SYNTHESIS OF 0.95$MgTiO_3$-0.05$CaTiO_3$ CERAMICS BY REACTION-SINTERING

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Abstract

0.95$MgTiO_3$-0.05$CaTiO_3$ (MCT) ceramics prepared using a reaction-sintering process were investigated. Without any calcination involved, the mixture of $Mg(OH)_2$, $CaCO_3$ and TiO_2 was pressed and sintered directly. MCT ceramics were obtained after 2-6 h sintering at 1150-1250^oC. Secondary phase $MgTi_2O_5$ as in $MgTiO_3$ prepared by the conventional mixed oxide route was not detected. The maximum density 3.62g/cm^3 (93.8% of the theoretical value) was obtained at 1230^oC/2 h. For 2 h sintering, grains of size less than 10 μm were formed. Abnormal grains (>70μm) were observed in pellets sintered for 4 and 6 h due to the secondary grain growth.

1 Introduction

Dielectric resonators used in microwave frequency have been widely investigated due to the fast growth of satellite and mobile communication systems. $MgTiO_3$ (MT) was reported to exhibit good dielectric properties of ε_r ~17, Q×f ~160,000 at 7 GHz and τ_f ~ -50 ppm/^oC. As $CaTiO_3$ (CT) with dielectric properties of ε_r~170, Q×f ~ 3,600 at 7 GHz and τ_f ~ 800 ppm/^oC was mixed into MT, τ_f near 0 ppm/^oC could be obtained [1-4].

Synthesis of MT-based ceramics has been reported in many studies by solid-state reaction methods [5-7], sol-gel [8], coprecipitation[9], thermal decomposition of peroxide precursors [10] and mechanochemical routes [11-12]. High temperature around 1400^oC is required in conventional solid-state synthesis from oxide precursors. Phase pure $MgTiO_3$ is difficult to obtain by solid-state reactions because of the formation of some metastable titanate phases. $MgTi_2O_5$ was still found in $MgTiO_3$ ceramic even by the mechanochemical process [11]. Dielectric properties of $MgTi_2O_5$ are ε_r ~17.4, Q×f ~47,000 GHz and τ_f ~ -66 ppm/^oC [13].

Reaction-sintering process is a simple and effective route to obtain ceramics with high density. The mixture of the raw materials is sintered directly with the calcination step bypassed. Liou and co-workers proposed $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) and $Pb(Fe_{0.5}Nb_{0.5})O_3$ (PFN) ceramics produced via a reaction-sintering process [14-16]. PMN ceramics with 99.5% of the theoretical density and high dielectric constant 19,900 (1 kHz) were obtained. This reaction-sintering process had also been successfully used to produce other complex perovskite relaxor ceramics [17-21]. Recently, Liou et al. produced some ceramics used for microwave dielectric components such as $BaTi_4O_9$, $Ba_5Nb_4O_{15}$, $Sr_5Nb_4O_{15}$, $CaNb_2O_6$ and $ZnNb_2O_6$ via this direct sintering method [22-25]. In this study, we try to obtain 0.95$MgTiO_3$-0.05$CaTiO_3$ ceramics by the reaction-sintering process.

2 Experimental procedure

All samples were prepared from reagent-grade powders: $Mg(OH)_2$ (95%), TiO_2 (99.9%), and $CaCO_3$ (99.9%). Appropriate amounts of raw materials for 0.95$MgTiO_3$-0.05$CaTiO_3$ (MCT) were weighed. The mixture was milled in acetone with zirconia balls for 12 h and then dried, pulverized and pressed into pellets of 12 mm in diameter and 1-2 mm thick. The pellets were heated at a rate 10^oC/min and sintered in a covered alumina crucible at temperatures ranging from 1150^oC to 1300^oC for 2-6 h in air.

Crystalline phases of the sintered pellets were identified with X-ray diffraction (XRD). Microstructures were analyzed by scanning electron microscopy (SEM). The density of sintered pellets was measured by the Archimedes method.

3 Results and discussion

Fig. 1 shows the XRD profiles of MCT ceramics using $Mg(OH)_2$ and with 1-3 mol% excess $Mg(OH)_2$ after sintered at 1250°C/2 h. The main phase $MgTiO_3$ formed and the minor phase $CaTiO_3$ was also found in the profiles. $MgTi_2O_5$ often formed in $MgTiO_3$ as a stable intermediate phase by mixed oxide route [2]. $MgTi_2O_5$ phase formed in MCT ceramics using MgO (Fig. 1 (a)) by the reaction-sintering process was not observed. This proves the $MgTiO_3$-based ceramics could be obtained by the reaction-sintering process. This simple process is effective not only in preparing $BaTi_4O_9$, $Ba_5Nb_4O_{15}$, $Sr_5Nb_4O_{15}$, $CaNb_2O_6$, $ZnNb_2O_6$ and Pb-based complex perovskite ceramics but also effective in preparing ceramics with MT and CT mixed phase.

