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Microwave dielectric characteristics of ceramics in Mg_2SiO_4–Zn_2SiO_4 system

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Abstract

$(Mg_{1-x}Zn_x)_2SiO_4$ ceramics were prepared and characterized. The densification temperatures of the present ceramics are much lower than those for Mg_2SiO_4 and Zn_2SiO_4 end-members. Small solid solution limits of Zn in Mg_2SiO_4 and Mg in Zn_2SiO_4 are observed, and the bi-phase structure is confirmed in $(Mg_{1-x}Zn_x)_2SiO_4$ ceramics with $x = 0.1$–0.9. Even though, it is clear that the Qf value of Zn_2SiO_4 ceramics can be significantly improved together with a suppressed temperature coefficient of resonant frequency τ_f by substituting Mg for Zn. $(Mg_{0.4}Zn_{0.6})_2SiO_4$ ceramics indicate a good combination of microwave dielectric characteristics: $\varepsilon_r = 6.6$ $Qf = 95{,}650$ GHz, and $\tau_f = -60$ ppm/°C.

Keywords: A. Sintering; B. X-ray methods; C. Dielectric properties; E. Functional application

1. Introduction

With the rapid development of telecommunication and radar systems, the utilized frequency has also correspondingly increased from kilometer-wave to submillimeter-wave, and even millimeter-wave where large quantity of information could be transported with rapid speed. The resonators and filters for such high-band microwave applications strongly require the microwave dielectric ceramics with high-quality factor (Q), low dielectric constant (ε_r) and nearly zero temperature coefficient of resonant frequency (τ_f) [1–9]. So far, a number of ceramics with low dielectric constant and high-Q value such as Al_2O_3, $MgTiO_3$, $MgAl_2O_4$, Y_2BaCuO_5 and Mg_2SiO_4 have been investigated [10–13]. Mg_2SiO_4 is an important member in this category of materials, and a low dielectric constant (6–7) and a high-Qf value (~241,500 GHz) were reported together with a temperature coefficient of resonant frequency of −67 ppm/°C [14]. Recently, the modification of microwave dielectric properties of forsterite ceramics have been reported by adding TiO_2 or forming solid solutions [14–16].

In the present paper, the microwave dielectric characteristics of $(Mg_{1-x}Zn_x)_2SiO_4$ ceramics were investigated together with their structure and densification behavior.

2. Experimental procedure

$(Mg_{1-x}Zn_x)_2SiO_4$ ceramics were prepared by conventional solid-reaction method using high-purity reagents. All the raw materials were first dried and MgO was fired at 700 °C for 3 h to avoid any water and CO_2 absorption. Then high-purity MgO (99.99%), ZnO (99.95%), and SiO_2 (99.99%) were weighed in nominal stoichiometric formula of $2(1-x)MgO\cdot 2xZnO\cdot SiO_2$. The powders were mixed and milled in a polyethylene bottle with zirconia balls in distilled water for 24 h. The wet slurries were dried and calcined at 1200 °C in air for 3 h, and then ground again for 24 h. The powders added with PVA organic binder (5 wt.%) were palletized into cylindrical compacts of 12 mm in diameter and 2–5 mm in thickness under uniaxial pressure of 98 MPa. The green compacts were firstly heated at 600 °C in air for 3 h to expel the organic binder, and subsequently sintered at 1200–1500 °C in air for 3 h.

The density was measured using Archimedes' method. The sintered samples were crushed, and the crystal structure and the phase constitution were studied using powder X-ray diffraction analysis (XRD, Rigaku D/max 2550 PC, Japan) using Cu Kα radiation. The polished samples were thermally etched at a

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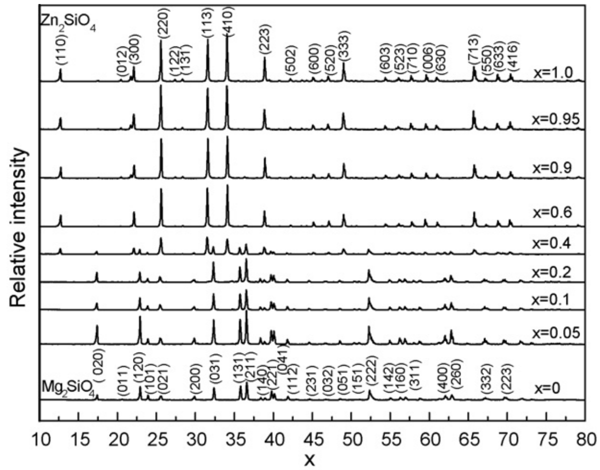

