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# Dielectric characteristics of composite ceramics in the $Ba(Mg_{1/3}Ta_{2/3})O_3$–$BaO \cdot Nd_2O_3 \cdot 5TiO_2$ system

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Dielectric characteristics of composite ceramics in the system $Ba(Mg_{1/3}Ta_{2/3})O_3$–$BaO \cdot Nd_2O_3 \cdot 5TiO_2$ were investigated to search for a new candidate system for microwave dielectric ceramics with modifiable dielectric constant, low dielectric loss and small temperature dependence. The dielectric constant could be adjusted in the range 25–81 by controlling the concentration of $BaO \cdot Nd_2O_3 \cdot 5TiO_2$, while the dielectric loss remained of the order of $10^{-4}$ for some compositions. Moreover, the dielectric properties in the present system could be significantly improved by post-densification thermal treatment.

## 1. Introduction

Recently, a number of microwave dielectric ceramics have been investigated because of their important applications in the microwave communication fields as dielectric ceramic resonators [1–9]. In such materials, high dielectric constant, low dielectric loss and small temperature coefficient of resonant frequency are generally required, and it has been the most important subject for many years to achieve higher dielectric constant and ultra-low dielectric loss. $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) and $BaO \cdot Nd_2O_3 \cdot 5TiO_2$ (BNT5) are well known as two typical microwave dielectric ceramics because of their ultra-low loss and high dielectric constant, respectively [5–9]. However, both these ceramics have their own problems (low dielectric constant for the former, and the relatively high dielectric loss for the latter), and these shortages greatly limit the scope of application of such materials. BMT is mainly used in situations where low loss is primarily required but minimization is not so important, and BNT5 is suitable for use at frequencies lower than 2 GHz.

In previous work [10], the challenging issue was addressed of trying to obtain a modifiable high dielectric constant combined with low dielectric loss through the production route for composite ceramics. The possibility of creating dielectric composite ceramics in the system $Ba(Mg_{1/3}Ta_{2/3})O_3$–$BaO \cdot Nd_2O_3 \cdot 5TiO_2$ (BMT/BNT5) was investigated, together with the densification characteristics of such composite ceramics. Dense BMT/BNT5 composite ceramics with homogeneous fine microstructures were successfully sintered from their end-member powders.

In this work, the dielectric characteristics of BMT/BNT5 composite ceramics were investigated together with the effects of post-densification thermal treatment on such properties, and the possibility of microwave applications of such materials has been discussed.

## 2. Experimental procedure

The compositions of 95BMT/5BNT5, 75BMT/25BNT5, 50BMT/50BNT5, 25BMT/75BNT5 and 5BMT/95BNT5 were investigated, and the dielectric composite ceramics were created by a solid-state reaction process. First, BMT and BNT5 powders were synthesized by the conventional solid-state reaction methods. Both powders were then pressed at 98 MPa into cylindrical compacts with dimensions of 12 mm diameter and 5–8 mm height, after mixing by ball-milling in ethanol for 24 h. Finally, the compacts were sintered at 1280–1450 °C (according to the compositions) in air for 3 h to create dense BMT/BNT5 composite ceramics.

The bulk density was evaluated by Archimedes' method for the sintered BMT/BNT5 composite ceramics. Scanning electron microscopy (SEM) observation and X-ray diffraction (XRD) analysis using $CuK_\alpha$ radiation were carried out for microstructural characterization, and the dielectric properties were determined using an LCR meter at 1 MHz. The microwave dielectric properties were evaluated by Hakki–Coleman's resonator method [11, 12] at the frequency of about 4 GHz.

