

# Sintering and Microwave Dielectric Properties of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ Ceramics Prepared by Precursor Method

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## ABSTRACTS

The phase development process of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  ceramics is not clearly known and frequently accompanies second phases which deteriorate dielectric properties. In synthesizing  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  ceramics, in order to trace the reaction sequence during conventional solid-state reaction in  $\text{BaO-TiO}_2$  system, different barium sources of  $\text{BaCO}_3$  and  $\text{BaTiO}_3$  precursor were used as starting materials. From the analysis of XRD patterns, different secondary phases could be identified depending on the barium source used, which might mean that the equilibrium phases in  $\text{BaO-TiO}_2$  system are very difficult to be synthesized. Because the  $\text{BaTiO}_3$  precursor provides short diffusion paths of ions, the system revealed less secondary phases during solid state reaction. In synthesizing  $\text{BaO-xSm}_2\text{O}_3\text{-4.5TiO}_2$  system using different barium sources, different secondary phases were developed also. Microstructure and dielectric properties were examined and discussed in terms of secondary phase development.

**Key words :**  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ , Precursor, Microwave, Dielectric, Secondary phase

## 1. Introduction

With recent progress in microwave telecommunication and satellite broadcasting industries, various microwave components such as band pass filter, duplexer and oscillator utilizing dielectric resonator are widely used in miniaturized filters and resonators. Since 1970s, microwave dielectric ceramics with dielectric constant ranging 20–40 such as  $\text{Ba}(\text{Mg},\text{Ta})\text{O}_3$ ,  $\text{Ba}(\text{Zn},\text{Ta})\text{O}_3$ ,  $\text{BaTi}_4\text{O}_9$ , and  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  systems have been developed and applied successfully to many commercial units.<sup>1,2)</sup> The research and development of  $\text{BaO-TiO}_2$  system with high dielectric performance have been followed.<sup>3-5)</sup> On the other hand, great attention has been paid on the phase development of  $\text{BaO-TiO}_2$  system as its application to microwave dielectrics is widely made.

In this system, it was, however, found that the secondary phases which are not readily eliminated by conventional ceramic manufacturing process are developed during heat treatment. Although many successive works have been focused on the phase development, the phase development as well as the phase relations is not clearly understood to date, which signifies that the equilibrium phases are hardly obtained.

It is well known that pyrochlore phases are easily formed during solid-state reaction of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN) ceramics.<sup>6)</sup> Once the pyrochlore phase is formed, it is not readily decomposed into the perovskite phase since the

pyrochlore phase is very stable. Therefore, the precursor method which alters the reaction sequence and leads to almost pyrochlore free material is often employed.<sup>7)</sup> The  $\text{BaO-TiO}_2$  binary system is the model case in which this kind of approach is routinely exercised since various intermediate phases of  $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ ,  $\text{BaTi}_5\text{O}_{11}$ ,  $\text{BaTi}_4\text{O}_9$ , and  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  co-exist along with  $\text{BaTiO}_3$ .<sup>3-5)</sup> Much interest has been taken in  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase among others due to its superior microwave dielectric properties. However, it is known that  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  single phase is hardly obtained by mixed oxide method with poor densification behavior.<sup>3-5)</sup> Therefore, the use of raw materials, i.e.,  $\text{BaTiO}_3$  and  $\text{TiO}_2$  are much more advantageous to obtain the single phase of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  rather than  $\text{BaCO}_3$  and  $\text{TiO}_2$ .<sup>3)</sup> Since a systematic phase development process and sintering behavior in  $\text{BaO-TiO}_2$  system have scarcely examined, it is necessary to compare the effect of different barium sources of  $\text{BaCO}_3$  and  $\text{BaTiO}_3$  for a detailed understanding of phase development.

In this study, to synthesize  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  ceramics by the general solid state reaction process, different barium sources of  $\text{BaCO}_3$  and  $\text{BaTiO}_3$  precursor were used as starting materials. The reaction sequence during conventional solid-state reaction process and the sintering behavior were examined. Microwave dielectric permittivity was also measured. Examination on  $\text{BaO-xSm}_2\text{O}_3\text{-4.5TiO}_2$  system, which is a good microwave dielectric material, was also conducted when different barium sources are used.

