Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 27 (2007) 3033–3037

www.elsevier.com/locate/jeurceramsoc

Low temperature sintering of $BaCu(B_2O_5)$-added $BaO–Re_2O_3–TiO_2$ (Re = Sm, Nd) ceramics

Min-Han Kim [a], Jong-Bong Lim [a], Sahn Nahm [a,*], Jong-Hoo Paik [b], Hwack-Joo Lee [c]

[a] Department of Materials Science and Engineering, Korea University, 1-5 Ka, Anam-Dong, Sungbuk-Ku, Seoul 136-701, Republic of Korea
[b] Korea Institute of Ceramic Engineering and Technology, 233-5, Gasan-Dong, Guemcheon-Gu, Seoul 153-801, Republic of Korea
[c] New Materials Evaluation Center, Korea Research Institute of Standard and Science, Deaduk Science Town, Taejeon 305-600, Republic of Korea

Abstract

The sintering temperature of $BaSm_2Ti_4O_{12}$ (BST) and $BaNd_2Ti_5O_{14}$ (BNT) ceramics was approximately 1350 °C and decreased to 875 °C with the addition of $BaCu(B_2O_5)$ (BCB) ceramic powder. The presence of the liquid phase was responsible for the decrease of the sintering temperature. The liquid phase is considered to have a composition similar to the BaO-deficient BCB. The bulk density and dielectric constant (ε_r) of the specimens increased and reached saturated value with increasing BCB content. The Q-value initially increased with the addition of BCB, but decreased considerably when a large amount of BCB was added, because of the presence of the liquid phase. Good microwave dielectric properties of $Q \times f = 4500\,\text{GHz}$, $\varepsilon_r = 60$ and $\tau_f = -30\,\text{ppm/°C}$ were obtained for the 16.0 mol% BCB-added BST ceramics sintered at 875 °C for 2 h. Moreover, the BST and BNT ceramics containing BCB show good compatibility with silver metal.

Keywords: Sintering; Dielectric properties; $BaO–(Sm,Nd)_2O_3–TiO_2$

1. Introduction

The development of communication systems such as mobile systems requires the miniaturization of devices. Low temperature co-fired ceramic (LTCC) multilayer devices have been extensively investigated for the miniaturization of microwave dielectric components.[1] For the application of LTCC multilayer devices, it is necessary to reduce the sintering temperature of the microwave dielectric ceramics so that they can be cofired with metallic electrodes such as silver and gold. Glass with low melting temperature was generally used to lower the sintering temperature of the microwave dielectric materials for LTCC applications.[2,3] However, it deteriorated the microwave dielectric properties of the ceramics, because it exists as an amorphous phase in the microwave dielectric materials. LTCCs based on oxides with a low melting temperature were investigated to overcome the problems caused by addition of glass.[4,5] Moreover, a small amount of oxide with a low melting temperature was also used as an additive to decrease the sintering temperature of microwave dielectric materials.[6,7]

$BaO–Re_2O_3–TiO_2$ ceramics (Re = Sm, Nd) are known to have good microwave dielectric properties.[8–12] However, their high sintering temperature of approximately 1350 °C needs to be decreased for application to LTCC technology. Although B_2O_3 and B_2O_3/GeO_2 have been used to decrease the sintering temperatures of BNT and BST ceramics, respectively, their sintering temperatures remains too high for the use of Ag metal as an electrode.[13,14] The composition of Ba–Nd–Sm–Ti–O ceramics was varied to reduce their sintering temperature, but the result was not satisfactory.[15] $B_2O_3–Bi_2O_3–SiO_2–ZnO$ glass-added $BaNd_2Ti_4O_{12}$ ceramics and $BaO–La_2O_3–4.7TiO_2$ ceramics with $PbO–B_2O_3–SiO_2$ glass were able to be sintered at 900 °C and exhibited good microwave dielectric properties.[16,17] However, their sintering temperature was still not reducible to below 900 °C as required for LTCC application.

