Microwave dielectric properties of Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ materials synthesized by inverse-microemulsion process

Yen-Chih Lee[a], Mei-Hui Liang[a], Chen-Ti Hu[a], I-Nan Lin[b],*

[a]*Department of Materials Science and Engineering, National Tsing-Hua University, Hsinchu, Taiwan 300, People's Republic of China*
[b]*Materials Science Center, National Tsing-Hua University, Hsinchu, Taiwan 300, People's Republic of China*

Abstract

Microwave dielectric properties of Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ (BMT) materials have been improved by using an inverse-microemulsion process for preparing the BMT powders. The as-prepared powders, which are amorphous clusters about 100 nm in size, can be converted into pure perovskite phase BMT materials without the formation of undesired secondary phase (Ba$_5$Ta$_4$O$_{15}$) by calcination process. BMT materials with high enough density [95% theoretical density (TD)] of BMT samples can be obtained only by sintering the materials at 1600 °C for 24 h. Low sinterability of thus prepared BMT powders is ascribed to the formation of aggregates in calcinations process. However, the sintered BMT samples exhibit very good microwave dielectric properties. The quality factor thus obtained, Q×f = 65 200 GHz, is markedly better than that of the BMT materials prepared by conventional mixed oxide routes. The prime factor improving the microwave dielectric properties of the inverse-microemulsion processed BMT materials is presumably the fine grain microstructure (1–2 μm) of the samples. © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$; Inverse-microemulsion; Microwave dielectrics

1. Introduction

Following the technology development trend in miniaturization of microwave communication circuits, the development of high performance dielectric materials is urgently needed.[1,2] Perovskite Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ (BMT), materials, which contain Mg- and Ta-ions orderedly arranged, possess highest Q-factor (∼35 000 at 10 GHz) among microwave dielectric materials, with low temperature coefficient of resonance frequency (τ_f = 5 ppm °C^{-1}) and large microwave dielectric constant (K = 25), and have great potential for device applications[3–6]. However, the sintering temperature needed (> 1600 °C) and the soaking time necessary (> 16 h) to achieve high enough sintered density for BMT materials is very stringent. The difficulty in preparing BMT materials by mixed oxide process is that the secondary phase, Ba$_5$Ta$_4$O$_{15}$, usually formed preferential in calcinations process. The presence of Ba$_5$Ta$_4$O$_{15}$ pronouncedly retards the densification process and markedly degrades the microwave dielectric properties of BMT materials. The secondary phase particles are very stable and can only be eliminated by sintering at high temperature for long soaking period. A process, which can prevent the formation of undesired secondary phase, is thus called for.[7–13]

In this paper, an inverse-microemulsion process[14–16] was utilized for preparing the BMT materials. The modification on powder characteristics and microwave dielectric properties of the sintered BMT materials will be described and the possible mechanism will be discussed.

2. Experimental

In the inverse-microemulsion process, the microemulsions of reactants and the co-precipitants were prepared separately, following the flow chart shown in Fig. 1. The aqueous solutions of Ba(NO$_3$)$_2$ and Mg(NO$_3$)$_2$ dissolved in water and the TaCl$_4$ dissolved in HCl solution were added to petroleum ether (PE), forming suspension containing microcells. The PE serves as oil phase, whereas the NP-5 was used as surfactant. Similarly, microemulsion of (C$_2$H$_5$)$_4$NOH solution of oxalic acid was prepared, also using PE as oil phase and NP-5 as surfactant. The ratio of solution, oil phase and surfactant is 15:42.5:42.5 (wt. %). The two microemulsions were mixed thoroughly by stirring for 7 h and then centrifuged at 10 000 rpm to separate out the ultra-fine particles thus obtained. The co-precipitants were then
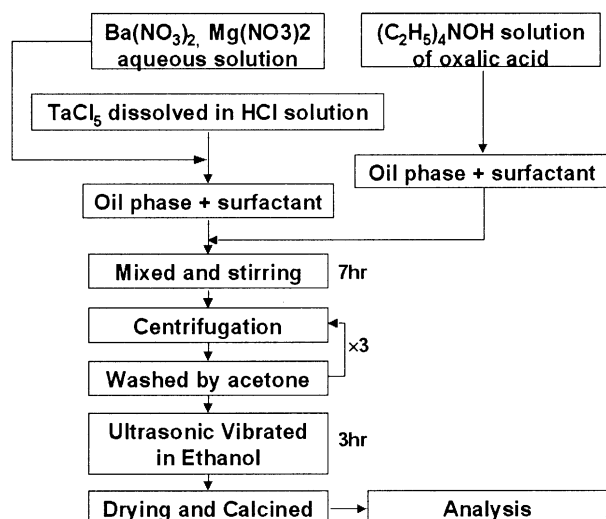
Fig. 1. Flow chart for preparing $Ba(Mg_{1/3}Ta_{2/3})O_3$ powders by the inverse-microemulsion process (oil phase: petroleum ether, PE; surfactant: NP-5).

