Crystal Structures, Modeling, and Dielectric Property Relationships of 2:1 Ordered Ba₃MM′₂O₉ (M = Mg, Ni, Zn; M′ = Nb, Ta) Perovskites

Michael W. Lufaso†
Ceramics Division, Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8520

Received January 31, 2004. Revised Manuscript Received March 10, 2004

The preparation, modeled and refined crystal structures, and structure–dielectric property relationships of five Ba₃MM′₂O₉ (M = Mg, Ni, Zn; M′ = Nb, Ta) perovskites are reported. Crystal structure modeling was used to generate initial structure models for Rietveld refinements of the neutron powder diffraction data. Bond valence sums calculated from the bond distances indicate Ba–O bonds are compressed and the M–O and M′–O bonds are expanded from ideal lengths. A shift of Ta⁵⁺ and Nb⁵⁺ out of center of the [M'O₆] octahedra forms three short and three long M′–O bonds. The octahedral distortion is driven by the asymmetry in the O bonding network and aided by the second-order Jahn–Teller distortion of the § Nb⁵⁺ and Ta⁵⁺ cations. Differences in the atomic coordination environments in the crystal structures were utilized to propose crystal structure–dielectric property relationships. The coordination of the divalent B-site cation (M²⁺) was correlated with the temperature coefficient of the resonant frequency (τf); a more under-bonded M²⁺ exhibited a more negative τf. Also, if the bond valences sums of the B-site cations were closer to the formal oxidations states, then a higher Q×f was observed.

Introduction

Dielectric ceramic materials are of considerable interest owing to their technically important properties and the relatively uncharted science surrounding the interactions between the crystal structures, chemistry, and useful physical properties. The dielectric ceramics are found as discrete components (e.g., dielectric resonators and filters) that are vital enabling devices in microwave communications systems.1 There are few known ceramic materials that meet the rigorous dielectric property requirements for use in device applications.2 The dielectric constant (ε) is only one of the key properties needing optimization; the temperature coefficient of the resonant frequency (τf) and dielectric loss (tan δ), often reported as the quality factor Q = (tan δ)⁻¹ or Q×f where f is the measurement frequency, are also critical properties. Obtaining optimal values of these three properties simultaneously is difficult; for example, high ε materials often possess a large τf and low Q.

Perovskites have been extensively investigated for use as microwave dielectric materials because of the outstanding and tunable dielectric properties present in a number of compositions. In the perovskite structure (AMO₃) the A-site cation is located in the cavity formed by the corner-sharing network of [M'O₆] octahedra. The fit of the A-site cation is described by the tolerance factor (t₀).3 If the tolerance factor is greater than unity, often no octahedral tilting is observed, whereas compositions with a tolerance factor less than unity typically undergo octahedral tilting distortions.4,5 The series of Ba₃MM′₂O₉ (M = Mg, Ni, Zn; M′ = Nb, Ta) perovskites that do not undergo an octahedral tilting distortion exhibit optimal dielectric properties. The perovskites Ba₃MgTa₂O₉ (BMT) and Ba₃ZnTa₂O₉ (BZT) possess high Q×f values and a near zero τf.6,7 The type of cation order influences the dielectric properties, with 2:1 order of the M and M′ cations exhibiting a larger Q×f than 1:1 ordered and disordered perovskites.7–9 Substitutions on the A-, M-, and M′-site have been made extensively, but no alternative compounds have emerged for high-Q applications.10–12 For example, B-site substitution of the identical ionic radius (0.78 Å) Nb⁵⁺ for Ta⁵⁺ results in crystallization of isostructural 2:1 ordered perovskites; however, the ε is higher, Q is lower, and τf is more positive. The origins of the dielectric property differences between the isostructural compounds are not well-understood.

Entanglement of synthetic variables (e.g., chemical composition, reagent purity, annealing and sintering temperatures and times, initial particle size, processing

References

1 E-mail: michael.lufaso@nist.gov.
(3) Goldschmidt, V. M. Naturwissenschaften 1926, 14, 477.
conditions, and partial O_2 pressure) and experimental observables (e.g., crystal structure, density, cation order inside of a domain, ordered domain size, domain boundaries, defects, and impurity phases) that influence the dielectric properties (i.e., ϵ, τ, and Q) complicate formation of structure–property relationships. One structure–property relationship that has been developed strongly relates the incidence of octahedral tilting to the magnitude and sign of τ. Also, substituting smaller A-site cations (i.e., A = Sr^{2+}, Ca^{2+}) in place of Ba^{2+} in Ba_3MM'_2O_9 perovskites is one approach to adjust the octahedral tilting and consequently the τ. Also, in general, a more negative temperature coefficient of the dielectric constant (τ) (thus typically a more positive τ) is observed with an increase in ϵ. The ϵ of dielectrics originates from the superposition of ionic and electronic polarization. Electronic polarization is considered a constant for a particular ion, whereas ionic polarization occurs because of lattice vibrations related to the crystal structure and is a particularly important contribution in high ϵ (>20) materials. Relationships between the crystal structure, dielectric properties, and crystal chemistry are prone to be complex; however, the elucidation of the structural differences between M' = Ta and M' = Nb compounds is a starting point in understanding the dielectric property differences.

Crystal structures reported in the literature indicate significant differences in the reported O fractional coordinates and cation coordination environments of BZT and BMT. The crystal structure of BZT was refined in space group P3m1 from neutron powder diffraction data and recently refined with combined neutron and X-ray powder diffraction data. The two crystal structures of BZT have significantly different B-site bond lengths (Å) [Zn-O 1.977(4) × 6, Ta-O 2.023(7) × 3, and 2.141(10) × 3] compared to [Zn-O 2.1246(22) × 6, Ta-O 1.9355(23) × 3, and 2.0827(13) × 3]. Similarly, the crystal structures of BMT refined from X-ray diffraction data show appreciably different B-site bond lengths (Å) [Mg-O 2.072(7) × 6, Ta-O 2.04(2) × 3, and 2.033(6) × 3] compared to [Mg-O 2.076(6) × 6, Ta-O 1.967(8) × 3, and 2.089(1) × 3]. Differences in the crystal structures of BMT may be partially attributed to the difficulty in refining accurate O positions from X-ray diffraction data. It is unclear from the reported crystal structures if Ta^{5+} shifts out of the center of the octahedra to form three short Ta-O bonds or retains Ta-O bonds.

