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Microwave Performance, Microstructure, and Crystallization of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ Ilmenite Ceramics

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Abstract: The sintering behavior, microstructure analysis, crystallization, and microwave performance of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ ($y = 0.01\text{--}0.2$) ceramics, processed with raw powders of MgO , NiO , ZnO , and TiO_2 via the conventional solid-state method, are investigated. The main phases of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ ceramics were obtained. With partial replacement by Ni^{2+} , the $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ could be well sintered at 1200°C , and the microwave performance was shown to be positively correlated with sintering temperature. The permittivity (ϵ_r) saturated at $18.7\text{--}19.3$, and the quality factor (Q_f) values approached $72,000\text{--}165,000$ (GHz) as the sintering temperatures increase from 1125 to 1250°C . The temperature coefficient of resonance frequency (τ_f) falls in a stable range of -62.9 to -66 ppm/ $^\circ\text{C}$ as sintering temperature rising. A permittivity (ϵ_r) of 19.3 , a maximum Q_f value of $165,000$ (GHz), and a temperature coefficient (τ_f) of -65.4 ppm/ $^\circ\text{C}$ were measured for the samples at $1200^\circ\text{C}/4$ h. $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ material system shows high potential for applications of high frequency-selection components in satellite communication and 5G wireless telecommunication systems.

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1. Introduction

Recent demands for high-frequency electronic components are increasing, and ceramic-based compositions are extensively used in satellite communications, including DBS TV, GPS, Internet of Things (IoT), etc., and 5G telecommunications, cell phone, cell site, etc. Furthermore, microwave dielectric ceramics are widely used for filters, resonators, and mixers in wireless communication systems [1–4]. In microwave telecommunications, microwave resonators fabricated by dielectric ceramics result in the miniaturization of microwave devices.

Materials possessing the following dielectric properties are suitable for dielectric resonators [5–8]: (1) Permittivity (ϵ_r) > 20 : The permittivity is an essential factor for component size reduction. (2) Quality factor ($\tan\delta$, the inverse of the dielectric loss) $> 30,000$ (GHz): Lower insertion loss and steeper cut-off can be obtained due to a higher Q_f value, which ensured the lower dielectric loss of components. (3) Temperature coefficient of resonance frequency (τ_f) $< \pm 10$ ppm/ $^\circ\text{C}$: A near-zero τ_f value ($< \pm 10$ ppm/ $^\circ\text{C}$) is necessary for the stability of device performance even temperature changes enormously in the environment. Generally speaking, three parameters strongly affect the size, frequency selectivity, and temperature stability of the device to the system, respectively.

MgTiO_3 -based ceramics, which possessed an ilmenite-type structure and trigonal space group R-3 have caught much attention and typical applications as dielectric resonators [9], filters, antennas, and so on for microwave communication systems due to its good microwave dielectric performance recently. MgTiO_3 sintered at 1350°C was demonstrated excellent dielectric performance in microwave frequency: $\epsilon_r \sim 17$, Q_f value $\sim 160,000$ (at 7 GHz) and temperature coefficients of resonance frequency (τ_f) ~ -51 ppm/ $^\circ\text{C}$ [10].

Furthermore, $(\text{Mg}_{0.6}\text{Zn}_{0.4})\text{TiO}_3$ sintered at $1200\text{ }^\circ\text{C}$ with $\epsilon_r \sim 19.8$, Qf value $\sim 144,000$ and $\tau_f \sim -66\text{ ppm}/^\circ\text{C}$ have also been demonstrated as promising titanate candidate for broad applications in this microwave frequency. Some researchers pay attention to comprehensively investigate the effects of relative contents between Mg and Zn in $(\text{Mg}_y\text{Zn}_{1-y})\text{TiO}_3$ system [11,12]. As a result, microwave dielectric performance of $(\text{Mg}_y\text{Zn}_{1-y})\text{TiO}_3$ highly depended on the content of Mg.

