Journal of the European Ceramic Society 21 (2001) 1705–1709
www.elsevier.com/locate/jeurceramsoc

Effect of $Ba_5Ta_4O_{15}$ on microstructural characteristics of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics and their microwave dielectric properties

I.-Nan Lin [a,*], Mei-Hui Liang [b], Chen-Ti Hu [b], John Steeds [c]

[a] Materials Science Center, National Tsing-Hua University, Hsinchu, Taiwan 300, ROC
[b] Department of Materials Science and Engineering, National Tsing-Hua University, Hsinchu, Taiwan 300, ROC
[c] Department of Physics, University of Bristol, Bristol BS8 1TL, UK

Received 4 September 2000; received in revised form 14 November 2000; accepted 10 December 2000

Abstract

Microstructures of the $Ba(Mg_{1/3}Ta_{2/3})O_3$, BMT, materials were examined using transmission electron microscopy. It is observed that small BMT grains usually contain very few defects, whereas large BMT grains always contain large proportion of dislocations, stacking faults and midribs of secondary phase. Incorporation of small amount (~0.1 mol%) of $Ba_5Ta_4O_{15}$ particles improves the uniformity of grains. However, the density of dislocations increases tremendously, resulting in tangling of dislocations and even the formation of networks, whereas the proportion of stacking faults decreases pronouncedly for the $Ba_5Ta_4O_{15}$ added BMT materials. Presumably, it is through the hindrance on the growth of grains and modification on the formation of defects that incorporation of $Ba_5Ta_4O_{15}$ particles alters the microwave dielectric properties of BMT materials.

Keywords: $Ba(Mg_{1/3}Ta_{2/3})O_3$; Microwave dielectrics; TEM microstructure

1. Introduction

In light of the technological development trends in the 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 arranged in an ordered fashion, possess the highest Q-factor ($Q \cong$ 5, 000 at 10 GHz) among the known microwave dielectric materials. These materials are also characterized by a low temperature coefficient of resonance frequency ($\tau_f = 5$ ppm/°C) and large microwave dielectric constant ($K = 25$) and thus have great potential for application devices. However, high sintering temperature (>1600°C) and long soaking time (>16 h) are required to achieve sufficiently high sintered density for the practical application of these BMT materials.[3–6] A two-step process consisting of the synthesis of intermediate-phase $MgTa_2O_6$ prior to the formation of BMT to improve the microwave dielectric properties has been observed to markedly reduce the sintering temperature and soaking time necessary to densify BMT materials, improving the microwave dielectric properties of the materials.[7] Incorporation of additives, such as Y_2O_3, $Ba_5Ta_4O_{15}$ or other second perovskite type materials, were also found beneficial for the formation of BMT materials.[8–14] However, the mechanism involved is still not well understood. To understand the mechanism, underlying the improvement in the densification kinetics of BMT materials prepared by the two-step process, the effect of $Ba_5Ta_4O_{15}$, BaT, incorporation on the characteristics of BMT materials prepared by such a process was systematically investigated. How the addition of BaT particles influence the microwave characteristics of BMT materials was investigated by examining the microstructure of these materials using transmission electron microscopy.

2. Experiments

To study the effect of the secondary-phase $Ba_5Ta_4O_{15}$ on the characteristics of BMT materials, $Ba_5Ta_4O_{15}$ and perovskite $Ba(Mg_{1/3}Ta_{2/3})O_3$ powders were synthesized separately. In the preparation of perovskite BMT powders, a two-step process was adopted: (i) $MgTa_2O_6$ powders were first prepared by the mixed oxide process, (ii) the powders were then mixed with $BaCO_3$ in a 1:3

* Corresponding author. Tel.: +886-3-5742573; fax: +886-3-5716977.
E-mail address: inlin@mx.nthu.edu.tw (I.-N. Lin).

0955-2219/01/$ - see front matter
PII: S0955-2219(01)00098-X

molar ratio for nominal composition $Ba(Mg_{1/3}Ta_{2/3})O_3$ and then calcined at 800°C for 2 h. Pure perovskite Ba $(Mg_{1/3}Ta_{2/3})O_3$ powders were thus obtained. $Ba_5Ta_4O_{15}$ powders were prepared by calcining a $BaCO_3/Ta_2O_5$ powder mixture in the molar ratio (5:2) at 1200°C (4 h). The perovskite BMT powders containing a small amount of $Ba_5Ta_4O_{15}$ powder (~0.1–3.0 mol%) were then pelletized, which were sintered at 1450-1600°C for 4 h. The sintered density was measured using Achimedas' method.