A group of five Ba_3M'M'_2O_9 (M = Mg, Ni, Zn; M' = Nb, Ta) perovskite compositions were synthesized and the crystal structures refined by the Rietveld method from neutron powder diffraction data. Idealized crystal structures were calculated by structure modeling in an effort to understand the differences in the reported crystal structures and to provide a starting structural model in the course of performing the Rietveld refinements. The Ba_3M'M'_2O_9 compositions in this paper all have tolerance factors greater than unity and do not exhibit the added variable of octahedral tilting; therefore, these compositions are good candidates for examining basic crystal structure–dielectric property relationships. A robust literature of dielectric characterization on these compositions was utilized to extend the suggested crystal structure–dielectric property relationships.

### Experimental Methods

#### Sample Synthesis

Single-phase Ba_3MgNb_2O_9 (BMN), Ba_3MgTaO_9 (BMT), Ba_3NiNb_2O_9 (BNN), Ba_3NiTaO_9 (BNT), and Ba_3ZnNb_2O_9 (BZN) perovskite compounds were prepared by a M'_2O_9 precursor route. Appropriate stoichiometric amounts of assayed MgCO_3 (Atomix), ZnO (Alfa Aesar, 99.99%), NiO (Alfa Aesar, 99.998%), Nb_2O_5 (Alfa Aesar, 99.998%), and Ta_2O_5 (Alfa Aesar, 99.993%) were ground and then heated overnight at 1100 °C. After the initial precursor heat cycle, a stoichiometric amount of BaCO_3 was added, intimately mixed, and calcined overnight to decompose the carbonate. Prior to each heat cycle, the samples were ground with an agate mortar and pestle, pelletized using a uniaxial press, and placed on sacrificial powder of the same composition on Pt foil on an alumina plate. The samples were covered with an inverted zirconia crucible prior to each heat cycle. These synthetic precautions were employed to suppress cation volatility and avoid formation of competing phases. In the synthesis of BZN the pellet was covered with a powder of the same composition and surrounded with a small excess of ZnO, which increases the ZnO partial pressure, to minimize Zn loss. Multiple (eight to nine) heat cycles, with intermediate grinding and repelletizing, were performed at increasing temperatures from 1100 °C to a final temperature of 1525 °C (BMN), 1575 °C (BMT), 1375 °C (BNN), 1475 °C (BNT), and 1250 °C (BZN).

#### Diffraction Data Collection

Phase purity was ascertained using X-ray powder diffraction data collected Cu Kα X-ray radiation with a Philips diffractometer equipped with incident Soller slits, theta compensating divergence slit, graphite monochromator, and scintillation detector. Equilibrium was assumed to occur when no further changes were evident in the relative intensities of the weak superlattice peaks associated with cation ordering and c/a lattice parameter ratio. Neutron powder diffraction data were collected using the BT-1 32 detector neutron powder diffraction at the NCNR, NBSR. The samples were loaded in vanadium sample containers of length 50 mm and diameter 12.4 mm. A Cu(311) monochromator with a 90° takeoff angle, λ = 1.5402(2) Å, and in-pile collimation of 15 min of arc were used. Data were collected under ambient conditions over the range of 3°–168° 2θ with a step size of 0.05°. The instrument is described in the NCNR Web site (http://www.ncnr.nist.gov/).

#### Crystal Structure Modeling

The SPuDS modeling software, which has been used to calculate the crystal structures.

---

(23) Crystal structure of the BZT-F powder sample.
(25) Crystal structure of the nonintercalated (polycrystalline) sample.
(27) Certain commercial equipment, instruments, or materials are identified in this paper to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.
fractional coordinates and lattice parameters are retained from the optimized structure in the previous calculation loop. Multiple (3–4) iterations are performed using successively smaller search steps until the ideal calculated crystal structure is obtained. The software program executes in a Microsoft Windows platform, and typical calculation times for each composition are on the order of minutes. The structure calculation procedure selects the crystal structure with the minimum GII, simultaneously optimizing the coordination of both the cation and the anions. Optimized lattice parameters, \( c / a \) lattice parameter ratio, fractional coordinates, tolerance factors, \( \text{M}^{2+} - \text{O} \) distances, and bond valence sums are shown in Table 1.

### Crystal Structure Refinement

The GSAS software package was used for Rietveld structural refinements using the EXPGUI interface. Initial lattice parameters were obtained from the indexing of the X-ray diffraction measurements and starting fractional coordinates were obtained from SPuDS calculations shown in Table 1. Default neutron scattering lengths and cross sections were utilized in the refinements. The data were refined in the range 10° < 2θ < 168° and the background was modeled using an 11-term Chebyshev polynomial. Peak profiles were modeled with a pseudo-Voigt function. The \( \text{M}^{2+} \) and \( \text{M}^{3+} \) ion were initialized with partially ordered occupancies on the \( 1b \) and \( 2d \) sites. The occupancy of the B-site was then refined under the constraint \( \sum [\text{M}^{2+}(1b)] + \sum [\text{M}^{3+}(2d)] = 2 \) and \( \sum [\text{M}^{3+}(1b)] + \sum [\text{M}^{2+}(2d)] = 2 \), where \( \chi \) is the fractional occupancy of the ion with the Wyckoff site shown in parentheses. The \( U_{\text{iso}} \) values were constrained to be equal for \( \text{M}^{2+} \) and \( \text{M}^{3+} \) for atoms located on the same crystallographic site. Refinement cycles involved 29–30 parameters including the scale factor, background, peak shape, unit cell, isotropic thermal parameters, and fractional coordinates. In BMN, BMT, and BNT the B-site occupancies refined to values slightly larger than unity, with an insignifi- cant improvement in the refinement and an \( R_{\text{wp}} \) improvement of 0.02% or less. In subsequent refinements of BMN, BMT, and BNT the \( \text{M}^{2+} \) and \( \text{M}^{3+} \) cation site occupancies were fixed at unity.

