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Low temperature sintering of $(Zn_{1-x}, Mg_x)TiO_3$ microwave dielectrics

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Abstract

The effects of glass additives and milling process on the microwave dielectric properties of (Zn_{1-x}, Mg_x) TiO_3 (ZMT) ceramics were investigated. Three glasses including B_2O_3–SiO_2–ZnO–Na_2O (B–Si–Zn–Na), B_2O_3–SiO_2–ZnO–K_2O (B–Si–Zn–K) and B_2O_3–K_2O–$MnCO_3$ (B–K–Mn) were selected for this study. Host material $(Zn_{0.6}Mg_{0.4})TiO_3$ was selected to be sintered with glasses in the temperature range of 900–1200 °C. For $(Zn_{0.6}Mg_{0.4})TiO_3$ with 5 wt.% glass B–Si–Zn–K sintered at 1100 °C, the ϵ_r and $Q \times f$ values were 18 and 29,375, respectively. Taking advantage of satellite milling, the ZMT ceramics can be sintered at 950 °C with the density of 4.21 g/cm^3, ϵ_r = 19, and $Q \times f$ = 18,957.

Keywords: A. Sintering; A. Milling; Microwave dielectrics; Zinc titanate; Glass additives

1. Introduction

Due to the rapid development of wireless communication services, the microwave ceramic devices with high performance are desired. The materials used in UHF microwave ceramic devices need to satisfy three requirements, namely the high dielectric constant, ϵ_r, high quality factor, Q, low and as close as possible to zero temperature coefficient of resonant frequency, τ_f. In order to miniaturize the microwave devices, the size of dielectric components must also be reduced. Multilayer devices have been developed to increase the volume efficiency. In multilayer structure, it is necessary to lower the sintering temperature of the dielectrics in order to co-fire with low melting point and highly conductive internal electrode metals, such as silver, copper, and their alloys [1–3].

Introducing low melting glass additives, chemical processing, and fining particle size of the starting materials are three of the methods used to reduce the sintering temperature of the dielectrics. Among these methods, glass additives used in liquid phase sintering is the most effective and least expensive [4]. Zinc titanate ($ZnTiO_3$) is a promising candidate for low temperature sintering dielectrics, because it can be sintered at 1100 °C without sintering aids and can be sintered at temperature <900 °C with B_2O_3 glass. But this phase will decompose as the sintering temperature is above 900 °C. Kim et al. studied in advance the phase stability by adding magnesium, and their microwave properties [5–8]. In order to extend the processing window, this paper studied the effect of ternary B–Si–Zn glass system on the sinterability and also discussed the effect of Mg content on the $ZnTiO_3$ phase stability, processing conditions, and microwave properties.

2. Experimental procedure

$(Zn_{1-x}, Mg_x)TiO_3$ (x = 0–0.5) powder as the host material was prepared by solid-reaction method. High purity oxides, TiO_2 (99.9% Showa Denko G1), ZnO (99.9% Umicore) and MgO (99% PCF) were mixed and then calcined at 700 °C for 2 h, followed by pulverization, pressing and then sintering in the temperature range of 950–1300 °C with intervals of 50 °C for 4 h. Three glasses were used in this study. The composition for glasses A–C are listed in Table 1. These

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Table 1
Chemical composition (wt.%) of glass

Glass	SiO_2	B_2O_3	Al_2O_3	ZnO	Metal oxide
A	10.4	45.3	2.5	35.2	Na_2O 6.6
B	9.5	44.0	4.5	33.5	K_2O 8.5
C	–	41.67	–	–	K_2O 41.67
					$MnCO_3$ 6.67

glasses were made by melting mixture of oxides at 1000 °C for 30 min and quenching. The calcined host material with 5 wt.% glasses were mixed by wet ball mill with water as the milling medium for 8 h. The dry-pressed and glass-doped samples were sintered at intervals of 50 °C over the temperature range of 950–1200 °C for 4 h. XRD analysis was undertaken for phase identification using Rigaku D/MAX-B. The microstructure was observed by SEM (Hitachi S-4700) attached with EDS (Horiba 7200-H). The densification behavior was evaluated by determining the bulk density using Archimedes technique. Dielectric properties were measured by a cavity method using Angilent 8722ES network analyzer.