## 2. Experimental Procedures

Conventional solid-state reaction process was used for

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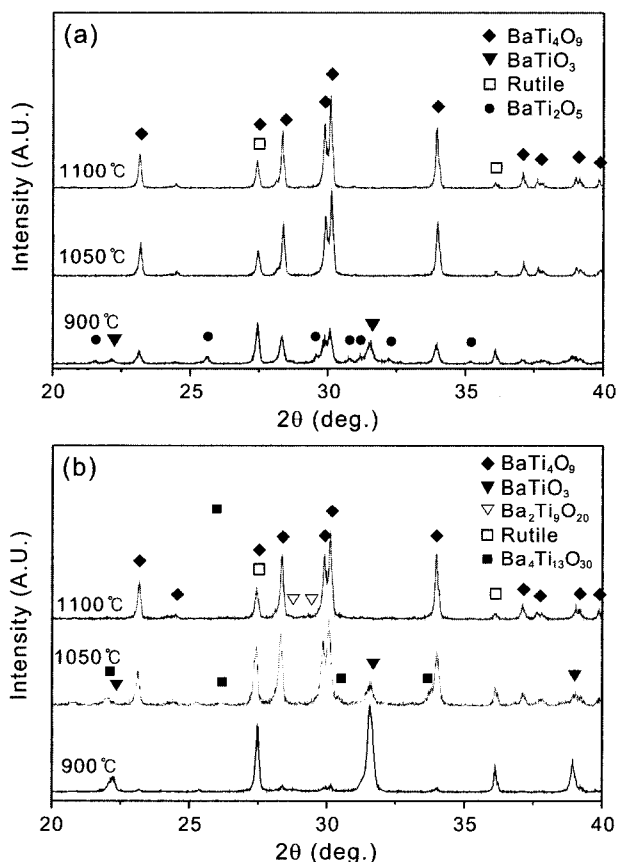
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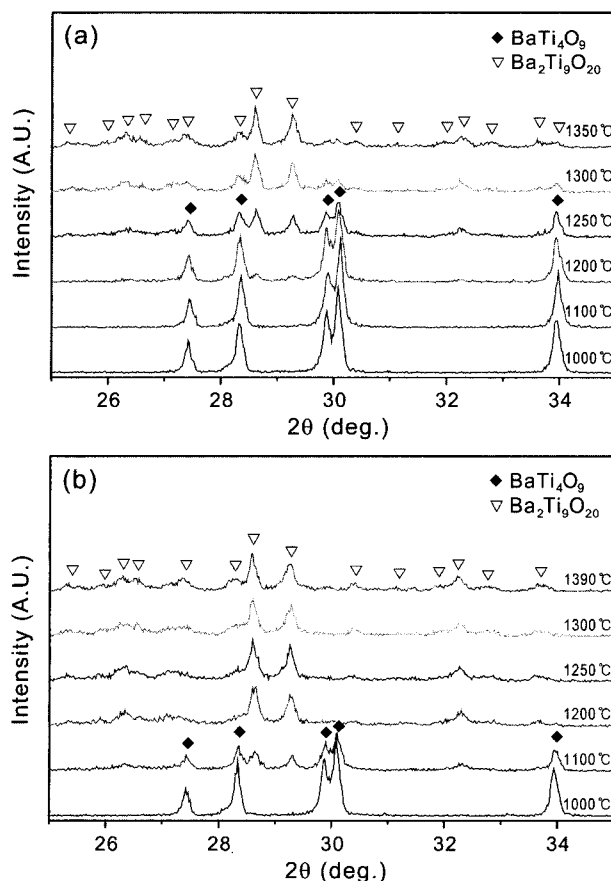
sample preparation. Two different synthesis methods were employed, i.e., mixed oxide method and precursor method. In the mixed oxide method,  $\text{BaCO}_3$  and  $\text{TiO}_2$  were used as raw materials, and in the precursor method,  $\text{BaTiO}_3$  and  $\text{TiO}_2$  were used. These different methods using  $\text{BaCO}_3$  and  $\text{BaTiO}_3$  are denoted as BCT and BTT, respectively.  $\text{BaO-xSm}_2\text{O}_3\text{-4.5TiO}_2$  system where  $x=0\sim 1.25$  was also prepared using different barium sources. After wet mixing using a ball-mill, the mixture was calcined in the temperature range of  $900\sim 1100^\circ\text{C}$  for 2 h. The granulated powders were then pressed into pellets under the pressure of  $1.5\text{ ton/cm}^2$ . The specimens were sintered in the temperature range of  $1200\sim 1390^\circ\text{C}$  for 2 h in air. The relative density of the sintered samples was measured using water immersion technique. The crystalline phases of calcined powders were determined by X-ray diffraction (XRD; Mac science, M03XHF, Yokohama, Japan). The microstructure of the sample surfaces was observed using a scanning electron microscope (SEM; JEOL, JML5400, Tokyo, Japan). The relative permittivity value of the samples in the microwave range was measured by the parallel plate method originally proposed by Hakki and Coleman<sup>8)</sup> utilizing  $\text{TE}_{01}$  resonant mode. The quality factor ( $Q\times f$ ) was measured by the open cavity resonator method<sup>9)</sup> using HP8720C network analyzer.

