittivity was measured perpendicular to (100), (010), or (001) planes using ac impedance spectroscopy and  $P$ - $E$  (polarization-electric field) hysteresis loops were determined. The near-divergence of dielectric constant ( $\gamma\gamma$  component) clearly indicated a Curie temperature of 747 K, slightly higher than the  $T_C$  of 703 K found in slightly Ti-rich single crystals.<sup>5</sup> The  $P$ - $E$  measurements showed a polarization of  $1.92 \mu\text{C}/\text{m}^2$  along  $b$  axis at room temperature<sup>4</sup> confirming ferroelectricity below  $T_C$ . As the ferroelectricity is not expected from the centrosymmetric structure of the space group  $C2/m$ , the crystal structure was refined with the model of  $C2$  (removal of the mirror plane perpendicular to the  $b$  axis<sup>5,6</sup> present in  $C2/m$ ) and an  $R$  value of 4.6%<sup>6</sup> was found. The switching field necessary for reversing the polarization of 0.244 MV/m is comparable to that in  $\text{BaTiO}_3$ . In the  $P$ - $E$  hysteresis curve it was found that the polarization does not saturate and this will be discussed in the following.

To confirm and understand the above-mentioned results, we obtain the energetics, polarization, and related properties of  $\text{BaTi}_2\text{O}_5$  using first-principles calculations based on density functional theory. These calculations are performed using *ab initio* ultrasoft pseudopotential<sup>10,11</sup> plane wave method with a local density approximation for the exchange-correlation energy of electrons.<sup>12</sup> This methodology has been used with good success in the study of perovskite oxides,<sup>13</sup> particularly in the determination of relative energetics of dif-

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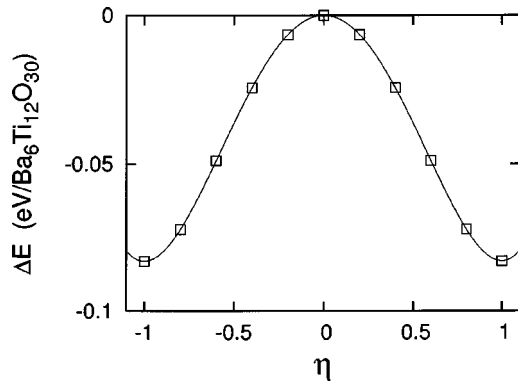


FIG. 1. Energy per  $\text{Ba}_6\text{Ti}_{12}\text{O}_{30}$  cell as a function of the ferroelectric order parameter  $\eta$  relative to the  $C2/m$  structure.  $\eta$  is zero for the undistorted  $C2/m$  structure and unity for the  $C2$  structure with optimized internal coordinates, for intermediate values of  $\eta$  atomic positions have been linearly interpolated. Lattice parameters are kept at the experimental values (Ref. 6).

ferent structures. In our calculations of  $\text{BaTi}_2\text{O}_5$ , we use a  $2 \times 6 \times 2$  Monkhorst–Pack  $k$ -points scheme for Brillouin zone integrations and an energy cutoff of 400 eV on the plane-wave representation of wave functions. Semicore  $p$  states of Ba and Ti have been included in the valence. Structural optimization is performed using conjugate gradient method and Hellmann–Feynman forces on the atoms. Born-effective charges were determined using density functional theory linear response implemented in the ABINIT<sup>14</sup> code and Teter pseudopotentials (semicore core states of Ba and Ti included) with an energy cutoff of 952 eV.

We focus our calculations on two structures of  $\text{BaTi}_2\text{O}_5$ : (a) with the experimentally refined<sup>6</sup> space group  $C2$  (space group 5) and (b) with the centrosymmetric structure with point group  $C2/m$  (space group 12). Maintaining the symmetries of these structures, we obtained the lowest energy structures at the experimental lattice constants (this is a standard practice in the first-principles study of ferroelectrics<sup>15,16</sup> and known to partially correct for the LDA errors in volume). In the study of stability, we use for reference the energies of ground state structures of rocksalt BaO and rutile  $\text{TiO}_2$  obtained using the same calculational parameters.

