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Dielectric properties of a low-loss $(1-x)(Mg_{0.95}Zn_{0.05})_2TiO_4$–$xSrTiO_3$ ceramic system at microwave frequencies

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ABSTRACT

Low-loss ceramics in the $(1-x)(Mg_{0.95}Zn_{0.05})_2TiO_4$–$xSrTiO_3$ system have been prepared by the conventional mixed oxide route and their microwave dielectric properties have been investigated. A two-phase system was confirmed by the XRD patterns, the EDS analysis and the measured lattice parameters. The addition of $SrTiO_3$, having a smaller grain size in comparison with that of $(Mg_{0.95}Zn_{0.05})_2TiO_4$, could effectively promote the densification in the $(Mg_{0.95}Zn_{0.05})_2TiO_4$ matrix. The specimen using $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.04SrTiO_3$ sintered at 1270 °C possesses an excellent combination of microwave dielectric properties: ε_r of ∼18, $Q \times f$ of ∼125,600 GHz (at 10 GHz), and τ_f of ∼0 ppm/°C. The dielectric is proposed as a candidate material for low-loss microwave and millimeter wave applications.

1. Introduction

There are three primary requirements for dielectric ceramics used at microwave frequencies: a high-dielectric constant to reduce the size of the components, a high quality factor to increase the frequency selectivity, and a near zero τ_f to ensure high temperature stability. However, increasing the carrier frequencies from 900 MHz to 2.4, 5.2, or even 5.8 GHz makes materials that have a high-dielectric constant become a less of interest. Low-dielectric-loss materials, instead, tend to play a more prominent role since the $Q \times f$ is almost constant in the microwave region [1–4].

Binary titanate ceramic Mg_2TiO_4 ($Q \times f$ of ∼150,000 GHz), having extremely low-dielectric loss, was first reported by Belous et al. [5,6]. In addition, $SrTiO_3$ (τ_f of ∼1700 ppm/°C) [7] was chosen as an τ_f compensator and mixed with Mg_2TiO_4 to achieve a near zero τ_f. The investigation on microwave dielectric properties of $0.94Mg_2TiO_4$–$0.06SrTiO_3$ composition was performed to possess an ε_r of ∼17.79, a $Q \times f$ of ∼70,900 GHz (at 10 GHz), and a τ_f of ∼−3.3 ppm/°C [8]. Recently, the $Q \times f$ of Mg_2TiO_4 was further boosted by using partially substituted $(Mg_{0.95}Zn_{0.05})_2TiO_4$ ceramic, which was found to have a much better combination of dielectric properties: an ε_r of ∼15.48, a $Q \times f$ of ∼275,300 GHz (at 11 GHz), and an τ_f of ∼−34 ppm/°C [9]. Consequently, the replacement of Mg_2TiO_4 by $(Mg_{0.95}Zn_{0.05})_2TiO_4$ in the ceramic system becomes an interesting issue.

In this study, the microwave dielectric properties of $(Mg_{0.95}Zn_{0.05})_2TiO_4$–$SrTiO_3$ system were investigated and discussed in terms of the compositional ratio, the densification and the sintering temperature of the specimens. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis were also employed to study the crystal structures and microstructures of the ceramics.

2. Experimental procedure

The starting materials were high-purity oxide powders (>99.9%): MgO, ZnO, TiO_2, and $SrCO_3$. The powders were separately prepared according to the desired stoichiometry of $(Mg_{0.95}Zn_{0.05})_2TiO_4$ and $SrTiO_3$, and ground in distilled water for 12 h in a ball mill with agate balls. The prepared powders were both dried and calcined at 1100 °C for 4 h in air. The calcined powders were mixed according to the molar fraction $(1-x)(Mg_{0.95}Zn_{0.05})_2TiO_4$–$xSrTiO_3$ and then re-milled for 12 h, together with 3 wt% of a 10% solution of polyvinyl alcohol (PVA 500, Showa, Japan) as a binder, and pressed into pellets with dimensions of 11 mm in diameter and 5 mm in thickness under a pressure of 200 MPa. These pellets were sintered in the temperature range 1210–1330 °C for 4 h in air. Both the heating and cooling rates were set at 10 °C/min.

