Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 27 (2007) 1053–1058
ELSEVIER
EC≋RS
www.elsevier.com/locate/jeurceramsoc

# Low temperature sintering of $BaO–Sm_2O_3–4TiO_2$ ceramics

Kyung-Hoon Cho[a], Jong-Bong Lim[a], Sahn Nahm[a,*], Hyo-Tae Kim[b],
Jong-Hee Kim[b], 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 Standards and Science, Daeduk Science Town, Taejon 305-600, Republic of Korea

## Abstract

The effect of $B_2O_3$ and CuO on the sintering temperature and microwave dielectric properties of $BaSm_2Ti_4O_{12}$ ceramics was investigated. The $BaSm_2Ti_4O_{12}$ ceramics were able to be sintered at 1000 °C when $B_2O_3$ was added. This decrease in the sintering temperature of the $BaSm_2Ti_4O_{12}$ ceramics upon the addition of $B_2O_3$ is attributed to the $BaB_4O_7$ second phase, whose melting temperature is around 900 °C. The $B_2O_3$ added $BaSm_2Ti_4O_{12}$ ceramics alone were not able to be sintered below 1000 °C, but were sintered at 875 °C when CuO was added. $BaCu(B_2O_5)$ second phase might be responsible for the decrease in the sintering temperature of the CuO and $B_2O_3$ added $BaSm_2Ti_4O_{12}$ ceramics. The $BaSm_2Ti_4O_{12} + 10.0$ mol% $B_2O_3 + 20.0$ mol% CuO ceramics sintered at 875 °C for 2 h have good microwave dielectric properties of $\varepsilon_r = 61.47$, $Q \times f = 4256$ GHz and $\tau_f = -9.25$ ppm/°C. The $BaCu(B_2O_5)$ is also a good additive for decreasing the sintering temperature of the $BaSm_2Ti_4O_{12}$ ceramics.

*Keywords:* Sintering; Microstructure; Dielectric properties

## 1. Introduction

The miniaturization and hybridization of microwave dielectric components are required for the development of mobile telecommunication systems, and various multi-layer devices have been extensively investigated in an attempt to satisfy these requirements. Multi-layer devices consist of alternating microwave dielectric ceramics and internal metallic electrode layers.[1] Ag has been widely used as the metallic electrode, because of its high conductivity and low cost. However, the melting temperature of Ag is low, about 961 °C, whereas the sintering temperature of the microwave dielectric ceramics is generally above 1400 °C. Therefore, for the fabrication of multilayer devices, it is necessary to develop microwave dielectric ceramics with a low sintering temperature, which can be co-fired with Ag.

$BaO–Sm_2O_3–TiO_2$ ceramics, consisting of two ternary phases, viz. $BaO–Sm_2O_3–5TiO_2$ and $BaO–Sm_2O_3–3TiO_2$, were first reported by Ouchi and co-workers and the crystal structure of these phases was identified as a tungsten–bronze type structure.[2–4] In particular, $BaSm_2Ti_4O_{12}$ ceramics show good microwave dielectric properties of $Q = 2289$ at 3.6 GHz and $\varepsilon_r = 78.91$.[5] However, the sintering temperature of this ceramic is relatively high, being approximately 1350 °C. Therefore, it is necessary to decrease sintering temperature for the application to LTCC technology. In a previous work, $B_2O_3/Ge_2O_2$ and $Bi_2O_3/MnO_2$ were used to reduce the sintering temperature of $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (where R = Sm, Nd, Pr or La) and [(Pb, Ca)La](Fe, Nb)$O_3$ ceramics, respectively, however their sintering temperatures were still too high for Ag metal to be used as an electrode.[6,7] Recently, many types of glasses were used to decrease the sintering temperature of $BaNd_2Ti_4O_{12}$ ceramics.[8–10] However, the microwave dielectric properties of the resulting ceramics were not satisfactory, because the addition of glass usually degraded their microwave dielectric properties.

In previous studies, the addition of a small amount of $B_2O_3$ and CuO was found to reduce the sintering temperature of $Ba(Zn_{1/3}Ta_{2/3})O_3$, and $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics to below 900 °C.[11,12] Therefore, it is also possible that these $B_2O_3$ and CuO additives would be effective in decreasing the sintering temperature of the $BaSm_2Ti_4O_{12}$ ceramics. In this work, small amounts of $B_2O_3$ and CuO additives were used to decrease the

---

[*] 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
doi:10.1016/j.jeurceramsoc.2006.05.061

sintering temperature of $BaSm_2Ti_4O_{12}$ ceramics and the variations in the microwave dielectric properties of these ceramics were investigated in terms of their microstructure.

