

The effect of calcination on the microwave dielectric properties of $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$

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Abstract

In this study, the role of calcination, its effect upon microstructural development and the correlation with dielectric losses at microwave frequencies were investigated. Ceramics with the composition $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BMT) were prepared by a conventional mixed-oxide route using controlled calcination. Commercial processing often uses sintering and calcination conditions to modify the dielectric properties of ceramics. However, the mechanism by which the calcination conditions influence the dielectric losses is not clear. The BMT powders were calcinated at 1000–1300 °C for 4–10 h in air or flowing oxygen. Resonator samples were then sintered at 1600–1650 °C for 3 h. Scanning electron microscopy and X-ray diffraction were used to examine the phase composition and the microstructure of the sintered bodies. The microwave dielectric properties were measured at 10 GHz. We found a significant influence of the calcination conditions on the quality factor (Qf) -value. The influences of the phase composition on dielectric losses appear to dominate those of the microstructure. A significant effect was also found for specimens calcinated in different atmospheres. By controlling the calcination and sintering a pure BMT ceramic with a dielectric constant of 24.5, a Qf -value of 120,000 GHz and an τ_f of 6 ppm/°C was obtained. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; Calcination; Microwave processing

1. Introduction

Microwave materials used as dielectric resonator materials have a high dielectric constant (20–100), low losses [high quality (Q) values] and a small temperature coefficient of resonant frequency (τ_f). A number of materials have been developed for microwave systems with some complex perovskites appearing suitable for applications at microwave frequencies. $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BMT) and $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BZT) have excellent microwave characteristics. BMT has the highest Q value among microwave materials,¹ however, the BMT ceramic is known to be difficult to sinter. Many parameters such as the degree of order, the sintered density, the composition and the processing have been suggested as influencing the quality factors Qf.^{2–9}

In this paper the calcination conditions such as temperature and atmosphere as well as the microstructure were investigated. The influence of calcination conditions on the sintering behavior and microwave dielectric

properties is discussed in terms of probable secondary phases.

2. Experimental procedures

The starting materials were high-purity powders of BaCO_3 , MgO and Ta_2O_5 (99.9%). The stoichiometric composition of BMT was first ball-milled in a polyethylene bottle with zirconia balls in deionized water for 24 h. After drying, mixed powders were calcinated at 1000, 1200, 1250 and 1300 °C in air or flowing oxygen for 4 and 10 h. Some samples were calcinated at 1250 °C for 10 h once, others were calcinated twice. After ball-milling again, the calcinated powders were pressed into pellets. The pellets were then sintered at 1600, 1630, 1650 and 1680 °C for 3 h.

Sintered samples were analyzed using an X-ray diffractometer. The bulk densities of the sintered samples were measured by the immersion method, with a theoretical density of 6.636 g/cm³ used to calculate the relative density. The microstructures were examined with a scanning electron microscope. The dielectric constant was measured by Hakki and Coleman's dielectric-resonator method at 6 GHz. The Q values and temperature

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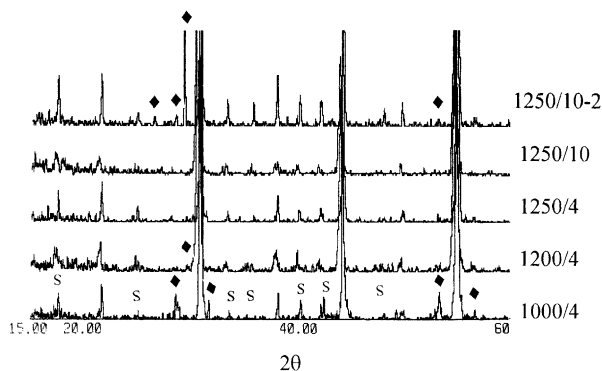


Fig. 1. XRD patterns for BMT calcinated under different conditions: at 1000 °C (1000/4), 1200 °C (1200/4) and 1250 °C for 4 h (1250/4), at 1250 °C for 10 h (1250/10) and twice at 1250 °C for 10 h (1250/10-2). All resonators were sintered at 1650 °C for 3 h. The reflections denoted by S correspond to superlattice reflections ($h \pm 1/3, k \pm 1/3, l \pm 1/3$), due to B-site ordering. ◆ Secondary phases.

coefficient of resonant frequency were measured by a reflection system at 10 GHz using a network analyzer (Hewlett Packard, Model HP 8510).

