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Ceramics International 28 (2002) 255–260

CERAMICS
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Effect of glass doping for the sinterability of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics

Chien-Min Cheng[a], Yuan-Tai Hsieh[b], Cheng-Fu Yang[c,*]

[a]*Department of Electronic Engineering, Southern Taiwan University of Technology, Yung-Kang City, Tainan, Taiwan, ROC*
[b]*Department of Electronic Engineering, Far East College, Hsin-Shih, Tainan, Taiwan, ROC*
[c]*Department of Electronic Engineering, Chinese Air Force Academy, PO Box 90277-4, Kangshan, Kaohsiung, Taiwan, ROC*

Received 18 December 2000; received in revised form 12 April 2001; accepted 24 September 2001

Abstract

Sintering of undoped $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) ceramics at 1500 °C gives BMT ceramics with 96.0% theoretical density and an ordering structure, but the satellite phases of $Ba_5Ta_4O_{15}$, $Ba_4Ta_2O_9$, $Ba_7Ta_6O_{22}$, and $Mg_4Ta_2O_9$ are difficult to eliminate completely. The addition of MgO–CaO–Al_2O_3–SiO_2 (MCAS) glass as a sintering aid not only decreases the satellite phases of BMT ceramics but also improves the sinterability of BMT ceramics. The densification of the BMT ceramics can be performed well at lower temperatures of 1300–1350 °C. The satellite phases of $Ba(Mg_{1/3}Ta_{2/3})O_3$ powder can almost be eliminated at 1350 °C when 3 wt.% MCAS is used as a sintering aid or at 1300 °C when 6 wt.% MCAS is used as a sintering aid. When the sintering temperature is higher than 1350 °C and the amount of MCAS addition is equal to or more than 3 wt.%, the densities of BMT ceramics decrease with the increase of sintering temperature because of the increase of satellite phases and the melting of MCAS glass.

Keywords: A. Sintering; B. X-ray methods

1. Introduction

A number of complex $A(B_{1/3}C_{2/3})O_3$ (A = Ba, Sr; B = Mg, Zn, Ni; C = Nb, Ta) perovskite compounds had been developed for high dielectric constant ε_r (25–40), high unloaded frequency Q (>3000), and low temperature coefficient of the frequency τ_f (0 ± 40 ppm/°C) [1–5]. Some papers also reported that extremely high Q values (36,000 at 10 GHz) were obtained for perfect $Ba(Mg_{1/3}Ta_{2/3})O_3$ (abbreviated as BMT) ceramics [6]. The usual process of preparing BMT materials by solid-state reaction of $BaCO_3$, MgO, and Ta_2O_5 was not the most appropriate method for the industrial production of ceramic dielectric resonators (DRs) because of the high calcining temperature, long calcining time, and poor sinterability of BMT ceramics [7,8]. The poor sinterability of BMT ceramics was thought to be due to some special satellite phases in the calcined powders. In order to eliminate such satellite phases of $Ba_5Ta_4O_{15}$, $Ba_4Ta_2O_9$, and $Ba_7Ta_6O_{22}$ from calcined BMT, a recalcination process was carried out [8]. However, the satellite phases remained residual in the recalcined BMT powder [8]. Due to the poor sinterability, the sintering temperature of BMT ceramics was higher than 1550 °C. Therefore, it was of increasing importance in the suppression or elimination of the satellite phases and lowering of the sintering temperatures.

