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Influence of Non-Stoichiometry on the Structure and Properties of $Ba(Zn_{1/3}Nb_{2/3})O_3$ Microwave Dielectrics: III. Effect of the Muffling Environment

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Abstract

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Comments

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Influence of Non-Stoichiometry on the Structure and Properties of $Ba(Zn_{1/3}Nb_{2/3})O_3$ Microwave Dielectrics: III. Effect of the Muffling Environment

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The effect of different muffling environments on the structure and dielectric losses of $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) microwave ceramics was investigated. The microwave dielectric losses of stoichiometric BZN pellets heated in ZnO-rich environments were severely degraded (e.g. $Q \times f$ ~15 000 in ZnO powder) compared with samples muffled in their own powder ($Q \times f$ ~80 000). Structure analyses and gravimetric measurements confirmed that the ceramics muffled in ZnO powder or vapor absorb excess ZnO to form non-stoichiometric solid solutions with reduced cation order and Q. By using starting compositions in the $(1-x)BZN-(x)BaNb_{4/5}O_3$ binary ($x = 0.04$), the stoichiometry can be tailored to ensure that after the uptake of ZnO, the ceramics remain well ordered and are located in a high Q region of the system. For example, ZnO-vapor-protected $(0.96)BZN-(0.04)BaNb_{4/5}O_3$ reached a very high $Q \times f$ (~1 05 000) after sintering at 1400°C for 5 h.

I. Introduction

The effects of changes in temperature, additives, and bulk crystal chemistry on the cation order of $BaZn_{1/3}Ta_{2/3}O_3$ (BZT), $BaZn_{1/3}Nb_{2/3}O_3$ (BZN), and other closely related phases have been widely studied.[1,2] The processing of these materials to yield an optimum performance is notoriously difficult as very small changes in bulk stoichiometry, cation ordering, and the degree of volatilization of ZnO at a high temperature can result in significant changes in the dielectric loss properties. In a previous paper, a narrow range of single-phase non-stoichiometric perovskites were identified in the BZN system[3]; this paper explores the effect of different muffling environments on their chemistry, structure, and dielectric properties.

Contradictions in previous studies of the effect of the loss of ZnO on the processing, structure, and properties of BZT, BZN, and other microwave perovskites were summarized previously.[3–9] However, there is universal agreement that unless appropriate protective measures are taken, excessive losses of ZnO during the processing of these systems can seriously undermine the integrity of their structure and dielectric losses. Four general methods have been used to prevent or limit the loss of ZnO from BZT or BZN ceramics during processing. These include the sintering and annealing of ceramic parts: (a) in protective, "sacrificial" powders of the same composition; (b) in an excess ZnO environment where the samples are covered with ZnO powder, or heated in a ZnO-rich vapor environment; (c) in a high pressure of pure O_2 that inhibits the loss of O_2 and Zn and, by association, ZnO; and (d) by adding sintering aids that promote rapid densification before major component losses.

Samples of BZT muffled in their own powder usually exhibit a higher degree of ordering and Q [6]; however, for larger scale production, the large amounts of powder required to inhibit the volatilization from the ceramic parts greatly increase the cost of processing and complicate their production. Although muffling with ZnO powder reduces the cost factor and is effective in preventing the formation of Zn-deficient impurities, some reports indicate that this method lowers the resultant $Q \times f$ values.[10] Most, if not all, studies of ZnO-protected ceramics have focused on the effect of the muffling on the loss of ZnO and the Q; their effect on the composition and structure of the perovskite and the possibility that the muffling, rather than preventing volatilization, leads to an increase in their ZnO content has not been examined.

Our recent study[3] demonstrated that BZN accommodates limited ranges of non-stoichiometry in several directions in the $BaO–ZnO–Nb_2O_5$ ternary. The non-stoichiometry is very limited (typically <1%), but has a surprisingly large effect on the extent and stability of the B-site order, the sintering, and the dielectric loss properties. The sensitivity of the structure and properties to such small changes in bulk chemistry may provide an explanation for the large variations in the $Q \times f$ values of BZN or BZT reported in the literature. For a small excess of ZnO, a single-phase perovskite structure was retained for samples of BZN; however, the $Q \times f$ values were lowered due to significant reductions in the degree of cation order. It was speculated that the lowering of Q previously reported for samples of BZN muffled in a ZnO-rich environment was in fact associated with a gain rather than a loss of ZnO.[3] The $Q \times f$ map of the nonstoichiometric BZN solid solutions developed in that work showed clear "hotspots," with the highest values occurring for compositions along the $BZN–Ba_5Nb_4O_{15}$ and $BZN–BaNb_2O_6$ joins. Furthermore, if the chemistry was to change through a gain or loss of ZnO during processing, the bulk composition of the nonstoichiometric samples would still lie within the high $Q \times f$ plateau, while stoichiometric BZN would be moved into a region with a significantly lower Q value.

In this paper, a systematic study was conducted on the effect of different muffling environments on the crystal structure, microstructure, and dielectric properties of stoichiometric and non-stoichiometric samples of BZN. It was confirmed that ZnO-rich muffling environments increase the ZnO content of BZN and can reduce $Q \times f$ to ~20 000; however, when a non-stoichiometric $BZN–Ba_5Nb_4O_{15}$ starting composition is processed in a ZnO-vapor environment, very high $Q \times f$'s (~1 05 000) could be obtained after just 5 h of processing at 1400°C.