3. Results and discussion

3.1. Material characteristics

Fig. 1 shows the X-ray diffraction patterns of BMT samples calcinated at 1000, 1200, 1250 °C for 4 h, 10 h, and at 1250 °C for 10 h two times; all samples were than sintered at 1650 °C for 3 h. The patterns of the sintered samples correspond to that of the perovskite structure with the space group $P\bar{3}m$ 1-characterized by weak superlattice reflections of the 1:2 ordering of Mg and Ta ions at B sites. The reflections due to secondary phases are indicated by ◆. These reflections, near to $2\theta = 30^\circ$, can be indexed to barium tantalite compounds such as $Ba_5Ta_4O_{15}$ and $Ba_7Ta_6O_{17}$, although some reflections may be due to unknown phases. It is clear that the 1000/4 and 1250/10-2 samples have a much higher intensity of second-phase reflections than the 1250/4 sample. The formation of secondary phases can introduce point defects into the matrix of sintered body. The probable defects are vacancies at the A and/or the B sites and interstitials in the perovskite structure.⁸ For this reason secondary phases will reduce the quality factor of ceramics, as can be seen for those samples shown in Fig. 2. In contrast, sample 1250/4 has the highest quality factor, probably due to stronger superlattice reflections and a reduced quantity of secondary phases, as shown in Fig. 1.

3.2. Microwave dielectric properties and calcination conditions

Fig. 2 shows the quality factor of a BMT sample fired at 1650 °C for 3 h as a function of calcination conditions.

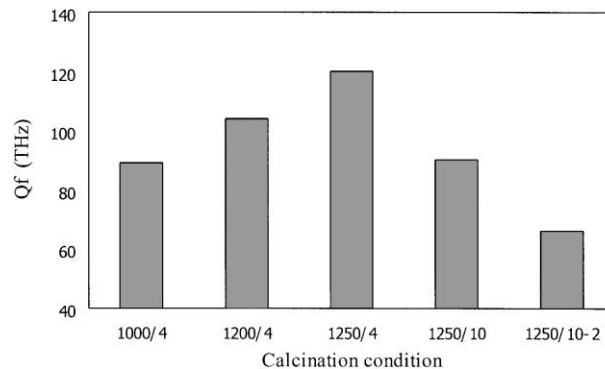


Fig. 2. Qf versus calcination temperature for different calcination times. All resonators were sintered at 1650 °C for 3 h.

The quality factor is sensitive to the calcination conditions. A maximum Qf value (120 THz) is found for the sample calcinated at 1250 °C for 4 h. The sample calcinated twice at 1250 °C for 10 h (1250/10-2) showed the lowest quality factor (70 THz) among these samples. This behavior could be attributed to more secondary phases in the latter sample.

This assertion was confirmed by X-ray analysis. Fig. 1 shows that the reflections from secondary phases at d close to 3.07 Å in calcinated powders disappeared after sintering due to a solid-state reaction in most samples. However, the reflections from secondary phase at this position for the 1250/10-2 sample continue to increase their intensity during sintering. Increasing amounts of secondary phases will reduce the quality factor due to the presence of point defects.

Fig. 3 shows scanning electron micrographs of the as-sintered surfaces of BMT samples. They were calcinated at 1000, 1200 and 1250 °C for 4 h, and twice at 1250 °C for 10 h, then sintered at 1650 °C for 3 h. Fig. 3(a) shows that the surface of the 1000 °C sample was covered with unknown secondary phases. This is consistent with the X-ray diffraction pattern for this sample, shown in Fig. 1. Fig. 3(b)–(d), shows that the grain growth was at the normal stage: grain sizes are in the 1–4 μm range. For BNT samples sintered at above 1600 °C, an abnormal grain growth was found.⁹ This is in agreement with the observation reported by Hyuk-Joon Youn et al.⁸ It is clear the 1250/4 sample [Fig. 3(c)] has the largest grain size among these samples. The 1250/10-2 sample [Fig. 3(d)] has a smaller grain size. Secondary phases or impurities in the grain boundary can restrain the grain growth. This difference in the grain growth behavior may be due to the different secondary phases in these samples. 1250/4 sample [Fig. 3(c)] has less secondary phases compared with the others. From the X-ray patterns of the BMT samples shown in Fig. 1, it is obvious that there is a stronger intensity of reflection for secondary phases near to the 2θ angle = 28.770 for the 1250/10-2 sample, whereas no second-phase reflections can be found at this angle for the 1250/4 sample.

