Phase, microstructure and microwave dielectric properties of $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics

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 $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics was prepared via conventional solid-state mixed-oxide route. The phase, microstructure and microwave dielectric properties of the sintered samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and a vector network analyzer. The microstructure comprised of circular and elongated plate-like grains. The semi quantitative analysis (EDS) of the circular and elongated grains revealed the existence of $Mg_{0.95}Ni_{0.05}T_2O_5$ as a secondary phase along with the parent $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ phase, which was consistent with the XRD findings. In the present study, $\epsilon_r \sim 17.1$, $Q_u f_o \sim 195855 \pm 2550$ GHz and $\tau_f \sim -46$ ppm/K was achieved for the synthesized $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics sintered at 1325 °C for 4 h.

Keywords: phase; microstructures; ceramics

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1. Introduction

Dielectric ceramics have been studied for more than 40 years since they were employed in the microwave devices, such as dielectric resonators, dielectric filters, dielectric antennas etc. The search for new materials has never stopped due to the development in wireless communication technology and devices, such as cellular phones, car telephones, Bluetooth technology, radar technology, global positioning system (GPS), direct TV broadcasting, intelligent transport system (ITS), and wireless local area network (WLAN) [1, 2].

Wireless communication is driven by the unique dielectric properties of ceramic puck that is used as resonator to filter and store microwave signals.

There are three key properties of ceramic dielectrics, which determine their functionality at microwave frequencies. These properties include high relative permittivity (ε_r) for reduction in size of the devices, high unloaded quality factor multiplied by the resonant frequency ($Q_u f_o$) for selectivity, and near zero temperature coefficient of resonant frequency (τ_f) for stability [3].

Low frequency bands have been occupied, i.e. the working frequencies have been increased from 900 MHz to 2.4, 5.2 or even to 5.8 GHz, which would render the interest in materials with high ϵ_r [4].

A number of dielectric materials with complex perovskite structure have been investigated for high frequency applications [5–9]. Among this types of materials, Ba(Zn_{1/3}Ta_{2/3})O₃ and Ba(Mg_{1/3}Ta_{2/3})O₃ showed the highest Q_uf_o values ranging from 100000 GHz to about 200000 GHz [9, 10]. Unfortunately, they contain Ta, which is very costly. Moreover, their high sintering temperature (1600 °C to 1650 °C), long soaking time (~50 h) for obtaining optimum densities also contribute to the high cost of preparation of these materials [9, 10]. Therefore, Ta free materials with low sintering temperature are desirable for the applications at high frequencies.

Magnesium titanate (MgTiO₃) is one of the low cost materials that has attracted much attention due to its good combination of microwave

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properties. MgTiO₃ possess $\varepsilon_r = 17$, Q_uf_o \sim 160000 GHz and a $\tau_{f} \sim -50$ ppm/K [11] but the high negative τ_f precludes its application. The Q_uf_o of MgTiO₃ has been improved by various cationic substitutions at the A and B sites causing local lattice distortion, which was greater than the effect of impurity in MgTiO₃. The partial replacement of Mg by Ni, Co, Mn and Zn at the A-site resulted in an improvement in the $Q_u f_o$ value (180000 to 264000 GHz) of pure MgTiO₃ [12, 13]. Ni based MgTiO₃, i.e. Mg_{0.95}Ni_{0.05}TiO₃ possess $\varepsilon_r \sim 17.2$, $Q_u f_o \sim 180000$ GHz and $\tau_f \sim -45$ ppm/K [13]. In a previous study, partial (5 %) Zr^{4+} substitution for Ti⁴⁺ at B-site of MgTiO₃ has resulted in a high increase (160,000 to 380,000 GHz) in the $Q_u f_o$ value of pure MgTiO₃ with almost unaffected $\tau_{\rm f}$ value, i.e. $\tau_f \sim -50$ ppm/K [14]. Therefore, it is important to improve the Qufo value of Mg_{0.95}Ni_{0.05}TiO₃ by partial (2 %) Zr^{4+} substitutions for Ti⁴⁺ at the B-site.

2. Experimental

Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O₃ ceramics was prepared by mixing high purity raw materials of TiO₂ (\geq 99 %, Sigma Aldrich), NiO (\geq 99.9 %, Sigma Aldrich), MgO (99.95 %, Aldrich), and ZrO₂ (99.5 %, Sigma Aldrich) in stoichiometric ratios and ball milling for 10 h using yttria-stabilized ZrO₂ balls as grinding media and isopropanol as lubricant to make a fine freely moving slurry. The slurry was dried overnight in an oven at ~95 °C followed by sieving to get fine powders. The milled powder was calcined at 1100 °C/5h at a heating/cooling rate of 5 °C/min followed by re-milling to dissociate the agglomerates if any. The finely grounded calcined powder was pressed into 4 to 5 mm high and 14.85 mm in diameter pellets and sintered in a range of temperature from 1275 °C to 1350 °C to get optimum density of the samples. The phase analysis of the calcined and sintered samples was carried out using XRD. The microstructure of an optimum density sample was investigated using scanning electron microscope (SEM).

