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Influence of Co substitution on the phase, microstructure, and microwave dielectric properties of $MgSiO_3$ ceramics

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Abstract

Solid-state sintering method was used for the synthesis of $Mg_{1-x}Co_xSiO_3$ (x = 0–0.25) ceramics. Phase, microstructure and microwave dielectric properties of the ceramics were investigated. With increase in Co^{2+} content, the increase was observed in the lattice parameters. The Q_uf_o value of $MgSiO_3$ was enhanced from 103,453 to 145,846 GHz with increasing the value of x content from 0 to 0.15. The Co^{2+} substitution also led to an obvious decrease in the sintering temperature by ~ 100 °C. Clino-enstatite phase formed for the composition with x = 0 while Proto-enstatite formed as the major along with minor clino-enstatite phase for the compositions with x > 0. Good dielectric properties at microwave frequencies i.e. $\varepsilon_r \sim 8.11$, Q_uf_o ~ 145,846 GHz and $\tau_f \sim -12$ ppm/°C were obtained for the composition with x = 0.15 sintered at 1350 °C for 9 h. This is suggested to be a very favorable dielectric material for millimeterwave applications.

1 Introduction

The advancement in the microwave telecommunication industry and technology has led to the rapid growth of information systems via wireless communication from the last few decades. The massive increase in the number of users of mobile phone is the common sign of its widespread applications [1–3]. The development in millimeterwave telecommunication is because of the frequent investigation of low dielectric constant materials. Low dielectric constant is needed to reduce the propagation time of the signal, a high Q_uf_o is needed for the stability, and a near zero τ_f is needed for the selectivity of resonant frequency besides the temperature changes.

Normally silicates have been reported to have low dielectric constant ($\varepsilon_r < 10$) because of their structural unit that consist of SiO_4 tetrahedrons with strong covalent bond characteristics. In recent years, many kinds of ceramic materials with SiO_4 tetrahedrons such as Mg_2SiO_4, Zn_2SiO_4 compounds have been reported as excellent materials for millimeter wave applications [4, 5]. Mg_2SiO_4 based ceramics has been widely investigated because of its high reported Q_uf_o value ~ 240,000 GHz, and low ε_r value ~ 6.80 [5–7]. However, they have high negative $\tau_f \sim -70$ ppm/°C which precluded its practical applications.

In 2008 Myung-Eun Song et al. reported that $MgSiO_3$ ceramic has outstanding microwave dielectric properties i.e. $\varepsilon_r \sim 6.5$, Q_uf_o ~ 120,000 GHz and $\tau_f \sim -19$ ppm/°C [2]. However, $MgSiO_3$ has low sinterability characteristics and its relatively high τ_f precluded its practical application. The sinterability of $MgSiO_3$ has been improved by Ni^{2+} substitution, and the τ_f of Ni based $MgSiO_3$ ceramics was tuned for its millimeter-wave range application [8]. An ionic substitution at A- and B-site is needed to improve the

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microwave properties and sinterability at commercial and scientific level. Previously, we reported excellent microwave dielectric properties of $MgSiO_3$ by partial substitution of Ni^{2+} and Zn^{2+} for Mg^{2+} [8, 9]. The increase in Q_uf_o value and a decrease in the sintering temperature were observed by partial substitution of Co^{2+} for Mg^{2+} in other different ceramics. For example partial substitution of Co^{2+} for Mg^{2+} in $MgTiO_3$ (i.e., $(Mg_{0.95}Co_{0.05})$ TiO_3)) enhanced the Q_uf_o value from 160,000 to 230,000 GHz [10, 11]. Similarly, in another study, partial Co^{2+} substitution enhanced the Q_uf_o value of Mg_2TiO_4 ceramic from ~ 150,000 to ~ 286,000 GHz [12–14]. In other studies Co substitution in Mg_2TiO_4 has improved the Q_uf_o value more in comparison to Ni and Zn substitution [12, 15, 16].

To the best of our knowledge, Co substitution for Mg in $MgSiO_3$ has not been studied. Therefore, the aim of the present study was to investigate the influence of Co^{2+} substitution for Mg on the phase microstructure and millimeter wave dielectric properties of $MgSiO_3$ ceramic.

