

Effect of B₂O₃ and CuO on the sintering temperature and microwave dielectric properties of the BaTi₄O₉ ceramics

Jong-Bong Lim · Sahn Nahm · Hyo-Tae Kim ·
Jong-Hee Kim · Jong-Hoo Paik · Hwack-Joo Lee

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Abstract The effect of B₂O₃ and CuO on the sintering temperature and microwave dielectric properties of BaTi₄O₉ ceramics was investigated. The BaTi₄O₉ ceramics were able to be sintered at 975°C when B₂O₃ was added. This decrease in the sintering temperature of the BaTi₄O₉ ceramics upon the addition of B₂O₃ is attributed to the formation of BaB₂O₄ second phase whose melting temperature is around 900°C. The B₂O₃ added BaTi₄O₉ ceramics alone were not sintered below 975°C, but were sintered at 875°C when CuO was added. The formation of BaCu(B₂O₅) second phase could be responsible for the decrease in the sintering temperature of the CuO and B₂O₃ added BaTi₄O₉ ceramics. The BaTi₄O₉ ceramics containing 2.0 mol% B₂O₃ and 5.0 mol% CuO sintered at 900°C for 2 h have good microwave dielectric properties of $\epsilon_r = 36.3$, $Q \times f = 30,500$ GHz and $\tau_f = 28.1$ ppm/°C

Keywords BaTi₄O₉ · BaCu(B₂O₅) · Electronic materials · Dielectric properties · Microstructure

J.-B. Lim · S. Nahm (✉)
Department of Materials Science and Engineering, Korea
University, 1-5 Ka, Anam Dong, Sungbuk-Ku, Seoul 136-701,
Korea
e-mail: snahm@korea.ac.kr

H.-T. Kim · J.-H. Kim · J.-H. Paik
Korea Institute of Ceramic Engineering and Technology, 233-5,
Gasan-Dong, Gueumcheon-Gu, Seoul 153-801, Korea

H.-J. Lee
New Materials Evaluation Center, Korea Research Institute of
Standards and Science, Daeduk Science Town, Taejon 305-600,
Korea

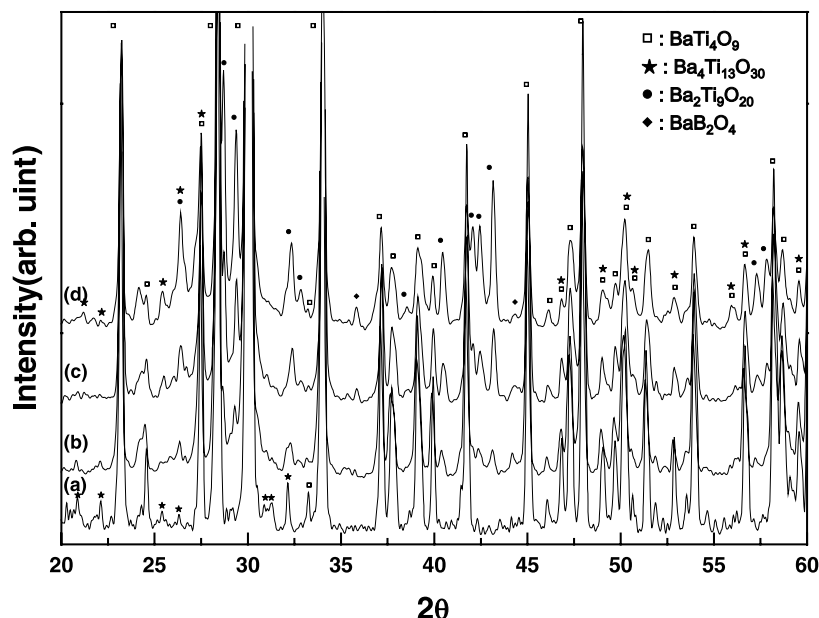
1 Introduction

The miniaturization and hybridization of microwave dielectric components are required for the development of mobile telecommunication system and multi-layer devices have been extensively investigated 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 a 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 microwave dielectric ceramics is generally above 1400°C. Therefore, for the fabrication of multi-layer devices, it is important to develop microwave dielectric ceramics with a low sintering temperature, which can be co-fired with Ag.

