The Effect of Symmetry Lowering on the Dielectric Response of BaZrO$_3$

Joseph W. Bennett, Ilya Grinberg, Andrew M. Rappe
The Makineni Theoretical Laboratories, Department of Chemistry
University of Pennsylvania, Philadelphia, PA 19104-6323
(Dated: June 28, 2018)

We use first-principles density functional theory calculations to investigate the dielectric response of BaZrO$_3$ perovskite. A previous study [Arkbarazdeh et al. Phys. Rev. B 72, 205104 (2005)] reported a disagreement between experimental and theoretical low temperature dielectric constant $\epsilon$ for the high symmetry BaZrO$_3$ structure. We show that a fully relaxed 40-atom BaZrO$_3$ structure exhibits O$_6$ octahedral tilting, and $\epsilon$ that agrees with experiment. The change in $\epsilon$ from high-symmetry to low-symmetry structure is due to increased phonon frequencies as well as decreased mode effective charges.

I. INTRODUCTION

Dielectric materials are important for wireless communications technology. These devices require a high dielectric constant, $\epsilon$, and low dielectric loss $\mu$. Barium zirconate, BaZrO$_3$ (BZ), is one of the constituent materials in the electroceramic capacitors used in wireless communications. BZ is a classic ABO$_3$ perovskite dielectric material that is both chemically and mechanically stable.

According to the well-established tolerance factor argument, BZ should have a stable cubic structure. Tolerance factor $t$ is given by

$$ t = \frac{R_{A-O}}{R_{B-O}\sqrt{2}} $$

where $R_{A-O}$ is the sum of A and O ionic radii and $R_{B-O}$ is the sum of B and O ionic radii. Tolerance factor $t < 1$ usually leads to the rotation and expansion of the B-O$_6$ octahedra. Such octahedral rotations often generate a low temperature anti-ferroelectric (AFE) phase (e.g., PbZrO$_3$). If $t > 1$, the B-O$_6$ octahedra are stretched from their preferred B-O bond lengths, promoting B-cation distortions by creating room for the B-cations to move off-center. Therefore, simple perovskites with $t > 1$ are usually ferroelectric (FE). For BZ, the sizes of the Ba and Zr ions ($R_{Ba} = 1.61$ Å and $R_{Zr} = 0.72$ Å), in their O$_{12}$ and O$_6$ cage ($R_0 = 1.35$ Å) exactly balance, leading to $t = 1$, so the cubic structure should have no driving force to deform to a lower symmetry. It also has a stable dielectric constant over a wide range of temperatures.

The total dielectric constant is a sum of two contributions, related to the electronic ($\epsilon_\infty$) and ionic polarizabilities ($\epsilon_\mu$). For most perovskites, $\epsilon_\infty$ is small ($\approx 5$) and $\epsilon_\mu$ is the dominant contribution at low frequency. Recent experimental studies of BZ at low temperature show that $\epsilon$ is 47 at 0 K and some interesting quantum effects are present, though not large in magnitude. Reference 3 also presents a DFT study which calculates $\epsilon$ of BZ to be 65 at 0 K, overestimating experimental results. DFT inaccuracies have been known for some time in describing ferroelectric systems. It is however surprising that DFT is inaccurate for a system as simple as paraelectric BZ.

Here, we show that at low temperatures, the ground state structure of BZ is not accurately represented by a five atom cell. A larger supercell with lower symmetry is energetically favored. The calculated value of $\epsilon$ for this low symmetry structure is in agreement with experimental results. Most importantly, the relationship between the breaking of structural symmetry and the change in dielectric response is elucidated.

II. METHODOLOGY

In this study, two first principles codes are used. An in-house solid state DFT code used in previous studies and the ABINIT software package are used to relax the ionic positions and lattice constants. Local density approximation (LDA) of the exchange correlation functional and a $4 \times 4 \times 4$ Monkhorst-Pack sampling of the Brillouin zone are used for all calculations. All atoms are represented by norm-conserving optimized pseudopotentials. All pseudopotentials generated using the OPIUM code. The calculations are performed with a plane wave cutoff of 50 Ry.