### 3. Results and Discussion

Fig. 1 shows XRD patterns of mixed powders calcined at different temperatures for 2 h. Fig. 1(a) is for the case of powders prepared by mixed oxide method (BCT) and (b) is of the precursor method (BTT). When BCT powder was calcined at  $900^\circ\text{C}$ ,  $\text{BaTi}_2\text{O}_5$ , rutile, and much more amount of  $\text{BaTi}_4\text{O}_9$  phases were coexisted. Over  $1050^\circ\text{C}$ ,  $\text{BaTi}_4\text{O}_9$  phase was appeared as a major phase and minor peaks from rutile were also observed. When BTT powder was calcined at  $900^\circ\text{C}$ ,  $\text{BaTiO}_3$ ,  $\text{TiO}_2$  and  $\text{BaTi}_4\text{O}_9$  phases were coexisted. Strong diffraction intensities from the raw materials of  $\text{BaTiO}_3$  and  $\text{TiO}_2$  were appeared while weak intensity from  $\text{BaTi}_4\text{O}_9$  was appeared signifying that solid state reaction is insignificant compared with BCT powder calcined at the same temperature. When the BTT powder was calcined at  $1050^\circ\text{C}$ , complex diffraction peaks from  $\text{BaTiO}_3$ ,  $\text{Ba}_4\text{Ti}_{13}\text{O}_{40}$ ,  $\text{TiO}_2$  and  $\text{BaTi}_4\text{O}_9$  phases were observed. In case of  $1100^\circ\text{C}$ , major peaks from  $\text{BaTi}_4\text{O}_9$  and minor peaks from  $\text{TiO}_2$  were observed. However, a trace of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase was appeared. From above results, it turned out that the initial stage of solid state reaction of BCT powder showed a superiority over the case of BTT powder when both powders are calcined at the same low temperature, i.e., in case of BTT, the raw powders of  $\text{BaTiO}_3$  and  $\text{TiO}_2$  were observed which



**Fig. 1.** X-ray diffraction patterns of (a) BCT and (b) BTT powders calcined at indicated temperature for 2 h.



**Fig. 2.** X-ray diffraction patterns of (a) BCT and (b) BTT specimens sintered at indicated temperature for 2 h.

signifies the solid state reaction was hardly proceeded. However,  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  was observed in BTT powder at  $1100^\circ\text{C}$  which was not observed in BCT powder.

