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Research Article

Phase microstructure evaluation and microwave dielectric properties of (1–x)$Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$–x$Ca_{0.6}La_{0.8/3}TiO_3$ ceramics

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Abstract: All the compositions in the $(1-x)Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3-xCa_{0.6}La_{0.8/3}TiO_3$ ($0 \leqslant x \leqslant 0.2$) series were fabricated using solid state sintering route. $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ possessed excellent microwave dielectric properties with $\varepsilon_r \approx 17.1$, $Q_u f_0 \approx 195855$ GHz, and $\tau_f \approx -46$ ppm/℃. τ_f was tuned through zero by mixing with $Ca_{0.6}La_{0.8/3}TiO_3$. In the present study, $\tau_f \approx -2$ ppm/℃ with $\varepsilon_r \approx 23.9$ and high $Q_u f_0 \approx 115870$ GHz was achieved for $x = 0.15$, i.e., for a mixture of 85% $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ and 15% $Ca_{0.6}La_{0.8/3}TiO_3$.

Keywords: phase; microstructure; density; ilmenite structure

1 Introduction

The development of microwave communication technology such as cellular phone, car telephone, bluetooth technology, radar technology, global positioning system (GPS), direct TV broadcasting, intelligent transport system (ITS), and wireless local area network (WLAN) has been promoted via microwave dielectric ceramics [1,2]. The shift of operating frequency band from 900 MHz to 2.4, 4, 5, 5.2 GHz, or even to 5.8 GHz renders high ε_r materials of less interest [3,4].

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Dielectric materials with complex perovskite structure have been extensively investigated for high frequency applications [4–7]. $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$ showed the highest $Q_u f_0$ values (Q_u is the unloaded quality factor and f_0 is the resonant frequency) ranging from 100000 to about 200000 GHz among these materials [8,9]. However, these contain Ta which is very costly. Moreover, these require high sintering temperature (1600 to 1650 ℃) and long soaking time (~50 h) for achieving optimum densities that also contribute to the high cost of preparation of these materials [8,9]. Therefore, Ta free materials with low sintering temperature are urgently desired for high frequency applications.

$MgTiO_3$ has attracted much attention due to its good combination of microwave properties and low cost. $MgTiO_3$ crystallizes in ilmenite structure [10]. ε_r = 17, $Q_u f_0$ ≈ 160000 GHz, and τ_f ≈ –50 ppm/℃ have been reported for $MgTiO_3$ [11,12]. The high negative τ_f precludes its application. Various cationic substitutions have improved the $Q_u f_0$ of $MgTiO_3$. Sn substitution for Ti enhanced $Q_u f_0$ of pure $MgTiO_3$ [13]. Similarly, Zr doped for Ti in $MgTiO_3$, i.e., $MgZr_{0.05}Ti_{0.95}O_3$ ceramic was reported to have ε_r ≈18.1, very high $Q_u f_0$ = 380000 GHz at 7 GHz, and τ_f = –50 ppm/℃ [14]. Addition of $CaTiO_3$ tuned the τ_f of $MgTiO_3$ through zero, and ε_r ≈ 20, $Q_u f_0$ ≈ 56000 GHz, and τ_f ≈ 0 ppm/℃ were achieved for $0.95MgTiO_3$–$0.05CaTiO_3$ [15]. Similarly, the addition of small amount of $SrTiO_3$ tuned the τ_f of $MgTiO_3$ through zero at the cost of a decrease in $Q_u f_0$ value, and ε_r ≈ 17.9, $Q_u f_0$ ≈ 30400 GHz, and τ_f ≈ 5 ppm/℃ were achieved for $0.96MgTiO_3$–$0.036SrTiO_3$ ceramic [16]. However, partial replacement of Mg by Ni, Co, Mn, and Zn at the A site resulted in improvement in the $Q_u f_0$ value (180000–264000 GHz) of pure $MgTiO_3$ without affecting the ε_r and τ_f value [17–19]. ε_r ≈ 17.2, $Q_u f_0$ ≈ 180000 GHz, and τ_f ≈ –45 ppm/℃ have been achieved for $Mg_{0.95}Ni_{0.05}TiO_3$ ceramic [19,20]. In our previous study, ε_r ≈ 17, $Q_u f_0$ ≈ 195000 GHz, and τ_f ≈ –46 ppm/℃ were obtained for $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ [21]. However, the high negative value of τ_f made $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ impractical for applications. Addition of $SrTiO_3$ to $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ resulted in tuning of τ_f through zero, and Manan *et al.* [22] reported ε_r ≈ 20, $Q_u f_0$ ≈ 85000 GHz, and τ_f ≈ 3 ppm/℃ for $0.04SrTiO_3$–$0.96Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ system. $CaTiO_3$ possessed ε_r ≈ 170, $Q_u f_0$ ≈ 3600 GHz at 7 GHz, and τ_f ≈ +800 ppm/℃ [23]. The addition of $CaTiO_3$ based ceramics to other materials has tuned the τ_f to 0 ppm/℃ [24,25]. After partial doping La in Ca site, $Ca_{0.6}La_{0.8/3}TiO_3$ ceramic having a pseudo-cubic perovskite structure has been reported to possess excellent dielectric ε_r ≈ 109, $Q_u f_0$ ≈ 17000 GHz, and τ_f ≈ 212 ppm/℃ [26]. Similarly the addition of $Ca_{0.6}La_{0.8/3}TiO_3$ to other $MgTiO_3$ based ceramics tuned their τ_f values through 0 ppm/℃ [27,28]. In order to tune the τ_f of $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ through zero, it is required to mix $Ca_{0.6}La_{0.8/3}TiO_3$ with $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ in appropriate ratio. Since $Ca_{0.6}La_{0.8/3}TiO_3$ ceramic has higher $Q_u f_0$ value than $SrTiO_3$, $Ca_{0.6}La_{0.8/3}TiO_3$ addition will result in much higher $Q_u f_0$ for the composite ceramics than $SrTiO_3$ added composite ceramics in our previous study [22].

