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

### Abstract

$(\text{Na}_{1/2}\text{La}_{1/2})(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  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 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 ( $\epsilon_r \sim 35$ ), they do have a significant effect on the value of the temperature coefficient of the capacitance.

### Comments

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

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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 a (111) 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 (001) 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 ( $\epsilon_r \sim 35$ ), they do have a significant effect on the value of the temperature coefficient of the capacitance.

## I. Introduction

COMPLEX perovskites with the general formula  $\text{A}^{2+}(\text{B}_{1/3}^{2+}\text{B}_{2/3}^{5+})\text{O}_3$  have received widespread interest in the wireless microwave communications community for their usage in low-loss dielectric resonators.<sup>1</sup> 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  $Q$  values ( $Q = 1/\tan \delta$ ) of all the microwave perovskites (e.g.,  $Q > 12000$  at 10 GHz) and are used extensively in commercial applications.<sup>1</sup> Previous research has demonstrated that the dielectric properties of these ceramics are closely tied to a number of factors including variations in density, component volatilization (in the ZnO-containing systems), and the degree of cation ordering on the B-site positions.<sup>2–4</sup> Given that all other factors are equal, the highest  $Q$ 's are typically observed when a system exhibits the highest degree of cation order. Many investigations have been made to assess the effect of different additives on the cation order and  $Q$  in these systems. Most research has focused on substituents that enter the B-site sublattice; A-site additives, other than the obvious replacement of Ba by other alkaline earths (Ca, Sr), have received less attention. This paper focuses on the effect of the coupled A-site substitution of  $\text{Na}_{1/2}^+\text{La}_{1/2}^{3+}$  on the cation order and dielectric properties of the niobate perovskite system,  $(\text{Na}_{1/2}\text{La}_{1/2})(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (NLMN).

Compared to their tantalate counterparts, mixed-metal niobates, such as  $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (BMN) and  $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (BZN), show respectable but lower  $Q$  values (e.g., BMN,  $Q = 5600$  at 10 GHz); however, they are still of commercial interest as they are cheaper to manufacture and have higher relative permittivities.<sup>5</sup> The B-site ordered structures of  $\text{A}^{2+}(\text{B}_{1/3}^{2+}\text{B}_{2/3}^{5+})\text{O}_3$  niobates with  $\text{A}^{2+} = \text{Ca}, \text{Sr}, \text{or Ba}$ , and  $\text{B}^{2+} = \text{Mg}, \text{Co}, \text{Ni}, \text{etc.}$  (space group

$P\bar{3}m1$ ,  $a = a_c\sqrt{2}$ ,  $c = a_c\sqrt{3}$ , where  $a_c$  is the length of the parent subcell) are identical to the corresponding tantalates and contain a 1:2  $\{\text{B}^{2+}\text{Nb}^{5+}\}$  layer repeat along the (111) direction (see Fig. 1).<sup>6,7</sup> It is well known that the introduction of ferroelectrically active  $\text{Pb}^{2+}$  ions onto the A-site destabilizes the 1:2 layered order, and lead-based systems such as  $\text{Pb}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$  and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  form a “partially ordered” 1:1 doubled perovskite structure with one site occupied by Ta (or Nb) and the other by a random 2:1 mixture of Mg and Ta(Nb).<sup>8</sup> Recently, it was shown that the coupled substitution of  $\text{Na}_{1/2}^+\text{La}_{1/2}^{3+}$  in  $(\text{Na}_{1/2}\text{La}_{1/2})(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$  (NLMT) also induces a transition to 1:1 type B-site order.<sup>9</sup> 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 ( $\sim 950^\circ\text{C}$ ) involving a (001) layering of the Na and La cations on the A-site position.<sup>9</sup>

In this paper we report on the synthesis, structure, and dielectric properties of  $(\text{Na}_{1/2}\text{La}_{1/2})(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (NLMN). The B-site order in NLMN 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 NLMN were prepared and their dielectric response was examined.

## II. Experimental Procedure

Samples of NLMN 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  $950^\circ\text{C}$  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, reheated at  $1200^\circ\text{C}$  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  $1300^\circ\text{C}$  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 postsintering 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  $\text{CuK}\alpha$  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.).

