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Effect of $Ba(Y_{1/2}Nb_{1/2})O_3$ and $BaZrO_3$ on the cation order and properties of $Ba(Co_{1/3}Nb_{2/3})O_3$ microwave ceramics

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Abstract

The effect of different solid solution additives and heat treatments on the cation order and dielectric properties of $Ba(Co_{1/3}Nb_{2/3})O_3$ (BCoN) were investigated. Pure $Ba(Co_{1/3}Nb_{2/3})O_3$ undergoes an order–disorder transition at ~1400 °C, the Q value of the ordered phase ($Q{\cdot}f = 64{,}400$) is significantly higher than the disordered variant ($Q{\cdot}f = 10{,}800$). The substitution of $BaZrO_3$ destabilizes the 1:2 order and a 1:1 ordered phase are formed for ~10–20 mol% BZ. The order–disorder temperatures for the 1:1 BCoN–BZ phases are quite low (<1300 °C) and lead to lower degrees of order and lower Q values. The substitution of $Ba(Y_{1/2}Nb_{1/2})O_3$ (BYN) also induces a transition to 1:1 ordering, but in this case the stability of the order is significantly higher and the samples remain ordered to at least 1550 °C. The greater degree of order in the BYN system is accompanied by a higher Q values compared to their BZ counterparts, however none of the samples reach the Q values of the pure ordered BCoN end-member. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cation order; Dielectric properties; Microwave ceramics; Niobates; Perovskite

1. Introduction

The continued development of wireless communication technologies will rely upon the identification of new microwave dielectric ceramics with enhanced quality factors. Most recent research of high-Q dielectrics has focused on complex perovskites with temperature compensated permittivities in the range 30 to 40, and very high $Q{\cdot}f$ values (~100,000). For example, the most widely used perovskite, $BaZn_{1/3}Ta_{2/3}O_3$ (BZT), has $\varepsilon \sim 29$, $Q{\cdot}f = 165{,}000$ at 11 GHz, and a near zero temperature coefficient of the resonance frequency.[1] However, the high cost of tantalum oxide and difficulties encountered in controlling the cation order and suppressing the volatility of Zn during processing have motivated investigations of lower cost replacements for BZT. The niobium-based analogues of the tantalate perovskites constitute one family of candidate materials. Compared to their tantalate counterparts, the niobates have higher permittivities and significantly lower raw material costs; however, although their Q values are typically quite good they have not reached the performance levels of the Ta systems. In this research we re-examine the structures and properties of several Nb based perovskites, focusing in particular on their sensitivity to various chemical additives and alterations in the thermal processing.

Several investigations of the Ta and Nb members of the 1:2 family of mixed metal perovskites (which have the general stoichiometry $A(M^{2+}_{1/3}M^{5+}_{2/3})O_3$, A = Ba, Sr, Ca; M^{2+} = Mg, Co, Ni, Zn, etc.; M^{5+} = Nb, Ta) have revealed that the ordering of the B-site cations into a 1:2 or 1:1 arrangement is an important factor in producing a high Q response.[2–9] At lower temperatures the most stable form of these systems has a 1:2 ordering of the M^{2+} and M^{5+} cations. While a perfectly ordered 1:2 state in BZT seems to exhibit the highest Q, a defect-free structure is difficult to achieve due to the formation of cation ordering induced domain boundaries and the volatilization of Zn during processing. Some of these problems can be alleviated by introducing low levels of $BaZrO_3$ (BZ) into BZT which allows high Q values to be reached in short processing times.[6] These substitutions were found to stabilize the domain boundaries and reduce their contribution to the loss properties.[8] A similar beneficial role of $BaZrO_3$ was also reported for the $Ba(Mg_{1/3}Nb_{2/3})O_3$ (BMN) niobate system.[9]

This paper focuses on the structure and properties of $Ba(Co_{1/3}Nb_{2/3})O_3$ (BCoN) based perovskites. Previous studies indicate this system can exhibit high Qs, can be

