Relaxational polarization in polar dielectric barium magnesium niobate

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Relaxor-like dielectric behavior, analogous to that found in lead magnesium niobate, has been induced in the polar dielectric barium magnesium niobate (BMN). In BMN, the dielectric constant was increased and the temperature of the maximum dielectric constant was shifted to a lower temperature with a decrease in measurement frequency with increasing A-site vacancy concentrations. The frequency dispersion of the permittivity maximum exhibited good agreement with the Arrhenius relationship. An activation energy of 0.15 eV and a preexponential factor $10^{14} \text{s}^{-1}$ were determined. No frequency dispersion in the imaginary part of the permittivity was found below the temperature of the dielectric maximum. A linear polarization-electric field dependence was observed at room temperature. A polarization of 0.3 $\mu\text{C/cm}^2$ was found under a field of 75 kV/cm at 25 °C. Phase analysis revealed a single phase perovskite structure with a hexagonal unit cell with $a = 5.77 \text{Å}$ and $c = 7.08 \text{Å}$. (110) selected area electron diffraction patterns revealed superlattice reflections along the (111). High resolution Z-contrast imaging was used to study the local ordering and the origin of the relaxational polarization. © 2000 American Institute of Physics. [S0021-8979(00)09017-4]

I. INTRODUCTION

Barium magnesium niobate (BMN) is a polar dielectric, which has a relative permittivity ($\varepsilon$) of 32 and a $Q$ factor ($1/\tan \delta$) of 5600 at 10 GHz. On the basis of ionic radii differences between B-site cations, BMN was conjectured to possess no B-site cation ordering, but in actuality it has tripled unit cell due to three B-site cation sublattices ordered (1:2) along the $\langle 111 \rangle$. Stoichiometric ordering influences the $Q$ factor. Due to the high $Q$ factor and dielectric constant, barium based perovskite materials are very suitable microwave dielectric resonators for commercial wireless technologies.

Recently this material has been explored for the optimization of its dielectric properties via chemical substitution, crystal structure, and microstructures. Viehland et al. studied the ordering behavior and Butcher and Thomas studied the transformation from relaxor to polar dielectric behavior in Ba-doped lead magnesium niobate. Here we report the relaxor-like dielectric characteristics in the polar dielectric BMN containing A-site vacancies. The frequency dispersion in the dielectric constant and the dissipation factor is analogous to that of lead magnesium niobate (PMN) and various dipolar glass systems. The relaxor behavior in BMN is explained by the Skanavi model.

II. EXPERIMENTAL PROCEDURE

The specimens studied in this investigation were fabricated according to the formula $\text{Ba}_1-2x(\text{Mg}_1/3\text{Nb}_{2/3})_{1+x}\text{O}_3$ (BMN-$x$) for $0<x<0.25$. The purity of the starting raw materials was 99.9% and the specimens were prepared by the columbite precursor method. The columbite precursor ($\text{MgNb}_2\text{O}_6$) was first prepared by mixing predetermined amounts of $\text{MgO}$ and $\text{Nb}_2\text{O}_5$ in isopropanol and ball milling for 5 h using a ZrO$_2$ grinding media. The slurry was dried at 80 °C and the powder was calcined at 1100 °C for 4 h. Single phase formation of $\text{MgNb}_2\text{O}_6$ was confirmed by x-ray diffraction (XRD). The columbite precursor was then mixed and ball milled with predetermined amounts of BaCO$_3$ powders and calcined at 1300 °C for 2 h. The calcined powders were mixed again and pressed into cylinders using polyvinyl alcohol as a binder at a hydrostatic pressure of ~172 MPa. These cylinders were fired at 1500 °C for 4 h in air after binder burnout at 450 °C for 2 h. The densities of all sintered pellets were measured volumetrically and determined to be above 95% of the theoretical. The calcined and sintered specimens were analyzed by a Rigaku x-ray diffractometer for second phase formation. The sintered blocks were then cut into thin disks and polished on different grades of emery papers to obtain parallel surfaces. The sintered blocks were then used as a binder for a silver paste to insure good electrical contact.

