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Structure and Dielectric Properties of the Ba(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–La(Mg$_{2/3}$Nb$_{1/3}$)O$_3$ System

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Abstract

A complete range of perovskite solid solutions can be formed in the $(1 - x)Ba(Mg_{1/3}Nb_{2/3})O_3$–$xLa(Mg_{2/3}Nb_{1/3})O_3$ (BMN–LMN) pseudobinary system. While pure BMN adopts a 1:2 cation ordered structure, 1:1 ordered phases are stabilized for $0.05 \leq x \leq 1.0$. Dark-field TEM images indicate that the La-doped solid solutions are comprised of large 1:1 ordered domains and no evidence was found for a phase-separated structure. This observation coupled with the systematic variations in the intensities of the supercell reflections supports a charge-balanced "random-site" model for the 1:1 ordering. The substitution of La also induces a transformation from a negative to positive temperature coefficient of capacitance in the region $0.25 \leq x \leq 0.5$.

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A complete range of perovskite solid solutions can be formed in the $(1 - x)$Ba(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–xLa(Mg$_{2/3}$Nb$_{1/3}$)O$_3$ (BMN–LMN) pseudobinary system. While pure BMN adopts a 1:2 cation ordered structure, 1:1 ordered phases are stabilized for $0.05 \leq x \leq 1.0$. Dark-field TEM images indicate that the La-doped solid solutions are comprised of large 1:1 ordered domains and no evidence was found for a phase-separated structure. This observation coupled with the systematic variations in the intensities of the supercell reflections supports a charge-balanced ''random-site'' model for the 1:1 ordering. The substitution of La also induces a transformation from a negative to positive temperature coefficient of capacitance in the region $0.25 \leq x \leq 0.5$.

I. Introduction

MIXED-METAL perovskites with the general formula Ba(B$^{2+}_{I,1/3}$B$^{5+}_{II,2/3}$)O$_3$ typically adopt a ''1:2'' ordered crystal structure in which the B-site cations are stoichiometrically ordered in a trigonal cell with a $\{$B$^{2+}_{I}$B$^{5+}_{II}$B$^{5+}_{II}\}$ layer repeat.[1–3] The Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ (BZT) and Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ (BMT) members of this family are widely used as resonators in commercial wireless technologies such as cellular phones and global positioning systems.[4] A successful microwave resonator must combine a high relative permittivity with a low dielectric loss and a near-zero temperature coefficient of resonant frequency.[4] For the perovskites these properties have a strong dependence on the degree and nature of the ordering of the metal cations on the octahedral sites. For example, the loss properties of Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ (BZT) and Ba(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (BMN) microwave ceramics can be improved by more than 100% by modifying the cation ordering through small substitutions of appropriate B-site dopants.[5,6] While many B-site substitutions have been examined, e.g., Zr^{4+}, Ti^{4+}, W^{6+},[5–8] the effect of A-site substitutions on the cation order and microwave properties has yet to be studied systematically.

Youn *et al.*[9] reported on the effect of small amounts of La ($x < 0.1$) on the B-site order in the Ba$_{1-x}$La$_x$(Mg$_{(1+x)/3}$Ta$_{(2-x)/3}$)O$_3$ (BLMT) system. In that work it was demonstrated that very small concentrations of La ($x = 0.05$) induce a transformation from 1:2 order to a structure with a 1:1 ordered cation distribution. We observed a similar transformation in the Ba$_{1-x}$La$_x$(Zn$_{(1+x)/3}$Nb$_{(2-x)/3}$)O$_3$ (BLZN) system[10] and found that single-phase perovskites could be formed for $0.00 < x < 0.6$, with a cubic 1:1 ordered Ba($\beta'_{1/2}\beta''_{1/2}$)O$_3$ structure being stabilized for solid solutions with $x \geq 0.05$.