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processed at temperatures close to 1400 °C, and can be tuned to a zero τ_f through partial replacement of Co by Zn.[10–13] The goal of this work is to characterize the effect of the cation ordering in BCoN on the dielectric properties and examine how the order is perturbed by different firing cycles and solid solution additives. One of the major and important differences between niobate and tantalate perovskites is the effect of temperature on the cation order. Athough most of the tantalates retain their 1:2 B-site order to temperatures well in excess of those used in sintering (~1550–1600 °C), many of the niobates undergo a transition to a disordered B-site arrangement below the sintering temperature. The reduced thermal stability of the order in the niobates has a major impact in designing a thermal processing scheme to optimize the cation order. For the tantalates cation order is thermodynamically favored during the entire processing and sintering cycle, for the niobates the ordering may only occur during the ramp down from the sintering temperature. The BCoN system provides an excellent example of the importance of the cooling rate. Recently we found that the order–disorder transition in BCoN occurs close to 1400 °C. As a result samples that are furnace cooled from the sintering temperature (~1425 °C) show a poorly ordered structure and quite low *Q*s ($Q{\cdot}f=10{,}800$). However, when the firing cycle is adjusted to allow sufficient residence time in the region of stability of the cation order, by slow cooling or by annealing at ~1380 °C, well-ordered samples with significantly higher *Q*s ($Q{\cdot}f=64{,}400$) can be obtained.

This paper describes the effect of solid solution additives on the structure and properties of $BaCo_{1/3}Nb_{2/3}O_3$ (BCoN). Two additives were investigated, one ($BaZrO_3$) contained a single B-site cation; the second, $BaY_{1/2}Nb_{1/2}O_3$ (BYN), has a 1:1 ordered arrangement of two different B site ions. It is shown that the two additives have opposite affects on the thermal stability of the cation order and that these differences are reflected by their dielectric loss properties.

2. Experimental procedure

Samples of the $(1-x)Ba(Co_{1/3}Nb_{2/3})O_3–(x)BaZrO_3$ and $(1–x)Ba(Co_{1/3}Nb_{2/3})O_3–(x)Ba(Y_{1/2}Nb_{1/2})O_3$ solid solutions were prepared from high purity $BaCO_3$, Co_3O_4, ZrO_2, Nb_2O_5 and Y_2O_3 powders using standard solid state methods. All powders were dried at 800ºC prior to mixing, except for $BaCO_3$ which was dried at 400 °C. The mixture was calcined for 6 h at 1050 °C in a corundum crucible, ball-milled for 12 h and then heated at 1200–1250 °C until a single phase material was obtained. Pellets were pressed at 80 kpsi using an isostatic press, wrapped in Pt envelopes filled with the precursor powder, and placed in a Pt crucible for further heat treatment. Sintering was conducted at temperatures ranging from 1380–1450 °C. Ordered specimens were obtained by cooling the pellets from the sintering temperature to 1100 °C at 2°/h.

The analyses of the phase content were performed by X-ray powder diffraction using a Rigaku D_{max} B diffractometer. The degree of order in the 1:1 ordered phases was calculated from experimental and calculated intensities of the (1/2,1/2,1/2) superstructure and (100) sub-cell reflections $(I_{111}/I_{200})_{obs}/(I_{111}/I_{200})_{calc}$. The calculated intensities $(I_{100}/I_{110})_{calc}$ were determined using Cerius^2-3.0 software with a random site model for the ordering. Oxygen displacements in the ordered structure, which can affect the intensity of the ordering reflections, were estimated from the difference in the average ionic radii of the two ordered positions in the structure.

The dielectric measurements at 1 MHz were performed using an HP LCR-meter. The temperature coefficient of the relative permittivity was calculated in the range of −20–+60 °C. Measurements at microwave frequencies made using standard reflection techniques by Mr. P. Lindell at Ericsson Radio Access.

