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Influence of Non-Stoichiometry on the Structure and Properties of $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ Microwave Dielectrics: I. Substitution of $\text{Ba}_3\text{W}_2\text{O}_9$

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Influence of Non-Stoichiometry on the Structure and Properties of Ba(Zn_{1/3}Nb_{2/3})O₃ Microwave Dielectrics: I. Substitution of Ba₃W₂O₉

Abstract

A narrow region of Zn-vacancy-containing cubic perovskites was formed in the (1-*x*)Ba₃(ZnNb₂)O₉-*x*Ba₃W₂O₉ system up to 2 mol% substitution (*x*=0.02). The introduction of cation vacancies enhanced the stability of the 1:2 B-site ordered form of the structure, Ba(Zn_{1-*x**x*})_{1/3}(Nb_{1-*x*W_{*x*}})_{2/3}O₃, which underwent an order-disorder transition at 1410°C, ~35° higher than pure Ba(Zn_{1/3}Nb_{2/3})O₃. The Zn vacancies also accelerated the kinetics of the ordering reaction, and samples with *x*=0.006 comprised large ordered domains with a high lattice distortion (*c/a*=1.226) after a 12 h anneal at 1300°C. The tungstate-containing solid solutions can be sintered to a high density at 1390°C, and the resultant ordered ceramics exhibit some of the highest microwave dielectric *Q* factors (*Q*×*f*=1 18 000 at 8 GHz) reported for a niobate-based perovskite.

Comments

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Influence of Non-Stoichiometry on the Structure and Properties of $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ Microwave Dielectrics: I. Substitution of $\text{Ba}_3\text{W}_2\text{O}_9$

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A narrow region of Zn-vacancy-containing cubic perovskites was formed in the $(1-x)\text{Ba}_3(\text{ZnNb}_2)\text{O}_9-(x)\text{Ba}_3\text{W}_2\text{O}_9$ system up to 2 mol% substitution ($x = 0.02$). The introduction of cation vacancies enhanced the stability of the 1:2 B-site ordered form of the structure, $\text{Ba}(\text{Zn}_{1-x}\square_{x/3})(\text{Nb}_{1-x}\text{W}_{x/3})_2\text{O}_3$, which underwent an order–disorder transition at 1410°C , $\sim 35^\circ$ higher than pure $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$. The Zn vacancies also accelerated the kinetics of the ordering reaction, and samples with $x = 0.006$ comprised large ordered domains with a high lattice distortion ($c/a = 1.226$) after a 12 h anneal at 1300°C . The tungstate-containing solid solutions can be sintered to a high density at 1390°C , and the resultant ordered ceramics exhibit some of the highest microwave dielectric Q factors ($Q \times f = 18\,000$ at 8 GHz) reported for a niobate-based perovskite.

I. Introduction

OVER the last 30 years, numerous studies have been performed on the design, structure, and properties of dielectric oxides for applications as resonators in microwave-based communications devices. To enable their development as a commercial microwave material, these oxides must have a relatively high relative dielectric constant (ϵ_r), a very low dielectric loss, or high Q , at microwave frequencies, and a temperature-independent coefficient of resonant frequency (τ_f). The most widely studied family of microwave ceramics are the so-called “1:2” perovskites where the $\text{A}(\text{B}_1^{2+}\text{B}_2^{5+})\text{O}_3$ stoichiometry is amenable to a broad range of chemical substitutions (e.g., $\text{A} = \text{Ba}, \text{Sr}, \text{Ca}$; $\text{B}^{2+} = \text{Mg}, \text{Zn}, \text{Ni}, \text{Co}, \text{Sr}, \text{Ca}, \text{Mn}$, etc; $\text{B}^{5+} = \text{Nb}, \text{Ta}$) that allow the tuning and optimization of their dielectric properties.^{1–4} The most widely studied member of this family, $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BZT), is utilized in several commercial systems and has a Q factor $> 15\,000$ at 10 GHz, a zero τ_f in its substituted form, and a relative dielectric constant close to 30.^{5–7} The many investigations of the chemistry, structure, and properties of BZT and the other 1:2 perovskites have led to the identification of several different issues that complicate the economically viable manufacturing of bulk resonators with reproducible loss properties. In some cases, these issues have been understood and resolved; however, several outstanding problems remain in optimizing their performance. This series of papers focus on the $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ system, in particular, on the effect of small levels of non-stoichiometry on the atomic- and micro-level structure, on the influence of different muffling environments on the volatilization of ZnO at high temperature, on the tuning of the τ_f to zero, and the dependence of their $Q \times f$ on frequency. The latter issue has complicated the production of large “puck-sized”

resonators that retain the “super Q ” properties of their smaller 10 GHz counterparts, for 2 GHz base station applications.

The dielectric loss properties of perovskite microwave materials are notoriously sensitive to a number of different processing and structural variables. The losses can vary from sample to sample even when they have the same nominal composition due to small differences in the intrinsic crystal structure, microstructure, density, and impurity concentration. Beginning with the first investigations of BZT and BMT, the ordering of the different B-site cations in the $\text{A}(\text{B}_1^{2+}\text{B}_2^{5+})\text{O}_3$ structure was identified as a critical factor in affecting their Q value.^{1,6,7} Given that all other factors are equal, the lowest losses are observed when the two different B cations adopt a long-range “1:2” ordered arrangement with a $\{\dots\text{B}^{2+}\text{B}^{5+}\dots\}$ repeat along the $[111]$ direction of the cubic perovskite sub-cell. Clear correlations between the dielectric loss and the degree of cation order, and/or the size of the resultant ordered domains have been established in systems such as $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BZT), $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BMT), $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BMN), and $\text{Ba}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BCN).^{1–4,8} The principal signatures of the cation ordering used to correlate the changes in structure to the Q value include the relative intensity of the superlattice peaks, the deviation of the c/a ratio of the ordered supercell from the value expected for an ideal undistorted cell (where $c/a = \sqrt{3/2} = 1.2247$), and the size of the ordered domains. Studies of the kinetics and mechanism of the ordering have established that the intensity of the superlattice reflections, the domain size, and the associated lattice distortion (c/a) in BZT-type perovskites increase with increasing annealing or sintering time and coincide with improvements in $Q \times f$.^{5–7,9,10}