Low melting glass additions and chemical processing of starting materials were used to improve the sinterability of the dielectric and reduction of the sintering temperature [6,9,10]. Renoult et al. used the sol-gel method to fabricate the BMT precursor, but 1400 °C for 10 h was needed to sinter the precursor [6]. Chen et al. reported that BMT ceramics had a bulk density of 0.98 theoretical density by adding NaF as a sintering aid [11]. In this paper, $Ba(Mg_{1/3}Ta_{2/3})O_3$ powder calcined at 1200 °C for 3 h was used as the precursor and efforts were made to lower the sintering temperature of BMT ceramics. In the calcined powder, $Ba(Mg_{1/3}Ta_{2/3})O_3$ was main phases, but the initial materials of MgO and Ta_2O_5 and the satellite phases of $Ba_5Ta_4O_{15}$, $Ba_4Ta_2O_9$, and $Ba_7Ta_6O_{22}$ also existed as minor phases. We used MgO–CaO–SiO_2–Al_2O_3 (MCAS) [12] glass powder as a

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* Corresponding author. Fax: +886 = 7 = 6114536.
E-mail address: cfyang@cc.cafa.edu.tw (C.-F. Yang).

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PII: S0272-8842(01)00087-6

sintering aid to improve the sinterability and lower the sintering temperature of BMT ceramics. Relationships among the sintering temperature, the microstructure evolution, and the phase formation of MCAS-fluxed BMT ceramics were presented.

2. Experimental procedures

In the present investigation, a homogeneous glass composition containing (in wt.%) MgO5%, CaO19%, $Al_2O_3$26%, and $SiO_2$50% (approximate stoichiometry $MgO{:}CaO{:}Al_2O_3{:}SiO_2 = 6.5{:}14.5{:}27.5{:}51.5$, abbreviated as MCAS) was prepared by the sol-gel method [12]. After the glass powder was formed in the solided format, the solids were collected by filtration and calcined at 300 °C for 1 h. The calcination step was desirable to decompose any ammonium nitrate present. The resulting material was the MCAS glass precursor.

Proportionate amounts of reagent-grade starting materials of $BaCO_3$, MgO, and Ta_2O_5 were mixed, according to the composition $Ba(Mg_{1/3}Ta_{2/3})O_3$, and ball-milled for 5 h. After drying, the reagent was ground with an agate mortar for 1 h. Then the powder was calcined at 1200 °C for 3 h. The crystal structure of calcined powder was examined by using an X-ray powder diffractometer. X-ray diffraction (XRD) patterns were taken at $2\theta = 4°$ per minute using CuK_α radiation. The calcined powder was used as the BMT precursor and mixed with 0, 1, 3 and 6 wt.% (abbreviated as BMT0, BMT1, BMT3, and BMT6) MCAS glass by ball milling. After drying, the powder was pressed into pellets uniaxially in a steel die. Sintering of these pellets was carried out at a temperature between 1200 and 1500 °C for a duration of 4 h. Crystallization of the MCAS–BMT ceramics was investigated using X-ray diffraction patterns. Densities of the sintered specimens, as a function of sintering temperature, were measured using the Archimedes method. The microstructural observations of the surfaces of sintered samples were directly observed from the SEM (scanning electronic micrograph).

3. Results and discussion

The conventional solid-state-reaction process for synthesizing BMT compounds was commonly based on the following reaction:

$$3BaCO_3 + MgO + Ta_2O_5 - 3Ba(Mg_{1/3}Ta_{2/3})O_3 + 3CO_2 \tag{R1}$$

However, the real solid reaction processes were usually more complex, and various satellite reactions might observe in the calcining and sintering process of BMT oxide system. The $Ba(Mg_{1/3}Ta_{2/3})O_3$ has hexagonal perovskite-typed structure with Mg and Ta showing 1:2 order in B site. If the Mg and Ta are in disorder, the compound will reveal a cubic perovskite-typed structure. As Fig. 1(a) shows, the calcination process leads to the formation of disordering $Ba(Mg_{1/3}Ta_{2/3})O_3$ phase, but the initial phases of MgO and Ta_2O_5 and the satellite phases of $Ba_5Ta_4O_{15}$, $Ba_4Ta_2O_9$, $Ba_7Ta_6O_{22}$, and $Mg_4Ta_2O_9$ are detected as the minor phase. As 1400 °C is used as sintering temperature, the initial phases consume and the satellite phases decrease, and the peaks for the ordering $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics are revealed in Fig. 1(b). Comparing the results shown in Fig. 1(b)–(c), the ceramics sintered at 1400 and at 1450 °C show largely different results. The 1450 °C-sintered $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics reveal an apparently ordering structure. Except the ordering structure of the $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics, satellite phases of $Ba_5Ta_4O_{15}$, $Ba_4Ta_2O_9$, $Ba_7Ta_6O_{22}$, and $Mg_4Ta_2O_9$ are still residual. Even 1500 °C is used as the sintering temperature, as Fig. 1(d) shows, the $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics reveal a more ordering structure and the intensities of satellite phases decrease but still residual.