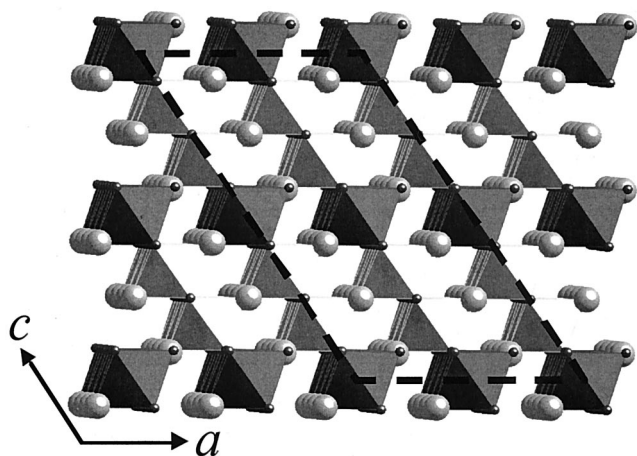
The relative permittivity,  $\epsilon_r$  (calculated from the capacitance using the sample dimensions at room temperature) and dielectric loss tangent,  $\tan \delta$ , were measured in the 100 Hz to 1 MHz frequency range by the parallel-plate method using a precision

G. S. Rohrer—contributing editor

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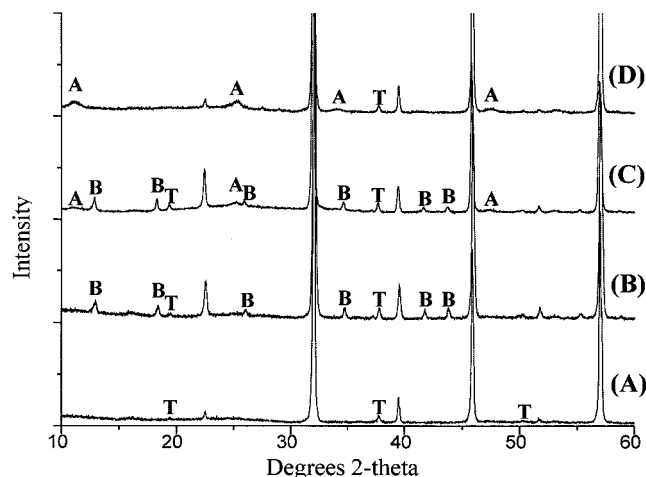


**Fig. 1.** Schematic illustration of 1:2 B-site order projected along  $[110]_c$ . Large spheres are A-site atoms, smaller spheres oxygen atoms; darker and lighter polyhedra represent the Mg and Nb octahedral, respectively. Hatched lines denote the monoclinic unit cell in the tilted, B-site ordered form of  $\text{Na}_{1/2}\text{La}_{1/2}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ; octahedral tilting is not shown.

LCR meter (HP 4284A, Hewlett-Packard, Palo Alto, CA). The temperature dependence of the capacitance  $\tau_c (= \Delta c/c_0 \Delta T$ , where  $c_0 = c_{25^\circ\text{C}}$ ) was measured from  $-25^\circ$  to  $80^\circ\text{C}$  in an environmental chamber (Delta 9920, Delta Design, San Diego, CA). Investigations 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 ( $1300^\circ\text{C}$ ) is shown in Fig. 2(a). The major peaks in the pattern could be indexed by a single-phase, cubic-disordered perovskite structure with  $a = 3.9609(5) \text{ \AA}$ . However, the presence of extra very weak reflections, for example at  $2\theta \approx 37.6^\circ$  (with a cubic index  $[3/2, 1/2, 1/2]$ ), suggested a reduced symmetry perhaps originating from octahedral tilting. The formation of a tilted structure would be consistent with the low tolerance factor of NLMN ( $t = 0.955$ ) which lies in a range where almost all known oxide perovskites have an  $b^-b^-c^+$  type tilt



