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Effect of B_2O_3 on the microstructure and microwave dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics

Beom-Jong Kim [a], Min-Han Kim [a], Sahn Nahm [a,*], Hyo-Tae Kim [b], Jong-Hee Kim [b], Jong-Hoo Paik [b], Hyun Ryu [c], Hwack-Joo Lee [c]

[a] *Department of Materials and Engineering, Korea University, 1-5 Ka, Anam Dong, Sung-buk-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*

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Abstract

$Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) ceramics have excellent microwave dielectric properties, but they are difficult to sinter because of their high sintering temperature of 1650 °C. However, in this study the addition of B_2O_3 to BMT ceramics enabled sintering to be performed at temperatures as low as 1300 °C. The BaB_4O_7 phase, which melts at approximately 900 °C, may have been responsible for the decrease of the sintering temperature. The presence of $Ba_3Ta_5O_{15}$ second phase was observed in the BMT ceramics containing a large amount of B_2O_3. The relative density and dielectric constant (ε_r) were considerably increased with the addition of a small amount of B_2O_3. The Q-value was also increased when a small amount of B_2O_3 was added, but was decreased when the B_2O_3 content exceeded 0.5 mol%. The decrease of $Q \times f$ was explained by the presence of the $Ba_3Ta_5O_{15}$ second phase. Excellent microwave dielectric properties of $Q \times f = 195{,}000$ GHz, $\varepsilon_r = 24$ and $\tau_f = 4.74$ ppm/°C were obtained by adding 0.5 mol% B_2O_3 to BMT ceramic and sintering at 1500 °C for 6 h.

Keywords: Dielectric properties; Perovskites; Sintering; Powders-solid state reaction

1. Introduction

For the application of dielectric ceramics to microwave devices, a high dielectric constant (ε_r), a high Q-value and a near-zero temperature coefficient (τ_f) are required.[1,2] $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) ceramics are known to have a high ε_r, a high Q-value, and a small τ_f. However, the sintering temperature of BMT ceramic is very high at above 1650 °C with a long sintering time, which makes it very difficult to sinter BMT ceramics. Many investigations have been carried out to reduce the sintering temperature and the sintering time of BMT ceramics without deteriorating their microwave dielectric properties. $BaSnO_3$-added BMT ceramics exhibited good microwave dielectric properties, but the sintering temperature remained high at about 1640 °C.[2] In the case of $BaWO_4$-added BMT ceramics, the sintering temperature was still high at approximately 1600 °C and the microwave dielectric properties were not improved.[3] BMT ceramics were also produced by a two-step process in which they were sintered at 1550 °C for 4 h, but the microwave dielectric properties were not satisfactory.[4] Fang et al. controlled the calcination process to improve the sinterability of the BMT ceramics but the resulting microwave dielectric properties of the BMT ceramics were poor.[5]

On the other hand, B_2O_3 is recognized as a good additive, which is able to reduce the sintering temperature of the ceramics. Previously, we reported that the addition of B_2O_3 decreased the sintering temperature of $Ba(Mg_{1/3}Nb_{2/3})O_3$, $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics.[6–8] Therefore, it is also possible that the addition of B_2O_3 would be effective in decreasing the sintering temperature of BMT ceramics. In this study, a small amount of B_2O_3 was added to reduce the sintering temperature of BMT ceramics while maintaining their good microwave dielectric properties. Furthermore, the variations of the microwave dielectric properties were investigated in terms of the microstructural changes.

