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Low-temperature sintering and microwave dielectric characteristics of $Ba_2Ti_9O_{20}$ ceramics

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Abstract

The effect of B_2O_3 and BaB_2O_4 additions on the low-temperature sintering and the microwave dielectric characteristics of $Ba_2Ti_9O_{20}$ have been investigated. The amounts of B_2O_3 and BaB_2O_4 were varied from 1 to 10 wt.% and the green compacts were sintered in the temperature range of 900–1100 °C for 2 h. As the amount of B_2O_3 increased, the bulk density decreased. In contrast to B_2O_3 addition, the density increased with the amount of BaB_2O_4. From the X-ray analysis of the sintered specimens, it was found that the borides of B_2O_3 and BaB_2O_4 promoted the formation of $Ba_2Ti_9O_{20}$ phase. Second phases of $BaTi(BO_3)_2$ and TiO_2 were observed when B_2O_3 was added. When BaB_2O_4 was added, however, TiO_2 was not observed regardless of the amount of BaB_2O_4. Dielectric characteristics were also examined and discussed in correlation with the densification, microstructure, and the second phase development.

Keywords: Sintering; Microstructure-final; Dielectric properties; Borides; $Ba_2Ti_9O_{20}$

1. Introduction

With recent progress in microwave telecommunication and satellite broadcasting industries, the miniaturization of dielectric devices such as band pass filters, duplexers and resonators has been a major requirement for volume efficiency. For the fabrication of miniaturized devices, multilayer co-firing process became an indispensable technology. Since most of the microwave dielectric ceramics usually need high sintering temperature and soaking time for densification, they are not compatible with the co-firing process.

Among the compounds in the BaO–TiO_2 system, $Ba_2Ti_9O_{20}$ possesses an excellent microwave dielectric characteristics of high quality factor ($Q = 8000$ at 4 GHz), moderate dielectric constant ($\varepsilon_r = 40$) and low-temperature coefficient of resonant frequency (0 ppm/°C). Because of these superior characteristics of $Ba_2Ti_9O_{20}$, a number of researches have been conducted. However, pure $Ba_2Ti_9O_{20}$ is difficult to be obtained through the general solid-state reaction process even at high temperatures around 1300–1400 °C.[1,2] Moreover, $Ba_2Ti_9O_{20}$ is hardly densified.

In order to reduce the sintering temperature of microwave dielectrics, liquid phase sintering has been frequently employed because liquid phase provides faster diffusion paths and low sintering temperature, which promote reaction and densification. Several studies have shown that the addition of B_2O_3 has the advantages of lowering sintering temperatures and improving dielectric properties of $Ba_2Ti_9O_{20}$.[3,4] It was also reported that B_2O_3 addition could enhance the formation of $Ba_2Ti_9O_{20}$. However, chemical reaction between the glass and ceramics should be considered because reaction induced compositional change or development of second phases might deteriorate the dielectric properties.

In this study, two kinds of boride liquid former—B_2O_3 and BaB_2O_4—were added in order to enhance the formation of the $Ba_2Ti_9O_{20}$ phase. The effect on densification, phase development, microstructural evolution and microwave dielectric characteristics was also examined and compared.

2. Experimental

$Ba_2Ti_9O_{20}$ was synthesized through the conventional solid-state reaction process using high-purity raw materials of $BaCO_3$ (99.95%) and TiO_2 (99.9%). The weighed powders were mixed for 16 h in a polyethylene bottle with zirconia balls and ethanol. After drying, the powders were calcined at 1200 °C for 2 h. The

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sintering aids of B_2O_3 and BaB_2O_4 were added to $Ba_2Ti_9O_{20}$ and the amount was varied from 1 to 10 wt.%. BaB_2O_4 was prepared using $BaCO_3$ and B_2O_3 (99.9%) through a heat treatment at 1150 °C for 1 h in a Pt crucible. Calcined $Ba_2Ti_9O_{20}$ and additives of B_2O_3 and BaB_2O_4 were dry-mixed for 24 h and sintered in the range of 900–1100 °C for 2 h. X-ray diffraction (M03XHF, Mac Science, Japan) analysis was carried out for phase identification of the sintered specimens. The microstructure of the specimens was observed using a scanning electron microscope (JEOL, JML5400, Japan). Microwave dielectric characteristics were measured by the Hakki–Coleman dielectric resonator method,[5] using a network analyzer (Agilent 8719ES S-parameter, USA).