The MCAS glass ceramics existed the anorthite and cordierite as two main crystalline phases [12]. The XRD patterns from the as-sintered surfaces of BMT3 and BMT6 ceramics as a function of sintering temperature are shown in Figs. 2 and 3. For BMT3 and BMT6 sintered at 1300 °C, the MCAS-doped $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics reveal a superstructure reflections corresponded to an ordering of Mg and Ta ions rather than a disordering structure. For BMT3 sintered at 1300–1400 °C and BMT6 at 1350 °C, the major phase is $Ba(Mg_{1/3}Ta_{2/3})O_3$, almost no satellite phases are observable. Comparing the patterns showing in Figs. 2 and 3, the crystalline

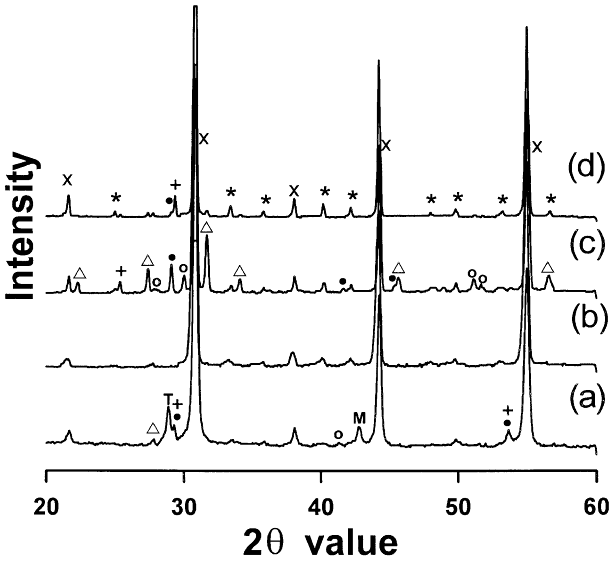

Fig. 1. X-ray patterns of $Ba(Mg_{1/3}Ta_{2/3})O_3$ (a) calcined powder, and ceramics sintered at (b) 1400 °C, (c) 1450 °C, and (d) 1500 °C. [×: $Ba(Mg_{1/3}Ta_{2/3})O_3$, *: ordering $Ba(Mg_{1/3}Ta_{2/3})O_3$, •: $Ba_5Ta_4O_{15}$, o: $Ba_4Ta_2O_9$, +: $Ba_7Ta_6O_{22}$, Δ: $Mg_4Ta_2O_9$, M:MgO, T:Ta_2O_5].

intensities of cordierite phase and satellite phases increase with the increase of MCAS content. For the same amount of MCAS glass addition, the crystalline intensities of cordierite phase slightly decrease and then increase with the increase of sintering temperatures. This suggests that too much MCAS glass addition is not necessary because the increase in satellite phases may cause poor densified process.