Microwave dielectric properties were measured using Agilent network analyzer (R3767CH) in the

range of 40 MHz to 8 GHz. The cylindrical samples were placed on a low-loss quartz single crystal at the center of the Au-coated 36 mm high and 40 mm in diameter brass cavity. τ_f values were measured by recording variations in the resonant frequency of TE_{01 δ} resonant mode over the temperature range of 20 °C to 80 °C and calculated using equation 1:

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

where f_1 and f_2 are the initial and final resonant frequencies at 20 °C and 80 °C, respectively.

3. Results and discussion

Fig. 1 shows the experimental (ρ_{exp}) and relative densities (ρ_r) of the sintered samples of Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O₃ ceramics. The density initially increased from 3.55 g/cm³ (89.8 %) to 3.63 g/cm³ (92.1 %) as the sintering temperature was increased from 1275 °C to 1325 °C. After that, a slight decrease in the density was observed at >1325 °C. The reason for the decrease in the sample density with increasing sintering temperature from 1325 °C to 1350 °C has ocurred, probably due to unstable grain growth at high temperatures [15]. The theoretical density of Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O₃ ceramics calculated from the XRD data was 3.95 g/cm³.



Fig. 1. Variation in ρ_{exp} and ρ_{r} of $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics as a function of sintering temperature.

The XRD patterns recorded from calcined and optimally sintered (1325 °C) $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics are shown in Fig. 2. In both the patterns, $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics crystallized in illmnite structure identical to $MgTiO_3$ trigonal (PDF#6-494) was observed as the major phase associated with a secondary $Mg_{0.95}Ni_{0.05}Ti_2O_5$ phase (PDF#35-792). The secondary $Mg_{0.95}Ni_{0.05}Ti_2O_3$ phase that developed as an intermediate phase during the growth of $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ phase was difficult to eliminate from the sample processed via mix oxide route.

The lattice parameters calculated manually for $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics sintered at 1325 °C/4 h were a = b = 0.5077 (5) nm and c = 1.3914 (7) nm. This shows an increase in the lattice parameters for $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics compared with the parameters of $Mg_{0.95}Ni_{0.05}TiO_3$, which are a = 0.5035 nm and c = 1.387 nm [3]. This is due to the larger ionic radius of Zr^{4+} than Ti^{4+} [16].



Fig. 2. XRD patterns recorded from (a) calcined and (b) optimally sintered (1325 °C) Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O₃ ceramics.

Fig. 3 shows the backscattered electron image from a thermally etched and gold coated bulk surface of $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics sintered at 1325 °C/4 h. The microstructure is comprised of slightly brighter and dark grains, indicating the occurrence of two phases. The grain morphology exhibits two different types of grains: circular grains and rod-shaped grains. A similar result was observed by Tseng [17], who suggested that the circular grains might be ilmenite phase and the rod-shaped grains could be $Mg_{0.95}Ni_{0.05}Ti_2O_5$ phase. The semi-quantitative SEM EDS (Table 1) of the grains labeled as "A" and "B" indicated that the composition of these grains was close to $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ and $Mg_{0.95}Ni_{0.05}Ti_2O_5$, respectively. The phase constitute can be confirmed by comparing with the results of XRD analysis of the ceramic sample.



Fig. 3. Backscattered electron image (BEI) of Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O₃ specimen sintered at 1325 °C/4 h.

Fig. 4 depicts the variation in ε_r of Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O₃ ceramics at different sintering temperatures. The ε_r increased with an increase in sintering temperature and reached a maximum at 1325 °C followed by a decrease with a further increase in the sintering temperature. This behavior was consistent with the trend observed in the apparent density (Fig. 1). It is known that ε_r is correlated strongly not only with the ionic polarization and the molar volume, but also with the densities and some second phases in the microwave frequency range. Therefore, the lower ε_r values for the samples sintered at lower (<1325 °C) and higher temperatures (>1325 °C) may be attributed to the lower densities at these temperatures. $Mg_{0.95}Ni_{0.05}TiO_3$ has $\epsilon_r \sim$ 17.2 with 88 % density [18], while Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O₃ has \sim 17.1 with 92 % density. This shows that the

Grain	MgK (wt.%)	NiK (wt.%)	TiK (wt.%)	ZrK (wt.%)	OK (wt.%)	
A	18.94	2.99	33.62	1.35	49.26	
B	12.04	1.30	43.24	0	43.42	

Table 1. EDS data of $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics sintered at 1325 °C/4 h.

reduction in ϵ_r could be attributed to the lower polarizability per unit volume of Zr^{4+} compared to Ti^{4+} [18]. A maximum $\epsilon_r \sim 17.1$ was obtained for $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics sintered at 1325 °C for 4 h. The variation in ϵ_r with sintering temperature is compared in Table 2.