## 3. Results and discussion

As shown in Fig. 1, the densification of BMT/BNT5 composite ceramics can be performed at the temperatures of 1300–1400 °C according to the composition, in air and for an identical holding time of 3 h. The lower densification temperature is needed for the composite ceramics with higher BNT5 concentrations, and

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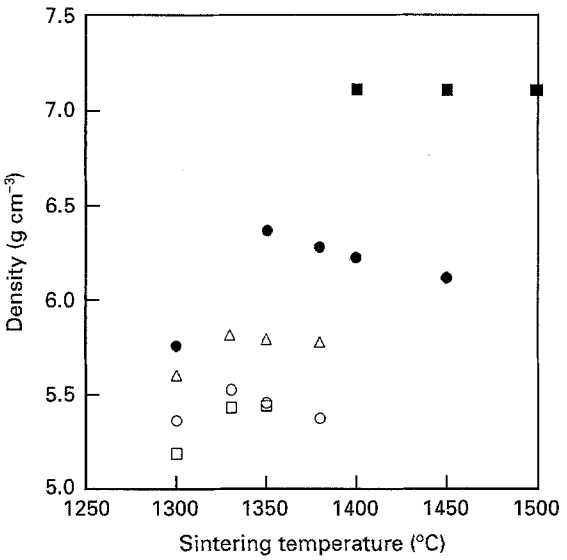


*Figure 1* Bulk density of BMT/BNT5 composite ceramics versus sintering temperature, for identical holding times of 3 h. (■) 95BMT/5BNT5, (●) 75BMT/25BNT5, (△) 50BMT/50BNT5, (○) 25BMT/75BNT5, (□) 5BMT/95BNT5.

there is a minimum densification temperature for 25BMT/75BNT5 composition. Each composition has its own suitable sintering temperature range, and too high a sintering temperature can lead to density decrease, which is considered to be due to the inhomogeneous microstructure evolution. This is also the situation for prolonged sintering.

In the present system, BMT is a stoichiometric compound with complex perovskite structure and equiaxial grain morphology. On the other hand, BNT5 is a solid solution phase, which tends to indicate columnar grain morphology [7]. Therefore, some information on the phase constituents of BMT/BNT5 composite ceramics can be obtained through observing the grain morphology. Fig. 2 shows the microstructures of BMT/BNT5 composite ceramics with various compositions. For 95BMT/5BNT5 and 75BMT/25BNT5 composite ceramics, clear two-phase structures are observed. The phase with columnar structures seems to be BNT5 or some similar phase, and the phase with equiaxial structures might be BMT. No clear information on phase constitution can be found from the scanning electron micrographs of 50BMT/50BNT5 and 25BMT/75BNT5 composite ceramics. It must be mentioned that microstructures may vary significantly with the processing conditions, and further examination is required to elucidate the details.

In order to evaluate the correct phase constitution of BMT/BNT5 composite ceramics, XRD analysis was performed. The results given in Table I conclude that 95BMT/5BNT5 and 75BMT/25BNT5 composite ceramics show two-phase structures, BMT and a new phase which can be assigned to $Ba_5NdTi_3Ta_7O_{30}$ (BNTT) based on the data of JCPDS Card 39-1445 for $Ba_5LaTi_3Nb_7O_3$. Other compositions generally indicate the phase constituents of BNT5 with an unidentified new phase. Moreover, the phase constitution of BMT/BNT5 composite ceramics appears to vary with sintering temperature and post-densification thermal treatment; the higher sintering temperature, prolonged sintering or post-densification thermal treatment tend to promote the evolution of new phases or occasionally to form some alternative new phases, and this is attributed to the possible reactions between the end-members which are promoted under such conditions.

For composite dielectric materials, several composite rules of the dielectric constant have been proposed [13]. In the present system, as shown in Fig. 3, the dielectric constant varies from 25–81, but never obeys any composite rule. With increasing concentration of BNT5, the dielectric constant first increases, then decreases slowly, and finally increases sharply when the concentration of BNT5 > 75 mol %. This suggests that some chemical reactions between the end-members may occur to generate some new phase during the sintering process. Meanwhile, the formation of possible solid solutions and crystal defects may also affect the dielectric properties. As shown in Fig. 3, the dielectric loss of BMT/BNT5 composite ceramics is greater than that of BMT. Even so, it is possible to obtain a modifiable dielectric constant combined with quite low dielectric loss of the order of $10^{-4}$ in some composition ranges of the BMT/BNT5 system, especially the compositions near to the end-members.

