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Communicating with wireless perovskites: cation order and zinc volatilization

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Abstract

The synthesis of new families of perovskites with a 1:2 ordered $Ba(Zn_{1/3}Ta_{2/3})O_3$-type structure was investigated. The compound $La(Li_{1/3}Ti_{2/3})O_3$ was prepared with a 1:2 ordered arrangement of Li and Ti and is the first reported titanate with this type of structure. A new family of ordered perovskites, $(Sr_{2/3}La_{1/3})(Li_{1/3}Ta_{2/3})O_3$ and $(Sr_{2/3}La_{1/3})(Li_{1/3}Nb_{2/3})O_3$, were also prepared with a 1:2 layered order of Li^+ and B^{5+} cations. All three compounds exhibit dielectric constants >25 and Q.f values $>20{,}000$. Studies were also made on the phase stability of Zn-deficient compositions of BZT. The hexagonal perovskite, $Ba_8ZnTa_6O_{24}$, was isolated in single-phase form and was found to be the stable phase formed as a result of the loss of ZnO from BZT. $Ba_8ZnTa_6O_{24}$ can be sintered to high density at temperatures considerably lower than pure BZT and exhibits very good microwave properties. In particular at GHz frequencies $\varepsilon = 30.5$, Q.f = 62,000, and $\tau f = +36$ ppm/°C.

Keywords: Dielectric properties; Niobates; Perovskites; Tantalates; $Ba(Zn,Ta)O_3$

1. Introduction

Dielectric resonators based on compounds with a complex perovskite structure have been extensively studied due to their very high quality factors in the microwave region. The $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) system has received the most attention and is utilized in a number of commercial applications. For the tantalate and niobate-based complex perovskites the highest reported Q values are observed in systems that exhibit the so-called "1:2" type of cation order on the B-sites [e.g. BZT and $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT)]. In this structure the cations are ordered in the $<111>$ layers with a 1:2 {ZnTaTa} (or {MgTaTa) repeat sequence (see Fig. 1). Although this ordered structure exhibits the highest Q's, aside from the recently reported ordering in $BaBi^{3+}_{2/3}Te^{6+}_{1/3}O_3$,[1] all of the known 1:2 ordered chemistries are restricted to the $A^{2+}(B^{2+}_{1/3}B^{5+}_{2/3})O_3$ family (where A^{2+} = Ba,Sr,Ca; B^{2+} = Sr, Ca, Mg, Mn, Fe, Co, Ni, Zn; B^{5+} = Nb, Ta). Furthermore, even in those systems the 1:2 ordering is destabilized by the incorporation of extremely small concentrations of cation substituents on the B-site. For example the addition of just 3% $BaZrO_3$ to BZT induces the formation of a partially ordered 1:1 doubled perovskite structure.[2] The first part of this paper describes investigations aimed toward identifying and preparing new families of 1:2 ordered perovskites that could themselves have interesting dielectric properties or could be utilized as substituents in preparing new 1:2 ordered BZT and BMT based solid solutions.

Although the effect of changes in temperature and bulk chemistry on the cation order in BZT (and BMT) are now relatively well understood, considerable disagreement remains concerning the effect of the volatilization of ZnO during processing on the structure and properties. The second part of this paper focuses on the identity, structure, and dielectric properties of the Zn-deficient impurity phases. Since the early report on the formation of Zn-deficient surface phases during sintering,[3] dozens of publications have reported on the impurity phases formed during the processing of BZT based systems (see, for example, Refs. 4–6). While there is general agreement that Zn-deficient impurities are formed at high temperature, particularly—though not exclusively—on the surfaces of the sintered ceramics, there is no consensus on their identity or how they effect the microwave properties of BZT. Almost all of the previous investigations have assigned the impurity peaks in the X-ray patterns of BZT to a variety of phases located along the BaO–Ta_2O_5 binary, for example

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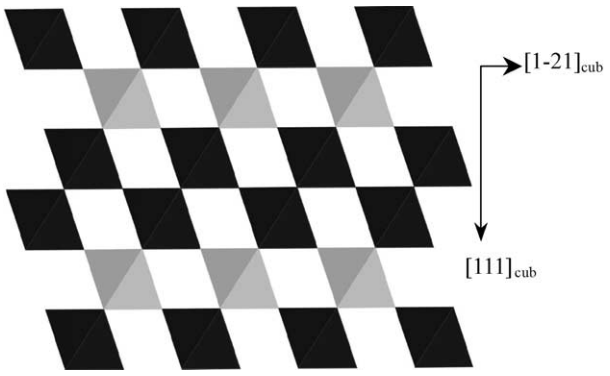