II. Experimental Procedure

Stoichiometric BZN was prepared by standard solid-state methods using high-purity oxide or carbonate powders (same as in Wu and Davies, submitted [11]). Batches of BZN pellets were sintered and annealed under different protections to examine their effect on the potential loss of ZnO. For samples muffled in their own "sacrificial" powders, the pellets were sealed in Pt bags

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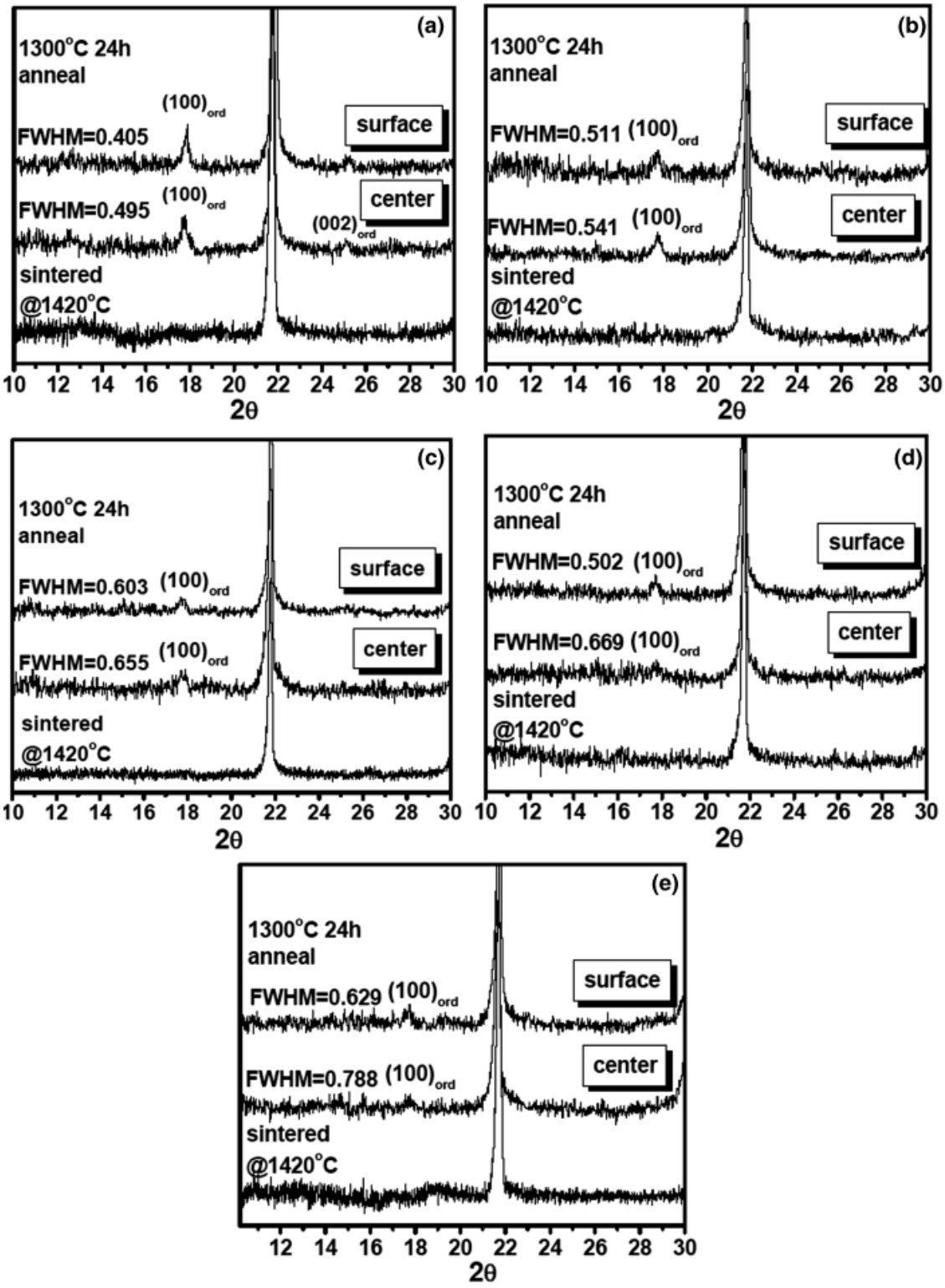

Fig. 1. X-ray diffraction patterns of the surface and interior of stoichiometric $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) pellets sintered at 1420°C for 5 h and annealed at 1300°C 24 h in muffling environments of: (a) their own powder, (b) sintered in their own powder and annealed in ZnO powder, (c) sintered and annealed in ZnO powder, (d) sintered and annealed in ZnO vapor, and (e) a pellet of BZN+0.5wt%ZnO sintered and annealed in ZnO vapor.