The BaTi₄O₉ phase was first reported by Rase and Roy [2] and the crystal structure of this phase was identified as orthorhombic with lattice parameters of $a = 1.453$ nm, $b = 0.379$ nm and $c = 0.629$ nm [3]. BaTi₄O₉ ceramics show good microwave dielectric properties of $Q = 2500$ – 5000 at 4–10 GHz, $\epsilon_r = 36$ – 39 and a τ_f of <20 ppm/°C, however, their sintering temperature is relatively high [4, 5]. Therefore, it is necessary to decrease their sintering temperature in order to use them in LTCCs. In previous studies, the sintering temperature of BaTi₄O₉ ceramics was reduced to 1200°C with the addition of MgO-CaO-SiO₂-Al₂O₃ or ZnO-B₂O₃ glass [6, 7]. However, this sintering temperature is still too high for Ag metal to be used as an electrode. Recently, it was reported that BaTi₄O₉ ceramics containing Zn-B-O glass were sintered at 900°C [8]. However, the microwave dielectric properties of these ceramics were not satisfactory.

In previous studies, the addition of a small amount of B₂O₃ and CuO was found to reduce the sintering temperature of Ba(Zn_{1/3}Ta_{2/3})O₃, Ba(Zn_{1/3}Nb_{2/3})O₃

Fig. 1 X-ray diffraction patterns of (a) BaTi_4O_9 ceramics calcined at 1100°C for 3 h, and the BaTi_4O_9 ceramics containing x mol% of B_2O_3 with $2.0 \leq x \leq 15.0$ mol% sintered at 975°C for 2 h: (b) $x = 2.0$, (c) $x = 10.0$ and (d) $x = 15.0$



and $\text{Ba}(\text{Mg}_{1/3}\text{Mn}_{2/3})\text{O}_3$ ceramics to below 900°C [9–11]. Therefore, it is also possible that these B_2O_3 and CuO additives would be effective in decreasing the sintering temperature of BaTi_4O_9 ceramics. In this work, small amounts of B_2O_3 and CuO additives were used to decrease the sintering temperature of BaTi_4O_9 ceramics and the variations of the microwave dielectric properties were investigated in terms of the microstructure.

2 Experimental procedure

BaCO_3 (High purity Chemicals, >99%, Japan) and TiO_2 (High purity Chemicals, >99%, Japan) were mixed in a nylon jar with zirconia balls for 24h, and then dried and calcined at 1100°C for 3 h. After remilling with B_2O_3 (High purity Chemicals, >99%, Japan) and CuO (High purity Chemicals, >99%, Japan) additives, the powder was dried and pressed into discs and sintered at 875 – 1000°C for 2 h. The microstructure of the specimens was studied using X-ray diffraction (XRD: Rigaku D/max-RC, Japan) and scanning electron microscopy (SEM: Hitach S-4300, 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 [13, 14]. The temperature coefficients of the resonant frequency were measured at 6.5 GHz in the temperature range of 25°C to 80°C .

3 Results and discussion

Figure 1(a) shows the X-ray diffraction patterns of the BaTi_4O_9 powder calcined at 1100°C for 3 h. Most of the

peaks were indexed as those of the orthorhombic BaTi_4O_9 phase. Peaks for the $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ second phase indicated by asterisks were also observed in the calcined BaTi_4O_9 specimen. Since the $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ second phase always exists as a low temperature phase in the BaTi_4O_9 phase formed below 1200°C , it was very difficult to avoid the formation of the $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ second phase completely. Figures 1(b)–(d) show the X-ray diffraction patterns of the BaTi_4O_9 ceramics containing x mol% of B_2O_3 with $2.0 \leq x \leq 15.0$ mol% sintered at 975°C for 2 h. When B_2O_3 was added to the BaTi_4O_9 ceramics, BaB_2O_4 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ second phases were formed and their amount increased with increasing B_2O_3 content. According to the phase diagram, the eutectic temperature of BaB_2O_4 is approximately 899°C [15]. Therefore, it can be inferred that the BaB_2O_4 phase existed as the liquid phase during the sintering and assisted in the densification of the BaTi_4O_9 ceramics. On the other hand, when B_2O_3 was added, the amount of the BaTi_4O_9 phase and the $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ second phase slightly decreased. Therefore, it is considered that some of the BaTi_4O_9 and $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ phases reacted with the B_2O_3 , resulting in the formation of the BaB_2O_4 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ second phases.

