

Synthesis of $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ microwave dielectrics by solid state processing

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Abstract

Synthesis and formation of $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BMT) from BaCO_3 , MgO and Ta_2O_5 was examined by thermal and X-ray diffraction analyses using quenching technique. Several reactions take place during heating process. BaCO_3 can react with Ta_2O_5 to form BaTa_2O_6 (BT_2) and B_4T_2 . BT_2 as an intermediate product was found at the first stage of the reaction, and then BaTa_2O_6 or B_4T_2 react with MgO to form BMT. The reaction of BMT formation was not complete until it was sintered at 1350 °C for 60 min. An intermediate reproduce cycle keeps company with the BMT formation in calcinations and sintering processing. The kinetics of solid-state reaction between powdered reactants for the reaction of BaTa_2O_6 formation was diffusion mechanism controlled, which can be described by Jander's model for three-dimensional diffusion. The activation energy was determined to be 235.6 kJ/mol. The BMT powders were sintered to ~96% of relative density after 3 h at 1650 °C. The final sintered ceramics exhibited a dielectric constant of 24.5, a $Q:f$ of 120,000 GHz, and a temperature coefficient of resonant frequency of 6 ppm/°C.

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1. Introduction

$\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BMT) is the only ternary compound in the $\text{BaO-MgO-Ta}_2\text{O}_5$ system.¹ The polymorphism and crystal structures of BMT have been widely studied.² In recent years considerable attention has been devoted to BMT by ceramists because of its potential application as a dielectric resonator material for microwave application. BMT exhibits ultra-low dielectric loss at microwave frequencies, with quality factor $Q:f$ of 150,000 to 350,000 GHz, dielectric constant of 25 and a near-zero temperature coefficient of frequency.^{3–6} These distinguishing features of BMT have resulted in considerable interest in the synthesis of this material.^{4–7} Usually BMT is made by a powder reaction route, but the sintering temperature is higher than 1600 °C. Solution chemistry offers an alternative approach for synthesis of BMT powders.^{5–7} Renoult et al.⁶ synthesized BMT powders by the sol-gel process,

obtaining a dense single-phase ceramics (96–98% theoretical density) after sintering at 1400 °C, but the $Q:f$ product was lower than that of the conventional solid-state reaction method.⁶ However, there is little information concerning the mechanism and kinetics of BMT formation.

Jander formulated the first theoretical model for the mechanism and kinetics of a solid-state reactions.⁸ Since then, a large number of rate equations (models) have been proposed and tested with varying success.^{9–15} Particle size, distribution of sizes and the previous history of the reactants can affect the measurements. In this study, we have worked with reactant particles having a narrow size distribution ($\approx 1\text{--}2\ \mu\text{m}$) and investigated the mechanisms and kinetics of BMT formation.

2. Experimental procedure

The reactant mixtures were prepared using high pure powders of BaCO_3 (99.9% purity), MgO (99.9% purity) and Ta_2O_5 (99.95% purity) in the ratio 3:1:1. The powders were wet milled (distilled water) using agate balls until the particles were reduced to $\approx 1\text{--}2\ \mu\text{m}$. The

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powders were then dried at 100 °C for 4 h. Reactants in the form of loose powder (~0.5 g) were placed within a small platinum crucible (10 mm diameter and 15 mm depth) and hung in the isothermal zone of a vertical quench furnace. Quenching experiments were carried out over the temperature range 600–1400 °C at heating rate of 600 °C/h. Two sets of experiments were designed. The first set is heating quenching to study the sequence of compounds formed during heating. The samples were quenched at desired temperature in air with no soaking time. The second set of experiments were isothermal quenching to determine the effect of time on reaction. Mixtures were heated at selected temperatures for various holding times and then air quenched.

During heating a weight loss occurs and this can be used as a measure of the extent of reaction. The extent of reaction, α , is defined as the ratio of the weight loss at a given temperature to the total weight loss after quenching. Phase present in the calcined powders were identified by X-ray diffraction using Philips diffractometer equipped with $\text{CuK}\alpha$ radiation ($\lambda = 0.154056$ nm). The intensities of the X-ray diffraction peaks were also used to characterize the extent of reaction. The powders were scanned between 2θ angles of 10 and 75° at 2θ - ω scanning mode using silicon powder as an internal standard.

