Microstructure and Microwave Characteristics of Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃-Based Dielectrics

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Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃ を基本とする誘電体の微細構造とマイクロ波特性

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[Received February 22, 1991; Accepted May 23, 1991]

The microstructure of the cubic perovskite Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃-based dielectric has been investigated. The secondary phase was determined to be Ba₅Nb₄O₁₅; this phase was detrimental to the microwave properties of Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃. Eliminating the secondary phase, the precise control of A-site/B-site ratio of the perovskite and long time annealing improved the microwave characteristics.

Key-words: Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃, Ba₅Nb₄O₁₅, Microwave dielectric, Perovskite structure, Microstructure

1. Introduction

Microwave application to automobile telephones and TV-receivers of satellite broadcasting has been increasing rapidly. Global Positioning System (GPS) for navigation of airplanes, cars, and mountain-climbers is also in the category of microwave application. Under these circumstances, the microwave dielectric properties with high-*Q*, low loss, as resonators and filters in the microwave equipment have been becoming extremely important. The cubic perovskite dielectrics have been studied for developing the high-*Q*, low loss, dielectric.¹⁾⁻⁸⁾ In order to study the mechanisms of microwave characteristics, far infrared reflection spectra,⁹⁾ phase transition,¹⁰⁾ and the effect of secondary phase on *Q*-value,¹¹⁾ Curie-Weiss-like behavior of the loss tangent,¹²⁾ the effect of dopants,^{13),14)} Ba reduced perovskite to improve sintering density,¹⁵⁾ B-site element control in perovskite ABO₃,¹⁶⁾ frequency and temperature dependence of grain size and density of polycrystalline perovskite,¹⁷⁾ and the techniques for microwave measurement¹⁸⁾ have been widely discussed. However, the relation between microstructural phases and the microwave properties has not been sufficiently discussed. The development of structural analysis equipment has made it possible to analyze the microstructures and the concentrations of constituent elements in grains and phases.¹⁹⁾⁻²¹⁾

Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃-based dielectrics usually synthesized have a very low *Q*-value. The authors considered that this might be caused by the existence of other phases in the dielectrics. The first pur-

pose of this study, therefore, is to analyze the microstructure of the Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃-based dielectrics, and to study the effects of the phases on the microwave properties of the dielectric body. The second purpose is to synthesize a high-*Q*, low loss, dielectric compound by controlling the A-site/B-site ratio and by long annealing process.

2. Experimental

Commercially available BaCO₃, MgCO₃, Co₃O₄, and Nb₂O₅ were used for the synthesis of Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃-based dielectrics. A mixture of 40 wt% concentration was ball-milled in deionized water for 17.5 h, dried, then calcined at 1270°C for 2 h in air atmosphere. After milling with polyvinyl alcohol as an organic binder, the calcined powder was pressed into a cylindrical shape, 12.5 mm in diameter and 15.0 mm in height. The pressed body was sintered at 1520°C for 2 h in air.

The sintered compacts were polished with 0.25 μm diamond paste then chemically etched by HCl+HF solution to reveal the grains and phases for microstructural observation with a scanning electron microscope (SEM: Hitachi S-800). Constituent elements of the microarea were mapped by means of a computer-aided micro analyzer (CMA: Jeol JCMA-733). A scanning transmission electron microscope (STEM: Jeol JEM-2000FXII) with energy dispersion X-ray (EDX) was used for quantitative analysis of composition of grains and phases in the microarea. The crystal structure of each phase was determined by an X-ray diffraction spectrometer (XRD: Mac Science MXP³) with Cu target.

In order to evaluate the microwave characteristics, each sintered body was precisely machined into a cylindrical shape, 10.00±0.03 mm in diameter and 5.00±0.01 mm in height. Microwave dielectric characteristics were measured by Hakki and Coleman's dielectric resonator method,²²⁾ and the *Q*-value was measured at 7.3 GHz.