The dielectric response was measured using a Hewlett Packard (HP) 4284A inductance-capacitance-resistance (LCR) bridge, which can cover a frequency range from 20 to 20 MHz.
10^6 Hz. For low temperature measurements, the samples were placed in a Delta Design 9023 test chamber, which can be operated between −180 and +250 °C. The temperature was measured using a HP 34401A multimeter via a platinum resistance thermometer device mounted directly on the ground electrode of the sample fixture. The LCR, test chamber and multimeter were interfaced with a computer to collect data while cooling at a rate of 4 °C/min at ten frequencies between 10^2 and 10^6 Hz.

Polarization electric field (P−E) measurements were made using a modified Sawyer–Tower circuit at 10 Hz. The voltage from the polarization change was fed into a voltage amplifier and then digitized by the computer.

Scanning electron micrographs were taken from the fractured surfaces. The fractured surfaces were sputtered by gold and palladium. The fractured surfaces were used for grain size and morphology determination. A qualitative study was carried out using energy dispersive x-ray spectroscopy (Link EDS System, Oxford X-ray System with detector resolution 133 eV) equipped with Zeiss DSM-960 scanning electron microscope (SEM).

Transmission electron microscopy (TEM) specimens were prepared by ultrasonically drilling 3 mm discs, which were mechanically polished to ~100 µm. The center portions of these discs were then further ground by a dimpler to ~10 µm and argon ion milled to perforation. Specimens were coated with carbon before examination. The TEM studies were done on a Phillips EM-420 microscope operating at an accelerating voltage of 100 kV. Quantitative energy dispersive x-ray (EDX) and line scans were carried out using Link energy dispersive spectroscopy, Oxford X-ray System with a Si–Li detector (resolution 136 eV) equipped with an Oxford virtual standards.

Specimens for Z-contrast imaging were prepared by the same method as the TEM specimens. In addition, low voltage argon ions were used during milling in order to reduce the thickness of the amorphous layers produced by ion milling. Amorphous layers broaden electron probes, thus reducing the spatial resolution of Z-contrast imaging. These samples were thinned to electron transparency using a 4 kV Ar ion beam at a 13° inclination and then cleaned at a lower voltage (1.5 kV) at a 10° inclination. Specimens were also plasma cleaned before examination.

Z-contrast images were obtained using a VG Microscope HB603 300 kV STEM with a 1.26 Å resolution. High resolution images were formed by scanning a 1.26 Å probe across a specimen aligned to a major zone axis. The Z-contrast signal was collected from a high-angle annular detector (typically 40–150 mrad). In this high-angle regime, lateral coherence between individual columns is destroyed and thus an incoherent image is formed. The resultant image is a map of the columnar scattering power, which in turn depends on the atomic number Z of each column. The scattered intensity can approach the compositional sensitivity of the atomic-number-squared dependence of Rutherford scattering, allowing for detection of compositional inhomogeneities on an atomic scale. The key aspect of this technique for structural determinations is that the intensity distribution in the high-resolution Z-contrast images provides direct interpretable images of atomic columns that are sensitive to both structure and composition on an atomic scale. In contrast, conventional high resolution TEM images are more difficult to interpret in such terms since reversals in image contrast as a function of defocus and specimen thickness can occur. Furthermore, in the (110) projections, the Mg and Nb columns are ~2.86 Å apart, whereas the Mg (or the Nb) and the Ba columns are ~2.02 Å apart. Thus, a 1.26 Å electron probe is sufficient to distinguish between Ba, Mg, and Nb columns. The resolution power is enhanced significantly due to the large difference in the average Z among the three columns. Contributions to the image intensity from O^2− anions were neglected due to its small atomic number.

### III. RESULTS AND DISCUSSION

#### A. Microstructural analysis

Figures 1(a)–1(d) show SEM pictures of the fracture surfaces for sintered MgNb2O6, BMN-0, BMN-10, and BMN-25, respectively. Intergranular fracture and unidirectional grains (approximately 10 µm in length) can be seen in Fig. 1(a). However, Figs. 1(b)–1(d) show intragranular fracture and well defined grains. The average grain size was approximately 1 µm. No unreacted starting elements or sec-

<table>
<thead>
<tr>
<th>Positions</th>
<th>Barium (at. %)</th>
<th>Magnesium (at. %)</th>
<th>Niobium (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain 1</td>
<td>50.7</td>
<td>11.8</td>
<td>37.5</td>
</tr>
<tr>
<td>Grain 2</td>
<td>50.3</td>
<td>12.3</td>
<td>37.4</td>
</tr>
<tr>
<td>Grain 3</td>
<td>50.0</td>
<td>13.4</td>
<td>36.6</td>
</tr>
<tr>
<td>Grain boundary</td>
<td>52.1</td>
<td>11.0</td>
<td>36.9</td>
</tr>
</tbody>
</table>