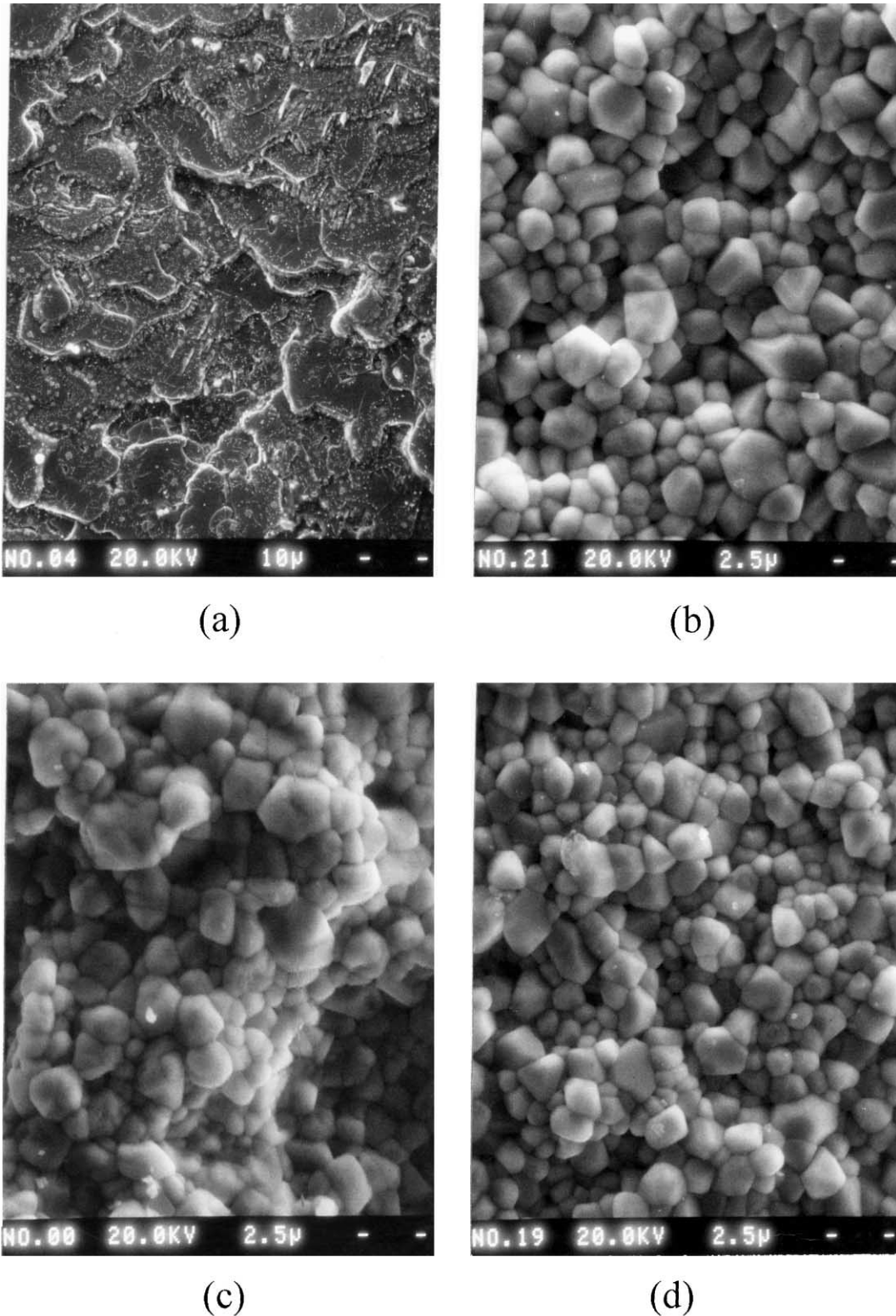


Fig. 3. Scanning electron micrographs of BMT Ceramics sintered at 1650 °C for 3 h for the powders calcinated under different conditions: (a) 1000 °C for 4 h, (b) 1200 °C for 4 h, (c) 1250 °C for 4 h, (d) 1250 °C for 10 h twice.

By controlling the calcination and sintering conditions, a BMT ceramic with a dielectric constant of 24.5, Qf of 120 THz and a temperature coefficient of resonant frequency of 6 ppm/°C was obtained.