The crystalline phases of the sintered ceramics were identified by XRD using Cu Kα (λ = 0.15406 nm) radiation with a Seimens D5000 diffractometer operated at 40 kV and 40 mA. The apparent densities of the sintered pellets were measured using the Archimedes method. The dielectric constant and the quality factor values at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method, as modified and improved by Courtney [10,11]. A system combining a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. The technique used for the measurement of the temperature coefficient of resonant frequency (τ_f) was the same as that for the quality factor measurement. The test cavity was placed over a thermostat and the temperature range used was from 25 °C to 80 °C. The τ_f (ppm/°C) was calculated by considering the change in resonant frequency (Δf):

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \qquad (1)$$

where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

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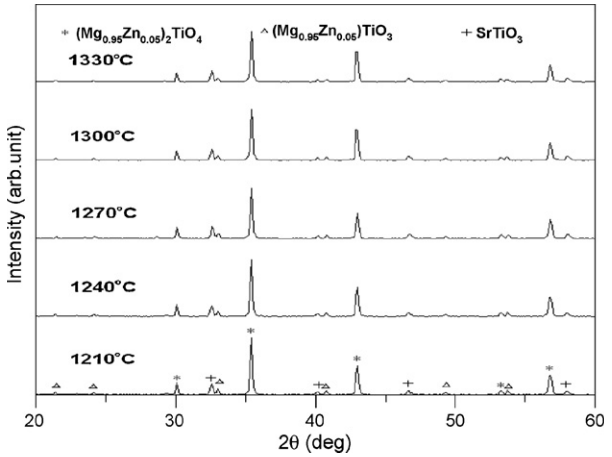

Fig. 1. X-ray diffraction patterns of $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ ceramics sintered at various temperatures for 4 h.

Table 1
Microwave dielectric properties of the $(1-x)(Mg_{0.95}Zn_{0.05})_2TiO_4$–$xSrTiO_3$ ceramics system sintered at 1270 °C for 4 h.

X value	Apparent density (g/cm^3)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
0	3.46	15.48	275,300	−34
0.02	3.49	16.21	182,600	−25
0.04	3.52	16.76	158,300	−11
0.06	3.56	18.00	125,600	0
0.08	3.59	18.98	104,900	14
0.1	3.66	19.95	75,700	32

3. Results and discussion

Table 1 demonstrates the microwave dielectric properties of $(1-x)(Mg_{0.95}Zn_{0.05})_2TiO_4$–$xSrTiO_3$ ceramic system sintered at 1270 °C for 4 h. Significant variation in the dielectric properties can be observed due to a different compositional ratio. It was mainly a result from a difference in the dielectric properties for each composition. Since the specimen using