Several investigations have also been made on the response of the structures of the corresponding Pb-based 1:2 perovskites, e.g., Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, to the substitution of La.[11–15] In contrast to their Ba- or Sr-based counterparts, the Pb perovskites adopt a structure comprised of 1:1 ordered nanodomains surrounded by a disordered matrix. This structure has generally been interpreted in terms of the so-called ''space charge'' model.[11,16] For this model the β' and β'' positions in the 1:1 ordered Pb($\beta'_{1/2}\beta''_{1/2}$)O$_3$ phases are claimed to be occupied exclusively by the B^{2+} and B^{5+} cations, respectively, and the resultant charge imbalance in the domains is assumed to be balanced by a B^{5+}-rich disordered matrix. Partial support for the space charge model has come from studies of the 1:1 ordering in PLMN solid solutions, Pb$_{1-x}$La$_x$[Mg$_{(1+x)/3}$Nb$_{(2-x)/3}$]O$_3$, where the observed increase in the size of the ordered domains with increasing x has been attributed to the reduction in the charge imbalance by the La^{3+} donor dopants.[11,15] Within the framework of this model a phase-separated microstructure would be expected for all solid solutions with $x < 0.5$; however, the published structure data for La-doped PMN,[11–15] and the recent studies of BLZN,[10] reveal that complete 1:1 ordering can be achieved for La concentrations as low 10 mol%.

For BLZN we have proposed that the 1:1 cation ordering is best described by a ''random-site'' structure.[10] In this model the 1:1 ordering is stoichiometric and the compositions of the solid solutions can be represented by Ba$_{1-x}$La$_x$$\{$[B$^{2+}_{(2+2x)/3}B^{5+}_{(1-2x)/3}$]$_{1/2}$[B^{5+}]$_{1/2}\}O_3$ where one cation position is occupied by the B^{5+} cations and the other by a random distribution of B^{2+} and B^{5+}. In this communication we examine the effect of the substitution of La^{3+} on the cation ordering in Ba(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ and report on the structure and dielectric properties of the perovskite solid solutions that form across the entire Ba(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–La(Mg$_{2/3}$Nb$_{1/3}$)O$_3$ pseudobinary system.

II. Experimental Methods

La-doped BMN (BLMN) ceramics were batched according to chemical formula, Ba$_{1-x}$La$_x$[Mg$_{(1+x)/3}$Nb$_{(2-x)/3}$]O$_3$, with $x = 0$, 0.05, 0.1, 0.15, 0.25, 0.5, 0.75, and 1. Stoichiometric quantities of high-purity (99.9%) predried oxides of Nb$_2$O$_5$, MgO, La$_2$O$_3$, and BaCO$_3$ were mixed in an agate mortar for 10 min and then precalcined at 1100°C for 12 h. The resultant calcine was ball-milled in a polyethylene jar for 3 h using yttria-stabilized zirconia balls and acetone as a milling medium. The slurry was dried and recalcined at 1250°C for 12 h, ball-milled for an additional 10 h, and then isostatically pressed at 600 MPa. The pellets were immersed in a powder of the same composition, placed in Pt-foil, and sintered at 1600°C for 10 h with a heating and cooling rate of 300°C/h.

The phase content of the samples was monitored by X-ray diffraction (Rigaku, Giegerflex, D-Max-B, Cu$K\alpha$ radiation produced at 45 kV and 30 mA) and the microstructure of the sintered pellets was characterized by TEM (Philips 400 EM, operated at 120 kV). The TEM samples were prepared by grinding the ceramic pellets to a thickness of approximately 30 μm and polishing both sides with 5, 3, 1, and 0.25 μm alumina powder. Copper support grids were then placed on the thin sections and the final thinning to perforation was conducted by

ion milling (Ar+, 5.5 kV and 5 mA, Gantan Dual ion Mill, Model 600). Finally, the thin foils were carbon coated to prevent charging.

The dielectric properties of the ceramics were characterized at 1 MHz using a high-precision LCR meter (HP42824A). During the measurements the samples were placed in an environmental chamber (Delta Design, Delta 9023) and the measurement temperature was monitored using a copper–constantan thermocouple (T type) placed next to the sample.