Recently, a small amount of B_2O_3 and CuO additives were used to decrease the sintering temperature of $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics.[18,19] They were well sintered at 870 °C and had good microwave dielectric properties. $BaCu(B_2O_5)$ second phase was observed in the B_2O_3- and CuO-added specimens and it was assumed to exist as a liquid phase and assist in the densification of the ceramics at low temperature. According to a previous work, $BaCu(B_2O_5)$ phase was formed at 700 °C and melted above 850 °C.[20] Moreover, the $BaCu(B_2O_5)$

---

* Corresponding author. Tel.: +82 2 3290 3279; fax: +82 2 928 3584.
E-mail address: snahm@korea.ac.kr (S. Nahm).

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.11.061

ceramic sintered at 810 °C had a dielectric constant (ε_r) of 7.4, a quality factor ($Q \times f$) of 50,000 GHz and a temperature coefficient of resonance frequency (τ_f) of −32 ppm/°C.[20] Since the $BaCu(B_2O_5)$ ceramic had a low melting temperature and good microwave dielectric properties, it could be used as a low temperature sintering aid in the microwave dielectric materials used for LTCC application. In this work, BCB ceramic powder was added to BST and BNT ceramics to reduce their sintering temperature and the effect of BCB addition on their microwave dielectric properties was studied.

2. Experimental procedures

$BaSm_2Ti_4O_{12}$ (BST) (or $BaNd_2Ti_5O_{14}$; BNT) + xBCB ceramics with $2.0 \leq x \leq 24.0$ mol% were prepared from oxides of >99% purity using conventional solid-state synthesis. To synthesize the BCB ceramic powder, BaO (High Purity Chemicals, >99%, Japan), CuO (Junsei Chemical Co., Tokyo, Japan) and B_2O_3 (High Purity Chemicals, >99%, Japan) were mixed for 24 h in a nylon jar with zirconia balls, then dried and calcined at 700 °C for 3 h. For the synthesis of the BST and BNT ceramics, $BaCO_3$ (High Purity Chemicals, >99%, Japan), Sm_2O_3 (High Purity Chemicals, >99%, Japan), Nd_2O_3 (High Purity Chemicals, >99%, Japan) and TiO_2 (High Purity Chemicals, >99%, Japan) were mixed in a nylon jar with zirconia balls for 24 h, and then dried and calcined at 1150 °C for 4 h. After remilling with the BCB additive, the powder was dried, pressed into discs and sintered at 850–900 °C for 2 h. The microstructure of the specimens was studied using X-ray diffraction (XRD; Rigaku D/max-RC, Japan), scanning electron microscopy (SEM; Hitachi S-4300, Japan) and transmission electron microscopy (TEM: Hitachi H-9000NAR Ibaraki, Japan). Composition analysis was performed using energy dispersive spectroscopy (EDS; Horiba EMAX, Japan). Shrinkage of the specimens during heating was measured using a horizontal loading dilatometer with aluminar rams and boats (Model M18XHF, Macscience Instruments, Japan). The densities of the sintered specimens were measured by a water-immersion technique. The dielectric properties in the microwave frequency range were measured by a dielectric post resonator technique suggested by Hakki-Coleman and Courtney.[21,22] The temperature coefficients of the resonant frequency were measured in the temperature range of 25–80 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns of the BST + xBCB ceramics with $2.0 \leq x \leq 20.0$ mol% sintered at 875 °C for 2 h. All the peaks were indexed to those of the tungsten bronze BST phase. Even though a large amount of BCB was added to the BST ceramics, no peaks were found for the second phases, including BCB phase. Similar results were also observed in the BCB-added BNT ceramics. Fig. 2 shows the TEM high resolution lattice image of the BST ceramics containing 20.0 mol% BCB sintered at 875 °C. The liquid phase was found at the grain boundary of the specimen. Therefore, the densification of the BST ceramics at low temperatures was attributed to the presence of the liquid phase. Furthermore, since the BCB phase starts to melt at approximately 850 °C, the liquid phase is considered to have a composition similar to the BCB. According to a previous work, liquid phase was also observed in the BCB-added $BaTi_4O_9$ ceramics with the $Ba_4Ti_{13}O_{30}$ second phase, but no peaks for the BCB second phase were found in the XRD patterns.[23] Therefore, it is considered that BCB liquid phase was formed during the sintering and the Ba ions in the BCB liquid phase were incorporated into the $BaTi_4O_9$ phase forming the $Ba_4Ti_{13}O_{30}$ second phase.[23] The composition of the liquid phase in the $BaTi_4O_9$ ceramics was not a BCB, but rather a CuO and B_2O_3 rich phase. Moreover, the BaO-deficient liquid phase existed as an amorphous phase after cooling.[23] For the BCB-added BST and BNT ceramics, even though liquid phase was observed in the TEM image, no peaks for the BCB second phase were found in the XRD patterns. Therefore, it is considered that the reaction that occurred in the BCB-added $BaTi_4O_9$ ceramics may have taken place in the BCB-added $BaO–Re_2O_3–TiO_2$ ceramics.

