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Relationships between Zr substitution for Ti and microwave dielectric properties in $Mg(Zr_xTi_{1-x})O_3$ ceramics

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ABSTRACT

The influence of Zr substitution for Ti on the microwave dielectric properties and microstructures of the $Mg(Zr_xTi_{1-x})O_3(MZ_xT)$ ($0.01 \le x \le 0.3$) ceramics was investigated. The quality factors of $Mg(Zr_xTi_{1-x})O_3$ ceramics with $x = 0.01$–0.05 were improved because the solid solution of a small amount of Zr^{4+} substitution in the B-site could increase density and grain size. An excess of Zr^{4+} resulted in the formation of a great deal of secondary phase that declined the microwave dielectric properties of MZ_xT ceramics. The temperature coefficient of resonant frequency (τ_f) of $Mg(Zr_xTi_{1-x})O_3$ ceramics slightly increased with increasing Zr content, and the variation in τ_f was attributed to the formation of secondary phases.

1. Introduction

The recent explosive growth in satellite and mobile communication has created a high demand for the development of microwave dielectric materials. The desirable properties in microwave dielectric materials are an optimum dielectric constant (ε_r) for use, a high quality factor ($Q \times f$) for better selectivity and a near-zero temperature coefficient of resonant frequency for stability (τ_f).

Magnesium titanate ($MgTiO_3$) ceramics are one among the leading dielectric materials for microwave frequency applications. $MgTiO_3$ has an ilmenite-type structure, belonging to the trigonal space group $R\bar{3}$, and shows excellent dielectric properties: $\varepsilon_r = 17$, $Q \times f = 160{,}000$ GHz and $\tau_f = -50$ ppm/°C [1,2].

Much attention has been paid to $MgTiO_3$ ceramics. A few studies were performed to improve $Q \times f$ of $MgTiO_3$ with the sintering aid Bi_2O_3–V_2O_5 [3]. Some authors carried out analogous work with M^{2+} ionic partial substitution in the A-site in $MgTiO_3$. Mg in $MgTiO_3$ ceramics was substituted with Ni, Mg, Co, and Mn to form $(Mg_{0.95}M_{0.052}{}^{2+})TiO_3$, which can improve the ε_r and $Q \times f$ due to the local lattice distortion and the size effect of cations more than the impurity effect in $MgTiO_3$ [4]. Huang et al. [5] reported $(Mg_{0.95}Zn_{0.05})TiO_3$ ceramics with the partial replacement of Mg by Zn that caused average grain size to increase leading to an increase of $Q \times f$ as compared with pure $MgTiO_3$ ceramics. The authors reported improvement in microwave dielectric properties of $MgTiO_3$ by the partial replacement of the A-site ions. However, similar improvement of properties with M^{4+} substitution at the B-site of the $MgTiO_3$ ceramics was not reported in the literature until the work of Tseng and coworkers [6,7]. It has been well documented that a small amount of impurity ion substitution can dramatically modify the microwave dielectric properties of $MgTiO_3$ ceramics; however, the dielectric properties of substitution of M^{4+} at the B-site in $MgTiO_3$ is better than those of the substitution of M^{2+} at the A-site.

It is interesting to study the influence of dielectric properties on the different Zr^{4+} substitutions in the B-sites in $MgTiO_3$ materials. In the present work, the $Mg(Zr_xTi_{1-x})O_3$ ceramics were prepared by using conventional solid-state methods and were characterized. Their microwave dielectric properties were discussed based on the results of the X-ray diffraction patterns and the microstructures of the MZ_xT ceramics.

2. Experimental procedure

Samples of $Mg(Zr_xTi_{1-x})O_3$ mixed according to the desired stoichiometry were synthesized by conventional solid-state methods from individual high-purity oxide powders (>99.9%) of MgO, ZrO_2 and TiO_2. The powders were ground in distilled water for 12 h in a ball mill with agent balls. All mixtures were dried, forced through a 200-mesh sieve and calcined at 1100 °C for 4 h. The calcined reagent was ground into fine powder for 12 h. The fine powder with 3 wt.% of a 10% solution of PVA as a binder was pressed into the pellets with dimensions of 11 mm in diameter and 5 mm in thickness under a pressure of 2000 kg/cm^2. These pellets were sintered at temperatures of 1360–1420 °C for 4 h in air. The heating rate and the cooling rate were both set at 10 °C/min. On the other hand, the X-ray diffraction (XRD, Siemens D5000) data of powder and bulk samples were collected using Cu Kα radiation and a graphite monochromator in the 2θ range of 20–60°. Lattice parameters of $Mg(Zr_xTi_{1-x})O_3$ were determined by referring to an external standard of silica. The microstructural observations and analysis of the sintered surface were performed using a scanning electron microscopy (SEM, Philips XL40FEG, Eindhoven, The Netherlands) and an energy dispersive X-ray spectrometer (EDS). The average grain size was determined by measuring the mean linear intercept of the grains as described by Mendelson [8]. The density of the sintered specimens, as a function of sintering tempera-