## 2. Experimental procedure

$BaCO_3$, $Sm_2O_3$ 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 1100 °C for 3 h. After remilling with the $B_2O_3$ and CuO (High purity Chemicals, >99%) additives, the powder was dried, pressed into discs and sintered at 875–1000 °C for 2 h. The microstructure of the specimens was studied using X-ray diffraction (Rigaku D/max-RC, Japan), scanning electron microscopy (SEM; Hitachi S-4300, Japan) and transmission electron microscopy (TEM; Hitachi H-9000NAR Ibaraki, 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 and Coleman[13] and Courtney.[14] The temperature coefficients of the resonant frequency was measured in the temperature range of 25–80 °C.

## 3. Results and discussion

The normal sintering temperature of the $BaSm_2Ti_4O_{12}$ ceramics is approximately 1350 °C, however they were able to be sintered at 1000 °C when $B_2O_3$ was added. Fig. 1 shows the X-ray diffraction patterns of $BaSm_2Ti_4O_{12}$ ceramics calcined at 1150 °C for 3 h and the $BaSm_2Ti_4O_{12} + xB_2O_3$ ceramics with $10.0 \leq x \leq 50.0$ mol% sintered at 1000 °C for 2 h. All of the peaks were indexed as those of the $BaSm_2Ti_4O_{12}$ phase with lattice parameters of $a = 2.23$ nm, $b = 1.21$ nm and $c = 0.38$ nm. Peaks for the $BaB_4O_7$ second phase, which are indicated by an asterisk, were also observed for the specimens with $x \geq 10.0$. According to the phase diagram, the eutectic temperature of the $BaB_4O_7$ ceramics is approximately 899 °C.[15] Therefore, the $BaB_4O_7$ phase existed as the liquid phase during the sintering process and assisted in the densification of the $BaSm_2Ti_4O_{12}$ ceramics. The unknown peaks which are indicated by the open circle were also observed and they might be related to the phase which is formed by the decomposition of the $BaSm_2Ti_4O_{12}$ ceramics due to the formation of the $BaB_4O_7$ phase.

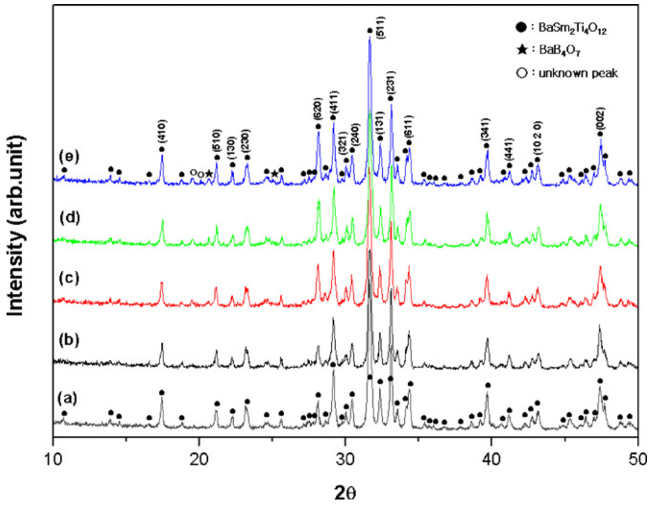

Fig. 1. X-ray diffraction patterns of (a) the $BaSm_2Ti_4O_{12}$ ceramics calcined at 1150 °C for 3 h and the $BaSm_2Ti_4O_{12} + xB_2O_3$ ceramics with $10.0 \leq x \leq 50.0$ mol% sintered at 1000 °C for 2 h: (b) $x = 10.0$ mol%, (c) $x = 20.0$ mol%, (d) $x = 30.0$ mol% and (e) $x = 50.0$ mol%.

The SEM images of the thermally etched $BaSm_2Ti_4O_{12} + xB_2O_3$ ceramics are shown in Fig. 2(a–c). For the specimen with $x = 5.0$ mol%, a porous microstructure with an average grain size of 0.2 μm was developed. A dense microstructure formed in the specimen with $x = 10.0$ mol%, but the microstructure was degraded when the amount of $B_2O_3$ exceeded 10.0 mol% as shown in Fig. 2(c). As the $B_2O_3$ content increased, the amount of liquid phase increased, and this liquid phase could have evaporated during the sintering process. Therefore, the porous microstructure formed in the specimens with a large amount of $B_2O_3$ might be due to the evaporation of the liquid phase during sintering.

