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A-Site and B-Site Order in \((Na_{1/2}La_{1/2})(Mg_{1/3}Nb_{2/3})O_3\) Perovskite

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A-Site and B-Site Order in (Na$_{1/2}$La$_{1/2}$)(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ Perovskite

Abstract

(NA$_{1/2}$La$_{1/2}$)(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ undergoes a series of phase transitions that involve cation order on the A- and B-sites of the parent perovskite structure. At high temperatures both sites contain a random distribution of cations; below 1275°C a $\langle 111 \rangle$ layering of Mg and Nb leads to the formation of a 1:2 ordered structure with a monoclinic supercell. A second transition was observed at 925°C, where the Na and La cations order onto alternate A-site positions along the $\langle 001 \rangle$ direction of the parent subcell. By quenching samples from above 1275°C to preserve the disorder on the B-site, a fourth variant of this compound was obtained by inducing A-site order through a subsequent anneal at 900°C. Although the changes in structure do not produce significant alterations in the relative permittivity ($\varepsilon_r \sim 35$), they do have a significant effect on the value of the temperature coefficient of the capacitance.

Comments

A-Site and B-Site Order in \((\text{Na}_{1/2}\text{La}_{1/2})(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\) Perovskites

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\((\text{Na}_{1/2}\text{La}_{1/2})(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\) undergoes a series of phase transitions that involve cation order on the A- and B-sites of the parent perovskite structure. At high temperatures both sites contain a random distribution of cations; below 1275°C, the ordering of Mg and Nb leads to the formation of a 1:2 ordered structure with a monoclinic supercub. A second transition was observed at 925°C, where the Na and La cations order onto alternate A-site positions along the \((001)\) direction of the parent perovskite. By quenching samples from above 1275°C to preserve the disorder on the B-site, a fourth variant of this compound was obtained by inducing A-site order through a subsequent anneal at 900°C. Although the changes in structure do not produce significant alterations in the relative permittivity \(\varepsilon_r \sim 35\), they do have a significant effect on the value of the temperature coefficient of the capacitance.

I. Introduction

Complex perovskites with the general formula \(A^{2+}(B^{3+}_1B^{3+}_2)O_3\) have received widespread interest in the wireless microwave communications community for their usage in low-loss dielectric resonators.\(^1\) In particular \(\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3\) (BMT) and \(\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3\) (BZT) show the highest response was examined. For NLMT the loss of 1:2 ordering was suggested to arise from local charge imbalances associated with the different valences of the A-site cations. The NLMT system also exhibited a low-temperature ordering transformation \((-950°C)\) involving a \((001)\) layering of the Na and La cations on the A-site position.\(^3\)

In this paper we report on the synthesis, structure, and dielectric properties of \((\text{Na}_{1/2}\text{La}_{1/2})(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\) (NLNM). The B-site order in NLNM was found to be different to NLMT and the cations retained a 1:2 ordered arrangement. An A-site ordering reaction was observed at lower temperature. By tailoring the processing, four different variants of NLNM were prepared and their dielectric response was examined.

II. Experimental Procedure

Samples of NLNM were prepared using solid-state techniques. Stoichiometric quantities of high-purity (>99% \(\text{Na}_2\text{CO}_3\), \(\text{La}_2\text{O}_3\), \(\text{Nb}_2\text{O}_5\), and \(\text{MgO}\) were mixed and calcined at 950°C for 18 h to remove \(\text{CO}_2\). The calcine was ball-milled for 14 h in ethanol with \(\text{Y}_2\text{O}_3\)-stabilized \(\text{ZrO}_2\) balls, reheat at 1200°C for 12 h, and then ball-milled for 15 h before being pressed into pellets. The pellets were pressed isostatically at 68 kpsi and sintered at 1300°C for 5 h. Any significant loss of sodium (monitored by the mass loss of the pellets) was avoided by embedding the pellets in the precursor powder before sintering. The densities of the pellets ranged from 92% to 96% of their theoretical value. The pellets were subjected to a variety of post-sintering heat treatments to assess their effect on the cation order, which are detailed below.

X-ray diffraction and transmission electron microscopy (TEM) aided in the structural analyses of the samples. The phase purity was determined by X-ray diffraction using a diffractometer (Rigaku DMAX-B, Tokyo, Japan) with a conventional CuK\(\alpha\) source. Data for the cell refinements was collected using an internal silicon standard and refined using standard least-squares procedures. Selected specimens were also examined by TEM operated at 120 kV (Model 420 EX, Philips Electronic Instruments, Mahwah, NJ). Samples for TEM were prepared by disaggregating the ceramic, followed by grinding under acetone. The powder was then suspended in acetone and dispersed onto a holey carbon 200-mesh TEM grid. Simulated X-ray patterns were calculated using a commercial software package (CrystalMaker Software Ltd., Yarnton, U.K.).