3. Result and discussion

Fig. 1 shows the X-ray diffraction patterns and SEM morphology of powders from raw material ($BaCO_3$:TiO_2 = 2:9) that are calcined at 1200 °C for 2 h. Single phase of $Ba_2Ti_9O_{20}$ was not obtained and considerable amount of $BaTi_4O_9$ phase coexisted. It is known that $Ba_2Ti_9O_{20}$ single phase is not easily obtained by the routine solid-state reaction method.

The temperature dependence of the phase development with the boride additives was examined. Fig. 2 shows the X-ray diffraction patterns of sintered specimens with 9 wt.% of B_2O_3 and BaB_2O_4 as a function of sintering temperature. In the case of B_2O_3 addition, three major phases such as $Ba_2Ti_9O_{20}$, $BaTi(BO_3)_2$ and TiO_2 coexisted at the sintering temperature of 800 °C. The intensity of the TiO_2 and $BaTi(BO_3)_2$ phases increased with the increase of sintering temperature and the $Ba_2Ti_9O_{20}$ phase remained as a minor phase. In the case of the specimen sintered at 800 °C with BaB_2O_4 addition, no considerable change in phase evolution was observed when compared with the calcined powders. However, as the sintering temperature increased, the dominant $BaTi_4O_9$ phase produced at the low sintering temperature of 800 °C disappeared and the $Ba_2Ti_9O_{20}$ phase was mainly obtained with a minor amount of $BaTi(BO_3)_2$. Note that TiO_2 phase was not produced when BaB_2O_4 was added. From this experimental result, it is confirmed that chemical reaction of B_2O_3 at low temperature is faster than that of BaB_2O_4 probably due to the difference in the melting temperatures of 450 and 899 °C for B_2O_3 and BaB_2O_4, respectively. Another notable thing is that the synthesis of $Ba_2Ti_9O_{20}$ phase is promoted at low and high temperatures when B_2O_3 and BaB_2O_4 were added, respectively.

The volume fraction of the phases in the specimen sintered at 1050 °C for 2 h as a function of B_2O_3 and BaB_2O_4 content is

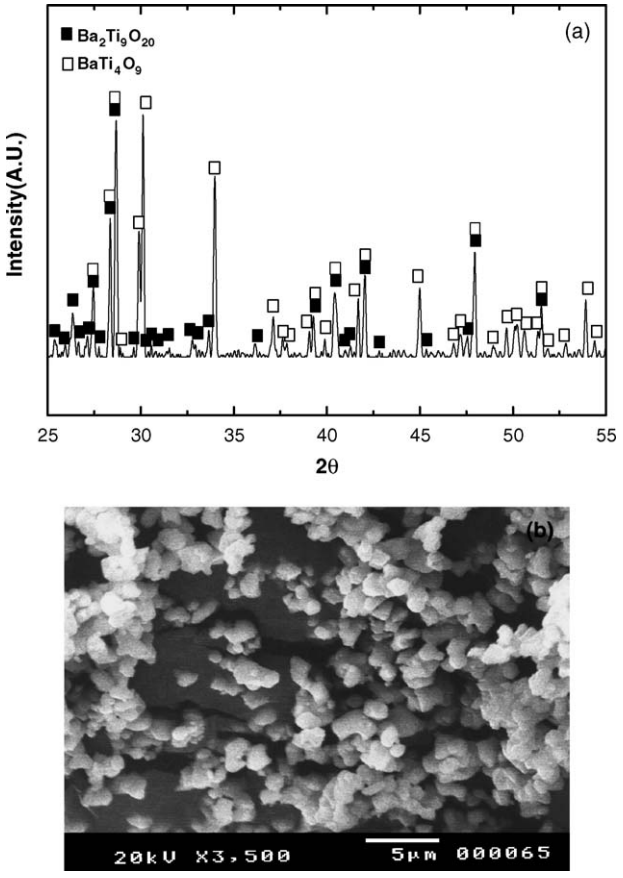

Fig. 1. (a) X-ray diffraction patterns of powders from raw material ($BaCO_3$:TiO_2 = 2:9) that were calcined at 1200 °C for 2h and (b) its SEM morphology.