It was reported that the partial replacement of Mg by B^{2+} ($\text{B}^{2+} = \text{Co}, \text{Ni}, \text{and Zn}$) increases the structural densification and upgrades the dielectric performance of MgTiO_3 . $(\text{Mg}_{0.95}\text{B}^{2+}_{0.05})\text{TiO}_3$ with an ilmenite-type structure has been documented to possess excellent dielectric performance [8,13,14]. Since the ionic radii of B^{2+} (0.0745 nm of Co^{2+} , 0.068 nm of Ni^{2+} , and 0.082 nm of Zn^{2+}) approach to that of Mg^{2+} (0.072 nm), Mg^{2+} ions can be replaced by B^{2+} ions to form $(\text{Mg}, \text{B}^{2+})\text{TiO}_3$ compound. However, the $(\text{Mg}_{0.95}\text{B}^{2+}_{0.05})\text{TiO}_3$ shows a negative temperature coefficient (τ_f). In the previous study, combining some large positive τ_f compensator with $(\text{Mg}_{0.95}\text{B}^{2+}_{0.05})\text{TiO}_3$ is effective to obtain near-zero τ_f value in the whole material system [14–21]. It is noted that the second phase of $\text{Mg}_{0.95}\text{B}^{2+}_{0.05}\text{Ti}_2\text{O}_5$ ($\text{B}^{2+} = \text{Co}, \text{Ni}, \text{and Zn}$) might deteriorate the dielectric performance of the $(\text{Mg}_{0.95}\text{B}^{2+}_{0.05})\text{TiO}_3$ system, and we could not precisely evaluate the effect of $\text{Mg}_{0.95}\text{B}^{2+}_{0.05}\text{Ti}_2\text{O}_5$ phase [22–27].

In this paper, with partial substitution of Mg^{2+} (0.072 nm) by Ni^{2+} (0.069 nm), the microstructure densification of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ was observed, and microwave dielectric performance of that was also further improved compared to $(\text{Mg}_{0.6}\text{Zn}_{0.4})\text{TiO}_3$. The $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ were fabricated via a solid-state method. The microwave dielectric performance was investigated according to the densification, the x-ray diffraction (XRD) analysis, and the samples' microstructures (SEM and EDS). The correlation between the microstructure and the Qf value was also investigated in detail.

2. Experimental Analysis

Conventional solid-state methods were utilized to synthesize samples of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ ($y = 0.01\text{--}0.2$) from high-purity oxide powders ($>99.9\%$): MgO , NiO , and TiO_2 . Raw MgO powder was fired at $600\text{ }^\circ\text{C}/1\text{h}$ to avoid moisture retention due to its hygroscopic characteristic. $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ ($y = 0.01\text{--}0.2$) compounds were made from mixed oxides stoichiometrically and ground in distilled water for 24 h in a ball mill with agate balls. The mixed solution was dried in the oven and calcined at $1100\text{ }^\circ\text{C}$ for 4 h in a high-temperature furnace. A 3.5 wt% of a 12% PVA solution as a binder (Polyvinyl alcohol 500, Showa) was added into the calcined powder, granulated by sieving through a 100 mesh, and pressed into pellets, 11 mm in diameter and 5 mm in thickness, under 200 MPa pressure. The pellets were sintered at temperatures ranging from 1125 to $1250\text{ }^\circ\text{C}$ for 4 h in the atmosphere. The heating and cooling rates of a high-temperature furnace were both set at $10\text{ }^\circ\text{C}/\text{min}$ to obtain high-quality samples.