**TABLE I. Compositional study of grains and grain boundaries for BMN-10.**
ond phases were observed in these samples. Relaxor-like characteristics have previously been reported in Bi$_2$O$_3$ doped SrTiO$_3$. In these samples bulk grains were depleted and grain boundaries (GB) were richer in Bi$^{3+}$ ions. To reveal the chemistry of grains and grain boundaries in BMN-$x$ samples, STEM study was performed. The resolution of the STEM was approximately 50 Å (beam size 10 Å), which was sufficient to measure the compositions at and near grain boundaries of 1 µm grains. The concentration of elements present at and near GB for BMN-10 are presented in Table I. It should be noticed from this table that grain boundaries and grains are of nearly the same composition. A STEM picture of BMN-10 is shown in Fig. 2. The points at which quantitative analysis were performed are marked in this figure.

To analyze the elemental gradient through the grain boundary between two adjacent grains, line scanning of Ba, Mg, and Nb elements was performed. Four line scans were taken at different positions on BMN-10 samples. One of the line scans is shown in Fig. 3 for BMN-10. No change in the concentrations of Ba, Mg, and Nb elements was observed. All four line scans revealed that there was no segregation of starting elements at the grain boundaries and that the grain compositions were nearly equivalent.

Qualitative energy EDX of MgNb$_2$O$_6$, BMN-0, BMN-10, and BMN-25 are shown in Figs. 4(a)–4(d), respectively. All the peaks in these spectra are identified. EDX spectra taken from the top of intragranular fractured surfaces and from well defined grains were identical. These results clearly reveal that grain boundaries are free from segregation of starting reagents or from second phase formation.

B. Phase analysis

X-ray diffraction was used to examine the phases present and the unit cell structure. Figures 5(a)–5(e) show XRD patterns for BMN-$x$ for $0<x<25$. All the major x-ray diffrac-
tion lines of BMN were identified with the reported Joint Committee on Powder Diffraction Standards (JCPDS) file.\textsuperscript{15} The perovskite structure of BMN has a hexagonal unit cell with $a = 5.77$ Å and $c = 7.08$ Å. Our results revealed that the cell dimensions remain unchanged with increasing A-site vacancy concentration. Additional peaks were identified as magnesium niobate. The intensity of these peaks were found to increase with increasing A-site vacancy concentration, as shown in Figs. 5(c)–5(e). The concentration of magnesium niobate was less than 5% in the BMN-10 specimens studied. It should be noticed from the x-ray data that no superlattice lines are present for the BMN-x specimens. The absence of superlattice lines indicates that the 1:2 ordered domains are small. Recently, Akbas and Davies\textsuperscript{5} found superlattice lines in pure BMN samples. Differences in ordered domain sizes can be attributed to variations in processing conditions. The sintering temperature was 1640 °C for 10 h in Davies’ samples, whereas our specimens were sintered at 1500 °C for 4 h.

C. Z-contrast imaging

The ordered structure of BMN has a trigonal supercell with a 1:2 \{\cdots Mg–Nb–Nb\cdots\} repeat sequence along the \langle 111 \rangle of the parent cubic cell. A \langle 110 \rangle projection of a fully 1:2 ordered structure of BMN-10 is shown in Fig. 6(a). In this case, the B\textsuperscript{I} and B\textsuperscript{II} columns are exclusively occupied by Mg and Nb cations, respectively. The B\textsuperscript{I} and B\textsuperscript{II} sublattices are indicated in the figure by solid lines. The intensity ratio between the B\textsuperscript{I}(Mg\textsuperscript{2+}) and B\textsuperscript{II}(Nb\textsuperscript{5+}) columns, $I(B\textsuperscript{I})/I(B\textsuperscript{II})$, is about 1/12. This is the same as that predicted by the structure of $A(B\textsuperscript{1/3},B\textsuperscript{2/3})O_3$ (BMN) and implies that the B\textsuperscript{I} columns are practically invisible. A high-resolution Z-contrast image of a micron-sized ordered domain in BMN-10 viewed along the \langle 110 \rangle is shown in Fig. 6(b). The bright spots are from the strongly scattering Ba\textsuperscript{2+} columns ($Z = 56$), whereas the light spots are from the weaker scattering Nb\textsuperscript{5+}(B\textsuperscript{II}) columns. Empty or invisible spots correspond to the scattering from Mg\textsuperscript{2+}(B\textsuperscript{I}) columns.