filled with the same powder; the Pt bags, together with a small amount of ZnO powder, were placed in Al_2O_3 crucibles covered with lids. For samples muffled in ZnO powder, the BZN pellet was completely buried in a large pile of zinc oxide. Samples were also muffled with a ZnO-rich vapor protection; in this case, the BZN pellets were covered with an inverted Al_2O_3 crucible that had been freshly washed with a dilute suspension of ZnO/water before the heat treatment. Experiments were also conducted on stoichiometric BZN powders where an excess of 0.5 wt% ZnO was added and blended before consolidation of the ceramic. The stoichiometric BZN pellets were all sintered at 1420°C for 5 h and then annealed at 1300°C for 24 h to improve the cation order. The nonstoichiometric samples of BZN, prepared with $x = 0.04$ in the $(1-x)BZN-(x)Ba_5Nb_4O_{15}$ system, were, unless stated otherwise, sintered and annealed at the same temperatures and under the same set of ZnO-loss protections used for BZN. The loss, or gain, of ZnO was monitored by weighing the samples before and after each heat cycle as well as by the

appearance of impurities in XRD patterns. XRD patterns were collected using a Rigaku DMAX-B diffractometer (The Woodlands, TX) with CuK_α radiation generated at 45 KV and 30 mA. The microstructures of the ceramics were studied on polished and thermally etched sintered pellets using a JEOL 6300F FEG HRSEM (Peabody, MA) operated at 10 kV. Dielectric loss measurements at microwave frequencies were conducted via standard cavity methods in the $TE_{01\delta}$ mode using an Agilent HP8720ES network analyzer (Palo Alto, CA).

III. Results

In most previous investigations, the XRD characterization of BZN ceramics has been conducted on either the pellet surface or on a powder obtained from a crushed pellet.[4,10,12] Significant differences have been noted in the structure, for example the c/a ratio, of the surface and the bulk, which, in certain cases, also showed differing degrees of impurity formation.[4] Differences in the ordered domain sizes in the bulk and surface have also been observed and ascribed to the possible influence of the loss of ZnO on the ordering kinetics.[5] Because ZnO-rich muffling powders or vapors are in direct contact with the pellet, it is also possible that the composition and structure of the surface and perhaps the interior of the ceramic can change during the high-temperature heat treatment. For all these reasons, in this study, the surface and interior of the pellet, which was sliced to different depths, were characterized by examining the structures of the resultant powdered slices.

Figure 1 shows XRD data collected from BZN pellets sintered at 1420°C for 5 h and then annealed at 1300°C for 24 h in different Zn-loss protective environments. The figures show the variation in the $(100)_{order}$ reflections collected from the XRD patterns of the surface and the interior of the BZN pellets. After sintering at 1420°C, all of the pellets had a disordered single-phase perovskite structure regardless of the depth or the muffling material. During the 1300°C annealing, the muffling environment had a significant effect on the degree of the cation order and domain coarsening. The BZN pellets that were sintered and annealed in their own powder showed a well-ordered structure with relatively sharp and intense ordering peaks (Fig. 1(a)). In comparison, pellets initially sintered in their own powder and then annealed in a ZnO muffling powder showed a sharply reduced degree of ordering (Fig. 1(b)). The ordering was further decreased in the BZN pellets that were sintered and annealed in a ZnO muffling powder (Fig. 1(c)) or in a ZnO-rich vapor atmosphere that was established by heating the ceramics in an inverted Al_2O_3 crucible coated with ZnO (Fig. 1(d)). Experiments were also conducted on samples of BZN that contained a 0.5 wt% excess of ZnO, a technique that has been used previously to compensate for the loss of ZnO at a high temperature. For these samples, the surface and interior only showed very weak and diffuse ordering reflections after sintering and annealing in a ZnO-rich vapor; see Fig. 1(e). The integrated relative intensity and the width of the $(100)_{order}$ supercell peak, which reflects the ordered domain size, in each of these samples are shown in Fig. 2. The highest intensity and sharpest ordering reflections were observed for the samples sintered and annealed in their own powder; pellets heated in a ZnO-containing muffling atmosphere (powder or vapor) all showed poorly ordered structures with a significantly lower degree of cation order and a smaller ordered domain size. It is also evident that for all the samples, the size of the domains in the interior of the pellets was reduced compared with the near-surface regions.

Experiments were designed to examine the effect of a ZnO-rich atmosphere on the structure of BZN ceramics that had first been annealed in their own powder to produce a well-ordered structure. The ordered sample was prepared by sintering (1420°C, 5 h) and annealing (1300°C, 24 h) BZN in its own powder to give the X-ray patterns shown in Fig. 1(a). This pellet was then buried in ZnO powder and re-annealed at 1300°C for 12 h. The X-ray patterns before and after the second anneal are compared in Fig. 3; the relative strength and sharpness of the $(100)_{order}$ peaks from the surface and interior are now reversed, with the ordering reflections from the surface being significantly broader and weaker.

