Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 26 (2006) 2885–2888

www.elsevier.com/locate/jeurceramsoc

Ordering structure of barium magnesium niobate ceramic with A-site substitution

Jong-Hoo Paik[a,*], Sei-Ki Kim[a], Mi-Jae Lee[a], Byung-Hyun Choi[a], Eun-Kyeong Lim[a], Sahn Nahm[b]

[a] Electronic Materials Technology Development Group, Korea Institute of Ceramic Engineering and Technology 233-5, Gasan-Dong, Guemcheon-Gu, Seoul 153-801, Republic of Korea
[b] Department of Materials Science and Engineering, Korea University, Seoul 136-701, Republic of Korea

Abstract

The ordering behaviour of $Ba(Mg_{1/3}Nb_{2/3})O_3$ ceramics (BMN) substituted by La^{3+}, Na^+, K^+ was investigated using X-ray powder diffraction and transmission electron microscopy. The 1:2 ordered structure of BMN can be transformed to 1:1 ordered structure by substituting a small amount of La cation ion into the A-site. Moreover, the degree of ordering was increased with La content in the compound, and reached almost unity at [La] = 50 mol%. When the La ion in $(Ba_{1-x}La_x)(Mg_{(1+x)/3}Nb_{(2-x)/3})O_3$ (BLMN) was substituted by Na or K ions, the 1:1 ordered structure of BLMN was transformed into the 1:2 ordered structure. The degree of 1:2 ordering was influenced by the sintering temperature and the size difference between the A and B site ions.

Keywords: Ordering; Perovskite

1. Introduction

The dielectric properties of the complex perovskite $A(B'_{1/3}B''_{2/3})O_3$ ceramics are largely affected by the 1:2 ordering and oxygen octahedral tilt. Galasso et al. reported that the 1:2 ordering, which is closely related to the *Q*-value, is influenced by the charge and size difference of B site ions.[1] Therefore, the complex perovskite materials with different compositions have been extensively studied to enhance the degree of 1:2 ordering. Oxygen octahedral tilt, on the other hand, is the major factor which influences the behaviour of the temperature coefficient of resonant frequency (τ_f). Oxygen tilt in simple perovskites has been studied by Glazer.[2,3] However, Glazer's model is not enough to describe the transformation of the 1:2 ordered complex perovskite structure. Recently, Nagai has expanded Glazer's model to make it applicable to 1:2 ordered perovskite compounds.[4]

For the present work, La and Na (or K) modified BMN ceramics were prepared and the transition of ordering structure and tilting of oxygen octahedra of BLMN and $(Ba_{1-x}K_{x/2}La_{x/2})(Mg_{1/3}Nb_{2/3})O_3$ (BKLMN) with K and La contents were studied.

2. Experimental

Specimens of $(Ba_{1-x}La_x)(Mg_{(1+x)/3}Nb_{(2-x)/3})O_3$, and $(Ba_{1-x}(K\text{ or }Na)_{x/2}La_{x/2})(Mg_{1/3}Nb_{2/3})O_3$ (BKLMN, BNLMN) with $0 \le x \le 1$ were synthesized by a conventional solid-state reaction method from $BaCO_3$ (Aldrich, 99%), La_2O_3 (Aldrich, 99%), Na_2CO_3 (Aldrich, 99%), K_2CO_3 (Aldrich, 99%), Nb_2O_5 (tritech, 99.9%), and MgO (Junsei, 99%). The materials were weighed in the appropriate molar ratio and mixed with ZrO_2 balls in ethanol media for 24 h. The mixture was calcined at a temperature of 1200 °C for 4 h, and pressed into discs. These pellets were sintered at various temperatures. All of the sintered pellets were analyzed using an X-ray diffractometer (XRD) (Rigaku D/max-RC X-ray diffractometer) with Cu Kα radiation. Microstructures of the specimens were studied using high-resolution transmission electron microscopy (HRTEM). TEM specimens were cut from discs, mechanically ground, and ion milled using argon. Hitachi H-9000NAR TEM was used to examine the specimens

---

* Corresponding author.
E-mail addresses: jhpaik@kicet.re.kr (J.-H. Paik), kimseiki@kicet.re.kr (S.-K. Kim), im1004@kicet.re.kr (M.-J. Lee), bhchoi@kicet.re.kr (B.-H. Choi), fresh003@hanmail.net (E.-K. Lim), snahm@korea.ac.kr (S. Nahm).