Fig. 3 shows the variations in the relative density, $\varepsilon_r$ value and $Q \times f$ value of the $B_2O_3$ added $BaSm_2Ti_4O_{12}$ ceramics sintered at 1000 °C for 2 h. The relative density of the specimen with 5.0 mol% of $B_2O_3$ was approximately 85% of the theoretical density and increased with increasing $B_2O_3$ content, showing a maximum value when $x = 10.0$ mol%. When $x$ exceeded 10.0 mol%, the relative density decreased, and this decrease is attributed to the development of the porous microstructure. The variation in the value of $\varepsilon_r$ is similar to that of the relative density and, thus, the density is an important factor in improving the value of $\varepsilon_r$. The $Q$-value decreased with increasing $B_2O_3$ content, even though the relative density increased. This decrease in the $Q$-value might be due to the increase of the $BaB_4O_7$ second phase. In addition, the decomposition of the $BaSm_2Ti_4O_{12}$ and the presence of cation deficiency in $BaSm_2Ti_4O_{12}$ due to the formation of $BaB_4O_7$ phase can also deteriorate the $Q \times f$ value of the specimens.

The sintering temperature of the $BaSm_2Ti_4O_{12}$ ceramics was reduced to 1000 °C when $B_2O_3$ was added. However, the $B_2O_3$ added $BaSm_2Ti_4O_{12}$ ceramics were not able to be sintered below 1000 °C and, thus, it is difficult to use Ag as the electrode for $B_2O_3$ added $BaSm_2Ti_4O_{12}$ ceramics. To overcome this difficulty, both CuO and $B_2O_3$ were added to the $BaSm_2Ti_4O_{12}$ ceramics, in order to reduce the sintering temperature below 900 °C. When CuO was added to the $BaSm_2Ti_4O_{12}$ ceramic containing 10.0 mol% $B_2O_3$, it was able to be sintered even at 850 °C. Fig. 4 shows the X-ray diffraction patterns of the $BaSm_2Ti_4O_{12}$ + 10.0 mol% $B_2O_3$ + $x$CuO ceramics where $5.0 \leq x \leq 50.0$ mol% sintered at 875 °C for 2 h. All of the peaks were identified as those of the $BaSm_2Ti_4O_{12}$ phase. The CuO itself cannot decrease the sintering temperature of $BaSm_2Ti_4O_{12}$ ceramics below 900 °C, because the CuO added $BaSm_2Ti_4O_{12}$ ceramics were not sintered below 1050 °C. Fig. 5 shows the TEM high resolution lattice image of the $BaSm_2Ti_4O_{12}$ + 10.0 mol% $B_2O_3$ + 20.0 mol% CuO ceramics sintered at 875 °C for 2 h. The liquid phase existed at the triple point of the $BaSm_2Ti_4O_{12}$ ceramics. According to a previous work, $BaCu(B_2O_5)$ second phase, which melts at a