2. Experimental procedure

BMT + xB_2O_3 ceramics with $0.0 \leq x \leq 20.0$ mol% were prepared by conventional solid-state synthesis. Oxide compounds

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

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of $BaCO_3$ (Kojundo Chemical, 99.95% purity), MgO (Kojundo Chemical, 99.95% purity) and Ta_2O_5 (Kojundo Chemical, 99.95% purity) were mixed for 24 h in a nylon jar with zirconia balls, then dried and calcined at 1200 °C for 3 h. After calcination, B_2O_3 (Junsei Chemical Co., Tokyo, Japan, ≥95% purity) and BaB_4O_7 additives were added and remilled for 24 h. The remilled B_2O_3- or BaB_4O_7-added BMT powders were ground and pressed into discs with a diameter of 10 mm. The green bodies were sintered at 1300–1650 °C for 6 h. $Ba_3Ta_5O_{15.5}$ ceramics were also produced by the same the processes and their calcination and sintering temperatures were 1000 and 1350 °C, respectively. The microstructures of the specimens were 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). Energy dispersive X-ray spectroscopy (EDS: Horiba EX-200, Japan) was used to analyze the composition of the specimen and Horiba software was used for the quantitative analysis of the composition of the specimen. The densities of the sintered specimens were measured by a water-immersion technique. The dielectric properties in the microwave frequency range were measured by the dielectric post resonator technique suggested by Hakki–Coleman and Courtney.[9,10] The τ_f value was measured in the range from 25 to 85 °C.

3. Results and discussion

Fig. 1 shows the SEM image of the fractured surface of the BMT + xB_2O_3 ceramics with $0.0 \leq x \leq 20.0$ mol% sintered at 1500 °C for 6 h. The BMT ceramics without B_2O_3 were not sintered at 1500 °C as shown in Fig. 1(a). When 0.5 mol% of B_2O_3 was added, a homogeneous and dense microstructure developed with an average grain size of 0.8–1.0 μm. When a large amount (≥5 mol%) of B_2O_3 was added, grain growth occurred, the microstructure became porous, and a rod-shaped second phase was formed indicated by arrow in Fig. 1(d). In order to identify the composition of the rod-shaped second phase, an energy dispersive spectroscopy (EDS) analysis was conducted on the second phase formed in the 20.0 mol% B_2O_3-added BMT ceramics, as shown in Fig. 2. High concentrations of Ba and Ta were detected and a small amount of Mg ion was also found in the rod-shaped second phase. Therefore, the rod-shaped second phase was considered to be a phase rich in Ba and Ta. According to the quantitative analysis shown in Table 1, the ratio of Ba to Ta was 0.6, which suggested that the rod-shaped second phase could be a $Ba_3Ta_5O_{15.5}$ phase and this phase was also detected

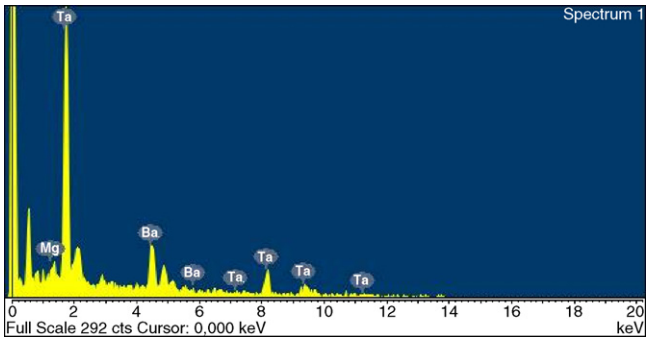

Fig. 2. EDS spectrum of the rod-shaped second phase formed in the 20.0 mol% B_2O_3-added BMT ceramics.