0955-2219/$ – see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2006.05.013

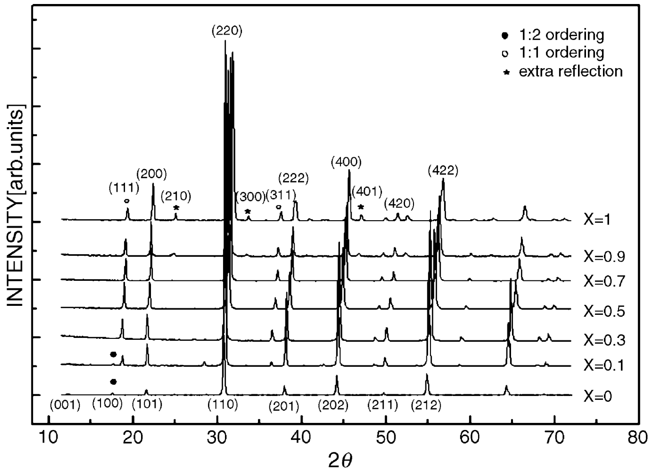
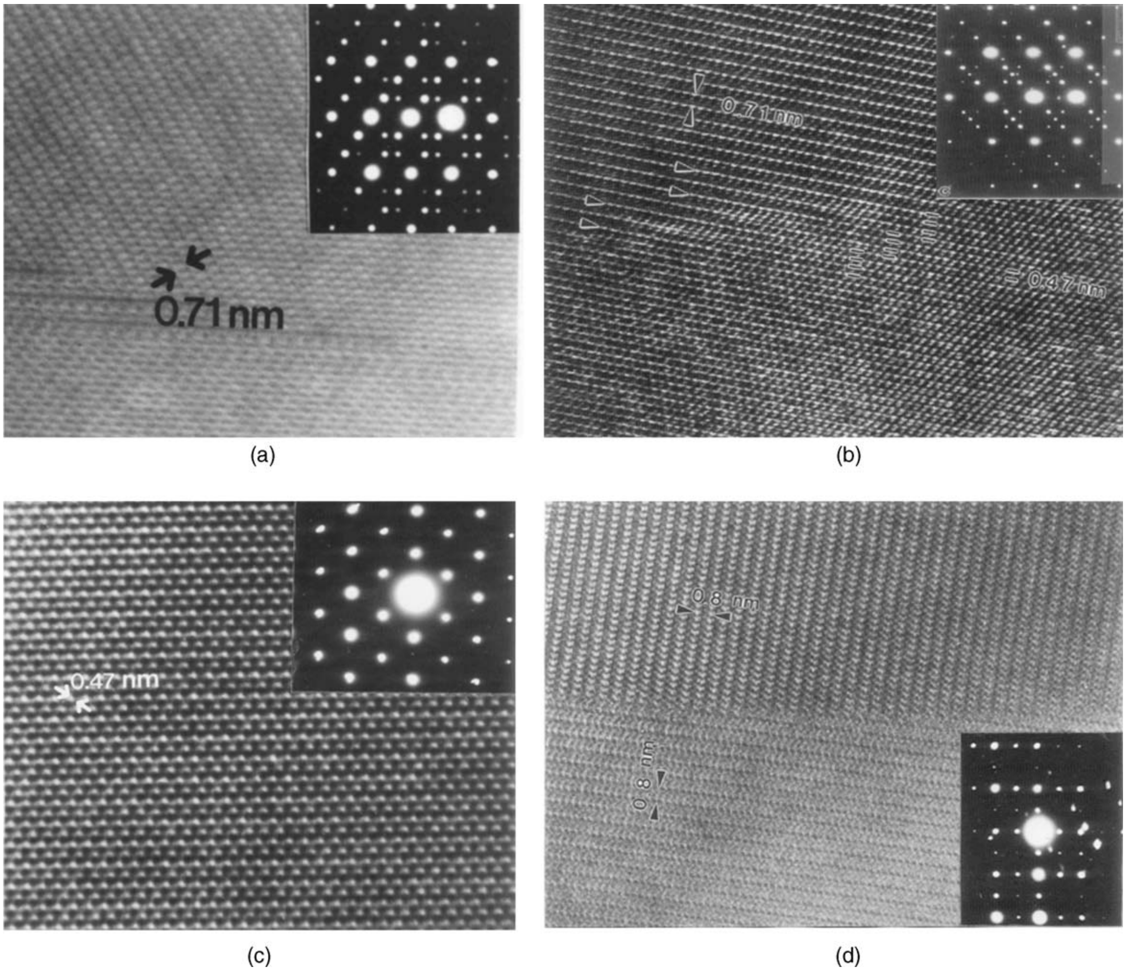