During the development of the 1:2 order, several types of planar defects (domain boundaries) can be formed. They include translational (antiphase) boundaries (APBs) that separate regions where the order nucleates on the same set of $\{111\}$ planes but is out of phase, and orientational (twin) boundaries separating regions that nucleate on different sets of $\{111\}$ planes; these have been described previously for 1:2 ordered BZT.¹⁰ Although it should be possible to remove the boundaries through extended annealing, in practice, the kinetically limited diffusion of the B-site cations prevents formation of a completely equilibrated state. The actual ceramic systems are usually comprised of domains of the various orientational and translational variants and their size depends considerably on the specific bulk chemistry and heat treatment.¹¹ In the absence of any additives, the high losses of partially ordered BZT were attributed to the formation of the elastically strained ordering-induced domain boundaries. Significant improvements in Q could be achieved through low-level substitutions (3 mol%) of BaZrO_3 ,⁶ where the partial segregation of Zr was suggested to stabilize the domain boundaries.¹

Other factors such as density, grain size, and the presence of secondary phases have made it difficult to establish a direct and unambiguous relationship between cation ordering and dielectric loss properties. While the relative density clearly affects the dielectric properties of any ceramic system, for the super Q microwave systems, it is particularly important as the losses of any pores or voids are higher than those of the perovskite grains. To

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focus on the effect of structure, it is critical that the properties be measured on samples of comparable and high density. Numerous investigations have been conducted on the effects of additives (e.g., V_2O_5 , ZrO_2 , Ga_2O_3 , NaF , Al_2O_3 , CdO , BaSnO_3 , WO_3) on the sinterability, microstructure, grain growth, and eventual dielectric loss of these systems (see, for example Yang and colleagues^{12–17}). In some cases, it has been claimed that the cation order is unimportant and that improvements in Q depend only on the density and grain size.^{12–14,17}

Another feature of these systems that complicates the structure–property relationship is their volatility at the high processing temperatures. In particular, for the Zn-containing perovskites, the volatility and loss of ZnO during sintering and annealing has been clearly established.^{5,7,10,18} The resultant changes in chemistry can produce secondary phases, affect the density, modify the bulk crystal chemistry, and change the $Q \times f$ properties. For BZT, many inconsistencies remain in identifying the chemistry of the secondary phases and understanding how the loss of ZnO affects the overall dielectric response. One of the original studies of BZT⁵ has reported that the loss of ZnO increased the Q value. In addition to the formation of secondary phases, identified as $\text{Ba}_3\text{Ta}_2\text{O}_8$, the authors noted that the c/a ratio of the ordered structure continued to increase even after the superlattice intensities had reached their maximum value. It was speculated this was associated with the partial replacement of the volatilized Zn^{2+} on the B sites by some of the A-site Ba cations. In that work, it was also suggested that the formation of secondary phases during the long-term annealing should reduce rather than increase the Q . The volatility of ZnO and secondary phase formation was reported to lower the Q , and density, of the closely related $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BZN) system.¹⁹ Recent reinvestigations of impurity formation in ZnO-deficient BZT identified the major impurity as a ternary hexagonal perovskite $\text{Ba}_8\text{ZnTa}_6\text{O}_{24}$, which also had a very high Q and would not be expected to deteriorate the overall loss properties severely.^{20,21}

Recently, high-resolution X-ray and neutron scattering techniques were utilized to study the changes in the structure of BZT during sintering and annealing. The resolution of these experiments revealed new details on the ordering, domain growth, and impurity formation.¹⁸ In addition to confirming the formation of $\text{Ba}_8\text{ZnTa}_6\text{O}_{24}$, two distinct trigonal 1:2 ordered phases with slightly different cell parameters and c/a distortions, and different superlattice intensities and widths, were identified in the diffraction profiles of BZT pellet and powder samples. Rietveld methods were used to ascertain the chemical differences between the two 1:2 ordered phases and these studies were the first to provide direct evidence for the formation of a Zn-vacancy-containing form of 1:2 ordered BZT. The small concentrations of Zn vacancies in the structure were suggested to play a role in accelerating the B-site diffusion and increasing the kinetics of the ordered domain growth.¹⁸

To minimize the loss of ZnO at high temperature, it is a common practice to process BZT and other related Zn-, Ni-, and Co-containing ceramics, in sacrificial “muffling” powders. In many laboratory studies, the muffling powders have the same composition as the pellet; in other laboratory studies and almost all larger scale investigations, more economical muffling environments consisting of ZnO powder or ZnO vapor (e.g., established by conducting the processing in inverted alumina crucibles soaked in ZnO) have been used. Some commercial processes also use high oxygen pressures to inhibit the loss of oxygen and therefore Zn from the samples. Although ZnO muffling has been shown to be effective in suppressing the volatilization, some studies have shown that the resultant Q values are reduced.²²

It is also well known that the dielectric losses of the BZT-related systems are very sensitive to the origin and purity of the raw materials. Several investigations (e.g., BZT,²³ $\text{Sr}_2\text{Al}(\text{Nb}/\text{Ta})\text{O}_6$,²⁴ BZN – $\text{Ba}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BNN),²⁵ BMT,²⁶ BZN, and BNN²⁷) have shown that defects associated with impure starting materials can have a profound effect on the mixing, reactivity, properties, and the degree of order. As a result, the processing of

these systems to achieve an optimum dielectric performance is notoriously difficult.

Although tantalate high Q perovskites such as BMT and BZT have been commercialized, in the last few years, economic factors associated with the high cost of Ta_2O_5 have increased the focus on their niobate counterparts. The processing of the $\text{Ba}(\text{B}_{1/3}^{2+}\text{Nb}_{2/3})\text{O}_3$ ($M = \text{Zn}, \text{Ni}, \text{Co}$) niobates can be further complicated by the reduced thermal stability of the cation order compared with their tantalate counterparts. In those cases, additional long-term (> 24 h) low-temperature heat treatments are required to convert the disordered structures of the sintered niobate samples into a well-ordered low-loss state; at lower annealing temperatures, the conversion can be affected by very slow kinetics.

Our investigations focus on the $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ system. The bulk crystal chemistry of BZN has been extensively investigated, and it undergoes a transition from a 1:2 ordered to disordered B-site arrangement at 1375°C .^{28–32} The reduced thermal stability of the cation order compared with BZT requires that the samples be annealed at a temperature below 1375°C to optimize the cation ordering and the loss properties. The literature values for the $Q \times f$ of BZN are quite varied; the highest reported value is 87 000 for a well-ordered sample.³³ Similar to BZT, the processing is further complicated by the volatility of ZnO, which can result in the formation of impurity phases. BZN has a higher permittivity (~ 40) compared with BZT (~ 30); however, it also has a relatively high-temperature coefficient (τ_f) of $\sim +30$ ppm/ $^\circ\text{C}$ that requires tuning, for example through the substitution of Co or Ni, prior to any practical application.