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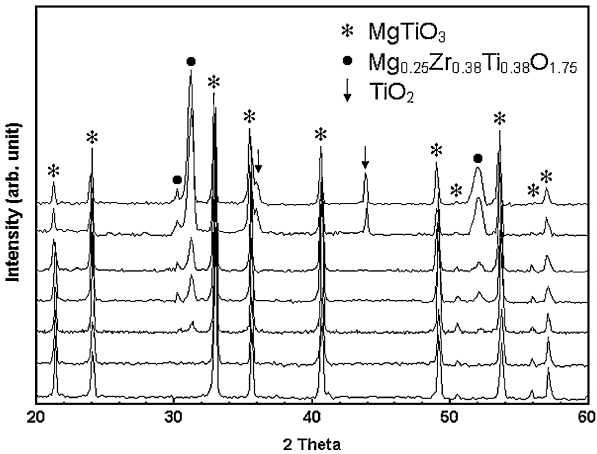

Fig. 1. XRD patterns of $Mg(Zr_xTi_{1-x})O_3$ ceramics.

ture, was measured by the liquid Archimedes method using distilled water as the liquid.

The dielectric constants (ε_r) and $Q \times f$ values at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method, as modified and improved by Courtney [9,10]. The dielectric resonator was positioned between two brass plates to form a cavity-like structure. The test cavity was placed over a thermostat, and the temperature range was +25 °C to +80 °C with the heating rates at 1 °C/min and the residence time was 10 min for each cycle. The τ_f (ppm/°C) was calculated by noting the change in resonant frequency by,

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

where f_1 is the resonant frequency at T_1 and f_2 is the resonant frequency at T_2.

3. Results and discussion

The X-ray diffraction patterns of $Mg(Zr_xTi_{1-x})O_3$ ($0.01 \leq x \leq 0.3$) ceramics sintered at 1360–1420 °C for 4 h are shown in Fig. 1. According to the XRD patterns, it is revealed that the single phase exists with the Zr concentration range of $0.01 \leq x < 0.05$, in which all the peaks can be indexed as ilmenite-type $MgTiO_3$ phase (ICDD-PDF#00-06-0494). For the composition range of $0.05 \leq x \leq 0.09$, the $Mg_{0.25}Zr_{0.38}Ti_{0.38}O_{1.75}$ (ICDD-PDF#00-77-2164) phase was detected, whereas the mixture of the two phases, $Mg_{0.25}Zr_{0.38}Ti_{0.38}O_{1.75}$ and TiO_2 was detected in the XRD patterns with x higher than 0.09. It can be noticed that the peak intensity of the secondary phases of $Mg_{0.25}Zr_{0.38}Ti_{0.38}O_{1.75}$ and TiO_2 increased with increasing x content. There are small shifts of diffraction peaks slightly toward the lower 2θ angle with increasing x content indicating that the lattice parameters of MZ_xT ceramics increased. The lattice parameters of $Mg(Zr_xTi_{1-x})O_3$ ceramics are given in Fig. 2 to clarify the effect of Zr substitution for Ti on the crystal structure of the MZ_xT ceramics. An expansion of the a-axis and c-axis is observed as the Zr content increased, due to the ionic radius of Zr^{4+} (0.72 Å) which is larger than that of Ti^{4+} (0.605 Å) when the coordination number is six. Similar trend of XRD patterns was observed when the x value varies.