3. Results and discussion

The XRD result of 700 °C and 2 h calcined powders of $(Zn_{1-x}, Mg_x)TiO_3$ with x = 0–0.5 shows that the major phase was hexagonal (Zn, Mg)TiO_3 and the TiO_2 and $Zn_2Ti_3O_8$ were minority. TiO_2 phase increased with the increasing Mg content. The existence of TiO_2 phase in Mg-rich systems seems to arise from the insufficient reaction of MgO with other oxides.

The $(Zn_{1-x}, Mg_x)TiO_3$ with $x = 0$ decomposed as the sintering temperature was greater than 950 °C as shown in Fig. 1(a–c). Fig. 2 shows the SEM photo of sample sintered at 1100 °C, where the dark rutile grain can be observed. The MgO additives could uplift the temperature of decomposition. The X-ray diffraction patterns of sample with $x = 0.4$ are showed in Fig. 1(d–f). The pure (Zn, Mg)TiO_3 can be kept until 1200 °C. The SEM photo of 1100 °C sintered sample with $x = 0.4$ in Fig. 2b shows the single phase of ZMT. Table 2 shows that the phase components of the ZMT with the different Mg content changing with the increasing temperature. The density of the sintered $(Zn_{1-x}, Mg_x)TiO_3$ ceramics increased with sintering temperature and decreased with the increasing Mg content as shown in Fig. 3. As sample with $x = 0.1$ sintered at 1000 °C and 1050 °C, the density decreased because of the hexagonal ZMT decomposing into cubic Zn_2TiO_4 and rutile. The

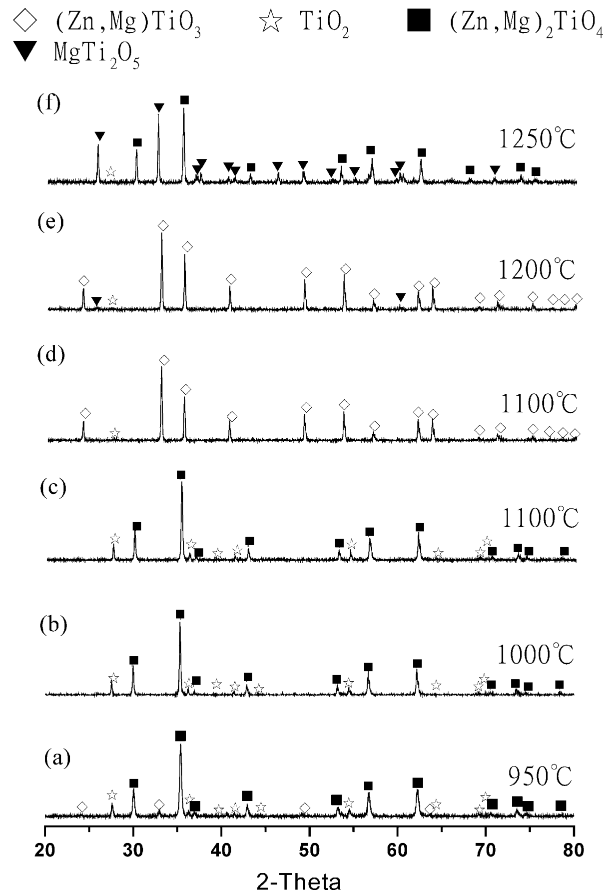

Fig. 1. XRD patterns of specimens with $x = 0$ (a–c) and $x = 0.4$ (d–f).

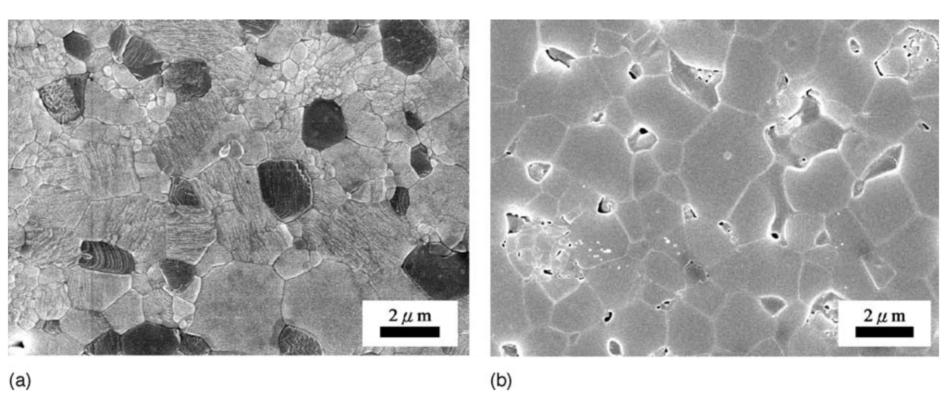

Fig. 2. SEM photos of $(Zn_{1-x}, Mg_x)TiO_3$ specimens of $x = 0$ (a) and $x = 0.4$ (b), both were sintered at 1100 °C for 4 h.