**Fig. 2.** X-ray patterns of  $\text{Na}_{1/2}\text{La}_{1/2}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  collected from samples: (A) quenched from  $1300^\circ\text{C}$ ; (B) annealed at  $1250^\circ\text{C}$ , slow-cooled and annealed at  $1200^\circ\text{C}$  for 8 h and then quenched; (C) annealed at  $1200^\circ\text{C}$  for 8 h and then slow-cooled and annealed at  $900^\circ\text{C}$  for 24 h; (D) quenched from  $1300^\circ\text{C}$  and then annealed at  $900^\circ\text{C}$  for 24 h. A = peaks from A-site order, B = peaks from 1:2 B-site order, T = peaks from tilting.

scheme and orthorhombic ( $Pbmn$ ) symmetry.<sup>10,11</sup> The positions and relative strengths of the additional reflections were similar to those observed in orthorhombic  $\text{SrZrO}_3$ ,<sup>12</sup> which has a tolerance factor (0.953) almost identical to NLMN, and all the peaks in the X-ray patterns of the high-temperature form of NLMN could be indexed using a cell with  $a = a_c\sqrt{2} = 5.5996(13) \text{ \AA}$ ,  $b = a_c\sqrt{2} = 5.5996(13) \text{ \AA}$ ,  $c = 2a_c = 7.9217(25) \text{ \AA}$ .

When the samples of NLMN were furnace cooled from the sintering temperature, the X-ray patterns showed evidence for additional peaks at  $2\theta \approx 12^\circ$  and  $17^\circ$ . Because the positions of these peaks were close to those typically observed in 1:2 chemically ordered perovskites,<sup>4,6,7</sup> a series of annealing treatments were conducted at lower temperature to examine their effect on the strength of the additional reflections. The X-ray pattern collected from a sample after an 8-h postsintering heat treatment at  $1250^\circ\text{C}$ , followed by an additional anneal for 8 h at  $1200^\circ\text{C}$ , is shown in Fig. 2(b). The set of additional reflections in this pattern could be indexed in terms of the formation of an ordered variant of NLMN with a 1:2  $\langle 111 \rangle$  layering of Mg and Nb on the B-site positions. In recent papers on a similar type of order in  $\text{Ca}(\text{Ca}_{1/3}\text{Nb}_{2/3})\text{O}_3$  Levin *et al.* showed that when a  $b^-b^-c^+$  type tilt is combined with 1:2 B-site order the structure has monoclinic symmetry ( $P2_1/c$ ) and a cell with the ideal parameters,  $a = a_c\sqrt{6}$ ,  $b = a_c\sqrt{2}$ ,  $c = a_c3\sqrt{2}$  and  $\beta = 125.3^\circ$ .<sup>13,14</sup> This cell was found to give excellent agreement with the experimental X-ray patterns (see Table I), with  $a = 9.701(1) \text{ \AA}$ ,  $b = 5.601(1) \text{ \AA}$ ,  $c = 16.804(2) \text{ \AA}$  and  $\beta = 125.26^\circ(1)$ . A series of heat treatments conducted between  $1200^\circ$  and  $1300^\circ\text{C}$  located the transformation from 1:2 order to disorder at  $1275^\circ\text{C}$ . 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  $1200^\circ$  to  $800^\circ\text{C}$ , another set of broad and weak additional peaks were observed at  $2\theta \approx 11^\circ$  and  $25^\circ$ ; see the X-ray scan in Fig. 2(c). Similar reflections had been reported for an A-site ordered form of NLMT.<sup>9</sup> 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  $\geq 24$  h at  $900^\circ\text{C}$ . They could be reversibly removed and reintroduced by annealing above and below  $925^\circ\text{C}$  respectively; however, below  $840^\circ\text{C}$  the samples were kinetically inert. The additional diffuse peaks are located at positions (e.g.,  $(0,0,1/2)_c$ ,  $(1,0,1/2)_c$ ,  $(1,1,1/2)_c$ ), 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.<sup>15</sup>