1.1 Sample preparation

$Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) ceramics were prepared via solid-state sintering route using high purity raw materials of MgO (≥ 99.90, Aladdin China) CoO (≥ 99.90, Aladdin China) and SiO_2 (≥ 99.90, Aladdin China). The raw materials were weighted in desired stoichiometric ratios followed by ball milling for 24 h in ethanol using Y-toughened ZrO_2 balls as the grinding media to make freely flowing slurries. The slurries were dried in an oven at 100 °C. The dried mixed powders were calcined at 1300 °C for 5 h. The calcined powders were remilled for 24 h to dissociate the agglomerates followed by passing the milled dried calcined powders by sieve to get fine powders. 5 wt % PVA was added to the grounded calcined powders of each composition as binder and then thoroughly mixed. The powders were then pressed into 5–6 mm thick and 12 mm in diameter pellets at 220 MPa in a steel dia. Vacuum rotary was used to eliminate the pores and to suck the air from the pellets. The green body pellets were heated at 600 °C for 2 h to expel the binder and then sintered in a range of temperature from 1325 to 1475 °C for 9 h. The optimum dense pellets were cut into halves and then finely polished followed by thermal etching of the polished surfaces of the samples at temperatures that were about 10% less than their sintering temperatures at a heating/cooling rate of 3 °C/min for 30 min. The thermally etched surfaces were gold coated for avoiding the charging effect under the electron beam in SEM. The microstructure of the optimally dense samples was examined using scanning electron microscope (Quanta 450 FEG, FEI, USA). The elemental compositions of the samples were made via energy dispersive spectroscopy (EDS) detector attached to SEM. The phase analysis of the calcined and sintered samples was carried out using X-ray diffraction (Panalytical Expert PRO).

Microwave dielectric properties were measured via Hakki–Coleman dielectric resonator method using Vector Network Analyzer [Agilent-8722ET (50 MHz to 40 GHz)] machine. The temperature coefficient of resonance frequency (τ_f) for each composition was calculated by noting the variation in the resonant frequency of TE_{011} resonant mode over the temperature range of 25 °C to 80 °C using Eq. (1).

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

where f_1 and f_2 are the initial and final resonant frequencies at T_1 (25 °C) and T_2 (85 °C) respectively.

2 Results and discussion

Figure 1a–e illustrate the X-ray diffraction (XRD) patterns of the optimum sintered crushed pellets of $Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) ceramics. For the composition with x = 0, the XRD pattern could be well indexed according to the PDF#035–0610 for $MgSiO_3$ (clinoenstatite system) crystalize in monoclinic structure with space group $P2_1/c$. By increasing the value of x from 0 to 0.25, protoenstatite (orthorhombic) formed as the major phase along with some minor clinoenstatite phase (monoclinic) [17, 18]. It has also been reported that protoenstatite occur at temperature below 1350 °C and transform to clinoenstatite above 1350 °C [2] which can be well explained from the XRD data of the composition with x = 0.15 at multiple temperatures as shown in

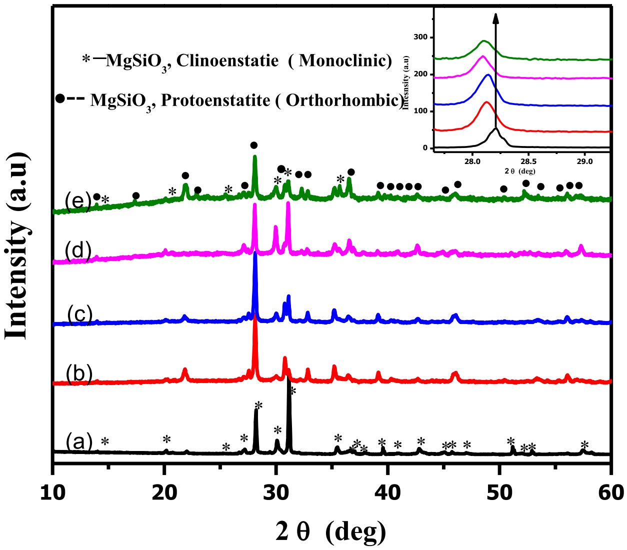

Fig. 1 XRD patterns of sintered crushed samples of $Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) ceramics (**a**) x = 0, sintered at 1450 °C for 9 h, (**b**) x = 0.1, (**c**) x = 0.15, (**d**) x = 0.2, and (**e**) x = 0.25 sintered at 1350 °C for 9 h

Fig. 2. Shifting of peaks position towards larger inter-planer (d) values or lower 2θ values was also observed which could be the result of the enlargement of unit cell by incorporation of larger Co (0.74 Å, CN-6) ion for smaller Mg (0.72 Å, CN-6) ion [19].