3. Results and discussion

3.1 Phase determination

Figure 1 shows a microstructure of the polished

Fig. 1. SEM photomicrograph of polished and etched surface of Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃ body. The white-colored secondary phase, and black-colored tertiary phase on the grain boundaries are observed.
Note : Etching solution was (1 : 1)HCl 250 ml + (1 : 9)HF 1 ml. Etching time was 100 s at 20°C.

and chemically etched surface of a sintered sample. The average grain size of the principal phase, Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃, is approximately 1.2 μm. The white-colored secondary phase, having straight edges and dihedral angles of 60 or 120 degrees, is stable against the HCl+HF solution. The black-colored tertiary phase with 0.2 μm diameter exists on the grain boundaries, particularly at the triple points. The tertiary phase is etched most easily by the solution among the three phases.

The constituent elements of the dielectric were mapped by CMA as shown in Fig. 2. It is significant that the concentrations of both Mg and Co in the secondary phase are extremely small. On the other hand, the concentration of Nb is much higher than that of the principal phase. Barium, as an A-site element in perovskite structure of ABO₃, shows no noticeable difference in concentration between principal and secondary phases. The constituent elements of each phase were quantitatively analyzed by using STEM-EDX as given in Table 1. The Ba/Nb ratio of the principal phase, Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃, is 52.04/35.95 (nearly 3/2). The secondary phase is 52.67/44.26 (nearly 5/4). Therefore, the most prob-

Table 1. Quantitative analysis by STEM-EDX (n=4).

		Concentration (at%)			
		BaO	(Nb ₂ O ₅)/2	CoO	MgO
Principal phase	ave.	52.04	35.95	5.84	2.74
	σ	±1.47	±3.63	±1.68	±2.00
Secondary phase	ave.	52.67	44.26	1.19	0.30
	σ	±2.85	±2.11	±1.20	±0.54
Tertiary phase	ave.	37.98	58.22	2.17	1.43
	σ	±2.29	±1.98	±0.35	±1.00

(a)

(b)

Fig. 2. (a) Composition image of the etched microstructure of Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃.
(b) Mg, Co, Nb, and Ba mapping image by CMA.

Fig. 3. X-ray diffraction spectra of (a) $\text{Ba}\{(\text{Mg}, \text{Co})_{1/3}\text{Nb}_{2/3}\}\text{O}_3$ -based dielectric, (b) $\text{Ba}_5\text{Nb}_4\text{O}_{15}$, and (c) $\text{Ba}\{(\text{Mg}, \text{Co})_{1/3}\text{Nb}_{2/3}\}\text{O}_3$ (75 wt%) + $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ (25 wt%). These samples were sintered at 1520°C for 2 h in air.

able compound of the secondary phase is determined to be $\text{Ba}_5\text{Nb}_4\text{O}_{15}$, which is a stable compound in the $\text{BaO}-\text{Nb}_2\text{O}_5$ binary system.^{23),24)}

Figures 3(a) and (b) show XRD patterns of $\text{Ba}\{(\text{Mg}, \text{Co})_{1/3}\text{Nb}_{2/3}\}\text{O}_3$ -based dielectric and the synthesized $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ (JCPDS: Card No. 14-28),²⁵⁾ respectively. The diffraction pattern of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ corresponds to the unknown peaks in Fig. 3(a). The $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ phase was milled and intentionally added to the principal phase at the concentration of 25 wt%, then the mixture was sintered at 1520°C for 2 h. The resulting XRD pattern in Fig. 3(c) is the same as that in Fig. 3(a). However, the former shows much higher intensity of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ than the latter. Consequently, this result convinces that the secondary phase has to be $\text{Ba}_5\text{Nb}_4\text{O}_{15}$. Furthermore, the hexagonal structure of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ agreed with the microstructural shape of the secondary phase in Fig. 1.

3.2 Model experiment of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ -doped $\text{Ba}\{(\text{Mg}, \text{Co})_{1/3}\text{Nb}_{2/3}\}\text{O}_3$

In order to study the influence of the secondary phase, a single phase of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ was synthesized from BaCO_3 and Nb_2O_5 under exactly the same processing conditions as the mother material. Below its calcination temperature of 1270°C, $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ shrunk considerably. When the temperature was

raised to 1520°C for sintering, $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ melted because the melting point of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ is 1320°C.^{23),24)} It is, thus, tenable that the secondary phase was formed during cooling process from the liquid phase.