The crystalline phases of the calcined powder and the sintered ceramics were distinguished by X-ray diffraction (XRD) using $\text{CuK}\alpha$ ($\lambda = 0.15406\text{ nm}$) radiation with a Siemens D5000 diffractometer (Siemens, Berlin/Munich, Germany). Scanning electron microscopy (SEM; Philips, Amsterdam, The Netherlands) was utilized to observe the sintered surface's microstructure, and an energy-dispersive X-ray spectrometer (Philips) was used to identify the existence of secondary phases. Calculation of lattice parameter was performed with the Rietveld method to fit at least five peaks from measured X-Ray patterns. The apparent densities were measured using the Archimedes method with the three sintered samples under the same process and average measured data to calculate relative densities. The permittivity (ϵ_r) and the quality factor (Q) at microwave frequencies were measured by the Hakki–Coleman dielectric resonator method [28,29]. This method utilizes parallel conducting plates and coaxial probes in TE_{011} mode, where TE represented transverse electric waves, the first two subscript integers denote the waveguide mode, and the third integer subscript indicates the order of resonance in an increasing set of discrete resonant lengths. The measurement system was connected to Anritsu network analyzer with model

MS46122B. The measurement technique for the temperature coefficient of resonance frequency (τ_f) is almost the same as that of the quality factor measurement except for using a thermostat. The τ_f at microwave frequencies was measured, and note change of resonance frequency from 30 °C to 80 °C. The following formula can calculate the τ_f value (ppm/°C),

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

where f_1 and f_2 mean the resonance frequencies at $T_1 = 25$ °C and $T_2 = 80$ °C, respectively.

3. Results and Discussion

Figure 1 shows the room-temperature XRD analysis of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ ($y = 0.01$ – 0.2) sintered at 1200 °C for 4 h. The $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ with an ilmenite-type structure, the same as $(\text{Mg}_{0.6}\text{Zn}_{0.4})\text{TiO}_3$: trigonal (ICDD #01-073-7752), were identified as the main phase associated with the apparent second phase $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{Ti}_2\text{O}_5$ identical to MgTi_2O_5 (JCPDS File No. 82-1125). MgTi_2O_5 , called the second phase, is typically formed as an intermediate phase during the crystal growth of what is challenging to eliminate from the sample when MgO and TiO_2 react in a 1:2 molar ratio [30–32].

Figure 1. XRD analysis of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ ($y = 0.01$ – 0.2) sintered at 1200 °C for 4 h. +: $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$, O: $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{Ti}_2\text{O}_5$.

The formation of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{Ti}_2\text{O}_5$ might degrade the microwave dielectric performance of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ ceramics. As expected, the second phase $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ was enhanced at high temperatures since the $\text{Mg}_{0.95}\text{Ni}_{0.05}\text{Ti}_2\text{O}_5$ requires a high sintering temperature of 1450 °C [26,33]. In other words, less $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{Ti}_2\text{O}_5$ phase would exist at lower sintering temperatures [34]. Similar XRD analysis was identified for the samples with $y = 0.05$ sintering at 1125–1250 °C for 4 h (Figure 2).

The lattice parameters of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ ceramics sintered at 1200 °C for 4 h with various y values were also calculated for further structure investigation and forming of solid solution (Table 1). A decrease in the lattice parameters was observed for $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ ceramics compared to that of $(\text{Mg}_{0.6}\text{Zn}_{0.4})\text{TiO}_3$ (ICDD #01-073-7752). The results explain that $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ would form a solid solution due to the replacement of Mg^{2+} , Zn^{2+} by 0.05 mole Ni^{2+} . Formation of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ would result in a fluctuation in the lattice parameters because the smaller Ni^{2+} ions (radii = 0.069 nm) relative to the size of the Mg^{2+} ions (radii = 0.072 nm) and Zn^{2+} ions (0.082 nm) are added in $(\text{Mg}_{0.6}\text{Zn}_{0.4})\text{TiO}_3$, lead to the lattice of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ locally distorted in A-site. These data indicated that with the partial replacement of Mg^{2+} , Zn^{2+} by 0.05 mole Ni^{2+} , formation of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ solid solution would demonstrate a decrease in the lattice parameters from ($a = 0.5064$, and $c = 1.3918$ nm) in $(\text{Mg}_{0.6}\text{Zn}_{0.4})\text{TiO}_3$ to ($a = 0.5063$, and $c = 1.3912$ nm).

