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Local cationic ordering behavior in $Ba(Mg_{1/3}Nb_{2/3})O_3$ ceramics

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Abstract

We have studied the effect of sintering temperature and time on cationic ordering in $BaMg_{1/3}Nb_{2/3}O_3$ (BMN) microwave dielectric ceramics using transmission electron microscopy. Energy-dispersive spectroscopy was used to analyze the local chemical compositions. It is revealed that according to the sintering conditions the BMN ceramics show diverse local cationic ordering behavior, such as the development of domain twinning and 'core-shell'-structured grains and the formation of local disordered domains, although generally having 1:2 cation ordering structure. The disordered structure is formed in Mg-excess regions. Such local chemical variation seems to be caused by the formation of $BaNb_2O_6$ second phase in the neighboring grain boundary. Microwave dielectric properties of the ceramics will also be discussed in relation to the structural variation.

Keywords: Capacitors; Dielectric properties; Electron microscopy; Perovskites; Sintering

1. Introduction

Ordering behaviour in $AB'_{1/3}B''_{2/3}O_3$-type complex perovskite ceramics has been extensively studied and it has been reported that the microwave dielectric properties of the ceramics are strongly dependent on the cationic ordering in the perovskite structure. B-site cationic ordering structute of the $AB'_{1/3}B''_{2/3}O_3$-type perovskites can be 1:2 ordering and 1:1 partial ordering.[1,2] In the latter structure $(B'_{2/3}B''_{1/3})_{1/2}$ and $B''_{1/2}$ are 1:1 partially ordered: In the two kinds of B-sites one is occupied by a cation B″ and the other is occupied by the two kind of cations statistically.[2] The $AB'_{1/3}B''_{2/3}O_3$-type complex perovskite may also have a disordered structure.

Most of the studies on order–disorder transitions in perovskite structure have been focussed on the transitions due to compositional variations. Recently, however, in some $AB'_{1/3}B''_{2/3}O_3$-type ceramics it is observed that their ordering structure may be changed locally by sintering temperatures. In $BaNi_{1/3}Nb_{2/3}O_3$ ceramics, which had been known to have disordered structure, it is found that the disordered structure transforms locally to 1:2 ordered structure according to heat-treatment conditions.[3]

In this study, we investigated the effect of heat-treatment on the cationic ordering behaviour in $BaMg_{1/3}Nb_{2/3}O_3$ (BMN) complex perovskite microwave ceramics which has been known to have 1:2 ordered structure. The effect of sintering temperature and time on the cationic ordering in the BMN ceramics was studied by using transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS). The relationship between the local structure and chemical composition was analysed. The effect of the structural variation on microwave dielectric properties of the ceramics were also studied.

2. Experimental procedure

The BMN ceramics were prepared using the columbite precursor method.[4] High-purity raw materials (>99.9%, High Purity Chem., Japan) of $BaCO_3$, MgO, and Nb_2O_5 were weighed and mixed by ball-milling for 24 h. The slurry was dried and calcined at 1200 °C for 4 h. The calcined powders were ground and pressed into disk shapes. Specimens were sintered in three different conditions: 1350 °C—4 h, 1350 °C—40 h, and 1500 °C—4 h.

For TEM analysis specimens were mechanically thinned by using micropolisher (Gatan, USA) and milled

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by using Ar^+ ion beam. Bright-field images and selected area electron diffraction (SAD) patterns were observed by using TEM (CM30, Philips) operated at the accelerating voltage of 200 kV. Local chemical compositions were analyzed by using EDS.