Fig. 2 shows the X-ray diffraction profile of the samples sintered at each temperature for 2 h. When the BCT powder was sintered at  $1000^\circ\text{C}$  and  $1100^\circ\text{C}$ , only  $\text{BaTi}_4\text{O}_9$  phase was observed as shown in Fig. 2(a). The diffraction intensity of the  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase appeared weak when the BCT powder was sintered at  $1200^\circ\text{C}$  and the intensity was increased drastically at  $1250^\circ\text{C}$ . The diffraction intensity of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase tends to increase slowly in case of the temperature over  $1300^\circ\text{C}$ . However,  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase was not existed as a single phase at the final sintering temperature due to the remains of  $\text{BaTi}_4\text{O}_9$  phase. Fig. 2(b) is the case of BTT powder. Only the  $\text{BaTi}_4\text{O}_9$  phase was observed at  $1000^\circ\text{C}$  while the  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase was drastically increased from  $1100^\circ\text{C}$  and almost single phase of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  was observed at the temperature over  $1200^\circ\text{C}$ . When the phase development process was compared during sintering process, more  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase was developed in BTT powder than in BCT at lower temperatures, which means the degree of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  formation retarded in BCT power compared to the case of BTT powder.

Fig. 3 shows the degree of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  formation in the sintered samples with the variation of the integrated intensity of X-ray diffraction as a function of sintering temperature. The relative amount of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase was estimated by

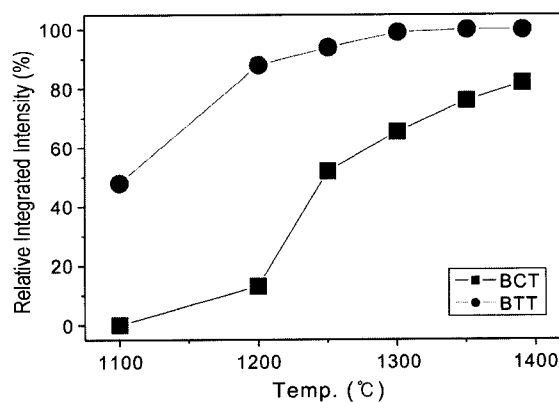


Fig. 3. The amount of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase evaluated from relative integrated intensity of (220) plane as a function of sintering temperature.

the integrated intensity of  $(2\bar{2}0)$  plane which reveals the biggest intensity of diffraction beam. In case of BCT, a little amount of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase was produced at  $1200^\circ\text{C}$  and the amount of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  increased sharply from  $1250^\circ\text{C}$ , then the increasing rate was reduced until it meets 82% of amount at  $1390^\circ\text{C}$ . However, in case of BTT, the amount of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase was already reached to 48% at  $1100^\circ\text{C}$  and became a single phase of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  from  $1300^\circ\text{C}$ .

When the BCT and BTT methods are applied to  $\text{BaO-xSm}_2\text{O}_3\text{-4.5TiO}_2$  system (where  $x=0\sim 1.25$ ), even the detail