Fig. 2. X-ray diffraction patterns of $Ba(Mg_{1/3}Ta_{2/3})O_3$ materials prepared by mixed oxide process: (a) as-calcined at 900 °C for 4 h, (b) sintered at 1550 °C for 4 h (inset shows the SEM microstructure of the sintered samples).

dried and calcined to form BMT powders, which were pressed into pellets and then sintered at 1450–1600 °C for 4–24 h. To facilitate the comparison, the BMT materials, were also prepared by mixed oxide process, i.e. via mixing, calcining, pulverizing, pressing and sintering process. Calcination was proceeded at 700–1200 °C for 4 h and sintenng was performed at 1500 °C for 4 h.

The size of the as prepared and calcined BMT powders was analyzed using dynamic laser scattering (DLS) techniques. The crystal structure and microstructure of the calcined powders and the sintered materials were examined using X-ray diffractometer (XRD; Rigaku D/max-II B) and scanning electron microscopy (SEM; Joel-JSM-5410), respectively. The microwave dielectric properties of the samples were measured by a cavity method using HP8722A network analyzer.

3. Results and discussion

In mixed oxide process, the BMT phase starts to form at 900 °C. However, a large proportion of the $Ba_5Ta_4O_{15}$ phase presents in accompany with the formation of the BMT perovskite phase (Fig. 2a). It requires high calcinations temperature ($\sim$1200 °C) to completely eliminate the undesired secondary phase. High density BMT materials [$>$95% theoretical density (T.D.)] can be obtained by sintering the samples at 1550 °C for 4 h (in air). X-ray analysis indicates that the BMT material, are highly ordered and no secondary phase was induced (Fig. 2b). SEM analysis reveals that the grain is small ($\sim$5 μm) and uniformly distributed (Fig. 2 inset). These materials possess high dielectric constant ($K\sim$26) and large quality factor ($Q\times f\sim$35,000 GHz) at 10 GHz.
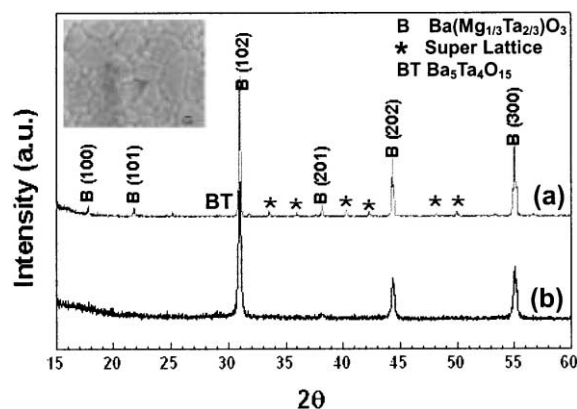
In contrast, the powders as-prepared by inverse microemulsion process are amorphous. The Perovskite, BMT phase starts to form when the inverse-microemulsion powders were calcined at 700 °C for 4 h. However, large proportion of the $BaCO_3$ phase forms preferentially (Fig. 3a). The high stability of $BaCO_3$ phase, as compared with the perovskite, will potentially induce the formation of an undesired secondary phase such as $Ba_5Ta_4O_{15}$ owing to the slow conversion rate from $BaCO_3$ to perovskite phase. Fortunately, the $BaCO_3$ phase occurred in inverse microemulsion process can be completely transformed into perovskite when calcined at 900 °C and higher temperature. The secondary phase, $Ba_5Ta_4O_{15}$, which usually formed preferentially when the BMT materials were prepared by mixed oxide process, is not observable when the BMT materials were synthesized via inverse-microemulsion routes. Presumably, this process, the ratio of the species in the micro-cell of the microemulsion favors the formation of perovskite such that the BMT phase is formed directly without the presence of $Ba_5Ta_4O_{15}$ secondary phase, even the $BaCO_3$ phase is preferentially formed. The advantage of localized reaction for the materials prepared by inverse-microemulsion route are clearly observed.