3. Results and discussion

3.1. Local cationic ordering

A bright-field image and SAD patterns for the specimen sintered at 1350 °C for 4 h are shown in Fig. 1. In the SAD patterns we can observe $1/3(111)_{cubic}$ and $2/3(111)_{cubic}$ superlattice diffraction spots due to the 1:2 ordering. From the arrangement of the superlattice spots, it is believed that the SAD patterns in Fig. 1 (b) are related to a single domain and the patterns in (c) and (d) are related to a twinned domain. We could not observe any local region which does not have 1:2 ordering though dozens of grains were invesigated. Any second phases were not found throughout the specimen. As the relative intensity of the superlattice diffraction spots compared to the fundamental ones in the patterns are not different significantly, the 1:2 ordering in this specimen seems to be rather uniform compared to that in the higher-temperature or longer-time heat-treated specimens, which will be discussed later.

When the sintering temperature of BMN specimen increased, diverse local ordering structures were developed. TEM analysis for the specimen heat-treated at 1500 °C for 4 h are shown in Figs. 2 and 3. As shown in the bright-field image in Fig. 2 (a), so-called "core-shell" structure is developed: the central area of the grain has imperfections such as dislocations and the marginal area has less imperfections. As shown in Fig. 2 (b)–(f), 1:2 superlattice diffractions due to the twinned domain were observed everywhere inside the grain. The relative intensity of the superlattice diffraction spots to the fundamental ones, however, increased significantly compared to that observed in the specimen heat-treated at 1350 °C for 4 h.

Fig. 3 shows the TEM analysis on another grain of the specimen sintered at 1500 °C for 4 h. In most regions inside the grain 1:2 ordered structures are identified; the "core" region has a twinned domain pattern [Fig. 3 (b)], while the "shell" region has a single domain pattern (Fig. 3 (c)). However, in a local region "3″ in Fig. 3 (a) simple cubic structure having no 1:2 superlattice diffraction spots is observed. The simple cubic structure means that in the local region the B sites are disordered. In addition a second phase is observed in some grain boundary triple points [for example, "4" in Fig. 3 (a)]. It is noteworthy that the disordered domain structure is adjacent to the second phase.

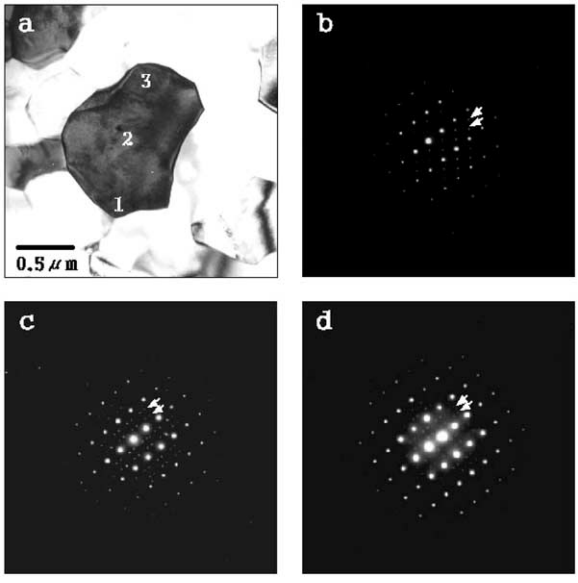

Fig. 1. Transmission electron micrographs of BMN ceramics sintered at 1350 °C for 4 h: (a) is a bright-field image; (b), (c) and (d) are $[110]_{cubic}$ zone axis SAD patterns for the regions marked by 1, 2 and 3, respectively in the image. Arrows indicate 1:2 order superlattice spots.