In this paper, $Ca_{0.6}La_{0.8/3}TiO_3$ was added to $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ to get temperature stable ceramics.

2 Experimental procedure

$Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ and $Ca_{0.6}La_{0.8/3}TiO_3$ ceramics were separately prepared via solid state route. High purity raw materials of TiO_2, NiO, MgO, and ZrO, and $CaCO_3$, La_2O_3, and TiO_2 were weighted in stoichiometry ratios and ball milled for 10 h using Y-stabilized ZrO_2 balls as grinding media and isopropanol as lubricant to make slurries. The slurries were dried over night in an oven at ~95 ℃. The dried powders were sieved and calcined at 1100 ℃ for 5 h at heating/cooling rate of 5 ℃/min. The calcined powders were re-milled to dissociate the agglomerates if any. $Ca_{0.6}La_{0.8/3}TiO_3$ was added according to the given compositions and milled again for 3 h. The finely grounded $Ca_{0.6}La_{0.8/3}TiO_3$ added powders were pressed into pellets of 14.85 mm in diameter and 6–8 mm in thickness and sintered at 1275–1350 ℃ to get optimum dense samples. The calcined powders of $Ca_{0.6}La_{0.8/3}TiO_3$ ceramic were sintered at 1400–1450 ℃. The crystalline phases of sintered samples were examined using X-ray diffraction (XRD, Panalytical Expert PRO). The apparent densities of the sintered pellets were measured using Archimedes method. The sintered samples were finely polished and thermally etched at temperatures 10% less than their corresponding sintering temperatures and gold coated for microstructural characterization. A JEOL 6400 SEM operating at 20 kV was used for microstructural examination.

Microwave dielectric properties were measured using Agilent network analyzer (R3767CH) under cavity method. The sintered pellets were placed on low loss quartz single crystal at the center of Au-coated brass cavity of 36 mm in height and 40 mm in diameter. The τ_f values were measured by noting the variation in resonant frequency of $TE_{01\delta}$ resonant mode over the temperature range of 20–80 ℃.

3 Results and discussion

The variation in experimental density of $(1-x)Mg_{0.95}$-

$Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$–$xCa_{0.6}La_{0.8/3}TiO_3$ (x = 0, 0.05, 0.1, 0.15, and 0.2) ceramics as a function of sintering temperature is shown in Fig. 1. The density of all samples increased as the sintering temperature increased to 1325 ℃ and thereafter decreased with further increase in sintering temperature to 1350 ℃. The first increase in density of the ceramics was due to elimination of pores under the mechanism of grain growth. Generally, at higher temperatures, abnormal grain growth occurs that causes inhomogeneous microstructure leading to porosity. Therefore, the final decrease in density above 1325 ℃ could be attributed to the abnormal grain growth. With the addition of $Ca_{0.6}La_{0.8/3}TiO_3$ ceramic, the density of sintered ceramics increased. The increase in density was expected since the theoretical density of $Ca_{0.6}La_{0.8/3}TiO_3$ is ~4.60 g/cm^3 [29] which is greater than the parent $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramic.