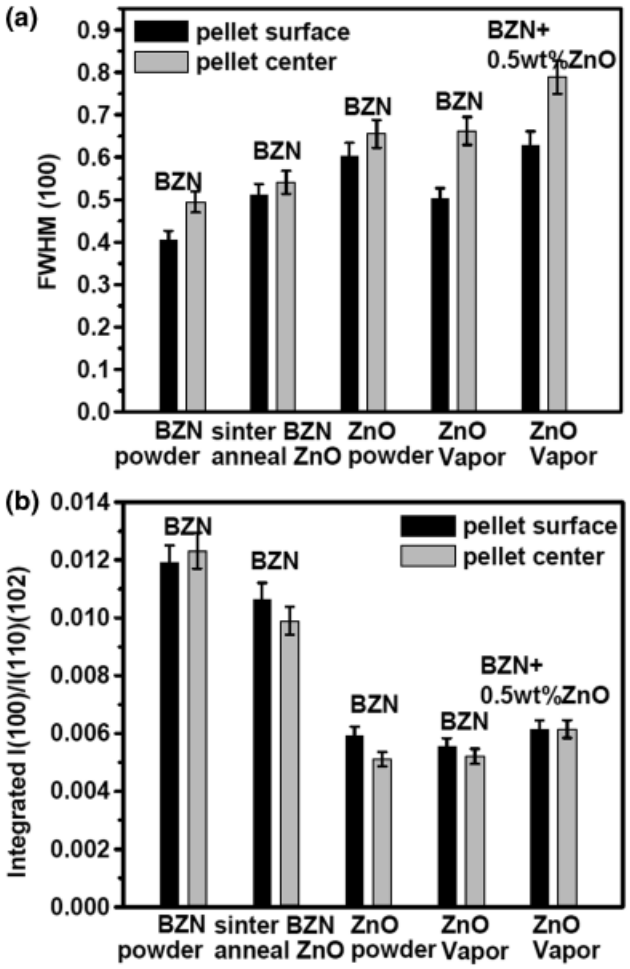

Fig. 2. (a) The width (full-width at half-maximum), and (b) the integrated relative intensity of the $(100)_{ord}$ reflection of $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) pellets after heating in the different ZnO-loss protective environments shown in Fig. 1. Data are included for the pellet surface and interior.

The effect of ZnO muffling on the microstructure was investigated by SEM examination using ceramics sintered at 1420°C for 5 h. Compared with a sample of BZN that was muffled in its own powder,[11] the ZnO-muffled pellet showed a slight increase in relative density (97% compared with 95%) and an increased grain size (~5 μm compared with 1–3 μm—see Fig. 4), and the microstructure was similar to those observed for the non-stoichiometric, ZnO-excess samples of BZN.[3] Similar results were obtained for the BZN pellets sintered in a ZnO-rich vapor atmosphere; a summary of the densities is given in Fig. 5.

The changes in structure led to significant alterations in the dielectric loss properties, which are summarized in Fig. 6. The highest $Q \times f$ (~85 000) was found in the samples of BZN that were muffled in their own powder during sintering and annealing. Even though they had slightly higher densities and larger grain sizes, the $Q \times f$'s of pellets sintered and annealed, or just annealed, with a ZnO powder or in a ZnO vapor were all decreased, and decreased to values as low as 15 000.

Recently, we characterized the changes in the $Q \times f$ properties over a narrow region of non-stoichiometric BZN solid solutions and suggested that some of these compositions could provide viable routes to higher $Q \times f$ ceramics.[3] The effectiveness of this method was investigated by using non-stoichiometric starting powders of $(1-x)BZN-(x)BaNb_{4/5}O_3$ with $x = 0.04$, which

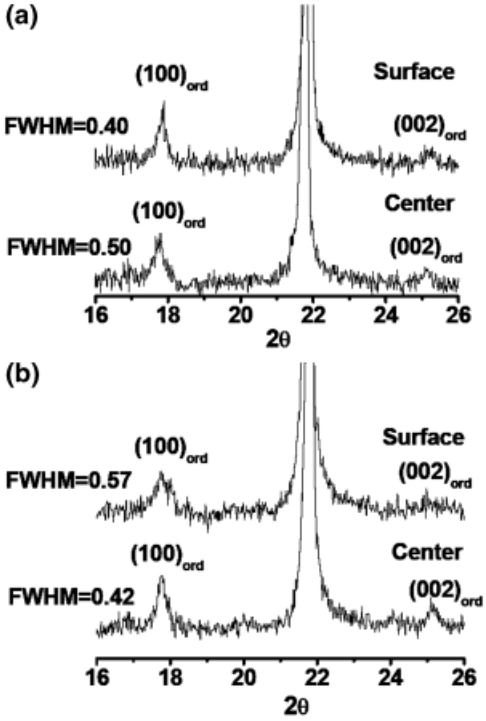

Fig. 3. X-ray diffraction patterns of stoichiometric $Ba(Zn_{1/3}Nb_{2/3})O_3$ sintered (1420°C, 5 h) in its own powder and then: (a) annealed at 1300°C for 24 h in its own powder, (b) re-annealed at 1300°C for 12 h in ZnO powder.

form a well-ordered structure with a high c/a (1.228) and a high $Q \times f$ (1 10 340 at 8 GHz). The samples were prepared and sintered using the same set of protections used for stoichiometric BZN. The XRD patterns collected from all of the muffled pellets were free of any peaks from secondary phases. The patterns from the $(1-x)$BZN$-(x)BaNb_{4/5}O_3$ ceramics sintered (1420°C, 5 h) and annealed (1300°C, 24 h) in their own powder contained sharp and intense $(100)_{order}$ peaks, and the $(226)_h$ and $(422)_h$ peak splitting at a high angle (Fig. 7) confirmed a well-defined c/a lattice distortion (= 1.2282). The pellets muffled in a ZnO-rich vapor also exhibited strong and sharp ordering peaks; however, they had a reduced high-angle peak splitting (Fig. 7) and a lower c/a (= 1.2271). The ordering peaks for samples muffled in ZnO powder were much weaker and broader and had a close to ideal c/a. The reduced c/a's for the ZnO-muffled ceramics suggest that the protective environment alters their composition. Gravimetric measurements indicated that rather than losing ZnO at a high temperature, the weight of the ZnO-protected ceramics increases during the heat treatment, while the samples annealed in their own powder show no detectable changes in mass. This is discussed later.