Table 1 represents, the lattice parameters and unit cell volume of $Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) ceramics calculated from the XRD data. As the x value increased from 0 to 0.25, the lattice parameters were increased. The increase in the lattice parameters could be the result of the substitution of larger Co^{2+} for smaller Mg^{2+} [19]. The increase in the lattices parameters resulted in an increase in unite cell volume (V_{unit}).

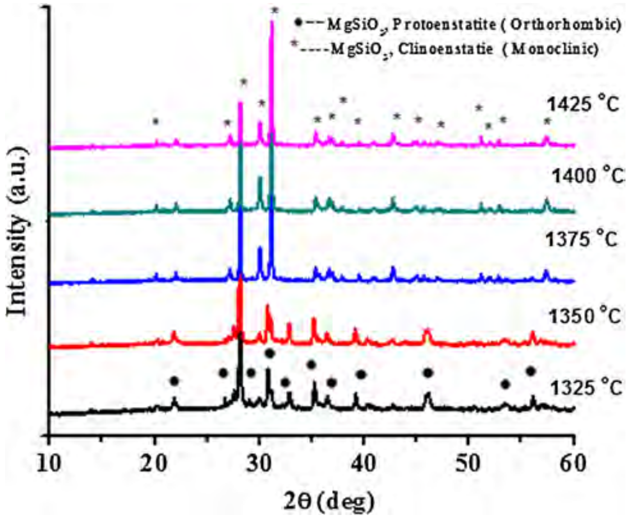

Fig. 2 XRD patterns of sintered crushed samples of $Mg_{0.85}Co_{0.15}SiO_3$ ceramics (**a**) 1325 °C for 9 h, (**b**) 1350 °C, (**c**) 1375 °C, (**d**) 1400 °C, and (**e**) 1425 °C for 9 h

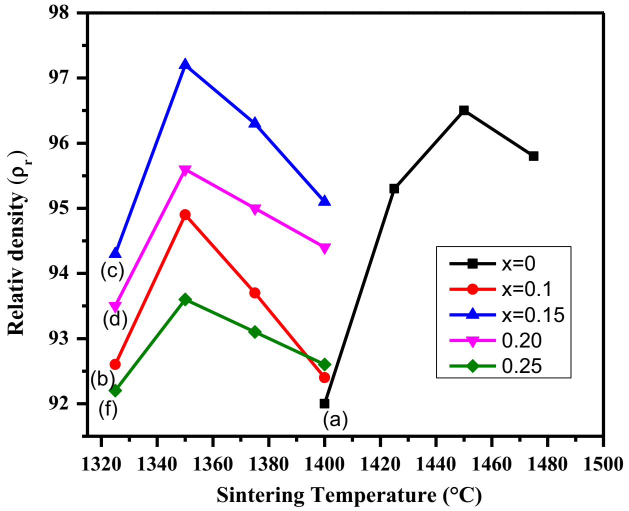

Fig. 3 Variation in the relative densities (ρ_r) of $Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) as a function of sintering temperature for 9 h

Figure 3 illustrate the variation of the relative density (ρ_r) of $Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) ceramics with sintering temperature. With increasing the sintering temperature from 1400 to 1450 °C, the relative density (ρ_r) of the composition with x = 0, first increased from 91.5 to 96.5%, while upon further increase in the sintering temperature up to 1475 °C, it slightly decreased. Therefore, it can be summed up that 1450 °C is the optimum sintering temperature to get the highest relative density (ρ_r) for composition with x = 0. The first increase in the density could be the result of the uniform grain growth illuminating the pores while the decrease in density above 1450 °C could be the result of the abnormal grain growth leading to pores formation. For the compositions with x > 0, first increase in the relative densities were observed with increasing the sintering temperature from 1325 to 1350 °C, however further increase in sintering temperature to 1400 °C showed a decrease in the relative density (ρ_r). This showed that for all Co^{2+} substituted compositions the maximum densities were obtained at sintering temperature of 1350 °C. Furthermore, the sintering temperature of $MgSiO_3$ was lowered by about 100 °C via Co^{2+} substitution which may be due to the low refractory nature of CoO then MgO. Maximum relative density greater than 97% was gained for the composition with x = 0.15, However, further increase in x value (i.e. x > 0.15) caused a decrease in the relative density.