Fig. 1. X-ray powder diffraction pattern of $(Ba_{1-x}La_x)(Mg_{(1+x)/3}Nb_{(2-x)/3})O_3$ with $0 \leq x \leq 1$ sintered at 1450 °C for 4 h.

3. Results and discussions

Fig. 1 shows the X-ray diffraction patterns of BLMN specimens sintered at 1450 °C for 4 h. As seen from the figure, the intensities of 1:2 ordering superlattice reflections decreased as La content, x, increased, eventually disappearing. When $x > 0.1$, a series of extra peaks at (1 1 1) and (3 1 1) positions, indicated by open circles, begin to grow, attaining a maxima at $x = 0.5$. When x is above 0.5, the intensity of the (1 1 1) extra peak gradually decreased, but the intensity of (3 1 1) peak did not change. The (1 1 1) extra peak arises from the 1:1 chemical ordering; the (3 1 1) peak formed as a result of either 1:1 ordering or anti-phase tilting of octahedra. Therefore, a 1:2 ordered hexagonal structure was transformed into the 1:1 ordered cubic structure when $x > 0.1$. Moreover, anti-phase tilting of the octahedra is considered to exist in the BLMN with $x > 0.5$.

As seen in Fig. 1, BLMN had a 1:1 ordered cubic structure when $0.1 < x < 0.7$. When x exceeded 0.7, however, new extra peaks appeared at the (2 1 0) and (3 0 0) positions, indicated by asterisks; at the same time, the (2 2 2) peak begins to split. The splitting of the (2 2 2) peak indicated that the specimen has a rhombohedral structure rather than a cubic structure. The crystal structure of BLMN thus evolved from a 1:1 ordered cubic perovskite to a 1:1 ordered rhombohedral perovskite when x exceeded 0.7. Because the (2 1 0) and (3 0 0) peaks are related to the anti-parallel shift of cations, the atomic displacement that occurred as BLMN changed from a cubic to rhombohedral structure was responsible for the formation of the extra (2 1 0) and



(a) (b)

(c) (d)

Fig. 2. HRTEM images and electron diffraction patterns of (a) $Ba(Mg_{1/3}Nb_{2/3})O_3$, (b) $(Ba_{0.9}La_{0.1})(Mg_{1.1/3}Nb_{1.9/3})O_3$, (c) $(Ba_{0.5}La_{0.5})(Mg_{1/2}Nb_{1/2})O_3$ and, (d) $(Ba_{0.1}La_{0.9})(Mg_{1.9/3}Nb_{1.1/3})O_3$.

(3 0 0) peaks. Therefore, according to the XRD results, rhombohedral BLMN has both the anti-phase tilt of oxygen octahedra and anti-parallel shift of cations.

