



Low-loss microwave dielectrics using $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x = 0.02\text{--}0.08$) solid solutions

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ABSTRACT

The microwave dielectric properties and microstructures of $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x = 0.02\text{--}0.08$) solid solutions prepared by the conventional solid-state route have been investigated. Lattice parameters of the ceramics were also measured and linearly increased with the increase of x . The formation of solid solutions $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x = 0.02\text{--}0.08$) was confirmed by the X-ray diffraction patterns, the EDS analysis and the measured lattice parameters. A substantial increase in the $Q \times f$ was achieved in the solid solution system whereas the dielectric constant and the temperature coefficient of resonant frequency retained similar compared to that of the pure $\text{Mg}_4\text{Nb}_2\text{O}_9$. A fine combination of microwave dielectric properties ($\epsilon_r \sim 13$, $Q \times f \sim 247,000$ GHz, $\tau_f \sim -67$ ppm/°C) can be achieved for specimen using $(\text{Mg}_{0.95}\text{Zn}_{0.05})_4\text{Nb}_2\text{O}_9$ ceramics sintered at 1340 °C for 4 h.

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1. Introduction

The increase of carrier frequency in the communication systems has been driving the need for new dielectric materials with a low loss (high quality factor, Q) in the last few years [1]. It is because the $Q \times f$ is almost constant in the microwave and millimeter wave regions. A high Q dielectric has become more prominent to prevent from the drop in the Q at high frequency. Research for such a material is therefore desired than ever and is being under investigation. In fact, several candidate dielectrics have been developed based on the requirement previously described [2–4]. For instance, compounds such as $(\text{Mg}_{1-x}\text{M}_x)\text{TiO}_3$ and $(\text{Mg}_{1-x}\text{M}_x)_2\text{TiO}_4$ (where $\text{M} = \text{Zn, Co, Ni or Mn}$), have been investigated to possess a $Q \times f$ higher than 200,000 GHz [5–9].

Due to its low dielectric loss, the corundum-type trigonal-structured $\text{Mg}_4\text{Nb}_2\text{O}_9$ ceramics [10] has been of great interest to the electronics and communication industries in the last few years. It had been investigated to exhibit excellent microwave dielectric properties by Yoshida et al. ($\epsilon_r \sim 12.4$, $Q \times f \sim 192,000$ GHz and $\tau_f \sim -70.5$ ppm/°C) [11]. Comparable results ($\epsilon_r \sim 16$, $Q \times f \sim 116,000$ GHz and $\tau_f \sim -66$ ppm/°C) were also reported by Khalam et al. [12]. Further research was accomplished to promote its $Q \times f$ by partially substituting Nb with Sb, Ta or V to form a solid solution [11,13–15]. Among those solid solutions, an extremely high $Q \times f$ ($\sim 350,000$ GHz) could be achieved from specimen using $\text{Mg}_4(\text{Nb}_{2-x}\text{Ta}_x)_2\text{O}_9$ [14]. However, the use of Ta limits its

practical application due to the expensive cost. In addition, A-site replacement (Mg by Zn or Ni) was also investigated for $\text{Mg}_4\text{Nb}_2\text{O}_9$ by Yoshida et al. [11]. They reported the $Q \times f$ of the specimen using $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ (with an increment of 0.125 in x) would decrease with increasing Zn content.

In this paper, $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x = 0.02\text{--}0.08$) solid solutions with a smaller increment in x were synthesized by solid-state method and its microwave dielectric properties and microstructures were also investigated. Consequently, the compound under study not only showed a tremendous lowering in the dielectric loss but also retained comparably decent values of ϵ_r and τ_f .

2. Experimental procedure

The solid solutions $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x = 0.02\text{--}0.08$) were synthesized using a solid-state mixed oxide route with starting materials of high-purity oxide powders (>99.9%): MgO , ZnO and Nb_2O_5 . Because MgO is hygroscopic, it was first fired at 600 °C to avoid moisture contain. The weighed raw materials were mixed by ball milling with agate media in distilled water for 24 h, and the mixtures were dried and calcined at 1100 °C for 4 h. Prepared powders were dried, ball-milled for 24 h with 5 wt% of a 10% solution of PVA as a binder, granulated by sieving through 100 mesh, and pressed into pellets with 11 mm in diameter and 5 mm in thickness. All samples were prepared using an automatic uniaxial hydraulic press at 2000 kg/cm². These pellets were sintered at 1310–1400 °C for 4 h in air.