Figure 4 shows an SEM photomicrograph of the sintered dielectric with the addition of 25 wt% secondary phase. The hexagonal-shaped secondary phase with 20 μm diameter and approximately 1 μm thick-

Fig. 4. SEM photomicrographs of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ (25 wt%) + $\text{Ba}\{(\text{Mg}, \text{Co})_{1/3}\text{Nb}_{2/3}\}\text{O}_3$ (75 wt%) dielectric sintered at 1500°C for 2 h in air.

ness is observed. Even when the dielectric was sintered without the intentional addition of the secondary phase, the same size of the hexagonal-shaped phase was still observed; but the number of the phase was smaller.

The microwave characteristics of Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃ containing secondary and tertiary phases were evaluated. The dielectric constant ϵ_r , the loss quality Q , and the temperature coefficient of resonating frequency τ_f (ppm/°C) of the Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃-based dielectric were 31.7, 1730 and 9.12, respectively, while those of Ba₅Nb₄O₁₅ were 27.3, 1100, and 54.56, respectively. In other words, Ba₅Nb₄O₁₅ possessed disadvantageous properties of low- ϵ_r , low- Q , and high τ_f . This case study, therefore, proves two points for improving the dielectric synthesis.

(1) The existence of Ba₅Nb₄O₁₅ in Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃ is detrimental to the microwave properties of ϵ_r , Q , and τ_f . Thus, Ba₅Nb₄O₁₅ has to be eliminated from the principal phase.

(2) Both Q -values of the principal and secondary phases were low. Chemical compositions, therefore, must be precisely controlled in order to obtain a high- Q microwave dielectric.

3.3 Effect of A-site/B-site ratio of Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃

Figure 5 shows the Q -value and ϵ_r of Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃, as a function of A-site/B-site ratio, which was determined by fluorescence X-ray analysis (Rigaku Simultics 3530). When the A/B value is over 1.018, Q -value is less than 1000; in this A-site rich zone, the porous microstructure of the dielectric was observed and thus both ϵ_r and Q had low values. At the point where $A/B=1.015$, the Q -value shows approximately 7000; this improved dielectric possesses much higher Q -value than that in the model experiment sample. As the A/B ratio decreases from 1.015 to 1.008, the Q -value increases to 11000 with the reduction of Ba₅Nb₄O₁₅ confirmed by XRD peak intensities. For the A/B ratio between 1.008 and 1.005, the Q -value declines dramatically to 2000; in this region, the quantity of Ba₅Nb₄O₁₅ increased. On the other hand, dielectric constant shows constant

Fig. 5. Q -value and dielectric constant versus A-site/B-site ratio of Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃.

Table 2. Effect of annealing on ϵ_r and Q .

annealing (h)	ϵ_r	Q
Conventional method		
2	32.90	8175
5	32.63	8529
10	32.82	8539
20	32.65	8743
40	32.62	9133
80	32.49	8985
A-site/B-site control		
40	32.66	11600

value of 32.8 in the A/B area between 1.013 and 1.005. It is, therefore, concluded that the Q -value is remarkably dependent on the A-site/B-site ratio of Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃.

3.4 Effect of annealing

Long-time annealing was carried out to enhance the Q -value of Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃, since the atomic arrangement of the constituent elements was considered to affect the microwave properties of the dielectric. Table 2 gives Q , ϵ_r , and annealing time of conventionally synthesized samples and those of the A-site/B-site controlled sample at 1390°C. The Q -value increases as annealing continues, although the ϵ_r shows to be almost constant. The atomic arrangement of the dielectric during annealing enhances the Q -value. However, when the sample is over-annealed more than 80 h, the Q -value decreases. Probably the composition has been altered because cobalt has priority over other elements in the vaporization during long annealing. Based on the result, long time annealing of 40 h for A-site/B-site modified sample was attempted. The result of Q -value is 11600 (Table 2), or the highest value in this experiment. The dielectric constant of this sample is almost the same as that of the conventional samples. Thus, in order to improve the microwave characteristics of Q -value, the precise control of the composition and long time annealing are of prime importance.

4. Concluding remarks

The microstructure and microwave properties of the cubic perovskite Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃-based dielectrics have been investigated.

(1) The secondary phase is determined to be hexagonal Ba₅Nb₄O₁₅. This phase is detrimental to the microwave properties of Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃.