The variation in the crystal structure of BLMN with La content was also investigated using transmission electron microscopy. Fig. 2(a)–(d) represent HRTEM images and electron diffraction patterns of BLMN with $x = 0$, 0.1, 0.5 and 0.9, respectively.

As seen in Fig. 2(a), the 1:2 ordered hexagonal structure was well developed in BMN, and that structure was found in the entire area of BMN. In the case of BLMN with $x = 0.1$, both 1:2 and 1:1 ordered structures coexisted, as shown in Fig. 2(b). Most of the area, however, has a 1:1 ordered cubic structure. These results indicate that a small amount of La substitution destroys the 1:2 ordered hexagonal structure and causes a 1:1 ordered cubic structure. The same results were found for the $(\mathrm{Ba}_{1-x}\mathrm{La}_x)(\mathrm{Mg}_{(1+x)/3}\mathrm{Ta}_{(2-x)/3})\mathrm{O}_3$ system.[5] Fig. 2(c) shows the HRTEM image and diffraction pattern of the specimen with $x = 0.5$. Only the 1:1 ordered cubic structure was found in that specimen. Similar results were obtained for the specimens with $0.1 \leq x \leq 0.7$. When x was >0.7, however, superlattice reflections, not revealed in the XRD pattern, were observed. Fig. 2(d) shows the HRTEM image of the [0 0 1] zone axis obtained from the BLMN with $x = 0.9$. The inset represents [0 0 1] electron diffraction pattern taken from the same area. The extra reflections at {2 1 0} and {3 0 0}, which existed in XRD pattern, also could be observed in this pattern. Moreover, {1 0 0}, and {1 1 0} superlattice reflections, that were not observed in the XRD pattern, were obtained in the electron diffraction pattern. The HRTEM image also shows a new type of modulation along the [1 0 0] and [0 1 0] directions with the wavelength of 0.8 nm which corresponds to the interplanar distance of (1 0 0) plane. Similar results were obtained from the LMN.

According to the previous investigation, {1 0 0} and {1 1 0} reflections arise from the anti-parallel shift of A site cations and in-phase tilt of oxygen octahedral.[6] Therefore, TEM results indicate that the 1:1 ordered rhombohedral BLMN and LMN have in-phase tilt of oxygen octahedra in addition to the anti-parallel shift of A site cations and anti-phase tilt of oxygen octahedra.

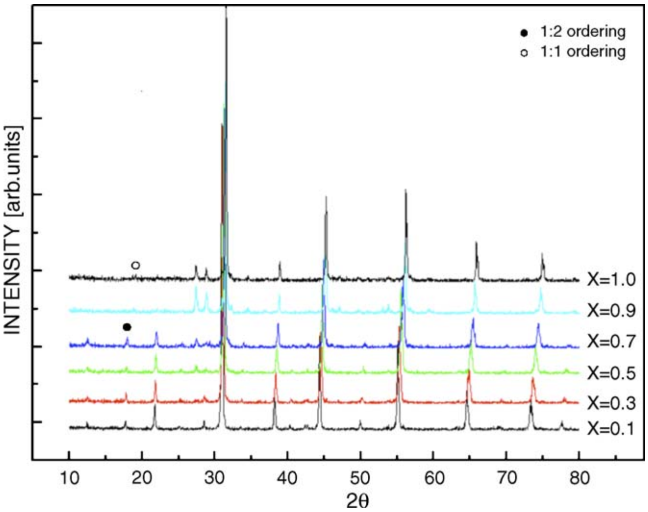


Fig. 3. X-ray diffraction pattern of $(\mathrm{Ba}_{1-x}\mathrm{K}_{x/2}\mathrm{La}_{x/2})(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$ with $0.1 \leq x \leq 1$ sintered at 1350 °C for 4 h.