This investigation examined the structure and properties of non-stoichiometric vacancy-containing BZN formed through the substitution of $\text{Ba}_3\text{W}_2\text{O}_9$ and through the preparation of a new family of non-stoichiometric phases identified in a narrow region of the BaO – Nb_2O_5 – ZnO system. The Q factors of the ordered non-stoichiometric phases are shown to be much higher than stoichiometric BZN. The following paper studies the effect of different muffling environments on the structure and properties of BZN; these experiments demonstrated that rather than inhibiting the loss of ZnO, in certain muffling atmospheres, the ceramics absorb excess ZnO. The final paper investigates the tuning of τ_f in the BZN – $\text{Ba}_3\text{W}_2\text{O}_9$ system using Ni and Co where a variation of $Q \times f$ with frequency was associated with gradients in the ordering in large dense ceramic parts.

This first paper examines the effect of the substitution of $\text{Ba}_3\text{W}_2\text{O}_9$ on the ordering, sintering, and Q factor of $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$. In this system, the substitution of W^{6+} for Nb is charge compensated by the introduction of vacancies on the Zn sites. The presence of high concentrations of B-site vacancies usually destabilize a cubic perovskite in favor of structures with hexagonal stacking sequences where the vacancies are ordered in the resultant face-shared octahedra. However, small ranges of vacancy formation are observed in some cubic perovskite systems, such as $\text{Ba}(\text{Ti}_{1-x}\text{Nb}_{4x/5}\text{Vac}_{x/5})\text{O}_3$, where 2 mole% of Ti vacancies can be introduced without secondary phase formation.³⁴ Although such low levels of vacancies might be assumed to have a negligible effect on the crystal chemistry or permittivity, they can enhance the kinetics of the B-site ordering process, which is important in improving the Q factor of systems such as BZN where the domain growth can be slow. The $\text{Ba}_3\text{W}_2\text{O}_9$ end member³⁵ is isostructural with $\text{Cs}_3\text{Ti}_2\text{Cl}_9$ space group $R\bar{3}c$, with the BaO_3 layers in hexagonally close packing and the resultant face-shared pairs of $\text{W}(\text{VI})\text{O}_3$ octahedra alternating with octahedra-containing metal vacancies. Because tungstates are widely used as sintering aids for complex perovskite oxide ceramics,^{22,36,37} these solid solutions also have the added advantage of aiding the densification of BZN.

II. Experimental Procedure

Samples in the $(1-x)\text{Ba}_3\text{ZnNb}_2\text{O}_9$ – $(x)\text{Ba}_3\text{W}_2\text{O}_9$ (BZN–BW) system were prepared with $x = 0, 0.005, 0.006, 0.007, 0.01$,

0.015, 0.02, 0.04, and 0.06 using standard solid-state methods. Stoichiometric amounts of BaCO₃ (Cerac, 99.9%), Nb₂O₅ (Cerac, 99.95%), ZnO (Cerac, 99.95%), and WO₃ (Cerac, 99.5%) were mixed and calcined at 1000°C to expel CO₂. The products were then ball milled in ethanol with Y-stabilized zirconia media for 4 h and annealed for 10 h at 1100°C to improve the homogeneity and produce single-phase starting powders. The powders were ball milled again for 6 h, dried, and then pressed isostatically into pellets at 80 000 psi. The pellets were covered with sacrificial powders of the same composition and sealed in Pt envelopes to avoid the loss of ZnO. During the heat treatment, the sealed Pt envelopes were placed in alumina crucibles covered with a small amount of ZnO, and the crucibles were covered with flat lids. Weighing the pellets before and after reaction confirmed the effectiveness of this method in inhibiting any volatilization of the components. BZN–BW samples with $x = 0.005$ – 0.06 could all be sintered to a high density ($>94\%$) after a 4–6 h fire between 1370° and 1400°C. Pure BZN could only be sintered to reasonable density ($>90\%$) above 1420°C using the same processing conditions. Annealing treatments were conducted on all the sintered pellets at 1300°C for various times (6–24 h) to observe the development of the ordering and its effect on the dielectric properties.

X-ray diffraction (XRD) patterns were collected with a Rigaku diffractometer (The Woodlands, TX) using a CuK_α source operated at 45 kV and 30 mA. Equilibration of the samples was gauged by the absence of any changes in the X-ray patterns with additional heating. The unit cell parameters were refined by a least-squares procedure using data collected over the range of 10°–150° 2θ with a slow scan speed (0.2°/min) and a step size of 0.02°. Thermally etched samples were examined by scanning electron microscopy (SEM) using a JEOL 6300F FEG HRSEM (Peabody, MA) operated at 10 kV; chemical analyses were obtained on a JEOL 6400 Analytical SEM equipped with an Oxford energy-dispersive X-ray spectrometer (EDS, Oxford Instruments Concord Nanoanalysis, Concord, MA) and wavelength-dispersive X-ray spectrometer (WDS). Samples for high-resolution transmission electron microscopy (HRTEM) were prepared by disaggregating the ceramic samples followed by grinding under acetone in an agate mortar. The powder was then suspended in acetone and dispersed onto a lacey carbon 400 mesh TEM grid. Structure imaging was performed using a JEOL 2010F TEM/STEM operated at 200 kV.

The relative permittivity of the samples, ϵ_r , was measured from 100 Hz to 1 MHz using the parallel-plate method, combined with an HP 4284A precision LCR meter and a Delta 9920 environmental chamber from –150° to 200°C. Measurements of the dielectric loss, $Q = 1/\tan \delta$, and the temperature coefficient of resonant frequency, τ_f , were made at microwave frequencies using cavity methods. The Q values are given by $Q = 2f_0/\Delta f$, where f_0 is the center frequency of the resonance response and Δf is the frequency between 3 dB points. The temperature coefficient of the resonant frequency (τ_f) was calculated from data collected at 25°–75°C according to $\tau_f = \Delta f/f_0 \Delta T$, where f_0 is the reference frequency at 25°C. To observe any fluctuations in the $Q \times f$ values resulting from small differences in density or aspect ratio and establish their reproducibility, property measurements were made on several samples prepared from different batches of each composition. For each composition, the data points shown in the figures represent the mean values and standard deviations of the measured $Q \times f$ s.