The relative permittivity, \(\varepsilon_r\) (calculated from the capacitance using the sample dimensions at room temperature) and dielectric loss tangent, \(\tan \delta\), were measured in the 100 Hz to 1 MHz frequency range by the parallel-plate method using a precision

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G. S. Rohrer—contributing editor
order, B
from 1300°C and then annealed at 900°C for 24 h. A
annealed at 1200°C for 8 h and then quenched; (C) annealed at 1200°C for
ples: (A) quenched from 1300°C; (B) annealed at 1250°C, slow-cooled and
X-ray patterns of Na_{1/2}La_{1/2}(Mg_{1/3}Nb_{2/3})O_3 collected from sam-

The temperature dependence of the capacitance
LCR meter (HP 4284A, Hewlett-Packard, Palo Alto, CA). The
tions of the dielectric loss at microwave frequencies were made
using cavity methods.

III. Results

The X-ray pattern of NLMN obtained from samples quenched from the sintering temperature (1300°C) is shown in Fig. 2(a). The major peaks in the pattern could be indexed by a single-phase, cubic-disordered perovskite structure with

The positions of the additional reflections in this pattern could be indexed in terms of the formation of an ordered variant of NLMN with a 1:2 (111) layering of Mg and Nb on the B-site positions. In recent papers on a similar type of order in Ca(Ca_{1/3}Nb_{2/3})O_3, Levin et al. showed that when a b^−b^−c^+ type tilt is combined with 1:2 B-site structure the perovskite has monoclinic structure (P2_1/c) and a cell with the ideal parameters, a = a_v/6, b = a_v/2, c = a_v/2 and β = 125.3°. A cell was found to give excellent agreement with the experimental X-ray patterns (see Table 1), with a = 9.701(1) Å, b = 5.601(1) Å, c = 16.8042(2) Å and β = 125.26(1°). A series of heat treatments conducted between 1200° and 1300°C located the transformation from 1:2 order to disorder at 1275°C. No evidence was found for the formation of a 1:1 B-site ordered form of NLMN at any of the investigated temperatures.

When the B-site ordered samples of NLMN were cooled slowly from 1200° to 800°C, another set of broad and weak additional peaks were observed at 20 = 11° and 25°; see the X-ray scan in Fig. 2(c). Similar reflections had been reported for an A-site ordered form of NLMT. After several annealing studies at low temperature, these reflections, though still very diffuse, were the strongest and most well-defined when the samples were held for ≥24 h at 900°C. They could be reversibly removed and reintroduced by annealing above and below 925°C respectively; however, below 840°C the samples were kinetically inert. The additional diffuse peaks are located at positions (e.g., (0,0,1/2)_c, (1,1/2)_c, (1,1/2)_c), typically observed in ordered mixed A-site perovskites where a (001) layering of the different A-site cations doubles the c axis of the parent perovskite cell.

A [110], electron diffraction pattern collected from a sample heat-treated at 1200°C to induce B-site order and then annealed for more than 24 h at 900°C is shown in Fig. 3. The superstructure reflections in this pattern arise from the 1:2 B-site order (k = ½[111]c^+), the octahedral tilt (k = ½[111]c^+), and the additional phase transformation at 925°C (at [h,h,1/2]_c). The pattern also contains several reflections originating from double diffraction and from the formation of orientational (twin) variants of the 1:2 B-site ordered structure. Because the 900°C transition is so similar to that observed in NLMT and of the A-site ordered perovskites, we believe it arises from a layered (001), ordering of Na and La on the A-site. All the reflections in the X-ray patterns of this low-temperature A- and B-site ordered form of NLMN were indexed using a monoclinic cell (space group P2c) with refined lattice parameters a = 9.704(1) Å, b = 5.603(1) Å, c = 16.809(2) Å and β = 125.26(1°). In this space group the strongest, though very diffuse, reflections associated with the A-site order at 20 = 11.1°, 25.1°, and 33.9°, are indexed as (100), (013)/(21–3), and (120), respectively.