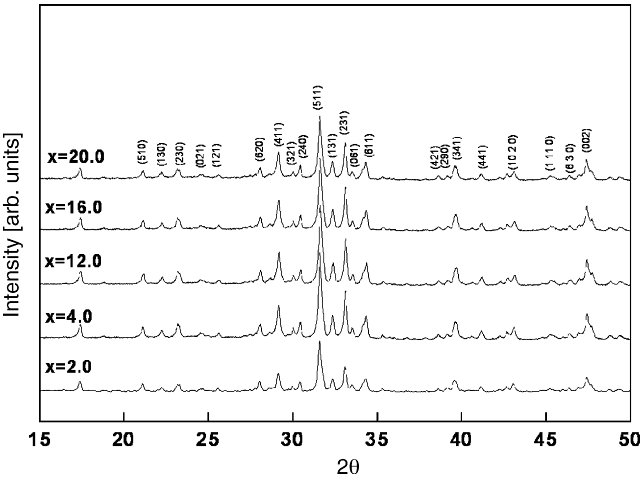

Fig. 1. XRD patterns of the BST + xBCB ceramics with $2.0 \leq x \leq 20.0$ mol% sintered at 875 °C for 2 h.

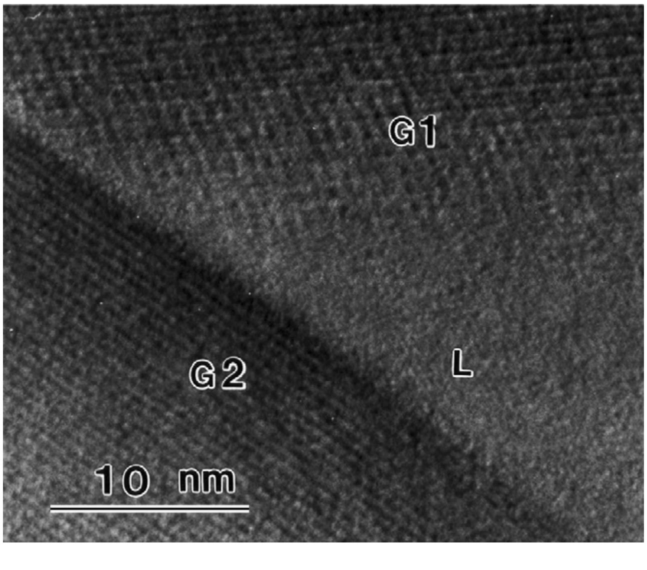

Fig. 2. TEM high resolution lattice image of the BST ceramics containing 20.0 mol% BCB sintered at 875 °C for 2 h.