A \langle 110 \rangle SAED pattern taken from an ordered domain of BMN-10 is shown in Fig. 6(c). This pattern reveals the presence of $1/3 \{111 \}$ superlattice reflections, which resulted from the 1:2 ordering of the B-site cation sublattices. Similar \langle 110 \rangle SAED pattern and $1/3\{111 \}$ superlattice reflections were also observed for BMN-0 specimens (SAED pattern not shown). No changes were observed in the superlattice reflections during cooling or heating in the temperature range between −180 and 50 °C. The presence of superlattice reflections in BMN-10 reveals that A-site vacancies have no effect on the 1:2 ordering. $1/3\{111 \}$ Superlattice reflections were also present in BMN-25.

The Z-contrast image in Fig. 6(b) provides direct atomic evidence of the structural model shown in Fig. 6(a). Determination of composition on an atomic scale is also possible using Z-contrast imaging, as long as the kinds of atoms present are known. Figure 6(d) shows an intensity profile measured along the \{002\} plane arrowed in Fig. 6(b). This plane contains both $B\textsuperscript{I}(Mg\textsuperscript{2+})$ and $B\textsuperscript{II}(Nb\textsuperscript{5+})$ columns. Statistically (more than 50 intensity ratios were measured from different areas), the average intensity ratio between the B\textsuperscript{I} and B\textsuperscript{II} columns was determined to be very close to the calculated ratio of 1/12. This demonstrates in the 1:2 ordered BMN that the B\textsuperscript{I} and B\textsuperscript{II} sublattices are occupied only by Mg\textsuperscript{2+} and Nb\textsuperscript{5+} cations, respectively. It should be mentioned that $I(B\textsuperscript{I})/I(B\textsuperscript{II})$ was independent of specimen thickness, as illustrated in Figs. 7(a) and 7(b). This figure shows two intensity profiles measured from thicker [Fig. 7(a)] and thinner areas [Fig. 7(b)], respectively. Although the thicker area had a higher total scattering intensity than the thinner one, the relative intensity ratios were the same. Therefore, the measured value of $I(B\textsuperscript{I})/I(B\textsuperscript{II})$ can be used to determine the local Mg and Nb distributions on an atomic scale in PMN. Ratios
larger than 1:12 would be indicative of partial occupation of Nb\(^{5+}\) on the B\(^1\) sublattices.

It is known that surface damage induced during sample preparation can cause statistical fluctuations in the intensities of atomic columns determined from \(Z\)-contrast images. Since there is no ordering on the Ba sites, the intensities measured from the Ba columns were used to estimate the fluctuations caused by surface damage. The intensities from over two hundred Ba sites were systematically measured. It was found that more than 90% of the columns had an intensity within \(\pm 10\%\) of the mean value and that no columns deviated by more than \(\pm 15\%\). In comparing two structural models, the expected \(I(B^1)/I(B^3)\) ratios differ by more than 300%. Thus, it can be concluded that fluctuations resulting from damaged surface layers do not affect the ability of \(Z\)-contrast imaging to distinguish between structural models.

Figure 8 shows the result of the maximum entropy analysis\(^{16}\) giving the best-fit object in both position and intensity. The Ba\(^{3+}\), Nb\(^{5+}\), and Mg\(^{2+}\) columns are marked on the basis of scattering. It should be noticed that the Nb\(^{5+}\) columns are displaced from their equilibrium position and are marked by arrows. The displacement in Nb\(^{5+}\) columns is due to a distortion of the octahedra, which can be attributed to the presence of lattice vacancies.\(^{12}\)