Fig. 1. Polyhedral representation of the 1:2 ordered $A^{2+}(B^{2+}_{1/3}B^{5+}_{2/3})O_3$ systems. B^{5+} octahedra are shown in black, B^{2+} octahedra in gray; oxygen and Ba atoms are omitted for clarity. Crystallographic directions are given for cubic sub-cell.

$BaTa_2O_6$, $Ba_5Ta_4O_{15}$, and $Ba_3Ta_2O_8$. The disagreement can be ascribed to several factors that include the weak intensity of the second phase peaks, and the considerable overlap with the reflections from the major BZT phase. In most cases there is less than satisfactory agreement between the peak positions of the cited impurity phases and the experimental patterns. Compared to the large number of reports citing impurity phases along the BaO–Ta_2O_5 binary, Zn-deficient ternary phases in the BaO–ZnO–Ta_2O_5 system have received little attention. However, one such phase, $Ba_8Zn_1Ta_6O_{24}$, was cited by Tolmer and Desgardin;[5] though in that work the importance of $Ba_8Zn_1Ta_6O_{24}$ was rejected in favor of the formation of $BaTa_2O_6$. The only other discussion of $Ba_8Zn_1Ta_6O_{24}$ has come recently from the groups of Hill (Trans-Tech Inc.) and Ibberson (University of Liverpool) who first discussed its formation during the course of our own studies (M. Hill, R.M. Ibberson, personal communications). The second half of this paper summarizes our results on the synthesis, structure, and dielectric properties of $Ba_8Zn_1Ta_6O_{24}$. Dense ceramic samples of $Ba_8Zn_1Ta_6O_{24}$ could be formed at temperatures considerably lower than BZT and were found to have high Q values. The X-ray patterns of this phase were found to give an excellent fit to the impurity peaks reported in previous studies of Zn-deficient BZT.

2. Experimental methods

All of the samples prepared in this work were prepared by standard solid state techniques using high purity oxide or carbonate powders. Details on the synthesis conditions are given in the results section for each compound. Ceramics were prepared from the ball-milled powders of the single-phase calcine after isotatic pressing at ~80,000 psi. The sintering temperatures were specific to each system and are detailed below. X-ray diffraction patterns were collected using a Rigaku DMAX-B diffractometer, using CuK_α radiation generated at 45 kV and 30 mA. Lattice parameters were calculated by least-squares refinement of powder diffraction data collected using silicon powder as an internal standard. Simulations of the X-ray patterns were conducted using commercially available software (CrystalMaker, Bicester, UK). Polished and thermally etched sintered pellets were examined using Scanning Electron Microscopy (JEOL 6300FV) and, after appropriate thinning, by TEM (Philips 420 TEM). The relative permittivity (ε_r) and dielectric loss tangent (tan δ) were measured in the 100 Hz to 1 MHz frequency range from −100 to 100 °C by the parallel-plate method using an LCR meter (Model HP 4284A precision LCR meter). Measurements of the dielectric properties at microwave frequencies were made using standard cavity techniques.

3. Results and discussion

3.1. New perovskites with 1:2 cation order

Compositions likely to produce 1:2 ordering of the B-site cations were targeted using crystal chemical designs that are described in detail elsewhere (Borisevich and Davies, in preparation). The critical factors responsible for the stabilization of this structure type include: (1) significant differences in the charge (usually >2) and size (typically >0.05 Å) of the two species occupying the octahedral position, (2) stability of the majority cation [B″ in $A(B'_{1/3}B''_{2/3})O_3$] in an off-centered/distorted octahedral coordination. The first factor is required for almost all ordered perovskites structures, the second is specific to the 1:2 ordered arrangement and accommodates the over-bonded character of the oxygen anions separating the two adjacent B″ layers.[1,7] The first new stoichiometry that was explored was $La(Li_{1/3}\ Ti_{2/3})O_3$. This compound had not been reported in an ordered form previously. To avoid the loss of lithium during the high temperature calcination and sintering (1300–1350 °C) platinum wrapped pellets of $La(Li_{1/3}\ Ti_{2/3})O_3$ were buried in a sacrificial Li-rich powder of Li_2TiO_3. Using this method it was possible to avoid any detectable formation of impurity phases (details are presented in Ref. 7). All of the peaks in the X-ray patterns of samples cooled rapidly from the synthesis temperature could be indexed using an orthorhombic Pbnm cell with $a=5.545$ Å, $b=5.561$ Å, $c=7.835$ Å. The patterns were essentially identical to those observed for tilted ($b^-b^-c^+$ in Glazer notation) disordered perovskites such as $LaFeO_3$.