Fig. 4 indicates the densification characteristics of BMT ceramics with various concentrations of MCAS addition. As Figs. 2 and 3 show, the MCAS glass will crystallize as independent cordierite phase. For that, the theoretical densities of the MCAS-doped $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics are estimated from the values of MCAS glass ceramics of 2.58 g/cm^3 [12] and $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics of 7.626 g/cm^3 (estimated from the X-ray patterns). The theoretical density for the MCAS–BMT ceramics is calculated using Eq. (1):

$$D = (W_1 + W_2)/(W_1/D_1 + W_2/D_2) \tag{E1}$$

where W_1 and W_2 are the weight percent of the BMT ceramics and MCAS glass in the mixtures, respectively; D_1 and D_2 are the densities of the $Ba(Mg_{1/3}Ta_{2/3})O_3$ and MCAS glass, respectively. The estimated densities for BMT1, BMT3, and BMT6 ceramics are 7.481, 7.216, and 6.868 g/cm^3, respectively. For all compositions, the densities of MCAS-ceramics increase with the increase of sintering temperature and the saturation densities are

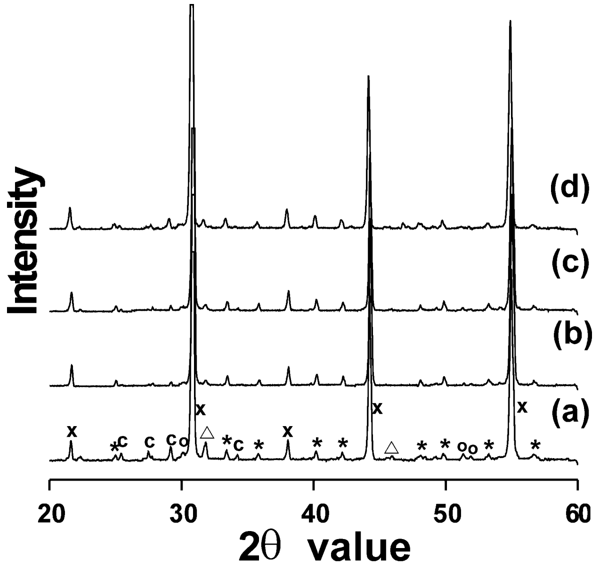

Fig. 2. X-ray patterns of BMT3 ceramics, sintered at (a) 1300 °C, (b) 1350 °C, (c) 1400 °C, and (d) 1450 °C. [×: $Ba(Mg_{1/3}Ta_{2/3})O_3$, *: ordering $Ba(Mg_{1/3}Ta_{2/3})O_3$, c: cordierite, •: $Ba_5Ta_4O_{15}$, o: $Ba_4Ta_2O_9$, +: $Ba_7Ta_6O_{22}$, Δ: $Mg_4Ta_2O_9$).

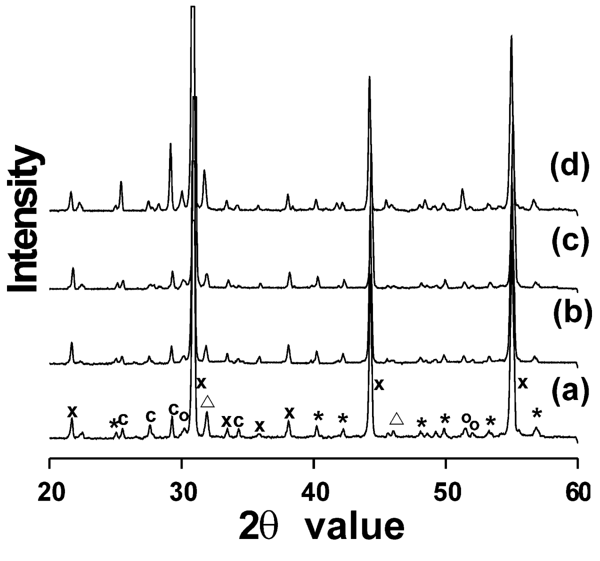

Fig. 3. X-ray patterns of BMT6 ceramics, sintered at (a) 1300 °C, (b) 1350 °C, (c) 1400 °C, and (d) 1450 °C. [×: $Ba(Mg_{1/3}Ta_{2/3})O_3$, *: ordering $Ba(Mg_{1/3}Ta_{2/3})O_3$, c: cordierite, •: $Ba_5Ta_4O_{15}$, o: $Ba_4Ta_2O_9$, +: $Ba_7Ta_6O_{22}$, Δ: $Mg_4Ta_2O_9$].