3.3. Number of calcination cycles

It was found that the Qf and relative density are sensitive to the number of calcinations at 1250 °C for 10 h.

Fig. 4 shows the variation of Qf for BMT samples with sintering temperature for samples first calcinated at 1250 °C for 10 h either once or twice. The samples calcinated once have a higher QF than that calcinated twice for all sintering temperatures. In the sintering temperature range from 1550 to 1650 °C for the twice-calcinated samples, the Qf does not change, from approximately 65 THz. When the sintering temperature reached 1680 °C, the Qf goes down to 35 THz. Such a large change occurring at this temperature might be due to a density decrease or a phase composition variation. The BMT powders which showed this behavior could be referred to as “dead fired” powders. The once-calcinated samples were very sensitive to sintering temperature and a maximum QF was found at 1650 °C (105 THz). A sharp decrease in Qf was observed at 1680 °C.

In order to explain the behavior of the samples, the bulk density was examined for some of the samples. Figs. 5 and 6 show the relative density of the BMT samples versus sintering temperature for the powder calcinated at 1250 °C for 10 h once and twice, respectively. The Q

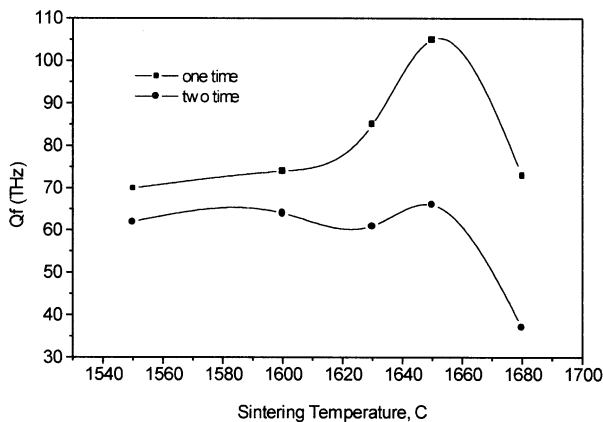


Fig. 4. Qf as a function of sintering temperature for BMT calcinated at 1250 °C for 10 h: once (■) and twice (●). All resonators were sintered at 1650 °C for 3 h.

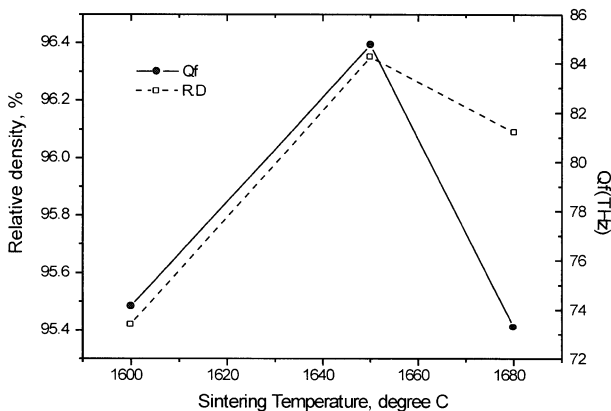


Fig. 5. Qf and relative density versus sintering temperature for BMT powders calcinated once at 1250 °C for 10 h.

value of the samples using the powder calcinated once at 1250 °C for 10 h increased with increasing relative density: their Q value depends on the relative density. However, Q values for the samples using the powder calcinated twice at 1250 °C for 10 h were independent of relative density as shown in Fig. 6. Although their relative density increased with increasing sintering temperature from 35 to 60% in the sintering temperature range from 1550 to 1650 °C the quality factor did not change at all for the twice-calcinated samples. This is due to using a “dead fired” powder. A similar behavior for relative density was found for both samples, There is a maximum at 1650 °C, which means the density does not affect the Qf for the samples using twice-calcinated powder.