When the samples were annealed below ~1180 °C an additional set of reflections appeared in the X-ray pattern (Fig. 2). These additional reflections were located at positions consistent with a 1:2 ordered arrangement of Li and Ti on the B sites. The X-ray pattern of the low

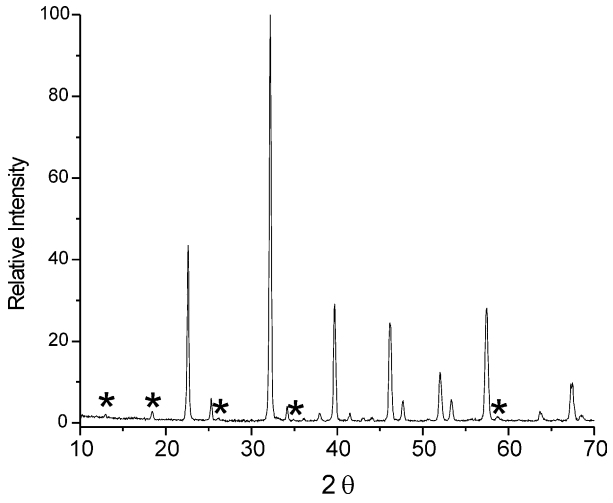

Fig. 2. Powder X-ray diffraction pattern of slow-cooled $La(Li_{1/3}Ti_{2/3})O_3$ (ordering peaks are marked with asterisks).

temperature form of $La(Li_{1/3}Ti_{2/3})O_3$ could be completely indexed using a monoclinic cell (space group $P2_1/c$) recently described for a 1:2 B-site ordered form of $Ca(Ca_{1/3}Nb_{2/3})O_3$ that exhibits the same type of tilt system.[8,9] Least squares refinement of the cell parameters yielded $a = a_c\sqrt{6} = 9.604$ Å, $b = a_c\sqrt{2} = 5.552$ Å, $c = a_c 3\sqrt{2} = 16.661$ Å, $\beta = 125.12°$. The presence of 1:2 type order was supported by the observation of strong ordering reflections at $k = {}^1/_3(111)^*_c$ in the electron diffraction patterns (see Fig. 3). Additional confirmation of the ordering of Li and Ti was obtained from calculations of the x-ray patterns of the 1:2 phase that yielded excellent agreement with the observed X-ray data.[7] By annealing and quenching samples at a variety of temperatures a reversible transition from 1:2 Li/Ti order to B-site disorder was located at 1180 °C.

$La(Li_{1/3}Ti_{2/3})O_3$ is the first example of a titanate perovskite with 1:2 B-site order. The addition of this compound to the short list of systems with this type of order is consistent with the criteria identified as critical in stabilizing this arrangement. In particular Li and Ti exhibit significant differences in charge and size, and Ti is well known to adopt stable off-centered geometries. The dielectric properties of the ordered form of $La(Li_{1/3}Ti_{2/3})O_3$ are currently being examined; the initial experiments gave a dielectric constant of approximately 40, and the ceramics showed relatively sharp resonance peaks in the microwave region. These preliminary measurements also indicate that the compound has a negative value of τf and may be useful in tuning other known 1:2 ordered systems such as BZN.