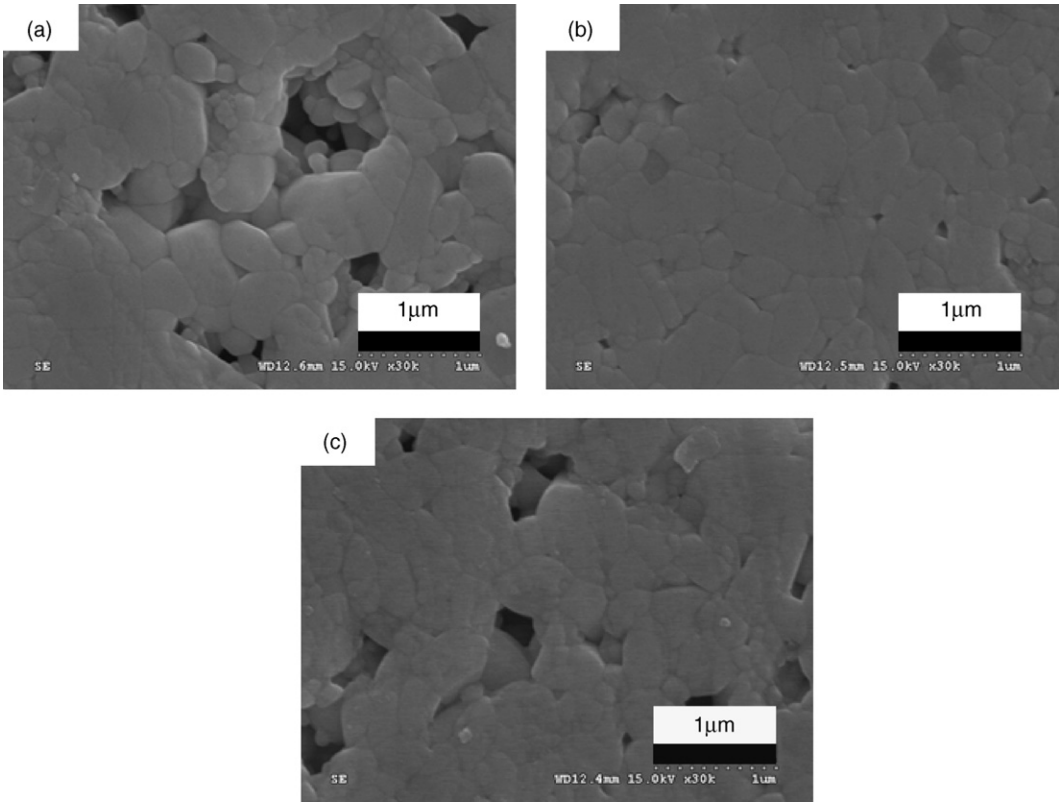

Fig. 2. SEM images of the thermally etched $BaSm_2Ti_4O_{12} + xB_2O_3$ ceramics: (a) $x = 5.0$ mol%, (b) $x = 10.0$ mol% and (c) $x = 20.0$ mol%.

temperature above 800 °C, existed in the CuO and $B_2O_3$ added $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics and assisted in the densification at low temperature.[12] For the $BaSm_2Ti_4O_{12}$ ceramics, even if it is difficult to find the peak for $BaCu(B_2O_5)$ in the X-ray diffraction pattern, it is possible that a small amount of the $BaCu(B_2O_5)$ liquid phase formed as shown in Fig. 5 and assisted in the densification of the $BaSm_2Ti_4O_{12}$ ceramic at low temperature. Furthermore, the $BaSm_2Ti_4O_{12}$ ceramics was well sintered even at 875 °C when a small amount of the $BaCu(B_2O_5)$ additive was added, as will be discussed later. Therefore, it is considered that the $BaCu(B_2O_5)$ second phase is responsible for the densification of the CuO and $B_2O_3$ added $BaSm_2Ti_4O_{12}$ ceramics at low temperature. In addition, the $CuB_8O_{13}$ phase melts at a temperature above 750 °C.[16] Therefore, we cannot completely exclude the possibility that the CuO reacted with the $B_2O_3$, resulting in the formation of CuO–$B_2O_3$ phase, which assisted in the sintering of the $BaSm_2Ti_4O_{12}$ ceramics below 900 °C.

Fig. 6(a–c) show the SEM images of the thermally etched surfaces of the $BaSm_2Ti_4O_{12}$ + 10.0 mol% $B_2O_3$ + $x$CuO ceramics with $5.0 \le x \le 20.0$ mol% sintered at 875 °C for 2 h. For the

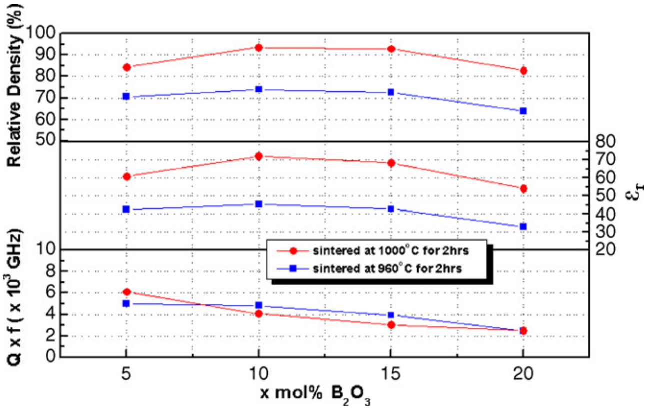

Fig. 3. Variations in the relative density, $\varepsilon_r$ value and $Q \times f$ value of the $B_2O_3$ added $BaSm_2Ti_4O_{12}$ ceramics sintered at 1000 °C for 2 h.

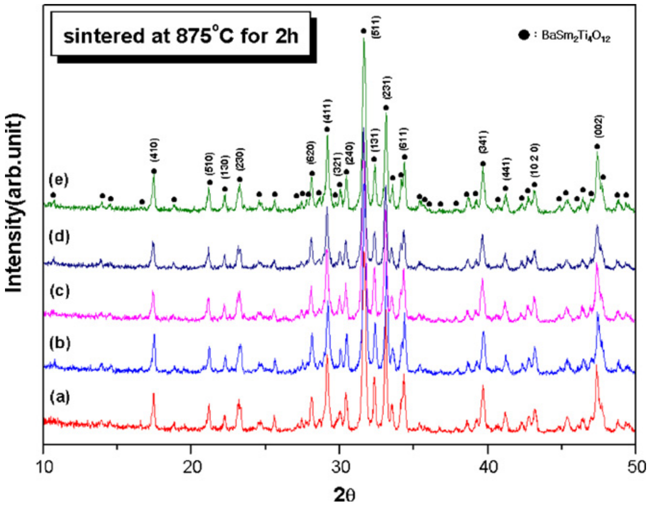

Fig. 4. X-ray diffraction patterns of the $BaSm_2Ti_4O_{12}$ + 10.0 mol% $B_2O_3$ + $x$CuO ceramics where $5.0 \le x \le 50.0$ mol% sintered at 875 °C for 2 h: (a) $x = 5.0$ mol%, (b) $x = 10.0$ mol%, (c) $x = 20.0$ mol%, (d) $x = 30.0$ mol% and (e) $x = 50.0$ mol%.