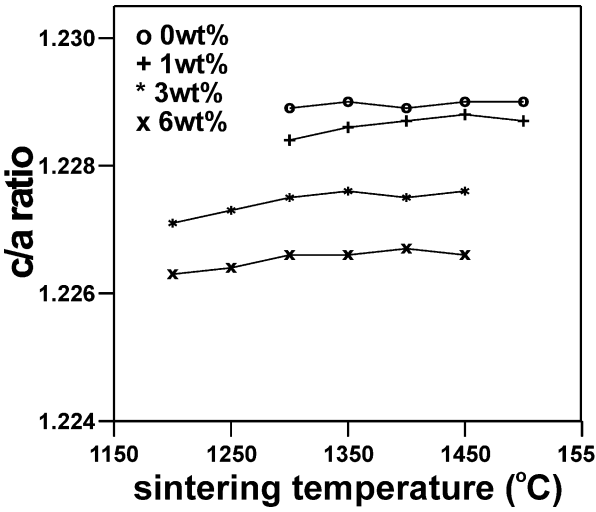

Fig. 4. The c/a ratios of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics as the functions of sintering temperature and amount of MCAS glass addition.

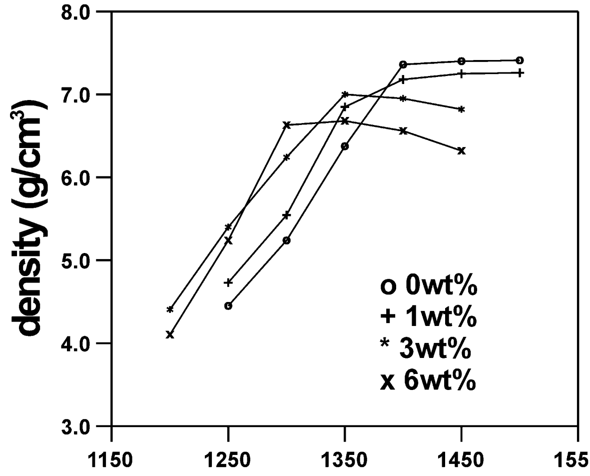

Fig. 5. Densities of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics as the functions of sintering temperature and amount of MCAS glass addition.