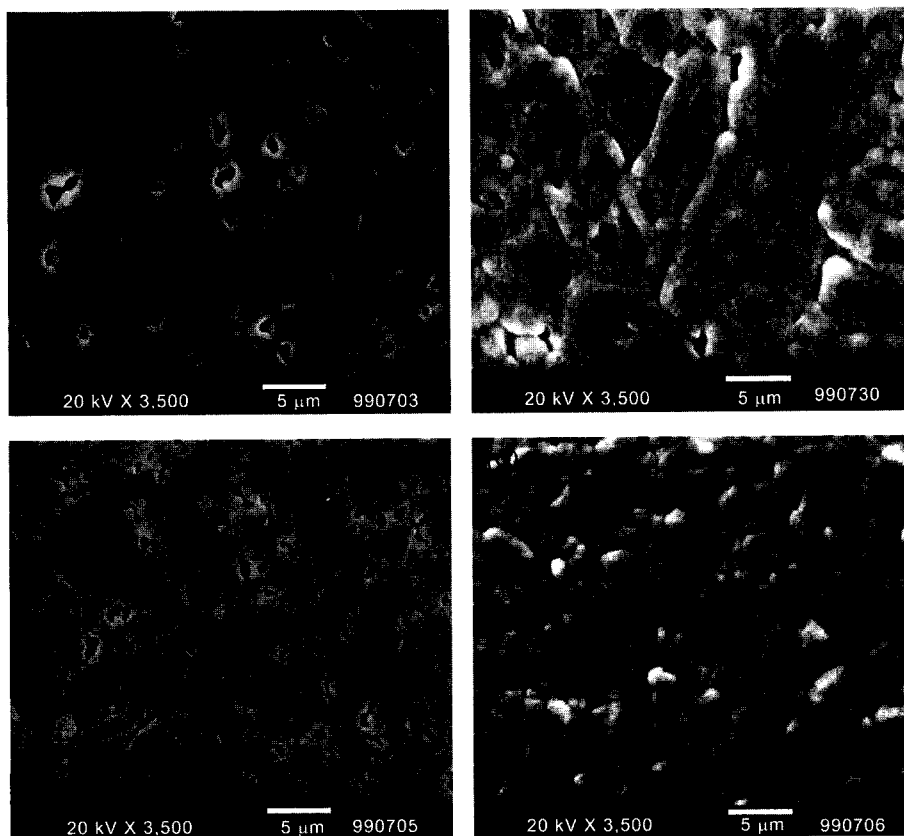


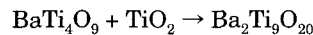
Fig. 4. SEM photographs of BCT (a, b) and BTT (c, d) specimens sintered at  $1250^\circ\text{C}$  (a, c) and  $1390^\circ\text{C}$  (b, d) for 2 h.

results are not presented in this paper, similar phase development behavior and dielectric characteristics were observed. When the samples were sintered at 1350°C for 4 h, different phases are developed by the two different processing methods of BCT and BTT. In the case where  $x=1$ ,  $\text{BaO-Sm}_2\text{O}_3\text{-4TiO}_2$  phase with the molar ratio of 1 : 1 : 4 (hereafter called 1 : 1 : 4 phase) appeared as a major phase in both the BCT and the BTT methods. However, different kinds of secondary phases were observed, i.e.,  $\text{BaTi}_4\text{O}_9$  and  $\text{TiO}_2$  in the BCT method and  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  in the BTT method.

The microstructure of sintered samples are represented in Fig. 4. Fig. 4(a) and (b), as BCT samples, are the cases of samples sintered at 1250°C and 1390°C for 2 h, respectively. The sample sintered at 1250°C shows small pores at grain boundaries and the porosity was  $6.42\pm 0.51\%$ . Large and small grains in the sample coexisted and the mean grain size was  $2.36\pm 0.62\ \mu\text{m}$ . The sample sintered at 1390°C has the porosity of  $3.22\pm 0.54\%$  and the mean grain size was  $8.76\pm 0.58\ \mu\text{m}$ . The size of pore and grain in case of the sample sintered at 1390°C was grown and the porosity decreased compared to the sample sintered at 1250°C. The pores were observed in the grain interior as well as in the grain boundaries. It is assumed that the trapped pores in the grain interior are due to the rapid grain growth. Different types of grains were seen in the microstructures of BCT samples sintered at different temperatures. We observe the surface of  $\text{BaTi}_4\text{O}_9$  phase was smooth, while the surface of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase was rough. The difference of microstructures of two phases was also reported from the analysis of EPMA image(WDX), EDX and X-ray diffraction by Nishigaki *et al.*<sup>10)</sup> In this study, EDS was also tried for the compositional

analysis but the satisfactory result was not obtained because the EDS energies from Ti and Ba are similar. Fig. 4 (c) and (d), as BTT samples, are the cases of samples also sintered at 1250°C and 1390°C for 2 h, respectively. The density of the sample (c) was low with porosity of  $18.62\pm 0.78\%$ . The density of sample (d) was high with low porosity of  $1.52\pm 0.27\%$  which leads to the conclusion that the full densification was almost achieved. Homogeneous and fine grains with the mean grain size of  $1.83\pm 0.25\ \mu\text{m}$  were observed compared to the case of BCT samples.

Fig. 5 shows the grain size distribution of BCT and BTT samples sintered at different temperatures. When BCT was sintered at 1390°C, the mean grain size was four times bigger and the grain size distribution was broader than BTT case. In BCT sample, following reaction is expected to be proceeded during sintering.