Other new examples of perovskites exhibiting 1:2 B-site order were found in systems containing Li and Nb/Ta on the B-sites. Fig. 4 shows the X-ray pattern collected from a composition $(Sr_{2/3}La_{1/3})(Li_{1/3}Ta_{2/3})O_3$. This compound was prepared in single-phase form at ~1350 °C. The X-ray pattern can be completely indexed in a tilted, 1:2 ordered structure (space group $P2_1/C$), with $a = 9.80$, $b = 5.65$, $c = 11.17$Å, $\beta = 125.2°$. Fig. 4 includes a theoretical x-ray pattern for the compound calculated assuming complete ordering of Li and Ta. The degree of tilting was estimated from the tolerance factor (details to be presented elsewhere). The good agreement between the experimental and theoretical patterns supports the assigned ordering, and direct structure refinement is in progress. Confirmation of the 1:2 type order was also obtained using electron diffraction. The B-site order was found to be stable up to the melting temperature, which lies close to ~1450 °C. Preliminary measure-

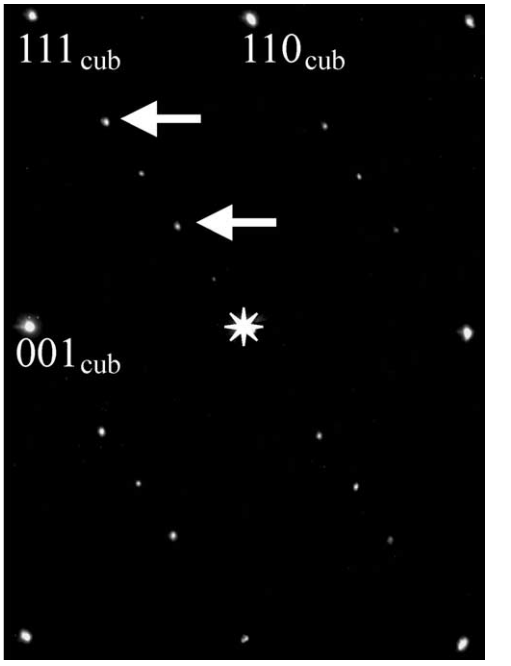

Fig. 3. $(110)_c$ zone axis electron diffraction pattern of ordered $La(Li_{1/3}Ti_{2/3})O_3$; examples of reflections associated with tripling of $(111)_c$ direction are arrowed.

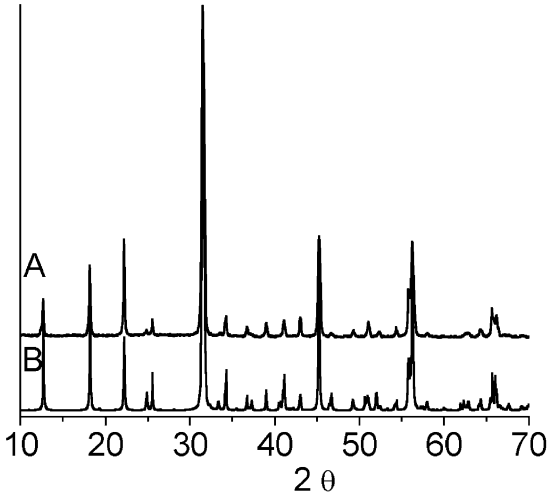

Fig. 4. Observed (A) and calculated (B) patterns for 1:2 ordered $Sr_{2/3}La_{1/3}(Li_{1/3}Ta_{2/3})O_3$.

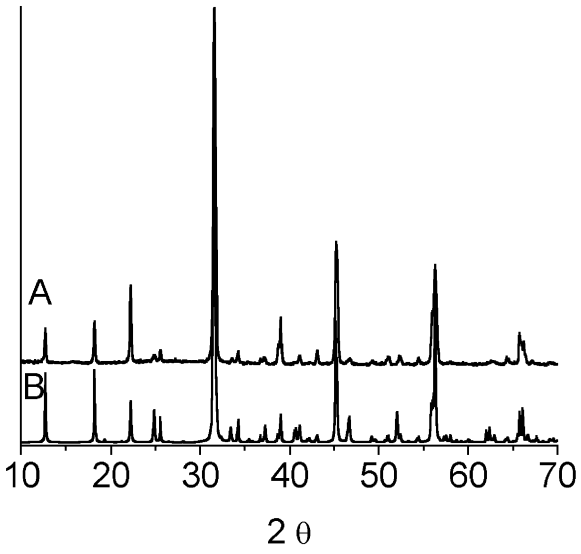

Fig. 5. Observed (A) and calculated (B) patterns for 1:2 ordered $Sr_{2/3}La_{1/3}(Li_{1/3}Nb_{2/3})O_3$.

ments of the dielectric properties at microwave frequencies yielded $\varepsilon' = 25$ and Q.f ~ 25,000.