Figures 2(a) and (b) show the SEM images of the BaTi_4O_9 ceramics containing x mol% of B_2O_3 with $x = 2.0$ and $x = 10.0$ sintered at 975°C , respectively. For the specimen with $x = 2.0$, a homogeneous and dense microstructure developed. However, for the specimen with $x = 10.0$, a porous microstructure was formed. As the B_2O_3 content increased, the amount of liquid phase increased and some of it could have evaporated during the sintering. Therefore, the porous microstructure formed in the specimens with a large amount of B_2O_3 is attributed to the evaporation of the liquid phase during the sintering process.

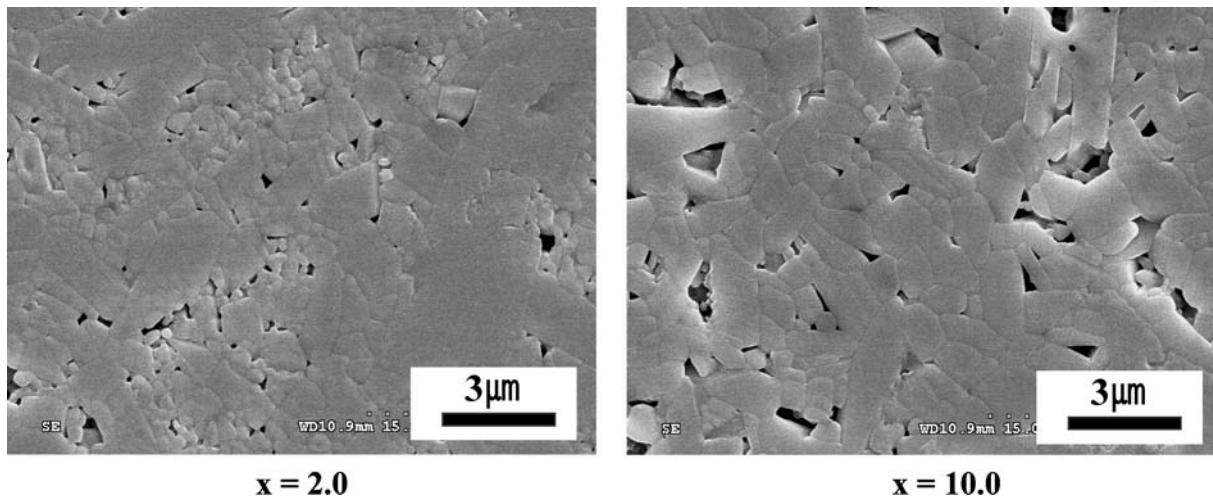


Fig. 2 SEM images of the BaTi₄O₉ ceramics containing x mol% of B₂O₃ with (a) x = 2.0 and (b) x = 10.0 sintered at 975°C

Figure 3 show the variations in the relative density, ϵ_r and $Q \times f$ value of the B₂O₃ added BaTi₄O₉ ceramics sintered at 975°C for 2 h. The relative density of the specimen with 2.0 mol% of B₂O₃ was approximately 87% of the theoretical density and decreased with increasing B₂O₃ content. This decrease in the density is attributed to the development of the porous microstructure. The ϵ_r and $Q \times f$ value also decreased with increasing B₂O₃ content. The variations in the ϵ_r and $Q \times f$ value are similar to that of the relative density. Therefore, the decrease in the dielectric properties could be explained by the decrease in the density. In addition, since the relative density of the specimen was lower than 90%, many pores could have developed which might also have contributed to the reduction in the microwave dielectric properties of the specimen. The B₂O₃ added BaTi₄O₉ ceramic was not able to be sintered below 975°C and, thus, it would be difficult to use Ag as the electrode for these B₂O₃ added BaTi₄O₉ ceramics. Therefore, both CuO and B₂O₃ were added to the BaTi₄O₉ ceramics, in an attempt to reduce the sintering temperature below 975°C.