Figure 2 shows the XRD patterns recorded for

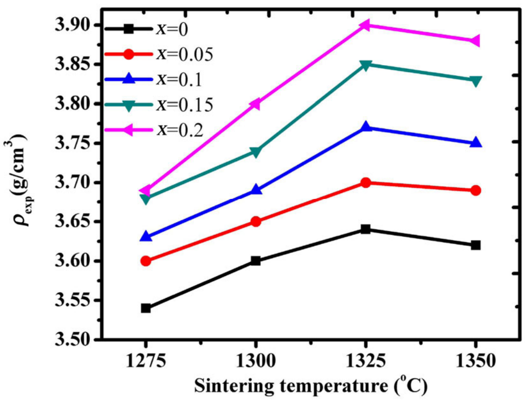

Fig. 1 Variation in experimental density (ρ_{exp}) of $(1-x)Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$–$xCa_{0.6}La_{0.8/3}TiO_3$ ($0 \leqslant x \leqslant 0.2$) ceramics with sintering temperature.

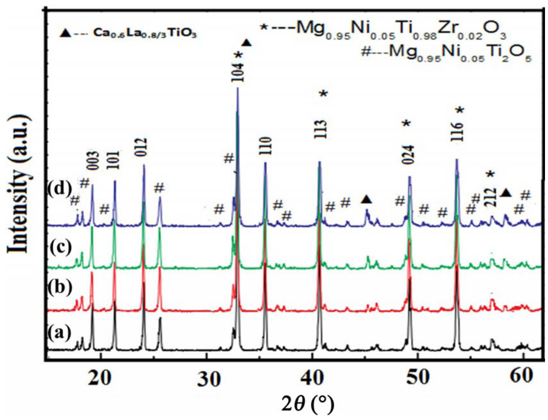

Fig. 2 XRD patterns of $(1-x)Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}$-$O_3$–$xCa_{0.6}La_{0.8/3}TiO_3$ ceramics sintered at 1325 ℃ for 4 h: (a) x = 0, (b) x = 0.05, (c) x = 0.1, (d) x = 0.15.

$Ca_{0.6}La_{0.8/3}TiO_3$ added $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics sintered at 1325 ℃. The inter-plane spacings and peak intensities of major peaks in the XRD patterns of all the compositions matched PDF#6-494 for $MgTiO_3$ with slight shifting of the peak positions towards larger 2θ angles due to incorporation of smaller Ni^{2+} (0.69 Å) for larger Mg^{2+} (0.72 Å) [30]. $MgTiO_3$ crystallized in rhombohedral crystal structure with unit cell parameters of $a = b$ = 5.054 Å and c = 13.898 Å [31]. A secondary $Mg_{0.95}Ni_{0.05}Ti_2O_5$ phase that crystallized in orthorhombic crystal structure with lattice parameters of a = 9.729 Å, b = 3.744 Å, and c = 99.25 Å [32] was also detected in all the XRD. $Ca_{0.6}La_{0.8/3}TiO_3$ was also identified as a minor phase for patterns of all compositions with $x > 0$. $Ca_{0.6}La_{0.8/3}TiO_3$ crystallized in pseudo-cubic structure with lattice parameters of $a = b = c$ = 3.872 Å [33]. The intensity of the peaks corresponding to $Ca_{0.6}La_{0.8/3}TiO_3$ phase increased with increase in the x value to 0.2.