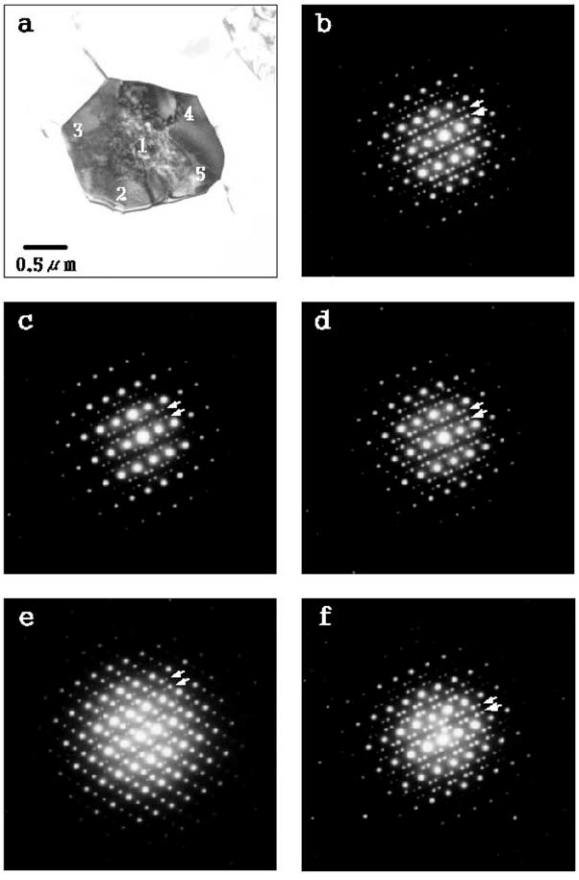

Fig. 2. Transmission electron micrographs of BMN ceramics sintered at 1500 °C for 4 h: (a) is a bright-field image; (b), (c), (d), (e) and (f) are $[110]_{cubic}$ zone axis SAD patterns for the regions marked by 1, 2, 3, 4 and 5, respectively in the image. Arrows indicate 1:2 order superlattice spots.

As the time of heat-treatment at 1350 °C increased to 40 h, the local structural behaviour is significantly changed from that of the 1350 °C—4 h sintered specimen. Figs. 4 and 5 show the TEM analysis on the specimen sintered at 1350 °C for 40 h. As shown in the bright-field image and SAD patterns in Fig. 4, the "core" region has a 1:2 ordered twinned domain pattern [Fig. 4 (b)] and most of the "shell" regions have a 1:2 ordered single domain pattern [Fig. 4 (d), (e) and (f)]. However, in a certain shell region "2″ in Fig. 4 (a), a disordered simple cubic pattern is observed (Fig. 4 (c)). It can also be observed that the relative intensity of the 1:2 superlattice diffraction spots to the fundamental ones varies significantly from region to region.

Fig. 5 shows the TEM analysis on another grain of the 1350 °C—40 h sintered specimen. In the figure, we can also observed the 1:2 ordered twinned domain pattern in the "core" region and the single domain pattern in the "shell" region. The grain in the "3" region in Fig. 5 (a) is revealed to a second phase.

3.2. Local order–disorder transition and second phase formation

Typical TEM–EDS results on the chemical compositions of the matrix grain regions and second phases discussed above are summarized in Table 1. As shown in the table, the chemical composition of the matrix grains is not far different from its ideal stoichiometry independent of sintering conditions as a whole. The composition of the second phases, which were developed in the specimens heat-treated at 1350 °C for 40 h