Additional support for a change in composition because of a gain of ZnO during annealing was obtained from observations of the microstructures using SEM. After sintering at 1420°C, all of the BZN–$Ba_5Nb_4O_{15}$ ($x = 0.04$) pellets were well densified (>96%) regardless of the muffling environment; however, the resultant grain sizes were quite different (Fig. 8). Pellets sintered in their own powder had a grain size in the range 2–5 μm (Fig. 8(a)), and those heated in the ZnO-rich atmospheres contain grains ~1–2 μm, Fig. 8(b). The ZnO vapor and powder protections were also found to reduce the temperatures required to achieve high levels of densification and in both environments the pellets could be sintered to >96% density at 1400°C.

Table I lists the $Q \times f$ values of the $(1-x)$BZN$-$x$BaNb_{4/5}O_3$ ($x = 0.04$) samples sintered and annealed in the different muffling atmospheres. The $Q \times f$'s of all the non-stoichiometric samples were higher than their stoichiometric BZN counterparts that were sintered and annealed under the same conditions. The highest $Q \times f$ was observed for samples heated in their own

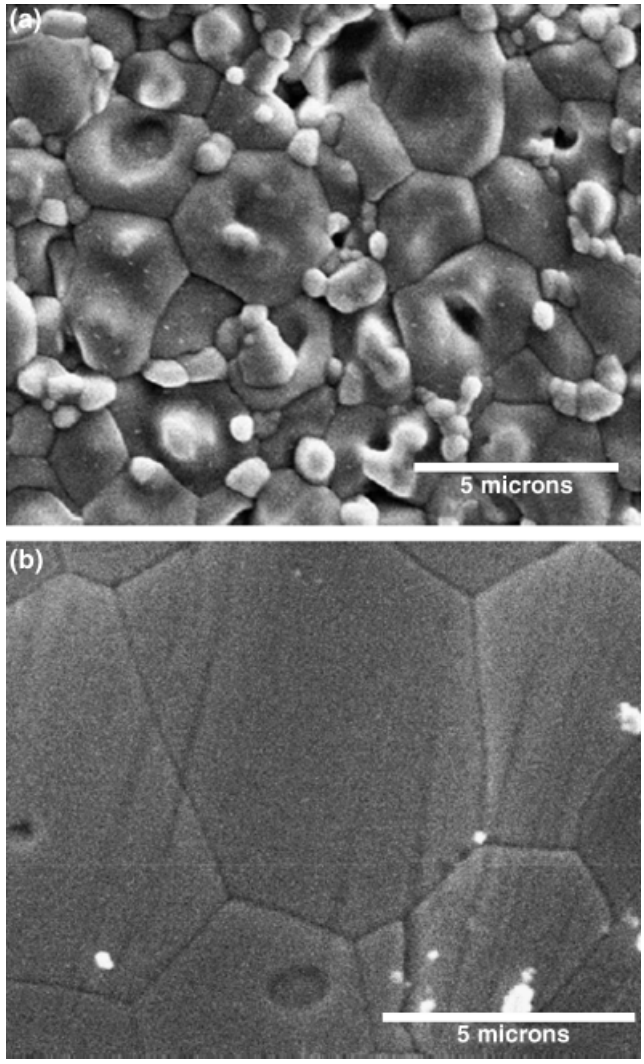

Fig. 4. Scanning electron microscope images of a stoichiometric $Ba(Zn_{1/3}Nb_{2/3})O_3$ pellet sintered in (a) its own powder, (b) in ZnO powder.

powder or in a ZnO-vapor atmosphere and reached a value of ~110 000 after annealing. The $Q \times f$ of ceramics prepared with ZnO powder protection was reduced to ~75 000, consistent with the accompanying reduction in the cation order. The ZnO-vapor samples also showed a very high $Q \times f$ (105 000) after the

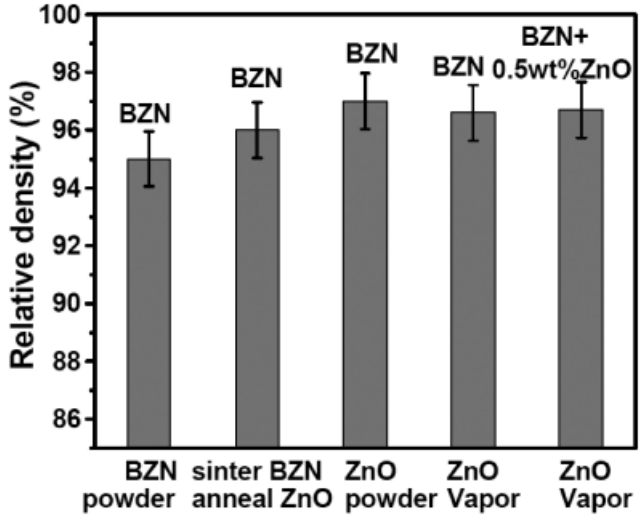

Fig. 5. Relative densities of stoichiometric $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) after sintering in different ZnO-loss-protective environments.