A  $[110]_c$  electron diffraction pattern collected from a sample heat-treated at  $1200^\circ\text{C}$  to induce B-site order and then annealed for more than 24 h at  $900^\circ\text{C}$  is shown in Fig. 3. The superstructure reflections in this pattern arise from the 1:2 B-site order ( $k = \frac{1}{3}[111]_c^*$ ), the octahedral tilting ( $k = \frac{1}{2}[111]_c^*$ ), and the additional phase transformation at  $925^\circ\text{C}$  (at  $[h,h,(l+1)/2]_c^*$ ). 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  $900^\circ\text{C}$  transition is so similar to that observed in NLMT and other A-site ordered perovskites, we believe it arises from a layered  $(001)_c$  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  $Pc$ ) with refined lattice parameters  $a = 9.704(1) \text{ \AA}$ ,  $b = 5.603(1) \text{ \AA}$ ,  $c = 16.809(2) \text{ \AA}$  and  $\beta = 125.26(1)$ . In this space group the strongest, though very diffuse, reflections associated with the A-site order at  $2\theta = 11.1^\circ$ ,  $25.1^\circ$ , and  $33.9^\circ$ , 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  $900^\circ\text{C}$ , a fourth variant of NLMN was prepared. The X-ray pattern of a specimen quenched from  $1300^\circ\text{C}$  and annealed at  $900^\circ\text{C}$  for  $\geq 24$  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  $[001]_c$  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  $925^\circ\text{C}$  transition in the B-site



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

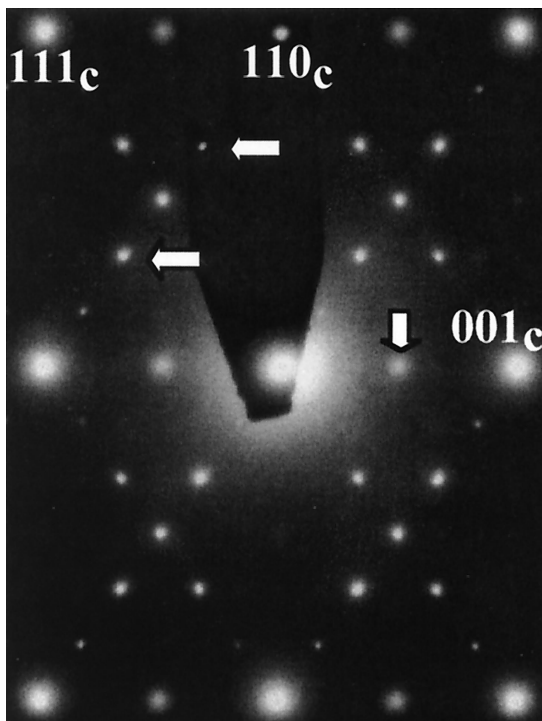
$2\theta_{\text{obs}}$ (deg)	$2\theta_{\text{calc}}$ (deg)	$I_{\text{obs}}$	$I_{\text{calc}}$	$hkl$	Type <sup>‡</sup>
12.84	12.89	5	5	002	B
18.26	18.27	4	6	202, 111	B
19.36	19.39	2	1	110	T
22.40	22.43	8	5	200, 111, 113, 204	F
	25.12		2	013, 213	T
25.88	25.95	3	1	004	B
31.92	31.93	100	100	113, 115, 206, 313, 020	F
34.58	34.56	3	2	311, 022, 315	B
37.06	37.03	2	1	404, 222	B
37.62	37.63	3	2	310, 023, 316, 223	T
39.38	39.37	8	5	006, 402, 220, 224, 406	F
41.60	41.59	3	2	311, 024, 316	B
43.68	43.73	3	1	204, 115, 117, 208	B
45.78	45.78	42	32	400, 222, 226, 408	F
50.08	50.05	2	2	515, 424, 131, 116, 223, 227	B
51.60	51.55	3	1	313, 026, 319, 422, 131, 517	F
55.10	55.15	2	1	402, 224, 228	B
56.90	56.89	44	38	206, 119, 420, 133, 606, 333, 519	F

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

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.,  $\Delta c/c_{25^\circ\text{C}}$ ) and was measured from  $-25^\circ$  to  $80^\circ\text{C}$ . 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).