### Table 1. Predicted Structural Parameters and Bond Valence Sums (v.u.) and \( \text{M}^{5+} - \text{O} \) Bond Distances (Å) Obtained from SPuDS Calculations

<table>
<thead>
<tr>
<th></th>
<th>( \text{Ba}_3\text{MgNb}_2\text{O}_9 )</th>
<th>( \text{Ba}_3\text{MgTa}_2\text{O}_9 )</th>
<th>( \text{Ba}_3\text{NiNb}_2\text{O}_9 )</th>
<th>( \text{Ba}_3\text{NiTa}_2\text{O}_9 )</th>
<th>( \text{Ba}_3\text{ZnNb}_2\text{O}_9 )</th>
<th>( \text{Ba}_3\text{ZnTa}_2\text{O}_9 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a ) (Å)</td>
<td>7.142(1)</td>
<td>7.142(1)</td>
<td>7.142(1)</td>
<td>7.142(1)</td>
<td>7.142(1)</td>
<td>7.153(1)</td>
</tr>
<tr>
<td>( b ) (Å)</td>
<td>7.142(1)</td>
<td>7.142(1)</td>
<td>7.142(1)</td>
<td>7.142(1)</td>
<td>7.142(1)</td>
<td>7.153(1)</td>
</tr>
<tr>
<td>( c ) (Å)</td>
<td>7.142(1)</td>
<td>7.142(1)</td>
<td>7.142(1)</td>
<td>7.142(1)</td>
<td>7.142(1)</td>
<td>7.153(1)</td>
</tr>
<tr>
<td>( \text{Ba}^+ )</td>
<td>0.6799(1)</td>
<td>0.6813(1)</td>
<td>0.6799(1)</td>
<td>0.6813(1)</td>
<td>0.6799(1)</td>
<td>0.6813(1)</td>
</tr>
<tr>
<td>( \text{M}^{3+} )</td>
<td>0.1800(1)</td>
<td>0.1833(1)</td>
<td>0.1800(1)</td>
<td>0.1833(1)</td>
<td>0.1800(1)</td>
<td>0.1833(1)</td>
</tr>
<tr>
<td>( \text{O}^2- )</td>
<td>2.02</td>
<td>2.04</td>
<td>2.02</td>
<td>2.04</td>
<td>2.02</td>
<td>2.04</td>
</tr>
</tbody>
</table>

\( ^a \) The fixed atomic positions are given in the text.
Results and Discussion

Crystal Structures, Coordination, and Bonding.

The refined fit of BMT to the diffraction pattern is shown in Figure 1. The Rietveld refined lattice parameters, fractional coordinates, site occupancies, and reliability factors for all compositions examined are shown in Table 2. The predicted fractional coordinates shown in Table 1 agree well with the refined values shown in Table 2, which illustrates the accuracy of the structure modeling calculations. Complete cation order was indicated for BMN, BMT, and BNT and nearly complete cation order for BNN and BZN. Selected interatomic bond distances and angles are given in Table 3. Standard uncertainties in the reported values are represented by one standard deviation. In contrast to many single and 1:1 ordered B-site cation perovskites, the crystal structures of 2:1 ordered perovskites exhibit an out-of-center distortion of $\text{M}^5+$ in $[\text{M}^5\text{O}_6]$. The crystal structure of $\text{Ba}_3\text{MgTa}_2\text{O}_9$ shown in Figure 2 illustrates the shift of Ta occurs toward the face of the $[\text{TaO}_6]$ octahedra toward a neighboring layer of $[\text{MgO}_6]$.

The source of the octahedral distortion may be understood using Pauling's Rules and assuming equidistant bonds in the first coordination sphere, with each

Table 2. Refined Structural Parameters, Fractional Site Occupancies, and Reliability Factors for $\text{Ba}_3\text{MM}'_2\text{O}_9$ ($\text{M} = \text{Mg, Ni, Zn}; \text{M}' = \text{Nb, Ta}$)

<table>
<thead>
<tr>
<th></th>
<th>exp. $\text{Ba}_3\text{MgNb}_2\text{O}_9$</th>
<th>exp. $\text{Ba}_3\text{MgTa}_2\text{O}_9$</th>
<th>exp. $\text{Ba}_3\text{NiNb}_2\text{O}_9$</th>
<th>exp. $\text{Ba}_3\text{NiTa}_2\text{O}_9$</th>
<th>exp. $\text{Ba}_3\text{ZnNb}_2\text{O}_9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>5.7754(5)</td>
<td>5.7738(5)</td>
<td>5.7549(6)</td>
<td>5.7551(8)</td>
<td>5.7820(7)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>7.0876(9)</td>
<td>7.0937(6)</td>
<td>7.0695(9)</td>
<td>7.0748(11)</td>
<td>7.0973(11)</td>
</tr>
<tr>
<td>$\text{Ba}2$ z</td>
<td>0.6681(3)</td>
<td>0.6650(3)</td>
<td>0.6638(6)</td>
<td>0.6635(7)</td>
<td>0.6661(4)</td>
</tr>
<tr>
<td>$\text{M}^5+$ z</td>
<td>0.1792(3)</td>
<td>0.1776(3)</td>
<td>0.1770(4)</td>
<td>0.1774(6)</td>
<td>0.1767(3)</td>
</tr>
<tr>
<td>$\text{O}2$ x</td>
<td>0.1706(1)</td>
<td>0.1708(1)</td>
<td>0.1698(2)</td>
<td>0.1695(2)</td>
<td>0.1711(1)</td>
</tr>
<tr>
<td>$\text{O}2$ z</td>
<td>0.3257(2)</td>
<td>0.3251(2)</td>
<td>0.3262(3)</td>
<td>0.3256(4)</td>
<td>0.3255(2)</td>
</tr>
<tr>
<td>$f$ ($\text{M}^5+$)</td>
<td>1</td>
<td>1</td>
<td>0.89(3)/0.11(3)</td>
<td>1</td>
<td>0.92(6)/0.08(6)</td>
</tr>
<tr>
<td>$f$ ($\text{M}^2+$)</td>
<td>1</td>
<td>1</td>
<td>0.94(2)/0.06(2)</td>
<td>1</td>
<td>0.96(3)/0.04(3)</td>
</tr>
<tr>
<td>$R_p$ (profile) (%)</td>
<td>4.24</td>
<td>4.27</td>
<td>3.93</td>
<td>4.22</td>
<td>4.14</td>
</tr>
<tr>
<td>$R_w$ (weighted profile) (%)</td>
<td>5.25</td>
<td>5.30</td>
<td>4.87</td>
<td>5.35</td>
<td>5.27</td>
</tr>
<tr>
<td>$\chi^2$ (Bragg) (%)</td>
<td>3.40</td>
<td>3.50</td>
<td>3.45</td>
<td>4.09</td>
<td>3.77</td>
</tr>
<tr>
<td>reduced $\chi^2$ (%)</td>
<td>2.10</td>
<td>1.60</td>
<td>1.38</td>
<td>1.08</td>
<td>2.01</td>
</tr>
</tbody>
</table>

The fixed atomic fractional coordinate positions are given in the text. Additional refined Rietveld fit parameters and isotropic thermal parameters are given in Supporting Information Table A.