IV. PROPERTIES STUDIES

A. Dielectric properties

The complex dielectric responses of BMN-\(x\) for \(0 < x < 25\) are shown in Figs. 9(a)–9(d). The dielectric constant increased with decreasing temperature for BMN-0, as shown in Fig. 9(a). No maxima in permittivity was observed for BMN-5 (data not shown). However, typical relaxor-like dielectric properties were observed for BMN-10, BMN-15, and BMN-25 specimens, as can be seen in Figs. 9(b)–9(d). The dissipation factor was lower for lower frequency, analogous to that observed in PMN. Interestingly, only very small changes in the dielectric constant (< 6) were observed between 100°C and \(T_c\) (temperature of \(\varepsilon_{\text{max}}\)). The dielectric permittivity at \(T_{\text{max}}\) of the BMN-15 ceramic was \(\sim 63\) (at 1 kHz), which was higher than that of BMN-0 (\(\varepsilon = 33\) at 1 kHz) or pure magnesium niobate (MN) (\(\varepsilon = 23\) at 1 kHz). The maximum dielectric constant for BMN-15 was \(\sim 33\) which is close to that expected from the dielectric mixing rules (parallel, series, or logarithmic) for a BMN containing 15 at. % magnesium niobate. The room temperature dc resistivity of MN (\(2 \times 10^{12} \Omega \text{ cm}\)) is comparable to BMN-0 (2.5 \(\times 10^{12} \Omega \text{ cm}\)), thus the Brick-wall model and space charge contributions to the low frequency dielectric constant are not reasonable. The temperature of \(\varepsilon_{\text{max}}\) was nearly equal for BMN-10, BMN-15, and BMN-25, whereas the dielectric
constant increased with increasing Ba$^{2+}$ vacancy concentration which can be attributed to weak coupling between dielectric dipoles.

The frequency dispersion of the permittivity maximum revealed close agreements to an Arrhenius relationship, as can be seen in Fig. 10(a). An activation energy of 0.15–0.16 eV and preexponential factor of $10^{14}$ s$^{-1}$ were calculated for BMN-10. No frequency dispersion in the imaginary part of permittivity, below the temperature of the dielectric maximum was observed. A fictitious freezing temperature, calculated using the Vogel–Fulcher relationship, was estimated to be near 0 K as shown in Fig. 10(b). The Curie constant for BMN-10, calculated using the Curie–Weiss law, was 1.77 × 10$^5$.

The dipole relaxation in BMN-15 and BMN-0 was studied at room and low temperatures and these data are shown in Figs. 11(a)–11(d). The value of $\varepsilon'$ remains unchanged up to a frequency of 10$^5$ Hz, but it decreased at higher frequencies for BMN-15. This decrease in $\varepsilon'$ occurred sharply at lower temperatures as can be seen in Fig. 11(b). No such relaxation was found for BMN-0 [Figs. 11(c) and 11(d)]. On comparing the data for BMN-15 and BMN-0, it is evident that higher concentrations of A-site vacancies result in dielectric relaxation at higher frequencies. The higher dielectric constant in BMN-15 can be attributed to contributions from a relaxational polarization due to Ba vacancy. The origin of this relaxational polarization can be explained using the Skanavi model, in which weakly bound ions displace from equilibrium positions and in this case Nb ions displace from its equilibrium position, as shown in the maximum entropy analysis image of BMN-10 in Sec. III C. The relaxor behavior arises because of the distorted octahedral containing unit cells in the matrix of nondistorted hexagonal unit cells. This then results in dipolar clusters, analogous to that found in dipolar glasses.

B. Field induced polarization

Electric field induced polarizations were measured for the MN and BMN-\(x\) (0<\(x<25\)) specimens. A linear $P$–$E$ curve was observed for all the samples, as shown in Fig. 12. The polarization under a field of 30 kV/cm was found to increase with increasing Ba-vacancy concentration. A polarization of 0.3 μC/cm$^2$ was found under a field of 75 kV/cm at 25 °C for BMN-10.

V. CONCLUSIONS

Relaxor-like dielectric characteristics have been induced in the polar dielectric BMN by creating A-site vacancies. High resolution Z-contrast and maximum entropy analysis images revealed 1:2 B-site cation ordering and Nb-ion displacement. Scanning transmission electron microscopy revealed homogeneous compositions between grains and grain
boundaries. No segregation of secondary phases was observed by SEM, but a small peak of a secondary phase was found by x-ray diffraction. An activation energy of 0.15 eV, a preexponential factor $10^{14} \text{s}^{-1}$, a fictitious freezing temperature near 0 K, and a Curie constant of $1.77 \times 10^5$ were calculated for BMN-10. A linear $P-E$ curve was observed at room temperature and the polarization was found to increase with increasing A-site vacancy concentration. The origin of the relaxational polarization in BMN is explained using the Skanavi model.

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