Table 2
Phase components of the ZMT changing with Mg content and temperature

Sintered temperature (°C)	$x = 0$	$x = 0.1$	$x = 0.2$	$x = 0.3$	$x = 0.4$	$x = 0.5$
1300	■, ☆	■, ☆	▼, ■, ☆	▼, ■, ☆	▼, ■, ☆	▼, ■, ☆
1250	■, ☆	■, ☆	▼, ■, ☆	▼, ■, ☆	▼, ■, ☆	◇, ▼, ■
1200	■, ☆	■, ☆	■, ☆, ◇	◇, ☆	◇, ☆, ▼	◇, ▼
1150	■, ☆	■, ☆	■, ☆, ◇	◇, ☆	◇, ☆	◇,▼
1100	■, ☆	■, ☆	◇	◇, ☆	◇, ☆	◇, ☆ ,▼
1050	■■, ☆	■, ☆, ◇	◇	◇, ☆	◇, ☆	◇, ☆
1000	■■, ☆	◇	◇	◇, ☆	◇, ☆	◇, ☆
950	◇ ■, ☆	◇	◇	◇	◇	◇, ☆

(◇) (Zn, Mg)TiO_3, (■) (Zn, Mg)$_2TiO_4$, (☆) TiO_2, (▼) $MgTi_2O_5$.

similar phenomena can be observed in the samples with $x = 0.3$ and 0.4 at the temperature greater than 1200 °C. The sample with $x \geq 0.2$ sintered at 1200 °C showed the decreasing of density because of the precipitation of $MgTi_2O_5$. The microwave dielectric properties are shown in Figs. 4 and 5. The ϵ_r values increased with the increasing temperature due to the more densification with higher temperature. The ϵ_r values decreased with the increasing of Mg content because of the $MgTiO_3$ component in the ZMT solid solution, which has a lower dielectric constant ($\epsilon_r = 17$). The $Q \times f$ values in Fig. 5 shows that, in general, the samples sintered below 1050 °C have lower $Q \times f$ values because of lower density, and the samples with lower Mg content and sintered at temperature higher than 1100 °C have the lower $Q \times f$ values because of the decomposition of hexagonal ZMT phase into cubic (Zn, Mg)$_2TiO_4$ phase and rutile. The higher $Q \times f$ values for the samples with higher Mg content sintered at higher temperature can be interpreted as that the Mg content stabilize the hexagonal ZMT phase and the higher sintering temperature enhance the densification. The excess Mg content (x > 0.4) caused to the lower bulk density and $Q \times f$ values.

Table 3
Dielectric properties of low fired ZMT

	ϵ_r	$Q \times f$
H.M. + 5 wt.% glass A	18.0	7721
H.M. + 5 wt.% glass B	18.0	29375
H.M. + 4 wt.% glass + 1 wt.% CuO	17.9	20424
H.M. + 5 wt.% glass C	15.7	1246

Considering the phase stability and the higher $Q \times f$ value, the ZMT with $x = 0.4$ was used as the host material. The density of ZMT with addition of 5 wt.% glass increased with sintering temperature range from 900 to 1100 °C, as shown in Fig. 6. The SEM photos of samples sintered at 950 °C are shown in Fig. 7. The density decreased as the sintering temperature greater than 1200 °C because of the decomposition of (Zn, Mg)TiO_3 and the precipitation of Zn_2TiO_4 and TiO_2. Specimens with glasses A and B had higher density than that with glass C. Glass A with 1 wt.% CuO addition failed to improve the densification and lower the sintering temperature. Due to the highest density was obtained at 1100 °C, the measurements of ϵ_r and Q values