The crystal structure and the microstructure of the sintered BMT samples were examined by X-ray diffraction analysis (XRD, Rigaku D/max-IIB) and scanning electron microscopy (SEM, Jeol JSM-840A), respectively. The microwave dielectric properties were measured using a H.P.8722A network analyzer in a resonant cavity or parallel plate test fixture.[15] The defects in the materials were examined using transmission electron microscopy (Joel, 200cx).

3. Results and discussion

The densification behavior is markedly improved for the $Ba(Mg_{1/3}Ta_{2/3})O_3$, BMT, samples pelletized from the powders prepared by the two-step calcination process such that a density of 7.29 g per cm^3, which is 95.5% T.D. (theoretical density, 7.636 g/cm^3) can be obtained by sintering the materials at 1550°C×4 h. The dielectric constant is around K = 24–25 and the quality factor reaches $Q \times f = 600,000$ GHz for high-density BMT materials. The temperature dependence of the resonance frequency is $(\tau_f)_I = 8.13$ ppm/°C. Incorporation of $Ba_5Ta_4O_{15}$ (BaT) powders significantly affects the densification behavior of the BMT samples. Addition of 0.1 mol% of BaT-powders markedly increases the sintered density of the BMT materials; that is, a density as high as 97.5% TD is achieved. Further increase in the BaT content beyond 0.5 mol% significantly degrades the sintering behavior. The density achievable for 1 or 3 mol% BaT-incorporated materials is only 96.2% TD. All the high density BMT materials, which contain 0.1–3% BaT, possess a high dielectric constant ($K = 26-28$) and stable temperature dependence of resonance frequency ($\tau_f = 8-12$ ppm per °C). However, the Q-factor, which is an indication of dielectric loss, decreases monotonously with the proportion of BaT powders.

SEM examinations indicate that the grains of BMT materials are very small, around 2.5 μm. Incorporation of 0.1 mol% $Ba_5Ta_4O_{15}$, BaT, materials markedly improves the uniformity of grain size distribution without altering the grain size of the materials. Addition of more BaT does not further modify the granular structure of the BMT samples, but the BaT particles, which are about 0.3 μm in size, start to aggregate.

Apparently, to understand the mechanism, which alters the microwave dielectric properties of BMT materials due to BaT-incorporation, information on detailed microstructures of these materials using TEM are needed. TEM-micrographs shown in Fig. 1(a) reveals that very few defects are observable for small BMT grains, but abundant defects appear when the grains are big. The contrast of the defects changes with orientation of grains, indicating that the clean image is not necessary defect free. Therefore, tilting of samples is needed in order to make sure that area is free of defects. However, TEM examinations on $Ba(Mg_{1/3}Ta_{2/3})O_3$ materials, BMT, using TEM is extremely difficult due to the highly insulating nature of the materials. The instability nature of the structure, which results in drastic phase changes due to electron irradiation during the tilting experiments for analyzing of defects, makes the analysis even more difficult.

Occasionally, there appear grains as large as 7.5 μm, which contains sub-areas (~2.5 μm) separated by diffuse boundaries [Fig. 1(b)]. Selected area diffraction (SAD) examinations indicate that all these sub-areas belong to the same grains. Probably, the large grain is a result of the coalescence of adjacent small grains, such that the boundaries of the original grains, a highly strained region, show vague contrast. Similarly, in the center of this grain, a wavy contrast is observed, which is, again, presumed to be the result of the coalescence of adjacent grains. Fig. 1(c) shows that plate-like defects, the stacking faults (labelled as "F") and the associated dislocations exist all over the grains. Occasionally, there exist defects of spherical geometry, which are probably the BMT material formed via the reaction of BaT particles with the surrounding materials.

In addition to the stacking faults and dislocations frequently seen in large BMT grains, huge midrib-like defects running across the whole grains are occasionally observed, as shown in Fig. 2. High-resolution TEM examinations indicate that the midribs are of similar composition as the BMT perovskite with different stacking sequence of the layers. They are of 8-layer periodicity, designated as 8L-phase, and may contain internal planar disorder. The image of the 8L midribs does not change contrast as the samples tilted, which is different from that of the stacking faults. It seems that once these midribs are nucleated, they grow laterally in a vary rapid rate, acrossing several grains. The mechanism triggering the formation of such kind of large periodicity phase is not clear yet.