When CuO was added to the BaTi₄O₉ ceramics containing 2.0 mol% B₂O₃, they were able to be sintered at temperatures as low as 875°C. Figure 4 shows the X-ray diffraction patterns of the BaTi₄O₉ ceramics containing 2.0 mol% of B₂O₃ and x mol% of CuO with 2.0 ≤ x ≤ 15.0 mol% sintered at 900°C for 2 h. Peaks for the Ba₂Ti₉O₂₀, BaB₄O₇ and CuO second phases were observed in all of the specimens. The intensity of the peaks for the Ba₄Ti₁₃O₃₀ second phase increased with increasing CuO content. The melting temperature of the BaB₄O₇ second phase is approximately 900°C, which is similar to that of the BaB₂O₄ second phase, thus the presence of the BaB₄O₇ second phase cannot explain the observed decrease in the sintering temperature of the BaTi₄O₉ ceramics to below 900°C. Moreover, it cannot be the CuO additive itself which causes the sintering temperature of the BaTi₄O₉ ceramics to drop below 900°C, because the CuO

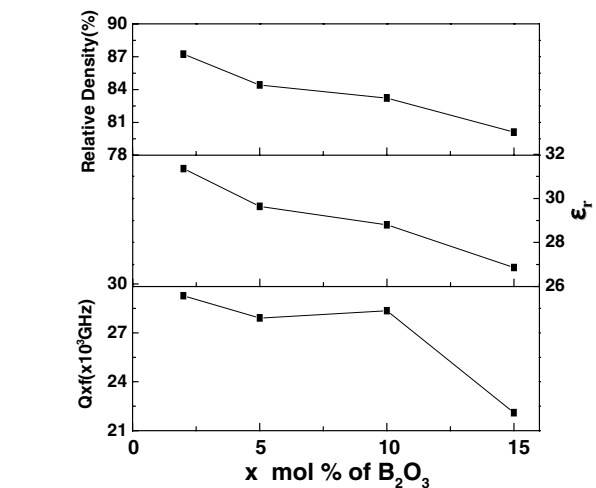


Fig. 3 Variations of the relative density, ϵ_r and $Q \times f$ value of the BaTi₄O₉ ceramics containing x mol% of B₂O₃ with 2.0 ≤ x ≤ 15.0 mol% sintered at 975°C for 2 h

added BaTi₄O₉ ceramics were not sintered below 950°C. In a previous work, it was reported that BaCu(B₂O₅) second phase, which melts above 800°C, existed in the CuO and B₂O₃ added Ba(Zn_{1/3}Nb_{2/3})O₃ ceramics and assisted in the densification of the specimens at low temperature [10]. In the case of the BaTi₄O₉ ceramics, however, it was difficult to identify the presence of the BaCu(B₂O₅) second phase, because the main X-ray peak for the BaCu(B₂O₅) second phase overlapped with that of Ba₂Ti₉O₂₀. To clarify the effect of the BaCu(B₂O₅) phase on the sintering temperature of the BaTi₄O₉ ceramics, we made BaCu(B₂O₅) powder at 700°C. When this BaCu(B₂O₅) was added, the BaTi₄O₉ ceramics were well sintered even at 850°C and had excellent microwave dielectric properties [12]. Therefore, it is considered that the BaCu(B₂O₅) second phase is responsible for the densification of the CuO and B₂O₃ added BaTi₄O₉ ceramics at low temperature.

Fig. 4 X-ray diffraction patterns of the BaTi_4O_9 ceramics containing 2.0 mol% of B_2O_3 and x mol% of CuO with $2.0 \leq x \leq 15.0$ mol% sintered at 900°C for 2 h