The crystalline phases of the sintered ceramics were identified by XRD using $\text{Cu K}\alpha$ ($\lambda = 0.15406$ nm) radiation with a Siemens D5000 diffractometer (Munich, Germany) operated at 40 kV and 40 mA. The lattice constant calculation was accomplished using GSAS software with Rietveld method to fit the XRD patterns [16]. The microstructural observations and analysis of the sintered surface were performed by scanning electron microscopy (SEM; Philips XL-40FEG, Eindhoven, The Netherlands) and an energy-dispersive X-ray spectrometer (EDS, Philips). The dielectric constant (ϵ_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki-Coleman dielectric resonator method [17,18]. A system combining a HP8757D network analyzer (Palo Alto, CA) and a HP8350B sweep oscillator

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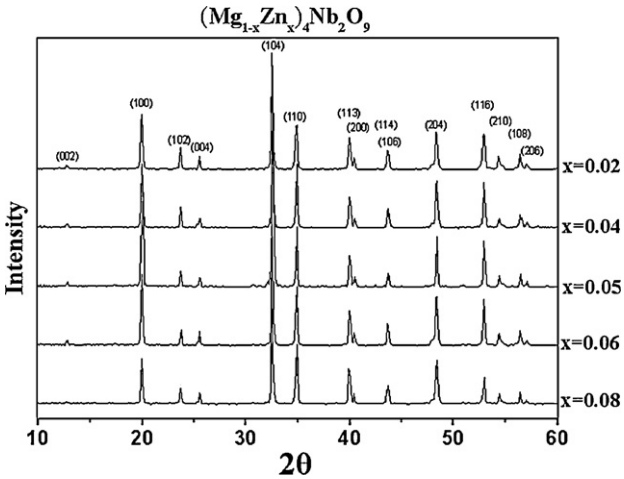


Fig. 1. X-ray diffraction patterns of $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x = 0.02\text{--}0.08$) solid solutions sintered at 1340°C for 4 h.

(Palo Alto, CA) was employed in the measurement. An identical technique was applied to the measurement of the temperature coefficient of resonant frequency (τ_f). The test set was placed over a thermostat in the temperature range of $25\text{--}80^\circ\text{C}$. τ_f (ppm/ $^\circ\text{C}$) can be calculated by considering the change in resonant frequency (Δf). The temperature coefficient of resonant frequency (τ_f) can be defined as

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

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

3. Results and discussion

Fig. 1 illustrates the room-temperature X-ray diffraction (XRD) patterns recorded from the $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x = 0.02\text{--}0.08$) ceramics sintered at 1340°C for 4 h. The single trigonal-structured $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ (can be indexed as $\text{Mg}_4\text{Nb}_2\text{O}_9$), belonging to the space group $P3c1$ (165), was identified throughout the entire tested range. The position and the relative intensity of the XRD peaks varied slightly implying the compound tends to form a continuous solid solution. In order to confirming the formation of solid solution, lattice parameters of $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x = 0.02\text{--}0.08$) ceramics sintered at 1340°C were measured and demonstrated in Table 1. The lattice parameters linearly increased from $a = 5.1616 \text{ \AA}$, $c = 14.0302 \text{ \AA}$ at $x = 0.02$ to $a = 5.1637 \text{ \AA}$, $c = 14.0346 \text{ \AA}$ at $x = 0.08$ in the $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ composition (Fig. 2). The variation of the lattice parameters of the specimens was a result from the incorporation of larger Zn^{2+} (0.74 \AA , CN=6) in place of Mg^{2+} (0.72 \AA , CN=6) under the same coordination number [19]. Moreover, significant variation was not detected from the X-ray diffraction patterns of the specimens using $(\text{Mg}_{0.95}\text{Zn}_{0.05})_4\text{Nb}_2\text{O}_9$ sintered at different temperatures in our experiment (Fig. 3).

Fig. 4 shows the scanning electron microscopy (SEM) micrographs of the specimens using $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ceramics sintered at different temperatures for 4 h. Well-developed microstructure was achieved for specimen using $(\text{Mg}_{0.95}\text{Zn}_{0.05})_4\text{Nb}_2\text{O}_9$

Table 1
Lattice parameters of $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ceramics sintered at 1340°C .