Table 3. Selected Interatomic Distances (Å) Determined from Refined Structural Parameters of $\text{Ba}_3\text{MM}'_2\text{O}_9$ ($\text{M} = \text{Mg, Ni, Zn}; \text{M}' = \text{Nb, Ta}$)

<table>
<thead>
<tr>
<th></th>
<th>$\times 6$ $\text{Ba}(1)-\text{O}(1)$</th>
<th>$\times 6$ $\text{Ba}(1)-\text{O}(2)$</th>
<th>$\times 3$ $\text{Ba}(2)-\text{O}(1)$</th>
<th>$\times 3$ $\text{Ba}(2)-\text{O}(2)$</th>
<th>$\times 6$ $\text{Ba}(2)-\text{O}(2)$</th>
<th>$\times 3$ $\text{M}(5)-\text{O}(1)$</th>
<th>$\times 3$ $\text{M}(5)-\text{O}(2)$</th>
<th>$\times 6$ $\text{M}(6)-\text{O}(2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ba}_3\text{MgNb}_2\text{O}_9$</td>
<td>2.8877(3)</td>
<td>2.8869(3)</td>
<td>2.8749(3)</td>
<td>2.869(4)</td>
<td>2.889(4)</td>
<td>2.899(4)</td>
<td>2.903(4)</td>
<td>2.893(2)</td>
</tr>
<tr>
<td>$\text{Ba}_3\text{MgTa}_2\text{O}_9$</td>
<td>2.8874(3)</td>
<td>2.8699(21)</td>
<td>2.859(4)</td>
<td>2.896(4)</td>
<td>2.895(4)</td>
<td>2.8757(4)</td>
<td>2.8753(27)</td>
<td>2.8762(16)</td>
</tr>
<tr>
<td>$\text{Ba}_3\text{NiNb}_2\text{O}_9$</td>
<td>2.8757(4)</td>
<td>2.8599(21)</td>
<td>2.8573(27)</td>
<td>2.8573(27)</td>
<td>2.8573(27)</td>
<td>2.875(4)</td>
<td>2.8753(27)</td>
<td>2.8762(16)</td>
</tr>
<tr>
<td>$\text{Ba}_3\text{NiTa}_2\text{O}_9$</td>
<td>2.8757(4)</td>
<td>2.8599(21)</td>
<td>2.8573(27)</td>
<td>2.8573(27)</td>
<td>2.8573(27)</td>
<td>2.8757(4)</td>
<td>2.8753(27)</td>
<td>2.8762(16)</td>
</tr>
<tr>
<td>$\text{Ba}_3\text{ZnNb}_2\text{O}_9$</td>
<td>2.8910(3)</td>
<td>2.893(2)</td>
<td>2.8984(22)</td>
<td>2.8984(22)</td>
<td>2.8984(22)</td>
<td>2.8910(3)</td>
<td>2.8984(22)</td>
<td>2.8984(22)</td>
</tr>
</tbody>
</table>

Selected interatomic bond distances and angles are given in Table 3. Standard uncertainties in the reported values are represented by one standard deviation. In contrast to many single and 1:1 ordered B-site cation perovskites, the crystal structures of 2:1 ordered perovskites exhibit an out-of-center distortion of $\text{M}^5+$ in $[\text{M}^5\text{O}_6]$. The crystal structure of $\text{Ba}_3\text{MgTa}_2\text{O}_9$ shown in Figure 2 illustrates the shift of Ta occurs toward the face of the $[\text{TaO}_6]$ octahedra toward a neighboring layer of $[\text{MgO}_6]$.

The source of the octahedral distortion may be understood using Pauling's Rules and assuming equidistant bonds in the first coordination sphere, with each
Table 4. Number of Bonds (N), Valence of Bond (\(\Delta E\)), Bond Valence Sums (BVS) of Ions in Ba\(_3\)ZnTa\(_2\)O\(_9\) with Distorted and Undistorted Octahedra, and the Experimental Crystal Structures

<table>
<thead>
<tr>
<th></th>
<th>undistorted octahedra</th>
<th></th>
<th>distorted octahedra</th>
<th></th>
<th>experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(s_{\text{M-O}}) (v.u.)</td>
<td>BVS (v.u.)</td>
<td>(s_{\text{M-O}}) (v.u.)</td>
<td>BVS (v.u.)</td>
<td>BVS (v.u.)</td>
</tr>
<tr>
<td>Zn–O</td>
<td>6</td>
<td>1/3</td>
<td>6</td>
<td>1/3</td>
<td>2.0</td>
</tr>
<tr>
<td>Ta–O</td>
<td>6</td>
<td>5/6</td>
<td>5.0</td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>O1–(Ta, Ba)</td>
<td>2.4</td>
<td>1/2, 1/6</td>
<td>2.87</td>
<td>2.87</td>
<td>1.93</td>
</tr>
<tr>
<td>O2–(Zn, Ta, Ba)</td>
<td>1, 1, 4</td>
<td>1/6, 1/6, 1/6</td>
<td>1.83</td>
<td>1.83</td>
<td>2.05</td>
</tr>
</tbody>
</table>

![Figure 2. Crystal structure of Ba\(_3\)MgTa\(_2\)O\(_9\). The large spheres represent Ba atoms and the small spheres oxygen atoms. Medium spheres represent Mg in pale [MgO\(_6\)] octahedra and Ta in dark [TaO\(_6\)] octahedra. Ta distorts out-of-center toward the octahedral face with O bonded to Mg.](image)