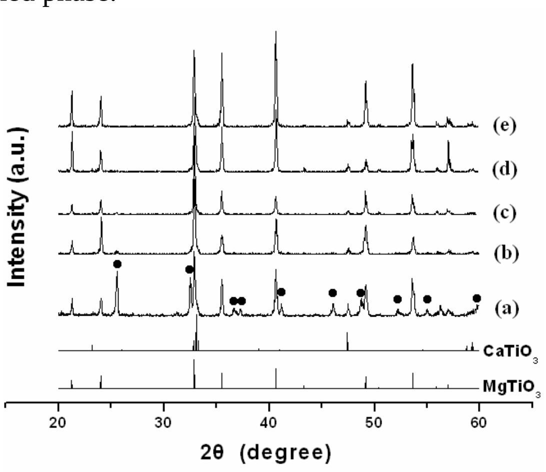

Fig. 1. XRD profiles of MCT ceramics using (a) MgO, (b) $Mg(OH)_2$ and with (c) 1, (d) 2 (e) 3 mol% excess $Mg(OH)_2$ and sintered at 1250°C/2 h. ($MgTiO_3$: ICDD # 00-006-0494, $CaTiO_3$: JCPDS # 89-8033, ●: $MgTi_2O_5$)

In Fig. 2, the density value of MCT increased with sintering temperature and saturated above 1230°C. The maximum density 3.62g/cm^3 (93.8% of the theoretical value) was obtained at 1230°C/2 h. Huang *et al*. reported MCT ceramics of density 3.49-3.72g/cm^3 with addition of sintering aids Bi_2O_3, CuO and B_2O_3. They used conventional mixed oxide route and pellets were calcined at 1100°C/3-4 h then sintered at 1200-1300°C/3-4 h [2-4]. Maximum density 3.85g/cm^3 could be obtained in MCT using MgO via the reaction-sintering process and sintered at 1250°C/4 h. Lower density in MCT using $Mg(OH)_2$ may caused by the fast grain growth and resulted in lots of isolated pores inside the pellets.

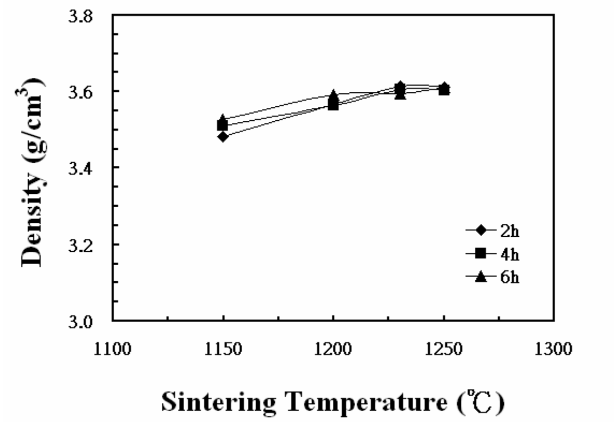

Fig. 2. Density of MCT ceramics with 2 mol% excess $Mg(OH)_2$ sintered at various temperatures and times.

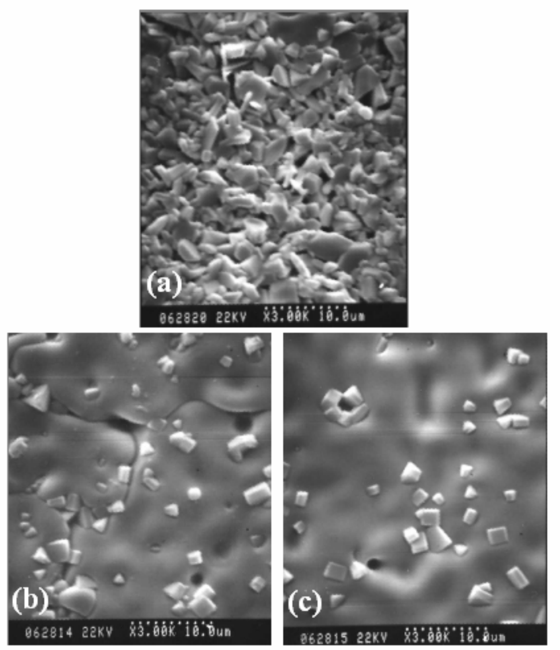

Fig. 3. SEM photos of MCT ceramics with 2 mol% excess $Mg(OH)_2$ sintered at 1150°C for (a) 2 h, (b) 4 h and (c) 6 h.

