Sintering and Microwave Dielectric Properties of Ba₇Ti₉O₂₀
Ceramics Prepared by Precursor Method

Je-Hong Sung, Joon-Hyung Lee, Jeong-Joo Kim,*, Hee Young Lee,* and Sang-Hee Cho

Department of Inorganic Materials Engineering, Kyungpook National University, Daegu 702-701, Korea
*School of Metallurgical and Materials Engineering, Yeungnam University, Kyongsan 712-749, Korea
(Received March 19, 2003; Accepted March 29, 2003)

ABSTRACTS

The phase development process of Ba₇Ti₉O₂₀ ceramics is not clearly known and frequently accompanies second phases which deteriorate dielectric properties. In synthesizing Ba₇Ti₉O₂₀ ceramics, in order to trace the reaction sequence during conventional solid-state reaction in BaO-TiO₂ system, different barium sources of BaCO₃ and BaTiO₃ 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 BaO-TiO₂ system are very difficult to be synthesized. Because the BaTiO₃ precursor provides short diffusion paths of ions, the system revealed less secondary phases during solid state reaction. In synthesizing BaO-xSm₂O₃-4.5TiO₂ 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: Ba₇Ti₉O₂₀, 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 Ba(Mg,Ta)O₃, Ba(Zn,Ta)O₃, BaTiO₃, and Ba₇Ti₉O₂₀ systems have been developed and applied successfully to many commercial units. The research and development of BaO-TiO₂ system with high dielectric performance have been followed. On the other hand, great attention has been paid on the phase development of BaO-TiO₂ system as its application to microwave dielectrics is widely made.

In this system, it was, however, found that the secondary phase 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 Pb(Mg₁₂Nb₂O₂₀)₃ (PMN) ceramics. 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. The BaO-TiO₂ binary system is the model case in which this kind of approach is routinely exercised since various intermediate phases of Ba₇Ti₉O₂₀, BaTiO₃, BaTiO₃, and Ba₇Ti₉O₂₀ co-exist along with BaTiO₃. Much interest has been taken in Ba₇Ti₉O₂₀ phase among others due to its superior microwave dielectric properties. However, it is known that Ba₇Ti₉O₂₀ single phase is hardly obtained by mixed oxide method with poor densification behavior. Therefore, the use of raw materials, i.e., BaTiO₃ and TiO₂ are much more advantageous to obtain the single phase of Ba₇Ti₉O₂₀ rather than BaCO₃ and TiO₂. Since a systematic phase development process and sintering behavior in BaO-TiO₂ system have scarcely examined, it is necessary to compare the effect of different barium sources of BaCO₃ and BaTiO₃ for a detailed understanding of phase development.

In this study, to synthesize Ba₇Ti₉O₂₀ ceramics by the general solid state reaction process, different barium sources of BaCO₃ and BaTiO₃ 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 BaO-xSm₂O₃-4.5TiO₂ 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

1Corresponding author: Jeong-Joo Kim
E-mail: jjkim@knu.ac.kr
Tel: +82-53-950-5635 Fax: +82-53-950-5645

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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, BaCO₃ and TiO₂ were used as raw materials, and in the precursor method, BaTiO₃ and Ba₃Ti₂O₇ were used. These different methods using BaCO₃ and BaTiO₃ are denoted as BCT and BTT, respectively. BaO-xSm₂O₃-4.5TiO₂ system where x=0-1.25 was also prepared using different barium sources. After wet mixing using a ball-mill, the mixture was calcined in the temperature range of 900–1100°C for 2 h. The granulated powders were then pressed into pellets under the pressure of 1.5 ton/cm². The specimens were sintered in the temperature range of 1200–1300°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, M03XH, 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 Coleman⁹ utilizing TE₀₁ resonant mode. The quality factor (Q×f) was measured by the open cavity resonator method⁹ 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°C, BaTiO₃, rutile, and much more amount of BaTi₃O₉ phases were coexisted. Over 1050°C, BaTiO₃ phase was appeared as a major phase and minor peaks from rutile were also observed. When BTT powder was calcined at 900°C, BaTiO₃, TiO₂ and Ba₃Ti₂O₇ phases were coexisted. Strong diffraction intensities from the raw materials of BaTiO₃ and TiO₂ were appeared while weak intensity from Ba₃Ti₂O₇ 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°C, complex diffraction peaks from BaTiO₃, Ba₃Ti₂O₇, TiO₂ and Ba₃Ti₂O₇ phases were observed. In case of 1100°C, major peaks from BaTiO₃ and minor peaks from TiO₂ were observed. However, a trace of Ba₃Ti₂O₇ 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 BaTiO₃ and TiO₂ were observed which

![Fig. 1. X-ray diffraction patterns of (a) BCT and (b) BTT powders calcined at indicated temperature for 2 h.](image1)