Figure 3 shows the backscattered electron images from thermally etched and gold coated bulk surface of $Ca_{0.6}La_{0.8/3}TiO_3$ added $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics sintered at 1325 ℃ for 4 h. The microstructure of the composition with x = 0 comprised of elongated and polygonal grains. A similar result was observed by Tseng and Hsu [13], who suggested that the polygonal grains are of ilmenite phase (Zr doped $Mg_{0.95}Ni_{0.05}TiO_3$) and the rod-shaped grains are of $Mg_{0.95}Ni_{0.05}Ti_2O_5$ phase. The polygonal type grains are labeled as "A" and elongated rod-shaped type grains are labeled as "B". The semi-quantitative SEM EDS (Table 1) of the grains labeled as "A" indicated that the composition of

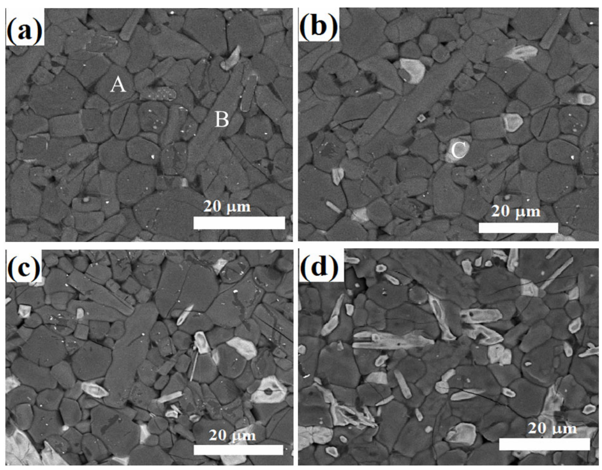

Fig. 3 Backscattered electron images of $(1-x)Mg_{0.95}Ni_{0.05}$-$Ti_{0.98}Zr_{0.02}O_3$–$xCa_{0.6}La_{0.8/3}TiO_3$ ceramics: (a) x = 0, (b) x = 0.05, (c) x = 0.1, (d) x = 0.15.

these grains is closed to $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ (ilmenite phase) and that of "B" indicated that the composition of these grains is closed to $Mg_{0.95}Ni_{0.05}Ti_2O_5$ phase consistent with the XRD findings (Fig. 2).

Similarly, the microstructures of the compositions with $x \geqslant 0.05$ comprised of elongated polygonal grains and some bright grains. The semi-quantitative SEM EDS (Table 1) of the bright grain labeled as "C" indicated that the composition of this type of grains was closed to $Ca_{0.6}La_{0.8/3}TiO_3$ phase. The concentration of the grains from $Ca_{0.6}La_{0.8/3}TiO_3$ phase increases with increase in x value. It has been reported that a material consisting of atoms with higher atomic weight deflects more electron beam than that with atoms having lower atomic weight, resulting in brightness of the grains using backscattered electron technique and detectors. Since $Ca_{0.6}La_{0.8/3}TiO_3$ contains La and Ca with higher atomic weight than Mg and Ni in $Mg_{0.95}Ni_{0.05}Ti_{0.9}8Zr_{0.02}O_3$, the grains of $Ca_{0.6}La_{0.8/3}TiO_3$ ceramic are brighter [28].

4 Microwave dielectric properties

Figure 4 shows ε_r values of $(1-x)Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$–$xCa_{0.6}La_{0.8/3}TiO_3$ ceramics as a function of $Ca_{0.6}La_{0.8/3}TiO_3$ content. The variation of dielectric constant (ε_r) was mainly consistent with density shown in Fig. 1. $\varepsilon_r \approx 17.1$ was obtained for $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramic sintered at 1325 ℃ and was also reported in our previous studies [20,21]. For $Ca_{0.6}La_{0.8/3}TiO_3$ ceramic, $\varepsilon_r \approx 106$ was obtained in the present study. For optimally dense ceramics in the present study, a nearly linear increase in ε_r is observed with increase in $Ca_{0.6}La_{0.8/3}TiO_3$ content. The ε_r increased from 17.1 to 26.3 with an increase in x value from 0 to 0.20. The reason for the increase in ε_r is due to the higher $\varepsilon_r \approx 106$ of $Ca_{0.6}La_{0.8/3}TiO_3$ than that of $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramic.