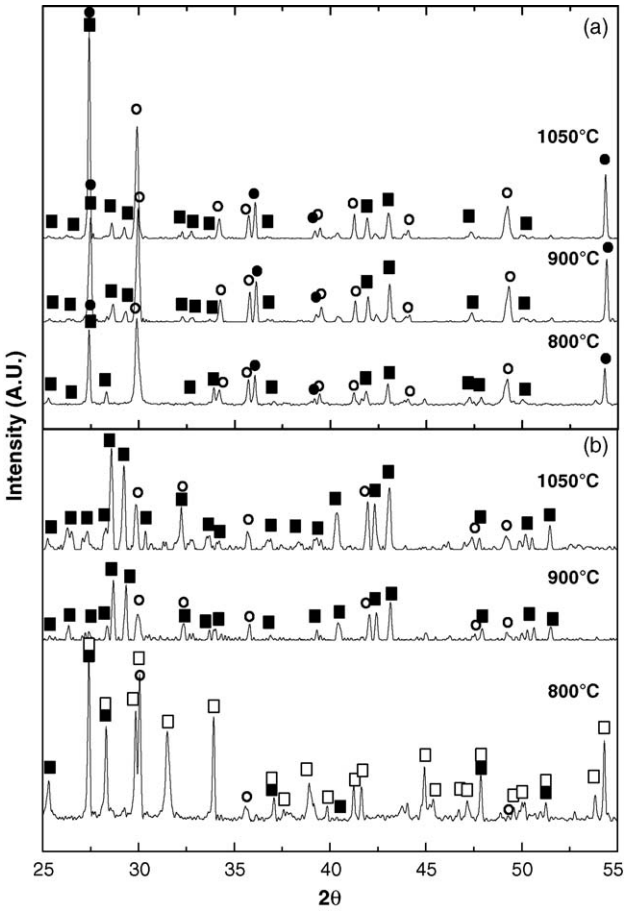

Fig. 2. X-ray diffraction patterns of sintered specimens with 9 wt.% of (a) B_2O_3 and (b) BaB_2O_4 as a function of sintering temperature ((◯) $BaTi(BO_3)_2$; (●) TiO_2; (■) $Ba_2Ti_9O_{20}$; (□) $BaTi_4O_9$).

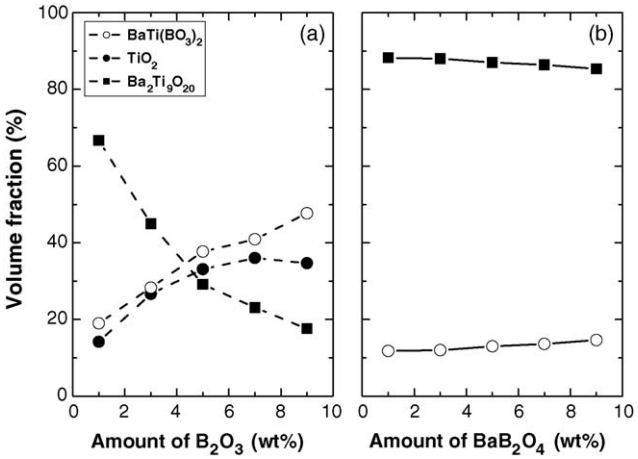

Fig. 3. Change in the volume fraction of the phases in the samples sintered at 1050 °C for 2 h as a function of the amount of (a) B_2O_3 and (b) BaB_2O_4.

shown in Fig. 3. Because the X-ray diffraction intensity can be used to estimate the volume fraction of the phases, the results were determined using the integrated X-ray diffraction intensity of the major peak of the respective phases. As the addition of B_2O_3 increased, the $Ba_2Ti_9O_{20}$ phase greatly decreased and both the $BaTi(BO_3)_2$ and TiO_2 phases increased. In contrast, when BaB_2O_4 was added, a high percentage of $Ba_2Ti_9O_{20}$ phase was obtained and was nearly independent of the amount of BaB_2O_4.