III. Results

The X-ray diffraction patterns collected from samples in the (1– x)BZN–(x)BW binary after sintering at 1390°C for 4 h are shown in Fig. 1(a). Single-phase perovskite solid solutions were formed over a very narrow region of composition with $0.0 \leq x \leq 0.02$. For $x > 0.02$, the patterns contained peaks from secondary phases of BaWO₄ and a recently discovered barium zinc niobate tetragonal tungsten bronze [T.A. Vanderah, NIST,

Fig. 1. X-ray diffraction (XRD) patterns of (1– x)BZN–(x)BW with $x = 0.0, 0.005, 0.006, 0.007, 0.008, 0.01, 0.02$, and 0.04 : (a) after sintering at 1390°C for 4 h (b) after annealing at 1300°C for 24 h for $x = 0.0$ and 12 h for $x > 0$.

private communication]. In contrast to the pure BZN end-member, which exhibited a disordered B-site structure at this sintering temperature, the single-phase BZN–BW solid solutions contained weak diffuse superlattice reflections at positions (e.g., $2\theta \sim 17.7^\circ$), consistent with the formation of 1:2 B-site order. To investigate the response of the ordering to lower temperature annealing, the single-phase samples were heated at 1300°C to improve the ordering. After a ≥ 24 h anneal at 1300°C, the XRD pattern of pure BZN contained relatively weak and broad peaks associated with the ordering. However, after only 12 h of annealing at 1300°C, the ordering peaks in the BZN–BW compositions ($0 < x \leq 0.02$) became much more intense and sharp (see Fig. 1(b)). The refined lattice parameters of all the ordered compositions, obtained from data collected over $2\theta = 10^\circ$ – 150° , are listed in Table I. The unit cell volumes of the annealed samples were generally smaller than the corresponding as-sintered samples, consistent with previous observations that the cation ordering results in a reduction in the volume of the perovskite sub-cell.²⁴

The kinetics of the ordering in the BZN–BW solid solutions was investigated by monitoring the changes in the degree of ordering. The extent of the ordering has been represented previously by an order parameter S ($s = \sqrt{(I_{(100)}/I_{(110)(102)})_{\text{obs}} / \sqrt{(I_{(100)}/I_{(110)(102)})_{\text{cal}}}$), by the deviation of the c/a ratio of the ordered trigonal structure from an ideal value of $\sqrt{3}/2$ ($= 1.2247$) for an undistorted cubic perovskite sub-cell, and

Table I. Lattice Parameters of 1:2 Ordered $(1-x)\text{Ba}_3\text{ZnNb}_2\text{O}_9-(x)\text{Ba}_3\text{W}_2\text{O}_9$

x	$a(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$	c/a
0	5.7870 (2)	7.0850 (3)	205.48	1.22425
0.005	5.7853 (7)	7.0874 (6)	205.43	1.22507
0.006	5.7850 (4)	7.0920 (2)	205.54	1.22593
0.007	5.7848 (5)	7.0900 (2)	205.48	1.22563
0.008	5.7835 (3)	7.0890 (4)	205.35	1.22573
0.01	5.7820 (7)	7.0857 (9)	205.38	1.22548
0.015	5.7850 (1)	7.0856 (2)	205.36	1.22482
0.02	5.7841 (2)	7.0830 (4)	205.21	1.22456

by the ordered domain size quantified using the Scherrer formula. The broadened superlattice reflections collected using our laboratory X-ray diffractometer sometimes yielded an S larger than unity and also prevented reliable determination of the ordered domain size from the corresponding FWHM. Instead, the evolution of the ordered structure was monitored through the variation in the integrated relative intensity of the $(100)_{\text{order}}$ reflection and by direct observation of changes in the ordered domain size using HRTEM.

Figure 2 shows the change in the intensity of $(100)_{\text{order}}$ with annealing time for $x = 0.0$ and 0.01 . Consistent with the observations in other BZT-type 1:2 ordered perovskites and in many ordered intermetallic alloys,^{5,7,10,38} the time dependence of the $(100)_{\text{order}}$ intensity followed an exponential trend, increasing rapidly in the early stage and then becoming constant and time independent; the data points were insufficient to determine the exponent accurately, which can be used to determine the growth mechanism, in the region before the ordering reaction is complete. It is clear from Fig. 2 that the kinetics of the ordering process in the W-containing sample were significantly faster than in pure BZN. The variation in the maximum intensity of the $(100)_{\text{order}}$ superstructure reflection, obtained after annealing BZN for 24 h at 1300°C and BZN–BW for 12 h at 1300°C , with the composition is presented in Fig. 3. The maximum intensity was observed in a sample with $x \sim 0.006$.

For the 1:2 ordered perovskites, the c/a ratio provides an effective measure of the development of long-range ordering, which is accompanied by a small expansion of the trigonal supercell along the c direction.^{5,6} Data for the c/a ratio of the ordered BZN–BW samples are shown in Fig. 4. The changes in c/a are consistent with the trends in the $(100)_{\text{order}}$ intensities, and further confirm the accelerated ordering kinetics in the W-containing solutions with a maximum again close to 0.006.

Fig. 2. Variation in the integrated relative intensity of $(100)_{\text{order}}$ with the time of annealing at 1300°C for $x = 0$ and 0.01 . **Fig. 3.** Variation in the maximum intensity of the $(100)_{\text{order}}$ reflection with x after annealing for 24 h ($x = 0$) and 12 h ($x > 0$) at 1300°C .

The ordered domain growth was monitored using HRTEM. Figure 5(a) shows a lattice image and electron diffraction pattern along the $[110]_c$ zone axis collected from an as-sintered sample with $x = 0.007$. Superlattice reflections at $(h \pm 1/3, k \pm 1/3, l \pm 1/3)$ and the associated superlattice fringes were observed along both of the allowed $\langle 111 \rangle$ directions, and the sample comprised a twinned, ordered domain structure. In the as-sintered sample (1390°C , 4 h), the majority of the domains were isotropic, with an average size in the range 10–20 nm. After the 12 h anneal at 1300°C , the domains were significantly larger (~ 50 –70 nm) and developed a clear anisotropic shape, with the correlation along c being shorter than in the basal plane. A higher resolution image of a domain in the annealed sample is shown in Fig. 5(c), which includes simulated images calculated for a fully ordered 1:2 structure using the atom positions reported in.³⁹ The simulations were in excellent agreement with the observed image contrast. HRTEM studies of all the annealed compositions yielded average domain sizes of 20–30, 60–75, and 50–60 nm for $x = 0$, $x = 0.006$, and $x = 0.01$, respectively. These again highlight the accelerated ordering kinetics in the tungsten-containing compositions.