This phase transformation in BCT sample is thought to be the reason of the rapid grain growth, and phase transformation accompanied grain growth has been reported.<sup>11,12)</sup> Concerning the molar volume of the  $\text{BaTi}_4\text{O}_9$ ,  $\text{TiO}_2$  and  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase, volume reduction of BCT sample is also expected after the reaction. This results in the pore generation which leads to the lower densification.

Fig. 6 shows the microwave dielectric characteristics of the samples sintered at 1390°C for 2 h. The relative permittivity value ( $\epsilon_r$ ) of BTT sample was almost 40 which is higher than that of BCT sample. The quality factor of BTT sample was outstandingly high. It is known that the dielectric permittivity is affected by the composition and density

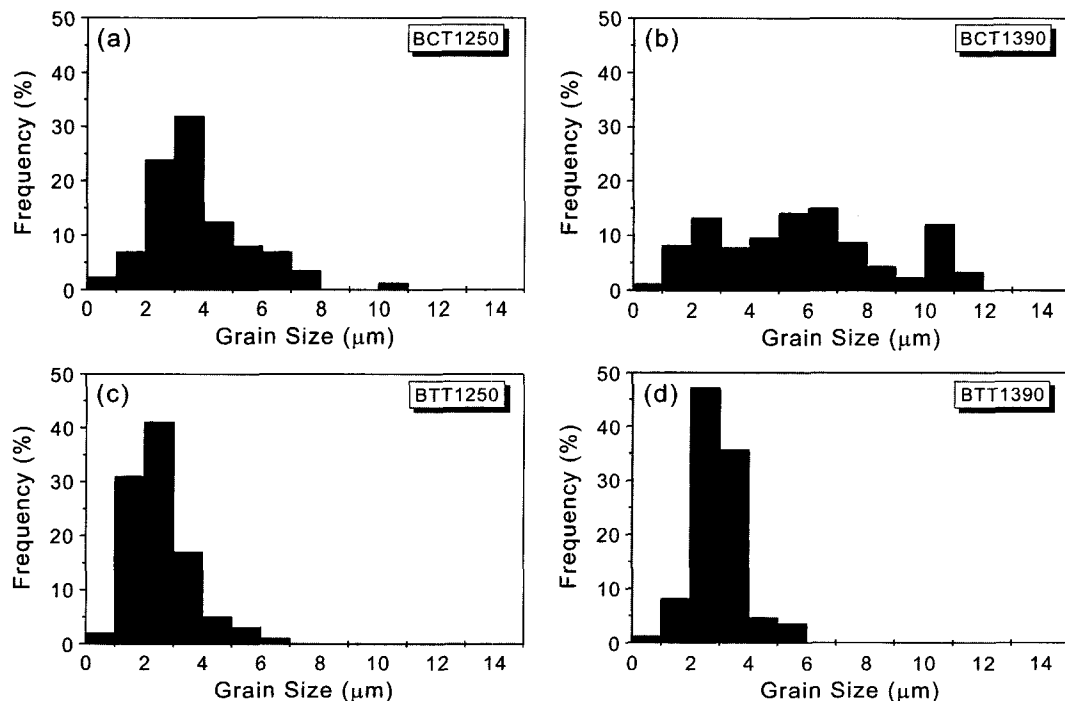


Fig. 5. Grain size distribution of BCT (a, b) and BTT (c, d) specimens sintered at 1250°C (a, c) and 1390°C (b, d) for 2 h.

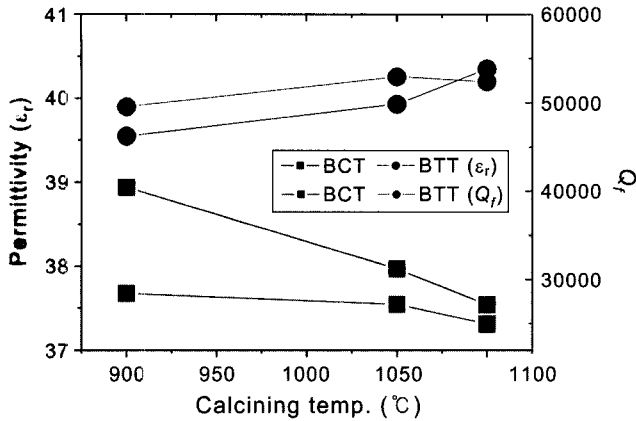


Fig. 6. Dielectric properties of BCT and BTT specimens as a function of calcining temperature.