Figure 2. XRD analysis of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ sintered at 1125–1250 °C for 4 h. [+; $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$, O: $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{Ti}_2\text{O}_5$].

Table 1. The calculated lattice parameter of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ ceramic with $y = 0.01$ –0.2.

y	Sintering	a (nm)	c (nm)
Value	Temperature (°C)		
0.01	1175	0.50656 ± 0.00051	1.39113 ± 0.00082
	1200	0.50702 ± 0.00900	1.39242 ± 0.00146
	1225	0.50481 ± 0.00055	1.38946 ± 0.00089
0.03	1175	0.50650 ± 0.00079	1.39209 ± 0.00170
	1200	0.50713 ± 0.00057	1.39041 ± 0.00121
	1225	0.50689 ± 0.00054	1.39147 ± 0.00087
0.05	1175	0.50671 ± 0.00057	1.39158 ± 0.00122
	1200	0.50670 ± 0.00032	1.39196 ± 0.00069
	1225	0.50545 ± 0.00063	1.39144 ± 0.00103
0.07	1175	0.50632 ± 0.00045	1.39188 ± 0.00096
	1200	0.50585 ± 0.00106	1.38861 ± 0.00227
	1225	0.50565 ± 0.00039	1.39175 ± 0.00064
0.1	1200	0.50577 ± 0.00068	1.39031 ± 0.00110
0.2	1200	0.50593 ± 0.00090	1.38992 ± 0.00146

The micrographs of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ sintered at different temperatures for 4 h are revealed in Figure 3. The microstructures of samples were not dense at 1125 °C. Grain size gradually increased with temperature and became highly uniform at 1200 °C. The growth of rod-shaped grain was enhanced at temperatures higher than 1225 °C and possibly the second phase. EDS analysis for Spot A–D and E–F identified the quantity composition of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ sintered at 1200 °C and $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{Ti}_2\text{O}_5$ sintered at 1250 °C for 4 h, as shown in Figure 4a,b, respectively. Two kinds of grains possessed Mg, Zn, Ni, Ti, and O ions with different stoichiometric compositions $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ and $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{Ti}_2\text{O}_5$, respectively, were clearly distinguished in the multiphase ceramics. The grain composition analysis observed from points A–F demonstrated that $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ and $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{Ti}_2\text{O}_5$ form solid solutions to a certain degree, which is consistent with XRD analysis.

Figure 3. SEM photographs of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ sintered at temperature range (a) 1125, (b) 1150, (c) 1175, (d) 1200, (e) 1225 and (f) 1250 °C for 4 h.

Spot	Atom(%)				
	MgK	ZnK	NiK	TiK	OK
A	10.86	11.10	1.44	26.17	50.43
B	11.67	7.21	1.21	21.92	57.99
C	12.15	10.25	2.00	20.53	55.07
D	8.21	4.21	0.58	24.44	62.55
E	10.71	6.77	0.71	35.34	46.47
F	12.33	7.32	0.71	40.85	38.79

Figure 4. The EDS analysis of (a) $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ sintered at 1200 °C (b) $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{Ti}_2\text{O}_5$ sintered at 1250 °C for 4 h.

The apparent and relative density of the $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ with $y = 0.01\text{--}0.2$ sintered at different temperatures (1125–1250 °C) for 4 h is demonstrated in Figure 5. The relative density of the $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ exceeded 91.6% of the theoretical density (TD) in all specimens. The apparent density of the samples increased when the temperature increased from 1125 to 1200 °C. This increase in the apparent density can be attributed to the formation of dense microstructures, as observed in Figure 3d. The apparent density decreased when the temperature exceeded 1200 °C.

Figure 5. Dependent relationship of apparent density(g/cm^3) and relative density (%) of the $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ ceramics with $y = 0.01\text{--}0.2$ under 1125–1250 °C.