The theoretical structure of  $\text{BaTi}_2\text{O}_5$  with  $C2$  symmetry agrees very well with the experimental structure.<sup>6</sup> The largest discrepancy in the structural parameters is about 0.02 Å in the position of four symmetry equivalent Ti atoms (which amounts to roughly 1% of Ti–O bond-lengths). All other structural parameters differ by less than a percent of their values determined experimentally. Energy of the ferroelectric  $C2$  structure is 13 meV per  $\text{BaTi}_2\text{O}_5$  formula unit lower than that of the fully optimized structure with  $C2/m$  symmetry, see Fig. 1. This confirms that the ferroelectric structure is indeed lower in energy than the nearest centrosymmetric structure. To get a realistic idea about the stability of compounds based on BaO and  $\text{TiO}_2$ , we compare its energy relative to the binary compounds  $\Delta E_{\text{form}}[(\text{BaO})_x(\text{TiO}_2)_{1-x}] = E[\text{Ba}_x\text{Ti}_{1-x}\text{O}_{2-x}] - xE[\text{BaO}] - (1-x)E[\text{TiO}_2]$ . Our calculations yield for  $\text{BaTi}_2\text{O}_5$ :  $\Delta E_{\text{form}}(\text{Ba}_{1/3}\text{Ti}_{2/3}\text{O}_{5/3}) = -0.498$  eV and for  $\text{BaTiO}_3$ :  $\Delta E_{\text{form}}(\text{Ba}_{1/2}\text{Ti}_{1/2}\text{O}_{3/2}) = -0.756$  eV. This means that  $\text{BaTi}_2\text{O}_5$  is on the line connecting the  $\text{TiO}_2$  and  $\text{BaTiO}_3$  ground states, suggesting that the  $\text{BaTi}_2\text{O}_5$  compound may

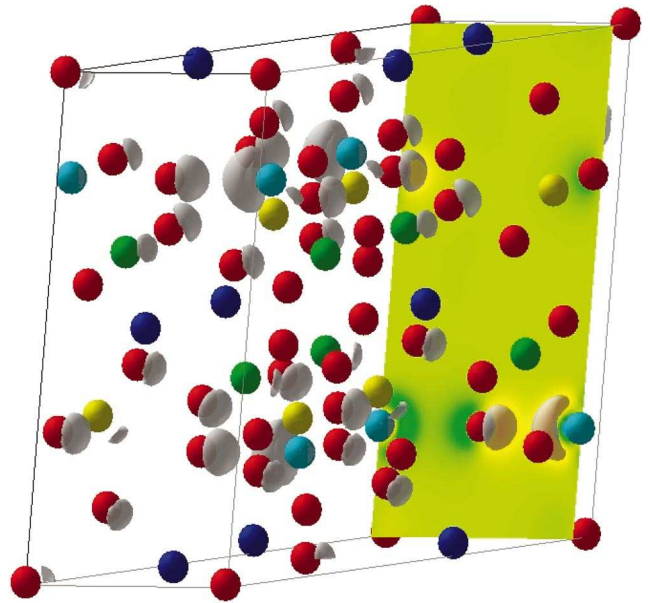


FIG. 2. (Color) Difference in electronic valence charge density between  $C2$  and  $C2/m$   $\text{BaTi}_2\text{O}_5$  with experimental cell parameters. Atoms are represented as colored spheres: Ba (dark blue), O (red), Ti1 (light blue), Ti2 (green), Ti3 (yellow). The isosurface is drawn at  $+0.5 e^- \text{Å}^{-3}$  and the image map, in the plane spanned by the horizontal  $b$  and the vertical  $c$  crystal axes, shows a yellow (dark green) color for excess (depletion) electronic density.

be synthesized only under carefully controlled circumstances such as chemically highly homogeneous starting material.