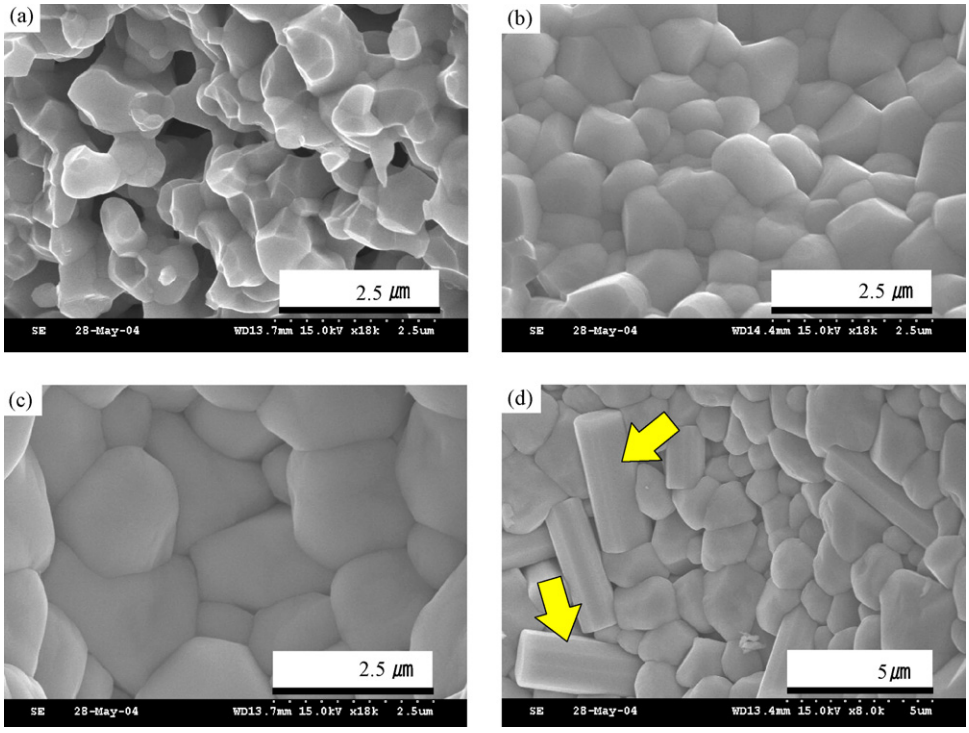

Fig. 1. SEM image of the fractured surface of the BMT + xB_2O_3 ceramics with $0.0 \leq x \leq 20.0$ mol% sintered at 1500 °C for 6 h: (a) $x = 0.0$ mol%, (b) $x = 0.5$ mol%, (c) $x = 10.0$ mol% and (d) $x = 20.0$ mol%.

Table 1
Quantitative analysis of the rod-shaped second phase formed in 20.0 mol% B_2O_3-added BMT ceramics sintered at 1500°C for 6 h

Element	Wt.%	At.%
Mg K	0.60	3.95
Ba L	29.96	34.81
Ta M	69.44	61.24
Total	100.00	100.00

in the X-ray diffraction pattern. In addition, since the Mg ion was detected in the rod-shaped second phase, the $Ba_3Ta_5O_{15.5}$ second phase contains a small amount of Mg ions and the explanation for its presence is given below.

Fig. 3(a–c) shows the X-ray diffraction patterns of the BMT + xB_2O_3 ceramics with $0.0 \leq x \leq 20.0$ mol% sintered at 1500 °C for 6 h. All of the peaks were indexed in terms of the 1:2 ordered hexagonal unit cell. For the specimens with $x = 0.5$ mol%, BMT peaks without a second phase were found, indicating the presence of a homogeneous BMT phase. Moreover, since the 1:2 ordering peak was present in the specimen with 20.0 mol% B_2O_3, BMT ceramics maintained the 1:2 ordered hexagonal structure even though a large amount of B_2O_3 was added. When x exceeded 0.5 mol%, however, peaks for the $Ba_3Ta_5O_{15.5}$ phase appeared as indicated by the asterisks in Fig. 3. Peaks for the other second phase were not observed in the BMT ceramics with a large amount of B_2O_3. It is generally accepted that the sintering temperature of BMT ceramics is very high at approximately 1650 °C, thus making them difficult to sinter. However, when B_2O_3 was added, the BMT ceramic was well sintered even at 1300 °C. According to our previous study, in which B_2O_3 was added to $Ba(Mg_{1/3}Nb_{2/3})O_3$ ceramics, the BaO–B_2O_3 second phase existed as a liquid phase during the sintering and assisted the densification of the $Ba(Mg_{1/3}Nb_{2/3})O_3$ ceramics.[6] A similar result was also observed when B_2O_3 was added to $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba(Zn_{1/3}Nb_{2/3})O_3$ and $Ba_5Nb_4O_{15}$ ceramics.[7,8,11] Therefore, it is considered that a second phase