Once the structure is fully relaxed, response function calculations are performed with ABINIT to generate $D_{\alpha\beta}(i,j)$, the mass weighted dynamical matrix.

$$ D_{\alpha\beta}(i,j) = \frac{\partial^2 E}{\sqrt{m_i m_j} \partial r_{i\alpha} \partial r_{j\beta}}. $$

Once normalized, each eigenvalue is $\nu_i^2$, the frequency squared of a normalized eigenvector $a_{\mu_i}^\alpha$. Born effective charge tensors, $Z_{i\alpha\beta}^*$ are also calculated for each atom. Each mode $\mu$ has a mode effective charge, $Z_{\mu\alpha}$, defined as

$$ Z_{\mu\alpha} = \sum_{i\beta} \frac{Z_{i\alpha\beta}^*(a_{\mu_i}^\alpha)_{i\beta}}{m_i^{1/2}}, $$

Contributions to the dielectric response arise only from the IR active modes. These modes have a non-zero
TABLE I: Forty-atom BZ phonon data for IR active modes in the high-symmetry cubic structure. Frequencies are in cm$^{-1}$, mode effective charges, $Z^*_{\mu\alpha}$, are in electrons. The contributions to the $\epsilon$ are calculated in SI units. Also reported are the motions which create the IR active mode.

| $\omega$ | $Z^*_{\mu\alpha}$ | Motion |
|---------|------------------|--------|
| 96      | 2.1              | Ba,Zr-O|
| 193     | 2.8              | 0$_6$  |
| 513     | 2.8              | 0$_6$  |

$Z^*_{\mu\alpha}$, and are used to calculate $\epsilon_{\mu\alpha}$, the contribution to the dielectric constant from mode $\mu$ [15] as

$$\epsilon_{\mu\alpha\beta} = \frac{Z^*_{\mu\alpha}Z^*_{\mu\beta}}{4\pi^2\epsilon_0V\nu^2_{\mu}}.$$ (4)

where the total ionic contribution is

$$\epsilon_{\mu} = \frac{1}{3} \sum_{\alpha} \epsilon_{\mu\alpha\alpha}.$$ (5)

III. RESULTS AND DISCUSSION

A. Five-Atom BZ calculations

The ground state five atom BaZrO$_3$ is a cubic perovskite structure where all ions occupy high symmetry positions. The relaxed DFT lattice constant of this cell was $a$ =4.157 Å. This structure was used to calculate both a phonon band structure (Figure 1) and $\epsilon$. The high-symmetry BaZrO$_3$ structure contains three IR active phonon modes in each direction.

The first set of phonon frequencies, occurring at 96 cm$^{-1}$ contribute the most to $\epsilon$, as shown in Table I. These three modes are mainly large Ba displacements against its O$_{12}$ cage into which some Zr displacement opposite its O$_6$ cage is mixed (Last mode). The ratio of Ba displacement to Zr displacement is about 9:1. However, due to the much larger $Z^*$ of Zr (6.3 for Zr versus 2.7 for Ba) even such a small Zr off-center displacement makes a significant contribution to the effective charge of the mode. The IR active modes are sometimes discussed in terms of purely A-O or B-O displacements, but that simple cation motion is not justified when describing the lowest frequency phonon modes of BZ.

The second set of phonon frequencies occurs at 193 cm$^{-1}$, consisting of Zr motion (Slater mode). A small amount of Ba motion is also present, but the ratio of Zr off-centering to Ba off-centering in this mode is about 20:1. Combined with the smaller $Z^*$ of Ba, this means that this mode is well-characterized as pure B-O. The final set of phonons, at 513 cm$^{-1}$ are caused by asymmetric O$_6$ cage motions. These contribute the least to $\epsilon$.

To obtain $\epsilon$, the contributions of $\epsilon_{\mu}$ from Table I are added to $\epsilon_{\infty}$, which was calculated as 4.94. The total zero temperature dielectric constant for the high symmetry structure is 65. This value is almost double previous experimental investigations [2], but agrees well with recent theoretical investigations [3].

The disagreement between experimental and theoretical $\epsilon$ results suggests either an inaccuracy of LDA or an inaccurate representation of ground-state BaZrO$_3$ structure by a five-atom high-symmetry unit cell. In Reference [3], the authors present a phonon band structure of BZ, which displayed a soft mode at R, but none at $\Gamma$. Our phonon band structure of five atom BZ, presented in Figure 1 confirms that there is no ferroelectric softening at $\Gamma$, but a rather large softening at R. The presence of an unstable mode indicates a driving force for symmetry breaking. To explore the effect of this, a larger BZ supercell is needed for accurate calculations.

B. Forty-Atom BZ calculations

The soft mode at R observed in the phonon band structure was induced in the high symmetry structure, and the supercell was then relaxed. The relaxed low symmetry structure had lattice constants $a$ = 8.306Å, $b$ = 8.313Å, and $c$ = 8.290Å. Thus, the relaxed volume is only 0.39% less than the high symmetry structure. None of the cations shift from their high symmetry positions, consistent with an O$_6$ tilt mode. Octahedral tilt angles range between 3.6 and 4.2°. A subsequent phonon response calculation on the tilted pseudo-cubic structure showed that no negative frequency modes were present. Unlike our calculations, low temperature x-ray diffraction and neutron scattering experiments are unable to detect this tilting in BZ [3]. Current experimental evidence is unclear.