3. Results and discussion

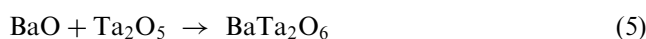
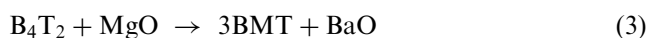
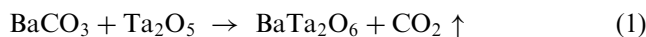
3.1. Sequence of compounds formed during heating

The mixtures were heated at 600 °C/h to various temperatures and quenched in air. The phases, as a function of temperature, are shown in Fig. 1. The notation used to identify the variety of compounds in this study is BaTa_2O_6 (BT_2), B_4T_2 , and $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BMT).

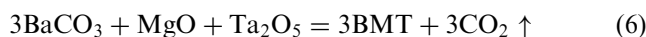
At 600 °C no new compounds were formed. At 700 °C, BaTa_2O_6 and B_4T_2 were found. When the temperature increased to 800 °C or above, the intensities

of BaTa_2O_6 and B_4T_2 increased and BMT appeared indicating the reaction of BaTa_2O_6 and B_4T_2 with MgO to form BMT. Above 1000 and 1100 °C, BaTa_2O_6 and B_4T_2 began to disappear as BaCO_3 and Ta_2O_5 were used up. The amount of BMT increases with temperature linearly, but the intermediates, BaTa_2O_6 and B_4T_2 , were present until 1400 °C.

Fig. 1 clearly shows that the following reactions took place during heating:

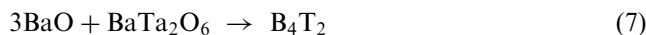


The resulting equation is



Reactions (1) and (2) start at 700 °C, while reactions (3)–(5) start at 800 °C. From 800 to 1000 °C three reactions of (1)–(3) proceed simultaneously. When the temperature higher than 1000 °C the reaction (3)–(5) control phase formation.

According to reaction (3)–(5), when one mole of BMT was formed, at the same time, some additional products such as Ta_2O_5 and BT_2 were reproduced. The reproduced BT_2 can react with adjacent BaCO_3 or BaO to produce new B_4T_2 via



Possibly this is the reason for why the second phases B_4T_2 is found at high temperature, up to 1400 °C. In this study, two main intermediates, BaTa_2O_6 and B_4T_2 , were formed instantly, but only BaTa_2O_6 was found in the solid-solid reaction of BaCO_3 , MgO , and Ta_2O_5 reported by Kakegawa et al. ⁵

3.2. Progress of reactions (1) and (2) with time

The fraction transformed (α) for BT_2 and B_4T_2 produced by reactions (1) and (2) was examined by determining the amount of unreacted reactant powders by weighing mixtures before and after quenching. The value for fraction transformed (α) was calculated via:

$$\alpha = \frac{(\text{wt})_i - (\text{wt})_t}{(\text{wt})_i} \quad (8)$$

Here, the subscripts *i* and *t* indicate the initial weight of sample and the weight of sample after heating time, *t* (min), respectively. The reactant mixtures were heated at 700, 800, 900 and 1000 °C and quenched. Fig. 2 shows relationships between the fraction transformed and holding time for the BT_2 and B_4T_2 synthesized from the mixture.

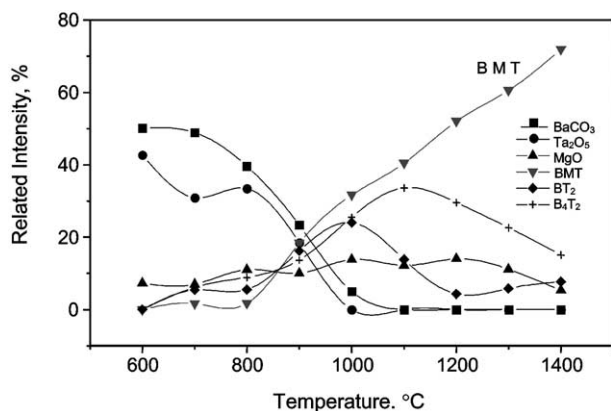


Fig. 1. Phase vs temperature for BMT samples heated at heating rate of 600 °C/h. Solids determined by X-ray diffractometry.