III. Results and Discussion

The X-ray patterns of compositions in the BMN–LMN system (Fig. 1) indicate that perovskite solid solutions can be formed across the entire pseudobinary. For the BMN end-member the formation of a trigonal 1:2 ordered structure was confirmed by the appearance of additional peaks in the XRD pattern (arrowed in Fig. 1) and by the reflections at ($h \pm 1/3$, $k \pm 1/3$, $l \pm 1/3$) in the [110] selected area electron diffraction patterns (inset in Fig. 2). Because the supercell reflections in the electron diffraction patterns are observed along both $\langle 111 \rangle$ directions, it is evident that BMN forms a twin related 1:2 ordered domain structure. The corresponding dark-field image (Fig. 2) confirms this interpretation and reveals a microstructure comprised of large (>100 nm) 1:2 ordered domains separated by twin related interfaces. Consistent with the previous studies of the BLZN system, small substitutions of lanthanum into BMN were found to stabilize a face-centered cubic ($Fm\bar{3}m$) 1:1 ordered structure with a doubled perovskite repeat. For $x = 0.05$ the samples adopt a two-phase, 1:2 + 1:1, assemblage, while compositions with $x \geq 0.1$ could all be indexed in terms of a single-phase 1:1 ordered $Ba_{1-x}La_x(\beta'_{1/2}\beta''_{1/2})O_3$ structure (Fig. 1). Although the homogeneity range of the 1:1 ordered structure extends all the way to the LMN end-member,
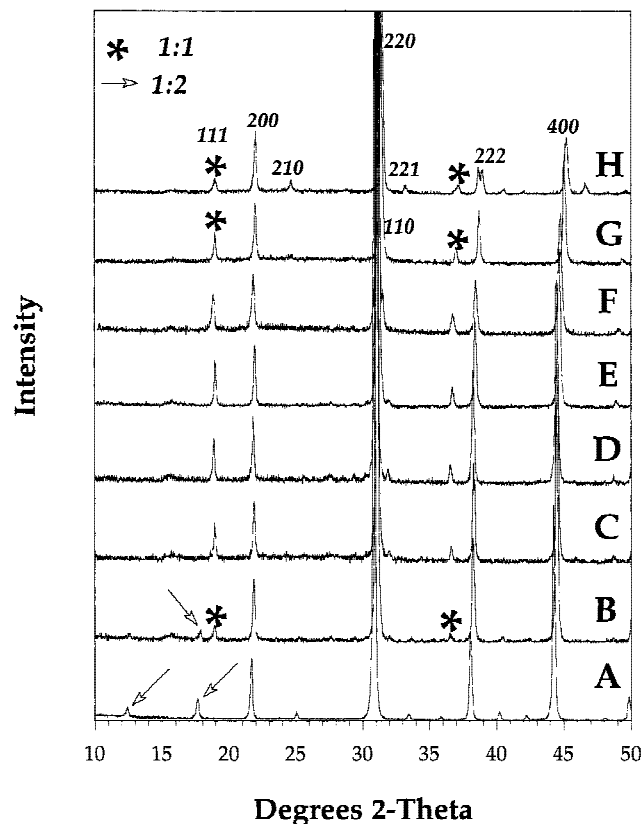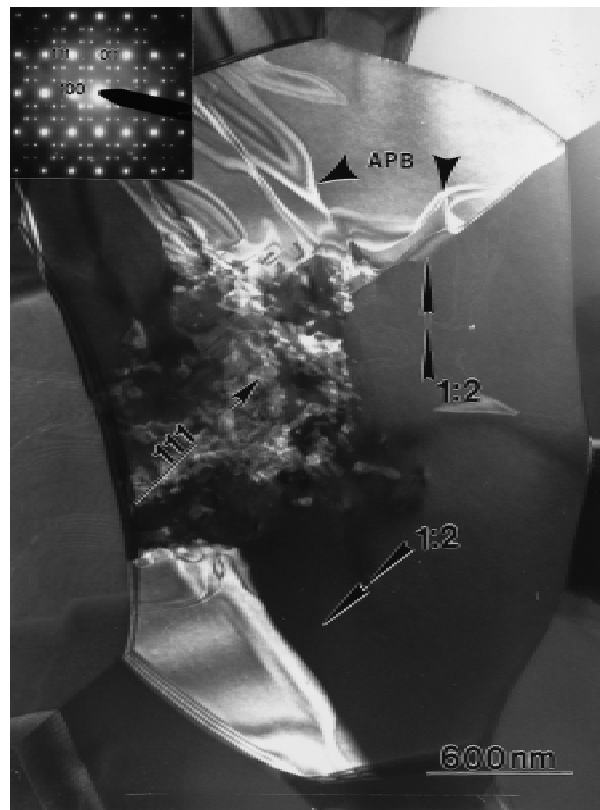

Fig. 2. Dark-field TEM image of pure BMN; image taken using 200 reflection.

a rhombohedral distortion from cubic symmetry was observed for $0.75 \leq x \leq 1.0$. This distortion is apparent from the broadening and/or splitting of the (hhh) reflections (Fig. 1), e.g., 222, in the X-ray patterns and had been noted previously in studies of the PLMN system.[13] The deviation from cubic symmetry is consistent with the decrease in the tolerance factor (t) of the perovskites with increasing concentrations of La ($t_{BMN} = 1.0$, $t_{LMN} = 0.94$).