A third new example of 1:2 order was found in the corresponding niobate system, $(Sr_{2/3}La_{1/3})(Li_{1/3}Nb_{2/3})O_3$ that was prepared in single-phase form at 1300 °C. The *x*-ray pattern of this compound is similar to its tantalate counterpart, see Fig. 5, and again good agreement was obtained with patterns calculated assuming complete 1:2 order of Li and Nb. The ordered arrangement of Li and Nb is stable up to the melting/decomposition temperature (>1400 °C) and the compound exhibits excellent sintering characteristics. Low frequency dielectric measurements yielded $\varepsilon' \sim 29$, higher frequency characterization will be reported later.

The successful formation of these new types of 1:2 ordered perovskites provides an opportunity for the synthesis of other new compounds in the same families. Their preparation will also enable the study of their use as end-members for the formation of 1:2 ordered solid solutions with BZT and BZN.

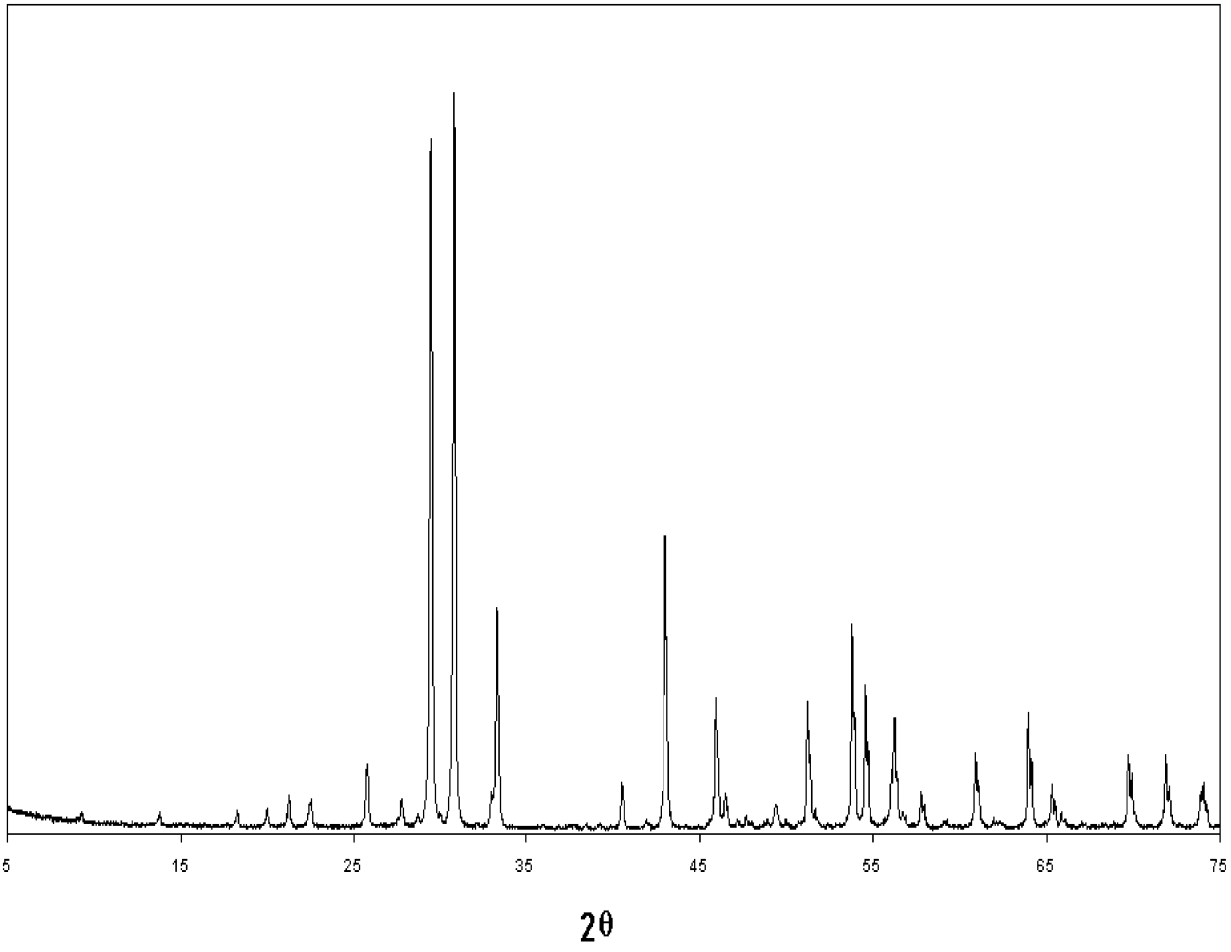

Fig. 6. Powder *x*-ray pattern of a single-phase sample of $Ba_8ZnTa_6O_{24}$.