This decrease in the apparent density could result from the formation of a porous microstructure with large pores, as observed in Figure 3e,f. The apparent density and its corresponding TD increased from 4.15 g/cm^3 (94.32% TD) to its maximum value of 4.39 g/cm^3 (99.77%TD), and then decreased to 4.33 g/cm^3 (98.41%TD) for the $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ ceramics.

The permittivity and quality factor (Q_f) of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ ceramics sintered at temperatures for 4 h with various y values (0.01–0.2) are shown in Figure 6. The relationship between permittivity (ϵ_r) values and temperature reveals the same trend between densities and temperature since higher density means lower porosity inside samples. The permittivity increased with increasing temperature, reaching a maximum of 19.3 at 1200 °C and after that decreasing. Thus, increasing sintering temperature does not always result in a higher permittivity (ϵ_r). The permittivity of the well-sintered $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ ceramics ranged from 17.9 to 19.3 at 1125–1200 °C. A maximum ϵ_r value of 19.3 was reached for the $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ sintered at 1200 °C for 4 h.

The Q_f value is a crucial index for microwave dielectric ceramics applications because a high Q_f value represented a lower dielectric loss for microwave devices. Q_f values increased when temperature increased from 1125 °C to 1200 °C (Figure 6), consistent with the variation of bulk density, as shown in Figure 5. The increase of Q_f value at low temperatures is attributed to the rise in density identical to grain growth uniformity, as shown in Figure 3. A maximum Q_f value of 165,000 (GHz) was observed for the $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ ceramics sintered at 1200 °C for 4 h. Q_f value reached a maximum at 1200 °C, and after that, it decreased. The Q_f value degraded due to the inhomogeneous grain growth, which leads to a reduction of density, as mentioned in Figure 3. There are several possible mechanisms to cause microwave dielectric loss, such as the lattice vibrational modes, the pores, second phases, impurities, and lattice defects [35]. Furthermore, apparent density also closely affects the dielectric loss and has also been demonstrated in microwave dielectric mate-

rials [35,36]. The Qf value and the variation of density of the $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ show a similar trend, and hence apparent density is one of the dominant factors to cause the dielectric loss in this ceramic system.

Figure 6. Permittivity and quality factor of the $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ with $y = 0.01\text{--}0.2$ under $1125\text{--}1250\text{ }^\circ\text{C}$.

As illustrated in Figure 7, the temperature coefficient of resonance frequency (τ_f) of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ at temperatures ranging from $1125\text{--}1250\text{ }^\circ\text{C}$ with $x = 0.01\text{--}0.2$. τ_f values fluctuate slightly at the whole temperature range. As expected, the synthesized composition persisted unchanged, and hence no noticeable fluctuation of the τ_f value was shown. As we know, τ_f is positively related to the synthesized composition, the second phase, and the material's additive. The measured τ_f values were from -62.9 to $-66\text{ ppm}/^\circ\text{C}$ as the $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ sintered at $1125\text{--}1250\text{ }^\circ\text{C}$. At $1200\text{ }^\circ\text{C}$, a τ_f of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ with 4 h sintering time was measured around $-65.4\text{ ppm}/^\circ\text{C}$. From the above discussion, microwave dielectric performance of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ with various y value sintered at $1200\text{ }^\circ\text{C}$ for 4 h was shown in Table 2 further demonstrated that best performance was found for $y = 0.05$. We also observed that Qf value is sensitive to Ni content, and however, permittivity and τ_f remain slightly fluctuate with varied Ni content. The sintering temperature affects the permittivity and Qf value to some extent. However, τ_f is not sensitive to sintering temperature. Table 3 revealed the comparison of the proposed dielectric with other similar documented dielectric ceramics. Among these three compositions, $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ can be sintered under the lowest thermal budget (12.5% reduction as compared to MgTiO_3) and measured highest Qf value (14.5% boost as compared to $(\text{Mg}_{0.6}\text{Zn}_{0.4})\text{TiO}_3$) with comparable ϵ_r and τ_f value. Overall, $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ was demonstrated with excellent microwave performance and possible to manufacture high-performance substrates utilized in the microwave devices and circuits.