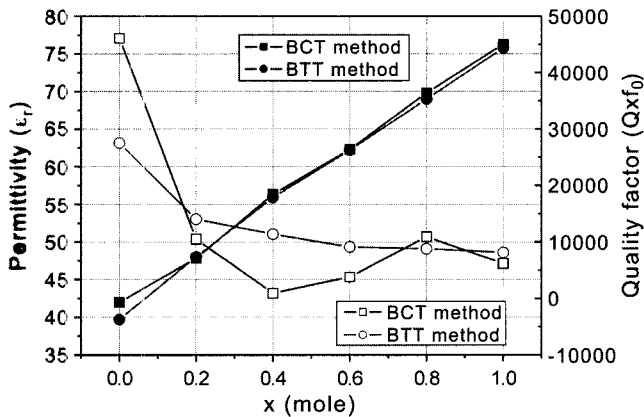


Fig. 7. Dielectric properties of BCT and BTT specimens of  $\text{BaO-xSm}_2\text{O}_3-4.5\text{TiO}_2$  system as a function of  $x$ .

while the quality factor is affected by the defects, pores, and second phases etc. Since BTT sample is composed of a single phase with higher density and more homogeneous microstructure than BCT, the dielectric constant and the quality factor of BTT were superior to those of BCT.

The dielectric characteristics of  $\text{BaO-xSm}_2\text{O}_3-4.5\text{TiO}_2$  system are shown in Fig. 7. The  $\epsilon_r$  increased linearly from 40 to 77 as the  $x$  value increased from 0.0 to 1.0, regardless of the different processing methods. It is because the  $\epsilon_r$  values of the secondary phases, i.e.  $\text{BaTi}_4\text{O}_9$  and  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ , are 40 and 38, respectively, which are very similar to the matrix 1 : 1 : 4 phase and each other.<sup>13-15</sup> However, the quality factor of the samples was affected by the different processing methods. As the  $x$  changed from 0 to 0.2, the quality factor decreased greatly. Because the 1 : 1 : 4 phase has low quality factor and the  $\text{BaTi}_4\text{O}_9$  and  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phases have high quality factors, the variation of volume fraction of the phases with respect to  $x$  seems to be the reason of decreased quality factor. In the samples prepared by the BCT method, the quality factor greatly decreased in the range of  $x=0.2-0.4$  since two different kinds of secondary phases of  $\text{TiO}_2$  and 1 : 1 : 4 coexisted. On the other hand, as  $\text{BaTi}_4\text{O}_9$  phase has higher quality factor than 1 : 1 : 4 phase, the decrease in

the volume fraction of  $\text{BaTi}_4\text{O}_9$  phase could have played a role in the decrease of the quality factor. However, the BTT method-derived samples that were close to the stoichiometric composition revealed stabilization in quality factors.

#### 4. Conclusions

In synthesizing  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  ceramics by different solid state reaction methods of BCT and BTT,  $\text{BaTi}_4\text{O}_9$  phase was easily formed when BCT method was used, while its formation was suppressed and a single phase of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  was obtained when BTT method was used. Because the  $\text{BaTiO}_3$  precursor provides short diffusion paths of ions, the system revealed less secondary phases during solid state reaction. Therefore,  $\text{BaTiO}_3$  and  $\text{TiO}_2$  system was considered to be closer to the equilibrium state than  $\text{BaCO}_3$  and  $\text{TiO}_2$  system. In case of BTT samples, homogeneous and fine grains were observed compared to the case of BCT samples. The grain size distribution of BCT was broader than BTT case. The relative permittivity value ( $\epsilon_r$ ) and the quality factor of BTT sample were superior to those prepared by the BCT method. In case of  $\text{BaO-xSm}_2\text{O}_3-4.5\text{TiO}_2$  system, as observed in  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  ceramics, the system prepared by BTT method was considered to be closer to the equilibrium state. It is therefore concluded that the BTT method using  $\text{BaTiO}_3$  precursor is highly advantageous in  $\text{BaO-TiO}_2$  containing microwave dielectrics.