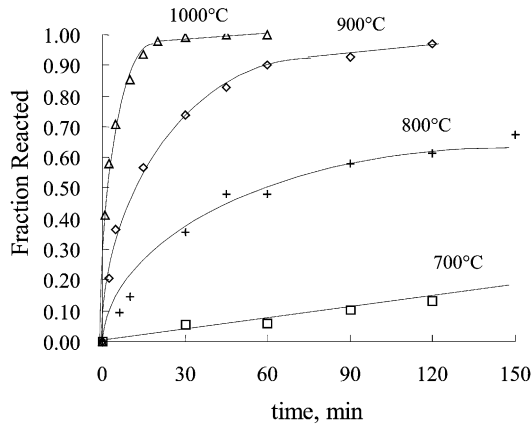


Fig. 2. Fraction reacted, α , vs soaking time for reaction (1) and (2) at various temperatures.

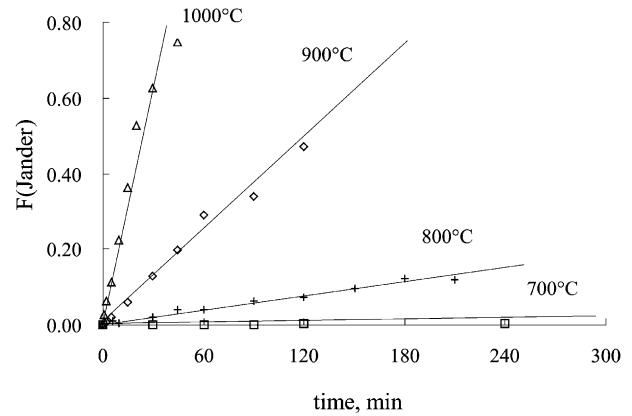


Fig. 3. Plots of $F(\alpha)$ vs time for Jander diffusion equation for $\text{BaCO}_3 + \text{Ta}_2\text{O}_5 \rightarrow \text{BaTa}_2\text{O}_6 + \text{CO}_2\uparrow$.

3.3. Graphical analysis and mechanism of reaction

Solid state reactions can be described by (a) diffusion-controlled reactions, (b) mechanisms controlled by nucleation and growth of the product, or (c) processes occurring at interfaces, i.e. phase boundary-controlled reactions and kinetic equations based on the order of reaction.¹⁴ The rate equations tested here are shown in Table 1. The notation from ϕ to D2 comes from Beretka et al.¹⁰ and additional equations come from Jander⁸ (D3), Ginstling and Brounshtein¹⁵ (D4), Cater⁹ (D5), Avam¹⁶ (A2), Sharp¹¹ (R2,R3). To identify rate equations, a given set of observations of fraction transformed α vs time is usually tested for linearity by plotting¹⁴ $f(\alpha)$ vs time. It was found that the results exhibit a near linear relationship, suggesting that only diffusion equations describe the reaction satisfactorily. The results fit the models D3, D4 and D5 almost equally well, but the best one is Jander equation, D3:

$$[1 - (1 - \alpha)^{1/3}]^2 = kt \tag{9}$$

Table 1
List of equations

Symbols	Model (type of process)	Equations		Ref.
		y	x	
ϕ	Zero order	α	t	10
D1	One-dimensional diffusion	α^2	t	10
D2	Two-dimensional diffusion	$(1-\alpha)\ln(1+\alpha) + \alpha$	t	10
D3	Diffusion (Jander)	$[1-(1-\alpha)^{1/3}]^2$	t	8
D4	Diffusion (Ginstling and Brounshtein)	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	t	15
D5	Diffusion (Carter)	$(1+\alpha)^{2/3} + (1-\alpha)^{2/3}$	t	9
F1	First-order kinetics (empirical)	$-\ln(1+\alpha)$	t	10
R2	Phase boundary (disk)	$1-(1+\alpha)^{1/2}$	t	11
R3	Phase boundary (sphere)	$1-(1-\alpha)^{1/3}$	t	11
A2	Nucleation (Avrami)	$[-\ln(1+\alpha)]^{1/2}$	t	16

where α is fraction transformed, k constant of reaction rate and t time. Fig. 3 shows the plots of $f(\alpha)$ vs time at various temperatures. Jander equation describes the reaction satisfactorily, and appears to follow the curves describing diffusion-controlled mechanism. It was found that reactions (1) and (2) will finish at 1000 °C after about 30 min.