As mentioned previously, a dielectric resonator's thermal stability is defined by the temperature coefficient of the resonance frequency. Dielectric materials systems with near-zero τ_f are crucial to fabricate substrates used in microwave frequency. In order to obtain near-zero τ_f dielectric material, SrTiO_3 [34] possessed ultrahigh positive τ_f ($\epsilon_r \sim 205$, Qf value ~ 4200 and $\tau_f \sim 1700\text{ ppm}/^\circ\text{C}$ under $1350\text{ }^\circ\text{C}$) was chosen to mix with $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ ($\tau_f \sim -66\text{ ppm}/^\circ\text{C}$ under $1200\text{ }^\circ\text{C}$). According to the mixture rules for τ_f , $0.94(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3 - 0.06\text{SrTiO}_3$ was fabricated and analyzed in advance. Figure 8 shows τ_f ranging from $+46.6$ to $68.5\text{ ppm}/^\circ\text{C}$ under $1125\text{--}1225\text{ }^\circ\text{C}$. Thus,

we believe a near-zero τ_f dielectric material with excellent microwave performance will be realized possibly after stoichiometry calculation and experiments in future work.

Figure 7. τ_f value V.S sintering temperature of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ with $y = 0.01\text{--}0.2$.

Table 2. Microwave dielectric performance of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ with various y values sintered at their optimized temperature for 4 h.

y Value	S.T.	Density	ϵ_r	Qf	τ_f
0.01	1200 °C/4 h	4.35	18.7	120,000	−66.5
0.03	1200 °C/4 h	4.36	18.8	140,000	−67.4
0.05	1200 °C/4 h	4.39	19.3	165,000	−65.4
0.07	1200 °C/4 h	4.37	19	155,000	−66
0.1	1200 °C/4 h	4.27	18.9	135,000	−59.7
0.2	1200 °C/4 h	4.25	18.6	90,000	−57.6

Table 3. Comparison of the proposed dielectric with other similar documented dielectric ceramics.

Composition	S.T.	ϵ_r	Qf	τ_f	Ref
MgTiO_3	1350 °C/4 h	17	160,000	−51	[10]
$(\text{Mg}_{0.6}\text{Zn}_{0.4})\text{TiO}_3$	1200 °C/4 h	19.8	144,000	−66	[12]
$(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$	1200 °C/4 h	19.3	165,000	−65.4	This work

Figure 8. Microwave performance of $0.94(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3 - 0.06\text{SrTiO}_3$ mixture.

4. Conclusions

The performance of the $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ at microwave frequency was investigated and analyzed. The dielectric ceramics with an ilmenite-type structure belonging to the trigonal space group R-3 could be founded in all samples. With the substitution of Ni^{2+} for Mg^{2+} and Zn^{2+} , the densification of $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{1-y}\text{Ni}_y\text{TiO}_3$ was significantly enhanced. Compared to documented dielectric ceramics, excellent microwave performance can be demonstrated for $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ sintered at $1200^\circ\text{C}/4\text{h}$ with $\epsilon_r \sim 19.3$, Qf value $\sim 165,000$ (GHz) and $\tau_f \sim -65.4$ ppm/ $^\circ\text{C}$. τ_f of $0.94(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3 - 0.06\text{SrTiO}_3$ shows $\sim +68.5$ ppm/ $^\circ\text{C}$ and, thus, a near-zero mixture could be obtained in future work. The $(\text{Mg}_{0.6}\text{Zn}_{0.4})_{0.95}\text{Ni}_{0.05}\text{TiO}_3$ microwave dielectric material system shows ultrahigh potential for applications in devices and systems of satellite and wireless communications.

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