3.2. Formation, structure, and properties of $Ba_8ZnTa_6O_{24}$

Because of the disagreement on the identity of the impurity phases in Zn-deficient BZT, we investigated the phase behavior of a series of compositions lying on the tie line between BZT and $Ba_5Ta_4O_{15}$. In particular the synthesis and properties of a composition $Ba_8ZnTa_6O_{24}$ (or $BaZn_{1/8}Ta_{3/4}O_3$) were explored in detail. A X-ray pattern collected from a sample after heating at 1350 °C is shown in Fig. 6. The pattern is very similar to that reported for the corresponding Ni compound, $Ba_8NiTa_6O_{24}$,[10] and can be indexed by a hexagonal cell with $a = 10.0825(14)$, $c = 19.0587(38)$ Å. Simulations of the X-ray pattern of $Ba_8ZnTa_6O_{24}$, conducted using the atom positions and occupancies reported for $Ba_8NiTa_6O_{24}$,[10] yielded excellent agreement with the experimental data and confirmed that these two compounds are isostructural (Thirumal and Davies, to be submitted). $Ba_8NiTa_6O_{24}$ has a hexagonal perovskite structure (space group P63cm) with an eight-layer $(cchc)_2$ close-packed arrangement of BaO_3 layers. The hexagonal layer produces a layer of face-sharing octahedra, see Fig. 7, occupied by Ta, Zn and vacancies. The ordering of the vacancies, Zn and Ta in this layer is discussed elsewhere (Ref. 10 and Thirumal and Davies, to be submitted). The diffraction pattern of $Ba_8ZnTa_6O_{24}$ was found to give an excellent match with the impurity peaks observed in previously published patterns of the Zn-deficient surface of BZT and it is likely that this phase, rather than the proposed binary Ba–Ta–O phases, was formed in those investigations.

The sintering properties of $Ba_8ZnTa_6O_{24}$ were investigated at 1350–1500 °C. By using a two-stage sintering process, in which the pellets obtained after a single sintering at 1400 °C were lightly ground, re-pressed, and re-sintered at the same temperature, ceramics with densities $\geqslant 94\%$ of the theoretical value were readily obtained. A SEM micrograph of the polished pellet surface is shown in Fig. 8. The microstructure exhibits minimal porosity and is comprised of "bar" and platelet-shaped grains. Detailed analysis of the grain structures and the sintering are provided in another publication (Thirumal and Davies, in preparation). Dielectric measurements were made on the pellets obtained from the two-stage sintering method. At low frequency (1 MHz) the dielectric constant was 30.3; when corrected for the density (94%) this yields a value of 32.2. The capacitance exhibited a small linear decrease with temperature over the range investigated (−100 to +100 °C) and the temperature coefficient of the capacitance was calculated to be−75 ppm/°C. At this frequency the losses were too low to be determined reliably. Measurements at microwave frequencies showed a strong and very narrow resonance peak consistent with a very high Q value. At 8.9 GHz the measured Q was 7025, yielding a Q.f of ~62,000. The value of the dielectric constant at this frequency (30.5) was in good agreement with the lower frequency data. The temperature coefficient of resonant frequency is +36 ppm/°C. The good Q value and excellent sintering characteristics of this phase suggest that it may have