HRTEM was also used to explore the nature of the domain boundaries in the ordered systems. Figures 6 and 7 show experimental images and schematics of the three mostly encountered domain boundaries in the annealed sample of $x = 0.007$, namely boundaries parallel to $(001)_{\text{sub}}$ (Fig. 6(a)), $(111)_{\text{sub}}$ (Fig. 6(b)),

Fig. 4. Variation in the c/a ratio with x after annealing for 24 h ($x = 0$) and 12 h ($x > 0$) at 1300°C .

Fig. 5. High-resolution transmission electron microscopy (HRTEM) lattice images selected area diffraction patterns collected along $[110]_c$ from BZN–BW ($x = 0.007$) after: (a) sintering at 1390°C for 4 h, (b) annealing at 1300°C for 12 h. A higher resolution image of a domain in the annealed sample is shown in (c); the insets show simulated images calculated for a thickness of 5.4 nm (1) and 6.2 nm (2), a defocus of 0.0 nm and $C_s = 1.0$ mm.

and $(110)_{\text{sub}}$ (Fig. 6(c)). The contrast modulations with a periodicity of ~ 0.71 nm corresponding to $1/3 \langle 111 \rangle$, i.e., $(001)_{\text{ordered}}$, are indicated in the different regions of the domains. In some regions of the sample defects associated with stacking faults or a localized face-sharing hexagonal stacking sequence, e.g., cation-vacancy-containing Ba₅Nb₄O₁₅-type sequences, were also observed; however, these were isolated structural features and were not present in any significant concentration.

The observation of weak ordering peaks in the X-ray patterns (Fig. 1(a)) of the as-sintered (1390°C) BW-containing solid solutions implied that although the levels of substitution are small, they are effective in stabilizing the ordered structure to temperatures higher than the disordering transition in BZN, which occurs at 1375°C . To confirm that such a stabilization was

Fig. 6. High-resolution transmission electron microscopy (HRTEM) lattice images of the three most common types of domain boundaries with orientations parallel to (a) $(001)_{\text{sub}}$; (b) $(111)_{\text{sub}}$; and (c) $(110)_{\text{sub}}$.

occurring, a series of quenching experiments were conducted to locate the order/disorder transition in the BZN–BW solid solutions. Samples with the same protections for ZnO loss described previously were equilibrated at temperatures ranging from 1375° to 1420°C (at intervals of 5°C) for 10 h and then water quenched. The ordering transition temperature, Fig. 8, showed a significant increase up to a maximum at $x \sim 0.007$ where the samples disordered at $\sim 1412^\circ$, $\sim 35^\circ\text{C}$ higher than pure BZN. The response of the stability of the order to the substitution provides indirect, but convincing, evidence that the W cations enter the ordered structure rather than forming small amounts of undetectable impurity phases.

Because tungstate additives such as WO₃ and BaWO₄ have been explored previously as sintering aids for BZT-type perovskites, it was not surprising that the addition of Ba₃W₂O₉ to BZN also facilitated the densification of the ceramics. For the same processing conditions, i.e., pre-calcination time and temperature, ball-milling time, pressing conditions, etc., the BZN–BW solid solutions with $0 < x \leq 0.02$ could be sintered to high density

Table 2. Energy Dispersive X-ray Spectrometer (EDS) Analysis of (1-*x*)BZN-(*x*)BW Ceramics

	Grain (atomic %)	Grain boundary (atomic %)	Ideal stoichiometry (atomic %)
(a) <i>x</i> = 0.01			
O (<i>Kα</i>)	59.93	59.35	60.04
Zn (<i>Kα</i>)	6.62	6.59	6.60
Nb (<i>Kα</i>)	13.28	13.48	13.21
Ba (<i>Lα</i>)	20.03	20.41	20.01
W (<i>Lα</i>)	0.14	0.17	0.13
(b) <i>x</i> = 0.02			
O (<i>Kα</i>)	59.93	59.89	60.08
Zn (<i>Kα</i>)	6.55	6.50	6.54
Nb (<i>Kα</i>)	13.10	13.02	13.08
Ba (<i>Lα</i>)	20.17	20.29	20.03
W (<i>Lα</i>)	0.25	0.30	0.27

the microstructure was found in the samples with *x* = 0.006, where new grains were observed to grow from the “liquid phase” and parent grains (Fig. 10); the EDS results also suggested that the grain boundary phase served as a source for the new grains with the ordered structure. This observation implies that the high-temperature phase equilibria of this composition involve some type of peritectic phase transformation.

As expected, given the small changes in bulk chemistry, the relative dielectric constant and temperature coefficient of resonant frequency of the BZN-BW solid solutions were all similar to that of pure BZN with $\epsilon_r \sim 38\text{--}40$, $\tau_f + 21 \sim +23$ ppm/°C. However, the changes in dielectric loss of the solid solutions caused by the small additions of Ba₃W₂O₉ were very large. Property measurements were made at microwave frequencies on samples that were of essentially identical relative densities ($\sim 95\%$ of their theoretical value). Figure 11 shows the $Q \times f$ values obtained from BZN and its BW solid solutions after sintering, and after the 1300°C annealing treatment. The $Q \times f$ s increased dramatically with *x*, and followed a trend that paralleled the change in the intensity of the (100)_{order} superlattice reflection (Fig. 3) and the *c/a* ratio (Fig. 4). For all compositions, the $Q \times f$ after annealing was approximately 100% higher than after sintering, with the maximum value of 118 500 (at 8 GHz) being recorded for specimens with *x* = 0.007. This value is the highest reported for a niobate perovskite.