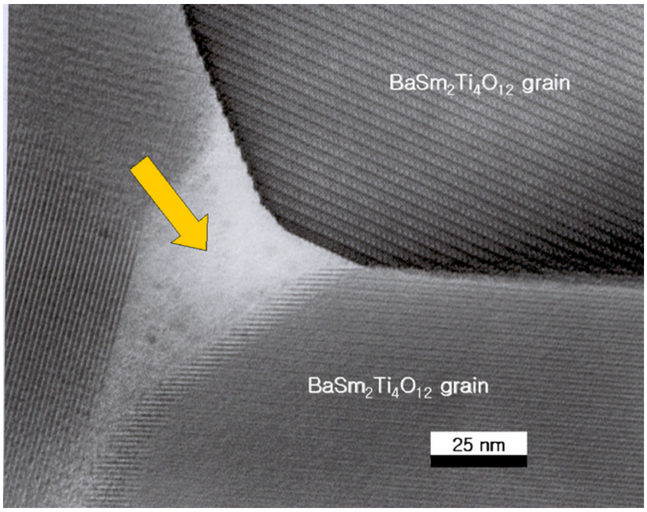

Fig. 5. TEM high resolution lattice image of the $BaSm_2Ti_4O_{12}$ + 10.0 mol% $B_2O_3$ + 20.0 mol% CuO ceramics sintered at 875 °C for 2 h.

specimen with 5.0 mol% of CuO, a porous microstructure was formed. However, when the CuO content exceeded 10.0 mol%, a dense microstructure developed. Moreover, the microstructure was not degraded when a large amount of CuO was added. Therefore, at least 10.0 mol% of CuO is required to ensure the densification of the $BaSm_2Ti_4O_{12}$ + 10.0 mol% $B_2O_3$ ceramics.

Fig. 7 shows the variations in the absolute density and $\varepsilon_r$ value of the $BaSm_2Ti_4O_{12}$ + 10.0 mol% $B_2O_3$ + $x$CuO ceramics with $5.0 \leq x \leq 50.0$ mol% sintered at various temperatures. For the specimens sintered at 875 °C, the absolute density increased with increasing CuO content and became saturated when the CuO content exceeded 15.0 mol%. The variation in the absolute density could be explained by that of the microstructure as shown in Fig. 6(a–c). A similar result was also obtained for the specimens sintered at 900 °C. For the specimens sintered at 850 °C, the density increased with increasing CuO content, but decreased when $x$ exceeded 20.0 mol%. This decrease in density is not completely understood at the present moment. The $\varepsilon_r$ value significantly increased with the addition of a small amount of CuO and became saturated for the specimens with 15.0 mol% added CuO sintered at 875 and 900 °C. In particular, the specimen with a CuO content of 15.0 mol% sintered at 900 °C exhibited a high $\varepsilon_r$ value of 70. In the case of the specimens sintered at 850 °C, the $\varepsilon_r$ value increased with increasing CuO content, but decreased when $x$ exceeded 15.0 mol%. In addition, the variation in the $\varepsilon_r$ value is the same as that of the density thus, density is an important factor which influences the $\varepsilon_r$ of the specimen.

Fig. 8 shows the variation in the $Q$-value of the $BaSm_2Ti_4O_{12}$ + 10.0 mol% $B_2O_3$ + $x$CuO ceramics with $5.0 \leq x \leq 50.0$ mol% as a function of the sintering temperature and CuO content. The $Q$-value increased with increasing sintering temperature, but decreased with increasing CuO content, even though the absolute density increased. This decrease in the $Q$-value might be related to the increase in the amount of the liquid phase with increasing CuO content. The variation in the $\tau_f$ value of