Composition	Lattice parameters		Ref.
	<i>a</i> (Å)	<i>c</i> (Å)	
<i>x</i> = 0.00	5.1612	14.0280	[10]
<i>x</i> = 0.02	5.1616	14.0302	This work
<i>x</i> = 0.04	5.1624	14.0311	This work
<i>x</i> = 0.05	5.1629	14.0320	This work
<i>x</i> = 0.06	5.1631	14.0326	This work
<i>x</i> = 0.08	5.1637	14.0346	This work

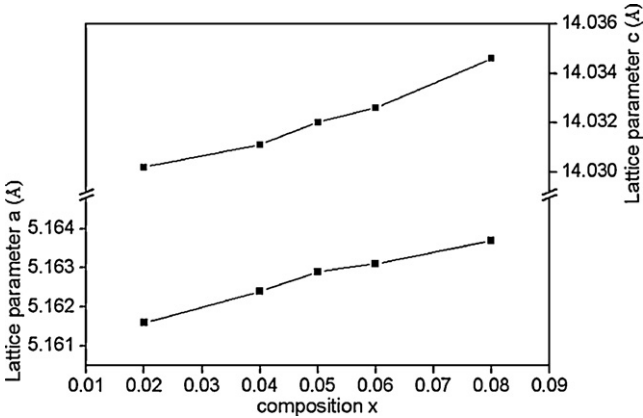


Fig. 2. The lattice parameters of $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x = 0.02\text{--}0.08$) solid solutions.

sintered at 1340°C whereas the porous one was observed at 1310°C . Further increase in the sintering temperature to $1370\text{--}1400^\circ\text{C}$ resulted in an over-grown grain morphology. It indicates a rapid grain growth of the ceramics occurs in the applied temperature range. Moreover, the grain size of $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ceramics slightly increased with increasing x value. However, the degradation in grain uniformity started to appear when the x value is higher than 0.05, which could damage its microwave dielectric properties. The corresponding EDX data (Table 2) of the SEM photo (Fig. 4b) illustrated all the examined grains showing $\text{Mg} + \text{Zn}:\text{Nb} = 2:1$, further confirming the formation of a solid solution. Notice that the evaporation of ZnO was observed from the EDX at high sintering temperature (spot D in Fig. 4d).

The relative density and dielectric constant of the $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x = 0.02\text{--}0.08$) solid solutions as a function of the sintering temperature for 4 h are shown in Fig. 5. Notice that the densities apparently increased with increasing sintering temperature to a maximum at 1340°C and slightly decreased thereafter. The increase in density was mainly a result from the grain growth as shown in Fig. 4. The lowering in the density of the specimen was due to the rapid grain growth as the sintering temperature increased to $1370\text{--}1400^\circ\text{C}$. It also might be a result from the evaporation of ZnO . In addition, specimen with $x = 0.05$ also possessed a higher relative density compared to those with other x values. By increasing the sintering temperature, the dielectric constants of all compositions increased to a maximum value at

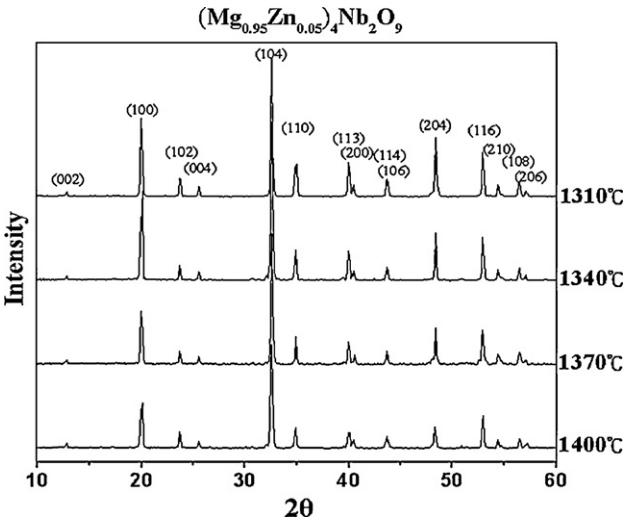


Fig. 3. X-ray diffraction patterns of $(\text{Mg}_{0.95}\text{Zn}_{0.05})_4\text{Nb}_2\text{O}_9$ solid solution sintered at different temperatures for 4 h.