Because the as-sintered phase structures of BMT/BNT5 composite ceramics are in a thermodynamically metstable state, and the post-densification thermal treatment can cause phase structure modification; the dielectric properties may, consequently, be controlled by such thermal treatment. As shown in Fig. 4, the thermal treatment causes an increase of dielectric loss but almost no change in the dielectric constant for 95BMT/5BNT5 composite ceramics. However, the thermal treatment significantly enhances the dielectric constant and lowers the dielectric loss in 75BMT/25BNT5 ceramics, as indicated in Fig. 5, where the dielectric constant can reach 65 after the thermal treatment. Fig. 6 shows a similar situation for 50BMT/50BNT5 composite ceramics, with increasing dielectric constant and lowering dielectric loss through the thermal treatment. For 75BMT/25BNT5 composite ceramics, as shown in Fig. 7, there is a more complex situation. Although the thermal treatment increases the dielectric constant remarkably, it also indicates a complex influence on the dielectric loss. As shown in Fig. 8, the thermal treatment indicates slight effects on the dielectric constant of 5BMT/95BNT5 composite ceramics, but improves the dielectric loss remarkably.

In order to discuss the possibility of microwave applications of BMT/BNT5 composite ceramics, the dielectric properties were evaluated at a frequency of about 4 GHz, and the results are shown in Table II. Although some optimization of processing is required to modify the microstructures and dielectric properties especially the $Q_f$ factor and $\tau_f$ (temperature coefficient of resonant frequency), it is believed that the present composite system is a potential microwave dielectric ceramic system because the high $Q_f$ factor (3100 GHz) was obtained, and further improvement of such properties is expected.