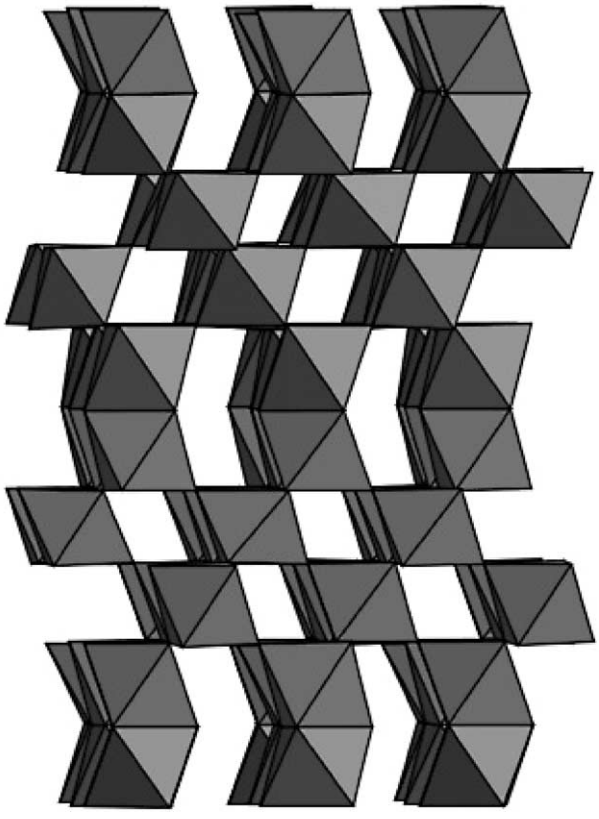

Fig. 7. Schematic representation of the arrangement of the octahedra in the 8H hexagonal perovskite $Ba_8NiTa_6O_{24}$ and $Ba_8ZnTa_6O_{24}$ structures. Ordering of the ions and vacancies in the face-shared octahedra is not shown.

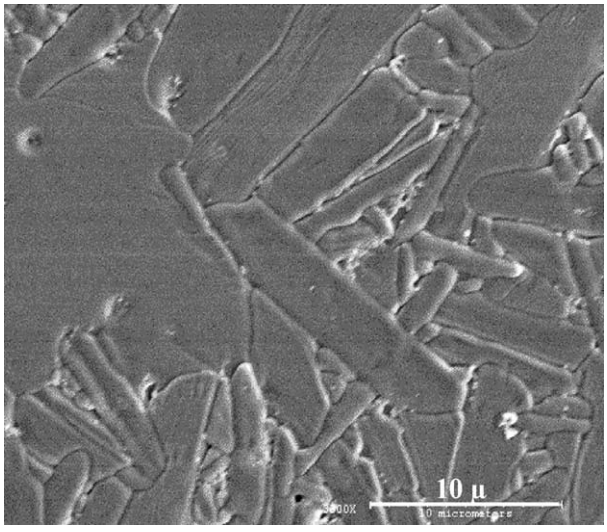

Fig. 8. SEM micrograph of a dense sample of $Ba_8ZnTa_6O_{24}$ after a two-stage sintering process.

useful applications, however additives will be needed to lower the temperature coefficient. We also investigated the behavior of sintered composites of $Ba_8ZnTa_6O_{24}$ and BZT and found these phases are compatible at high temperature and form stable two-phase mixtures. There is also evidence that $Ba_8ZnTa_6O_{24}$ is beneficial in lowering the sintering temperature of BZT.

4. Conclusions

While all previously identified perovskites exhibiting 1:2 type cation order were restricted to niobates and tantalates in the $A^{2+}(B^{2+}_{1/3}B^{5+}_{2/3})O_3$ family, this study shows that new ordered stoichiometries can be designed and prepared. For example, the first 1:2 ordered titanate ($LaLi_{1/3}Ti_{2/3}O_3$) was isolated and characterized, and two members of a new family of 1:2 ordered $(A^{2.33+})(B^{+}_{1/3}B^{5+}_{2/3})O_3$ systems were prepared with $A=(Sr_{2/3}La_{1/3})$, $B^{+}=Li$, and $B^{5+}=Nb$ and Ta. All three systems exhibit good microwave properties and may be useful as new ordering enhancing additives to BZT. Studies were also made on the identity of the stable phases formed as a result of the loss of ZnO from BZT. Single phases samples of the Zn-deficient hexagonal perovskite, $Ba_8ZnTa_6O_{24}$, were prepared for the first time and found to exhibit excellent sintering characteristics and very good microwave properties. The reflections in the X-ray patterns from this phase give an excellent fit to the impurities observed in several previous studies, and it was observed to be thermodynamically compatible with BZT.

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