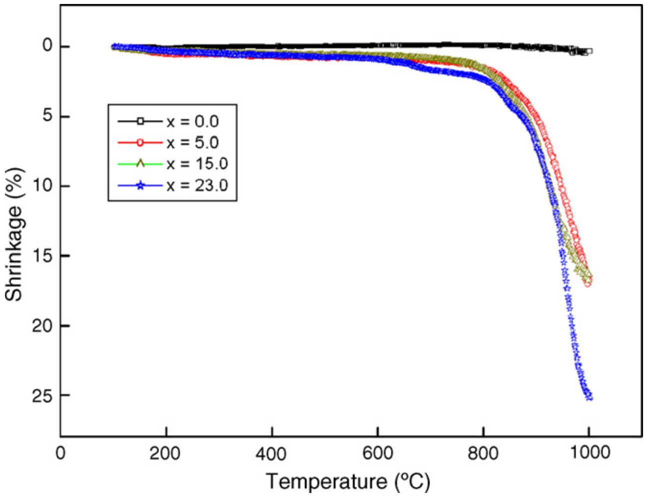

Fig. 3. Shrinkage of the BCB-added BST ceramics.

The shrinkage behavior of the BCB-added BST ceramics is shown in Fig. 3. For the BCB-added BST ceramics, shrinkage started approximately 800 °C. These results implied that the BCB acted as a good low temperature sintering aid for BST ceramics. The similar results were observed in the BCB-added BNT ceramics.

The variations of the density, ε_r, Q-value and τ_f value of the BCB-added BST ceramics sintered at 875 °C are shown in Fig. 4(a). The bulk density was comparatively low at low BCB content. However, it increased with increasing BCB content reached a saturated value when 16.0 mol% BCB was added. The variation of ε_r was similar to that of the bulk density and a saturated ε_r value of 60 was obtained for the specimens with 16.0 mol% BCB. The $Q \times f$ value increased with the addition of a small amount of BCB, due to the increased density, and a maximum $Q \times f$ value of 4700 GHz was obtained for the specimen with 12.0 mol% BCB. In contrast to the ε_r value, the Q-value decreased at a high BCB content, because of the increase in the amount of the liquid phase. Therefore, the density is also an important factor determining the Q-value, although the presence of the liquid phase can deteriorate the Q-value even at a high bulk density. For BST ceramic with 4.0 mol% BCB, the τ_f value was about 5.0 ppm/°C and decreased with increasing BCB content. At 16.0 mol% BCB, the τ_f value reached the saturated value of −30 ppm/°C.

The variations of the density, ε_r, Q-value and τ_f value of the BCB-added BNT ceramics sintered at 875 °C are shown in Fig. 4(b). The variation in bulk density with the BCB content was similar to that of the BST ceramics. For the specimens sintered at 875 °C, the saturated bulk density corresponding to 95% of the theoretical value was obtained when 23.0 mol% BCB was added. The variations of the ε_r and Q-value of the BCB-added BNT were similar to those of the BCB-added BST. It is interesting to note that the BNT ceramics required a greater amount of BCB to obtain the saturated value of ε_r. For the specimen sintered at 875 °C, at least 23.0 mol% BCB was required to reach the saturated value of ε_r, 58. However, the Q-value of this specimen was very low, despite its exhibiting a high bulk density, because it contained a large amount of the liquid phase. Therefore, it was difficult to obtain BNT ceramics with both large ε_r and