Concerning the phase development process in this system, B_2O_3 liquid phase will be produced during the sintering process at elevated temperatures. When $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ grains are surrounded by B_2O_3 liquid, Ba and Ti ions will be concurrently dissolved out into B_2O_3 melts from $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ grains and then forms Ba–Ti–B–O glass. In the Ba–Ti–B–O glass, B and Ba component acts as glass network former and modifier, respectively. However, because the solubility of Ba in B_2O_3 glass is higher than that of Ti, more Ba will be dissolved out from the $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$, which will eventually result in the formation of TiO_2 and Ba-rich B_2O_3 glasses.[6,7] At the same time, another reaction between the solid grains and Ba-rich B_2O_3 glass will be proceeded that leads to the formation of the $BaTi(BO_3)_2$. $Ba_2Ti_9O_{20}$ phase also can be produced through the reaction between $BaTi_4O_9$ and Ba-rich B_2O_3 glass. On the other hand, when BaB_2O_4 is added, less Ba will be dissolved out from the solid grains comparing to the case of B_2O_3 addition because BaB_2O_4 can be considered as a material that Ba component already dissolved in B_2O_3. In this case, no TiO_2 will be produced but $BaTi(BO_3)_2$ will be produced as observed in Fig. 2b.

Fig. 4 shows the bulk density and porosity of specimens sintered at 1050 °C for 2 h with different amounts of B_2O_3 and BaB_2O_4. Bulk densities of the specimens increased with the sintering temperature and the density of the specimens with BaB_2O_4 addition was higher than that of B_2O_3 addition. The increase of B_2O_3 from 1 to 9 wt.% decreased the bulk density from 4.2 ± 0.1 to 3.3 ± 0.1 g/cm^3 and increased the porosity of sintered specimens. When considering the theoretical densities of $Ba_2Ti_9O_{20}$ (4.6 g/cm^3), $BaTi(BO_3)_2$ (4.2 g/cm^3) and TiO_2

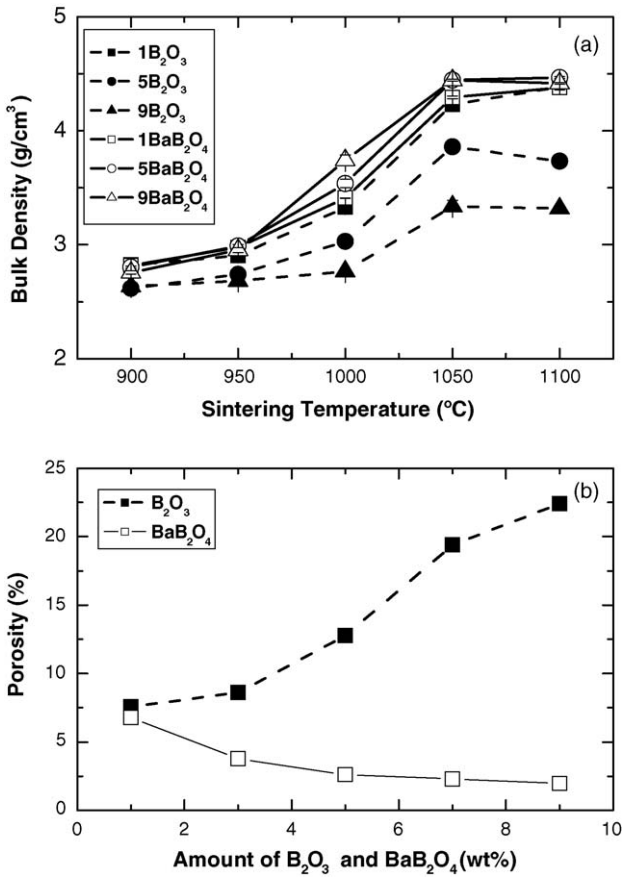

Fig. 4. (a) Bulk density of $Ba_2Ti_9O_{20}$ specimens as functions of temperature and the amount of B_2O_3 and BaB_2O_4, (b) porosity of the specimens sintered at 1050 °C for 2 h as a function of the amount of B_2O_3 and BaB_2O_4.

(4.2 g/cm^3), the increase of $BaTi(BO_3)_2$ and TiO_2 phases also caused the decrease in the bulk density as the amount of B_2O_3 increased. When the amount of BaB_2O_4 is increased, the bulk density slowly increased. The addition of BaB_2O_4 decreased the porosity and enhanced the densification of sintered specimen.