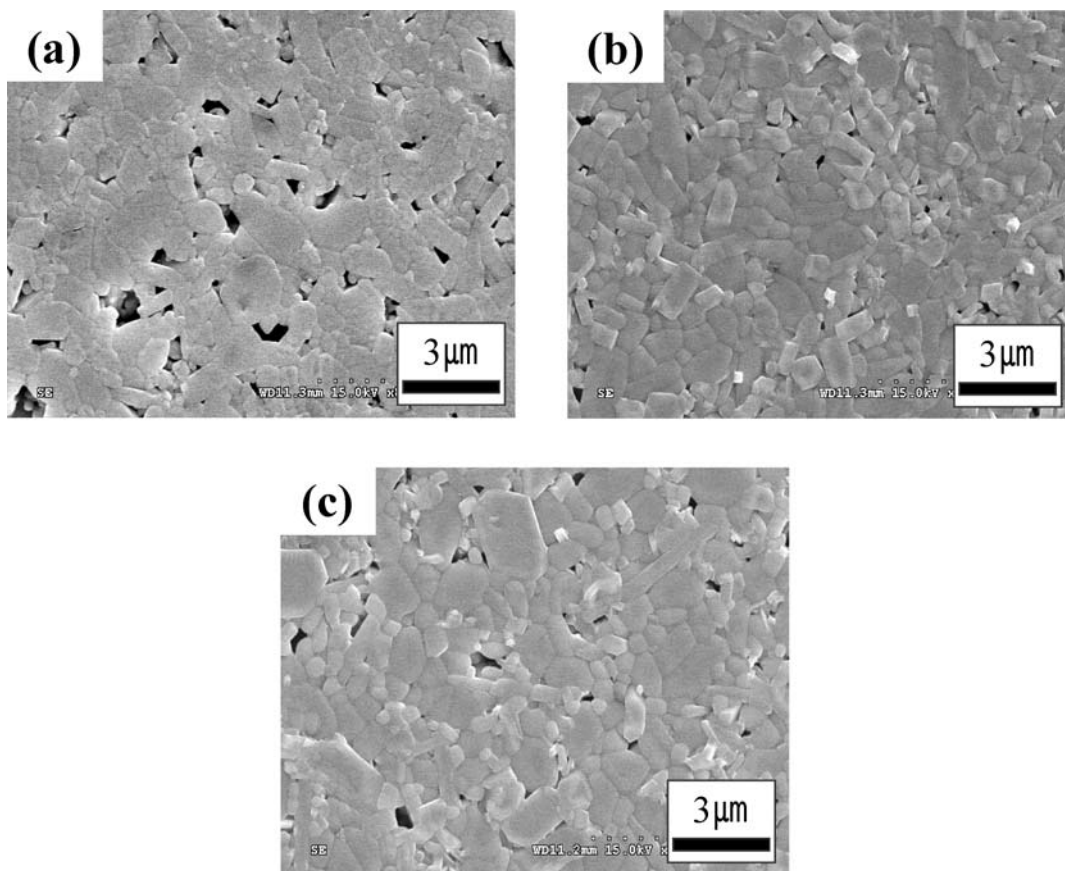
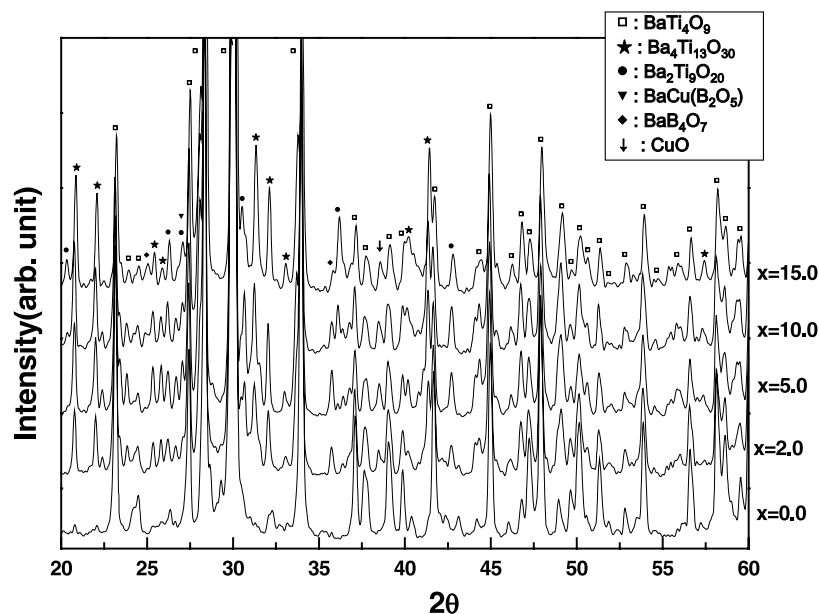


Fig. 5 SEM images of the fracture surface of the BaTi_4O_9 ceramics containing 2.0 mol% of B_2O_3 and x mol% of CuO with (a) $x = 2.0$, (b) $x = 5.0$ and (c) $x = 15.0$ mol% sintered at 900°C for 2 h

Figures 5(a)–(c) show the SEM images of the thermally etched surfaces of the BaTi_4O_9 ceramics containing 2.0 mol% of B_2O_3 and x mol% of CuO with $2.0 \leq x \leq 15.0$ mol% sintered at 900°C for 2 h. For the specimen

containing 2.0 mol% of CuO , a porous microstructure was formed. However, when 5.0 mol% CuO was added, a dense microstructure developed. Therefore, the densification occurred when x exceeded 2.0 mol%.