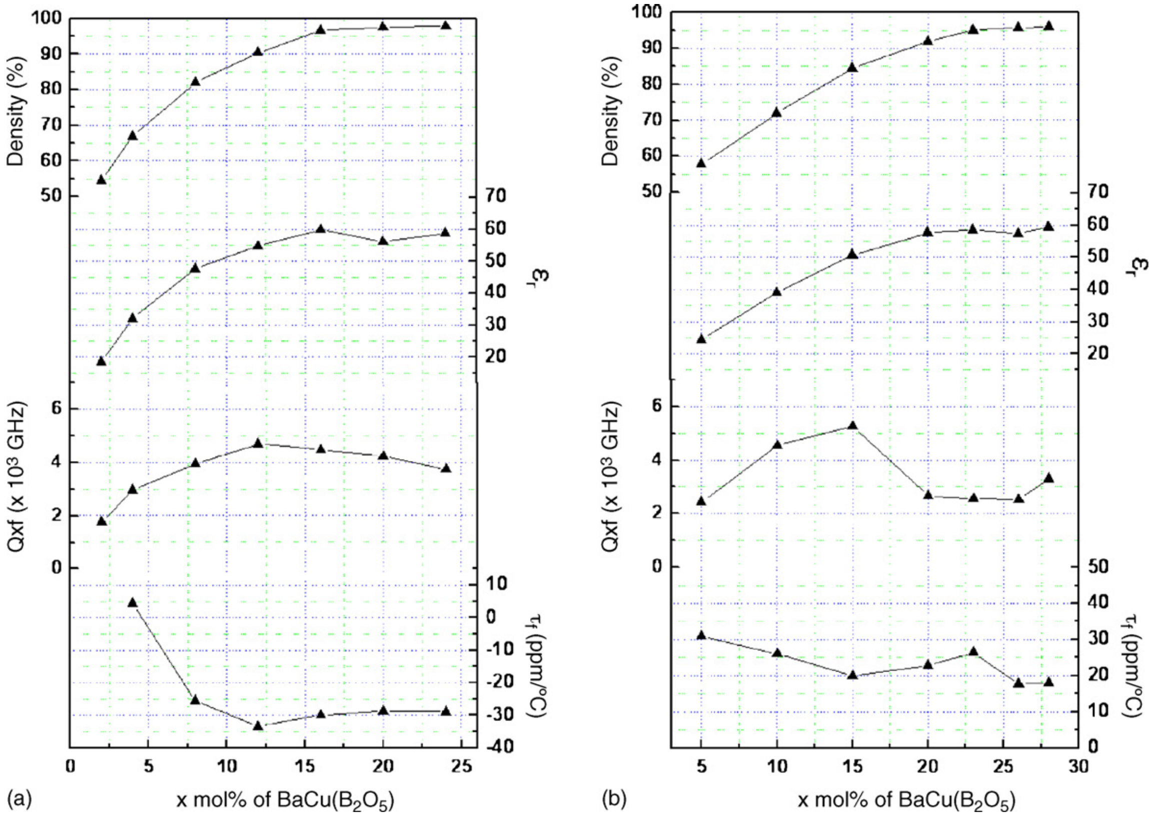

Fig. 4. Density, ε_r, Q-value and τ_f value of (a) BST and (b) BNT ceramics containing x mol% of BCB with $2.0 \leq x \leq 28.0$ sintered at 875 °C for 2 h.

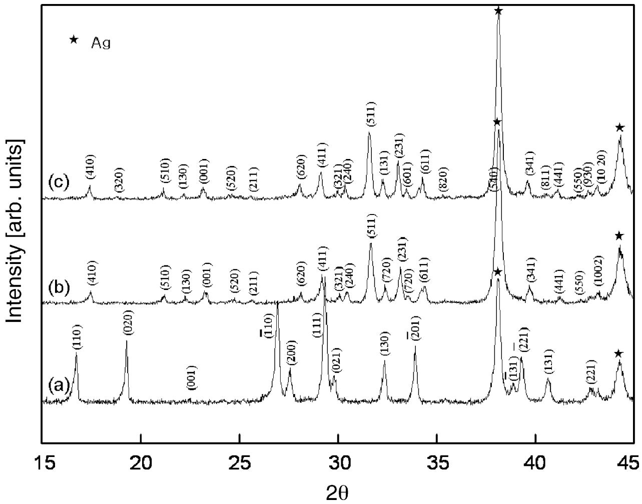

Fig. 5. XRD patterns of the (a) BCB, (b) 23.0 mol% of BCB-added BST and (c) 24.0 mol% BCB-added BNT ceramics sintered with Ag metal at 875 °C for 2 h.

a high Q-value. The τ_f value of the BCB-added BNT ceramics decreased with the addition of BCB, but showed a slight increase for $14.0 < x < 26.0$.