The SEM photos of MCT ceramics sintered at 1150°C for 2 h are shown in Fig. 3. For 2 h sintering, grains of size less than 10 μm were formed. Abnormal grains (>70μm) were observed in pellets sintered for 4 and 6 h due to the secondary grain growth. It can be noted that grains with two different sizes formed in MCT pellets. The larger grains are $MgTiO_3$ and the smaller grains are $CaTiO_3$ or $MgTiO_3$. In the study of Huang and Weng, large grains in MCT ceramics with B_2O_3 addition were recognized as $MgTiO_3$ and small grains might be

$CaTiO_3$ or $MgTiO_3$ [2]. In doped $MgTiO_3$-$CaTiO_3$ prepared via conventional solid-state reaction method, Woo et al. found that large grains were identified as $MgTiO_3$, containing dispersed small $CaTiO_3$ crystallites inside. $CaTiO_3$ and $MgTiO_3$ phases were separated due to virtually no solid solubility between them because of different crystal structures [26]. Wing et al. also observed similar morphology in calcium magnesium titanate system. Large-scale inhomogeneities occurred on the scale of 100–200 μm and showed very little calcium content [27].

4 Conclusions

0.95$MgTiO_3$-0.05$CaTiO_3$ ceramics have been obtained successfully by a reaction-sintering process using $Mg(OH)_2$. Secondary phase $MgTi_2O_5$ as in $MgTiO_3$ prepared by the conventional mixed oxide route was not detected. The maximum density 3.62g/cm^3 (93.8% of the theoretical value) was obtained at 1230^{o}C/2 h. For 2 h sintering, grains of size less than 10 μm were formed. Abnormal grains (>70μm) were observed in pellets sintered for 4 and 6 h due to the secondary grain growth.

References

[1] Wakino K. "Recent development of dielectric resonator materials and filters in Japan". *Ferroelectrics*, Vol. 91, pp 69-86, 1989.

[2] Huang C.L. and Weng M.H. "Improved high Q value of $MgTiO_3$–$CaTiO_3$ microwave dielectric ceramics at low sintering temperature". *Mater. Res. Bull.*, Vol. 36, pp 2741-2750, 2001.

[3] Huang C.L., Pan C.L. and Shium S.J. "Liquid phase sintering of $MgTiO_3$–$CaTiO_3$ microwave dielectric ceramics". *Mater. Chem. & Phys.*, Vol. 78, pp 111-115, 2002.

[4] Huang C.L. and Pan C.L. "Low-temperature sintering and microwave dielectric properties of (1-x)$MgTiO_3$-x$CaTiO_3$ ceramics using bismuth addition". *Jpn. J. Appl. Phys.*, Vol. 41, pp 707-711 , 2002.

[5] B. Naylor, A. Cook, "High-temperature heat contents of the metatitanates of calcium, iron and magnesium". *J. Am. Chem. Soc.*, Vol. 68, pp 1003-1005, 1946.

[6] B. Wechsler, A. Navrotsky, "Thermodynamics and structureal chemistry of compounds in the system MgO-TiO_2". *J. Solid State Chem.*, Vol. 55, pp 165-180, 1984.

[7] C. L. Huang and M. H. Weng, "Improved high Q value of $MgTiO_3$–$CaTiO_3$ microwave dielectric ceramics at low sintering temperature". *Mater. Res. Bull*. Vol. 36, pp 2741–2750, 2001.

[8] I. R. Abothu, A. V. P. Rao and S. Komarneni, "Nanocomposite and monophasic synthesis routes to magnesium titanate". *Mater. Lett.*, Vol. 38, pp 186-189, 1999.

[9] M. P. Baura-Pena, M. J. Martinez-Lope, M. E. Garcia-Claval, "Synthesis of the mineral geikielite $MgTiO_3$". *J. Mater. Sci.*, Vol. 26, pp 4341-4343, 1991.

[10] G. Pfaff, "Peroxide route for synthesis of magnesium titanate powders of various compositions". *Ceram. Int.*, Vol. 20, pp 111-116, 1994.

[11] J. Liao, M. Senna, "Crystallization of Titania and magnesium titanate from mechanically activated $Mg(OH)_2$ and TiO_2 gel mixture", *Mater. Res. Bull.*, Vol. 30, pp 385-392, 1995.