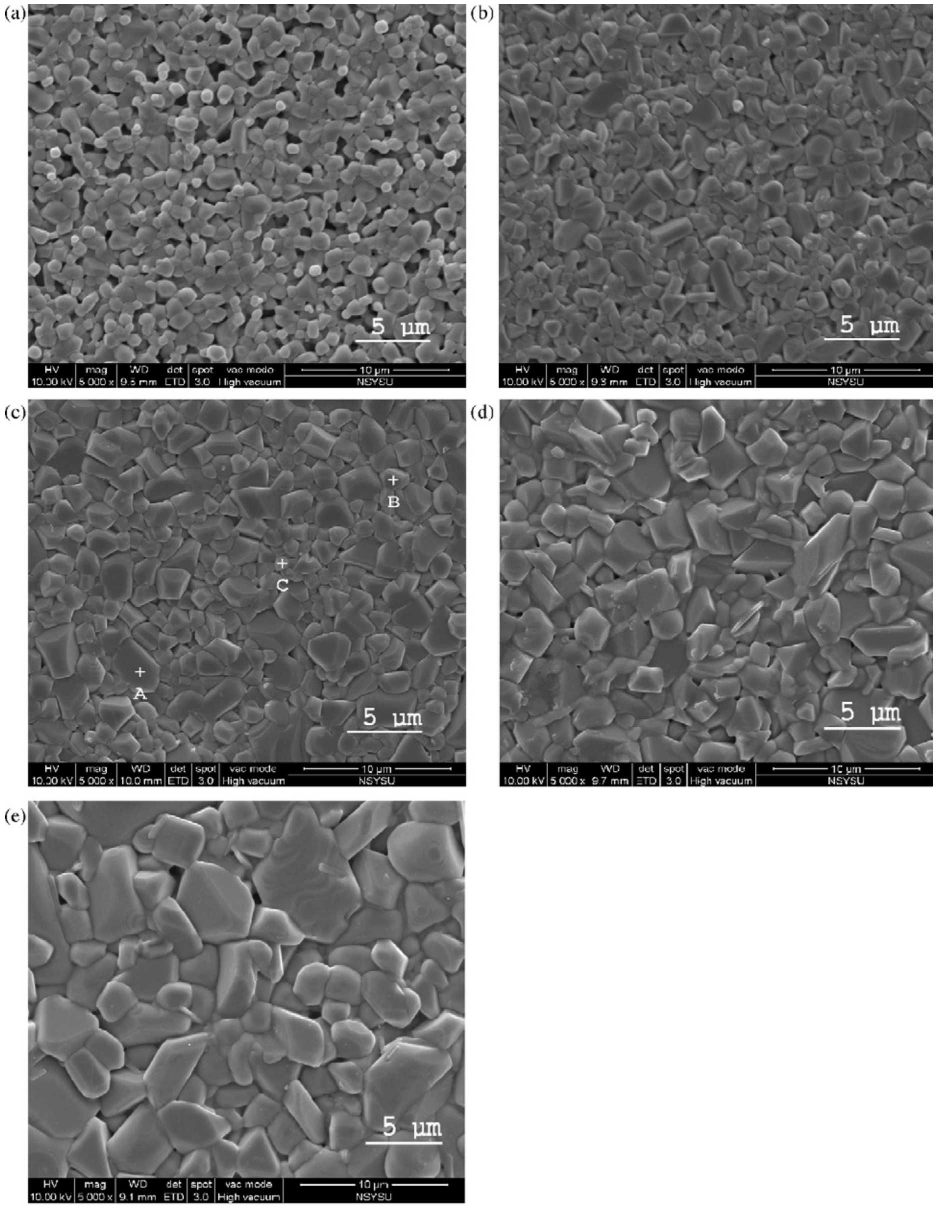

Fig. 2. SEM micrographs of $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ ceramics sintered at (a) 1210, (b) 1240, (c) 1270, (d) 1300, and (e) 1330 °C for 4 h.

Table 2
EDX data of the $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ ceramic sintered at 1270 °C for Spots A, B, and C shown in Fig. 2(c).

Spot	Atom (%)				
	Mg K	Zn L	Sr L	Ti K	O K
A	36.82	1.95	0	20.19	41.04
B	22.68	1.25	0	24.72	51.35
C	0	0	23.56	23.12	53.32

$0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ shows a good temperature stability with τ_f of ~0 ppm/°C, a more comprehensive and closer investigation on the microwave dielectric properties of $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ was then conducted.

Fig. 1 shows the XRD patterns of the $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ ceramic sintered at various temperatures for 4 h. The XRD patterns show a two-phase system with a main crystalline phase $(Mg_{0.95}Zn_{0.05})_2TiO_4$ (can be indexed as Mg_2TiO_4) and a minor phase $SrTiO_3$. A second phase $(Mg_{0.95}Zn_{0.05})TiO_3$ (can be indexed as $MgTiO_3$) is also detected throughout the complete range of mixtures. Petrova et al. proposed the following thermal decomposition mechanism to explain the formation of the $MgTiO_3$ phase [12]:

$$Mg_2TiO_4 \rightarrow Mg_{2+2\delta}Ti_{1-\delta}O_4 + MgTiO_3 \qquad (2)$$

The thermal decomposition of Mg_2TiO_4, however, becomes negligible when the temperature exceeds 1400 °C [5,12]. However, the formula should be modified for this experiment as follows :

$$(Mg_{0.95}Zn_{0.05})_2TiO_4 \rightarrow (Mg_{0.95}Zn_{0.05})_{2+2\delta}Ti_{1-\delta}O_4 + (Mg_{0.95}Zn_{0.05})TiO_3 \qquad (3)$$

It is found that crystal structures of Mg_2TiO_4 and $SrTiO_3$ are spinal cubic (ICDD-PDF #00-025-1157) and cubic (ICDD-PDF #01-084-0443), respectively. In addition, significant variance was not monitored in the XRD patterns for specimens using $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ ceramic at different sintering temperatures. Lattice parameters of $(1-x)(Mg_{0.95}Zn_{0.05})_2TiO_4$–$xSrTiO_3$ ceramics at 1270 °C were also measured in this study. It was found that $(Mg_{0.95}Zn_{0.05})_2TiO_4$ showed the following lattice parameters; $a = b = c = 0.8443$ nm and retained invariable with the addition of $SrTiO_3$ to form the ceramic system $(1-x)(Mg_{0.95}Zn_{0.05})_2TiO_4$–$xSrTiO_3$. This finding confirms the existence of a two-phase system. The results are in good agreement with those from XRD analysis.