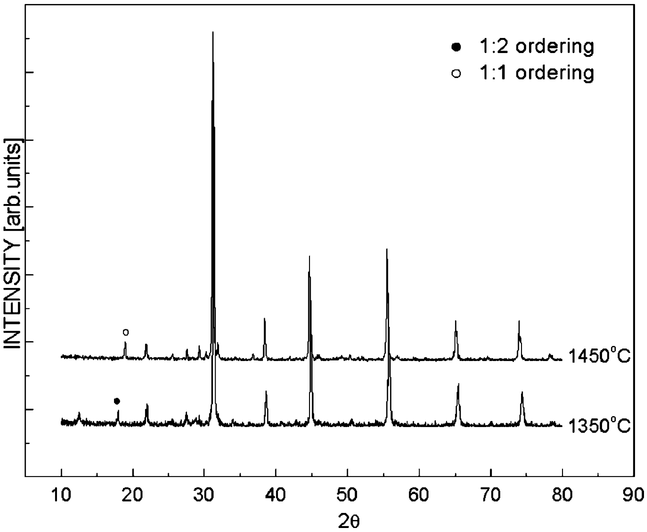


Fig. 4. X-ray diffraction pattern of $(\mathrm{Ba}_{0.5}\mathrm{K}_{0.25}\mathrm{La}_{0.25})(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$ sintered at 1350 and 1450 °C for 4 h.

In order to investigate the ordering behaviour of the BLMN ceramics, the La ion in BLMN was substituted by Na or K ions. Fig. 3 shows the X-ray diffraction pattern of BKLMN specimens sintered at 1350 °C for 4 h. As seen from the figure, When the K content (x) is less than 0.9, the 1:1 ordered structure of BLMN is transformed into the 1:2 ordered structure. When x is above 0.9, however, the 1:1 ordered cubic structure of BLMN was maintained.

Galasso et al. suggested that a 1:2 ordering increased with the increase of the size difference between B site ions.[7] According to our results (shown in Fig. 3) the large difference in the size between A and B site ions also seems to increase the 1:2 ordering because the size difference between A and B site ions decreases with the increase of K content. Fig. 4 shows the XRD pattern of BKLMN sintered at 1350 °C and 1450 °C for 4 h. The 1:2 ordered hexagonal structure, shown in Fig. 3, was transformed

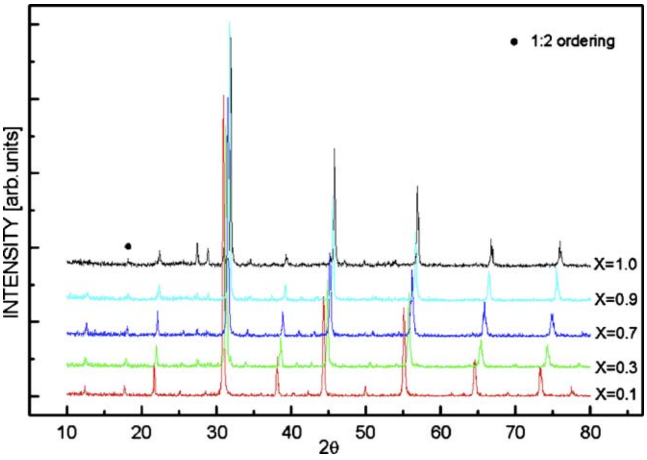


Fig. 5. X-ray diffraction pattern of $(\mathrm{Ba}_{1-x}\mathrm{Na}_{x/2}\mathrm{La}_{x/2})(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$ with $0.1 \leq x \leq 1$ sintered at 1400 °C for 4 h.

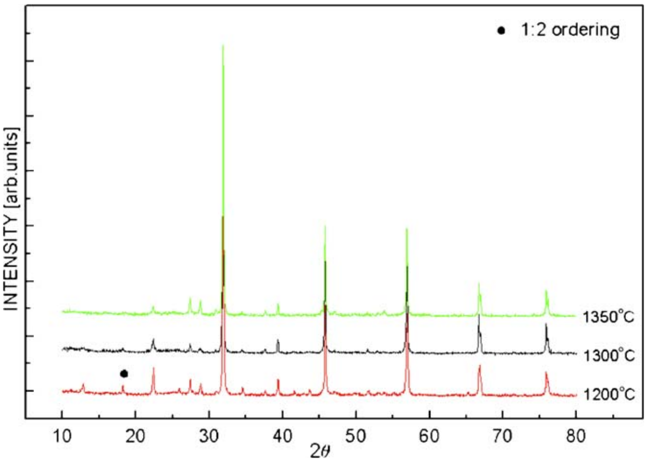


Fig. 6. X-ray diffraction pattern of $[Na_{0.5}La_{0.5}](Mg_{1/3}Nb_{2/3})O_3$ sintered at various temperatures for 4 h.