Ag is generally used as the electrode in LTCC devices, because of its high conductivity and low cost. Thus, it is important to study the reaction between Ag electrode and BCB-added BaO–Re_2O_3–TiO_2 ceramics. Fig. 5(a) shows the XRD pattern of the BCB ceramics sintered with Ag metal at 875 °C. Only peaks for the BCB ceramics and Ag metal were observed without any peaks for the second phase. Therefore, Ag metal did not react with the BCB ceramics at 875 °C. The XRD patterns of 24.0 mol% BCB-added BST and BNT ceramics are also shown in Fig. 5(b) and (c), respectively. All the peaks can be indexed in terms of those of BST (or BNT) and Ag and no peaks were observed for the second phase. Therefore, Ag metal did not react with the BST (or BNT) ceramics at 875 °C. The interface between Ag and BCB ceramics was also studied using SEM and EDS line scan, as shown in Fig. 6. The interface between the Ag metal and BCB ceramics is well developed and the sliver profile sharply decreased at the interface, indicating that no diffusion of silver occurred into the BCB ceramics. Moreover, since the concentrations of Ba and Cu in the Ag metal were very low, it is considered that there was no reaction between the Ag metal and BCB ceramics. The interface between the Ag metal and the BST ceramics containing 24.0 mol% BCB was also investigated, as shown in Fig. 7. The silver profile sharply decreased at the interface between BST ceramics and Ag metal. The concentrations of Ba, Sm and Ti ions in the Ag metal were very low. Therefore, no reaction occurred between BCB-added BST ceramics and Ag electrode. Similar results were also obtained from the BNT ceramics containing BCB. Therefore, it can be concluded that the $BaCu(B_2O_5)$ phase constitutes a good additive for decreasing the sintering temperature of BST and BNT ceramics. Furthermore, BCB-added BST and BNT ceramics are good candidates for LTCC because of their low sintering temperature, good microwave dielectric properties and good compatibility with the Ag electrode.

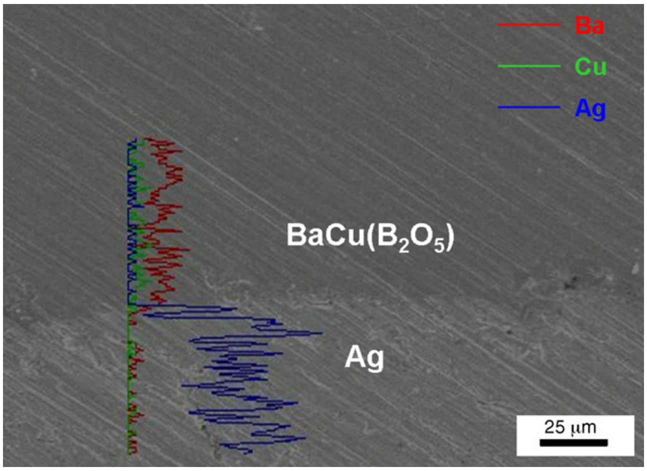

Fig. 6. SEM image and EDS line scan of the interface between BCB ceramics and Ag metal.