The surface microstructure photographs of $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ ceramics at various sintering temperatures are presented in Fig. 2. Energy dispersive X-ray (EDX) analysis was also used in combination with scanning electron microscopy to distinguish each grain for $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ ceramics, as shown in Fig. 2(c). The grain morphology of the specimens can be grouped into three types: larger grains (Spot A) are identified as $(Mg_{0.95}Zn_{0.05})_2TiO_4$, medium (Spot B) and small ones (Spot C) are represented as $(Mg_{0.95}Zn_{0.05})TiO_3$ and $SrTiO_3$ phases, respectively (Table 2). Porous microstructures were observed at 1210 °C. The grains, however, started to grow at 1240 °C and a significant increase in the grain size was observed at 1270 °C. Inhomogeneous grain growth was observed at temperatures higher than 1270 °C, which might degrade the microwave dielectric properties of the ceramics.

Fig. 3 shows the apparent densities and ε_r of the $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ ceramics sintered at various temperatures for 4 h. With the increase in temperature, the apparent density increases to a maximum value of 3.75 g/cm^3 at 1270 °C, and decreases thereafter. The reduction in the density is due to the abnormal grain growth as shown in Fig. 2. The variation of ε_r is consistent with that of the density. The dielectric constant also increased with the increase in sintering temperature. After reaching a maximum at 1270 °C, it starts to decrease. A maximum ε_r value of 18 was obtained for $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ ceramics sintered at 1270 °C for 4 h. Moreover, the highest density of added ceramic occurs at 1270 °C, which is 60 °C lower than that of the pure one, indicating that the addition of $SrTiO_3$, having a smaller grain size in comparison with that of $(Mg_{0.95}Zn_{0.05})_2TiO_4$, could effectively promote the densification in the $(Mg_{0.95}Zn_{0.05})_2TiO_4$ matrix [2].

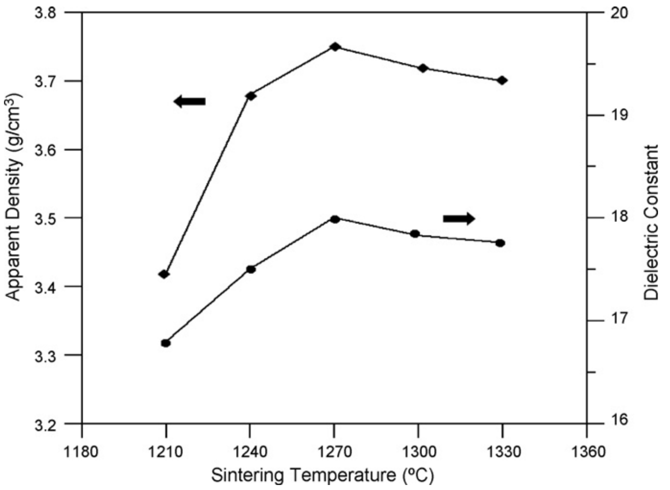

Fig. 3. Apparent density and dielectric constant of $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ ceramics as a function of the sintering temperature.

Fig. 4 shows the $Q \times f$ and τ_f values of the $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ ceramics sintered at various sintering temperatures. With the increase in sintering temperature, the $Q \times f$ value increased to a maximum value and then decreased. Several factors contribute to the dielectric loss at microwave frequencies, such as density, porosity, second phases, grain boundaries, and inclusions in real homogeneous ceramics [13]. The $Q \times f$ of the second phase $(Mg_{0.95}Zn_{0.05})TiO_3$ ($Q \times f$ of ~264,000 GHz) [14] was similar to that of the primary phase $(Mg_{0.95}Zn_{0.05})_2TiO_4$ ($Q \times f$ of ~275,300 GHz) and the variation of $Q \times f$ was consistent with that of density, suggesting that $Q \times f$ was most likely in response to the apparent density. A maximum $Q \times f$ value of 125,600 GHz

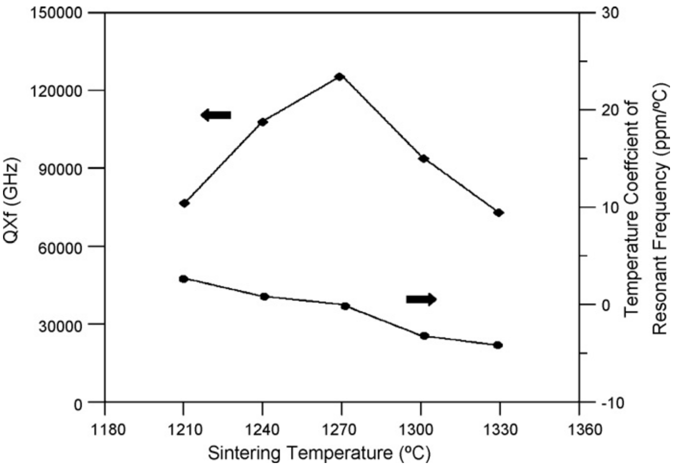

Fig. 4. $Q \times f$ and τ_f values of $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ ceramics as a function of the sintering temperature.