By quenching samples from temperatures above the B-site ordering transition, and then annealing them at 900°C, a fourth variant of NLMN was prepared. The X-ray pattern of a specimen quenched from 1300°C and annealed at 900°C for ≥24 h is shown in Fig. 2, scan D. The annealing temperature is too low to permit any ordering on the B-site sublattice, but lies in a region where the [001], ordering of Na and La can still take place on the A-sites. The positions of the additional reflections in this sample are the same as those associated with the 925°C transition in the B-site

![Fig. 1](image-url) - Schematic illustration of 1:2 B-site order projected along [110]_c. Large spheres are A-site atoms, smaller spheres oxygen atoms; darker and lighter polyhedra represent the Mg and Nb octahedral, respectively. Hatched lines denote the monoclinic unit cell in the tilted, B-site ordered form of Na_{1/2}La_{1/2}(Mg_{1/3}Nb_{2/3})O_3; octahedral tilting is not shown.

![Fig. 2](image-url) - X-ray patterns of Na_{1/2}La_{1/2}(Mg_{1/3}Nb_{2/3})O_3 collected from samples: (A) quenched from 1300°C; (B) annealed at 1250°C, slow-cooled and annealed at 1200°C for 8 h and then quenched; (C) annealed at 1200°C for 8 h and then slow-cooled and annealed at 900°C for 24 h; (D) quenched from 1300°C and then annealed at 900°C for 24 h. A = peaks from A-site order, B = peaks from 1:2 B-site order, T = peaks from tilting.
ordered sample. The X-ray patterns of this A-site ordered, B-site disordered variant of NLMN could be indexed by doubling the c axis of the parent cubic subcell and using a tetragonal cell with \( a = 3.9614(4) \) Å and \( c = 7.9222(5) \) Å.

The dielectric properties of NLMN were investigated on samples that had first been sintered to relative densities between 92% and 95% at 1300°C. Four different structural variants of the NLMN ceramics were examined: (a) A-site ordered/B-site disordered, quenched from 1300°C; (b) A-site disordered/B-site ordered, annealed, and quenched from 1200°C; (c) A-site disordered/B-site ordered, annealed at 1200°C, slow-cooled, and annealed at 900°C; (d) A-site ordered/B-site disordered, quenched from 1300°C, and annealed at 900°C. The relative permittivity of the four different samples calculated from the capacitance at 1 MHz and 25°C, is shown in Table II. After correcting for the density, the permittivity ranged from 35.6 to 33.5 in the different specimens. The values of the permittivity were subject to 1–2% error and the sample-to-sample variations are probably not significant. Although the dielectric losses at 1 MHz were less than 10–4 for all four samples, measurements at microwave frequencies failed to detect any significant resonance peaks indicating that their Q values in the gigahertz range are quite low. The temperature dependence of the capacitance of the different structural forms of NLMN is shown in Fig. 4. In this figure the change in the capacitance is scaled to the value at 25°C (i.e., \( \Delta \varepsilon /\varepsilon_{25^\circ C} \)) and was measured from –25°C to 80°C. The temperature coefficient of the capacitance clearly changes with the type of order and ranges from +122 ppm/°C for complete disorder to +236 ppm/°C for A-site order/B-site disorder (see Table II and Fig. 4).

### Table I. Indexed XRD Pattern of B-Site Ordered Na\(_{1/2}\)La\(_{1/2}\)(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)