The data in Fig. 3 was analysed via a standard Arrhenius equation where k is the reaction rate constant, related to the temperature (T) with apparent activation energy (Q):

$$k = A \exp(-Q/RT), \tag{10}$$

From a plot of $\ln k$ versus $1/T$ an activation energy of 235.6 kJ/mol was obtained for the formation of BT_2 .

3.4. Reaction at various temperatures for 60 min

With mixtures of BaCO_3 , $1/3\text{MgO}$ and $1/3\text{Ta}_2\text{O}_5$ a series isothermal quenching experiments were performed. Reactant mixtures heated at temperature range from 600 to 1350 °C for 60 min. Fig. 4 shows the X-ray patterns as a function of temperature. At 700 °C no new phases were found. BMT and B_4T_2 phases were found at 800 °C. At 1000 °C reactants BaCO_3 and Ta_2O_5 disappear but MgO remained until 1250 °C.

Further experiments showed that B_4T_2 is also present in the samples heated at 1350 °C for 60 min. Fig. 5 plots the relative intensity of phases as a function of temperature for the samples heated for 60 min. BMT and B_4T_2 were found at 800 °C. However, BT_2 was not found in this set of samples. As indicated earlier, BT_2 existed in all samples in the heating-quenching experiments with no holding time. Thus BT_2 should be produced in the reaction process but disappears in a very short time. Reaction (1) and (6) may form BT_2 . It was noted that in the isothermal process, all unreacted BT_2 should react with BaO to form B_4T_2 by reaction (7).

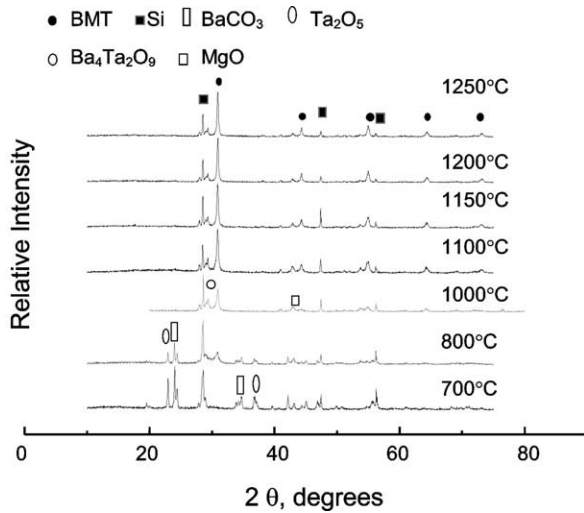


Fig. 4. X-ray patterns for BMT samples heated at various temperatures for 60 min.

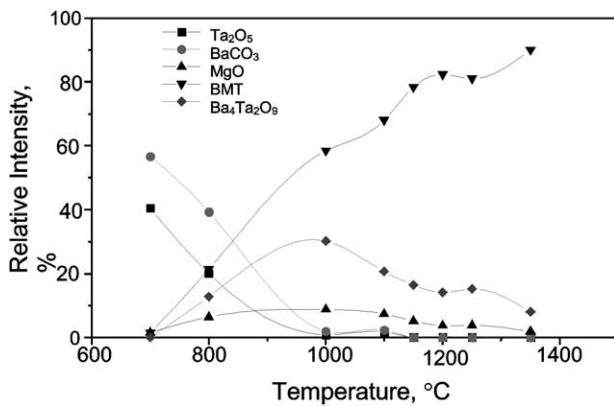
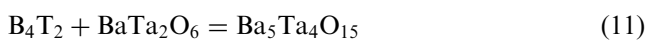


Fig. 5. Phase relative intensity vs temperature for samples heated at various temperature for 60 min.