In some papers, it has been suggested that many of the Q improvements in the 1:2 perovskites are associated with changes

Fig. 10. Scanning electron microscopy (SEM) image collected from (1-*x*)BZN-(*x*)BW with *x* = 0.006, showing the formation of new grains from the liquid phase and parent grains. **Fig. 11.** Change in the $Q \times f$ of (1-*x*)BZN-(*x*)BW with *x* after sintering (square data points) and annealing (circles). The highest reported $Q \times f$ value for pure BZN³² is indicated by a star.

in density and grain size rather than the cation order; in this context, it is important to note that the annealing of BZN-BW only results in an alteration in the cation order and does not change the density or the grain size. The direct correlation between the improvements in Q and the change in structure is further confirmed by the data in Fig. 12, where the Q value of pure BZN and BZN-BW with *x* = 0.01 was monitored as a function of the time of annealing at 1300°C. The increase in the Q values with annealing time mirrors the increase in the intensity of the ordering reflections presented in Fig. 2 and change in *c/a*, with the BW-containing composition reaching a higher degree of order, a higher *c/a*, and a higher Q in a shorter time.

IV. Discussion

The data in the previous section indicate that the addition of Ba₃W₂O₉ to Ba(Zn_{1/3}Nb_{2/3})O₃ can be used to engineer ceramics with some of the highest Q values ($Q \times f = 118\,000$) reported for a niobate-based perovskite, and the losses for this system rival those of its “super Q ” BZT counterpart. The effectiveness of Ba₃W₂O₉ as an additive to BZN in realizing these superior properties is closely linked to the enhanced kinetics of the ordering process in the system, which in turn appear to be related to the presence of small concentrations of zinc vacancies on the B-site sub-lattice. This discussion focuses on the stability of the vacancy-containing cubic perovskite BZN-BW phases, on

Fig. 12. Change in $Q \times f$ of BZN and (1-*x*)BZN-(*x*)BW (*x* = 0.01) with the time of annealing at 1300°C.

the effect of vacancies and W on the stability and kinetics of the cation ordering, on the key aspects of the ordering responsible for the improvement in Q , and on the possible phase relations that lead to the reduction in the sintering temperature and formation of dense microstructures.

The single-phase, cubic perovskite-forming region in the $(1-x)\text{BZN}-(x)\text{BW}$ system is very narrow, with the X-ray patterns containing reflections from secondary phases for $x > 0.02$. In addition to the impurity-free XRD patterns, support for the substitution of BW into BZN for $x < 0.02$ comes from the EDS analyses and from the changes in the stability of the ordering, which are discussed below. The solubility limit of $x = 0.02$ corresponds to $\sim 0.67\%$ vacancies on the B-site lattice; this is similar to previous studies of the limits of B-site vacancy formation in other cubic perovskite systems such as Nb-doped BaTiO_3 .³⁴ Given the similar size and charge of Nb and W, the most likely arrangement of the cations in the 1:2 ordered form of the BZN-BW solid solutions is one in which the W^{6+} cations substitute onto the Nb sites and the vacancies occupy the Zn position. This distribution maintains the largest possible size and charge difference between the two ordered cation sites in the $\text{Ba}(\text{B}_{1/3}^{\text{I}}\text{B}_{2/3}^{\text{II}})\text{O}_3$ structure and gives an ordered stoichiometry: $\text{Ba}[(\text{Zn}_{1-x}\text{Vac}_x)_{1/3}(\text{Nb}_{1-x}\text{W}_x)_{2/3}]\text{O}_3$.

While the substitution of small levels of BW into BZN clearly enhances the kinetics of the cation ordering, the increase in the temperature of the order-disorder transition indicates that the small changes in stoichiometry induce a remarkably large enhancement in the relative stability of the 1:2 ordered phase. Many cation substitutions have been explored in BZN and its related ordered perovskites; in all cases, alterations in the stoichiometry of the B-site sub-lattice (e.g., through the substitution of BaZrO_3 , BaTiO_3 , $\text{La}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$, $\text{Ba}(\text{Y}_{1/2}\text{Nb}_{1/2})\text{O}_3$,¹⁻⁴ etc.) reduce the stability of the 1:2 order, which is usually destabilized in favor of 1:1 ("random-site") order or complete B-site disorder. Therefore, the enhancement in the thermal stability of the 1:2 order in BW-substituted BZN is unique.

It is well known that the charge (Δq) and size (Δr) difference of the two B-site positions is the primary crystal chemical factor affecting the stability of the ordered variants of these and many other mixed-metal perovskites. Therefore, it is possible that the change in stability in BZN-BW could be due to an increase in Δq and Δr that accompanies the substitution of vacancies and W^{6+} on the $\text{B}^{\text{I}}(\text{Zn})$ and $\text{B}^{\text{II}}(\text{Nb})$ sites, respectively. However, for the low levels of substitution observed here ($< 2\%$), the change in Δq (3.03 for $x = 0.01$, 3.0 for BZN) and Δr (0.1004 Å for $x = 0.01$, 0.10 Å for BZN) seem far too small to be responsible for the resultant $\sim 35^\circ\text{C}$ increase in T_{order} . Instead, we propose that the changes in T_{order} reflect the different degree of destabilization induced in the ordered and disordered phases by the Zn vacancies. As noted previously, B-site vacancies have very limited regions of stability in a cubic perovskite structure; significant concentrations ($\geq 2\%$) produce alterations in the stacking of the AO_3 layers and formation of the so-called "hexagonal perovskite" structures (e.g., $\text{Ba}_5\text{Nb}_4\text{O}_{15}$, etc.) where the vacancies order in the resultant layers of face-shared octahedra. Therefore, the introduction of an octahedral vacancy will undoubtedly increase the absolute free energy of the disordered and ordered variants of BZN-BW. However, the increase in T_{order} of BZN-BW suggests that the adverse effect of the vacancies on the energetics of the disordered phase is far greater than their effect on the 1:2 ordered structure.

In seeking an explanation for this effect, it is useful to consider the local bonding configurations in both forms of the BZN-based solid solutions. For the purposes of this argument, the small concentration of W on the Nb sites, which maintain complete oxygen stoichiometry, can be ignored. In the perovskite structure, each oxygen anion has two B-site and four A-site cations as nearest neighbors. For a random B-site arrangement in BZN, the probability of a given anion being coordinated two Zn, one Zn and one Nb, or two Nb cations is 11.2%, 44.4%, and 44.4%, respectively. For a fully ordered structure with a $\{\text{Zn}, \text{Nb}, \text{Nb}\}$ layered repeat, two-thirds of the anions are coordinated

by one Zn and one Nb, and one-third by two Nb cations; no anions have two Zn nearest neighbors. When a vacancy is present on the Zn site, the nearest-neighbor anions become underbonded (for an ideal octahedron, the valence of one Zn-O bond corresponds to a charge of 2/6) and local displacements of the remaining neighbors are required to compensate for the missing cations. Both factors reduce the bulk stability; however, the degree of destabilization will depend upon the specifics of the local coordination.