3.4. The influence of calcination atmosphere

Fig. 7 shows the Qf variation with calcination temperature for sample calcinated in air and flowing oxygen. All samples were sintered at 1650 °C for 3 h in air. The Qf for the sample calcinated in flowing oxygen shows no

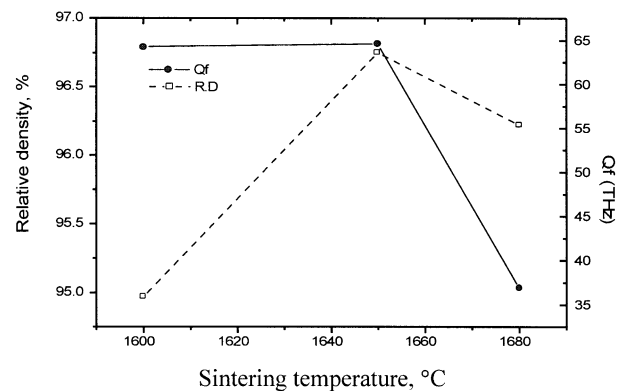


Fig. 6. Qf and relative density versus sintering temperature for BMT powders calcinated twice at 1250 °C for 10 h.

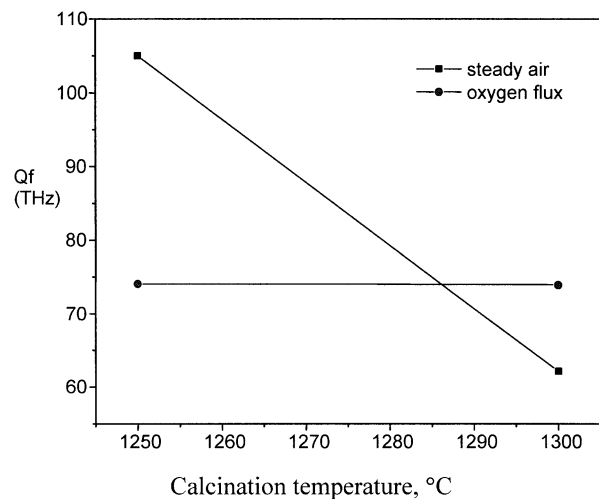


Fig. 7. Qf as a function of calcination temperature and atmosphere. All resonators were sintered at 1650 °C for 3 h.

change with calcination temperature while the sample calcinated in air showed that their quality is sensitive to the calcination temperature. The sample calcinated at 1300 °C has a much lower value compared with the sample calcinated at 1250 °C. This means that samples calcinated in flowing oxygen will result in a highly stable BMT powder. This behavior may be due to calcination in oxygen leading to the formation of less oxygen vacancies in the powders or the formation of some stable secondary phases in the powders. This affect clearly needs further study.

3.5. Secondary phases, properties, grain growth and solid-state reaction

From the discussion above, we see that secondary phases, dielectric properties and grain growth depend on the calcination condition for the powder. This is due to the formation of BMT by a diffusion-controlled solid-state reaction. We have investigated the mechanism and kinetics of BMT formation by solid-state reaction in the system $\text{BaCO}_3 + 1/3 \text{MgO} + 1/3 \text{Ta}_2\text{O}_5$ using a quenching technique, thermal analysis and X-ray diffractometry.¹⁰ The whole reaction can be simply described by the following reaction:



The real reaction is, however, very complex and never follows this scheme. The reaction mechanism is similar to the formation of BaTiO_3 by solid-state reaction in a mixture of $\text{BaCO}_3 + \text{TiO}_2$. Many parallel reactions occur leading to the formation of other compounds such as BaTa_2O_6 , $\text{Ba}_4\text{Ta}_2\text{O}_9$, $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ and $\text{Ba}_7\text{Ta}_6\text{O}_{22}$. Some of these $\text{BaO}-\text{Ta}_2\text{O}_5$ -system compounds are presented as intermediate compounds in the process. The main intermediates are BaTa_2O_6 and $\text{Ba}_4\text{Ta}_2\text{O}_9$. Fig. 8 shows these following reactions took place during heating:

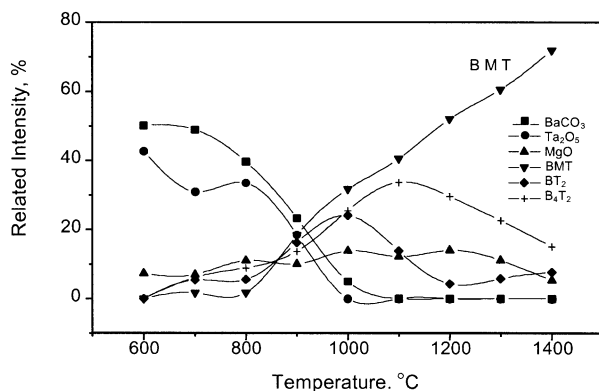
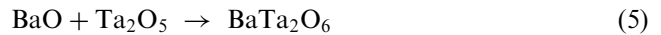
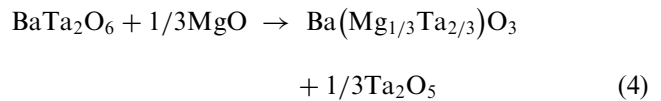
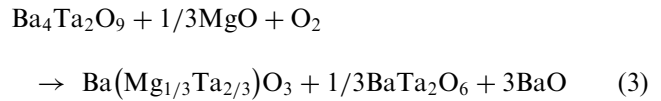
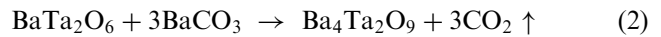
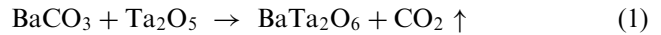
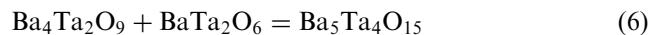


Fig. 8. Phase vs temperature for BMT samples heated at a heating rate of 600 °C/h. Solids determined by X-ray diffractometry.



Reactions (1) and (2) start at 700 °C and the rate of these two reactions is very rapid, as a result, BaTa_2O_6 was not found in the sintered bodies. Reactions (3)–(5) start at 800 °C. From 800 to 1000 °C, the three reactions (1)–(3), proceed simultaneously. When the temperature is higher than 1000 °C the reactions (3)–(5) control the formation reaction. According to reactions (3)–(5), as 1 mol of BMT is formed, 0.33 mol Ta_2O_5 or BaTa_2O_6 is produced. Maybe this is the reason why the secondary phases can be found at higher temperatures. At 1400 °C intermediate products reaction also exists, maybe because the rate of the reactions in Eqs. (3) and (4) are too slow, and reaction (5) is very quick. $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ and $\text{Ba}_7\text{Ta}_6\text{O}_{22}$ can be found in the sintered bodies, therefore, the following reactions might form $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ and $\text{Ba}_7\text{Ta}_6\text{O}_{22}$:



From $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ and $\text{Ba}_7\text{Ta}_6\text{O}_{22}$, it is very difficult to form BMT because the reactants are stable at high temperature and the reaction requires going through a solid-diffusion process. The mechanism for these reactions is not clear; however, it is reasonable to assume that they have to make contact with MgO to form BMT by long-distance diffusion. If these two compounds are formed in the calcinated powder during the calcination processes they will maintain growth during sintering and finally be present as secondary phases in the sintered body. This is why BMT, even when sintered at 1650 °C for a long time, has various kinds of secondary phases present as previously reported.^{8,11} This kind of calcinated powder is called “dead fired” powder. In this work, we found the powder calcinated twice at 1250 °C for 10 h two times is “dead fired” powder, while the powder calcinated at 1250 °C for 4 h is “active fired” powder. Compared with the “active fired” powder, the “dead fired” powder has a lot more secondary phases as shown in Fig. 1 (see sample 1250/10-2), a lower Q value (Fig. 2) and a low density (Fig. 4). A smaller grain size

was also found for the “dead fired” powder sample in Fig. 3 (d) because it has more secondary phases as inclusions, which play a role as grain growth inhibitors during sintering.¹² It can be seen from Fig. 3 that the 1250/4 sample has a slightly larger grain size (Fig. 3c) than the others because it has less secondary phases than the others as shown in Fig. 1 do.

4. Conclusion

Control of the calcination conditions is very important for the Qf of BMT ceramics. The calcination conditions are one of the important parameters, which influence the microwave structure, second-phase formation and the microwave properties of pure BMT ceramics. By controlling calcination and sintering conditions a BMT ceramic with a dielectric constant of 24.5, Qf of 120 THz and a temperature coefficient of resonant frequency of 6 ppm/°C was obtained. Calcination at higher temperatures, in an oxygen atmosphere or twice at high temperature is not good for the Qf and the density. It leads to the formation of stable secondary phases in the calcinated powders. These secondary phases will not disappear even after sintering at high temperature. In this work, secondary phases play a greater role in controlling the Qf of BMT than the density. The secondary phases play an important role in controlling the microstructure, density, grain growth and microwave dielectric properties because the BMT was formed by a complex solid-state reaction controlled by a diffusion mechanism.

Acknowledgements

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