(2) The precise control of A-site/B-site ratio is significant in eliminating the secondary phase Ba₅Nb₄O₁₅ and therefore in improving the Q -value of Ba{(Mg, Co)_{1/3}Nb_{2/3}}O₃.

(3) Long time annealing is also effective for the

enhancement of the Q -value of $\text{Ba}\{(\text{Mg}, \text{Co})_{1/3}\text{Nb}_{2/3}\}\text{O}_3$.

Acknowledgments The authors thank Y. Izumi and Y. Yamamoto for their analytical support, and A. Okamoto for his comment. The advice on the sample preparation by M. Yahagi, T. Kikuchi, S. Taguchi, and Y. Iijima is also gratefully acknowledged.

References

- 1) S. Kawashima, M. Nishida, I. Ueda and H. Ouchi, *J. Am. Ceram. Soc.*, **66**, 421–23 (1983).
- 2) K. Endo, K. Fujimoto and K. Murakawa, *J. Am. Ceram. Soc.*, **70**, C215–18 (1987).
- 3) H. Tamura, T. Konoike, Y. Sakabe and K. Wakino, *J. Am. Ceram. Soc.*, **67**, C59–61 (1984).
- 4) H. Banno, F. Mizuno and T. Takeuchi, *Jpn. J. Appl. Phys.*, **24**, Supplement 24–3, 87–89 (1985).
- 5) S. Nomura and F. Kojima, *Jpn. J. Appl. Phys.*, **14**, 907–98 (1975).
- 6) F. Galasso and J. Pyle, *J. Phys. Chem.*, 533–34 (1963).
- 7) Y. Hikichi, Z. Chen, R. E. Newnham and L. E. Cross, *Mat. Res. Bull.*, **17**, 1371–77 (1982).
- 8) K. Sasazawa and N. Yamaoka, *Jpn. J. Appl. Phys.*, **24**, Supplement 24–2, 1022–24 (1985).
- 9) K. Wakino, M. Murata and H. Tamura, *J. Am. Ceram. Soc.*, **69**, 34–37 (1986).
- 10) G. Rupprecht and R. O. Bell, *Phys. Rev.*, **125**, 1915–20 (1962).
- 11) K. Kageyama, J. Takahashi and M. Takata, *Seramikkusu Ronbunshi*, **98**, 824–30 (1990).
- 12) A. J. Pointon and R. M. Henson, Proc. 3rd IMF, *Ferroelectrics*, **7**, 359–60 (1974).
- 13) S. Neirman and I. Burn, *J. Mater. Sci.*, **19**, 737–44 (1984).
- 14) B. D. Silverman, *Phys. Rev.*, **125**, 1921–30 (1990).
- 15) K. Endo, M. Tsurumi and K. Murakawa, *Seramikkusu Ronbunshi*, **98**, 934–37 (1990).
- 16) S. B. Desu and H. M. O'Bryan, *J. Am. Ceram. Soc.*, **68**, 546–51 (1985).
- 17) S. Ikegami, *J. Phys. Soc. Jpn.*, **18**, 1203–13 (1963).
- 18) M. T. Lanagan, J. H. Kim, S.-J. Jang and R. E. Newnham, *J. Am. Ceram. Soc.*, **71**, 311–16 (1988).
- 19) S. Sumita, M. Ikeda, Y. Nakano, K. Nishiyama and T. Nomura, to be published in *J. Am. Ceram. Soc.*
- 20) S. Sumita, *Seramikkusu Ronbunshi*, **99**, 538–42 (1991).
- 21) S. Sumita, A. Fukuno, S. Yamashita and T. Yoneyama, *J. Jpn. Soc. Powder & Powder Metal.*, **32**, 253–58 (1985).
- 22) B. W. Hakki and P. D. Coleman, IRE Transaction on Microwave Theory and Techniques, 402–10 (1960).
- 23) "Phase Diagram for Ceramists", Vol. VI, Am. Ceram. Soc. (1987) p. 101, Fig. 6371.
- 24) "Phase Diagram for Ceramists", Vol. I, Am. Ceram. Soc. (1964) p. 99, Fig. 214.
- 25) Powder Diffraction File, Card No. 14–28, Joint Committee on Powder Diffraction Standards.