The effect of substitution of Zr^{4+} on the microstructure of the $MgTiO_3$ ceramic is given in Fig. 3(a)–(g). All ceramics had a dense structure with low porosity in the whole composition range of $0.01 \leq x \leq 0.3$. There was a significant change in crystal microstructure. It can be clearly seen that the grain size increased with increasing of Zr content (x), $x \geq 0.05$, especially. The grain size of MZ_xT samples with small Zr content substituting $MgTiO_3$ was between 2 and 3 μm, whereas the grain size of the MZ_xT ceramic rapidly increased to more than 18 μm when $x \geq 0.05$. This change led to the enhancement of the dielectric properties. For $x \geq 0.05$, not only rapid grain growth is observed but also an increase in the powdery phase in the grain or melt-like phase in the boundary. Moreover, the abnormal grain growth can be detected at high x content. Small grains started to appear in the MZ_xT specimens as the Zr content became higher than 0.09. An energy-dispersive spectroscopy was employed on the grains (A–G) of the MZ_xT ceramics. As shown in Table 1, the large grains were that of MZ_xT and the powdery grain or melt-like phase were that of $Mg_{0.25}Zr_{0.38}Ti_{0.38}O_{1.75}$. In addition, the small grain was identified as the TiO_2 phase. This correlates well with the XRD analyses.

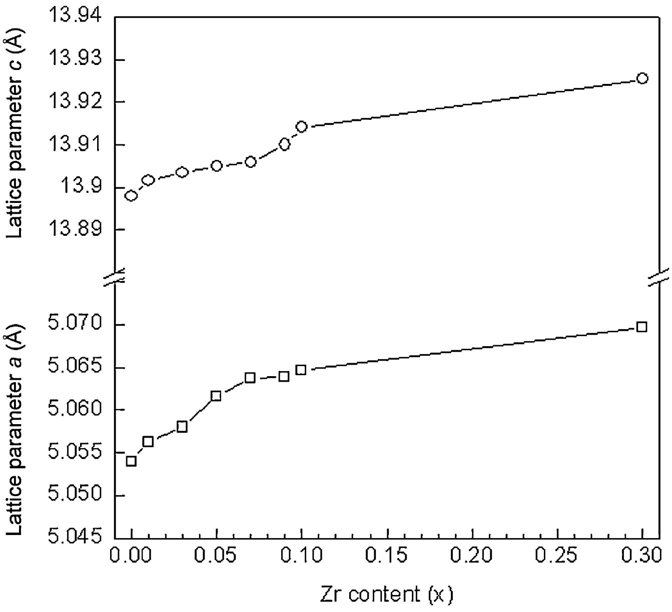

Fig. 2. The lattice parameters of $Mg(Zr_xTi_{1-x})O_3$ ceramics as a function of composition x.

Fig. 4 presents the microwave dielectric properties of $Mg(Zr_xTi_{1-x})O_3$ ceramics as functions of x. The densities and dielectric constants of well-sintered MZ_xT ceramics with the composition range of $0.01 \leq x \leq 0.3$ are represented in Fig. 4(a). The densities of MZ_xT ceramics increased with the increase of the x content, moreover, it sharply increased from 3.81 to 4.53 g/cm^3 as the x value increased from 0.01 to 0.05 and then reached saturation. The densities of $MgTiO_3$, $Mg_{0.25}Zr_{0.38}Ti_{0.38}O_{1.75}$ and TiO_2 were around 3.7, 4.6 and 4.2 g/cm^3, respectively. When $x \geq 0.05$, the densities of the ceramics increased obviously because of the existence of $Mg_{0.25}Zr_{0.38}Ti_{0.38}O_{1.75}$ with higher density. For $0.05 \leq x \leq 0.3$, the densities only had a small change. This might be because the densities of $Mg_{0.25}Zr_{0.38}Ti_{0.38}O_{1.75}$ and of TiO_2 are similar. The ε_r value of Zr substitution for Ti ranging from 17 to 18.1, and an increase of the ε_r value are in agreement with those of density in the composition ranging from 0 to 0.05. For $0.05 < x \leq 0.09$, a decrease of the ε_r value occurs and is attributed to the melting $Mg_{0.25}Zr_{0.38}Ti_{0.38}O_{1.75}$ impurity phase. Further by increasing the Zr (x) value, the ε_r value

Table 1
EDS analysis result of $Mg(Zr_xTi_{1-x})O_3$ ceramics marked in Fig. 3.