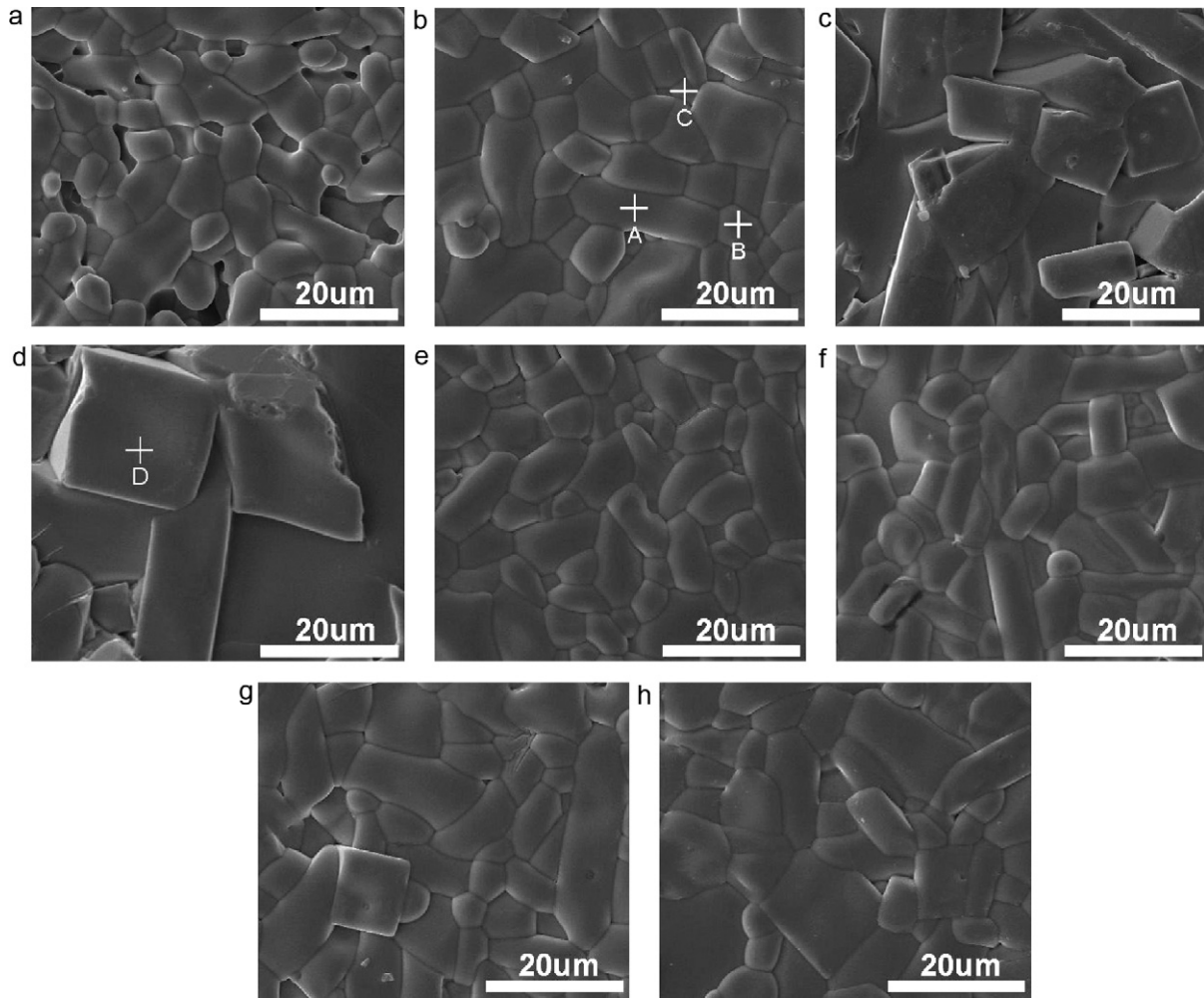


Fig. 4. The scanning electron microscopy (SEM) micrographs of $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ceramics with $x=0.05$ sintered at (a) 1310 °C, (b) 1340 °C, (c) 1370 °C, and (d) 1400 °C for 4 h, and with (e) $x=0.02$, (f) $x=0.04$, (g) $x=0.06$, and (h) $x=0.08$ sintered at 1340 °C for 4 h.