Fig. 4. Variation in ε_r of Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O₃ ceramics as a function of sintering temperature.

The variation in Q_uf_o of Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O₃ ceramics with sintering temperature with error bars is shown in Fig. 5. The trend in the variation of $Q_u f_o$ of Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O₃ ceramics also follows the density. The increase in Qufo value is attributed to an increase in the density. The decrease in $Q_u f_o$ value at temperatures >1325 °C is attributed to a decrease in the density due to non-uniform grain growth. A maximum Qufo value of 195855 ± 2550 GHz was obtained for Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O₃ ceramics sintered at 1325 °C/4 h, which is higher than for Zr free $Mg_{0.95}Ni_{0.05}TiO_3$ (Q_uf_o ~ 188000 GHz) [16]. The Qufo value is affected by both the way of sharing



Fig. 5. Variation in $Q_u f_o$ of $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics as a function of sintering temperature.

the oxygen octahedral and the packing fraction of ions in the unit cell volume. In general, the formation of secondary MgTi₂O₅ phase reduces the Qufo value of MgTiO₃ ceramics significantly, although pure MgTiO₃ exhibits a high Qufo value due to the isolation of the TiO_6 octahedron by cation vacancies and the depolarization of the MgO₆ octahedron. Additionally, the slight increase in lattice constants, which can reduce ionic polarizability and ε_r , is identified as the dominant reason for the high Qufo value in MgTiO3. Thus, some authors carried out studies on M2+ (where ionic partial substitu-Μ Ni or Zn) = tion in the A-site in MgTiO₃ to form $(Mg_{0.95}M_{0.05})TiO_3$ [12, 13], which revealed a greater improvement in the Q_uf_o value due to the local lattice distortion and the size effect of cations higher than the impurity effect in MgTiO₃. The secondary Mg_{0.95}Ni_{0.05}Ti₂O₅ phase has been reported to have lower $Q_u f_o \sim 50000$ GHz [19], much lower than that of the parent Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O₃ phase. This suggests that the formation of secondary Mg_{0.95}Ni_{0.05}Ti₂O₅ phase has densities

and

S.T. (°C)	$\begin{array}{c} \rho_{exp} \\ (g/cm^3) \end{array}$	ε _r	Q _u f _o (GHz)	τ _f (ppm/K)	f _o (GHz)	Diameter (mm)
1275/4 h	3.52	16.1	165540 ± 2040	-43.2	6.93819334 ± 0.035	12.56
1300/4 h	3.59	16.5	186160 ± 2260	-45.5	6.94519334 ± 0.043	12.50
1325/4 h	3.64	17.1	195855 ± 2550	-46.2	6.898695334 ± 0.051	12.42
1350/4 h	3.61	16.9	192655 ± 2160	-45.8	6.928695334 ± 0.032	12.45

Table 2. Preparation conditions, experimental of $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics.

lowered the $Q_u f_o$ of $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$. Therefore, Zr⁴⁺ substitution for Ti⁴⁺ has resulted in an increase of the Qufo value of $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$. The temperature coefficient of resonant frequency (τ_f) is known to be related to the composition and secondary phase formation. No significant change has been observed in the value of τ_f with sintering temperature and the secondary Mg_{0.95}Ni_{0.05}Ti₂O₅ phase formation as it had nearly the same τ_f ~ -48 ppm/K [19]. The $\tau_{\rm f} \sim -46$ ppm/K was obtained for Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O₃ sintered at 1325 °C for 4 h. For practical applications, tuning of τ_f to 0 ppm/K is necessary. Therefore, further work is in progress to tune the τ_f to zero.

4. Conclusions

Zr substitution for Ti in $M_{0.95}Ni_{0.05}TiO_3$ ceramics enhanced the $Q_u f_o$ in spite of the formation of $Mg_{0.95}Ni_{0.05}Ti_2O_5$ phase that developed as an intermediate phase. $Mg_{0.95}Ni_{0.05}Ti_2O_5$ phase by itself degraded the $Q_u f_o$ value drastically. In the present study, $\varepsilon_r \sim 17.1$, $Q_u f_o \sim 195855 \pm 2550$ GHz and $\tau_f \sim -46$ ppm/K was achieved for the synthesized ceramics sintered at 1325 °C for 4 h.

Acknowledgements

The authors acknowledge the financial support of the Directorate of Science and Technology (DOST) under its developmental Scheme "Promotion and Support of R&D in Public & Private Sector, Phase 1 in Khyber Pakhtunhwa (R&D)" Funded Project 2011 – 2012 Peshawar, Pakistan.

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Received 2014-06-04 Accepted 2014-11-28

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