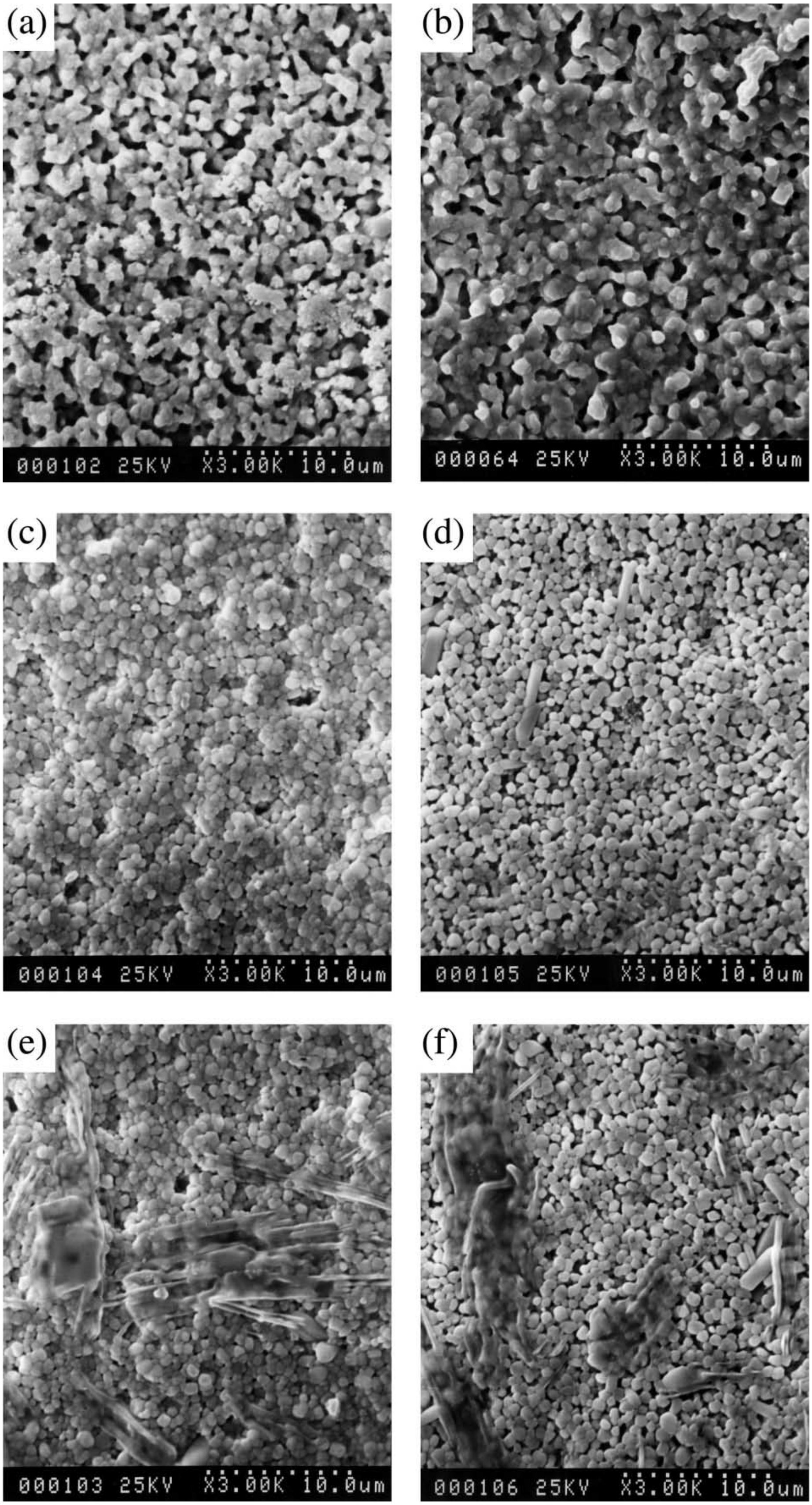

Fig. 6. Sintered morphologies of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics sintered at (a) 1300 °C and (b) 1450 °C with 0 wt.% MCAS addition, sintered at 1300 °C with (c) 3 wt.% and (d) 6 wt.% MCAS addition, and sintered at 1400 °C with (e) 3 wt.%, and (f) 6 wt.% MCAS addition.

shifted to lower temperatures as the amount of MCAS addition increases. As sintering temperature is higher than 1350 °C, the densities of BMT3 and BMT6 ceramics decrease with the increase of sintering temperature, probably due to the melting of MCAS glass and the increase of satellite phase. These results imply that as MCAS glass is used as sintering agent, $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics can be sintered at considerably lower temperature than that for undoped BMT powders derived from a sol-gel process [6]. The apparent density of the sintered samples are about 97.1 (1450 °C), 97.2 (1350 °C), and 96.7% (1300 °C) of the theoretical densities of 1, 3, and 6 wt.%-MCAS-added-$Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics.

The ordering of Mg and Ta expands the original perovskite unit cell along the $<111>$ direction of the original perovskite unit cell, so that c/a ratio has a value greater than $(3/2)^{1/2}$ (=1.2247). As Fig. 5 shows, the *c*/*a* ratios decrease with the increase of MCAS glass addition. The *c*/*a* ratios for BMT0 and BMT1, fired at 1250 to 1500 °C, are about 1.229 and the *c*/*a*s ratio for BMT3 and BMT6, fired at 1200 to 1450 °C, are smaller than 1.229 but larger than 1.225. Fig. 5 also shows that the c/a ratios increase slightly with the sintering temperature and saturate at higher sintering temperature.