Figure 4 shows the scanning electron microscope images of optimally sintered $Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) ceramics. Figure 4a shows the dense microstructure of the composition with x = 0 sintered at 1450 °C for 9 h. The EDS analysis of the grain "A" shows 1:1 atomic ratio of Mg and Si elements that indicates that the such grain belongs to $MgSiO_3$ phase which is in good agreement with XRD findings.

Table 1 Structural data of $Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) ceramics

(x)	ST (°C)	α (Å)	b (Å)	c (Å)	β	V_{unit} (Å^3)
0	1450	9.38949	8.80975	5.18146	103.9444	416.00
0.1	1350	9.3923	8.8102	5.1822	103.9473	416.04
0.15	1350	9.3929	8.8109	5.1824	103.9561	416.24
0.20	1350	9.3934	8.8119	5.1827	103.9595	416.47
0.25	1350	9.4045	8.8135	5.1831	103.9665	416.71

Fig. 4 SEM images of $Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) ceramics (**a**) x = 0 ($MgSiO_3$) sintered at 1450 °C for 9 h and (**b**) x = 0.1, (**c**) x = 0.15, (**d**) x = 0.2, (**e**) x = 0.25 sintered at 1350 °C for 9 h

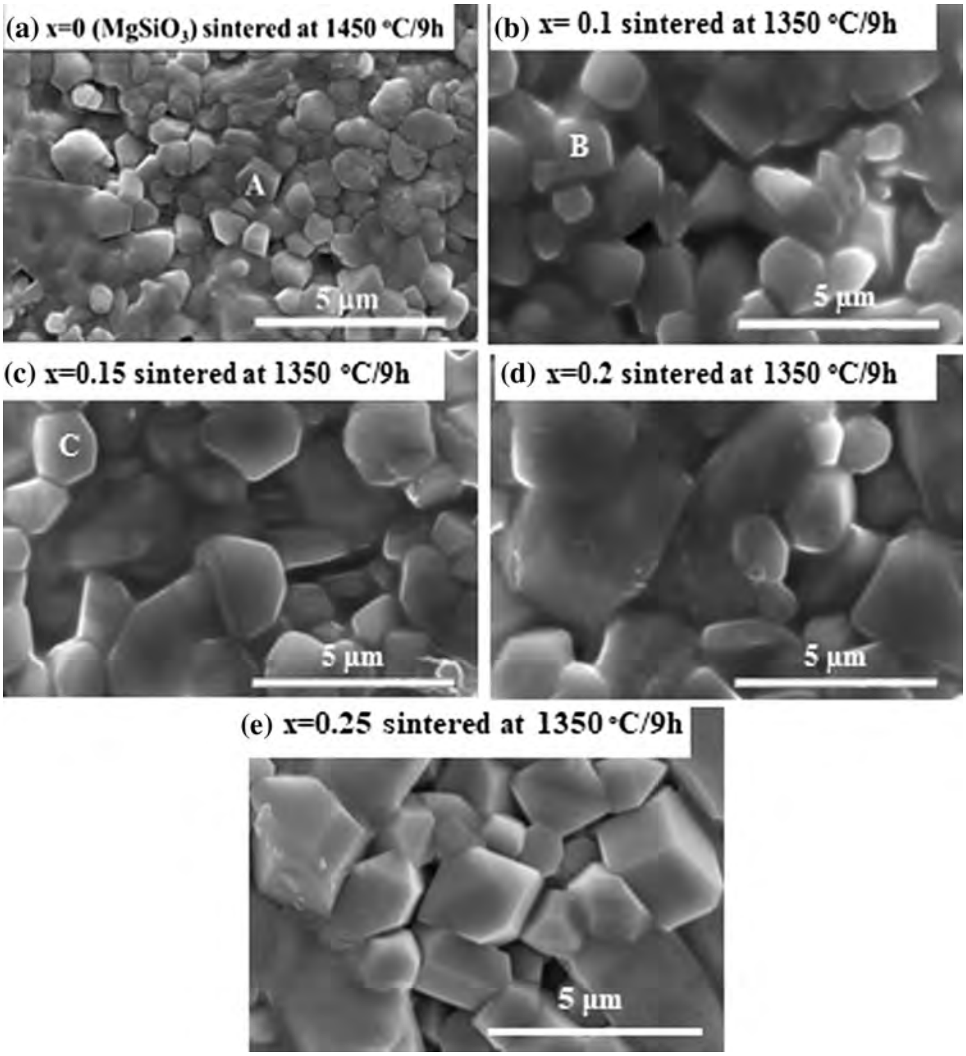

Figure 4b–e illustrate the SEM micrographs of the ceramics with x = 0.1, 0.15 and 0.20, 0.25 sintered at 1350 °C for 9 h, respectively. From the SEM micrographs, it is obvious that uniform grain growth occurred with increasing the x value from 0 to 0.15 that led to an increase in the density. However, for x > 0.15, an abnormal growth is observed which could be the cause of the decrease in the relative densities for these compositions (Fig. 3). This suggests that substitution of Co for Mg caused an increase in the grain size. The