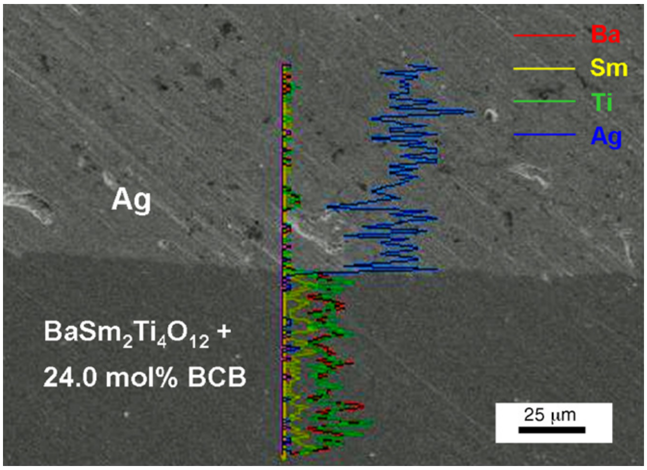

Fig. 7. SEM image and EDS line scan of the interface between 24.0 mol% BCB-added BST ceramics and Ag metal.

4. Conclusion

BCB ceramic powder melted during the sintering and assisted the densification of the BST and BNT ceramics at low temperature. The ε_r of the specimens increased and reached the saturated value with increasing BCB content and its increase can be explained by the increase of the bulk density. The Q-value also increased at low BCB content, but decreased considerably at a high BCB content, due to the presence of the liquid phase. The BST ceramics needed a relatively small amount of BCB to obtain the saturated value of ε_r, while still maintaining a high $Q \times f$ value. However, a large amount of BCB was needed for BNT to obtain the saturated of ε_r and the resulting specimen had a large amount of liquid phase, which deteriorated the Q-value. Good microwave dielectric properties of $Q \times f = 4500$ GHz, $\varepsilon_r = 60$ and $\tau_f = -30$ ppm/°C were obtained for the 16.0 mol% BCB-added BST ceramics sintered at 875 °C for 2 h. BCB-added BST and BNT ceramics show good compatibility with the Ag electrode thus, are good candidates for the LTCC.

Acknowledgements

This work was supported by the Ministry of Commerce, Industry and Energy and one of the authors also acknowledges the financial support provided by the Ministry of Science and Technology through the NRL Project.