Fig. 6 gives the typical morphology of the BMT ceramics with different amount of MCAS addition and sintered at different temperatures. For BMT0 sintered 1300 °C, pores and isolated BMT particles are easily observed in Fig. 6(a). Even the sintering temperature increases to 1450 °C, the BMT0 ceramics also shows a porous surface. With the addition of MCAS glass, a much easier densification of BMT ceramics is evidenced. For BMT3 and BMT6 sintered at 1300 °C, the size of pores can be easily decreased and the microstructures are more homogeneous, as Fig. 6(c) and (d) show. For BMT3 and BMT6 sintered at 1400 °C, as Fig. 6(e) and (f) show, the glass melting out is obvious, but the ceramics still show densified surfaces.

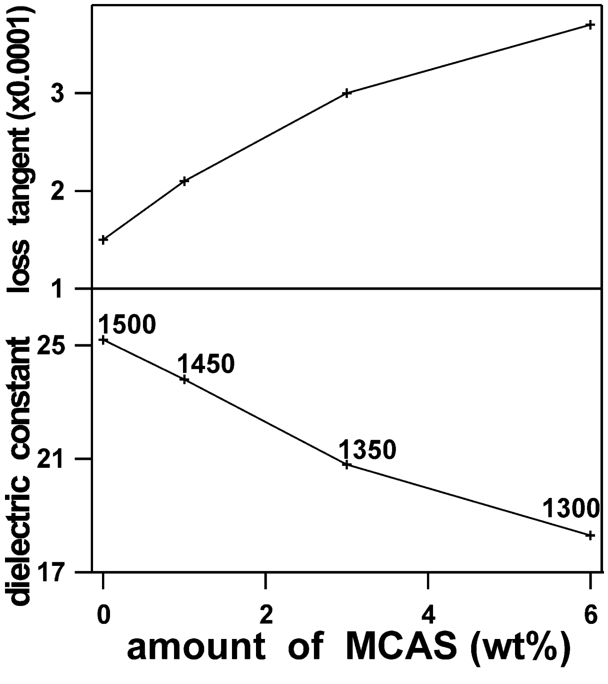

Fig. 7. Dielectric constant and loss tangent of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics as the functions of sintering temperature and amount of MCAS glass addition.

The dielectric constant (ε_r) and loss tangent ($\tan\delta$) of MCAS-added BMT dielectric are measured at 1 MHz, and the results are shown in Fig. 7. The ε_r value increases and the $\tan\delta$ decreases with the increase of sintering temperature, and the saturation values shift to lower temperature as the amount of MCAS glass increases. This maybe caused by the increase of sintered density with the increase of sintering temperature. At 1 MHz, values of $\varepsilon_r = 25.2$ and $\tan\delta = 10^{-4}$ are observed for pure densified BMT dielectric (sintered at 1500 °C). The deleterious effect of the MCAS glass on the dielectric constant is apparent in Fig. 7. At 1 MHz, dielectric constant decreases from 25.2 for pure BMT dielectric to 17.8 for BMT dielectric with 6 wt.% MCAS glass added. The addition of MCAS glass has no deleterious effect, however, on the dielectric loss. For the densified 1-, 3, and 6 wt.%-MCAS-added BMT ceramics the $\tan\delta$ are 2.1×10^{-4}, 3.0×10^{-4}, and 3.7×10^{-4}, respectively.

4. Conclusions

In this study, the optimum temperatures needed to sinter $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics is 1300–1350 °C for 6 wt.% MCAS glass and 1350–1400 °C for 3 wt.% MCAS glass because of the higher densities. Too much MCAS addition is not necessary because of the decrease of dielectric constant and the increase of dielectric loss with the increase of MCAS glass. In this study, $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics with 3 wt.% MCAS glass addition have the optimum sintering results, because they own the low temperatures of 1350–1400 °C, the less satellite phases, the maximum theoretical density, and the acceptable dielectric constant and dielectric loss.

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