The relevant X-ray reflections for oxygen-based symmetry breaking would be weak, due to the scattering factor of O. We propose the tilted structure based on quantum mechanical energy minimization and conse-
Comparison of the $\mu$ values in Tables I and II shows that the contribution of the mainly Ba modes to $\epsilon$ has decreased by half, whereas the contribution of the Zr modes and the $O_6$ modes has remained the same. The new modes around 300 cm$^{-1}$ do not contribute as much to $\epsilon_\mu$ as the three previously mentioned sets of modes.

Comparison of the $\epsilon_\mu$ values in Tables I and II shows that the contribution of the mainly Ba modes to $\epsilon$ has decreased by half, whereas the contribution of the Zr modes and the $O_6$ modes has remained the same. The new modes around 300 cm$^{-1}$ do not contribute significantly.

The total $\epsilon_\mu$ is 45, in contrast with 60 calculated for the 5-atom cell. We find that $\epsilon_\infty$ is still 4.94, and the total $\epsilon$ is 50, in agreement with experimental data. Thus, we find that it is necessary to include the $O_6$ tilt to correctly represent the dielectric response of BZ at low temperature.

We now discuss the physical reasons behind the changes in the dielectric response induced by octahedral tilting. As noted above, the weaker dielectric response of the low-symmetry BaZrO$_3$ structure is caused by the 40% drop in the contribution of the low frequency Last mode. To some extent, this effect can be rationalized by the rattling cation model. As the $O_6$ cages tilt, the O atoms are brought closer to the Ba atom. This reduces the volume of the Ba-O$_{12}$ cage leaving less room for Ba to rattle around in response to an applied electric field. More precisely, the shorter Ba-O distances lead to a stiffening of the potential energy surface felt by the Ba. This gives rise to a smaller dielectric response, as $\epsilon_\mu$ is proportional to $1/\omega^2$. However, examination of Ba-O modes shows that $\omega$ shifts up by about 10%. This should lead to about 27% decrease in $\epsilon_\mu$, accounting for about half of the Ba-O mode $\epsilon_\mu$ change. The other factor that weakens the dielectric response is the decrease in the mode effective charge $Z^*_\mu$, which is significantly smaller for the low-symmetry structure than for the 5-atom high-symmetry structure. Since Eqns. 3 and 4 shows that $\epsilon_\mu$ is proportional to the square of $Z^*_\mu$, distribution of $Z^*_\mu$ over multiple modes leads to a 20% decrease in $\epsilon_\mu$.

Comparison of the Ba-O phonon eigenvectors for the two structures shows that induced Zr off-centering is smaller for the Last mode in the 40-atom low symmetry structure than in the 5-atom high-symmetry mode. It is this reduction in the induced Zr displacement that gives rise to the smaller $Z^*_\mu$. Physically, the smaller induced Zr displacement points to a weakened coupling between Ba and Zr displacements. The coupling between Ba and Zr displacement is most likely due to Pauli repulsion [16]. In the low-symmetry structure $O_6$ tilting as well as increased O motion in $x$ and $y$ directions in the Last mode eigenvector moves an O atom between Ba and Zr. This partially screens the Ba-Zr interactions, leading to a smaller $Z^*_\mu$.

| $\omega$ (cm$^{-1}$) | $Z'_{xx}$ | $Z'_{yy}$ | $Z'_{zz}$ | $\epsilon_{xx}$ | $\epsilon_{yy}$ | $\epsilon_{zz}$ | Motion |
|---------------------|-----------|-----------|-----------|----------------|----------------|----------------|--------|
| 106                 | 1.3       | 1.3       | 0.5       | 12.1          | 11.7           | 1.9            | Ba-O   |
| 107                 | 0.5       | 0.5       | 0.2       | 2.0           | 1.9            | 0.3            | Ba-O   |
| 114                 | 0.4       | 0.4       | 1.8       | 1.0           | 0.8            | 21.8           | Ba-O   |
| 125                 | 1.2       | 1.3       | 0.0       | 8.5           | 9.0            | 0.0            | Ba-O   |
| 184                 | 0.2       | 0.3       | 0.1       | 0.1           | 0.2            | 0.0            | Zr-O   |
| 192                 | 0.3       | 0.7       | 0.0       | 0.3           | 1.1            | 0.0            | Zr-O   |
| 195                 | 1.3       | 2.3       | 1.0       | 3.6           | 12.2           | 2.2            | Zr-O   |
| 196                 | 0.3       | 1.0       | 2.7       | 0.2           | 2.0            | 16.3           | Zr-O   |
| 197                 | 2.5       | 1.3       | 0.2       | 14.1          | 3.5            | 0.1            | Zr-O   |
| 211                 | 0.6       | 0.6       | 0.0       | 0.7           | 0.6            | 0.0            | Zr-O   |
| 307                 | 0.2       | 0.1       | 0.6       | 0.1           | 0.0            | 0.3            | Ba,Zr-O |
| 308                 | 0.4       | 0.4       | 0.2       | 0.2           | 0.1            | 0.1            | Ba,Zr-O |
| 501                 | 1.5       | 1.9       | 1.2       | 0.8           | 1.2            | 0.5            | O$_6$   |
| 502                 | 0.8       | 0.9       | 2.4       | 0.2           | 0.3            | 1.9            | O$_6$   |
| 505                 | 2.1       | 1.7       | 0.0       | 1.4           | 0.9            | 0.0            | O$_6$   |