References

1. Tummala, R. R., Ceramic and glass–ceramic packaging in the 1990s. *J. Am. Ceram. Soc.*, 1991, **74**(5), 895–908.
2. Takada, T., Wang, S. F., Yoshikawa, S., Jang, S. J. and Newham, R. E., Effects of glass additions on (Zr,Sn)TiO_4 for microwave applications. *J. Am. Ceram. Soc.*, 1994, **77**, 2485–2488.
3. Yang, C. F., The microwave characteristics of glass–$BaTi_4O_9$ ceramics. *Jpn. J. Appl. Phys.*, 1994, **38**, 3576–3579.
4. Udovic, M., Valant, M. and Suvorov, D., Dielectric characterization of ceramics from the TiO_2–TeO_2 system. *J. Eur. Ceram. Soc.*, 2001, **21**, 1735–1738.
5. Valant, M. and Suvorov, D., Processing and dielectric properties of sillenite compounds $Bi_{12}MO_{20-\delta}$ (M = Si, Ge, Ti, Pb, Mn, $B_{1/2}P_{1/2}$). *J. Am. Ceram. Soc.*, 2001, **84**, 2900–2904.
6. Yamamoto, H., Koga, A., Shibagaki, S. and Ichinose, N., Low temperature firing of $MgTiO_3$–$CaTiO_3$ microwave dielectric ceramics modified with B_2O_3 or V_2O_5. *J. Ceram. Soc. Jpn.*, 1998, **106**(3), 339–343.
7. Kagata, H., Inoue, T., Kato, J. and Kameyama, I., Low-fire bismuth-based dielectric ceramics for microwave use. *Jpn. J. Appl. Phys.*, 1992, **31**(9B), 3152–3155.
8. Wersing, W., Microwave ceramics for resonators and filters. *Solids State Mater. Sci.*, 1996, **1**, 715–731.
9. Ohsato, H., Nishigaki, S. and Okuda, T., Superlattice and dielectric properties of BaO–R_2O_3–TiO_2 (R = La, Nd and Sm) microwave dielectric compounds. *Jpn. J. Appl. Phys.*, 1992, **31**, 3136–3138.
10. Chen, X. M., Suzuki, Y. and Sato, N., Preparation and densification of $BaNd_2Ti_5O_{14}$ dielectric ceramics. *Mater. Lett.*, 1993, **16**, 75–78.
11. Kolar, D., Gaberscek, S. and Volavsek, B., Synthesis and crystal chemistry of $BaNd_2Ti_3O_{10}$, $BaNd_2Ti_5O_{14}$, and $Nd_4Ti_9O_{24}$. *J. Solid State Chem.*, 1981, **38**, 158–164.
12. Choi, J. H., Kim, J. H., Lee, B. T., Kim, Y. M. and Moon, J. H., Microwave dielectric properties of Ba–Nd–Ti–O system doped with metal oxides. *Mater. Lett.*, 2000, **44**, 29–34.
13. Lu, C. H. and Huang, Y. H., Densification and dielectric properties of barium neodymium titanium oxide ceramics. *Mater. Sci. Eng.*, 2003, **B98**, 33–37.
14. Ota, Y., Kakimoto, K., Ohsato, H. and Okawa, T., Low-temperature sintering of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ microwave dielectric ceramics by B_2O_3 and GeO_2 addition. *J. Eur. Ceram. Soc.*, 2004, **24**, 1755–1760.
15. Cheng, C. C., Hsieh, T. E. and Lin, I. N., The effect of composition on Ba–Nd–Sm–Ti–O microwave dielectric materials for LTCC application. *Mater. Chem. Phys.*, 2003, **79**, 119–123.
16. Dernovsek, O., Naeini, A., Preu, G., Wersing, W., Eberstein, M. and Schiller, W. A., LTCC glass–ceramic composites for microwave application. *J. Eur. Ceram. Soc.*, 2001, **21**, 1693–1697.
17. Lee, C. C. and Lin, P., Effect of glass addition on microwave properties of $BaO\cdot La_2O_3\cdot 4.7TiO_2$. *Jpn. J. Appl. Phys.*, 1998, **37**, 6048–6054.
18. Kim, M. H., Nahm, S., Lee, W. S., Yoo, M. J., Kang, N. K., Kim, H. T. *et al.*, Effect of B_2O_3 and CuO on the sintering temperature and microwave dielectric properties of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics. *Jpn. J. Appl. Phys.*, 2005, **44**(5A), 3091–3094.
19. Kim, M. H., Jeong, Y. H., Nahm, S., Kim, H. T. and Lee, H. J., Effect of B_2O_3 and CuO additives on the sintering temperature and microwave dielectric properties of $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics. *J. Eur. Ceram. Soc.*, 2006, **26**, 2139–2142.
20. Kim, M. H., Lim, J. B., Kim, J. C., Nahm, S., Paik, J. H. and Kim, J. H., *J. Am. Ceram. Soc.*, 2006, **89**, 3124-3128.
21. Hakki, B. W. and Coleman, P. D., A dielectric resonator method of measuring inductive in the millimeter range. *IEEE Trans. Microwave Theory Tech.*, 1960, **8**, 402–410.
22. Courtney, W. E., Analysis and evaluation of a method of measuring the complex permittivity and permeability of microwave insulators. *IEEE Trans. Microwave Theory Tech.*, 1970, **18**, 476–485.
23. Lim, J. B., Kim, M. H., Kim, J. C., Nahm, S., Paik, J. H. and Kim, J. H., Effect of $BaCu(B_2O_5)$ additive on the sintering temperature and microwave dielectric properties of $BaTi_4O_9$ ceramics. *Jpn. J. Appl. Phys.*, 2006, **45**, L242–L244.