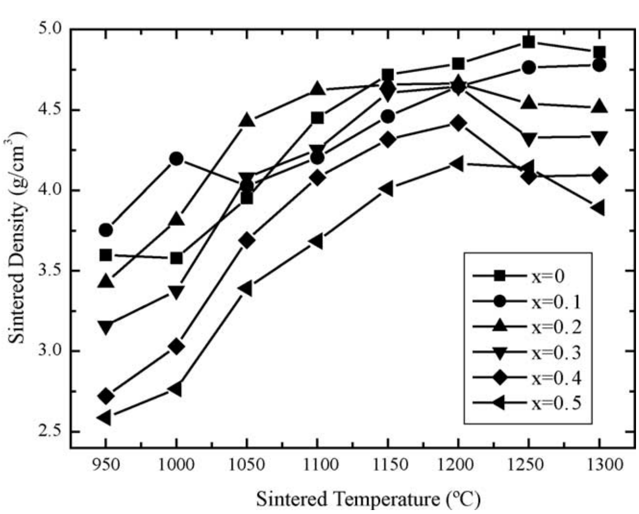

Fig. 3. Density curves for the(Zn$_{1-x}$, Mg$_x$)TiO_3 (x = 0–0.5) powder sintered from 950 to 1300 °C.

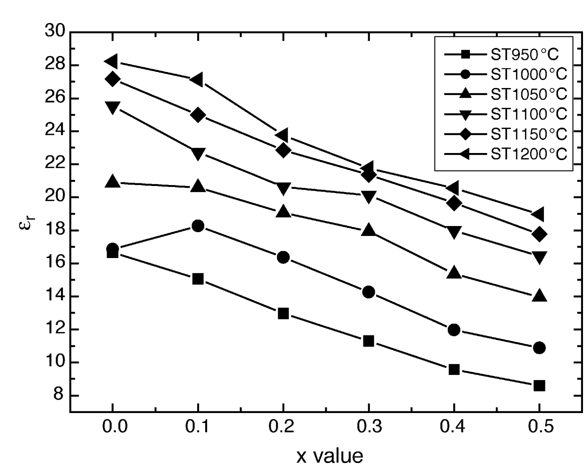

Fig. 4. Dielectric constant of (Zn$_{1-x}$, Mg$_x$)TiO_3 (x = 0–0.5) sintered from 950 to 1200 °C.

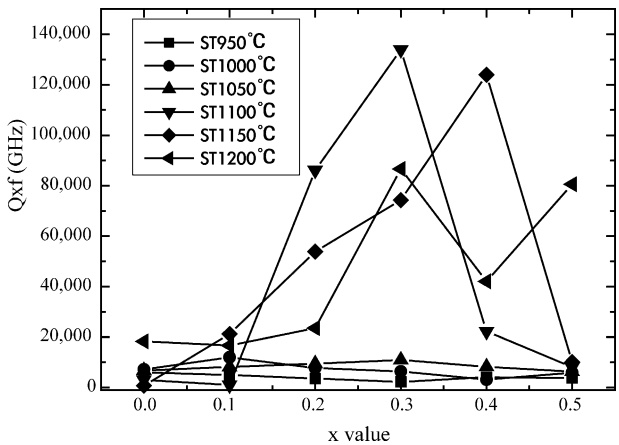

Fig. 5. $Q \times f$ of $(Zn_{1-x}, Mg_x)TiO_3$ ($x = 0$–0.5) sintered from 950 to 1200 °C.

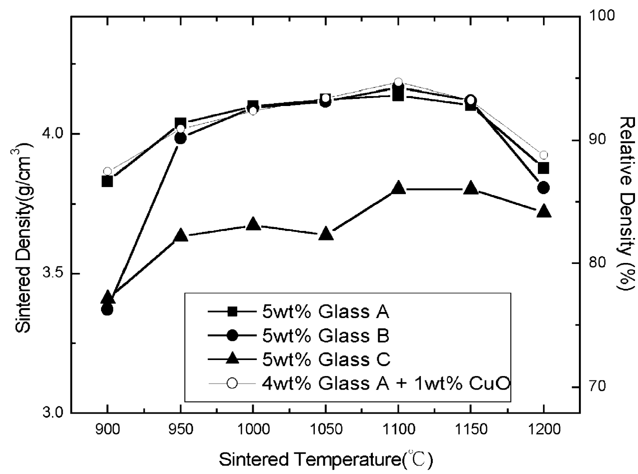

Fig. 6. Density curves of ZMT with addition of 5 wt.% glass sintered with intervals of 50 °C in the temperature range of 900–1200 °C.