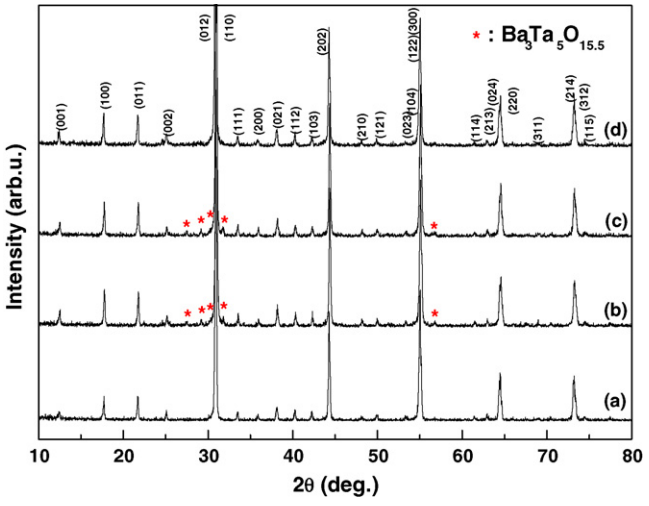

Fig. 3. X-ray diffraction patterns of the BMT + xB_2O_3 ceramics with (a) $x = 0.5$ mol%, (b) $x = 5.0$ mol%, (c) $x = 20.0$ mol% and (d) BMT + 20.0 mol% BaB_4O_7 sintered at 1500 °C for 6 h.

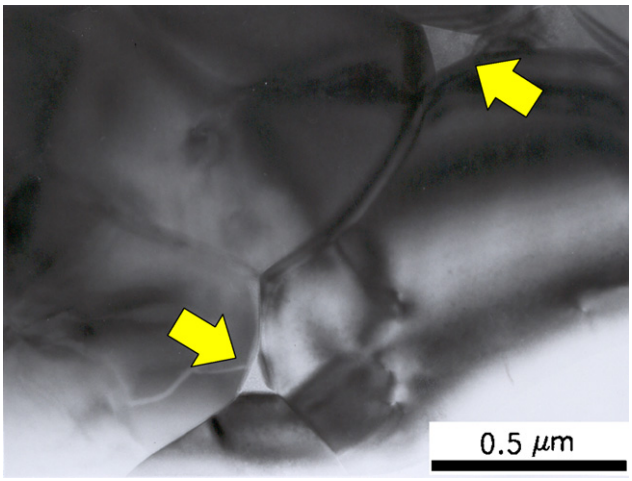

Fig. 4. TEM bright field image of the 20.0 mol% B_2O_3-added BMT ceramics sintered at 1300 °C for 6 h.

containing BaO and B_2O_3 formed when B_2O_3 was added and this facilitated the sintering of the BMT ceramics.

A TEM analysis was conducted to identify the liquid phase formed in the B_2O_3-added BMT ceramics. Fig. 4 shows the TEM bright field image of the 20.0 mol% B_2O_3-added BMT ceramics sintered at 1300 °C. The liquid phase indicated by the arrow was found at the triple point. Therefore, the densification of the BMT ceramics at low temperatures was attributed to the presence of the BaO–B_2O_3 liquid phase. Moreover, when a BaB_4O_7 additive was added to the BMT ceramics, they were well sintered at 1300 °C and the $Ba_3Ta_5O_{15.5}$ second phase, which appeared in the B_2O_3-added BMT ceramics, was not observed, as shown in Fig. 3(d). Therefore, it can be inferred that when B_2O_3 was added to the BMT ceramics, the B^{3+} ion reacted with the Ba^{2+} ion in the BMT ceramics and the BaB_4O_7 and $Ba_3Ta_5O_{15.5}$ second phases were formed through the reaction shown below. Furthermore, BaB_4O_7 existed as a liquid phase during the sintering and assisted the densification of the BMT ceramics at low temperature:

$$\mathrm{BMT} + 2xB_2O_3 \rightarrow xBaB_4O_7 + (3-5x)/8\,Ba_3Ta_5O_{15.5} + (5-3x)/24\,\mathrm{BMT} + (19+3x)/24\,\mathrm{MgO}$$

However, since the BaB_2O_4 phase was also observed in the B_2O_3 added BMN ceramics, we cannot exclude the possibility of the formation of BaB_2O_4 second phase or other BaO–B_2O_3 second phase in the B_2O_3 BMT ceramics. In addition, MgO should be released from the B_2O_3 added BMT phase and therefore would be detected in the XRD patterns. However, no peaks for the MgO phase were found even in the 20 mol% B_2O_3 added BMT ceramics. On the other hand, the Mg^{2+} ion was detected in the rod-shaped $Ba_3Ta_5O_{15.5}$ second phase and, thus, a small amount of the Mg^{2+} ions must have existed in the $Ba_3Ta_5O_{15.5}$ second phase. It is also possible that the Mg^{2+} ions were incorporated into the liquid phase. Recently, it was reported that the cation non-stoichiometry exists in BMT.[12] Therefore, it is possible that the BMT phase contains the excess Mg^{2+} ions when a large amount of B_2O_3 was added.

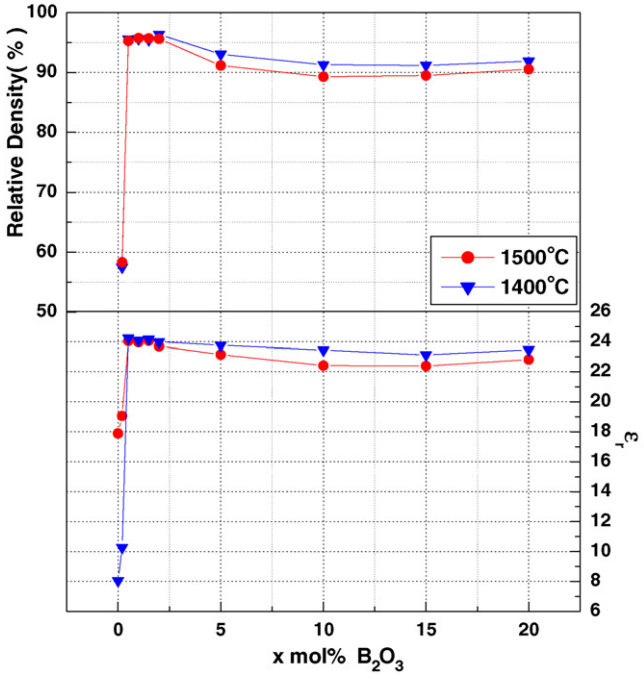

Fig. 5. Relative density and ε_r of the B_2O_3-added BMT ceramics sintered at various temperatures for 6 h.