3. Results

Several compositions in the $(1-x)Ba(Co_{1/3}Nb_{2/3})O_3–(x)BaZrO_3$ (BCoN–BZ) system ($x=0.005$, 0.02, 0.05, 0.1, 0.15, 0.20) were prepared to monitor the effect of zirconium substitution on the B-site cation ordering. In a recent study we found that pure $Ba(Co_{1/3}Nb_{2/3})O_3$ undergoes a transition from a 1:2 ordered to disordered B-site arrangement at ~1425 °C. After air quenching the BCoN–BZ samples from 1380 °C ordering reflections were only observed for $x<0.02$, the XRD patterns of all the other specimens were characteristic of a cubic disordered perovskite structure. In an attempt to induce cation order at lower temperature the samples were slow cooled at 2°/h from 1380 to 1100 °C. The XRD patterns collected from the slow cooled compositions are shown in Fig. 1 together with the pattern of the 1:2 ordered BCoN end member. The superstructure reflection at $2\Theta = 17.6°$ that originates from the 1:2 order is not visible in samples with $x>0.005$, however a new series of broad and weak peaks that correspond to 1:1 type order appear for $x=0.1$, 0.15 and 0.2. The 1:1 order in this system can be described by the random site model where the ordered structure has the general composition $Ba(Co_{2(1-x)/3}Nb_{(1-4x)/3}Zr_{2x})_{1/2}Nb_{1/2}$.[7] The degree of order calculated as defined previously, is <10, 43, 58, and 34% for the phases with 5, 10, 15 and 20% BZ, respectively. The systematic shift of the peaks to lower angles indicates an increase in the cell parameter for increasing *x*.

The temperature of the order–disorder phase transition in the BCoN–BZ solid solution was determined by annealing and quenching the slow cooled samples at progressively higher temperatures. By monitoring the disappearance of the ordering peaks it was possible to establish the order-disorder transition temperature. A schematic diagram illustrating the fields of stability of the 1:2, 1:1 and disordered phases is shown in Fig. 2. The ordering temperatures for the BCoN–BZ samples are all quite low ($T_{\mathrm{ord}}\sim1300$ °C) and the conditions required during sintering (~1380–1425 °C depending upon the composition) lie within the disordered phase field.

Fig. 3 shows the dielectric losses for the BCoN–BZ system measured at 1 MHz. Similar to the BCoN end member, the 1MHz losses are higher for the disordered samples than for the slow cooled ones. The microwave loss data for the slow-cooled samples is shown in Fig. 4. It is apparent that while the Q values of the Zr containing samples are slightly higher than that of disordered BCoN, none of them approach the Q of the ordered end-member.

Solid solutions in the $(1\text{–}x)\mathrm{Ba(Co_{1/3}Nb_{2/3})O_3}\text{–}(x)\ \mathrm{Ba(Y_{1/2}Nb_{1/2})O_3}$ system could be prepared across the entire range of composition. To allow direct comparison to the behavior of the BCoN–BZ system, the effect of BYN on the ordering in BCoN was examined on samples sintered at 1380 °C and slow cooled to 1100 °C. XRD patterns collected from selected compositions with this heat treatment are shown in Fig. 5. The addition of BYN induces a transformation to 1:1 order at $x\sim0.08$. The intensity of the ordering reflections in the BCoN–BYN solid solutions is considerably stronger than those observed for the BCoN–BZ system. Comparison of the observed intensity to those calculated for a 1:1 ordered random site structure, where the stoichiometry is described by $\mathrm{Ba(Co_{2(1-x)/3}Nb_{(1-x)/3}Y_x)_{1/2}Nb_{1/2},O_3}$, indicates that all the slow-cooled BCoN–BYN specimens are fully ordered.