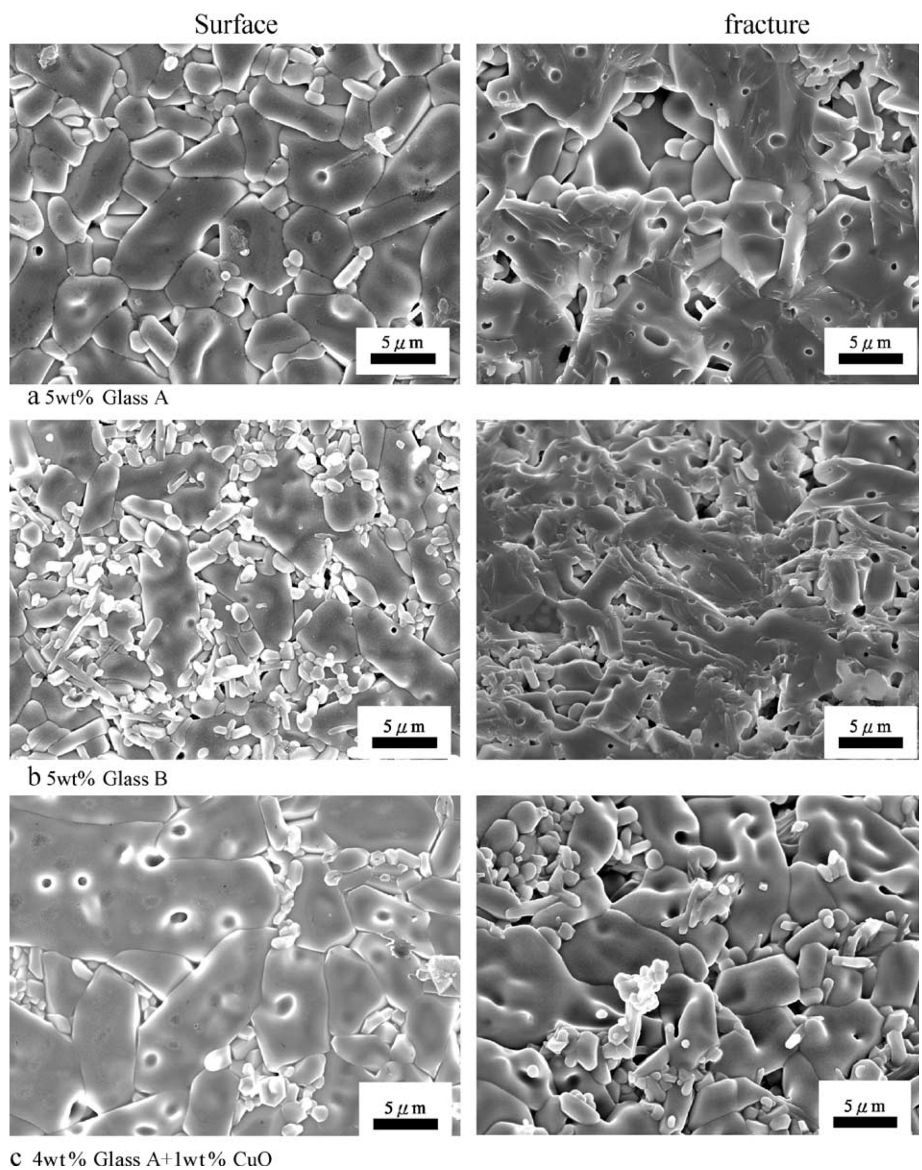

Fig. 7. SEM photos of surface and fracture microstructure of host material with glasses sintered at 950 °C.