Anions coordinated by two Zn^{2+} cations, Zn-O-Zn, are already severely underbonded (for ideal polyhedra, the bond valence sum on this oxygen = $4(2/12) + 2(2/6) = 4/3$); therefore, a Zn vacancy will severely compromise the local stability, which could not be significantly improved by displacements of the remaining Zn^{2+} neighbor due to its relatively small contribution to the overall bond valence. Anions coordinated by one Zn^{2+} and one Nb^{5+} undergoes a very small degree of underbonding (for ideal polyhedra, the bond valence sum = $4(2/12) + 1(2/6) + 1(5/6) = 11/6$), which is accommodated in the stoichiometric structure through a small displacement in the Nb cations toward the underbonded anion. While a missing Zn cation would again reduce the overall energetic stability, the impact will be far less than for the Zn-O-Zn clusters, and could be accommodated more easily through an additional displacement of the remaining Nb neighbor. The impact would be further reduced when the Nb site is occupied by W^{6+} . Anions with a Nb-O-Nb coordination are not directly impacted by the presence of a Zn vacancy.

Because Zn-O-Zn linkages are completely avoided in the ordered structure, but are present in a significant concentration in the disordered arrangement, we believe that these differences in the local bonding arrangements are the primary factor responsible for the increase in the free energy difference of the ordered and disordered phases, i.e., $\Delta G_{\text{(order)}} = G_{\text{(ordered)}} - G_{\text{(disordered)}}$, and for the increase in T_{order} when Zn vacancies are introduced into the structure. The magnitude of the increase in T_{order} of BZN when BW is substituted, combined with the reduction in sintering temperature, directly impacts the processing of high Q ceramics as the initial sintering can be conducted in the stability field of the ordered phase.

We now turn to the effect of the vacancies on the kinetics of the ordering transformation and on the development of microstructures comprised of well-ordered domains with a maximum c/a distortion and a very high Q value. The mechanism of the ordering process for BZN-BW ceramics during the fixed temperature annealing below T_{order} is similar to that in many metallic alloy systems (see, e.g., Cu_3Au Nagler *et al.*³⁸) and can be divided into three steps: nucleation, ordering, and coarsening. Two important stages for the perovskite systems are the ordering process, where isolated ordered clusters grow in size, and the domain-coarsening process (domain growth), which proceeds after the impingement of the ordered domains.

Studies of the $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ system^{10,18} found that small concentrations of Zn vacancies, in that case introduced through the volatilization of ZnO, promote the cation diffusion process. The results presented in the previous section demonstrate that all the structural signatures of the ordering, the intensity of the superlattice reflections, the size of the ordered domains, and the degree of c/a "distortion," are accelerated and enhanced in the vacancy-containing BZN-BW solid solutions.

The transition from the disordered ($P\bar{3}m1$) to 1:2 ordered trigonal structure ($Pm\bar{3}m$) is first order, and the intensity of the superlattice reflections primarily arises from the ordering of Zn and Nb onto the B^{I} and B^{II} sites. However, the symmetry relationship allows for the formation of energetically degenerate orientational variants of the ordered cell where the c -axis lies along one of the four equivalent $[111]$ directions of the parent cubic cell. Therefore, the intra-grain structures are comprised of ordered nano-domains separated by domain boundaries. Localized disorder and strains at the boundaries can also affect the intensities (and shapes) of the superlattice diffraction peaks. The early stage of the ordering involves the nucleation and growth of all possible variants of the structure until the domains

impinge at domain boundaries. In this stage, the superlattice intensity for BZN (see Fig. 4) increases rapidly; however, the c/a ratio of the ordered structure remains close to that expected for an undistorted cubic sub-cell ($\sqrt{3}/2$). The TEM images of the sintered sample of BZN–BW also show that at this stage the shape of the small ordered domains is essentially isotropic (see Fig. 5(a)). After impingement of the domains, the subsequent coarsening occurs through the disappearance and reorientation of the domain boundaries. In the BZN–BW ceramics, the growth of the domains is accompanied by a continuous expansion of the c -axis and the c/a ratio approaches, but does not reach, the value reported in the literature for well-ordered powdered samples of BZN (1.2275) and other 1:2 tantalates and niobates.³⁹ For the ceramic samples of pure BZN, even after extended annealing, the domains show very limited growth, the c/a only undergoes a very small increase from its ideal value (Fig. 4), and neither approach the values observed for BZN–BW.

The HRTEM images of the annealed BZN–BW ceramics indicate that the domain growth and c/a distortion is accompanied by the development of an anisotropic domain shape and the correlation length along the ordered c direction is two to three times shorter than in the (100)_{order} basal plane. Similar anisotropies have been observed in HRTEM investigations of the ordered domains in other “well-ordered” 1:2 systems.^{1,40} The domain shape and limited c/a distortion suggest that the growth along c_{ord} is constrained by the elastic strains induced by the expansion of the superstructure. Because the increase in c/a will result in a rhombohedral distortion of the parent cubic sub-cell, it introduces a “ferroelastic-type” component to the phase development, with the resultant twin boundaries accommodating the elastic strains. The boundaries (Fig. 6) in the annealed BZN–BW sample become more defined during the domain-coarsening stage and their primary orientation, (110)_{cubic} and (100)_{cubic}, is the same as those observed for the twin boundaries in perovskites such as LaAlO₃ that undergo a cubic to rhombohedral ferroelastic transformation.^{41,42} For the pure BZN ceramic specimens, even after 24 h of annealing, the kinetic limitations of the B-site diffusion inhibit the domain coarsening and formation of well-defined boundaries, and prevent the development of an equilibrium c/a distortion.

The expansion of the 1:2 ordered structure along c is associated with the under- and overbonded character of the oxygen anions, which was cited above to understand the effect of the B-site vacancies on the order–disorder transition. For ideal polyhedra, anions between the two Nb cation layers are overbonded (bond valence = $4(2/12) + 2(5/6) = 7/3$), while those between a Zn and Nb layer are slightly underbonded. This situation is remedied by movements of the Nb cations toward the Zn layers to create an off-centered coordination with three short (~ 1.9382 Å) and three long (~ 2.0877 Å) Nb–O bonds.³⁹ The off-centering in the equilibrium structure increases the mean Nb–O bond length and expands the lattice along c . The formation of ordered domains with a “constrained” c -axis and an ideal cubic c/a would inhibit the off-centering of Nb, increase the free energy of the structure, and presumably increase the dielectric loss. Because the constraints on the domain growth and lattice distortion are greater in a dense ceramic pellet compared with a powdered sample, a set of experiments were designed to test this hypothesis and examine whether the c/a of the annealed BZN pellets would relax when they were re-annealed in a disaggregated powder form.