The TEM micrograph in Fig. 3 indicates that the uniformity of the grain size has been markedly improved due to the addition 0.1 mol% of BaT particles into BMT materials, which is in accord with SEM examinations. The average grain size is also around 2.5 μm for the BaT incorporated BMT materials. A large proportion of defects, including stacking faults, and dislocations, also appear in the large grains. Small spherical regions of the same composition and structure as the BMT matrix are

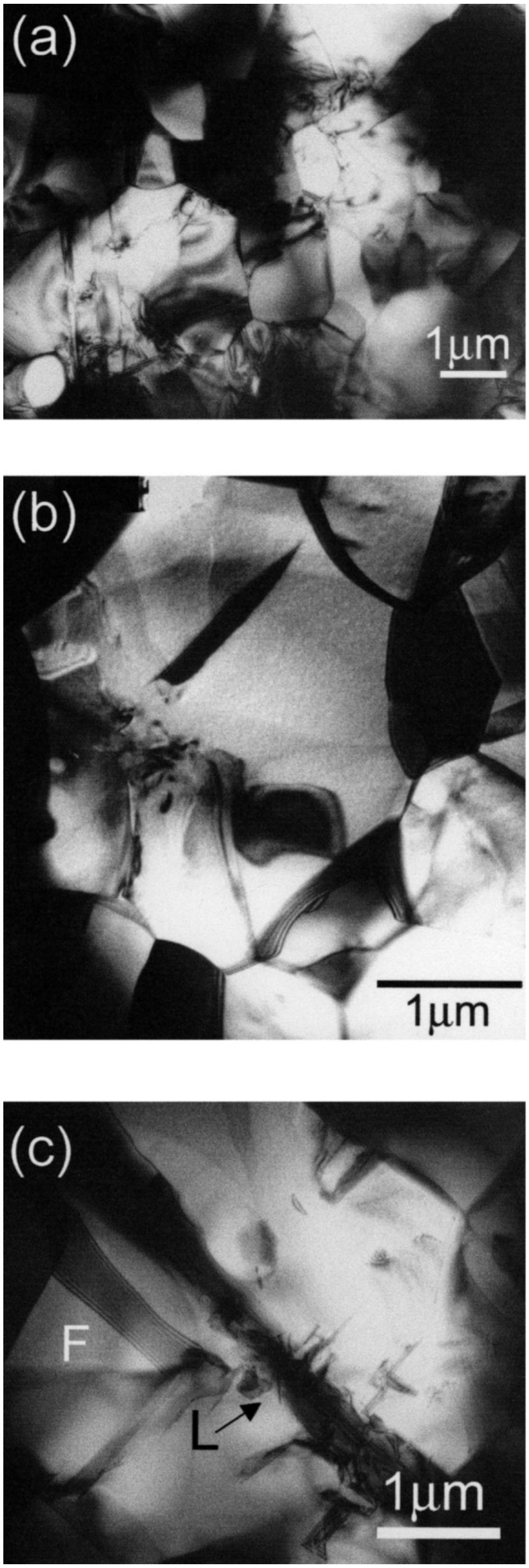

Fig. 1. TEM micrographs of $Ba(Mg_{1/3}Ta_{2/3})O_3$ materials incorporated with 0 mol% $Ba_5Ta_4O_{15}$, BaT, materials showing: (a) typical overall microstructure; (b) microstructure of a large grain, and (c) the stacking fault, F, and dislocation loops, L.

Fig. 2. TEM micrograph of $Ba(Mg_{1/3}Ta_{2/3})O_3$ materials incorporated with 0 mol% $Ba_5Ta_4O_{15}$, BaT, materials; showing a midrib running across the whole grains, which are of 8 layer periodicity.

Fig. 3. TEM micrographs of $Ba(Mg_{1/3}Ta_{2/3})O_3$ materials incorporated with 0.1 mol% $Ba_5Ta_4O_{15}$, BaT, showing fine grain microstructure of the materials.

also observed in these samples. The stacking faults in these materials are simpler in structure, that is, short, straight and associated with dislocations only at the edge or the joints of the faults. Midribs of 8L secondary phase are also observable. The most intriguing phenomenon in BaT-incorporated samples is that, in the big grains, high density of dislocations is present [Fig. 4(a)]. These dislocations may tangle together and even form dislocation networks [Fig. 4(b)].