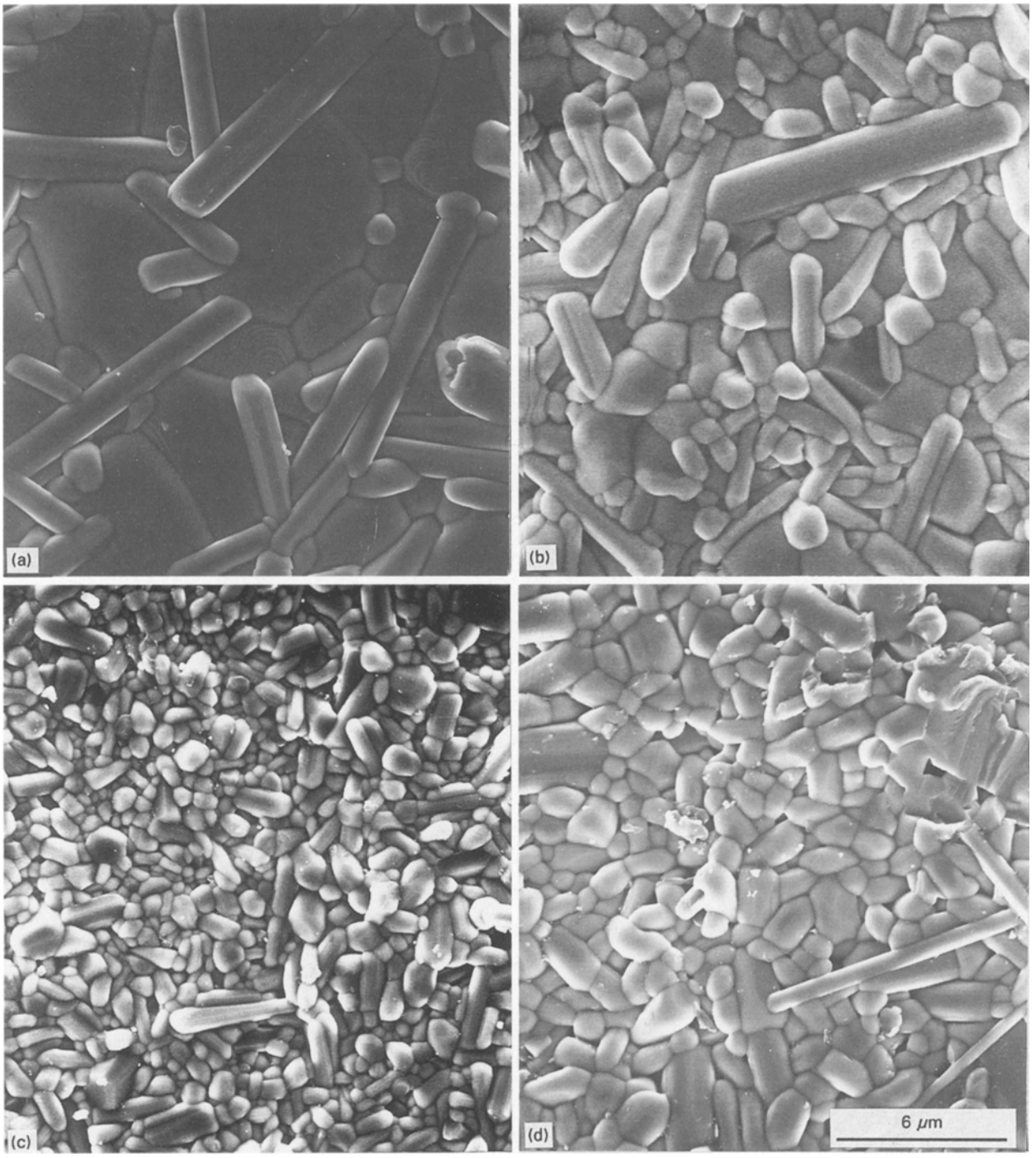


*Figure 2* Scanning electron micrographs of as-sintered surfaces of BMT/BNT5 composite ceramics: (a) 95BMT/5BNT5, 1500 °C, 3 h; (b) 75BMT/25BNT5, 1380 °C, 3 h; (c) 50BMT/50BNT5, 1330 °C, 3 h; (d) 25BMT/75BNT5, 1350 °C, 3 h.

TABLE I Phase analysis of BMT/BNT5 composite ceramics by XRD technique

| Composition | Sintering condition | Thermal treatment | Phase present[a] |
|---|---|---|---|
| 95BMT/5BNT5 | 1400 °C, 3 h, in air | | BMT + BNTT(s) |
| 75BMT/25BNT5 | 1400 °C, 3 h, in air | | BNTT + BMT |
| 50BMT/50BNT5 | 1350 °C, 3 h, in air | | BNT5 + ? |
| 25BMT/75BNT5 | 1350 °C, 3 h, in air | | BNT5 + ? |
| 5BMT/95BNT5 | 1330 °C, 3 h, in air | | BNT5 + ? |
| 95BMT/5BNT5 | 1400 °C, 3 h, in air | 1100 °C, 1 h, in air | BMT + BNTT(s) + ?(s) |
| 75BMT/25BNT5 | 1400 °C, 3 h, in air | 1100 °C, 1 h, in air | BMT + BNTT(s) + ?(s) |
| 50BMT/50BNT5 | 1350 °C, 3 h, in air | 1100 °C, 1 h, in air | ? + BNT5 |
| 25BMT/75BNT5 | 1350 °C, 3 h, in air | 1100 °C, 1 h, in air | ? + BNT5 |
| 5BMT/95BNT5 | 1330 °C, 3 h, in air | 1100 °C, 1 h, in air | BNT5 + ? |

[a] BNTT, suggested to be $Ba_5NdTi_3Ta_7O_{30}$ with a structure similar to $Ba_5NdTi_3Ta_7O_{30}$ (JCPDS Card 39-1445); ?, unknown phase; s, small amount.