was obtained for $0.94(Mg_{0.95}Zn_{0.05})_2TiO_4$–$0.06SrTiO_3$ ceramics sintered at 1270 °C for 4 h. The temperature coefficient of resonant frequency (τ_f) is known to be governed by the composition, the additives, and the second phase of the material. Because the τ_f values of $(Mg_{0.95}Zn_{0.05})_2TiO_4$ and $SrTiO_3$ are −34 and 1700 ppm/°C, respectively, increasing $SrTiO_3$ content makes the τ_f value become more positive. In addition, the τ_f values of $(Mg_{0.95}Zn_{0.05})TiO_3$ (τ_f of ∼−41 ppm/°C) [13] and $(Mg_{0.95}Zn_{0.05})_2TiO_4$ (τ_f of ∼−34 ppm/°C) are similar to each other, implying that the second phase factor can be excluded. With $x = 0.06$, a zero τ_f value was achieved for the $(1-x)(Mg_{0.95}Zn_{0.05})_2TiO_4$–$xSrTiO_3$ ceramic system sintered at 1270 °C for 4 h.

4. Conclusion

A new microwave dielectric ceramic system was synthesized by combining $(Mg_{0.95}Zn_{0.05})_2TiO_4$ and $SrTiO_3$. The $(1-x)(Mg_{0.95}Zn_{0.05})_2TiO_4$–$xSrTiO_3$ ceramic system showed a mixed-phase with a $(Mg_{0.95}Zn_{0.05})_2TiO_4$) as the main crystalline phase, a minor phase of $SrTiO_3$, and a second phase of $(Mg_{0.95}Zn_{0.05})TiO_3$. The microwave dielectric properties are strongly related to the density and matrix of the specimen. At $x = 0.06$, the proposed system exhibits a good combination of microwave dielectric properties: ε_r of ∼18, $Q \times f$ of ∼125,600 GHz (at 10 GHz), and τ_f of ∼0 ppm/°C, which makes it a very promising candidate material for low-loss microwave and millimeter wave applications.

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References

[1] C.L. Huang, J.J. Wang, J.J. Chang, J. Am. Ceram. Soc. 90 (2007) 858–862.
[2] C.L. Huang, J.J. Wang, C.Y. Huang, J. Am. Ceram. Soc. 90 (2007) 1487–1493.
[3] W. Lei, W.Z. Lu, J.H. Zhu, X.H. Wang, Mater. Lett. 61 (2007) 4066–4069.
[4] A. Kan, H. Ogawa, H. Ohsato, J. Alloys Compd. 337 (2002) 303–308.
[5] A. Belous, O. Ovchar, D. Durilin, M.M. Krzmanc, M. Valant, D. Suvorov, J. Am. Ceram. Soc. 89 (2006) 3441–3445.
[6] A. Belous, O. Ovchar, D. Durilin, M. Valant, M.M. Krzmanc, D. Suvorov, J. Eur. Ceram. Soc. 27 (2007) 2963–2966.
[7] P.H. Sun, T. Nakamura, Y.J. Shan, Y. Inaguma, M. Itoh, T. Kitamura, Jpn. J. Appl. Phys. 37 (1998) 5625–5629.
[8] C.L. Huang, S.S. Liu, J. Alloys Compd. 471 (2009) L9–L12.
[9] C.L. Huang, S.S. Liu, J. Am. Ceram. Soc. 91 (2008) 3428–3430.
[10] B.W. Hakki, P.D. Coleman, I.E.E.E. Trans, Microwave Theory Tech. 8 (1960) 402–410.
[11] W.E. Courtney, IEEE Trans. Microwave Theory Tech. 18 (1970) 476–485.
[12] M.A. Petrova, G.A. Mikirticheva, A.S. Novikova, V.F. Popova, J. Mater. Res. 12 (1997) 2584–2588.
[13] A. Feteira, D.C. Sinclair, M.T. Lanagan, J. Mater. Res. 20 (2005) 2391–2399.
[14] C.L. Huang, S.S. Liu, Jpn. J. Appl. Phys. 46 (2007) 283–285.