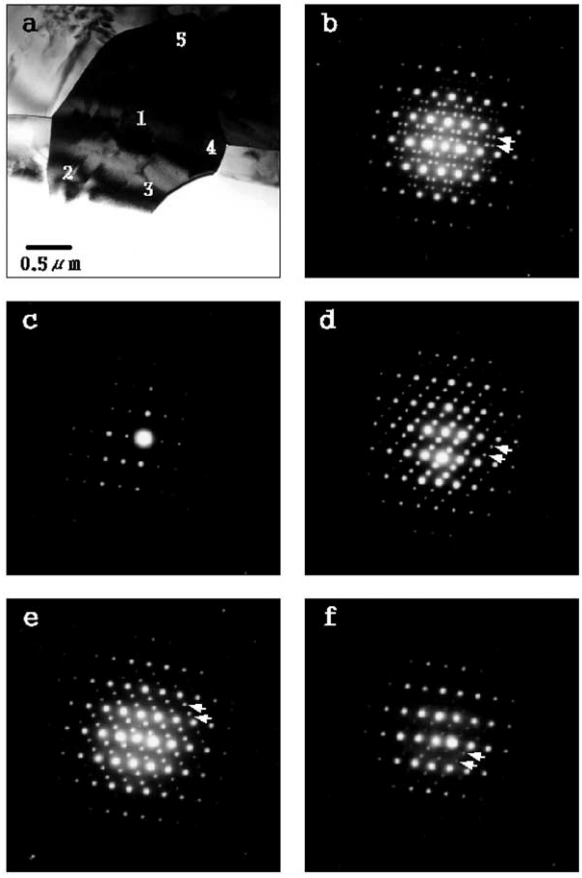

Fig. 4. Transmission electron micrographs of BMN ceramics sintered at 1350 °C for 40 h: (a) is a bright-field image; (b), (c), (d), (e) and (f) are $[110]_{cubic}$ zone axis SAD patterns for the regions marked by 1, 2, 3, 4 and 5, respectively in the image.

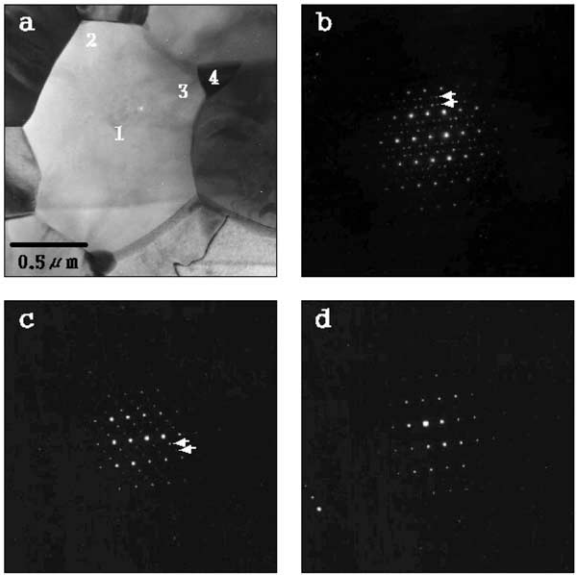

Fig. 3. Transmission electron micrographs of BMN ceramics sintered at 1500 °C for 4 h: (a) is a bright-field image; (b), (c) and (d) are $[110]_{cubic}$ zone axis SAD patterns for the regions marked by 1, 2 and 3, respectively in the image. Arrows indicate 1:2 order superlattice spots.

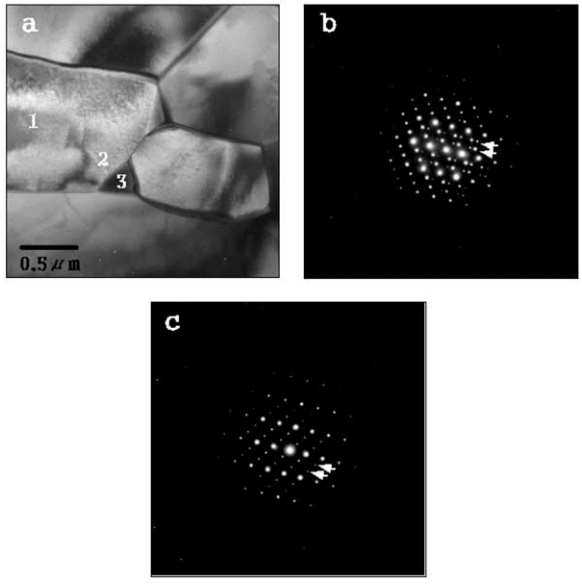

Fig. 5. Transmission electron micrographs of BMN ceramics sintered at 1350 °C for 40 h: (a) is a bright-field image; (b) and (c) are $[110]_{cubic}$ zone axis SAD patterns for the regions marked by 1 and 2, respectively in the image. Region 3 is a second phase.