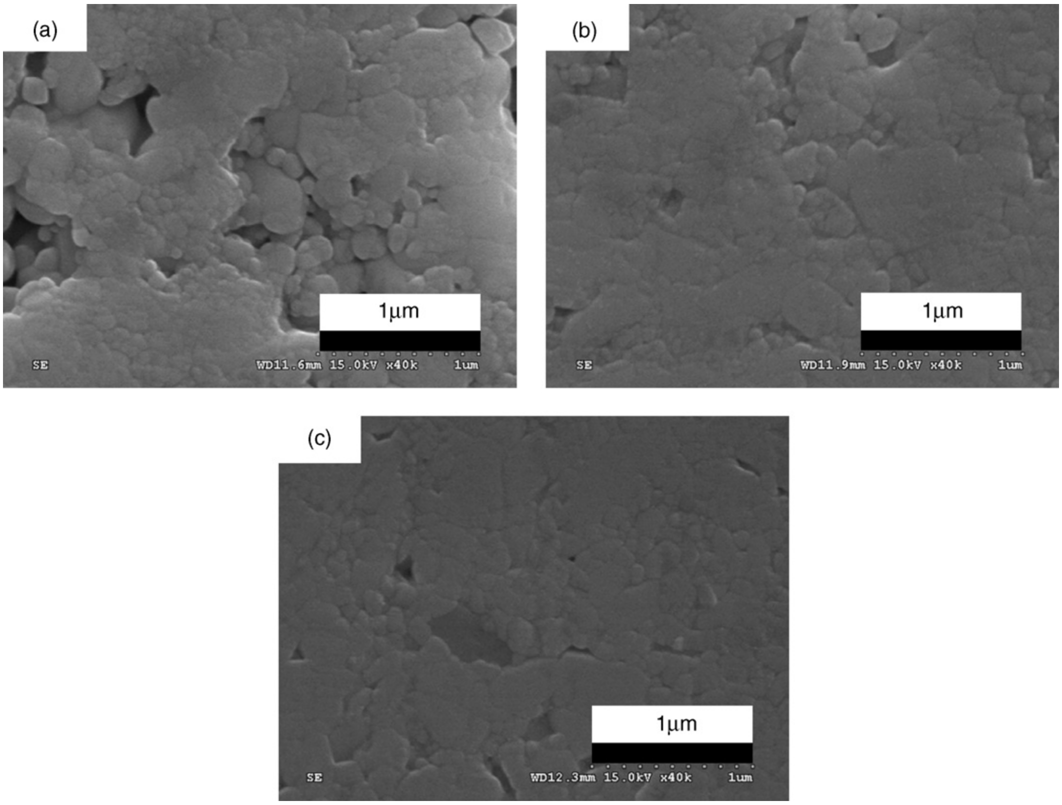

Fig. 6. SEM images of the thermally etched surfaces of the $BaSm_2Ti_4O_{12}$ + 10.0 mol% $B_2O_3$ + $x$CuO ceramics sintered 875 °C for 2 h: (a) $x$ = 5.0 mol%, (b) $x$ = 10.0 mol% and (c) $c$ = 20.0 mol%.

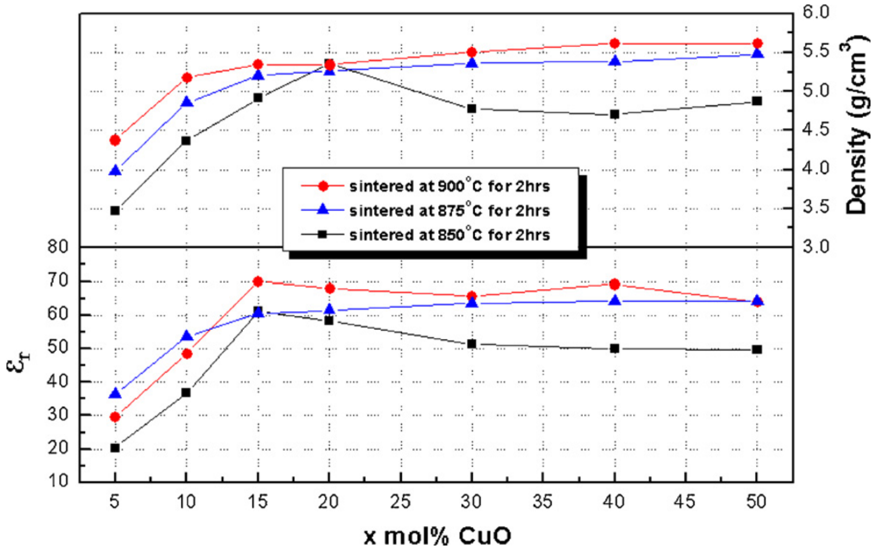

Fig. 7. Variations in the absolute density and $\varepsilon_r$ value of the $BaSm_2Ti_4O_{12}$ + 10.0 mol% $B_2O_3$ + $x$CuO ceramics where $5.0 \leq x \leq 50.0$ mol% sintered at various temperatures.

the specimens sintered at 875 °C is also shown in Fig. 8. The $\tau_f$ value of the $BaSm_2Ti_4O_{12}$ + 10.0 mol% $B_2O_3$ + 5.0 mol% CuO ceramics is about −11 ppm/°C and varied slightly, but non-significantly, with the CuO content. Good microwave dielectric properties of $\varepsilon_r$ = 61.47, $Q \times f$ = 4256 GHz and $\tau_f$ = −9.25 ppm/°C, were obtained for the $BaSm_2Ti_4O_{12}$ + 10.0 mol% $B_2O_3$ + 20.0 mol% CuO ceramics sintered at 875 °C for 2 h.