Although the out-of-center distortion primarily occurs because of the asymmetry in the bond network, the connectivity in the bond network is not the sole driving force for the distortion. In general, a distortion depends on both electronic and structural components in the nature of the bond network. Ta\(^{5+}\) or Nb\(^{5+}\) cations have low-lying d orbitals that are able to mix with the filled p orbitals of the oxygen. In the extended perovskite structure this results in a number of different electronic configurations with closely spaced energies. A spontaneous distortion can remove any near degeneracy, which is known as a second-order Jahn-Teller distortion. In general, second-order Jahn–Teller distortions that occur for d\(^{0}\) cations (e.g., Ti\(^{4+}\), Nb\(^{5+}\), Ta\(^{5+}\), W\(^{6+}\)) exhibit a tendency for multiple bond lengths. It is noteworthy that substitution of the similar six-coordinate ionic radius Sb\(^{5+}\) (r = 0.74 Å) for Ta\(^{5+}\) and Nb\(^{5+}\) in perovskites with a 1:1 “NaCl”-type ordered cation arrangement, which has no connectivity asymmetry for an off-center distortion, results in formation of a perovskite phase. However, substitution of Sb\(^{5+}\) in 2:1 compositions with the A-site cation Ba\(^{2+}\) results in the crystallization of a phase that does not contain corner-sharing octahedra. For example, Ba\(_3\)MgSb\(_2\)O\(_9\) (M = Mg, Ni) crystallize in space group P6\(_3\)/mmc with corner- and face-sharing octahedra. The d\(^{10}\) Sb\(^{5+}\) does not have empty d orbitals to mix with the O 2p orbitals to stabilize the off-center distortion. Compositions with 2:1 ratio of B-site cations with M\(^{+}\) cations that contain partially filled d shells adopt a non-stoichiometric 1:1 order. Perovskites which exhibit the nonstoichiometric 1:1 order include space group Fm\(_3\)m, Ba\(_3\)MM\(_2\)O\(_9\) (M = Mo, W; M\(^{+}\) = Dy, Gd), Ba\(_3\)WSm\(_2\)O\(_9\), \(\text{As}_2\text{Te}_2\text{O}_9\) (A = Sr, Ba), Sr\(_3\)WCO\(_2\)O\(_9\), Sr\(_3\)WM\(_2\)O\(_9\) (M\(^{+}\) = Cr, Fe), \(\text{As}_2\text{UF}_2\text{O}_6\) (A = Sr, Ba), and Ba\(_3\)UF\(_2\)O\(_6\), space group I4/m, Sr\(_3\)MF\(_2\)O\(_6\) (M\(^{+}\) = Mo, W, Te, U), and space group I4mm and Pnmm Sr\(_3\)NiSb\(_2\)O\(_9\). Formulation of 2:1 ordered perovskites appears to require a d\(^{0}\) cation on the M\(^{+}\) site, which may undergo a second-order Jahn–Teller off-center distortion to create a more favorable coordination for the O.
There were additional differences observed between the M' = Nb and M' = Ta crystal structures. It is well-known that with increasing 2:1 cation order the c/a lattice parameter ratio becomes larger than \(3/2\).\(^{49,50}\) The c/a lattice parameter ratios shown in Table 5 are slightly smaller for M' = Nb compounds compared to the corresponding M' = Ta in compounds, even with a similar degree of cation order. Bond valence sums were calculated using the SPuDS software with modern bond valence parameters.\(^{51}\) Bond valence sums and the GII shown in Table 5 were calculated using bond distances of M' = Nb compounds.52 These compounds have a large tolerance factor and are near the ideal value. The GII values shown in Table 5 are large while the O bond valence sums remain near the formal valence. The GII values shown in Table 5 are in good agreement with the reported bond valence sums from ideal values. The BVS of M = Ni\(^{2+}\) for BNN and BNT show the largest deviation from two and the largest stretching of the Ni–O bonds was also predicted by the structure modeling shown in Table 1. Smaller bond valence sums are observed for M' = Nb\(^{5+}\) compared to those for M' = Ta\(^{5+}\). Bond strain is distributed through both the A-site cation via compression and the B-site cations via expansion, while the O bond valence sums remain near the formal value. The GII values shown in Table 5 are large because of the significant strain in the bonds. Crystal structures are noted to have a GII as large as 0.2 v.u. in structures with lattice-induced strains, whereas crystal structures with a GII greater than 0.2 v.u. are often found to be unstable.\(^{52}\) These compounds have a relatively large GII, which may also be a factor in the reason competing phases are often observed in syntheses.\(^{53,54}\) The Ba\(_2\)MM'\(_2\)O\(_9\) (M = Mg, Ni; M' = Nb, Ta) compounds have a large tolerance factor and are near the edge of the perovskite stability range, which is illustrated by the formation of a nonperovskite structure type in Ba\(_3\)MSb\(_2\)O\(_9\) (M = Mg, Ni) when the slightly smaller Sb\(^{5+}\) is substituted for Nb\(^{5+}\) or Ta\(^{5+}\), but a nonstoichiometric 1:1 type ordered perovskite is observed for Sr\(_3\)NiSb\(_2\)O\(_9\).

The second-order Jahn–Teller distortion is expected to be influenced by the degree of overlap between the low-lying empty d orbitals and the filled O 2p orbitals. Electronic structure calculations and experimental measurements in a wide range of perovskite and related compounds indicate Nb\(^{5+}\) is more covalent than Ta\(^{5+}\).\(^{55}\) Calculations on KTa\(_{1-x}\)Nb\(_x\)O\(_3\) also indicate more covalent bonding for Nb\(^{5+}\) and show increased preference and energy stability gain for Nb\(^{5+}\) by an off-center displacement, whereas the Ta\(^{5+}\) preferentially remained in a more symmetric environment.\(^{57}\) Similar experimental coordination preferences are observed in KTaO\(_3\) (space group Pm\(_3m\))\(^{58}\) with Ta–O bond distances (Å) of 1.994(2) \(\times \) 6 and in NaTaO\(_3\) (space group Pbnm)\(^{59}\) with Ta–O bond distances (Å) 1.976(2) \(\times \) 2, 1.977(2) \(\times \) 2, and 1.980(2) \(\times \) 2. In contrast, the bond distances (Å) in

\[
\Delta d = \frac{1}{6} \sum_{n=1,6} [d_n - (d)]^2
\]

where (d) is the mean M–O bond distance and d\(_n\) are the individual M–O bond distances.\(^{55}\) A slightly larger distortion of the Nb\(^{5+}\) coordination environment for M = Mg, Zn is revealed by a larger \(\Delta d\) for M' = Nb than for M' = Ta shown in Table 5. Partial B-site disorder of BNN and BZN yields a slightly smaller \(\Delta d\) than in a fully ordered composition because of the preference of Ni\(^{2+}\) and Zn\(^{2+}\) to occupy a more symmetric octahedral coordination.