Disordering experiments similar to those discussed above for BCoN–BZ were conducted on the BCoN–BYN system. After quenching from temperatures as high as 1580 °C complete order was retained in all compositions. The stability of the cation order is clearly enhanced by the substitution of BYN and the transition temperatures are significantly higher than those observed for the BCoN–BZ system or for the BCoN end-member. Preliminary data for the dielectric properties of selected BCoN–BYN compositions are shown in Table 1; because of the high order/disorder temperatures, it was not possible to

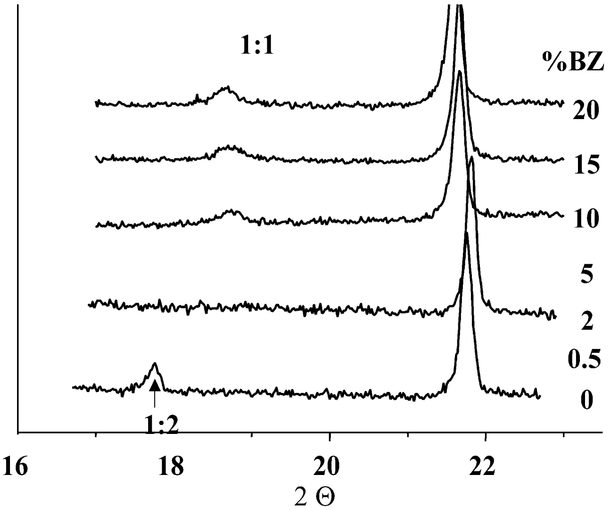

Fig. 1. Low angle regions in diffraction patterns collected from slow-cooled compositions in the $\mathrm{Ba(Co_{1/3}Nb_{2/3})O_3\text{–}BaZrO_3}$ system, reflections from 1:2 and 1:1 order are highlighted.

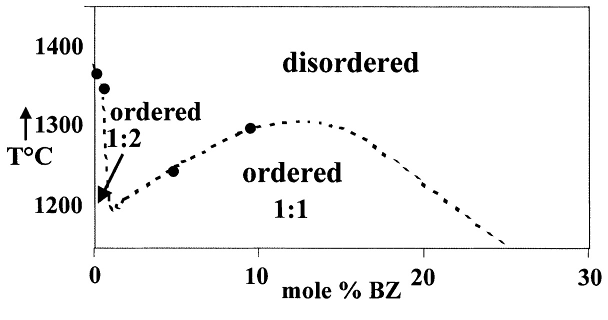

Fig. 2. Phase stabilities for $\mathrm{Ba(Co_{1/3}Nb_{2/3})O_3\text{–}BaZrO_3}$. Order–disorder boundary is indicated, points represent experimental data.

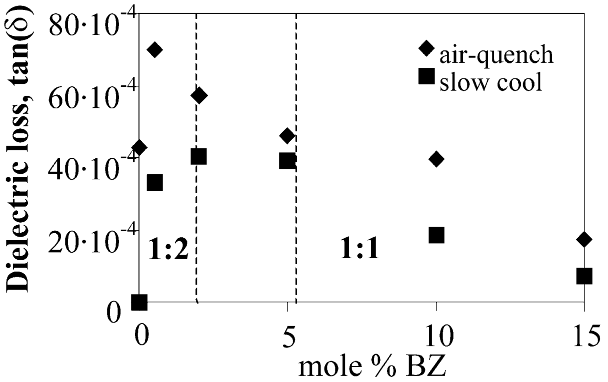

Fig. 3. 1 MHz losses for $\mathrm{Ba(Co_{1/3}Nb_{2/3})O_3\text{–}BaZrO_3}$.

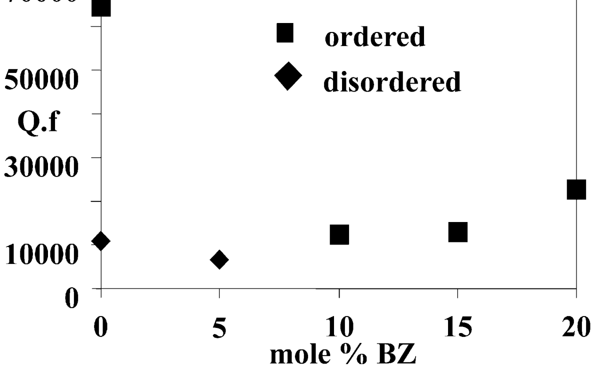

Fig. 4. Microwave quality factors for $\mathrm{Ba(Co_{1/3}Nb_{2/3})O_3\text{–}BaZrO_3}$.