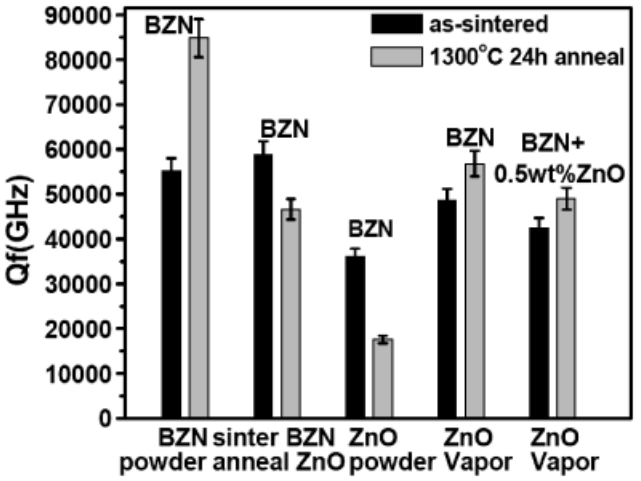

Fig. 6. $Q \times f$ values of stoichiometric $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) after heat treatments in different ZnO-loss-protective environments.

initial sintering, which could be conducted at temperatures 20 degrees lower (1400°C) than the pellets muffled in their own powder. In a previous paper, we showed that the small degree of non-stoichiometry along the $(1-x)BZN-xBaNb_{4/5}O_3$ line induced a relatively large change in the temperature of the order–disorder transition, which increased from ~1375°C for pure BZN to ~1415°C for $x = 0.04$.[3] Because the ZnO-vapor atmosphere allows the samples to reach a high density at a temperature below the disordering transformation, they sinter in an ordered, rather than disordered, state. Correspondingly, the effect of the subsequent 1300°C anneal on the $Q \times f$ was quite small compared with the ceramics annealed in their own powder, which are disordered after sintering at 1425°C and only order during the annealing. The reduction in the sintering

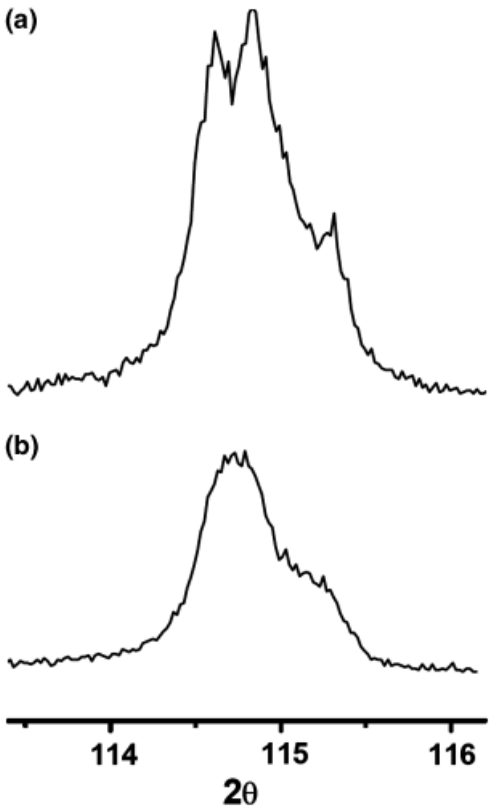

Fig. 7. High-angle peak splitting of $(1-x)Ba(Zn_{1/3}Nb_{2/3})O_3 - xBaNb_{4/5}O_3$ ($x = 0.04$) after sintering and annealing at 1300°C for 24 h in: (a) a powder of the same composition, (b) ZnO vapor.

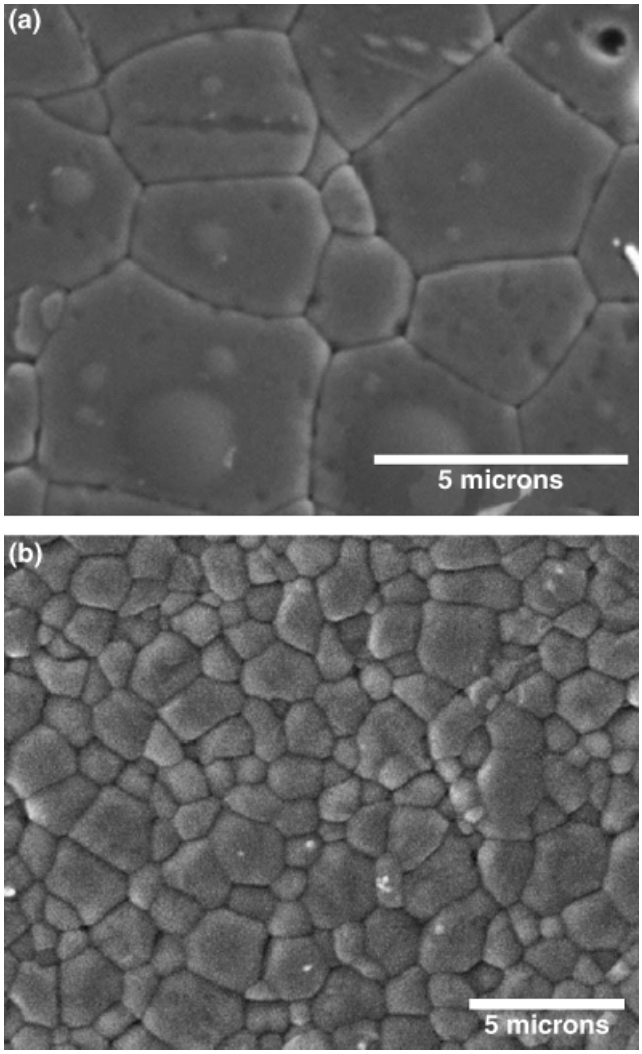

Fig. 8. Scanning electron microscope images of the $(1-x)Ba(Zn_{1/3}Nb_{2/3})O_3-xBaNb_{4/5}O_3$ ($x = 0.04$) sintered in (a) its own powder (b) ZnO vapor.

temperature to a value that lies within the stability field of the ordered state is particularly important as it allows the formation of ceramics with excellent Q values after a very short firing (5 h at 1400°C).