into a 1:1 ordered cubic structure. Therefore, the 1:2 ordered structure is stable at low temperature.

To clarify the effect of the size difference between A and B site ions on 1:2 ordering, Na ion, which is smaller than K ion, was substituted for K in BKLMN specimens. Fig. 5 shows the XRD pattern of BNLMN sintered at 1400 °C for 4 h. All the specimens had the 1:2 ordered structure even though they were sintered at a higher temperature. Therefore, this result confirms that the size difference between A and B site ions also influence the 1:2 ordering.

Fig. 6 shows the XRD pattern of LNMN specimens sintered at various temperatures. As seen in Fig. 6, the splitting of (2 2 2) and (2 1 0) peaks, shown for LMN, disappeared in this case. However, the (3 1 1) peak still exists in LNMN. Therefore, LNMN has the 1:2 ordered structure, which is distorted by the anti-phase tilting of oxygen octahedra.

Nagai et al. found a similar structure in $Sr(Mg_{1/3}Ta_{2/3})O_3$ (SMT) and a 1:2 ordered monoclinic structure was suggested for SMT.[8] Therefore it can be concluded that with the addition of Na or K ion, the 1:1 ordered structure of BLMN was transformed into 1:2 ordered hexagonal structure; the 1:1 ordered rhombohedral structure, on the other hand, was transformed into the 1:1 ordered monoclinic structure.

4. Conclusions

Variation in the crystal structure of $(Ba_{1-x}La_x)(Mg_{(1+x)/3}Nb_{(2-x)/3})O_3$ with $0 \le x \le 1$ was investigated in the present study. A 1:2 ordered hexagonal structure was found in the whole region of BMN. With increasing La content, the structure changes to 1:1 ordered cubic. When $x = 0.1$, both 1:1 and 1:2 ordered structures were found but most of the sample had the 1:1 ordered cubic structure. The 1:1 ordered cubic structure was maintained up to $x = 0.7$. When x exceeds 0.7, however, BLMN is transformed from a cubic to a rhombohedral structure. The rhombohedral BLMN had anti-parallel shifting of A site cations and in-phase tilting and anti-phase tilting of oxygen octahedra. When the La ion in BLMN was substituted by the K or Na ion, the 1:1 ordered structure of BLMN was transformed into 1:2 ordered structure. Sintering temperature and size difference of A and B site ions influenced the degree of 1:2 ordering.

References

1. Galasso, F. and Pyle, J., *Inorg. Chem.*, 1963, **2**(3), 482.
2. Glazer, A. M., *Acta Cryst.*, 1972, **B28**, 3384.
3. Glazer, A. M., *Acta Cryst.*, 1975, **A31**, 756.
4. Nagai, T., Sugiyama, M., Sando, M. and Nihara, K., *Jpn. J. Appl. Phys.*, 1997, **36**(3A), 1146.
5. Youn, H. J., Hong, K. S. and Kim, H., *J. Mater. Res.*, 1996, **12**(3), 589.
6. Reaney, I. M., Colla, E. L. and Setter, N., *Jpn. J. Appl. Phys.*, 1994, **33**, 3984–3990.
7. Galasso, F. and Pyle, J., *Inorg. Chem.*, 1963, **2**(3), 482–484.
8. Nagai, T., Sugiyama, M., Sando, M. and Nihara, K., *Jpn. J. Appl. Phys.*, 1997, **36**(3A), 1146.