compare the properties of these ordered ceramics to their disordered counterparts. The permittivity increases for increasing BYN and at microwave frequencies they show good *Q·f* values (e.g. $Q \cdot f = 38.700$ for $x = 0.01$). Although these *Q*s are higher than those observed for BCoN–BZ or for disordered BCoN, they are still not as high as the *Q* of pure 1:2 ordered BCoN.

4. Discussion

In pure $Ba(Co_{1/3}Nb_{2/3})O_3$ the B-site cations undergo a transition from a 1:2 ordered to a disordered arrangement at temperatures close 1400 °C. Consistent with the behavior of other similar perovskites, the ordering transition is accompanied by a large reduction in the dielectric loss in the microwave region (ordered $Q \cdot f = 64{,}400$, disordered $Q \cdot f = 10{,}800$). The effect of the substitution of $BaZrO_3$ into BCoN also parallels the behavior of other perovskites and induces a transition from 1:2 to 1:1 B-site order. However, in contrast to the tantalate BZT[6,8] and niobate BMN systems[9] where high *Q* values are retained or even improved by the Zr additive, for BCoN this substitution produces a significant deterioration in the loss properties. For example, 5% BZ reduces *Q·f* to 6,640, a value that is lower than either the ordered or disordered forms of BCoN, and for 15% BZ the *Q·f* is still only ~13,000.

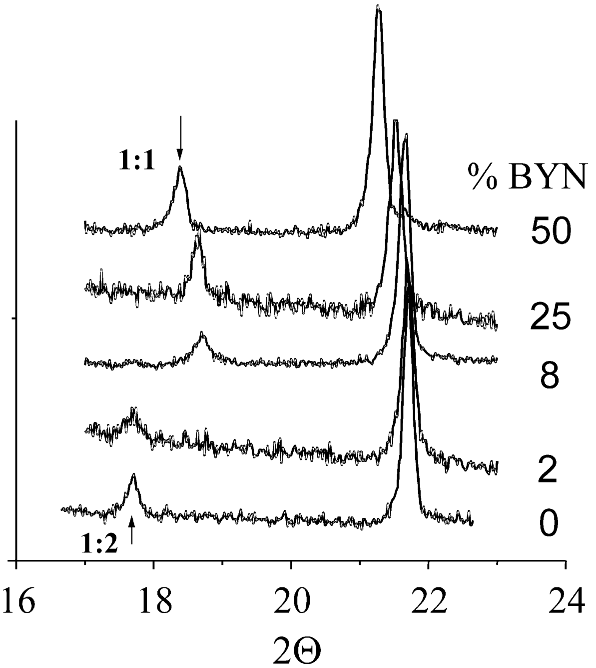

Fig. 5. Low angle region of the diffraction patterns collected from several slow-cooled $Ba(Co_{1/3}Nb_{2/3})O_3$–$Ba(Y_{1/2}Nb_{1/2})O_3$ compositions; 1:2 and 1:1 ordering reflections are highlighted.

Table 1
Dielectric properties of the BCoN–BYN system

% BYN	ρ_{rel} (%)	ε	τ_ε (ppm)	tan(δ) (1 MHz)	*Q·f*
0 (Disordered)	93	35.7	61	$22 \cdot 10^{-4}$	10800 (8.4 GHz)
0 (Ordered)	93	32.9	13.0	$<10^{-4}$	64400 (8.6 GHz)
1	95	34.1	12.3	$7 \cdot 10^{-4}$	38690 (8.5 GHz)
5	93	33.9	6.6	$<10^{-4}$	
10	94	37.1	5.8	$19 \cdot 10^{-4}$	25560 (7.8 GHz)
25	94	40.5	−115.2	$<10^{-4}$	