We further characterized the ferroelectric state through calculation of its macroscopic polarization. We use the Berry phase method,<sup>17</sup> as implemented in VASP.<sup>11,18</sup> The meaningful value of polarization is obtained by removing the ambiguity in this calculation through comparison with values of polarization calculated for the centrosymmetric  $C2/m$  structure. Our calculations yield polarization values along  $b$  axis of 2.0 and 8.7  $\mu\text{C}/\text{cm}^2$  for the experimental and fully relaxed structures, respectively. These are indeed in good agreement with the values determined in the measurement of polarization hysteresis.

The cause for polarization along the  $b$  crystal axis is easily visualized by inspecting the charge density. In Fig. 2 the difference of the electronic valence charge densities  $\rho(C2) - \rho(C2/m)$  is shown. Around Ti atoms excess electrons occur toward the left, and depletion of electronic charge occurs toward the right while for O atoms the reverse holds. Clearly the inhomogeneity occurs exclusively along the  $b$  crystal axis as expected. To determine the structural origin of  $P$ , we compare the paraelectric  $C2/m$  and ferroelectric ( $C2$ ) structures. We find that most of the contribution to  $P$  comes from the four symmetry equivalent Ti-atoms occupying Ti1 site.<sup>6</sup> In fact, based on the effective charges  $Z_i^*$ , listed in Table I, we find that a simple formula  $P = (1/V) \sum_i Z_i^* d_i$ ,  $d_i$  being displacements of an ion  $i$  from the high symmetry sites of  $C2/m$  gives an estimated polarization of about 15  $\mu\text{C}/\text{cm}^2$ , 76% of which is contributed by Ti1 and its neighboring oxygen atoms. The Born effective charge ( $yy$  component) of these two atoms is clearly (Table I) far more anomalous than those of the rest, which confirms their special role in the ferroelectricity of  $\text{BaTi}_2\text{O}_5$ . There are three kinds of Ti sites in  $\text{BaTi}_2\text{O}_5$ . A Ti1 centered octahedron links

TABLE I. Born effective charge tensor  $Z^*$  (atomic units) for each unique atom in  $\text{BaTi}_2\text{O}_5$ . The Cartesian coordinates were defined such that the base centered monoclinic cell parameters  $a$  and  $b$  were aligned with the  $x$  and  $y$  axes, respectively.

Atom	$Z_{xx}^*$	$Z_{yy}^*$	$Z_{zz}^*$	$Z_{xy}^*$	$Z_{yz}^*$	$Z_{zx}^*$
Ba <sub>1</sub>	2.801	2.736	3.050	0.176	-0.184	0.001
Ba <sub>2</sub>	2.842	2.736	3.050	-0.176	-0.189	-0.001
Ba <sub>3</sub>	3.070	2.736	3.199	0.000	0.019	0.000
Ti <sub>1</sub>	5.584	6.115	5.392	0.147	0.059	-0.018
Ti <sub>2</sub>	5.429	4.523	4.460	0.079	0.759	0.029
Ti <sub>3</sub>	4.924	4.988	4.240	0.002	-0.485	-0.109
O <sub>1</sub>	-1.755	-6.780	-1.773	-0.254	0.083	-0.050
O <sub>2</sub>	-3.465	-1.342	-2.806	-0.044	-0.159	-0.097
O <sub>3</sub>	-2.753	-1.371	-3.172	-0.186	-0.827	0.020
O <sub>4</sub>	-2.719	-4.214	-1.195	0.099	0.256	-0.055
O <sub>5</sub>	-2.073	-3.456	-2.192	0.063	0.197	0.026
O <sub>6</sub>	-1.725	-1.347	-3.209	-0.006	-0.333	0.094
O <sub>7</sub>	-5.048	-1.650	-1.779	0.177	0.846	-0.098
O <sub>8</sub>	-1.582	-1.748	-5.303	0.000	-0.315	0.000