![Fig. 2. X-ray diffraction patterns of (a) BCT and (b) BTT specimens sintered at indicated temperature for 2 h.](image2)
signifies the solid state reaction was hardly proceeded. However, Ba$_2$Ti$_2$O$_{20}$ was observed in BTT powder at 1100°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°C and 1100°C, only BaTi$_4$O$_9$ phase was observed as shown in Fig. 2(a). The diffraction intensity of the Ba$_2$Ti$_2$O$_{20}$ phase appeared weak when the BCT powder was sintered at 1200°C and the intensity was increased drastically at 1250°C. The diffraction intensity of Ba$_2$Ti$_2$O$_{20}$ phase tends to increase slowly in case of the temperature over 1300°C. However, Ba$_2$Ti$_2$O$_{20}$ phase was not existed as a single phase at the final sintering temperature due to the remains of BaTi$_4$O$_9$ phase. Fig. 2(b) is the case of BTT powder. Only the BaTi$_4$O$_9$ phase was observed at 1000°C while the Ba$_2$Ti$_2$O$_{20}$ phase was drastically increased from 1100°C and almost single phase of Ba$_2$Ti$_2$O$_{20}$ was observed at the temperature over 1200°C. When the phase development process was compared during sintering process, more Ba$_2$Ti$_2$O$_{20}$ phase was developed in BTT powder than in BCT at lower temperatures, which means the degree of Ba$_2$Ti$_2$O$_{20}$ formation retarded in BCT powder compared to the case of BTT powder.

Fig. 3 shows the degree of Ba$_2$Ti$_2$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 Ba$_2$Ti$_2$O$_{20}$ phase was estimated by the integrated intensity of (220) plane which reveals the biggest intensity of diffraction beam. In case of BCT, a little amount of Ba$_2$Ti$_2$O$_{20}$ phase was produced at 1200°C and the amount of Ba$_2$Ti$_2$O$_{20}$ increased sharply from 1250°C, then the increasing rate was reduced until it meets 82% of amount at 1390°C. However, in case of BTT, the amount of Ba$_2$Ti$_2$O$_{20}$ phase was already reached to 48% at 1100°C and became a single phase of Ba$_2$Ti$_2$O$_{20}$ from 1300°C.

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

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

![Fig. 4. SEM photographs of BCT (a, b) and BTT (c, d) specimens sintered at 1250°C (a, c) and 1390°C (b, d) for 2 h.](image)
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 $x=1$, BaO-Sm$_2$O$_3$-TiO$_2$ 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., BaTi$_4$O$_9$ and TiO$_2$ in the BCT method and Ba$_2$Ti$_3$O$_{10}$ 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±0.51%. Large and small grains in the sample coexisted and the mean grain size was 2.36±0.62 μm. The sample sintered at 1390°C has the porosity of 3.22±0.54% and the mean grain size was 8.76±0.58 μm. 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 BaTi$_4$O$_9$ phase was smooth, while the surface of Ba$_2$Ti$_3$O$_{10}$ 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. 108 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±0.78%. The density of sample (d) was high with low porosity of 1.52±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±0.25 μm 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.

$$\text{BaTi}_4\text{O}_9 + \text{TiO}_2 \rightarrow \text{Ba}_2\text{Ti}_3\text{O}_{10}$$

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. 11,12 Concerning the molar volume of the BaTi$_4$O$_9$, TiO$_2$ and Ba$_2$Ti$_3$O$_{10}$ 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 ($\varepsilon_r$) 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.](image-url)
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 BaO-xSm2O3-4.5TiO2 system are shown in Fig. 7. The \( \varepsilon_r \) 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 \( \varepsilon_r \) values of the secondary phases, i.e. BaTi3O9 and Ba7Ti4O20, are 40 and 36, respectively, which are very similar to the matrix 1:1:4 phase and each other.13,14 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 BaTi3O9 and Ba7Ti4O20 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 \( x=0.2 \) to 0.4 since two different kinds of secondary phases of TiO2 and 1:1:4 coexisted. On the other hand, as BaTi3O9 phase has higher quality factor than 1:1:4 phase, the decrease in the volume fraction of BaTi3O9 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 Ba\(_2\)Ti\(_3\)O\(_9\) ceramics by different solid state reaction methods of BCT and BTT, BaTi3O9 phase was easily formed when BCT method was used, while its formation was suppressed and a single phase of Ba\(_2\)Ti\(_3\)O\(_9\) was obtained when BTT method was used. Because the BaTiO\(_3\) precursor provides short diffusion paths of ions, the system revealed less secondary phases during solid state reaction. Therefore, BaTiO\(_3\) and TiO\(_2\) system was considered to be closer to the equilibrium state than BaCO\(_3\) and 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 (\( \varepsilon_r \)) and the quality factor of BTT sample were superior to those prepared by the BCT method. In case of BaO-xSm2O3-4.5TiO2 system, as observed in Ba\(_2\)Ti\(_3\)O\(_9\) 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 BaTiO\(_3\) precursor is highly advantageous in BaO-TiO\(_2\) containing microwave dielectrics.

REFERENCES


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 BaO-xSm2O3-4.5TiO2 system as a function of x.