Fig. 1. XRD patterns of $(Mg_{1-x}Zn_x)_2SiO_4$ ceramics with various x values.

temperature 100 °C below that of sintering temperature, and the surface morphology was studied by scanning electron microscopy (SEM) with the back scattering electron images (SIR10N-100, FEI, Netherland). The microwave dielectric characteristics were evaluated at about 10 GHz using a network analyzer (Aglient PNA E8363B). The ε_r and Qf value were evaluated by a cavity method [17], and τ_f was evaluated by the Hakki–Coleman method [18] and calculated by the following equation:

$$\tau_f(\text{ppm}/^\circ\text{C}) = \frac{f_{85\,^\circ\text{C}} - f_{20\,^\circ\text{C}}}{65\,f_{20\,^\circ\text{C}}} \times 10^6 \qquad (1)$$

3. Results and discussion

The densification temperature of $(Mg_{1-x}Zn_x)_2SiO_4$ ceramics decreases from 1450 to 1250 °C with increasing x up to $x = 0.6$, and then turns to increase. Zn-substitution for Mg decreases the sintering temperature of Mg_2SiO_4 ceramics, and Mg-substitution for Zn in Zn_2SiO_4 ceramics has the similar effect. Fig. 1 shows the XRD patterns of $(Mg_{1-x}Zn_x)_2SiO_4$ ceramics with various x. Mg_2SiO_4- and Zn_2SiO_4-based phases are observed as the major phases for the compositions of $x < 0.4$ and $x \geq 0.6$, respectively, and the obvious co-presence of such two phases are determined at $x = 0.4$. It is difficult to discern the peaks of Zn_2SiO_4 for $x = 0.05$, and minor amount of Zn_2SiO_4 was detected for $x = 0.1$. With increasing x, Zn_2SiO_4 becomes the major phase, while Mg_2SiO_4 becomes to the secondary phase and finally disappears at $x = 0.95$. These results agree well with those reported by Segnit et al. [19,20]. That is, the solid solution limit in both end of $(Mg_{1-x}Zn_x)_2SiO_4$ is small. The small solid solution limit is because of the large difference between the crystal structure of Mg_2SiO_4 and Zn_2SiO_4. Though Mg_2SiO_4