TABLE II: Forty-atom low-symmetry BZ phonon data for IR active modes. Frequencies are in cm$^{-1}$, mode effective charges, $Z^*$, are in e. The contributions to $\epsilon$ are calculated in SI units. For each IR active mode, the atomic motions are described, mode.

FIG. 2: Gamma-point phonon DOS of the high-symmetry BaZrO$_3$ structure, solid black line, and the fully relaxed pseudo-cubic supercell, dashed blue line. The most important changes are the upshift in Ba-O mode frequencies (from 96 cm$^{-1}$ to 100-130 cm$^{-1}$) and the appearance of new modes around 300 cm$^{-1}$.
IV. CONCLUSIONS

We have presented calculations that reveal interesting structural and dielectric properties in the seemingly simple material BaZrO$_3$. At zero temperature, the high-symmetry model proved inadequate for calculating the dielectric constant. Large supercells were used in order to find the equilibrium structure, which exhibits octahedral tilts. These tilts have a significant effect on the low frequency Ba-O Last mode and its contribution to the dielectric constant. Allowing octahedral tilts in the first principles modeling of BaZrO$_3$ resolves the discrepancy between recent theoretical and experimental investigations of low temperature dielectric constant. Moreover, the understanding of how octahedral tilting can change dielectric response should give insight into alloying strategies for future dielectric materials design.

V. ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research under Grant No. N-00014-00-1-0372, the Center for Piezoelectric Design, a GAAAN fellowship from the University of Pennsylvania, and the IMI Program of the National Science Foundation under Award No. DMR 0409848. We also acknowledge the support of the DoD HPCMO, DURIP and NSF CRIF program, Grant No. CHE-0131132.

VI. REFERENCES

[1] W. Fortin, G. E. Kugel, J. Grigas, and A. Kania, J. Appl. Phys. 79, 4273 (1996).
[2] I. Levin, T. G. Amos, S. M. Bell, L. Farber, T. A. Vanderah, R. S. Roth, and B. H. Toby, J. Solid State Chem. 175, 170 (2003).
[3] A. R. Akbarzadeh, I. Kornev, C. Malibert, L. Bellaiche, and J. M. Kiat, Phys. Rev. B. 72, 205104 (2005).
[4] R. E. Cohen, J. Phys. Chem. Solids 57, 1393 (1996).
[5] I. Grinberg and A. M. Rappe, AIP Conf. Proc., pp. 130–8 (2003), ISSN 0094-243X, URL [http://dx.doi.org/10.1063/1.1609946](http://dx.doi.org/10.1063/1.1609946).
[6] S. E. Mason, I. Grinberg, and A. M. Rappe, Phys. Rev. B Rapid Comm. 69, 161401(R) (2004).
[7] X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, et al., Comp. Mater. Sci. 25, 478 (2002).
[8] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
[9] A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, Phys. Rev. B Rapid Comm. 41, 1227 (1990).
[10] N. J. Ramer and A. M. Rappe, Phys. Rev. B 59, 12471 (1999).
[11] http://opium.sourceforge.net.
[12] X. Gonze and C. Lee, Phys. Rev. B 55, 10355 (1997).
[13] P. Ghosez, J.-P. Michenaud, and X. Gonze, Phys. Rev. B 58, 6224 (1998).
[14] E. Cockayne and B. P. Burton, Phys. Rev. B 62, 3735 (2000).
[15] E. Cockayne, Journal of the European Ceramic Society 23, 2375 (2003).
[16] I. Grinberg, V. R. Cooper, and A. M. Rappe, Nature 419, 909 (2002).