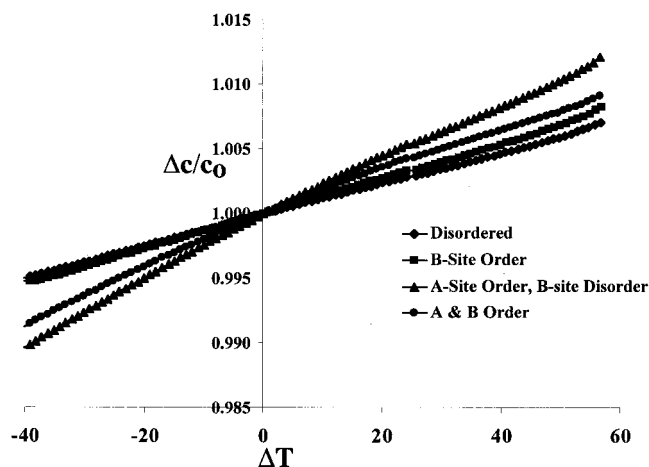
**Fig. 3.**  $[110]_c$  electron diffraction pattern collected from an A- and B-site ordered sample of  $\text{Na}_{1/2}\text{La}_{1/2}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ . Horizontal arrows highlight examples of reflections from B-site order; vertical arrows indicate an example of a reflection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

#### IV. Discussion

Above 1275°C, NLMN adopts an orthorhombic  $\text{SrZrO}_3$ -type perovskite structure with a disordered arrangement of Na/La 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  $\langle 111 \rangle \{ \dots \text{MgNbNb} \dots \}$  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 ( $b^-b^-c^+$ ),  $\text{Ca}(\text{Ca}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -type, monoclinic cell (space group  $P2_1/c$ ) with the ideal cell parameters,  $a = a_c\sqrt{6}$ ,  $b = a_c\sqrt{2}$ ,  $c = a_c3\sqrt{2}$  and  $\beta = 125.3^\circ$ .<sup>13,14</sup> 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.<sup>4</sup> The size of the B-site ordered domains, calculated from the peak widths using the Scherrer formula, is  $\sim 300$  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.

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

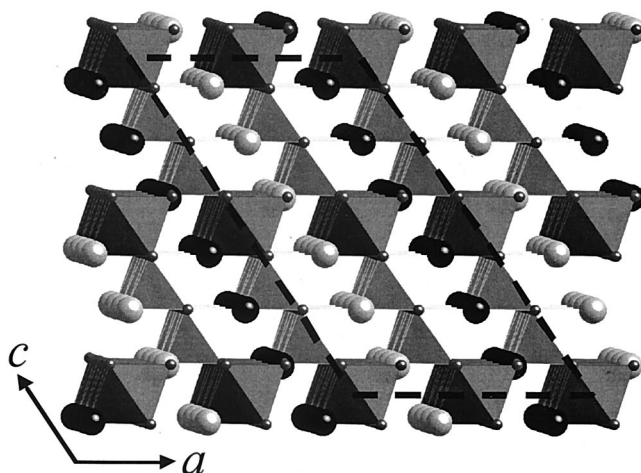
Ordering	$\rho_{\text{rel}}$ (%)	$\epsilon_{25^\circ\text{C}}$	$\tan(\delta)$ (1 MHz)	$\tau_c$ (ppm/°C)
BMN 1:2	97	34	$<10^{-4}$	-70
NLMN 1:1 A, 1:2 B	96	35.6	$<10^{-4}$	196
NLMN 1:1 A	92	35	$<10^{-4}$	236
NLMN 1:2 B	96	33.5	$<10^{-4}$	137
NLMN Disordered	92	34	$<10^{-4}$	122



**Fig. 4.** Temperature dependence of the capacitance for the four structural variants of  $\text{Na}_{1/2}\text{La}_{1/2}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ;  $c_0 = c_{25^\circ\text{C}}$ ,  $\Delta c = c - c_0$ ,  $\Delta T = T - 25^\circ\text{C}$ .