Table 4
Microwave dielectric properties of samples milled for 8 h and sintered in temperature range of 900 to 1200 °C

	Sintered temperature (°C)						
	900	950	1000	1050	1100	1150	1200
ϵ_r	17.8	19.0	19.8	19.7	18.9	18.6	17.3
$Q \times f$	18547	18957	20101	21179	17937	15253	18532

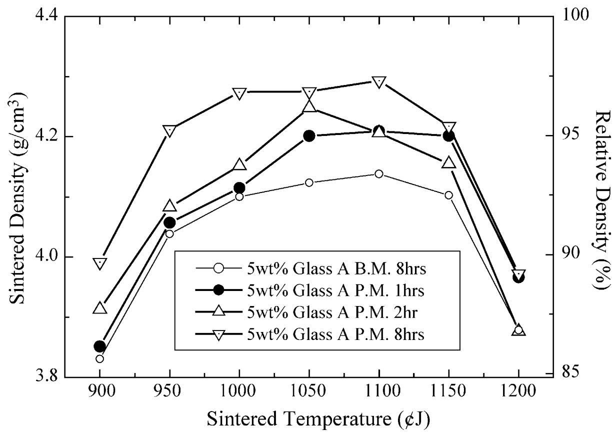

Fig. 8. Sintered density curves of samples milled by satellite mill.

were performed on these samples. Table 3 shows the properties of low fired ZMT. The ϵ_r and $Q \times f$ values for sample with glass B were reduced to 18 and 29,375, respectively.

The sample with glass A had higher density and, therefore, was chosen to be milled by satellite ball mill. After milling for 1, 2 and 8 h, the grain size (d_{50}) were 1.37, 1.21 and 0.83 μm, respectively. As shown in Fig. 8, compared to the sample milled by traditional ball mill, the densification of samples milled by satellite mill were significantly improved and the sintering temperature can be lowered to 950 °C. After 8 h milling, the density of 4.21 g/cm^3 (95% relative density) can be obtained at 950 °C. Table 4 shows the microwave dielectric properties of samples milled for 8 h and sintered at temperature range from 900 to 1200 °C. $\epsilon_r = 19$ and $Q \times f = 18{,}957$ can be obtained at sintering temperature 900 °C.

4. Conclusion

Microwave material $(Zn_{0.6}Mg_{0.4})TiO_3$ were sintered in the temperature range of 900–1200 °C with the addition of B_2O_3–SiO_2–ZnO glass system. For $(Zn_{0.6}Mg_{0.4})TiO_3$ sintered with 5 wt.% glass B at 1100 °C, the ϵ_r and $Q \times f$ values were 18 and 29,375, respectively. Taking advantage of satellite milling, the ZMT ceramics can be sintered at 950 °C with the density of 4.21 g/cm^3, $\epsilon_r = 19$, and $Q \times f = 18{,}957$.

References

[1] A.J. Moulson, J.M. Herbert, Electroceramics, Chapman and Hall, New York, 1990.

[2] K. Wakino, T. Nishikawa, Y. Ishikawa, H. Tamura, Dielectric resonator materials and their applications for mobile communication systems, Br. Ceram. Trans. J. 89 (1990) 39–43.

[3] H. Kagata, T. Inoue, J. Kato, T. Ishizaki, Low-fire microwave dielectric ceramics and multilayer devices with silver internal electrode, in: K.M. Nair, J.P. Guha, A. Okamoto (Eds.), Dielectric Ceramics Processing, Properties, and Applications: Vol. 32: Ceramic Transactions, American Ceramic Society, Westerville, OH, 1993, pp. 81–90.

[4] T. Takada, S.F. Wang, S. Yoshicawa, S.J. Jang, R.E. Newnham, Effect of glass additions on BaO–TiO_2–WO_3 microwave ceramics, J. Am. Ceram. Soc. 77 (9) (1994) 2485.

[5] H.T. Kim, J.D. Byun, Y. Kim, Microstructure and microwave dielectric properties of modified zinc titanates(I), Mater. Res. Bull. 33 (1998) 963–973.

[6] H.T. Kim, J.D. Byun, Y. Kim, Microstructure and microwave dielectric properties of modified zinc titanates(II), Mater. Res. Bull. 33 (1998) 975–986.

[7] H.T. Kim, S.H. Kim, S. Nahm, J.D. Byun, Low-temperature sintering and microwave dielectric properties of zinc metatitanate–rutile mixtures using boron, J. Am. Ceram. Soc. 82 (11) (1999) 3043–3048.

[8] H.T. Kim, S. Nahm, J.D. Byun, Low-fired (Zn, Mg) TiO_3 microwave dielectrics, J. Am. Ceram. Soc. 82 (12) (1999) 3476–3480.