<table>
<thead>
<tr>
<th>(2\theta_\text{obs} (\text{deg}))</th>
<th>(2\theta_\text{calc} (\text{deg}))</th>
<th>(I_\text{obs})</th>
<th>(I_\text{calc})</th>
<th>(h\bar{k}l)</th>
<th>Type</th>
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<tbody>
<tr>
<td>12.84</td>
<td>12.89</td>
<td>5</td>
<td>5</td>
<td>002</td>
<td>B</td>
</tr>
<tr>
<td>18.26</td>
<td>18.27</td>
<td>4</td>
<td>6</td>
<td>202, 111</td>
<td>B</td>
</tr>
<tr>
<td>19.36</td>
<td>19.39</td>
<td>2</td>
<td>1</td>
<td>110</td>
<td>T</td>
</tr>
<tr>
<td>22.40</td>
<td>22.43</td>
<td>8</td>
<td>5</td>
<td>200, 111, 113, 204</td>
<td>F</td>
</tr>
<tr>
<td>25.12</td>
<td>25.12</td>
<td>2</td>
<td>2</td>
<td>013, 213</td>
<td>T</td>
</tr>
<tr>
<td>25.88</td>
<td>25.95</td>
<td>3</td>
<td>1</td>
<td>004</td>
<td>B</td>
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<tr>
<td>31.92</td>
<td>31.93</td>
<td>100</td>
<td>100</td>
<td>113, 115, 206, 313, 020</td>
<td>F</td>
</tr>
<tr>
<td>34.58</td>
<td>34.56</td>
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<td>311, 022, 315</td>
<td>B</td>
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<tr>
<td>37.06</td>
<td>37.03</td>
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<td>1</td>
<td>404, 222</td>
<td>B</td>
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<td>37.62</td>
<td>37.63</td>
<td>3</td>
<td>2</td>
<td>310, 023, 316, 223</td>
<td>T</td>
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<tr>
<td>39.38</td>
<td>39.37</td>
<td>8</td>
<td>5</td>
<td>006, 402, 220, 224, 406</td>
<td>F</td>
</tr>
<tr>
<td>41.60</td>
<td>41.59</td>
<td>3</td>
<td>2</td>
<td>311, 024, 316</td>
<td>B</td>
</tr>
<tr>
<td>43.68</td>
<td>43.73</td>
<td>3</td>
<td>1</td>
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</tr>
<tr>
<td>45.78</td>
<td>45.78</td>
<td>42</td>
<td>32</td>
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<tr>
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<td>2</td>
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<td>B</td>
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<tr>
<td>51.60</td>
<td>51.55</td>
<td>3</td>
<td>1</td>
<td>313, 026, 319, 422, 131, 517</td>
<td>F</td>
</tr>
<tr>
<td>55.10</td>
<td>55.15</td>
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<td>402, 224, 228</td>
<td>B</td>
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<td>56.90</td>
<td>56.89</td>
<td>44</td>
<td>38</td>
<td>206, 119, 420, 133, 606, 333, 519</td>
<td>F</td>
</tr>
</tbody>
</table>

† Space group \( P2_1/c \), \( a = 9.701(1) \), \( b = 5.601(1) \), \( c = 16.804(2) \), \( \beta = 125.26(1) \). ‡ \( T \) = tilt reflection, \( B \) = B-site order, \( F \) = fundamental.

### Table II. Dielectric Properties of NLMN at 1 MHz

<table>
<thead>
<tr>
<th>Ordering</th>
<th>(\varepsilon_{25^\circ C})</th>
<th>tan((\delta)) (1 MHz)</th>
<th>(\tau_a) (ppm/°C)</th>
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</thead>
<tbody>
<tr>
<td>BMN</td>
<td>1:2</td>
<td>97</td>
<td>34</td>
</tr>
<tr>
<td>NLMN</td>
<td>1:1 A, 1:2 B</td>
<td>96</td>
<td>35.6</td>
</tr>
<tr>
<td>NLMN</td>
<td>1:1 A</td>
<td>92</td>
<td>35</td>
</tr>
<tr>
<td>NLMN</td>
<td>1:2 B</td>
<td>96</td>
<td>33.5</td>
</tr>
<tr>
<td>NLMN</td>
<td>Disordered</td>
<td>92</td>
<td>34</td>
</tr>
</tbody>
</table>

**Fig. 3.** [110], electron diffraction pattern collected from an A- and B-site ordered sample of Na\(_{1/2}\)La\(_{1/2}\)(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\). Horizontal arrows highlight examples of reflections from B-site order; vertical arrows indicate an example of a reflection with a contribution from the A-site order.