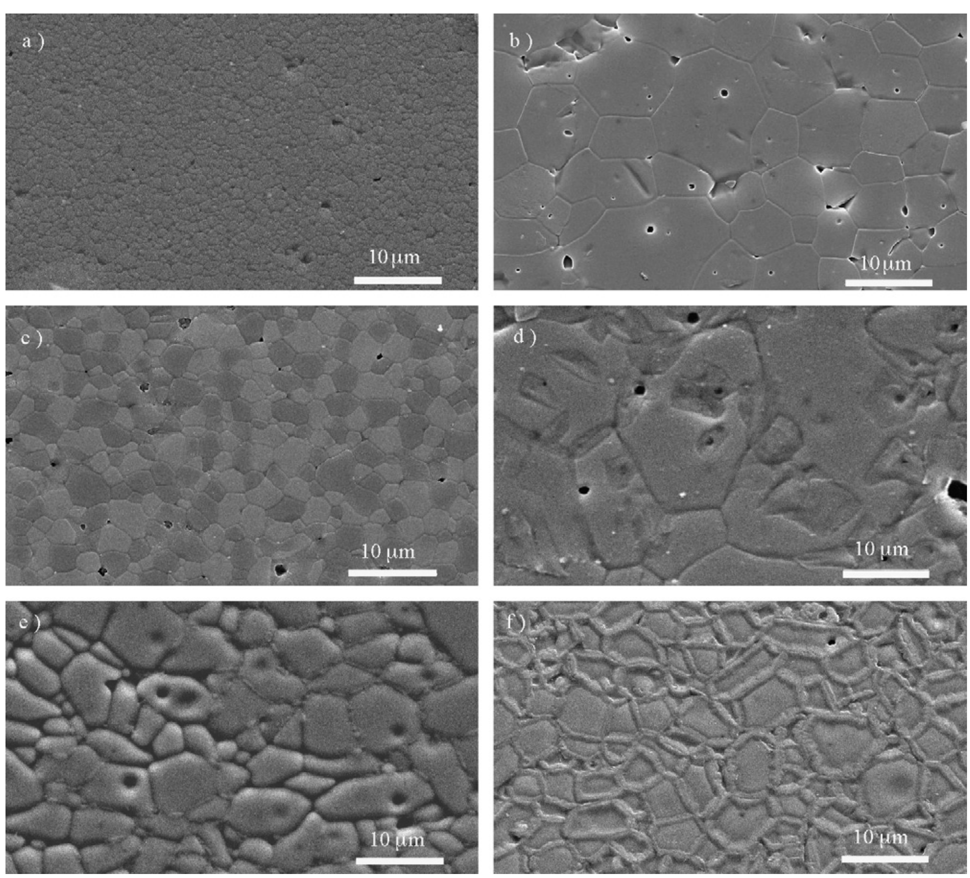

Fig. 2. SEM micrographs of $(Mg_{1-x}Zn_x)_2SiO_4$ ceramics with various x: (a) $x = 0$ sintered at 1450 °C; (b) $x = 0.1$ sintered at 1400 °C; (c) $x = 0.4$ sintered at 1250 °C; (d) $x = 0.6$ sintered at 1250 °C; (e) $x = 0.8$ sintered at 1375 °C; (f) $x = 1.0$ sintered at 1400 °C.

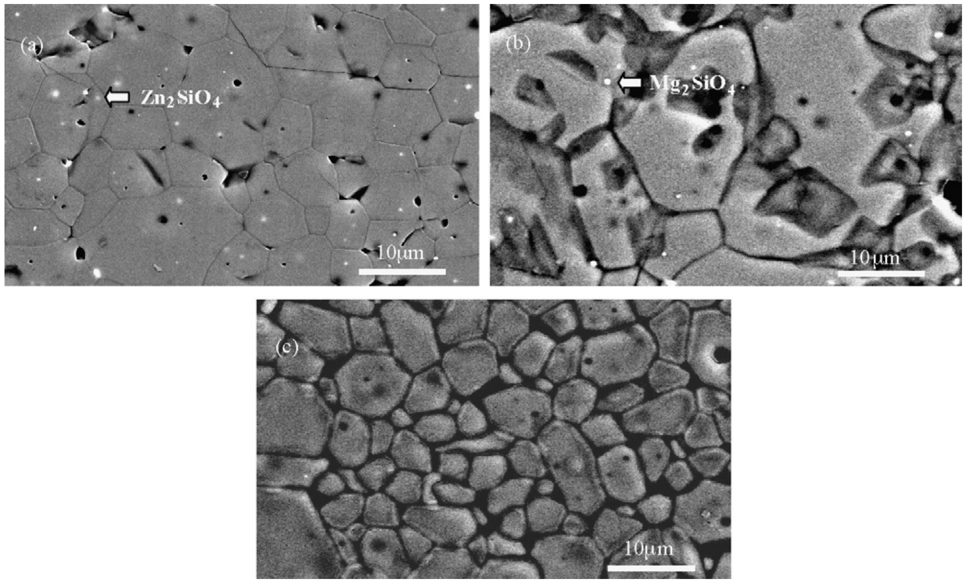

Fig. 3. Back scattering electron micrographs of $(Mg_{1-x}Zn_x)_2SiO_4$ ceramics with various x: (a) $x = 0.1$ sintered at 1400 °C; (b) $x = 0.6$ sintered at 1250 °C; (c) $x = 0.9$ sintered at 1375 °C.

and Zn_2SiO_4 are both island silicate compound with the similar formula, the former generally known as ''forsterite'' has an orthorhombic structure belonging to space group *Pmnb*, and the latter known as ''willemite'' has a rhombohedral structure belonging to space group $R\overline{3}$ (148) [21,22]. Mg_2SiO_4 is composed of connection of Mg–O octahedron with Si–O tetrahedron by sharing vertex and edge, Zn_2SiO_4 is built on connection of Zn–O tetrahedron with Si–O tetrahedron by sharing vertex.