The slight differences in the coordination of Nb\(^{5+}\) and Ta\(^{5+}\) may result from differences in covalent bonding. The second-order Jahn–Teller distortion is expected to be influenced by the degree of overlap between the low-lying empty d orbitals and the filled O 2p orbitals. Electronic structure calculations and experimental measurements in a wide range of perovskite and related compounds indicate Nb\(^{5+}\) is more covalent than Ta\(^{5+}\).\(^{55}\) Calculations on KTa\(_{1-x}\)Nb\(_x\)O\(_3\) also indicate more covalent bonding for Nb\(^{5+}\) and show increased preference and energy stability gain for Nb\(^{5+}\) by an off-center displacement, whereas the Ta\(^{5+}\) preferentially remained in a more symmetric environment.\(^{57}\) Similar experimental coordination preferences are observed in KTaO\(_3\) (space group Pm\(_3m\))\(^{58}\) with Ta–O bond distances (Å) of 1.994(2) \(\times \) 6 and in NaTaO\(_3\) (space group Pbnm)\(^{59}\) with Ta–O bond distances (Å) 1.976(2) \(\times \) 2, 1.977(2) \(\times \) 2, and 1.980(2) \(\times \) 2. In contrast, the bond distances (Å) in

\[
\Delta d = \frac{1}{6} \sum_{n=1,6} [d_n - (d)]^2
\]

where (d) is the mean M–O bond distance and d\(_n\) are the individual M–O bond distances.\(^{55}\) A slightly larger distortion of the Nb\(^{5+}\) coordination environment for M = Mg, Zn is revealed by a larger \(\Delta d\) for M' = Nb than for M' = Ta shown in Table 5. Partial B-site disorder of BNN and BZN yields a slightly smaller \(\Delta d\) than in a fully ordered composition because of the preference of Ni\(^{2+}\) and Zn\(^{2+}\) to occupy a more symmetric octahedral coordination.

The slight differences in the coordination of Nb\(^{5+}\) and Ta\(^{5+}\) may result from differences in covalent bonding. The second-order Jahn–Teller distortion is expected to be influenced by the degree of overlap between the low-lying empty d orbitals and the filled O 2p orbitals. Electronic structure calculations and experimental measurements in a wide range of perovskite and related compounds indicate Nb\(^{5+}\) is more covalent than Ta\(^{5+}\).\(^{55}\) Calculations on KTa\(_{1-x}\)Nb\(_x\)O\(_3\) also indicate more covalent bonding for Nb\(^{5+}\) and show increased preference and energy stability gain for Nb\(^{5+}\) by an off-center displacement, whereas the Ta\(^{5+}\) preferentially remained in a more symmetric environment.\(^{57}\) Similar experimental coordination preferences are observed in KTaO\(_3\) (space group Pm\(_3m\))\(^{58}\) with Ta–O bond distances (Å) of 1.994(2) \(\times \) 6 and in NaTaO\(_3\) (space group Pbnm)\(^{59}\) with Ta–O bond distances (Å) 1.976(2) \(\times \) 2, 1.977(2) \(\times \) 2, and 1.980(2) \(\times \) 2. In contrast, the bond distances (Å) in

\[
\Delta d = \frac{1}{6} \sum_{n=1,6} [d_n - (d)]^2
\]

where (d) is the mean M–O bond distance and d\(_n\) are the individual M–O bond distances.\(^{55}\) A slightly larger distortion of the Nb\(^{5+}\) coordination environment for M = Mg, Zn is revealed by a larger \(\Delta d\) for M' = Nb than for M' = Ta shown in Table 5. Partial B-site disorder of BNN and BZN yields a slightly smaller \(\Delta d\) than in a fully ordered composition because of the preference of Ni\(^{2+}\) and Zn\(^{2+}\) to occupy a more symmetric octahedral coordination.

The slight differences in the coordination of Nb\(^{5+}\) and Ta\(^{5+}\) may result from differences in covalent bonding. The second-order Jahn–Teller distortion is expected to be influenced by the degree of overlap between the low-lying empty d orbitals and the filled O 2p orbitals. Electronic structure calculations and experimental measurements in a wide range of perovskite and related compounds indicate Nb\(^{5+}\) is more covalent than Ta\(^{5+}\).\(^{55}\) Calculations on KTa\(_{1-x}\)Nb\(_x\)O\(_3\) also indicate more covalent bonding for Nb\(^{5+}\) and show increased preference and energy stability gain for Nb\(^{5+}\) by an off-center displacement, whereas the Ta\(^{5+}\) preferentially remained in a more symmetric environment.\(^{57}\) Similar experimental coordination preferences are observed in KTaO\(_3\) (space group Pm\(_3m\))\(^{58}\) with Ta–O bond distances (Å) of 1.994(2) \(\times \) 6 and in NaTaO\(_3\) (space group Pbnm)\(^{59}\) with Ta–O bond distances (Å) 1.976(2) \(\times \) 2, 1.977(2) \(\times \) 2, and 1.980(2) \(\times \) 2. In contrast, the bond distances (Å) in

\[
\Delta d = \frac{1}{6} \sum_{n=1,6} [d_n - (d)]^2
\]
KNbO	extsubscript{3} (space group Amn	extsubscript{2}) are more diverse 1.873(5)×2, 1.996(1)×2, and 2.169(5)×2 as the Nb	extsuperscript{5+} moves toward an edge. Multiple phases occur for NaNbO	extsubscript{3}, and the Nb–O bond distances (Å) for the room-temperature phase	extsuperscript{62} range from 1.881(11) to 2.112(9). In a variety of structure types, the coordination environment distortion is typically larger for Nb	extsuperscript{5+} than for Ta	extsuperscript{5+}.	extsuperscript{37} Other factors being equal, the more ionic Ta	extsuperscript{5+} has less driving force than the more covalent Nb	extsuperscript{5+} to adopt a distorted coordination environment because of the reduced mixing of the O 2p and M	extsuperscript{5+} d orbitals and decreased second-order Jahn–Teller distortion. The significance of the coordination differences and reduced second-order Jahn–Teller distortion on the dielectric properties is explored in the subsequent sections.

### Dielectric Constant

In general, the measured \( \varepsilon \) are larger for Nb	extsuperscript{5+} than for Ta	extsuperscript{5+}-containing perovskites.	extsuperscript{63,64} The increase in the \( \varepsilon \) results from a larger polarizability of Nb	extsuperscript{5+} compared to that of Ta	extsuperscript{5+}. Dielectric properties and average values for 2:1 perovskites in this study are shown in Supporting Information Table C and additional \( V_m \) and \( \varepsilon \) perovskite data are given in Supporting Information Table D. The average \( \varepsilon \) increase for M	extsuperscript{′} = Nb	extsuperscript{5+} perovskites compared to M	extsuperscript{′} = Ta	extsuperscript{5+} for Group A perovskites with a tolerance factor less than unity is 4.0(9,2), whereas the average increase for Group B perovskites with a tolerance factor larger than unity is 5.6(9,2). The larger increase of \( \varepsilon \) in Group B compared to Group A perovskites is attributed to a larger ionic contribution to the total polarizability resulting from the smaller BVS of Nb	extsuperscript{5+} than Ta	extsuperscript{5+}. An ion with a smaller BVS is expected to give a larger ionic polarization contribution to the \( \varepsilon \) because an ion with longer and weaker bonds is expected to have a more facile polarization than an ion with a more ideal BVS.