Table 1
Typical TEM–EDS results on chemical composition of matrix grains and second phase present in the sintered BMN samples

Sintering condition	Analysis region	Structural feature	Atomic%			Atomic ratio	
			Ba	Mg	Nb	Nb/Mg	(Mg + Nb)/Ba
Ideal BMN			50.0	16.7	33.3	2	1
1350 °C—4 h	Fig. 1(a) "1"	Matrix 1:2	49.6	15.5	34.9	2.25	1.02
1500 °C—4 h	Fig. 3(a) "1"	Matrix 1:2	52.8	14.4	32.8	2.28	0.89
	Fig. 3(a) "3"	Matrix disorder	44.4	20.0	35.7	1.79	1.25
	Fig. 3(a) "4"	Second phase	37.3	3.6	59.1	16.42	1.68
	Fig. 2(a) "1"	Matrix 1:2	52.2	15.2	32.6	2.14	0.92
1350 °C—40 h	Fig. 5(a) "3"	Second phase	38.5	7.3	54.2	7.42	1.60
	Fig. 4(a) "1"	Matrix 1:2	56.4	15.1	28.5	1.89	0.77
	Fig. 4(a) "2"	Matrix disorder	50.6	19.1	30.3	1.59	0.98

and 1500 °C for 4 h, is significantly Nb-rich and Mg-deficient. The disordered region "3" in Fig. 3 (a), which is adjacent to the second phase "4", is Mg-excess compared to the 1:2 ordered region. The same phenomenon is observed in the disordered region "2" in Fig. 4 (a). From these results, it may be postulated that the second phase was generated by the Ba and Nb ions diffused from the matrix. Thus, the local chemical composition of the region adjacent to the second phase became Mg-excess, which resulted in disordering. It is noteworthy that the disordering occurs only when the ratio of Nb/Mg is less than 1.8, even though there are significant variations in the ratio of (Mg + Nb)/Ba.

Considering the resolution of EDS probe and superimposing effects from the matrix, the second phase seems to be $BaNb_2O_6$ (or $Ba_3Nb_5O_{15.5}$). The formation of this second phase in this study is thought to be coincident with the formation of the second phases, $BaNb_2O_6$ and $BaTa_2O_6$ in high-temperature and long-time sintered $Ba(Ni_{1/3}Nb_{2/3})O_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics, respectively.[5–6]

3.3. Microwave dielectric properties

Microwave dielectric properties of the BMN ceramics sintered at various conditions are summarized in Table 2. It is noteworthy that the lowest quality factor was measured in the specimen heat-treated at 1500 °C for 4 h. This can be attributed to the structural and chemical inhomogeneity and diversity such as the formation of second phase, local disordering, and domain twinning. The microwave dielectric quality factor of $BaNb_2O_6$ was reported as poor as 2900.[6]

Table 2
Microwave dielectric properties of BMN ceramics sintered with various sintering conditions

Sintering condition	Dielectric constant	Quality factor ($Q \times f$: GHz)	Temperature coefficient of resonant frequency (ppm/°C)	Sintered density (%)
1350 °C—4 h	31.2	46,000	+18	96.9
1500 °C—4 h	31.5	15,300	+20	96.0
1350 °C—40 h	31.0	28,600	+18	96.0

The high quality factor observed at the specimen heat-treated at 1350 °C for 4 h can be attributed to its higher structural and chemical homogeneity than those sintered at a higher temperature or for a longer time.

4. Conclusion

It is revealed that according to the sintering conditions the BMN ceramics show very diverse local cationic ordering behaviour, such as the development of domain twinning, "core-shell" structured grains and local disordered structure, though having 1:2 cationic ordering structure basically. When the BMN ceramics were sintered at 1350 °C for 40 h and 1500 °C for 4 h, a local order–disorder transition was observed in Mg-excess regions, especially where the ratio of Nb/Mg is less than 1.8. It is postulated that the formation of $BaNb_2O_6$-like second phase at grain boundary triple points resulted in local compositional change in the 1:2 ordered matrix grain and thus caused the local disordering.

The microwave dielectric quality factor of the ceramics decreases greatly with the increase of the structural and chemical inhomogeneity.

Acknowledgements

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