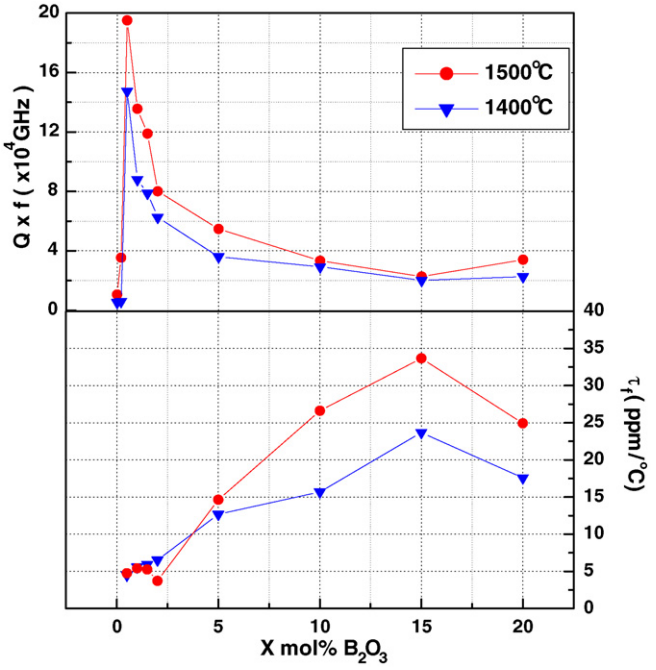

Fig. 6. Variations of the Q-value and τ_f of the B_2O_3-added BMT ceramics as a function of the B_2O_3 content.

Fig. 5 shows the variation in the relative density of the BMT + xB_2O_3 ceramics as a function of the B_2O_3 content. The relative density considerably increased up to 95% with the addition of a small amount of B_2O_3, but decreased slightly when the B_2O_3 content exceeded 5.0 mol%. The SEM image revealed that the microstructure of the specimens became dense with the addition of a small amount of B_2O_3 but it became porous when a large amount of B_2O_3 was added. Therefore, the variation of the density could be explained by the changes in the microstructure. In addition, it is interesting to note that the relative densities of the specimens sintered at 1500 °C were lower than those of the specimens sintered at 1400 °C when the B_2O_3 content exceeded 2.5 mol%. The evaporation of the BaB_4O_7 liquid phase and the formation of the $Ba_3Ta_5O_{15.5}$ second phase increased with increasing sintering temperature, thereby lowering the relative density for the specimens sintered at higher temperature. The ε_r values of the B_2O_3-added BMT ceramics are also shown in Fig. 5. The ε_r value was increased significantly with the addition of a small amount of B_2O_3 and the BMT ceramic with 0.2 mol% B_2O_3 had a high ε_r value of 24. In addition, the behavior of ε_r was similar to that of the relative density, indicating that the density is the important factor influencing the ε_r value of the specimens.

The variation of the Q-value is illustrated in Fig. 6. The Q-value was increased with the addition of a small amount of B_2O_3 and the maximum $Q \times f$ value of 195,188 GHz was obtained from the BMT ceramic with 0.5 mol% B_2O_3. The increase in the Q-value could be explained by the increase in the relative density. However, the Q-value was decreased when x exceeded 0.5 mol%. According to the X-ray diffraction pattern, the $Ba_3Ta_5O_{15.5}$ second phase existed in the BMT ceramic with a large amount of B_2O_3. We made $Ba_3Ta_5O_{15.5}$ ceramics whose relative density was approximately 94% of the theoretical density and measured their microwave dielectric properties. The $Ba_3Ta_5O_{15.5}$ ceramics have the microwave dielectric properties of $Q \times f = 9681$ GHz, $\varepsilon_r = 54$ and $\tau_f = 124$ ppm/°C. Therefore, the decrease in the $Q \times f$ value was attributed to the presence of the $Ba_3Ta_5O_{15.5}$ second phase. Fig. 6 also shows the τ_f value of the B_2O_3-added BMT specimens. The τ_f value was increased with the addition of B_2O_3 and since that of the $Ba_3Ta_5O_{15.5}$ ceramics was about 124 ppm/°C, this increased τ_f could also be explained by the presence of $Ba_3Ta_5O_{15.5}$. The BMT ceramic with 0.5 mol% B_2O_3, which showed the maximum Q-value, had a low τ_f value of 5.0 ppm/°C.