The Clausius–Mossotti (C–M) equation,\textsuperscript{65} although strictly valid only for cubic structures in isotropic environments, may be used to estimate the \( \varepsilon \) of a material and is shown in (5),

\[
\alpha_D = \frac{V_m(\varepsilon - 1)}{b(\varepsilon + 2)}
\]

where \( \alpha_D \) is the total dielectric polarizability, \( b = 4\pi/3 \), and \( V_m \) is the molar volume. The total dielectric polarizability is assumed to be equal to the sum of individual ion polarizabilities determined from dielectric data of single-crystal oxides and fluorides and noncubic compounds if the dielectric anisotropy was determined.\textsuperscript{18} The agreement between the C–M equation calculated \( \varepsilon \) with the measured \( \varepsilon \) was approximately 0.5% in well-behaved compounds. In nonisotropic perovskite structures the macroscopic polarizability not only is the sum of the ion polarizabilities but also contains additional components from the crystal structure. C–M calculated (\( \varepsilon_{\text{calc.}} \)) and measured (\( \varepsilon_{\text{meas.}} \)) dielectric constants are plotted in Figure 3. There is relatively good agreement in the calculated and measured dielectric constants for Group A (tol. ∼ 1) perovskites, but significant error with Group B (tol. > 1) perovskites shown in the inset. One source of the discrepancy is the relatively small \( V_m \) of the Group B perovskites; the \( V_m \) are much smaller than expected from the predicted lattice parameters, which is illustrated by comparing Tables 1 and 2. The \( \varepsilon \) calculated using the \( V_m \) from SPuDS modeling and standard ion polarizabilities are in better agreement with \( \varepsilon_{\text{meas.}} \) shown in Table 6. The constraints imposed by the corner-sharing octahedra and the resulting compression of the A-site and slight expansion of the B-site results in an overall compression in the bonds, with the sum of the discrepancy factors being larger than zero. The weighted average discrepancy factor \( \langle d \rangle \) gives the average deviation from ideal bond valence sums and was calculated by using the following eq 6,

\[
\langle d \rangle = \frac{1}{N} \sum_{j=1}^{n} w_j d_j
\]

where \( w \) is the Wyckoff site multiplicity, \( d_j \) is the discrepancy factor for each of the \( n \) ions on a distinct crystallographic site, and \( N \) is the number of atoms in...
1. Ordered Ba$_3$MM'O$_9$ Perovskites

Figure 4. Average $T_f$ versus average $\epsilon$. Error bars represent one standard deviation.

Figure 5. Average $T_f$ versus $M^{2+}$ bond valence sum. Error bars represent one standard deviation.

the unit cell. The positive (d) values listed in Table 5 indicate the ions are, on average, over-bonded.

The similar M$^{3+}$ ionic radii and $V_m$ but larger $\epsilon$ of Nb$^{5+}$ compared to Ta$^{5+}$ perovskites leads one to expect a larger ion polarizability for Nb$^{5+}$. However, the tabulated ion polarizabilities$^{18}$ are $\alpha$(Nb$^{5+}$) = 3.97 Å$^3$ and $\alpha$(Ta$^{5+}$) = 4.73 Å$^3$. These values are inaccurate relative to each other for use in perovskites. The calculation of Nb$^{5+}$ and Ta$^{5+}$ ion polarizabilities applicable for perovskites was obtained using only compositions from Group A to calculate the total dielectric polarizabilities. With use of the C–M equation and the experimental $V_m$ and $\epsilon$, the ion polarizabilities of Nb$^{5+}$ and Ta$^{5+}$ for each composition were calculated by subtracting standard ion polarizabilities of the non-M$^{5+}$ ions from the C–M calculated total dielectric polarizability. Updated average ion polarizabilities values for Nb$^{5+}$ and Ta$^{5+}$ are 4.65(80) and 4.55(89) Å$^3$, respectively. The average ion polarizability value obtained for Nb$^{5+}$ exhibits the largest deviation from the tabulated value, whereas the value for Ta$^{5+}$ is in closer agreement. The updated ion polarizabilities for Nb$^{5+}$ and Ta$^{5+}$ may only be usable for well-behaved perovskite systems with a tolerance factor less than unity and may not be applicable to other structure types.

**Temperature Coefficient of the Resonant Frequency ($T_f$).** The $T_f$ is related to the temperature coefficient of the dielectric constant ($\epsilon_r$) and the linear thermal expansion coefficient ($\alpha$) by $T_f = -1/2(\epsilon_r + \alpha)$. Low $\epsilon$ materials typically have a positive $\epsilon_r$, and high $\epsilon$ materials ($>20$) generally have a more negative $T_f$.$^{66,17}$ Assuming a typical $\alpha$ for perovskites, a larger $\epsilon$ and more negative $T_f$ is expected to result in a more positive $T_r$ and has been observed previously in a wide range of dielectrics.$^{67,68,69}$ For the 2:1 perovskites examined in this study, the general trend of more positive $T_r$ with increasing $\epsilon$ is also observed and shown in Figure 4.

However, the general relationship between $T_f$ and $\epsilon$ does not rationalize the relatively large $T_f$ differences observed between BNT and BMT and BNN, BMN, and BZT, which respectively have similar $\epsilon$. In these compounds, ion coordination and bonding are proposed to be the source of the difference in $T_f$.$^{69}$ The most significant coordination difference is in M$^{2+}$ and the BVS of M$^{2+}$ versus $T_f$ shown in Figure 5. The coordination of M$^{2+}$ displays a trend in which a more underbonded (smaller BVS) M$^{2+}$ exhibits a more negative $T_f$.