Microstructures of $Ba_2Ti_9O_{20}$ with 9 wt.% of B_2O_3 and BaB_2O_4 sintered at 1050 °C for 2 h are shown in Fig. 5. The phases in the microstructure were identified with the energy dispersive spectroscopy (EDS). The SEM images indicate that large pores are produced in the specimen with B_2O_3 while the addition of BaB_2O_4 achieved high densification of specimen. During sintering over the eutectic temperature of B_2O_3, the melts of B_2O_3 will soak into the solid skeleton of $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ grains leaving behind voids at the place where the B_2O_3 existed. Because of the reaction between B_2O_3 liquid and solid grains of $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$, most of the B_2O_3 melts disappeared and the liquid filling of pores is not available. Since large voids are not easily eliminated during sintering, pores are frequently produced as observed in Fig. 5a. Moreover, once rectangular shaped grains of $BaTi(BO_3)_2$ is formed, densification through particle rearrangement process is almost impossible because the particles hinder moving and sliding of grains.

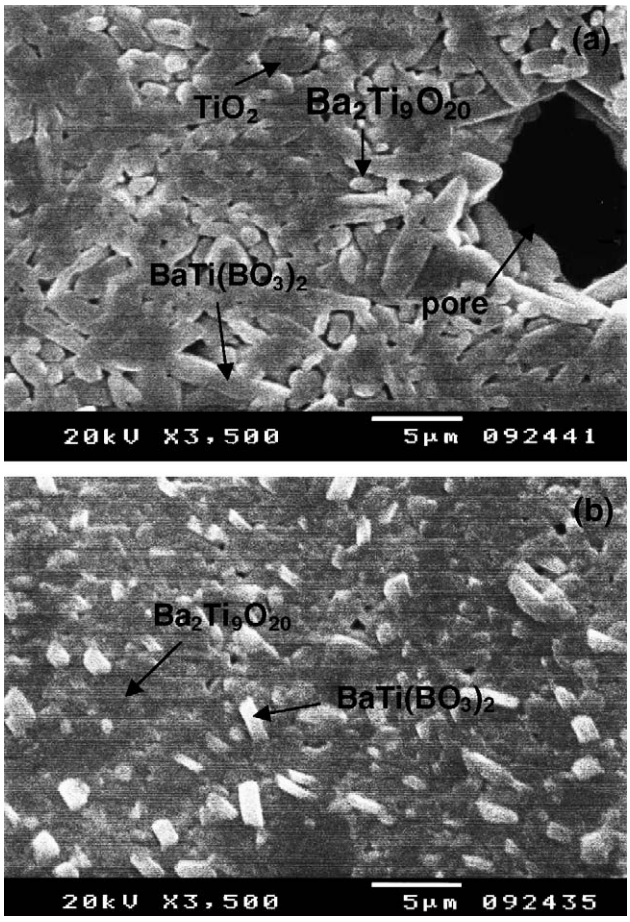

Fig. 5. Microstructures of $Ba_2Ti_9O_{20}$ specimens sintered at 1050 °C for 2 h with addition of (a) 9 wt.% B_2O_3 and (b) 9 wt.% BaB_2O_4.

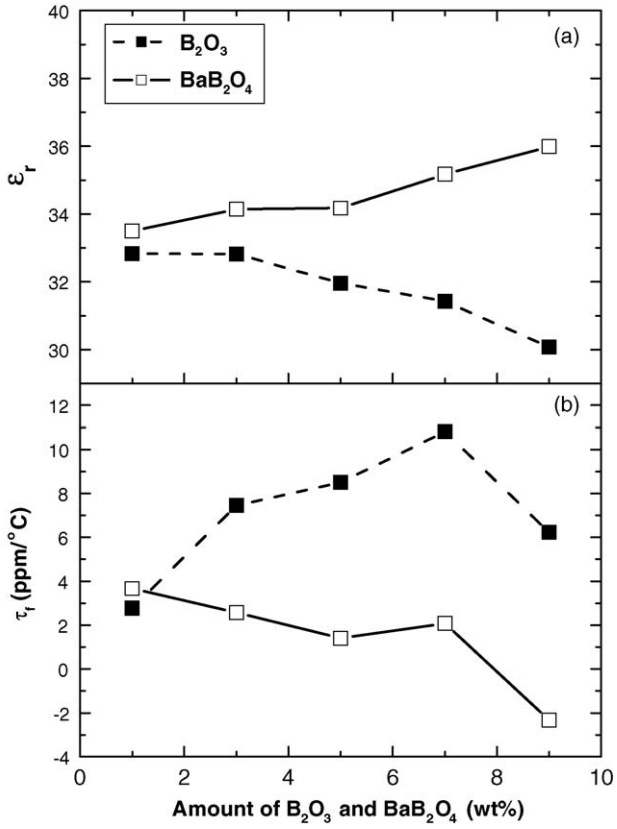

Fig. 6. Dielectric constant and temperature coefficient of resonant frequency of specimens sintered at 1050 °C for 2 h as a function of the amount of (a) B_2O_3 and (b) BaB_2O_4.