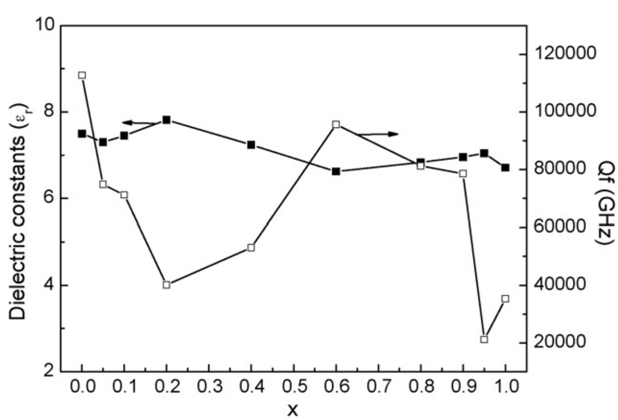

Fig. 4. Dielectric constants and *Qf* of $(Mg_{1-x}Zn_x)_2SiO_4$ ceramics as functions of x.

Table 1
Microwave dielectric characteristics of $(Mg_{1-x}Zn_x)_2SiO_4$ ceramics as functions of x

x	f_0 (GHz)	ε_r	Qf (GHz)	τ_f (ppm/°C)
0	10.7	7.5	112,780	−63
0.05	10.0	7.3	74,830	−67
0.1	10.1	7.5	71,210	−69
0.2	10.2	7.8	40,140	−68
0.4	10.5	7.2	53,010	−59
0.6	10.9	6.6	95,650	−60
0.8	10.8	6.8	81,320	−55
0.9	10.8	7.0	78,540	−58
0.95	10.7	7.0	21,170	−53
1.0	11.0	6.7	35,330	−58

Fig. 2 shows the SEM micrographs of $(Mg_{1-x}Zn_x)_2SiO_4$ ceramics with various x. The accelerated grain growth is observed for $x = 0.1$ and 0.9, and fine-grained structures are determined for $x = 0.4$ where the co-presence of Mg_2SiO_4 and Zn_2SiO_4 two phases are confirmed by XRD analysis. Moreover, the porosities indicate the occurrence of ZnO evaporation at higher sintering temperatures. The presence of secondary phase is confirmed by the back-scattering electron images shown in Fig. 3, where the secondary phases are pointed by arrows.

Fig. 4 and Table 1 show the microwave dielectric characteristics of $(Mg_{1-x}Zn_x)_2SiO_4$ as a function of x. Dielectric constant various little in the present ceramics with various x, but the composition has significant effects upon *Qf*. A serious decrease of *Qf* value is observed in the $(Mg_{1-x}Zn_x)_2SiO_4$ ceramics at the vicinity of Mg_2SiO_4 end-member, however, the *Qf* value much great than that in Zn_2SiO_4 end-member is obtained in the compositions of $x = 0.6$–0.9. Moreover, a suppressed temperature coefficient of resonant frequency τ_f is obtained by substituting Mg for Zn. The good combination of microwave dielectric characteristics is achieved in the composition of $x = 0.6$, $\varepsilon_r = 6.6$, $Qf = 95{,}650$ GHz, and $\tau_f = -60$ ppm/°C.

4. Conclusions

$(Mg_{1-x}Zn_x)_2SiO_4$ ceramics can be sintered at a temperature much lower than that for Mg_2SiO_4 and Zn_2SiO_4 end-members. Small solid solution limits of Zn in Mg_2SiO_4 and Mg in Zn_2SiO_4 are observed, and the $(Mg_{1-x}Zn_x)_2SiO_4$ ceramics with $x = 0.1$–0.9 generally indicate the ''forsterite + willemite'' bi-phase structure. Though a serious decrease of *Qf* value is observed in $(Mg_{1-x}Zn_x)_2SiO_4$ ceramics at the vicinity of Mg_2SiO_4 end-member, it is clear that the *Qf* value of Zn_2SiO_4 ceramics can be significantly improved together with a suppressed temperature coefficient of resonant frequency τ_f by substituting Mg for Zn. $(Mg_{0.4}Zn_{0.6})_2SiO_4$ ceramics indicate a good combination of microwave dielectric characteristics: $\varepsilon_r = 6.6$, $Qf = 95{,}650$ GHz, and $\tau_f = -60$ ppm/°C.

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