with Ti3 and Ti1 centered ones by sharing corners and with Ti2-centered octahedron by sharing an edge. The Ti2 and Ti3 centered octahedra share six and three edges, respectively. This indicates that the off-centering of Ti ions is most favored by the octahedra that share corners rather than edges with neighbors. This is consistent with the strong anisotropy in  $Z^*$  (illustrated in Fig. 3) of the oxygen sites around the Ti1 sites common to the corner sharing octahedra and its anomalously large  $yy$  component. Based on the structure, we find that contributions of Ti2 and Ti3 sites to the polarization are small and partially cancel that of the Ti1 sites (somewhat like a ferroelectric) and this results in a relatively small magnitude of spontaneous polarization in spite of a relatively high  $T_C$ . This is also responsible for the lack of saturation in the  $P$ - $E$  curve and unusual dependence of polarization on temperature found in experiments.<sup>4</sup> The high-frequency dielectric tensor was computed using linear response as  $\epsilon_{xx}, \epsilon_{yy}, \epsilon_{zz}, \epsilon_{xy}, \epsilon_{yz}, \epsilon_{zx} = 5.43, 5.51, 5.13, 0.00, 0.00, 0.02$ .

Calculations of polarization can be used to estimate the piezoelectric constant of  $\text{BaTi}_2\text{O}_5$ . We optimize the internal structure (atomic positions) for crystal unit cells strained along  $b$  axis ( $e_{yy} = 0.01$  and  $-0.01$ ) and subsequently determine their polarization using geometric phase formula. The

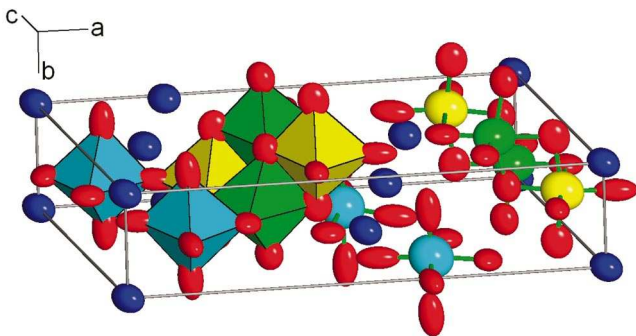


FIG. 3. (Color) Born effective charge tensors displayed as ellipsoids. Atoms are colored as in Fig. 2.

slope of a simple linear fit to calculated polarization as a function of strain gives the piezoelectric constant  $e_{22} = 2.02 \text{ C/m}^2$ . This is comparable with the calculated<sup>19</sup> value of  $e_{33} = 3.3 \text{ C/m}^2$  for  $\text{PbTiO}_3$ . We note that the calculated estimate is for the low temperatures piezoelectric response. Given that the Curie temperature of  $\text{BaTi}_2\text{O}_5$  is rather high, it should be a lower bound on the room temperature piezoelectric response.

As the spontaneous polarization of  $\text{BaTi}_2\text{O}_5$  is relatively small, we expect the switching field needed for reversing it to be small, making it useful for nonvolatile computer memory applications. Its piezoelectric response is found to be quite comparable to that of  $\text{PbTiO}_3$ , and could be improved with possible substitutions for Ba and Ti to be explored further.

In summary, we confirm and explain recently discovered ferroelectricity in  $\text{BaTi}_2\text{O}_5$  using first-principles calculations. While the polarization of  $\text{BaTi}_2\text{O}_5$  is somewhat smaller than the perovskite ferroelectrics, its Curie temperature is high and comparable to that of  $\text{PbTiO}_3$ . Our calculated piezoelectric constant is  $e_{22} = 2.02 \text{ C/m}^2$ . We believe there is room to improve on the properties of  $\text{BaTi}_2\text{O}_5$  and it appears a promising material for future lead-free high-temperature ferroelectrics.

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