The annealing study was conducted on BZN pellets that had been sintered to a high density at 1425°C (6 h) and then annealed in pellet form for 24 h at 1300°C. These pellets were crushed, and the resultant powder was re-annealed at 1300°C for times varying from 12 to 60 h. The cell parameters of the powders derived from the pellet, Fig. 13, were compared with those collected from powder samples of BZN that had never been consolidated into a dense pellet, and to data where all of the annealing was conducted in a dense pellet form. For all heat treatments, the same precautions described earlier were taken to avoid any loss of ZnO and all the final XRD patterns were single

Fig. 13. Variations in a , c , and c/a of BZN with the time of annealing at 1300°C for: (a) a free powder (squares); (b) a dense ceramic pellet (triangles), and re-annealed powders (circles) obtained from pellets that were sintered to high density and annealed in pellet form for 24 h at 1300°C.

phase. To avoid any ambiguity in differences in the quality of patterns obtained from a pellet surface and a powder, after their annealing treatment the pellet samples were crushed into a powder for the X-ray analysis.

As shown in Fig. 13, large differences were observed in the variation of a , c , and c/a for the different samples of BZN. The free powder samples had a higher degree of order, a larger ordered domain size, and a much larger c/a distortion compared with the dense pellet samples. For example after 84 h annealing at 1300°C for the free powders, $c/a = 1.2268$ and for the dense pellets $c/a = 1.2251$. Even though the free powders of BZN showed a much larger distortion, from the change in c/a with time (Fig. 13), it is clear that 84 h were still insufficient for complete equilibrium, and the values were still lower than those reported for BZN powders prepared and annealed at 1250°C for approximately 140 h where $a = 5.782$ (Å), $c = 7.097$ (Å), and $c/a = 1.2275$.³⁹ The data for the powder obtained from the crushed pellet, which was annealed for 24 h in pellet form and had an essentially undistorted $c/a = 1.2247$, support the hypothesis of the constraints on the ordering and showed an immediate increase in c/a after annealing in an “unconstrained” powder form. We believe that these experiments provide convincing support for the formation of constrained ordered phases in the dense pellets of BZN with a c -axis that is shorter than the equilibrium value and a c/a ratio close to the “ideal cubic value.” We also propose that this is the primary factor in mediating the dielectric loss properties of BZN and prevents dense stoichiometric ceramic samples from reaching their highest possible Q values.

The major benefit of the addition of BW is the controlled introduction of Zn vacancies that enhance the relative stability

Fig. 14. A schematic pseudo-binary phase diagram for the $(1-x)$ $\text{Ba}_3\text{ZnNb}_2\text{O}_9$ – (x) $\text{Ba}_3\text{W}_2\text{O}_9$ system.

of the ordered structure, increase the kinetics of the ordering and coarsening process, and allow dense ceramic samples to adopt a structure where the c/a distortion approaches its maximum equilibrium value. We propose that these structural changes are primarily responsible for the exceptionally high Q values of the BZN–BW system, and every signature of the ordering process, the integrated intensities, the domain sizes, and the c/a distortion shows a direct relationship with the increase in Q . Recent papers have claimed that the importance of ordering is secondary to that of density and grain size; while they are clearly important for all high Q systems, for BZN–BW all of the samples have essentially the same relative density and although the grain size does change with the addition of very small amounts of BW, it does not scale with the detailed variation of Q presented in any of the previous figures.

Finally, we have used the observations of an increase in the ordering temperature and change in the microstructure to construct a schematic pseudo-binary phase diagram (Fig. 14) to represent the behavior of the $(1-x)$ $\text{Ba}_3\text{ZnNb}_2\text{O}_9$ – (x) $\text{Ba}_3\text{W}_2\text{O}_9$ system. The main features represented in the diagram are an increase in T_{order} , the appearance of a liquid phase in the compositions with $x \geq 0.005$ at $\sim 1410^\circ\text{C}$, and the appearance of a peritectic-type reaction in the sample of $x = 0.006$. The diagram contains a peritectic reaction at 1410°C involving the formation of an ordered $x = 0.006$ phase from a W-rich liquid and a disordered perovskite phase. For simplicity, the peritectic is portrayed as an invariant reaction at 1410°C . In fact, the $(1-x)$ BZN– (x) BW “pseudo-binary” is a section through the BaO – ZnO – Nb_2O_5 – WO_3 quaternary system and the additional degrees of freedom could give a temperature-, and composition-, dependent peritectic. This would explain the small decrease in the ordering temperatures observed for the compositions with $x > 0.007$ (Fig. 8). The appearance of a liquid phase in the system at 1410°C for $x \sim 0.005$ – 0.007 , or below for $x > 0.007$, is consistent with the lowering of the sintering temperatures and the corresponding increase in the grain size of the BW-containing ceramics.

V. Conclusions

Single-phase perovskite solid solutions are formed within a very limited range $0 \leq x \leq 0.02$ in the $(1-x)$ BZN– (x) BW system and form B-site vacancy-containing ordered structures with a stoichiometry, $\text{Ba}(\text{Zn}_{1-x}\square_x)_{1/3}(\text{Nb}_{1-x}\text{W}_x)_{2/3}\text{O}_3$. In contrast to other substituted 1:2 perovskites, the small concentrations of BW enhance the relative stability of the 1:2 ordered structure and increase the order–disorder temperature of BZN by 35°C . The stabilization of the order was ascribed to the instability of the

local bonding of oxygen in vacancy-containing Zn–O–Zn “clusters.” The Zn vacancies also increase the kinetics of the ordering and coarsening process and allow the c/a distortion of dense ceramic samples to approach their maximum equilibrium value. $\text{Ba}_3\text{W}_2\text{O}_9$ also lowers the sintering temperature of BZN by $\sim 50^\circ\text{C}$ through a mechanism that involves a liquid phase. All of these factors combine to produce a dramatic enhancement in the $Q \times f$ value of BZN, which reaches 118 500 at 8 GHz for $x = 0.007$ and rivals that of its “super Q ” tantalate counterpart.

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