Dense BMT ceramics can be obtained by sintering the samples made of inverse-microemulsion BMT powders. No secondary phase is observable, and the ordering of the Mg- and Ta- cations resulted for the samples sintered at 1500 °C (4 h), as shown in (Fig. 3b). Unfortunately, the density of the 1500 °C (4 h) sintered BMT samples is only about 89.6% TD. Increase the sintering temperature to 1600 °C (4 h) does not result in higher density for the BMT materials. It takes longer soaking time (24 h) at 1600 °C sintering temperature to raise the density of the materials to a value higher then 96% TD (Fig. 4.). Increasing the sintering temperature to 1600 °C and soaking time to 24 h does not induce any degradation on the crystallinity and phase purity for the materials.
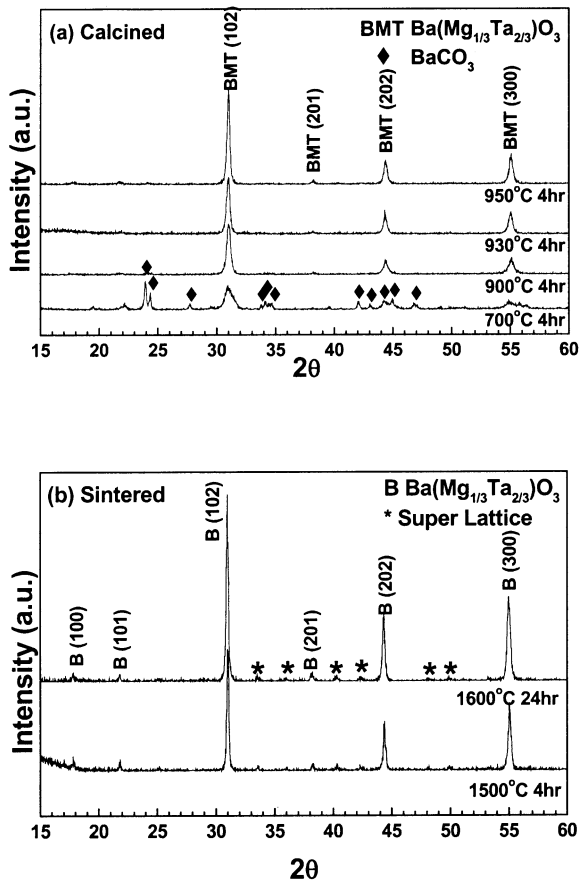
Fig. 3. X-ray diffraction patterns of (a) $Ba(Mg_{1/3}Ta_{2/3})O_3$ powders prepared by the inverse-microemulsion process and (b) sintered $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics.

Fig. 4. Variation of sintered density for the $Ba(Mg_{1/3}Ta_{2/3})O_3$ materials prepared by the inverse-microemulsion process and sintered at 1450–1600 °C (4–16 h).

Fig. 5. Particle size of the powders analyzed using dynamic laser scattering (DLS) technique: (a) as prepared and (b) calcined at 930 °C for 4 h.

Fig. 6. SEM micrographs of the $Ba(Mg_{1/3}Ta_{2/3})O_3$ powders calcined at 930 °C for 4 h.

To understand the mechanism retarding the densification of thus obtained BMT materials, the characteristics of the powders made of inverse-microemulsion process were further examined (Figs. 5a and b) and reveals that nano-sized powders, about 50–100 nm, have been successfully synthesized, but the size of the powders increases markedly, to about 500 nm, after calcinations at 930 °C (4 h). SEM micrographs in Fig. 6 indicate that the size of the powders is, in fact, still very small, about 100 nm in size, but they are seriously aggregated. The aggregation of ultra-fine powders, apparently, is the cause resulting in low sintered density for BMT materials made of these powders. Fig. 7a shows that the samples sintered at 1500 °C (4 h), which is around 89.6% TD, possess large proportion of voids.