The M$^{2+}$–O and M$^{5+}$–O bond lengths change at different rates. In general, for the same coordination number, the M–O bond distances change more slowly with temperature for higher valent (i.e., M$^{5+}$) ions than for lower valent (i.e., M$^{2+}$) ions.$^{70}$ This will change the polarizability differently at each B-site and hence $\epsilon$ and $T_f$ with temperature. The A-site is over-bonded and the O has nearly ideal bonding; therefore, the ionic component of the polarization is not expected to change as significantly with temperature as the underbonded B-site cations. A detailed analysis of the differences in the chemistry and bonding influences on the $T_f$ of the alkaline earth (Mg$^{2+}$), d$^0$ transition metal (Ni$^{2+}$), or the full d$^{10}$ shell (Zn$^{2+}$) cations would need to be considered in a comprehensive analysis of the structure–property relationships. However, the coordination trends are a useful guide in understanding the dielectric property differences and may be used to estimate the $T_f$ for space group P3$m_1$ perovskites based on the $\epsilon$ and atomic coordination environment of M$^{2+}$.

**Dielectric Loss and Q$\times$f.** Extracting the primary influences on Q values is difficult because of the complexity of separating intrinsic (e.g., cation order and phonon modes) and extrinsic (e.g., defects, impurity, processing, and sintering conditions) contributions to dielectric loss. Intrinsinc dielectric loss originates from anharmonic interactions of the electric field with the phonon system.$^{71}$ The Q$\times$f product is approximately equal for measurements performed on samples with different sizes and enables a comparison of Q measured

---

at different frequencies. The large variance in $Q\times f$ observed in ceramics shown in the large standard deviation in Supporting Information Table C results from the combination of both intrinsic and extrinsic effects. In many systems it is possible that slightly higher $Q\times f$ could be obtained with additional processing studies; however, considering the significant research and computational costs, it may be more efficient to manipulate the B-site coordination environment in order to achieve $Q\times f$ values very likely to be near the optimal intrinsic values.

An interesting correlation is observed with the sum of the differences between the B-site cation calculated BVS and the formal oxidation state $\Sigma_{B} = 2 \times [5 - \text{BVS(M)}] + [2 - \text{BVS(M)}]$. The smaller the sum of the B-site discrepancy factors, the higher the maximum reported $Q\times f$ values shown in Figure 6. Weakly bonded B-site cations in an expanded coordination environment may be one source of intrinsic dielectric loss. In a classical sense the more under-bonded B-site ions contribute to the dielectric loss because the ions “rattle” more freely in the octahedral cage and may interact more strongly with the anharmonic phonons. The precise nature of the contribution of the expanded coordination environment of [MO$_6$] and [M$'$O$_6$] to the dielectric loss is beyond the scope of this paper, but the correlation is presented to base future efforts on understanding intrinsic sources of dielectric loss in the 2:1 ordered perovskites.

**Conclusions**

Crystal structures of five Ba$_3$MM$'$$_2$O$_9$ (M = Mg, Ni, Zn; M$'$ = Nb, Ta) isostructural perovskites with 2:1 B-site ordering are reported from Rietveld refinements of neutron powder diffraction data. The perovskites crystallize in space group P3$_{1}$m1 with ordered (111) planes of M and M$'$ cations with a {M$'$M'M} layer repeat unit. Crystal structure modeling was used to generate a starting structural model for the Rietveld refinements. Constraints imposed by the space group symmetry combined with the optimization of the GI allow accurate prediction of the fractional coordinates. The coordination environments of Ba$^{2+}$ are compressed and the [MO$_6$] and [M$'$O$_6$] octahedra are expanded, resulting in bond valence sums that are larger for Ba$^{2+}$ and smaller for M$^{2+}$ and M$'$ than the formal oxidation states, whereas the O BVS are near ideal values. The modeling predicts the d$^0$ cations (i.e., Ta$^{5+}$ and Nb$^{5+}$) shift out of the center of the [MO$_6$] octahedron, forming three short and three long M$'$–O bonds, which is analogous to the experimental distortion.

Both of the M$'=$ Nb$^{5+}$ and Ta$^{5+}$ B-site cations undergo an out-of-center distortion to simultaneously satisfy the coordination requirements of both the O and cations. The out-of-center distortion is driven by the bond connectivity asymmetry and is allowed electronically by the second-order Jahn–Teller distortion of the d$^0$ M$'$ cations. The 2:1 ordered perovskite is not observed by substituting a d$^{10}$ M$'=$ Sb$^{5+}$ or 2:1 compositions with partially occupied d orbitals on the M$'$ cation; instead, other structures types or non-2:1 ordering is observed. Electronic contributions to bonding should be considered in experimental efforts to manipulate dielectric properties via B-site substitution to retain the high-Q 2:1 ordered state, rather than the lower-Q 1:1 ordered state of perovskites. The more covalent Nb$^{5+}$ has a higher preference for occupying a more distorted coordination environment revealed by an enhanced off-center shift (i.e., increased $\Delta d$), while Ta$^{5+}$ typically crystallizes with a more symmetric coordination environment. The observed coordination environment combined with smaller bond valence sums of Nb$^{5+}$ is used to suggest a more facile ionic polarization is present for the M$'=$ Sb$^{5+}$ perovskites. A larger ionic polarization component to the total polarizability of M$'=$ Nb$^{5+}$ is present compared to that of M$'=$ Ta$^{5+}$, resulting in a larger measured $\epsilon$. A detailed bond valence analysis reveals similar Ba and O coordination between compositions, and interesting relationships of the B-site coordination environments and dielectric properties. In addition to the general increase in $r_f$ with an increase in $\epsilon$, a composition with a smaller bond valence sum of M$^{2+}$ exhibits a more negative $r_f$. The smaller the sum of the discrepancy factors for the B-site correlates well with a larger measured $Q\times f$ maximum. The phenomenological relationships presented here are also a potential starting point in further investigations into the crystal structure–dielectric property relationships of 2:1 ordered perovskites.

**Acknowledgment.** This work was supported in part by a postdoctoral fellowship administered by the National Research Council. The author thanks T. A. Vanderah and P. W. Barnes for useful discussions.

**Supporting Information Available:** Crystallographic information files (CIF) for Ba$_3$MgNb$_2$O$_9$, Ba$_3$MgTa$_2$O$_9$, Ba$_3$NiNb$_2$O$_9$, Ba$_3$NiTa$_2$O$_9$, and Ba$_3$ZnNb$_2$O$_9$. Table containing Rietveld refinement parameters and isotropic thermal parameters; table containing selected bond angles; table containing $\epsilon$, $r_f$, and $Q\times f$ for 2:1 perovskites; table containing $V_m$, $V_m'$, $f_{acc}$, $\alpha$, and references for Group A and Group B perovskites (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM049831K