Within the region of stability of the 1:1 ordering the intensity of the supercell reflections increases with x up to $x = 0.5$, and then decreases as x approaches 1 (Fig. 1). While this observation could be interpreted in terms of a variable volume fraction of the 1:1 ordered phase, dark-field TEM images reveal that the microstructures of the samples are all fully 1:1 ordered (Fig. 3). The image in Fig. 3, collected from a sample with $x = 0.1$, shows the typical microstructure of the 1:1 ordered BLMN samples which are comprised of large (>100 nm) 1:1 ordered domains separated by APBs.

The observation of a fully 1:1 ordered microstructure for all lanthanum concentrations cannot be rationalized in terms of the space charge model in which the charge imbalance requires a significant fraction of a disordered perovskite matrix for all compositions except $x = 0.5$. Instead our experimental results for BLMN favor the charged balanced ''random-site'' model that was previously used to explain the behavior of the BLZN and other related systems.[6,7,10,17,18] In this model the 1:1 ordered $(1 - x)$BMN–xLMN solid solutions with $x < 0.5$ contain one cation site (β'') occupied exclusively by Nb^{5+}, and another (β') occupied by a random distribution of Mg and Nb with the stoichiometry $[Mg_{(2+2x)/3}Nb_{(1-2x)/3}]$. When $x = 0.5$, the two cation positions are occupied by a single type of cation (Mg and Nb) and the supercell reflections exhibit their maximum intensity. For compositions with $x > 0.5$ we proposed that the 1:1 phases also adopt a random site structure but that in this case the mixing of the cations occurs on the β'' positions.[10] For BLZN the very limited stability ($x \leq 0.6$) of these La-rich

Fig. 1. XRD patterns of $Ba_{1-x}La_x[Mg_{(1+x)/3}Nb_{(2-x)/3}]O_3$ for (A) $x = 0$, (B) $x = 0.05$, (C) $x = 0.1$, (D) $x = 0.15$, (E) $x = 0.25$, (F) $x = 0.50$, (G) $x = 0.75$, and (H) $x = 1$. The arrowed peaks correspond to the 1:2 ordering, the peaks marked by an asterisk to the 1:1 order.

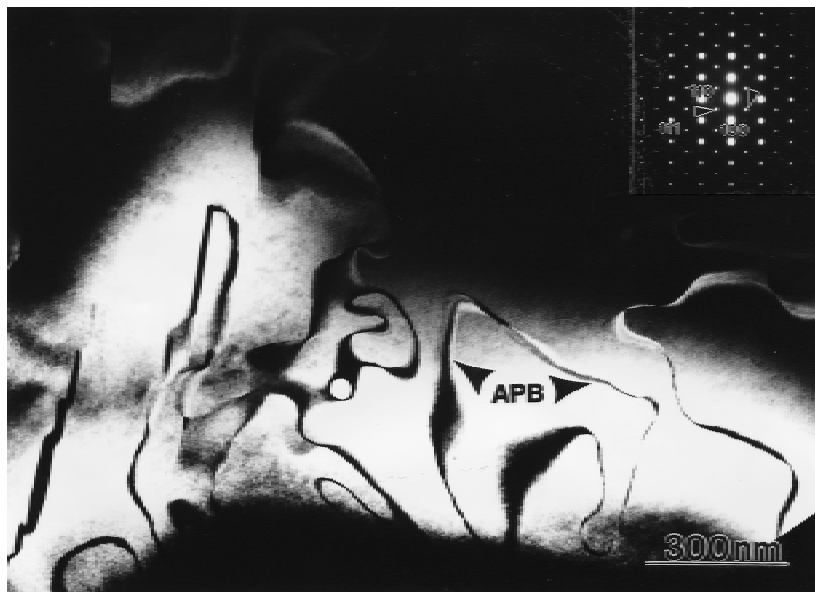**Fig. 3.** Dark-field TEM image of $Ba_{1-x}La_x[Mg_{(1+x)/3}Nb_{(2-x)/3}]O_3$ with $x = 0.1$; image taken using (3/2,3/2,3/2) supercell reflection.

phases impeded definitive correlations between the strength of the supercell reflections and composition. However, for BLMN the 1:1 order persists all the way to the LMN end-member and it is clear that in this region of the system the intensity of the ordering reflections decreases with increasing x. This observation, coupled with the completely 1:1 ordered microstructures, adds further credence to the random β'' site description where the stoichiometry of the solid solutions with $x \geq 0.5$ can be represented by $Ba_{1-x}La_x\{[Mg]_{1/2}[Nb_{(4-2x)/3}Mg_{(2x-1)/3}]_{1/2}\}O_3$.