The different effect of Zr on the *Q* values in these systems may be related to the differences in the stability of the cation order. In BCoN the introduction of Zr reduces the temperature of the order–disorder transition to <1300 °C. Because this temperature is below the conditions used to sinter the ceramics (~1400 °C) and also lies in a region where kinetic barriers to cation diffusion are severe, it is difficult to prepare samples with an equilibrated fully ordered structure. The calculations of the degree of order show that the order parameter *S* $(=\sqrt{I_{expt}/I_{calc}})$ is <0.76 in any of these samples. For BZT and BMN Zr also reduces the thermal stability of the ordering, however the order–disorder temperatures are still high and lie in a region where the equilibration of well ordered samples can be still be achieved.

Further support for this conclusion comes from the behavior of the BYN substituted BCoN system. In contrast to BZ, BYN induces a significant enhancement in the stability of the cation order, particularly in the 1:1 phase field, and the order–disorder temperatures now lie well above those used during sintering (see Fig. 6).

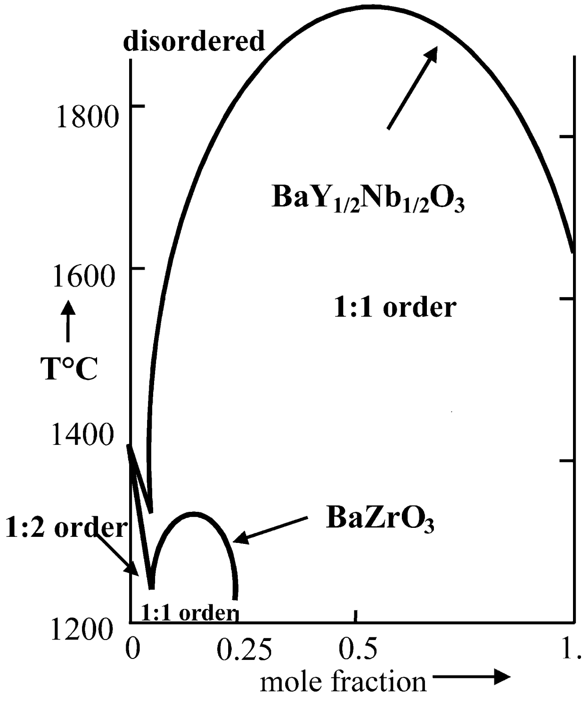

Fig. 6. Schematic comparison of phase stabilities in the $Ba(Co_{1/3}Nb_{2/3})O_3$–$BaZrO_3$ and $Ba(Co_{1/3}Nb_{2/3})O_3$–$Ba(Y_{1/2}Nb_{1/2})O_3$ systems.

Correspondingly, the Q values for the more ordered BYN solid solutions are higher than the BZ system; in the region of stability of 1:2 order (1% BYN) $Qf=\sim 39{,}000$, and for a sample with 1:1 order (10% BYN), $Q{\cdot}f\sim 26{,}000$. Again, neither of these values approach that of pure ordered BCoN, but they are higher than the Qs observed for disordered BCoN or the BCoN–BZ solid solutions. The observed relationship between the stability of the order and Q may permit the design of lower loss compositions through the introduction of other solid solution additives. However, any improvements in the Q value of ordered BCoN will probably require additives that can retain, extend, and stabilize the 1:2 cation ordered phase field.

5. Conclusions

BCoN undergoes an order–disorder transition close to 1400 °C, the ordered form has a significantly higher Q value. The introduction of BZ promotes a transition to a 1:1 cation ordered arrangement with reduced thermal stability. The BCoN–BZ samples show relatively poor Q values. The substitution of BYN into BCoN also induces 1:1 type order, but in this case with significantly higher order–disorder transition temperatures. The BYN samples achieve a high degree of order and correspondingly show higher Q values as compared to their BZ substituted counterparts.

Acknowledgements

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