The rate of BMT is very slow. Fig. 5 indicated that the BMT mixtures calcinated at 1350 °C for 1 h, only 90% BMT could be obtained. It means that about 10%-calcined powders were MgO and second phases. The most of them was B_4T_2 . The result shows that it is impossible to obtain a single phase BMT calcined powder by oxide method. Therefore, it could be expected that the BMT formation reaction would be continued in the sintering processing.

3.5. The path of BMT formation reaction

A Ba-rich second phases, B_5T_4 was also found in calcined powders and sintered bodies.¹⁹ B_4T_2 can further react with B_2T to form B_5T_4 . A reaction for this compound formation would be expected:



As discussed above it is difficult to get a single phase of BMT calcined powder by solid state reaction process. An IRRC keeps company with the BMT formation. The second phase formation reactions will continue during sintering. Therefore controlling calcination of reactant powders and sintering is very important. We have investigated the effect of calcination on phase composition and microwave dielectric properties of BMT.⁴ A strong effect of calcination on the second phase formation and microwave dielectric properties of BMT was found. The amount of second phases in sintered bodies depends strongly on calcination condition as shown in Fig. 6. Several kind of second phases were presented in the sintered samples. The intensity of second phase peaks for the powder calcined two times at 1250 °C for 10 h was much strong compared with that of 1250 °C for 10 h one time powder. These observations revealed that intermediate reproduced cyclical reactions were continued both in the calcination and sintering processing. In present work, a single phase (XRA) BMT ceramic was obtained by using the powders calcined at 1250 °C for 4 h, and then sintered at 1650 °C for 3 h. The BMT pellets were sintered to ~96% of relative density. The sintered ceramics exhibited a dielectric constant of 24.5, a $Q \cdot f$ of 120,000 GHz and a temperature coefficient of resonant frequency of 6 ppm/°C.

The formation of BMT could be considered as a multipath process in which each path contains several steps. Two intermediates, BT_2 and B_4T_2 , can react with MgO to form BMT. Therefore, there are two possible paths to form BMT. Path 1 (called $BaTa_2O_6$) contains two steps: R_{1a} ; first $BaCO_3$ reacts with Ta_2O_5 by reactions (1) to form BT_2 , and then R_{1b} ; BT_2 react with $BaCO_3$ to form BMT by reaction (4). Path 2 (called B_4T_2) path is a parallel path in which there is three steps in the process. R_{2a} ; $BaCO_3$ reacts with Ta_2O_5 by reaction (1) to form BT_2 , then R_{2b} ; BT_2 reacted with $BaCO_3$ to form B_4T_2 by reaction (2), and finally R_{2c} ; B_4T_2 reacted with MgO to form BMT by reaction (3). Therefore, overall processes are complex and require a series of individual separate unit steps. BT_2 was found as a first intermediate in the heating quenching samples, but was not found in all isothermal heating samples. The disappearance of BT_2 indicated that B_4T_2 is the main intermediate and the B_4T_2 path is the main path to form BMT. There are three steps in this path. The reaction with the lowest virtual maximum rate controls the overall rate if it is much lower than other steps.¹⁷ B_4T_2 as a main intermediate in the process, the rate of the slowest individual step should be R_{2c} . Therefore, the overall reaction rate of BMT formation should be determined by step R_{2c} , the reaction (3). In the reaction process B_4T_2 increases with temperature until 1000 °C. BMT increases with the increase in temperature until 1350 °C. However, even at 1350 °C, MgO and B_4T_2 still present.

3.6. A second phase partially reproduced cycle

There is an intermediate partially reproduced reaction cycle (IRRC) in the BMT formation processing. According to reaction (3), the main BMT formation reaction, B_4T_2 reacts with MgO to form BMT. When 1 mol BMT was formed, 0.33 mol BaO will be produced at the same time. The reproduced BaO can react with BT_2 to form new B_4T_2 by reaction (7). The experimental result in Fig. 5 shows that only B_4T_2 could be found in the isothermal samples. Therefore, there is an intermediate (B_4T_2) partially reproduced reaction cycle (IRRC) in the BMT formation processing.