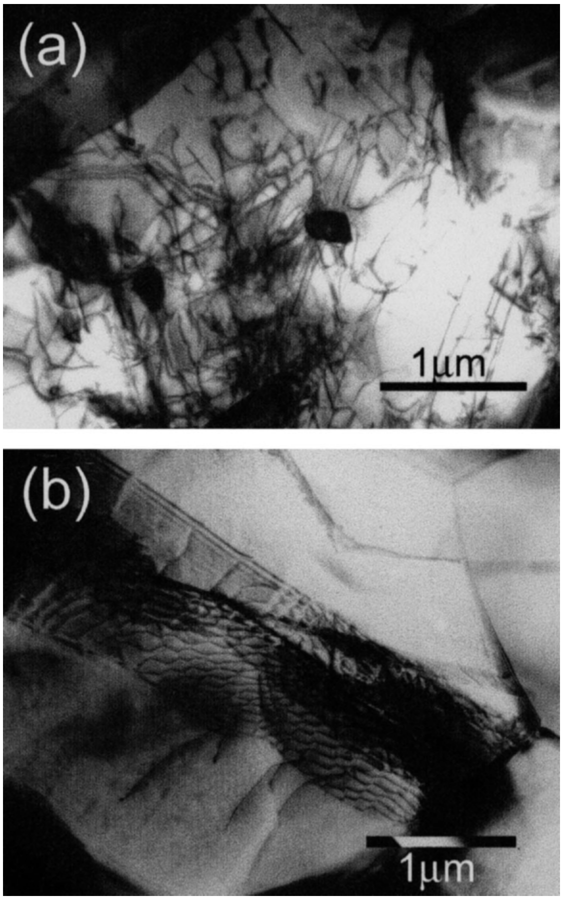

Fig. 4. TEM micrographs of $Ba(Mg_{1/3}Ta_{2/3})O_3$ materials incorporated with 0.1 mol% $Ba_5Ta_4O_{15}$, BaT, materials shows the (a) tangling of dislocations and (b) forming dislocation networks.

It should be noted that the density of the stacking faults in BaT-incorporated BMT samples is pronouncedly lower than those in undoped BMT materials. Presumably, a stacking fault was formed when a partial dislocation, which was dissociated from a perfect dislocation, was swept away. Tangling of dislocations prohibit their gliding capability such that the formation of stacking fault is suppressed. Such a model account for the different characteristics of defects observable in BMT materials, viz. the undoped materials contain large proportion of stacking faults but less density of dislocations, whereas the BaT-doped materials contain high density of dislocation but fewer stacking faults. Apparently, large proportion of defects contained in the big grains will degrade the quality factor (Q) of the materials. Only the small grains ($\leqslant 2$ μm), which are free of defects can have a high Q-value. The implication of these results is that the suppression on the formation of defect via the reduction on grain size is a possible approach for improving the microwave dielectric properties for these materials.

4. Conclusion

$Ba(Mg_{1/3}Ta_{2/3})O_3$, BMT, materials prepared by the two-step process possess good microwave dielectric properties. The $Ba_5Ta_4O_{15}$, BaT, incorporated into pure BMT perovskite prepared by such a two-step process was found to significantly influence the densification behavior and microwave dielectric chacteristics of the BMT materials. The sintered density of BMT materials decreases with the proportion of secondary-phase $Ba_5Ta_4O_{15}$. The dielectric constant (K) and temperature coefficient of resonance frequency (τ_f) are insignificantly changed, but the Q-factor of the BMT materials decreases as the $Ba_5Ta_4O_{15}$ concentration increases. The defects existing in $Ba(Mg_{1/3}Ta_{2/3})O_3$ materials were examined using transmission electron microscopy, which reveals that both the undoped and BaT-incorporated materials posses similar microstructures, except that the dislocation density increases and the stacking fault density decreases, whenever BaT particles were incorporated.

Acknowledgements

The financial support of National Science Councils, ROC through project No. NSC 89-2622-E-007-005 is gratefully appreciated.

References

1. Wakino, K., High frequency dielectric and their application. *IEEE Proc. 6th ISAF*, 1986, 97–106.
2. Matsumoto, H., Tamura, H. and Wakino, K., Ba(Mg,Ta)–$BaSnO_3$ high-Q dielectric resonator. *Jpn. J. Appl. Phys.*, 1991, **30**, 2347–2349.
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. Phys.*, 1982, **21**, 624–626.
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. *Jpn. J. Appl. Phys.*, 1982, **21**, 624–626.
7. Liang, M. H., Hu, C. T., Chiou, C. G., Tsai, Y. N. and Lin, I. N., Effcet of $Ba_5Ta_4O_{15}$ 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*, 1965, 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 $Ba(Zn_{1/3}Ta_{2/3})O_3$–$BaZrO_3$ perovskite microwave dielectrics. *J. Am. Ceram. Soc.*, 1997, **80**, 1727–1740.
11. Galasso, F. and Pyle, J., Ordering in compounds of the $A(B'_{0.33}Ta_{0.67})O_3$ 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 $Ba(Ni_{1/3}Ta_{2/3})O_3$. *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. Youn, H. J., Kim, K. Y. and Kim, H., Microstructure characteristics of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics and its related microwave dielectric properties. *Jpn. J. Appl. Phys.*, 1996, **35**, 3947–3953.
15. Hakki, B. W. and Coleman, P. D., A dielectric resonator method of measuring inductive capacities in the millimeter range. *IRE Trans. Microwave Theory Technol.*, 1960, **MTT-8**, 402–410.