1340 °C, corresponding to the optimum densification temperature, and decreased thereafter. The variation of ε_r was consistent with that of the relative density. A maximum ε_r value of ~ 13 was obtained for specimen using $(\text{Mg}_{0.95}\text{Zn}_{0.05})_4\text{Nb}_2\text{O}_9$ sintered at 1340 °C for 4 h. It is comparable with that of pure $\text{Mg}_4\text{Nb}_2\text{O}_9$ ($\varepsilon_r \sim 12.4\text{--}16$), implying the forming of solid solution will not bring much variance in the ε_r of the specimen using pure $\text{Mg}_4\text{Nb}_2\text{O}_9$. In addition, the ε_r is a function of the composition, which could also be correlated to the relative density of the ceramics.

The ionic polarizabilities (α_D) of $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x=0.02\text{--}0.08$) were also estimated in order to clarify the effects of the Zn substitution for Mg on the dielectric constant using the Clausius–Mosotti equation:

$$\alpha_D = \frac{1[\nu_m(\varepsilon - 1)]}{b(\varepsilon + 2)} \quad (2)$$

Table 2

The EDX data of the $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ceramics for spots A, B and C in Fig. 4b.

Spots	Atom (%)			
	Mg K	Zn K	Nb L	O K
A	20.87	1.03	11.51	66.59
B	20.09	0.87	11.03	68.01
C	21.09	0.95	10.62	67.34
D	21.02	0.53	11.23	67.22

where V_m and ε represent the molecular volume and measured dielectric constant, respectively and constant value $b=4\pi/3$. By increasing the compositions x , the obtained ionic polarizability (α_D) slightly increases to a maximum at $x=0.05$ and decreases thereafter as shown in Fig. 6. It exhibits the similar variations in the dielectric constant although the molecular volume linearly increases with increasing x value suggesting that in addition to the relative den-

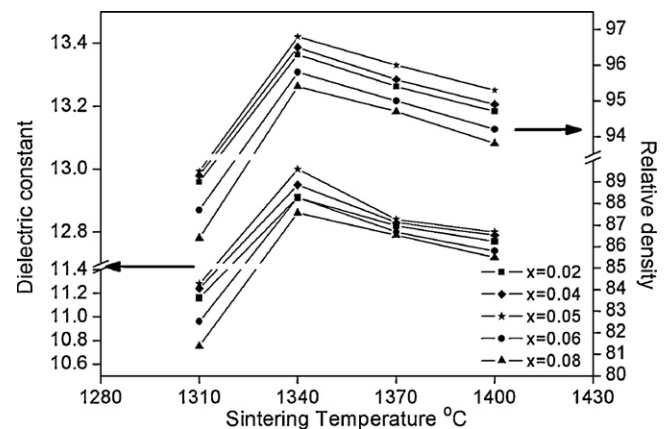


Fig. 5. The relative density and dielectric constant of the $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x=0.02\text{--}0.08$) solid solutions as a function of sintering temperature for 4 h.

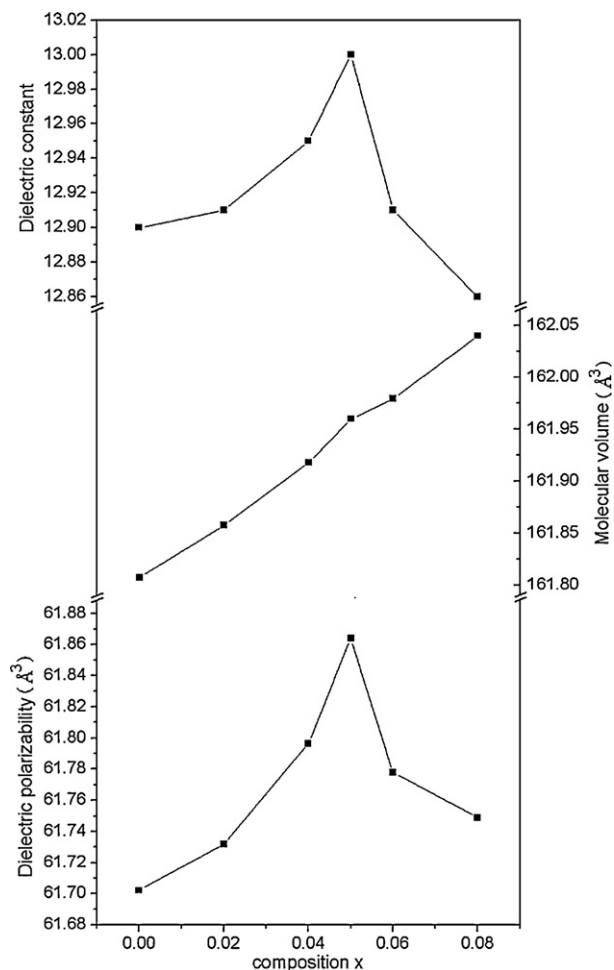


Fig. 6. The ϵ_r , molecular volume and polarizability of $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x = 0.02\text{--}0.08$) solid solutions as a function of sintering temperature for 4 h.