IV. Discussion

Significant variations in the structure and Q value were observed when BZN ceramics were processed in different muffling environments. The $Q \times f$ of stoichiometric BZN pellets muffled in ZnO powder or ZnO vapor were seriously degraded compared with samples heated in their own powder (Fig. 6) even though the ZnO-rich environments improved the density and grain size (Figs. 4 and 5). The reduction in $Q \times f$ was accompanied by a large decrease in the cation order (Fig. 2). In contrast, non-stoichiometric samples of BZN prepared in the $(1-x)BZN-xBaNb_{4/5}O_3$ system with $x = 0.04$ showed excellent $Q \times f$ values in their as-sintered state when they were fired in a ZnO vapor and did not require any additional annealing to reach $Q \times f$'s greater than 100 000. In this section, we discuss the effect of the muffling materials on the bulk composition, crystal chemistry, microstructure, and $Q \times f$ value of BZN and the importance of non-stoichiometry in optimizing the processing and dielectric loss properties of these and other high Q complex perovskites.

In a recent paper,[3] it was demonstrated that BZN can accommodate small degrees of non-stoichiometry along a variety

Table I. *Qf* Values of $(1-x)BZN-xBaNb_{4/5}O_3$ ($x = 0.04$)

Pellet composition	Muffling environments	*Qf* (at 8 GHz) Assintered (T_{sinter})	*Qf* (at 8 GHz) Annealed for 24 h at 1300°C	Relative density (%)
BZN–$Ba_5Nb_4O_{15}$ ($x = 0.04$)	Same composition	50 010 (at 1420°C)	110 350	94.6
BZN–$Ba_5Nb_4O_{15}$ ($x = 0.04$)	ZnO powders	60 880 (at 1400°C)	75 500	95.5
BZN–$Ba_5Nb_4O_{15}$ ($x = 0.04$)	ZnO-rich vapor	104 690 (at 1400°C)	109060	95.6

of different directions in the BaO–ZnO–Nb_2O_5 system and that these can induce very large changes in the stability and the kinetics of the cation ordering. For an excess of ZnO, solid solutions can be formed in the $(1-x)BaZn_{1/3}Nb_{2/3}O_3-(x)ZnO$ system for $0 \leq x \leq 0.02$. The small increase in the Zn:Nb stoichiometry reduces the charge difference of the two ordered B sites and destabilizes the cation order. Therefore, the observation of a large reduction in the degree of order and the ordered domain size when stoichiometric BZN is muffled in ZnO-powder or vapor suggests that rather than inhibiting the loss of ZnO, in these protective environments, the pellets form a non-stoichiometric perovskite with an excess of ZnO. The reaction of ZnO with the pellets was confirmed by measurements of a small weight gain of ~0.07 and 0.5 wt% after the vapor and powder muffling, which corresponds to a gain of 0.2 and 1.7 mol% excess ZnO, respectively. No weight change was observed for the BZN ceramics muffled in their own powders. As the degree of weight gain increases, the degree of cation order and the domain size decreases and, given that the reaction is initiated at the ZnO/BZN interface, the pellet surfaces show a lower degree of order (Fig. 3). The change in stoichiometry and reduced cation order significantly reduces the $Q \times f$ of the ZnO-muffled samples even though they have slightly higher densities and larger grain sizes than the samples annealed in their own powder.

In all of the muffling environments, the size of the ordered domains in the pellets, as gauged by the full-width at half maximum of the $(100)_{order}$ reflection, is larger at the surface than in the interior (Fig. 2). Previous studies of the closely related BZT system found that loose powders exhibit larger domain sizes than their pellets. For BZT, it was suggested that this is associated with the enhanced volatilization of ZnO in the powders with the small concentration of resultant Zn vacancies accelerating the cation diffusion process.[5] This argument could also be applied to the BZN pellets, with the larger losses of ZnO in the near-surface regions being responsible for a distribution of domain sizes throughout the pellet. However, in our experiments no loss of ZnO was observed and in fact the BZN pellets with ZnO-rich protections showed small weight gains. Furthermore, the relative distribution of the domain size of a BZN pellet that was first sintered and annealed in its own powder to produce a well-ordered structure with larger surface domains was reversed after a subsequent anneal with a ZnO muffling powder (Fig. 3).

Alternate explanations have to be considered for the different extents of cation order observed at the surface and the interior of the dense BZN pellets. In our study of the BZN–BW system, the domain growth and the lattice distortion of the 1:2 ordered structure were found to be constrained by elastic strains associated with the expansion of the superstructure along the *c* axis.[11] Because the constraints on the domain growth are greater in a dense pellet than in a powder, free powders exhibited higher *c*/*a* distortions. We propose that the distributions of domain size observed in the ceramic samples shown in Fig. 1 are also due to the increased constraints on the ordering in the interior of the pellets. For pellets muffled in ZnO-rich powders or vapor, the constrained order in the interior and the ZnO-excess composition near the surface will combine to suppress the ordering. The reversal of the domain coring when pre-ordered pellets are reannealed in a ZnO-muffled environment reflects the reduction in the stability of the order in the ZnO-rich near-surface regions. Other aspects of the ordering gradients, in particular, their impact on *Q*, will be discussed in a separate publication.[13]