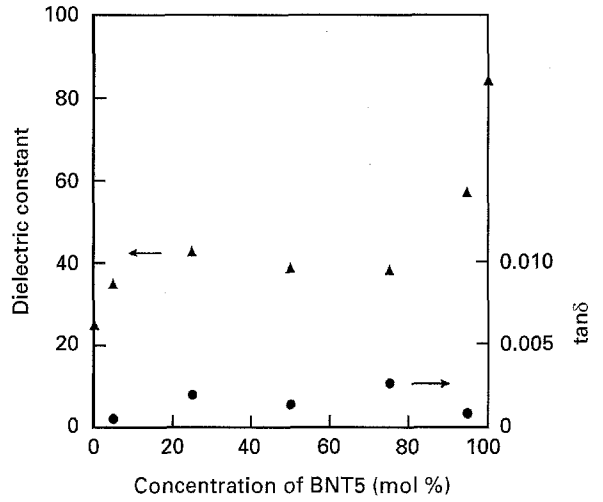


*Figure 3* Dielectric properties (at 1 MHz) of BMT/BNT5 composite ceramics versus composition. (▲) dielectric constant, (●) dielectric loss.

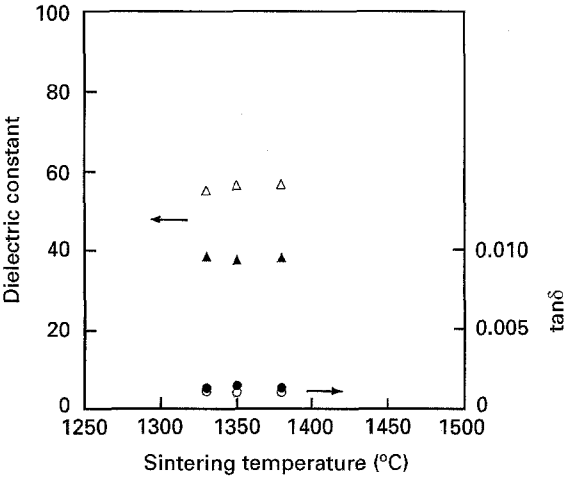


*Figure 6* Effects of thermal treatment on dielectric properties of 50BMT/50BNT5 ceramics sintered at various temperatures. (▲, ●) As-sintered, (△, ○) after thermal treatment.

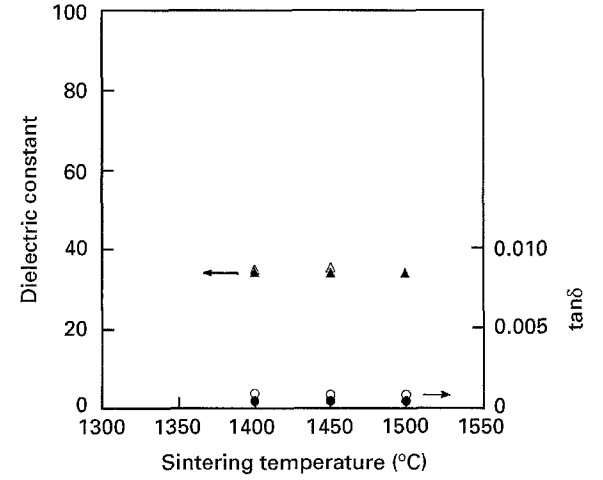


*Figure 4* Effects of thermal treatment on dielectric properties of 95BMT/5BNT5 ceramics sintered at various temperatures. (▲, ●) As-sintered, (△, ○) after thermal treatment.

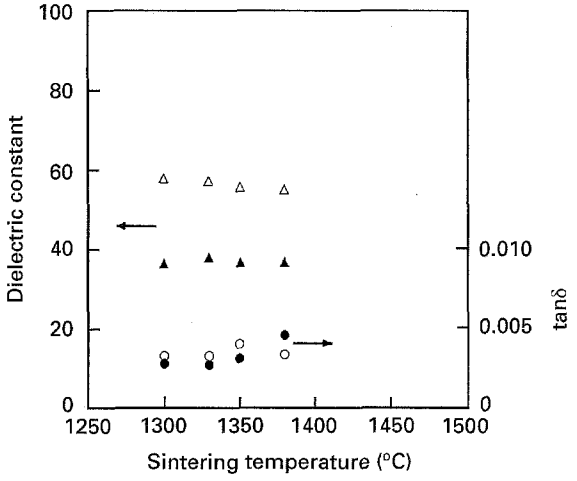


*Figure 7* Effects of thermal treatment on dielectric properties of 25BMT/75BNT5 ceramics sintered at various temperatures. (▲, ●) As-sintered, (△, ○) after thermal treatment.