To clarify the effect of the $BaCu(B_2O_5)$ phase on the sintering temperature of the $BaSm_2Ti_4O_{12}$ ceramics, we made $BaCu(B_2O_5)$ and added it to the $BaSm_2Ti_4O_{12}$ ceramics. When $BaCu(B_2O_5)$ was added, the $BaSm_2Ti_4O_{12}$ ceramics were well sintered even at 875 °C. Fig. 9 shows the variations in absolute density, $\varepsilon_r$ value and $Q$-value of the $BaCu(B_2O_5)$ added $BaSm_2Ti_4O_{12}$ ceramics sintered at various temperatures for 2 h. The density increased with increasing $BaCu(B_2O_5)$ content and became saturated when 16.0 mol% of $BaCu(B_2O_5)$ was added. Similar variations were also observed for the $\varepsilon_r$ value and $Q$-value. Good dielectric properties of $\varepsilon_r$ = 60.0 and $Q \times f$ = 4500 GHz were obtained for the $BaSm_2Ti_4O_{12}$ ceramic with 16.0 mol% of $BaCu(B_2O_5)$ sintered at 875 °C. From this result, it can be inferred that $BaCu(B_2O_5)$ second phase was formed in the $B_2O_3$ and CuO added $BaSm_2Ti_4O_{12}$ ceramics and helped in the densification at low temperature. Moreover, it can be concluded that the $BaCu(B_2O_5)$ phase is a good additive for decreasing the sintering temperature of the $BaSm_2Ti_4O_{12}$ ceramics without deteriorating the microwave dielectric properties. However, more investigation is required before it can be used in practical applications.

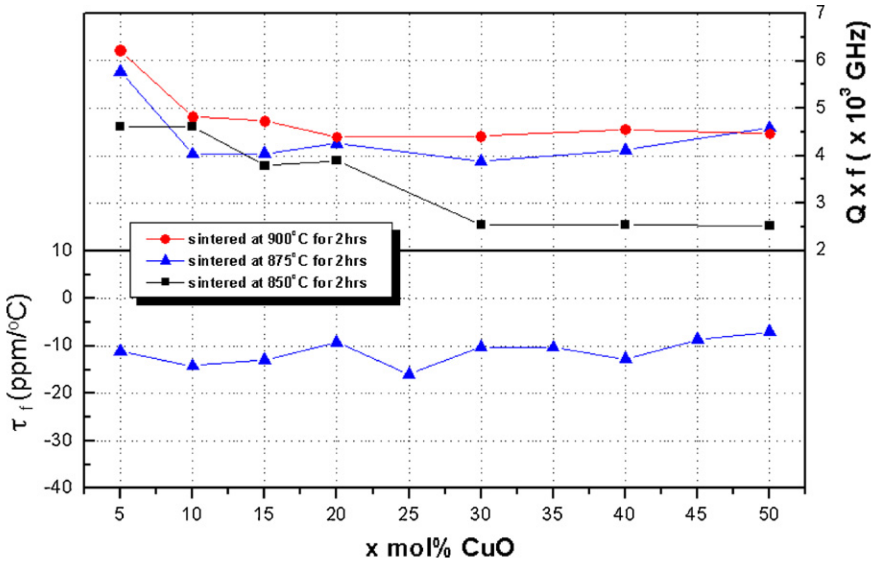

Fig. 8. Variations in the $Q$-value and $\tau_f$ value of the $BaSm_2Ti_4O_{12}$ + 10.0 mol% $B_2O_3$ + $x$CuO ceramics where $5.0 \leq x \leq 50.0$ mol% as a function of the sintering temperature and CuO content.