Spot	Atom (%)			
	MgK	ZrL	TiO	OK
A	20.03	1.09	18.85	60.03
B	9.23	13.72	13.87	63.18
C	20.12	1.13	18.54	60.21
D	9.09	13.66	13.72	63.53
E	9.14	13.75	13.89	63.22
F	0	0	32.98	67.02
G	0	0	33.34	66.66

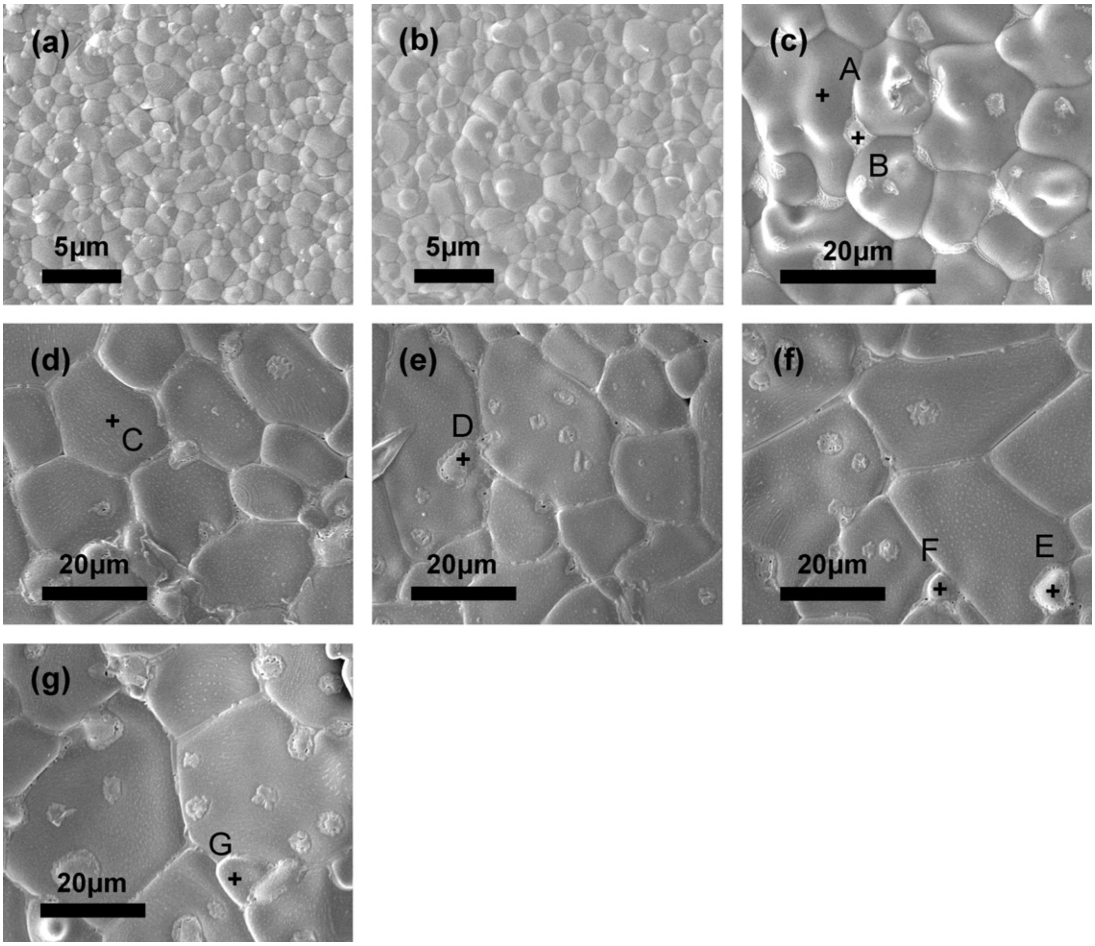

Fig. 3. SEM micrographs of $Mg(Zr_xTi_{1-x})O_3$ composite ceramic samples: (a) $x = 0.01$; (b) $x = 0.03$; (c) $x = 0.05$; (d) $x = 0.07$; (e) $x = 0.09$; (f) $x = 0.1$; (g) $x = 0.3$.

