September, 1987] © 1987 The Chemical Society of Japan NOTES *Bull. Chem. Soc. Jpn.*, **60**, 3433—3434 (1987) 3433

Ordering of Cations in $\mathrm{Ba(Mg_{1/3}Nb_{2/3})O_3}$ and $\mathrm{Ba(Zn_{1/3}Nb_{2/3})O_3}$

Hideki YOSHIOKA
Industrial Research Institute of Hyogo Prefecture, Yukihira-cho 3-1-12, Suma-ku, Kobe 654

(Received March 16, 1987)

Synopsis. The ordering of B-site cations in $\mathrm{Ba(Mg_{1/3}Nb_{2/3})O_3}$ (BMN) and $\mathrm{Ba(Zn_{1/3}Nb_{2/3})O_3}$ (BZN) was studied from superlattice reflections in X-ray diffraction patterns. The degree of ordering in BMN increases with increasing sintering temperature. While in BZN an ordered structure was observed up to 1673 K, and an order-disorder phase transition was found below 1773 K.

The ordering of B-site cations has been studied by Galasso et al.[1] for a number of $\mathrm{A(B'B'')O_3}$ type complex perovskite oxides. $\mathrm{Ba(Mg_{1/3}Nb_{2/3})O_3}$ (BMN) and $\mathrm{Ba(Zn_{1/3}Nb_{2/3})O_3}$ (BZN) were also synthesized by Galasso et al.[2] and their ordering properties were investigated by X-ray powder diffraction analysis. They reported that $\mathrm{Mg^{2+}}$ and $\mathrm{Nb^{5+}}$ in BMN are hexagonally ordered, while BZN has a disordered structure in terms of its B-site $\mathrm{Zn^{2+}}$ and $\mathrm{Nb^{5+}}$ cations.

It was considered that the ordering of B-site cations depends upon the defferences in their ionic charges and ionic radii.[2] Since the differences in the ionic charges are equal for BMN and BZN, their ordering properties may depend upon the differences in the ionic radii of B-site cations. As the ionic radii of $\mathrm{Mg^{2+}}$, $\mathrm{Zn^{2+}}$, and $\mathrm{Nb^{5+}}$ are 0.066, 0.074, and 0.069 nm, respectively,[3] the differences are 0.003 nm for BMN and 0.005 nm for BZN, which are also very close. Therefore, it is considered that the ordering properties of these compounds are located near the boundary of stability between order and disorder, and that the possibility of changing the degree of ordering by a heat treatment exists for these compounds. In this study the ordering of B-site cations for BMN and BZN under various heat treatments was investigated using superlattice reflections in the X-ray powder diffraction patterns.

BMN and BZN were prepared by solid state reactions. The mixtures of stoichiometric proportions of $\mathrm{BaCO_3}$, MgO or ZnO, and $\mathrm{Nb_2O_5}$ (purity>99.99%) were calcined at 1273 K for 8 h. The obtained powders gave X-ray patterns of a cubic perovskite structure. After pressing into pellets, these were sintered under various conditions, as shown in Table 1. The ordering of B-site cations produces superlattice reflections such as (1/3 1/3 1/3) and (2/3 1/3 1/3) with an original perovskite unit cell in the X-ray powder diffraction patterns. If B-site cations are completely ordered, the unit cell can be described as a hexagonal lattice and the superlattice reflections, (1/3 1/3 1/3) and (2/3 1/3 1/3), can be indexed as (001) and (100), respectively, with this hexagonal unit cell.

Table 1. Sintering Conditions of BMN and BZN

BMN	T/K	t/h	BZN	T/K	t/h
1	1473	16	1	1473	16
2	1573	4	2	1573	16
3	1673	4	3	1573	4
4	1773	4	4	1673	4
5	1833	4	5	1773	4

X-Ray diffraction patterns of the superlattice reflections (001) and (100) in BMN with Cu $K\alpha$ radiation are shown in Fig. 1. In all samples, (100) reflections are about twice as large in peak heights as the (001) reflections. The lattice spacings of (001) and (100) obtained from the diffraction angles are 0.71 and 0.50 nm, respectively; these are constant among samples under various sintering conditions. However, with increasing sintering temperature, the increase in peak heights and the sharpening of peaks are evident in Fig. 1. The degree of ordering can be represented by the intensity of the superlattice peak, while the ordered domain size can be calculated from the broadening of the peak. To estimate the degree of ordering in samples, the intensity ratio of the (100) reflection, which is the strongest superlattice reflection, to (110) and (102) reflections, which are overlapped and the strongest of all reflections, was calculated. The ordered domain sizes were obtained from the half widths of the superlattice reflections. The results are listed in Table 2. An increase in the degree of ordering was observed for a sample sintered at more than 1773 K; this is attributed to an enhancement of the rate of ordering with increasing temperature. Since the intensity ratio in a sample sintered at 1833 K is comparable with the theoretical value calculated from the completely ordered arrangement, the ordering of $\mathrm{Mg^{2+}}$ and $\mathrm{Nb^{5+}}$ in BMN is almost achieved by sintering at 1883 K for 4 h. The

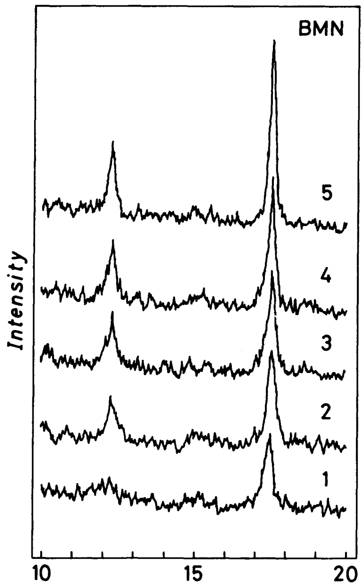

Fig. 1. X-Ray diffraction patterns of superlattice reflections for BMN.