**IV. Discussion**

Above 1275°C, NLMN adopts an orthorhombic SrZrO\(_3\)-type perovskite structure with a disordered arrangement of NaLa and Mg/Nb on the A-site and B-site sublattice, respectively. Below this temperature, the B-site cations undergo a transformation to a 1:2 ordered arrangement with a (111) \( f \ldots \text{MgNbNb} \ldots \) layering of Mg and Nb. The X-ray (and electron) diffraction patterns of the ordered phase are in very good agreement with those calculated using a 1:2 ordered, tilted \((b^* b^- c^-)\), Ca(Ca\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-type, monoclinic cell (space group \( P2_1/c \)) with the ideal cell parameters, \( a = a_\text{ideal}/6 \), \( b = a_\text{ideal}/\sqrt{2} \), \( c = a_\text{ideal}/\sqrt{2} \) and \( \beta = 125.3^\circ \). The experimental peaks associated with the B-site order were noticeably broader than those from the perovskite subcell, implying that the microstructure is comprised of small domains of the various orientational and anti-phase variants of the 1:2 ordered structure. The size of the B-site ordered domains, calculated from the peak widths using the Scherrer formula, is \(<300\) Å. This estimate of the domain size is in good agreement with direct observations of the domain structure made using TEM and with the twinning observed in the corresponding electron diffraction patterns.
The formation of long-range 1:2 Mg/Nb order in NLMN is not unusual and almost all other non-Pb-based 1:2 \(A^2\) \((B_{2/3}^+/B_{2/3}^{2+})O_3\) perovskites adopt the same structure. However, this type of order was somewhat surprising as the closely related mixed A-site compound NLMT was reported to form a 1:1 ordered, “random site” doubled perovskite structure \((A(Mg_{2/3}Ta_{1/3})^{1/2}(Ta)^{1/2}O_3)\).\(^9\) The instability of 1:2 B-site order in NLMN was rationalized in terms of its incompatibility with the different valences of the Na\(^+\) and La\(^{3+}\) cations on the A-site. This type of order creates two different environments for the A-site cations; the two A-sites located between B\(^{5+}\) and B\(^{5+}\) layers have five B\(^{5+}\) and three B\(^{5+}\) neighbors, while the A-site between two B\(^{5+}\) layers has six B\(^{5+}\) and two B\(^{5+}\) neighbors. The formal ionic charge at these two A-site positions is 2.125 and 1.75, respectively. For NLMT it was argued that when the two positions are occupied by a 1:1 mixture of Na\(^+\) and La\(^{3+}\), the resultant local charge imbalance \((\Delta q)\) is responsible for the destabilization of the 1:2 B-site order (Na\(^+\), \(\Delta q = -1.125\) and \(-0.75\); La\(^{3+}\), \(\Delta q = +0.875\) and +1.25 for each respective A-site).\(^9\) Although the formal ionic charges at the A-sites in NLMN are identical to those in NLMT, apparently they are not as effective in reducing the stability of the 1:2 B-site order. The different behavior of NLMT and NLMN can be explained in terms of the covalency of Ta and Nb. It is well known that the Nb–O bond is more covalent than its tantalate counterpart; therefore, the actual charges on the A-site positions in NLMN will be less than in NLMT. The resultant reduction in the local charge imbalance is apparently sufficient to stabilize the 1:2 ordered form of NLMN. Even though a 1:2 ordered structure does form for NLMN the order–disorder temperature \((1275\,^\circ\text{C})\) is much lower than in Sr\((Mg_{1/3}Nb_{2/3})O_3\) or Ba\((Mg_{1/3}Nb_{2/3})O_3\), which retain an ordered B-site arrangement to temperatures \(>1650\,^\circ\text{C}\). This difference provides direct evidence for the reduced stability of the chemical order in NLMN. Because the two energy of the ordered and disordered phases are equal at the transition temperature \((T_{\text{trans}} = 1548\,\text{K})\), the enthalpy of the ordering reaction \((\Delta H_{\text{ord}})\) can be estimated from the change in the configurational entropy \((\Delta S_{\text{conf}})\) associated with the B-site ordering using \(\Delta H_{\text{ord}} = T_{\text{trans}}\Delta S_{\text{conf}}\). If the B-site ions are assumed to be mixed randomly in the disordered phase then \(\Delta S_{\text{conf}} = S_{\text{ordered}} - S_{\text{disordered}} = 0 - (-1.25 \\text{ln} 0.33 + 0.875 \\text{ln} 0.875) = -2.125\,\text{ln} 0.67\). The changes in the structure of NLMN do not cause any appreciable alterations in the dielectric constant, which was \(\approx 35\) for all forms. This value is similar to that of BMN\(^{34}\) (see Table I). However while BMN has a negative temperature coefficient of capacitance \((\tau_c = -70 \,\text{ppm}/\text{°C})\), see Table II) \(\tau_c\) is positive for all the forms of NLMN, implying that a solid solution between the two could be tuned to a zero value. The actual value of \(\tau_c\) exhibits significant changes with the type of order and increases in the A-site ordered forms of both the ordered and disordered B-site phases. It is possible that the alterations in the temperature coefficient originate from localized changes in the tilting of the oxygen octahedra that might accompany the different ordering reactions. This interpretation is consistent with previous studies of several other perovskite oxides where the temperature dependence of the dielectric response was found to change systematically with the degree and type of octahedral tilting.\(^{16}\)

V. Conclusions

By tailoring the thermal annealing, four different structural variants of the NLNM system can be prepared. Above 1275°C, the A- and B-sites contain a random distribution of the different metal cations. Below 1275°C, Mg and Nb adopt a 1:2 ordered arrangement on the B-sites, and Na/La order can be induced on the A-site by annealing at 900°C. Samples quenched from 1300°C and then annealed at 900°C form a fourth variant of NLNM with B-site disorder and A-site order. The changes in structure do not have any significant effect on the relative permittivity of NLNM, but do induce quite large alterations in the temperature dependence of the dielectric properties.

Acknowledgment

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References