The different muffling environments also affect the structure and dielectric properties of the non-stoichiometric samples of BZN in the $(1-x)$ $BZN-(x)BaNb_{4/5}O_3$ system. However, in contrast to stoichiometric BZN, excellent $Q \times f$ values were obtained for the ZnO-vapor-protected samples as well as for those muffled in their own powder. The samples protected by their own powder again showed no evidence for a change in weight or composition, whereas a small weight gain was observed for the pellets muffled in ZnO powder and ZnO vapor. During processing, the mass of the vapor protected pellets increased by 0.15 wt%, which corresponds to the addition of 0.495 mole% ZnO. The movement of the composition toward pure ZnO is illustrated in Fig. 9, where the starting composition of $x = 0.04$ $(1-x)$ $BZN-xBaNb_{4/5}O_3$ (where the molar ratio of BaO:ZnO:Nb_2O_5 = 0.604:0.193:0.203) corresponds to point A, and the final composition, calculated from the gain in mass, is given by point B (where BaO:ZnO:Nb_2O_5 = 0.602:0.196:0.202). Because the initial powders are non-stoichiometric, after the uptake of ZnO, the composition of the samples remains in the high *Q* region of the system identified in[11]. However, if the uptake of ZnO from the muffling environment becomes too high, which is the case for the ZnO-powder muffled samples where the gain in mass was 0.5 wt%, the final stoichiometry can lie outside the high *Q* region. This is also illustrated in Fig. 9, where the final composition of the ZnO-powder samples, indicated by point C, have a molar ratio BaO:ZnO:Nb_2O_5 = 0.598:0.201:0.201. The crystallographic (i.e., degree of order, domain size, and *c*/*a*) and microstructural (i.e., grain size, density) features of the final compositions are consistent with those observed in our prior work where the properties of non-stoichiometric solid solutions of BZN were characterized and any changes in composition were avoided by using their own powders as a muffling agent.

The *Q* factor of ZnO-vapor muffled BZN–$Ba_5Nb_4O_{15}$ ($Q \times f$ = 109 060 at 8 GHz) is almost twice that of a ZnO-vapor-protected stoichiometric BZN pellet (58 000 at 8 GHz), and 36% higher than a stoichiometric pellet protected in its own powder (~80 000 at 8 GHz). Because the ZnO-rich vapor atmosphere improves the sintering properties, the non-stoichiometric BZN pellets can be sintered at a temperature (1400°C) that lies within the region of stability of the cation order (T_{order}

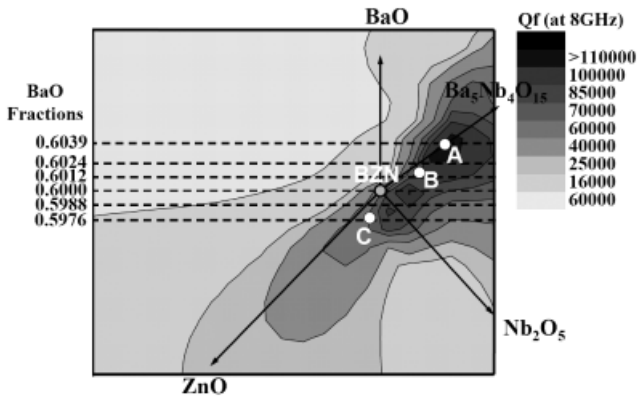

Fig. 9. $Q \times f$ map illustrating the movement of the composition of $(1-x)Ba(Zn_{1/3}Nb_{2/3})O_3$ $-xBaNb4/5O3$ ($x = 0.04$) toward ZnO: (A) starting composition; (B) muffled in ZnO-vapor, (C) muffled in ZnO powder.

$= 1415°C$). This permits the preparation of a dense, single-phase, well-ordered, high Q ($Q \times f = 104\,690$) ceramic after a single heat treatment of just 5 h at 1400°C and avoids the need for an additional low-temperature anneal to promote the formation of cation order. From the perspective of their exceptional loss properties, these non-stoichiometric BZN compositions could be very promising candidates for niobate-based ceramic resonators. However, before any commercial application partial replacement of the Zn content by Ni or Co would be necessary to tune their temperature coefficient of resonant frequency, which, for the Zn system, is $\sim +20$ ppm/°C, to a zero value. The final part of this series of papers explores this possibility for a family of Zn, Ni, Co perovskites where the non-stoichiometry is controlled through the addition of $Ba_3W_2O_9$.

V. Conclusions

The effect of different muffling protective environments on the bulk crystal structure, microstructure, and dielectric losses of BZN ceramics was investigated. The $Q \times f$ values of stoichiometric BZN pellets heated in ZnO-rich environments are severely degraded compared with the samples muffled in their own powder even though the ZnO-rich environments improve the density and grain size. The reduction in $Q \times f$ coincides with a large decrease in the cation order. Gravimetric measurements confirmed that in ZnO powder and vapor environments, the degradations in the order and properties are due to an uptake of ZnO from the muffling agent. The different muffling environments also affect the structure and dielectric properties of non-stoichiometric samples of $(1-x)$BZN$-x$BaNb$_{4/5}$O$_3$ with $x = 0.04$. However, even after the partial reaction with ZnO vapor, the composition remains in the high Q region ($Q \times f > 110\,000$ at 8 GHz). The ZnO vapor lowers the sintering temperature of these non-stoichiometric compositions to a value that lies in the stability field of the cation ordered structure. As a result, they also have a very high Q ($Q \times f = 105\,000$) in their as-sintered, ordered state.

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