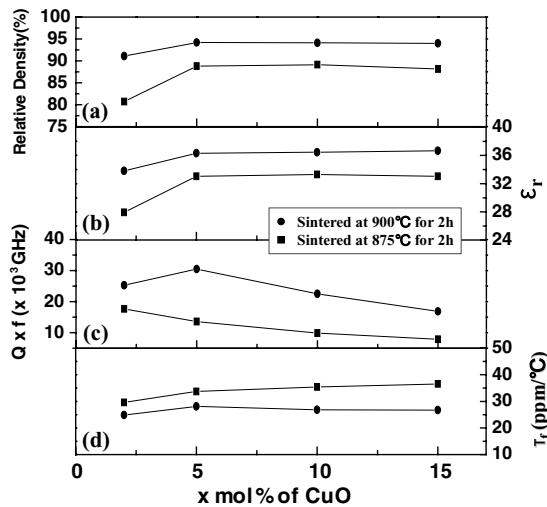


Fig. 6 Variations of the relative density and the dielectric properties of the BaTi_4O_9 ceramics containing 2.0 mol% of B_2O_3 and x mol% of CuO with $2.0 \leq x \leq 15.0$ mol% sintered at various temperatures for 2 h

Figures 6(a) and (b) show the variations in the relative density and the ϵ_r value of the BaTi_4O_9 ceramics containing 2.0 mol% of B_2O_3 and x mol% of CuO with $2.0 \leq x \leq 15.0$ mol% sintered at various temperatures. The relative density of the specimens sintered at 900°C was comparatively low when a small amount of CuO was added, i.e. approximately 91% of the theoretical density, but it increased considerably when x exceeded 2.0 mol%. The variation in the relative density is closely related to the microstructure, as shown in Figures 5(a)–(c). A similar result was also obtained for the specimens sintered at 875°C , although the relative density of all these specimens is low. The variation of the ϵ_r is shown in Fig. 6(b). For the specimens sintered at 900°C , 5.0 mol% of CuO was sufficient to obtain a high ϵ_r value of 36, and this value was slightly increased with the addition of CuO. In addition, the variation in the ϵ_r is similar to that of the density and, thus, it can be concluded that the density is the most important factor contributing to the improvement of the ϵ_r value of the specimen. Figure 6(c) shows the variation in the Q -value of the specimens. For the specimen sintered at 900°C , the Q -value of the specimens increased with the addition of CuO and showed a maximum value of 30,500 GHz when $x = 5.0$ mol%. The increase in the Q -value with the addition of a small amount of CuO is attributed to the increase in the density. However, the Q -value decreased when x exceeded 5.0 mol%. According to the X-ray diffraction pattern, the amount of $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ second phase, whose Q -value is low approximately 8138 GHz, increased with increasing CuO content. Therefore, the decrease in the Q -value is due

to the increasing amount of $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ second phase. The τ_f of the B_2O_3 added BaTi_4O_9 ceramics sintered at 900°C is about 25 ppm/°C and slightly increased with the addition of CuO, as shown in Fig. 6(d). The τ_f of the $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ ceramics is 51.3 ppm/°C. Therefore, the increase in the τ_f could be due to the presence of the $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ second phase.

4 Conclusions

The B_2O_3 added BaTi_4O_9 ceramics were not able to be sintered below 975°C . However, when B_2O_3 and CuO were added, the BaTi_4O_9 ceramics were sintered even at 875°C . It is suggested that the $\text{BaCu}(\text{B}_2\text{O}_5)$ phase existed as the liquid phase during the sintering and assisted in the densification of the specimens. The ϵ_r and the Q -value increased with the addition of a small amount of CuO. The BaTi_4O_9 ceramics containing 2.0 mol% B_2O_3 and 5.0 mol% CuO sintered at 900°C for 2 h had good microwave dielectric properties of $\epsilon_r = 36.3$, $Q \times f = 30,500$ GHz and $\tau_f = 28.1$ ppm/°C.

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