The formation of long-range 1:2 Mg/Nb order in NLMN is not unusual and almost all other non-Pb-based 1:2  $\text{A}^{2+}(\text{B}_{1/3}^{2+}\text{B}_{2/3}^{5+})\text{O}_3$  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  $(\text{A}(\text{Mg}_{2/3}\text{Ta}_{1/3})_{1/2}(\text{Ta})_{1/2}\text{O}_3)$ .<sup>9</sup> The instability of 1:2 B-site order in NLMT was rationalized in terms of its incompatibility with the different valences of the  $\text{Na}^+$  and  $\text{La}^{3+}$  cations on the A-site. This type of order creates two different environments for the A-site cations; the two A-sites located between  $\text{B}^{2+}$  and  $\text{B}^{5+}$  layers have five  $\text{B}^{5+}$  and three  $\text{B}^{2+}$  nearest neighbors, while the A-site between two  $\text{B}^{5+}$  layers has six  $\text{B}^{5+}$  and two  $\text{B}^{2+}$  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  $\text{Na}^+$  and  $\text{La}^{3+}$  the resultant local charge imbalance ( $\Delta q$ ) is responsible for the destabilization of the 1:2 B-site order ( $\text{Na}^+$ ,  $\Delta q = -1.125$  and  $-0.75$ ;  $\text{La}^{3+}$ ,  $\Delta q = +0.875$  and  $+1.25$  for each respective A-site).<sup>9</sup> 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  $\text{Sr}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  or  $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ , which retain an ordered B-site arrangement to temperatures  $\gg 1650^\circ\text{C}$ . This difference provides direct evidence for the reduced stability of the chemical order in NLMN. Because the free 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  $\Delta S_{\text{conf}} = S_{\text{ordered}} - S_{\text{disordered}} = 0 - \{-nR(0.33 \ln 0.33 + 0.67 \ln 0.67)\}$ , and  $\Delta H_{\text{ord}} = -8.2\text{ kJ/mol}$ .

Although the B-site order in NLMN and NLMT is different, both compounds undergo a phase transition at lower temperature that involves an ordering of Na and La on the A-site. This transition was observed at  $\sim 925^\circ\text{C}$  for both the ordered and disordered B-site forms of NLMN. In all known A-site ordered perovskites the chemical order arises from an  $[001]_c$  layering of the different cations, and the arrangement of Na and La in NLMN seems to follow that pattern. For the disordered B-site phase, the A-site order yields a tetragonal cell with a doubled  $c$



**Fig. 5.** Schematic illustration of one variant of the A- and B-site ordered form of  $\text{Na}_{1/2}\text{La}_{1/2}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ . Darker and lighter spheres represent Na and La, respectively. Tilting of octahedra is not shown.

axis. In the monoclinic 1:2 ordered phase the  $[001]_c$  A-site order removes the center of symmetry and can propagate in three unique directions with respect to the parent  $P2_1/c$  cell. A schematic picture of one possible A-site ordered variant (space group  $Pc$ ) is shown in Fig. 5. In both of the A-site ordered forms of NLMN the peaks associated with the ordering are extremely broad and the calculated average size of the ordered domains is  $\sim 30\text{ \AA}$ .

The changes in the structure of NLMN do not cause any appreciable alterations in the dielectric constant, which was  $\sim 35$  for all forms. This value is similar to that of  $\text{BMN}$ <sup>34</sup> (see Table I). However while  $\text{BMN}$  has a negative temperature coefficient of capacitance ( $\tau_c = -70\text{ ppm}/^\circ\text{C}$ , 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.<sup>16</sup>

## V. Conclusions

By tailoring the thermal annealing, four different structural variants of the NLMN system can be prepared. Above  $1275^\circ\text{C}$ , the A- and B-sites contain a random distribution of the different metal cations. Below  $1275^\circ\text{C}$ , 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  $900^\circ\text{C}$ . Samples quenched from  $1300^\circ\text{C}$  and then annealed at  $900^\circ\text{C}$  form a fourth variant of NLMN with B-site disorder and A-site order. The changes in structure do not have any significant effect on the relative permittivity of NLMN, but do induce quite large alterations in the temperature dependence of the dielectric properties.

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