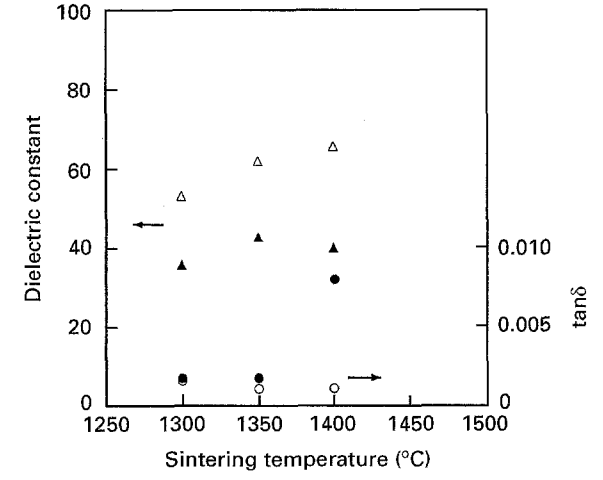


*Figure 5* Effects of thermal treatment of dielectric properties of 75BMT/25BNT5 ceramics sintered at various temperatures. (▲, ●) As-sintered, (△, ○) after thermal treatment.

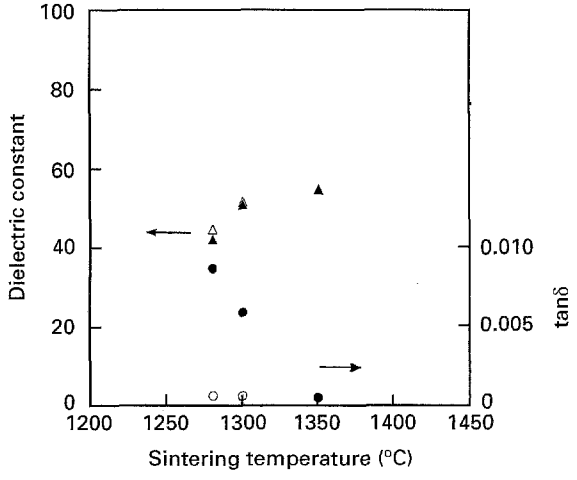


*Figure 8* Effects of thermal treatment on dielectric properties of 5BMT/95BNT5 ceramics sintered at various temperatures. (▲, ●) As-sintered, (△, ○) after thermal treatment.

TABLE II Microwave dielectric characteristics of BMT/BNT5 composite ceramics (at 4 GHz)

| Composition | Sintering condition | $\varepsilon$ | $Q_f$ (GHz) | $\tau_f$ (p.p.m.° $C^{-1}$) |
|---|---|---|---|---|
| 75BMT/25BNT5 | 1380 °C, 3 h, in air | 42.8 | 2400 | 460 |
| 50BMT/50BNT5 | 1330 °C, 3 h, in air | 39.7 | 2000 | 160 |
| 25BMT/75BNT5 | 1350 °C, 3 h, in air | 36.7 | 3100 | 97 |

## 4. Conclusion

BMT/BNT5 composite ceramics indicate the modifiable dielectric constant from 25–81 combined with a quite lower dielectric loss. The initial data on microwave dielectric properties suggest that the present composite system might be a potential candidate for microwave dielectric ceramics, though the important issue remains of how to improve the temperature coefficient of resonant frequency and the dielectric loss by optimizing the processing conditions and modifying the microstructures.

Because some reactions between BMT and BNT5 and the consequent phase modification might occur during the sintering process, the dielectric constant of the composite ceramics does not obey any composite rule in the present system. Moreover, the dielectric properties of the present composite ceramics can be improved significantly by the post-densification thermal treatments as a consequence of the modification of microstructures and phase constitution.

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