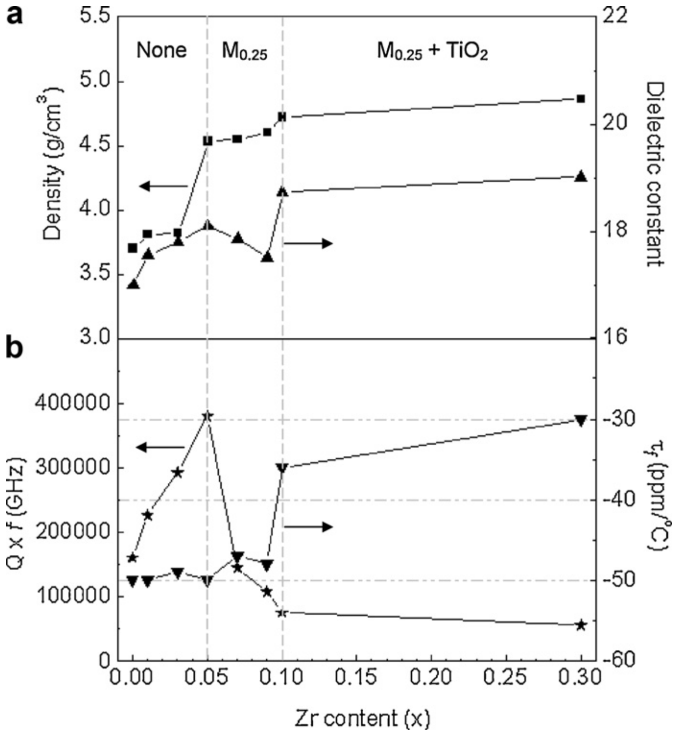

Fig. 4. Microwave dielectric properties of $Mg(Zr_xTi_{1-x})O_3$ ceramics as a function of Zr content (x).

increased to 19 for $x = 0.3$. The existence of the TiO_2 second phase contributes to enhance the ε_r (=100) [11], as shown by the XRD data.

Fig. 4(b) shows the $Q \times f$ and τ_f value of $Mg(Zr_xTi_{1-x})O_3$ ceramics. The microwave dielectric loss is caused not only by the lattice vibrational modes, but also by the pores, the grain morphology and the secondary phase [12]. As x increased from 0 to 0.05, the $Q \times f$ value increased from 225,000 to 380,000 GHz, which is higher than that of pure $MgTiO_3$. The reason for improved $Q \times f$ value ($x = 0.05$, especially) was that the grain sizes of MZ_xT were lager than those of pure $MgTiO_3$. Moreover, the grain sizes were relatively average. Yang et al. reported that the improvement of the Q value was observed and it was explained by the increase in the grain size [13]. As the grain size increased, the pores and the grain boundary area decreased, thus reducing the lattice imperfections and increasing the $Q \times f$ values [12,14]. Further by increasing the Zr substitution content, it can be observed that the $Q \times f$ value decreased rapidly to 55,000 GHz for $x = 0.3$. The decrease in the $Q \times f$ value might be caused by the existence of secondary phases and the abnormal grain growth, as shown in Fig. 3. The τ_f values of $Mg(Zr_xTi_{1-x})O_3$ ceramics are also represented in Fig. 4(b). For $x \leq 0.09$, no remarkable variations in the τ_f were observed. The τ_f values of MZ_xT ceramics varied from −47 to −50 ppm/°C. Nevertheless, with further increase of x, the TiO_2 phase was formed in the MZ_xT ceramics. The TiO_2 phase possesses high τ_f value (420 ppm/°C) [11], which leads to an increase in the τ_f values of the MZ_xT ceramics.

4. Conclusion

The microwave dielectric properties of Zr substituted for Ti to form $Mg(Zr_xTi_{1-x})O_3$ ceramics have been investigated in this study. Substitution in the B-site occurred in the composition of $0.01 \leq x \leq 0.3$. Single phase ceramics were obtained at the composition's x range from 0.01 to 0.05. $Mg_{0.25}Zr_{0.38}Ti_{0.38}O_{1.75}$ second phase was observed in the boundary or in the grain as $x \geq 0.05$, whereas the TiO_2 phase was formed in specimens with other compositions. The Zr substitution was capable of improving the grain growth of the ceramics, which enhanced the $Q \times f$ value compared with the pure $MgTiO_3$. With an excess of Zr substitution, however, it can be seen that the abnormal grain growth and secondary phases made the $Q \times f$ value to slow down. Although the secondary phases damaged the $Q \times f$ value at high x content, τ_f values of the MZ_xT ceramics varied from about −50 to −30 ppm/°C in the ranges $x = 0.05$–0.1 by the influence of the secondary phase. When $x = 0.05$, the specimen exhibited excellent properties of $\varepsilon_r = 18.1$, $Q \times f = 380{,}000$ GHz and $\tau_f = -50$ ppm/°C.

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