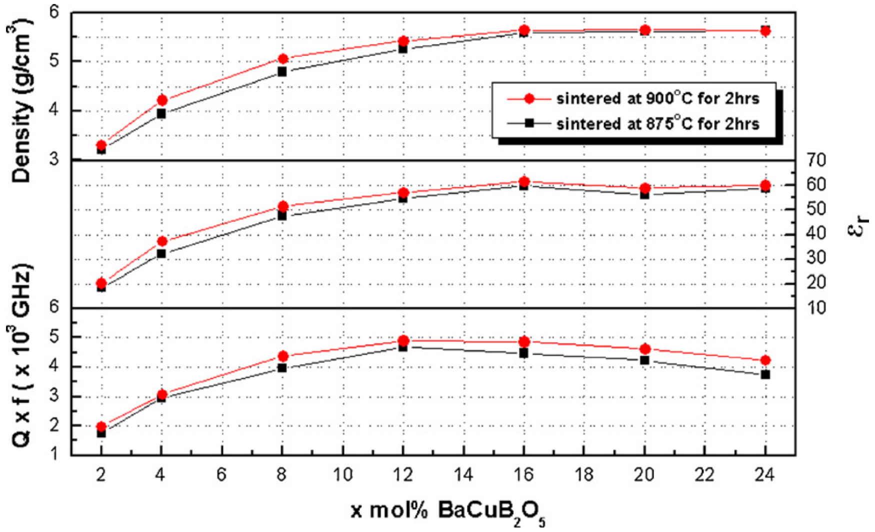

Fig. 9. Variations in the absolute density, $\varepsilon_r$ value and $Q$-value of the BaCu($B_2O_5$) added $BaSm_2Ti_4O_{12}$ ceramics sintered at various temperatures for 2 h.

## 4. Conclusions

The $B_2O_3$ added $BaSm_2Ti_4O_{12}$ ceramics were not able to be sintered below 1000 °C. However, when both $B_2O_3$ and CuO were added, the $BaSm_2Ti_4O_{12}$ ceramics were sintered even at 850 °C. It is suggested that the BaCu($B_2O_5$) phase existed as the liquid phase during the sintering process, and assisted in the densification of the $BaSm_2Ti_4O_{12}$. However, it is possible that the liquid phase can have the composition other than BaCu($B_2O_5$). The $\varepsilon_r$ value and $Q$-value increased with the addition of a small amount of CuO. Good microwave dielectric properties of $\varepsilon_r = 61.47$, $Q \times f = 4256$ GHz and $\tau_f = -9.25$ ppm/°C were obtained for the $BaSm_2Ti_4O_{12}$ + 10.0 mol% $B_2O_3$ + 20.0 mol% CuO ceramics sintered at 875 °C for 2 h.

## 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. Okawa, T., *Sumitomo Search*, 1991, **47**, 117.
2. Kawashima, S., Nishida, M., Ueda, I. and Ouchi, H., Dielectric Properties at Microwave Frequencies of the Ceramics in BaO–$Sm_2O_3$–$TiO_2$ System, *Presented at the 87th Annual Meeting*, American Ceramic Society, Cincinnati, OH, May 6, 1985 (Electronics Division Paper No. 15-E-85).
3. Ohsato, H., *J. Eur. Ceram. Soc.*, 2001, **21**, 2703–2711.
4. Ohsato, H., Mizuta, M., Ikoma, T., Onogi, Z., Nishigaki, S. and Okuta, T., *J. Ceram. Soc. Jpn.*, 1998, **106**(2), 178–184.
5. Ohsato, H., Nishigaki, S. and Okuda, T., *Jpn. J. Appl. Phys*, 1992, **31**, 3136.
6. Ota, Y., Kakimoto, K., Ohsato, H. and Okawa, T., *J. Eur. Ceram. Soc.*, 2004, **24**, 1755–1760.
7. Hu, M. Z., Zhou, D. X., Gu, H., Wang, H., Zhang, T. and Zhou, B., *Mater. Sci. Eng. B*, 2005, **117**, 199–204.
8. Dernovsek, O., Naeini, A., Preu, G., Wersing, W., Eberstein, M. and Schiller, W. A., *J. Eur. Ceram. Soc.*, 2001, **21**, 1693.
9. Cheng, C. C., Hsieh, T. E. and Lin, I. N., *J. Eur. Ceram. Soc.*, 2003, **23**, 2553.
10. Cho, I. S., Kim, D. W., Kim, J. R. and Hong, K. S., *Ceram. Int.*, 2004, **30**, 1181–1185.
11. Kim, M. H., Nahm, S., Lee, W. S., Yoo, M. J., Kang, N. K., Kim, H. T. *et al.*, *Jpn. J. Appl. Phys.*, 2005, **44**, 3091–3094.
12. Kim, M. H., Jeong, Y. H., Nahm, S., Kim, H. T. and Lee, H. J., *J. Eur. Ceram. Soc.*, 2006, **26**, 2139–2142.
13. Hakki, B. W. and Coleman, P. D., *IEEE Trans. Microwave Theor. Tech.*, 1960, **8**, 402.
14. Courtney, W. E., *IEEE Trans. Microwave Theor. Tech.*, 1970, **18**, 476.
15. Levin, E. M. and McMurdie, H. F., *J. Res. Natl. Bur. Stand.*, 1949, **42**, 131.
16. Shuster, N. S., Zeinalova, Kh. L. K., Zargarova, M. I. and Zh. Neorg, *Khim.*, 1982, **27**(7), 1837–1841;
    Shuster, N. S., Zeinalova, Kh. L. K., Zargarova, M. I. and Zh. Neorg, *Russ. J. Inorg. Chem.* (Engl. Transl.), 1982, **27**(7), 1037–1040.