The IRRC includes three steps. Firstly, B_4T_2 reacts with MgO by reaction (3) to BMT and reproduced BaO. The secondly, the new BaO reacts with Ta_2O_5 reproduced from reaction (4) to form new BT_2 by reaction (5). The third, the new BT_2 reacts with BaO from reaction (3) to form new B_4T_2 by reaction (7). Finally, the new B_4T_2 as a reactant go back to the first step and starts at reaction (3) to begin a new cycle. This is an intermediate (second phases) reproduced reaction cycle followed in the BMT formation processing. Second phases reproduced reaction is the nature of the cyclical reaction. The cycle reaction never stops in the limited time. The time needed to transfer all second phases into BMT is unlimited. Possibly this is a reason for B_4T_2 presented at high temperature.

Due to the B_4T_2 partial cyclical reaction the second phases reproduced continuously in the BMT formation processing, it implies that even though at high temperature prolonging time is also difficult to finish the reaction of BMT. Based on this standpoint, the intermediate cyclical reaction will be continued from calcination to sintering processing. This is consistent result with X-ray diffraction patterns for sintered bodies where remained reflections due to second phases are still visible as shown in Fig. 6. Second phases could be observed in sintered

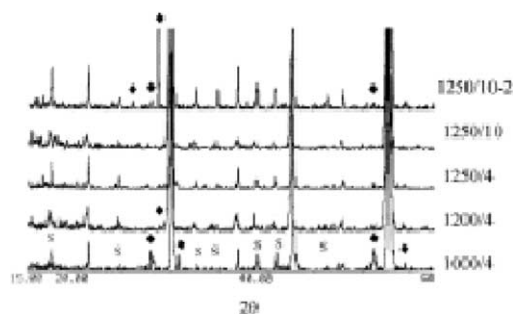


Fig. 6. XRD patterns for BMT calcined under different conditions: at 1000 °C (1000/4), 1200 °C (1200/4) and 1250 °C for 4 h (1250/4), at 1250 °C for 10 h (1250/10) and twice at 1250 °C for 10 h (1250/10-2). All samples were sintered at 1650 °C for 3 h. The reflections denoted by S correspond to superlattice reflections ($h \pm 1/3, k \pm 1/3, l \pm 1/3$), due to B-site ordering secondary phases.

BMT ceramics even though for the samples sintered at 1650 °C for 2 to 20 h.^{4,18,19}

$BaTa_2O_6$, $Ba_3TaO_{5.5}$, B_4T_2 , $Ba_5Ta_4O_{15}$ (B_5T_4) and $Ba_7Ta_6O_{22}$ (B_7T_6) are compounds in Ba-Ta-O system. In general, these five compounds are possible as second phases presented in the calcined BMT powders and sintered bodies. Due to the difference in thermodynamics and kinetics of formation reaction, different combination of compounds presented in the calcined powder and sintered bodies were observed.^{4,19} In the present work BT_2 was found in the heating quenching samples but not in the isothermal quenching samples as shown in Figs. 1 and 5. The disappearance of $BaTa_2O_6$ would be attributed to form BMT by reaction (4) and B_4T_2 by reaction (2) and (7), respectively.

4. Conclusions

(a) The formation of BMT by solid state reaction is a complex process. There are six reactions taking place. Reactions (1), (2) and (3) dominate BMT formation. This involves three consecutive steps. At temperatures above 1000 °C, the overall rate of the reaction is controlled by reaction (3).

(b) There are two intermediates in the BMT formation process. BT_2 is the first intermediate product in the process. B_4T_2 , the main intermediate, was present until 1350 °C. Reactions (1) and (2) to form BT_2 and B_4T_2 started at 700 °C. BMT was found at 800 °C. After heating at 1350 °C for 60 min 90% BMT can be obtained.

(c) B_4T_2 can be found at higher temperatures, possibly due to BMT formed by reaction (3) and (4). New MgO and Ta_2O_5 appeared after BMT formation.

(d) The formation of BT_2 and B_4T_2 is diffusion-controlled mechanism. The kinetics can be described by the Jander Equation. The activation energy was determined to be 235.6 kJ/mol.

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