It is interesting to note that the ''1:2'' $La(Mg_{2/3}Nb_{1/3})O_3$ end-member adopts a 1:1 ordered structure rather than forming a phase with ''stoichiometric'' 2:1 order. The difference in the crystal chemistry of LMN and BMN provides some additional insights into the competing mechanisms that are responsible for the stabilization of the different cation ordering schemes. In the 1:2 structure of BMN and the other related Ba- and Sr-based perovskites, the ordering of the divalent and pentavalent cations in separate $\langle 111 \rangle$ layers permits the adjacent anion layers to undergo a concerted displacement toward the smaller B^{5+} cations. However, the resultant layer sequence of the structure, for BMN{MgNbNb}, requires that the Nb cations have an asymmetric anion environment with three shorter and three longer bonds. For LMN a similar type of stoichiometric 2:1 ordering would lead to a {MgMgNb} layer sequence and an asymmetric environment for Mg. This type of distorted local environment is rarely observed for Mg compounds and its instability is confirmed by the crystal chemistry of LMN where the formation of a 1:1 ordered random site structure, despite its lack of complete positional order, is compatible with a symmetric octahedral environment for Mg.

The effect of the changes in structure on the dielectric properties of the BLMN solid solutions were examined by measuring their capacitance at 1 MHz. At 25°C the relative permittivity of BMN was 32, which is in good agreement with previously reported values. The transformation from 1:2 to 1:1 cation order was found to be accompanied by an increase in the relative permittivity and approached 35 for small concentrations of La ($x = 0.05$, 0.1, 0.15). For higher La concentrations the permittivity decreased systemically to a value of 29 for the LMN end-member (Fig. 4). The change in the ordering also affected the temperature coefficient of the capacitance (τ_{cap}), which was determined between 10° and 75°C. The transformation from 1:2 to 1:1 order reduced the temperature coefficient of BMN to $\sim$−200–250 ppm/°C for $x = 0.1$–0.2; however, a transition to a positive τ_{cap} was observed for higher La concentrations and for pure LMN $\tau_{cap} = +150$ (Fig. 4). The
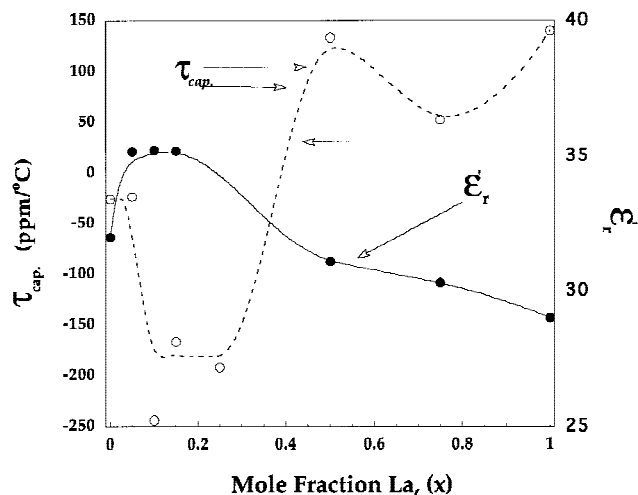

Fig. 4. Relative permittivity and temperature coefficient of capacitance (τ_{cap}) versus composition for the BMN–LMN system.

changes in sign of τ_{cap} demonstrate that the substitution of La could be utilized to tune the temperature coefficient of BMN to a zero value.

IV. Conclusions

A complete range of perovskite solid solutions were formed in the $Ba(Mg_{1/3}Nb_{2/3})O_3$–$La(Mg_{2/3}Nb_{1/3})O_3$ system. For $0.05 < x \leq 1.0$ the B-site cations in the $Ba_{1-x}La_x[Mg_{(1+x)/3}Nb_{(2-x)/3}]O_3$ solid solutions adopt a 1:1 ordered arrangement and their microstructures are comprised of large chemically ordered domains. The crystal chemistry of these phases can be interpreted through the formation of a ''random-site'' structure in which one cation site is occupied by a single type of cation and the other contains a random distribution of Mg and Nb. The temperature coefficient of capacitance in the system is a sensitive function of the La concentration and a transition from negative to positive T_c was observed for $x > 0.25$.

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