The variation in Q_uf_0 values of $(1-x)Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$–$xCa_{0.6}La_{0.8/3}TiO_3$ ceramic system as a function of $Ca_{0.6}La_{0.8/3}TiO_3$ content is shown in Fig. 5. There are basically two main loss mechanisms that contribute to dielectric loss at microwave frequencies. The intrinsic loss which comes from crystal structure is generally regarded as the lower limit of dielectric loss. Pores, second phases, impurities, grain morphologies, and lattice defects contribute to extrinsic loss. The extrinsic loss plays a significant role in microwave dielectric loss. The Q_uf_0 value decreased from 195855 to 95403 GHz with increase in $Ca_{0.6}La_{0.8./3}TiO_3$ content from 0 to 0.2. The decrease in Q_uf_0 was expected since the Q_uf_0 obtained in the present study for $Ca_{0.6}La_{0.8/3}TiO_3$ (~15000 GHz) is much lower than $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramic ($Q_uf_0 \approx$ 195800 GHz).

Table 1 EDS data of $Ca_{0.6}La_{0.8/3}TiO_3$ added $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramics sintered at 1325 ℃ for 4 h

Grain	Mg (wt%)	Ni (wt%)	Ca (wt%)	La (wt%)	Ti (wt%)	Zr (wt%)	O (wt%)
A	18.94	2.99	0	0	33.62	1.35	49.26
B	12.04	1.30	0	0	43.24	0	43.42
C	1.1	0	10.30	47.09	20.73	0	20.72

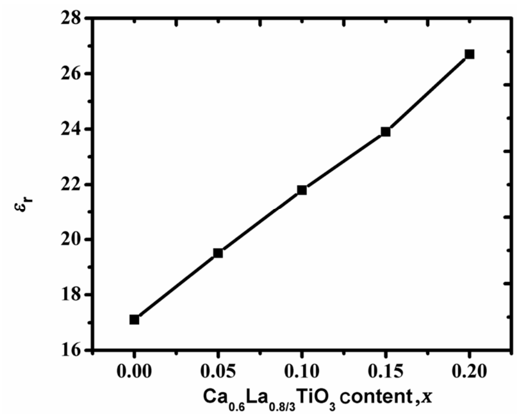

Fig. 4 ε_r of $(1-x)Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$–$xCa_{0.6}La_{0.8/3}TiO_3$ ($0 \leqslant x \leqslant 0.2$) ceramics as a function of x value.

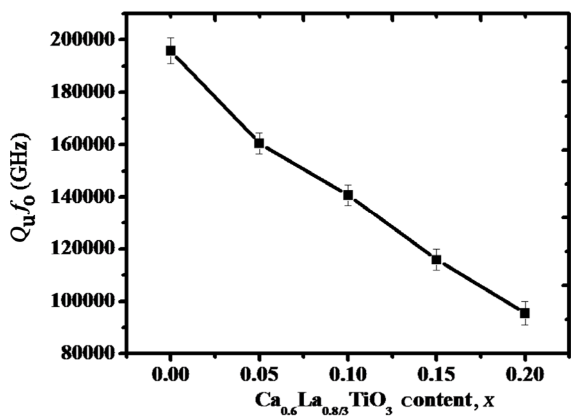

Fig. 5 Q_uf_0 of $(1-x)Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$–$xCa_{0.6}La_{0.8/3}TiO_3$ ($0 \leqslant x \leqslant 0.2$) ceramics as a function of x value.

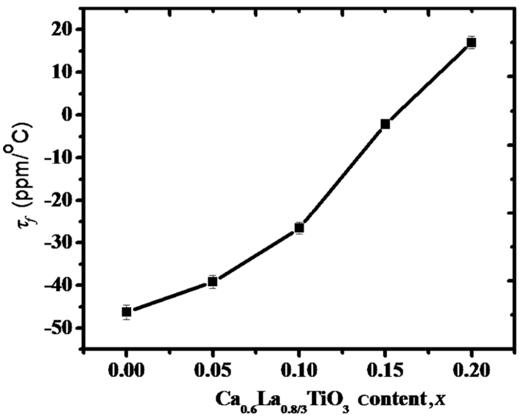

Fig. 6 τ_f of $(1-x)Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3–xCa_{0.6}La_{0.8/3}TiO_3$ ($0 \leqslant x \leqslant 0.2$) ceramics as a function of x value.