Table 2. Intensity Ratio of Superlattice Peak and Size of Ordered Domains for BMN

	$(I_{100}/I_{110,102})\times 100$	L/nm
1	2.18	62
2	2.38	73
3	2.28	75
4	2.78	>100
5	3.27	>100

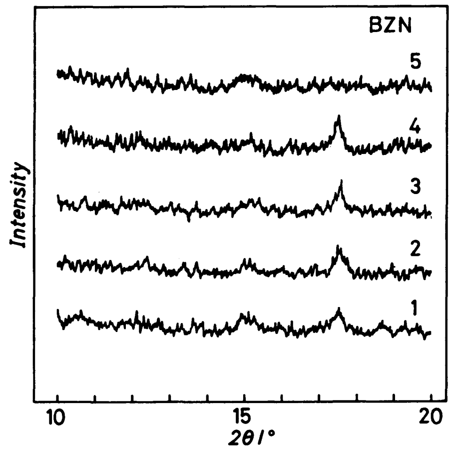

Fig. 2. X-Ray diffraction patterns of superlattice reflections for BZN.

ordered domain sizes increase steadily with increasing sintering temperature, reaching more than 100 nm at 1773 K.

Superlattice peaks of (1 0 0) reflections were detected for BZN sintered at less than 1673 K (Fig. 2), corresponding to the cation ordering, although Galasso et al.[2] reported that BZN was a disordered perovskite. Scattering factors of Zn^{2+} and Nb^{5+} are so close that the (1 0 0) reflections are much smaller than those in BMN and that the (0 0 1) reflections, which are considered to be about half as much as the (1 0 0) reflections in intensities like in BMN, are invisible. Since no significant difference with sintering time was observed between the diffraction patterns of samples 2 and 3 in Fig. 3, it seems that sintering for 4 h is sufficient for investigating the ordering property of BZN. One characteristic is the fact that the peak intensities increase with increasing sintering temperature for a sample sintered at less than 1673 K, and that no superlattice reflection could be observed for a sample sintered at 1773 K. This indicates that below 1673 K the ordered arrangement is stable, but above 1773 K the disordered arrangement is stable for BZN. This could be confirmed by X-ray diffraction patterns of the samples subjected to two-step heat treatments. In Fig. 3, the diffraction pattern of a sample sintered at 1573 K for 4 h (labeled as 3) in which the (1 0 0) reflection can be clearly observed. After sintering this sample again at 1773 K for 4 h (represented by 3 R in Fig. 3), the (1 0 0) reflection could. no longer be detected. Though the sample first sintered at 1773 K for 4 h showed no superlattice reflection (labeled as 5 in Fig. 3), a weak superlattice reflection was detected when reheated to 1573 K for 4 h (5 R in Fig. 3). This result clearly indicates that the ordered structure is stable up to 1573 K, but that the disordered structure is stable above 1773 K. Also, there is a reversible phase transition between the ordered and disordered structures in the temperature range from 1573 to 1773 K.

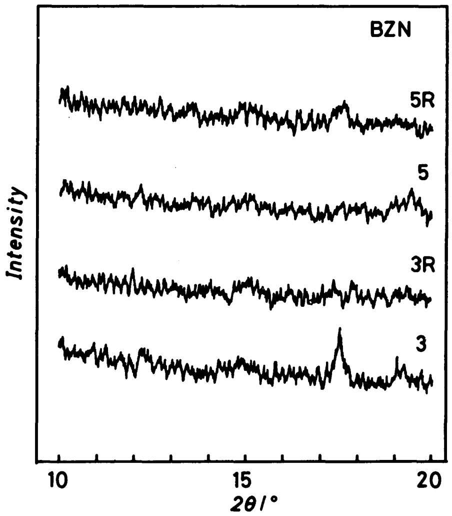

Fig. 3. Superlattice reflections of BZN subjected to two-step heat treatments.

Few of the complex perovskite oxides, which show an order-disorder phase transition like BZN, are known except for $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) studied by N. Setter et al.[4] They found that the degree of Sc^{3+} and Ta^{5+} ordering in PST sintered at 1833 K increases from 0.37 to more than 0.80 after annealing at 1273 K for 4 h; this strongly suggests that there is an order-disorder phase transition between 1273 and 1833 K.

The appearance of the order-disorder phase transition can be explained in terms of an increase in the entropy contribution to the free energy at high temperatures. The free energy of the ordered structure in BMN is lower than that of the disorderd structure (up to 1833 K); however, in BZN that of the disordered structure is lower than that of the ordered structure in 1773 K. The free energies of these materials mainly consist of the Madelung energy, due to an electrostatical interaction, and the entopy contribution which increases at high temperatures. Both are very close between BMN and BZN at the same temperature. Thus, it is noted that as G. Patrat et al.[5] pointed out for $Sr(Fe_{1/2}Ta_{1/2})O_3$, that the polarization energy and the displacement energy, which are caused by the size and the polarizability of the constituent ions, must be included in calculations of their free energies.

References

1) F. Galasso and J. Pint, *Nature (London)*, **207**, 70 (1965).
2) F. Galasso and J. Pyle, *J. Phys. Chem.*, **67**, 1561 (1963).
3) L. H. Ahrens, *Geochim. Cosmochim. Acta*, **2**, 155 (1952).
4) N. Setter and L. E. Cross, *J. Appl. Phys.*, **51**, 4356 (1980).
5) G. Patrat, M. Brunel, and F. de Bergevin, *J. Phys. Chem. Solids*, **37**, 285 (1976).