#### REFERENCES

1. K. Wakino, "Recent Development of Dielectric Resonator Materials and Filters in Japan," *Ferroelectrics*, **91** 69-86 (1989).
2. G. H. Jonker and W. Kwestroo, "The Ternary Systems  $\text{BaO-TiO}_2\text{-SnO}_2$  and  $\text{BaO-TiO}_2\text{-ZrO}_2$ ," *J. Am. Ceram. Soc.*, **41** [10] 390-94 (1958).
3. H. M. O'Bryan and J. Thomson, " $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  Phase Equilibria," *J. Am. Ceram. Soc.*, **66** [1] 66-8 (1983).
4. J. M. Wu and H. W. Wang, "Factors Affecting the Formation of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ," *J. Am. Ceram. Soc.*, **71** [10] 869-75 (1988).
5. J. Yu, H. Zhao, Z. Wang, and F. Xia, "Effect of  $\text{Al}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_3$  on the Formation Mechanism of Sn-doped  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ," *J. Am. Ceram. Soc.*, **77** [4] 1052-56 (1994).
6. S. L. Swartz, T. R. Shrout, W. A. Schulze, and L. E. Cross, "Dielectric Properties of Lead-magnesium Niobate Ceramics," *J. Am. Ceram. Soc.*, **67** [5] 311-14 (1984).
7. S. L. Swartz and T. R. Shrout, "Fabrication of Perovskite Lead Magnesium Niobate," *Mat. Res. Bull.*, **17** [10] 1245-50 (1982).
8. B. W. Hakki and P. D. Coleman, "A Dielectric Resonator Method of Measuring Inductive Capacities in the Millimeter Range," *IRE Trans. on Microwave Theory Tech.*, MTT-8, 402-10 (1960).
9. Y. Kobayashi and M. Katoh, "Microwave Dielectric Properties of Low-loss Materials by the Dielectric Rod Resonator Method," *IEEE Trans. on Microwave Theory Tech.*,

- MTT-33, 7 (1985).
10. S. Nishigaki, S. Yano, H. Kato, T. Hirai, and T. Nonomura, "BaO-TiO<sub>2</sub>-WO<sub>3</sub> Microwave Ceramics and Crystalline BaWO<sub>4</sub>," *J. Am. Ceram. Soc.*, **71** [1] C-11-C17 (1988).
  11. B. C. Kim, S. M. Kim, J. H. Lee, and J. J. Kim, "Effect of Phase Transformation on the Densification of Coprecipitated Nanocrystalline ITO Powders," *J. Am. Ceram. Soc.*, **85** [8] 2083-88 (2002).
  12. J. H. Lee and Y.-M. Chiang, "Pyrochlore-perovskite Phase Transformation in Highly Homogeneous (Pb,La)(Zr,Sn,Ti) O<sub>3</sub> Powders," *J. Mat. Chem.*, **9** [12] 3107-11 (1999).
  13. H. M. O'Bryan Jr., J. Thomson, and J. K. Plourde, "A New BaO-TiO<sub>2</sub> Compound with Temperature-stable High Permittivity and Low Microwave Loss," *J. Am. Ceram. Soc.*, **57** [10] 450-53 (1974).
  14. S. G. Mhaisalkar, D. W. Readey, and S. A. Akbar, "Microwave Dielectric Properties of Doped BaTi<sub>4</sub>O<sub>9</sub>," *J. Am. Ceram. Soc.*, **74** [8] 1894-98 (1991).
  15. J. K. Plourde, D. F. Linn, H. M. O'Bryan, Jr., and J. Thomson, Jr., "Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> as a Microwave Dielectric Resonator," *J. Am. Ceram. Soc.*, **58** [9-10] 418-20 (1975).