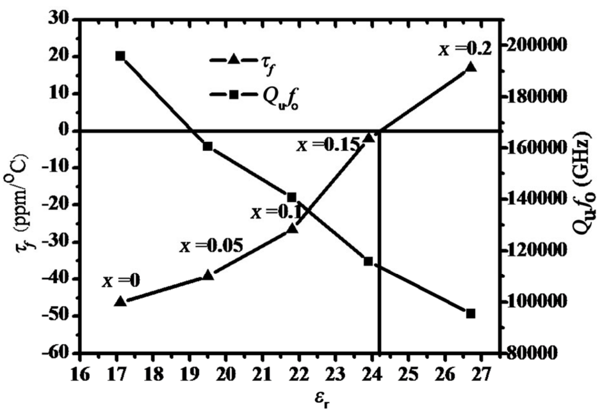

Fig. 7 Relationship of ε_r and $Q_u f_0$ and τ_f of $(1-x)Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3–xCa_{0.6}La_{0.8/3}TiO_3$ ($0 \leqslant x \leqslant 0.2$) ceramics as a function of ε_r.

Table 2 Preparation conditions, experimental densities, and microwave dielectric properties of $(1-x)Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3–xCa_{0.6}La_{0.8/3}TiO_3$ ceramics

x	ST (℃)	ρ_{exp} (g/cm³)	f_0 (GHz)	Diameter (mm)	Thickness (mm)	ε_r observed	$Q_u f_0$ (GHz)	τ_f (ppm/℃)
0	1325	3.64	6.98	12.80	7.80	17.1±1.2	195855±5000	–46.3±1.6
0.05	1325	3.70	7.15	12.7	6.80	19.5±1.1	160505±4000	–39.2±1.5
0.1	1325	3.77	6.83	12.65	6.70	21.8±1.4	140668±4020	–26.6±1.4
0.15	1325	3.85	6.46	12.6	6.85	23.9±1.3	115870±4000	–2.1±1.1
0.2	1325	3.90	6.24	12.7	6.56	26.7±1.5	95430±4503	17±1.5
1	1450	4.47	3.45	12.8	5.56	106±3.5	15450±600	205±4.5

The secondary $Mg_{0.95}Ni_{0.05}Ti_2O_5$ phase has lower ($Q_u f_0 \approx 50000$ GHz) [27] than $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramic. Therefore, some other factors such as $Mg_{0.95}Ni_{0.05}Ti_2O_5$ phase and pores also contribute to the decrease in $Q_u f_0$ value along with $Ca_{0.6}La_{0.8/3}TiO_3$ phase in the present study.

The third important characteristic is the temperature coefficient of resonant frequency (τ_f) which is mainly related to the additive, composition, and second phase of a material. In the present study, $\tau_f \approx 205$ ppm/℃ was obtained for $Ca_{0.6}La_{0.8/3}TiO_3$. Thus by increasing the amount of $Ca_{0.6}La_{0.8/3}TiO_3$, the τ_f of $(1-x)Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3–xCa_{0.6}La_{0.8/3}TiO_3$ ceramics was made more and more positive and a near zero $\tau_f \approx -2$ ppm/℃ was achieved for the composition with x = 0.15 sintered at 1325 ℃ for 4 h as shown in Fig. 6. However, from the nearly linear relationship of the properties with $Ca_{0.6}La_{0.8/3}TiO_3$ content from the analysis of the data, it could be seen that $\tau_f \approx 0$ ppm/℃, $Q_u f_0 \approx 114000$ GHz, and $\varepsilon_r \approx 24.3$ could correspond to x = 0.16 as shown in Fig. 7. The material is a suitable candidate for applications at high frequencies.

The microwave dielectric properties are also summarized in Table 2.

5 Conclusions

Both the ceramics were separately prepared and the microwave dielectric properties of $(1-x)Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3–xCa_{0.6}La_{0.8/3}TiO_3$ ($0 \leqslant x \leqslant 0.2$) ceramics were investigated in order to get temperature stable low loss ceramics. $\varepsilon_r \approx 106.9$, $Q_u f_0 \approx 15450$ GHz, and $\tau_f \approx 205$ ppm/℃ were obtained for $Ca_{0.6}La_{0.8/3}TiO_3$ ceramic. The addition of $Ca_{0.6}La_{0.8/3}TiO_3$ ceramic tuned the τ_f value of $Mg_{0.95}Ni_{0.05}Ti_{0.98}Zr_{0.02}O_3$ ceramic through zero, and $\varepsilon_r \approx 23.9$, $Q_u f_0 \approx 115870$ GHz, and $\tau_f \approx -2.1$ ppm/℃ were achieved for the composition with x = 0.15 in the present study. The material is a suitable candidate for high frequency applications.

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