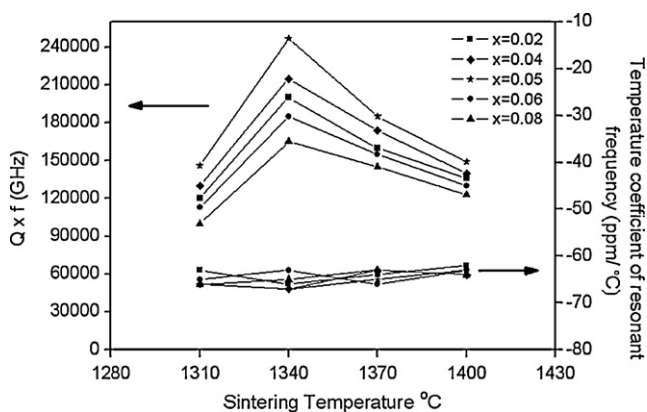


Fig. 7. The plots of the room-temperature $Q \times f$ and τ_f values of the $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x = 0.02\text{--}0.08$) solid solutions as a function of the composition and sintering temperature administered for duration of 4 h.

sity, the variance in the dielectric constant can be attributed to the change in ionic polarizability.

Fig. 7 shows the plots of the room-temperature $Q \times f$ and τ_f values of the presented ceramics as a function of the composition and sintering temperature administered for duration of 4 h. The varia-

tion of $Q \times f$ was also consistent with that of relative density. The initial increase in x from 0 to 0.05 tremendously promoted the $Q \times f$ from 192,000 to 247,000 GHz whereas a further increase in the x to 0.08 reduced the $Q \times f$ to 165,000 GHz, indicating the initial increase in the concentration of Zn has a more prominent effect on the $Q \times f$ than subsequent additions. Similar behavior has also been reported in other solid solutions [5–9]. It implied the variation of $Q \times f$ was most likely in response to that of relative density. Also, a relatively uniform morphology contributes to the lowering of dielectric loss. The maximum $Q \times f$ value of 247,000 GHz was obtained for specimen using $(\text{Mg}_{0.95}\text{Zn}_{0.05})_4\text{Nb}_2\text{O}_9$ sintered at 1340 °C for 4 h, indicating a tremendous lowering in the dielectric loss compared to that of both end members, pure $\text{Mg}_4\text{Nb}_2\text{O}_9$ and $\text{Zn}_4\text{Nb}_2\text{O}_9$. In addition, the τ_f is known to be governed by the composition, the additives, and the second phase of the material. It was not sensitive to the sintering temperature since there was no alternate composition in the experiment. Significant variation in the τ_f was also not observed for specimens at different sintering temperatures. Consequently, the τ_f would retain in the range from –62 to –67 ppm/°C for specimens with $x = 0.02\text{--}0.08$ at 1310–1400 °C. It is also comparable with that of the pure $\text{Mg}_4\text{Nb}_2\text{O}_9$.

4. Conclusion

Well-sintered ceramics in the $(\text{Mg}_{1-x}\text{Zn}_x)_4\text{Nb}_2\text{O}_9$ ($x = 0.02\text{--}0.08$) system were investigated and the forming of continuous solid solutions was confirmed. A tremendous loss reduction can be achieved for specimen using $(\text{Mg}_{0.95}\text{Zn}_{0.05})_4\text{Nb}_2\text{O}_9$ whereas the ϵ_r and τ_f retain similar compared to that of pure $\text{Mg}_4\text{Nb}_2\text{O}_9$. The $Q \times f$ can be boosted from 192,000 GHz of pure $\text{Mg}_4\text{Nb}_2\text{O}_9$ to 247,000 GHz in the $(\text{Mg}_{0.95}\text{Zn}_{0.05})_4\text{Nb}_2\text{O}_9$. It is expected to receive more attention than both end members, pure $\text{Mg}_4\text{Nb}_2\text{O}_9$ and $\text{Zn}_4\text{Nb}_2\text{O}_9$. The proposed dielectric, having extremely low loss has made it a very promising material for microwave and millimeter wave applications.

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