[12] J. G. Baek, T. Isobe and M. Senna, "Mechanochemical effects on the precursor formation and microwave dielectric characteristics of $MgTiO_3$". *Solid State Ionics*, Vol. 90, pp 269-279, 1996.

[13] H. Shin, H. K. Shin, H. S. Jung, S. Y. Cho, K. S. Hong, "Phase evolution and dielectric properties of $MgTi_2O_5$ ceramic sintered with lithium borosilicate glass". *Mater. Res. Bull.*, Vol. 40, pp 2021-2028, 2005.

[14] Y. C. Liou and K. H. Tseng, "Stoichiometric $Pb(Mg_{1/3}Nb_{2/3})O_3$ perovskite ceramics produced by reaction-sintering process". *Mater. Res. Bull.*, Vol. 38(8), pp 1351-1357, 2003.

[15] Y. C. Liou, "Stoichiometric perovskite PMN-PT ceramics produced by reaction-sintering process". *Mater. Sci. and Eng. B.*, Vol. 103(3), pp 281-284, 2003.

[16] Y. C. Liou, C. Y. Shih and C. H. Yu, "Stoichiometric $Pb(Fe_{1/2}Nb_{1/2})O_3$ perovskite ceramics produced by reaction-sintering process". *Mater. Lett.*, Vol. 57(13-14), pp 1977-1981, 2003.

[17] Y. C. Liou, "PMN-PFN relaxor ferroelectric ceramics by a reaction-sintering process". *J. Electroceram.*, Vol. 12, pp 187-190, 2004.

[18] Y. C. Liou, "$Pb((Mg_{0.7}Zn_{0.3})_{1/3}Nb_{2/3})O_3$ relaxor ferroelectric ceramics by a reaction-sintering process". *J. Electroceram.*, Vol. 13, pp 453-456, 2004.

[19] Y. C. Liou, C. J. Chuang and Y. C. Shih, "Low-firing PZN-PFN-PFW relaxor ferroelectric ceramics produced by a reaction-sintering process". *Mater. Chem. & Phys.*,Vol. 93[1], pp 26-30, 2005.

[20] Y. C. Liou, J. H. Chen, Y. C. Huang, C. T. Wu and Y. R. Chen, "Synthesis of $Pb(Ni_{1/3}Nb_{2/3})_{0.72}Ti_{0.28}O_3$ Perovskite ceramics by a reaction-sintering process". *J. Electroceram.*, Vol. 16(3), pp 213-220, 2006.

[21] Y. C. Liou, Y. C. Huang and C. T. Wu, "Preparation and phase formation of perovskite $Pb(Ni_{1/3}Nb_{2/3})O_3$ by a reaction-sintering process". *J. Mater. Sci.*, in press. 2007.

[22] Y. C. Liou, C. T. Wu, K. H. Tseng and T. C. Chung, "Synthesis of $BaTi_4O_9$ ceramics by reaction-

sintering process". *Mater. Res. Bull.*, Vol. 40[9], pp 1483-1489, 2005.
[23] Y. C. Liou and W. H. Shiu, Chung-Yu Shih, "Microwave ceramics $Ba_5Nb_4O_{15}$ and $Sr_5Nb_4O_{15}$ prepared by a reaction-sintering process". *Mater. Sci. and Eng. B*, Vol. 131[1-3], pp 142-146, 2006.
[24] Y. C. Liou, M. H. Weng and C. Y. Shiue, "$CaNb_2O_6$ ceramics prepared by a reaction-sintering process". *Mater. Sci. and Eng. B*, Vol. 133[1-3], pp 14-19, 2006.
[25] Y. C. Liou, Y. L. Sung, "Preparation of Columbite $MgNb_2O_6$ and $ZnNb_2O_6$ ceramics by reaction-sintering". *Ceram. Int.*, in press, 2007.
[26] D. C. Woo, H. Y. Lee, J. J. Kim, T. H. Kim, S. J. Lee, J. R. Park and T. G. Choy, "Microwave dielectric properties of doped-$MgTiO_3$ ceramics". ISAF '96 Proceedings of the Tenth IEEE International Symposium on Applications of Ferroelectrics Volume 2, Issue, 18-21 Aug, 1996, 863-866.
[27] Z. N. Wing, J. W. Halloran, Q Zhang and P. J. McGinn, "Variable dielectrics in the calcium magnesium titanate system characterized with scanning microwave microscopy". *J. Am. Ceram. Soc.*, Vol. 89 [5], pp 1610–1614, 2006.