They are of fine grain microstructure, about 1–2 μm in size. By contrast, Fig. 7b reveals that the samples sintered at 1600 °C (4 h) own high density and are almost pore free. It is interesting to observe that the size of grains is still very small, even though the sintering time was increased to 24 h at 1600 °C. The significance of such a phenomenon is that the grains of the BMT materials synthesized via inverse-microemulsion route will contain fewer proportion of defects, since it has
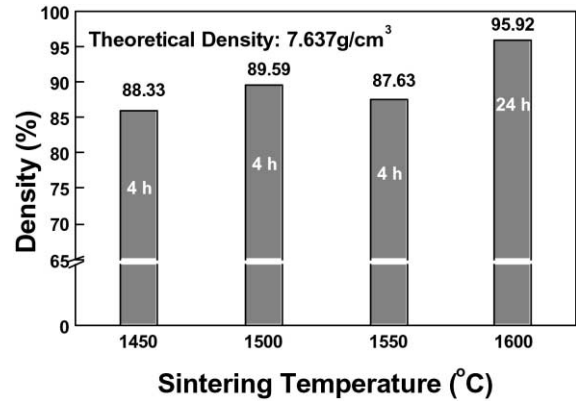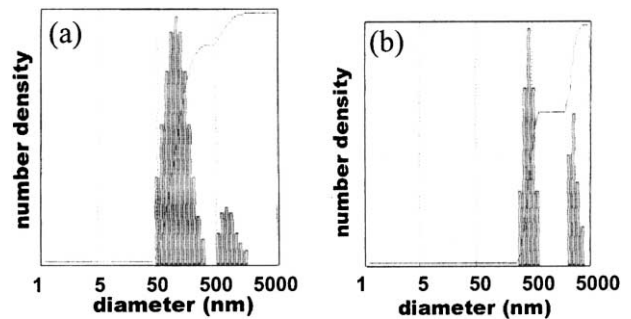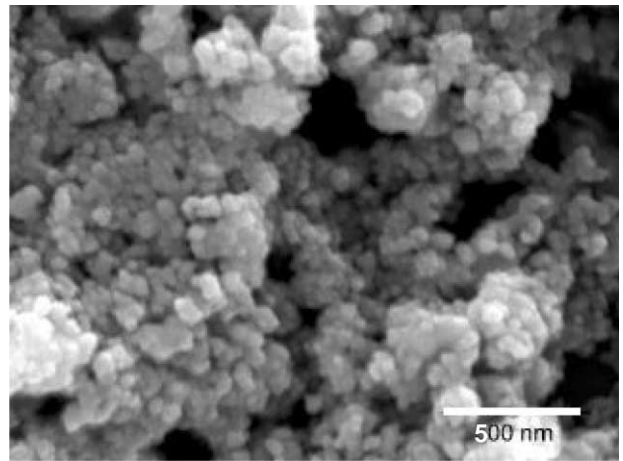
been observed that large proportion of defects, such as dislocations, and stacking faults, will be induced only when the grains are large.[17] The suppression on the formation of defects will apparently improve the quality factor for the BMT materials. The microwave dielectric properties of materials prepared via inverse-microemul-
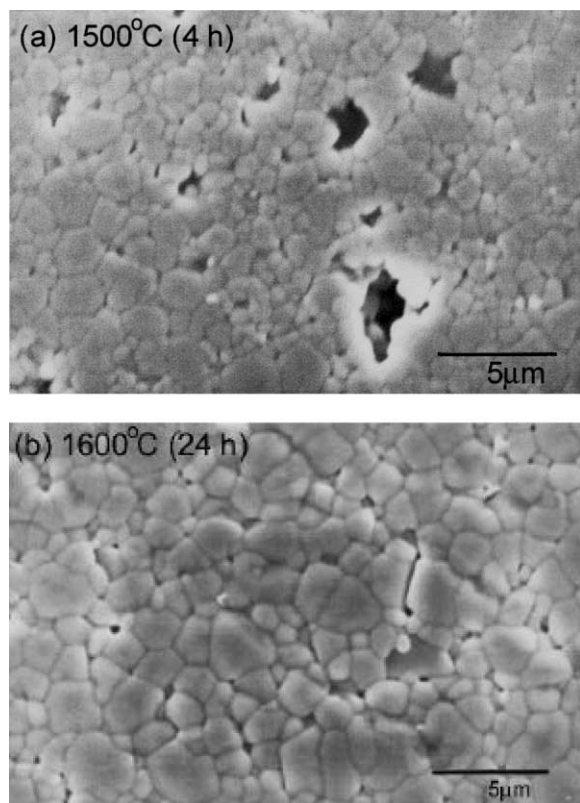
Fig. 7. SEM micrographs of the Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ ceramics sintered at (a) 1500 °C for 4 h and (b) 1600 °C for 24 h.

sion route ($K = 25.2$ and $Q \times f = 65\ 200$ GHz) are thus markedly better than those of the samples prepared by conventional mixed oxide routes ($K = 27.4$ and $Q \times f = 33\ 600$ GHz).

4. Conclusion

Microwave dielectric properties of BMT materials have been improved by using inverse-microemulsion process for preparing the BMT powders. The BMT powders, which are amorphous clusters about 100 nm in size when as-prepared, can be converted into pure perovskite phase BMT materials without the formation of undesired secondary phase (Ba$_5$Ta$_4$O$_{15}$) by calcination processes at 900 °C (4 h). Highly ordered structure of BMT materials can be obtained by sintering the samples at 1500 °C (4 h) and higher temperature. However, high enough density (95% TD) of BMT samples can be obtained only when they were sintered at 1600 °C for 24 h. Low sinterability of thus prepared BMT powders is ascribed to the formation of aggregates in calcinations process. However, the sintered BMT samples exhibit very good microwave dielectric properties, viz, the dielectric constant is $K = 25.2$ and the quality factor is $Q \times f \sim 65\ 200$ GHz, which are markedly better than the BMT materials prepared by conventional mixed oxide routes.