In order to clarify the effect of the BaB_4O_7 additive on the sintering temperature and the microwave dielectric properties of BMT ceramics, a small amount of BaB_4O_7 was added. Fig. 7 illustrates the variations in the ε_r, $Q \times f$ and τ_f values of the BaB_4O_7-added BMT ceramics. The ε_r value was considerably increased with the addition of a small amount of BaB_4O_7. The Q-value increased when x was less than 1.0 mol% but it decreased when the BaB_4O_7 content further increased. The maximum $Q \times f$ value of 199,500 GHz was obtained for the BMT ceramic with 0.5 mol% BaB_4O_7. The τ_f value of the BaB_4O_7-added BMT ceramics was small and slightly decreased with the addition of B_2O_3. These results suggest that the variations of the ε_r, $Q \times f$ and τ_f values are similar to those of the B_2O_3-added BMT ceramic. Therefore, it can be concluded that the BaB_4O_7 phase assisted the densification and improved the microwave dielectric properties of the B_2O_3 added BMT ceramics sintered at low temperature. Moreover, the BaB_4O_7 can be a good additive to enhance the sinterability and microwave dielectric properties of BMT ceramics. However, more investigation is required for the BaB_4O_7-added BMT ceramics.

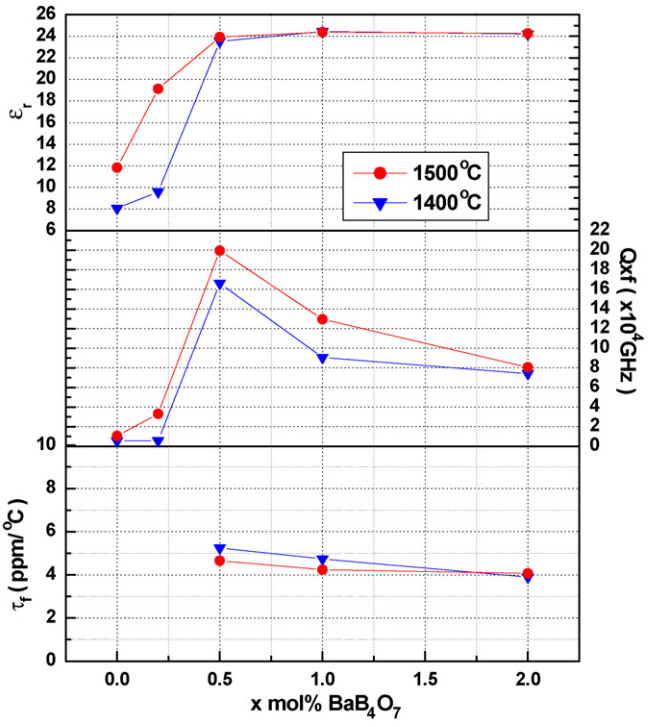

Fig. 7. Variations of ε_r, $Q \times f$ and τ_f of the BaB_4O_7-added BMT ceramics sintered at various temperatures for 6 h.

4. Conclusions

The effects of B_2O_3 on the sintering temperature and microwave dielectric properties of BMT ceramics were investigated. The sintering temperature of BMT ceramics is approximately 1650 °C but the B_2O_3-added BMT ceramics were well sintered even at 1300 °C. The presence BaB_4O_7 second phase may have been responsible for the decrease in the sintering temperature of the BMT ceramics. The ε_r value and Q-value were significantly improved with the addition of a small amount of B_2O_3. Excellent microwave dielectric properties of $\varepsilon_r = 24$, $Q \times f = 195{,}000$ GHz and $\tau_f = 4.74$ ppm/°C were obtained for the 0.5 mol% B_2O_3-added BMT ceramic sintered at 1500 °C for 6 h. A similar result was also obtained for the BaB_4O_7-added BMT ceramic sintered at 1500 °C for 6 h. This indicates that BaB_4O_7 is also a good additive to improve the sinterability of the BMT ceramics.

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