The dielectric constants of specimens sintered at 1050 °C for 2 h with different amounts of B_2O_3 and BaB_2O_4 are shown in Fig. 6. As sintering temperature increased, the dielectric constant of specimens sintered with B_2O_3 gradually decreased from 32.9 to 30.1 with the amount of B_2O_3. In the case of BaB_2O_4 added specimens, the dielectric constant slowly increased from 33.5 to 36.0 with the amount of additive. The change in dielectric constant with addition of B_2O_3 and BaB_2O_4 can be explained by the density of sintered specimens. The temperature coefficient of resonant frequency (τ_f) of the specimens revealed that the τ_f increased from 3 to 11 with increase of B_2O_3 from 1 to 7 wt.%. The increased τ_f is believed to be caused from the generation of TiO_2 which has high positive τ_f value. Since B_2O_3 hinders densification of the specimens, further increase of B_2O_3 to 9 wt.% reduced the τ_f. When BaB_2O_4 is added, the τ_f slowly decreased as the amount of $BaBa_2O_4$ increased. Because more BaB_2O_4 addition produced more $BaTi(BO_3)_2$ phase in the specimen, it is thought that the $BaTi(BO_3)_2$ phase probably has negative τ_f. Concerning $Q \times f$ values of the specimens, it decreased from 16,800 to 12,600 as the amount of BaB_2O_4 increased from 1 to 9 wt.%. B_2O_3 addition also showed a decreasing tendency with the values from 14,500 to 13,700 as the amount increased from 1 to 9 wt.%.

4. Conclusion

The chemical reaction of B_2O_3 at low temperature is faster than that of BaB_2O_4. B_2O_3 and BaB_2O_4 addition promoted the synthesis of $Ba_2Ti_9O_{20}$ phase at low temperatures. However, the amount of the second phases increased as the amount of boride additives increased. Even though the addition of BaB_2O_4 contributed to the densification of the specimens through the liquid phase sintering, B_2O_3 produced many large pores. The dielectric constant showed a close relationship with the porosity of the specimens, while the temperature coefficient of resonant frequency (τ_f) was dependent on the second phase.

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References

1. O'Bryan Jr., H. M. and Thomson, J., Temperature-dependent phase boundaries for $BaTi_4O_9$ $Ba_4Ti_{13}O_{30}$ and $Ba_6Ti_{17}O_{40}$. *J. Am. Ceram. Soc.*, 1985, **68**, C70–C72.

2. Negas, T., Yeager, G., Bell, S., Coats, N. and Minis, I., $BaTi_4O_9/Ba_2Ti_9O_{20}$-based ceramics resurrected for modern microwave applications. *Am. Ceram. Soc. Bull.*, 1993, **72**, 80–89.
3. Wang, S. G., Chiang, C. C., Wang, C. H. and Chu, J. P., Phase stability of B_2O_3-added $Ba_2Ti_9O_{20}$ ceramic: processing effects. *J. Mater. Res.*, 2003, **18**, 201–207.
4. Wang, S. G., Chiang, C. C., Wang, C. H. and Chu, J. P., Effects of B_2O_3 on the phase stability of $Ba_2Ti_9O_{20}$ microwave ceramic. *J. Am. Ceram. Soc.*, 2002, **85**, 1619–1621.
5. Hakki, B. W. and Coleman, P. D., A dielectric resonator method of measuring inductive capacities in the millimeter range. *IRE Trans. Microwave Theory Tech.*, 1960, **MTT-8**, 402–410.
6. Kuromitsu, Y., Wang, S. F., Yoshikawa, S. and Newnham, R. E., Evolution of interfacial microstructure between barium titanate and binary glasses. *J. Am. Ceram. Soc.*, 1994, **77**, 852–856.
7. Hirata, A. and Yamaguchi, T., Interfacial reaction of $BaTiO_3$ ceramics with $PbO–B_2O_3$ glasses. *J. Am. Ceram. Soc.*, 1997, **80**, 79–84.