The prime factor is presumably the fine grain microstructure (1–2 μm) of thus obtained BMT samples.

Acknowledgements

References

1. Matsumoto, H., Tamura, H. and Wakino, K., Ba(Mg,Ta)–BaSnO$_3$ high-Q dielectric resonator. *Jpn. J. Appl. Phys.*, 1991, **30**, 2347–2349.
2. Wakino, K., High frequency dielectric and their application. In *IEEE Proc. 6th ISAF*, 1986, pp. 97–106.
3. Nomura, S., Toyama, K. and Kaneta, K., Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ ceramics with temperature-stable high dielectric constant and low microwave loss. *Jpn. J. Appl. Phy.*, 1982, **21**, L624–L626.
4. Lu, C. H. and Tsai, C. C., Reaction kinetics, sintering characteristics, and ordering behavior of microwave dielectrics: Barium magnesium tantalite. *J. Mater. Res.*, 1996, **11**, 1219.
5. Chen, X. M., Suzuki, Y. and Sato, N., Sinterability improvement of Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ dielectric ceramics. *J. Mater. Sci.*, 1994, **5**, 244–247.
6. Nomura, S., Toyama, K. and Kaneta, K., Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ ceramics with temperature-stable high dielectric constant and low microwave loss. *Jap. J. Appl. Phys.*, 1982, **21**, 624–626.
7. Liang, M. H., Hu, C. T., Chiou, C. G., Tsai, Y. N. and Lin, I. N., Effect of Ba$_5$Ta$_4$O$_{15}$ incorporation on sintering behavior and microwave dielectric properties of Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ materials. *Jpn. J. Appl. Phys.*, 1999, **38**, 71–75.
8. Galasso, F. and Pinto, J., Growth of single crystals of Ba(B′$_{0.33}$Ta$_{0.67}$)O$_3$ perovskite-type compounds. *Nature*, 70–72.
9. Barber, D. J., Moulding, K. M. and Zhou, J., Structural order in Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$, Ba(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ and Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ microwave dielectric ceramics. *J. Mater Sci.*, 1997, **32**, 1531–1544.
10. Davies, P. K. and Tong, J., Effect of ordering-induced domain boundaries on low-loss Ba(Zn$_{13}$Ta$_{23}$)O$_3$–BaZrO$_3$ perovskite microwave dielectrics. *J. Am. Ceram. Soc.*, 1997, **80**, 1727–1740.
11. Galasso, F. and Pyle, J., Ordering in compounds of the A(B′$_{0.3}$Ta$_{0.67}$)O$_3$ type. *J. Am. Chem. Soc.*, 1959, **81**, 482–484.
12. Tochi, K., Ohgaku, T. and Takeuchi, N., Long-wavelength phonons and effective charges in complex perovskite compounds Ba(Mn$_{1/3}$Ta$_{2/3}$)O$_3$ and Ba(Mn$_{0.33}$Ta$_{2/3}$)O$_3$. *J. Mater. Sci. Lett.*, 1989, **8**, 1331–1333.
13. Youn, H. J., Hong, K. S. and Kim, H., Coexistence of 1:2 and 1:1 long-range ordering types in La-modified Ba(Mg$_{0.33}$Ta$_{0.67}$)O$_3$ ceramics. *J. Mater Res.*, 1997, **12**, 589–592.
14. Bandow, S., Kimura, K. and Kon-No, K., Dispersion stability of nonaqueous calcium catbonate dispersion prepared in water core W/O microemulsion. *Jpn. J. Appl. Phys.*, 1987, **5**, 713–716.
15. Chhabra, V., Pillai, V., Mishra, B. K., Morrone, A. and Shah, D. O., Nanophase BaFel$_2$O$_{19}$ synthesized from a nonaqueous microemulsion with Ba- and Fe-containing surfactants. *Langmuir*, 1995, **11**, 3307–3311.
16. Lim, G. K., Wang, J., Ng, S. C. and Gan, L. M., Processing of fine hydroxyapatite powders via an inverse microemulsion route. *Materials Letters*, 1996, **28**, 431–436.
17. Liang, M.-H., Hu, C.-T., Cheng, H.-F., Lin, I.-N. & Steeds, J., Effect of sintering process on microstructure characteristics of Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ ceramics and their microwave dielectric properties. *J. Eur. Ceram. Soc.*, 2001, **21**(15), 2759–2763.