average grain size was measured by Image J software. The average grain size of $MgSiO_3$, $Mg_{0.90}Co_{0.1}SiO_3$ and $Mg_{0.85}Co_{0.15}SiO_3$ was about 2 µm, 2.7 µm and 3.3 µm respectively. This shows that Co substitution for Mg influences the grain size of the specimen.

The elemental analysis of the grains of $Mg_{1-x}Co_xSiO_3$ ceramics with different x value sintered at 1350 °C for 9 h, results are shown in Table 2. From the semi-quantitative SEM EDS data of grains labeled as A, B, C, in the samples of the compositions with x = 0, 0.1, and 0.15 respectively shows that the compositions of these grains in closed to $MgSiO_3$, $Mg_{0.90}Co_{0.10}SiO_3$ and $Mg_{0.85}Co_{0.15}SiO_3$ respectively. This is good agreement with the theoretical calculations and XRD findings.

Table 2 Elemental composition (in moles) calculated from semi-quantitative EDS data for spots A, B, C, in Fig. 4a–c

Grain	Mg (wt.%)	Co (wt.%)	Si (wt.%)	O (wt.%)
A	25.15	0	27.2	47.65
B	20.5	6.7	26.2	46.6
C	18.7	8.6	25.9	46.8

2.1 Microwave dielectric properties

The variation in the dielectric constant (ε_r) of $Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) ceramics as a function of Co content is shown in Fig. 5. An increase in the dielectric constant

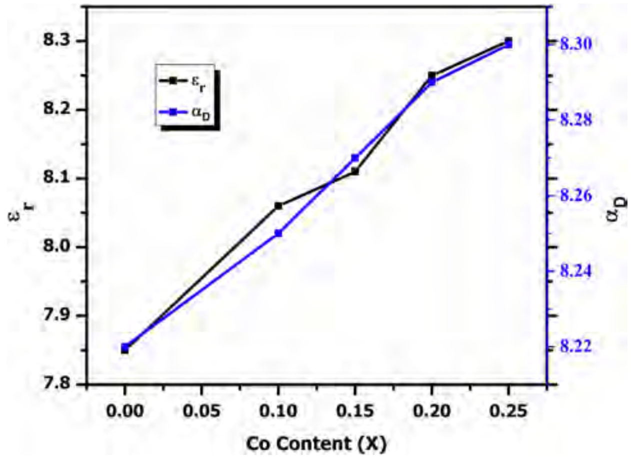

Fig. 5 Variation in the dielectric constant (ε_r) and ionic polarizability (α_D) of $Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) ceramics sintered at 1350 °C for 9 h as a function of Co Content

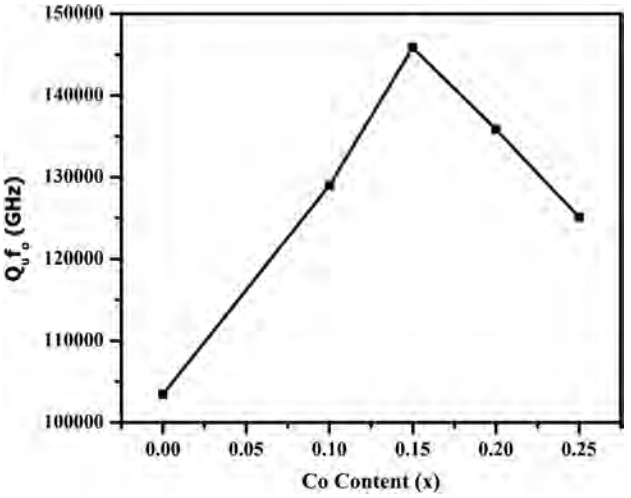

Fig. 6 Variation in the Q_uf_o value of $Mg_{1-x}Co_xSiO_3$(x = 0, 0.1, 0.15, 0.2, 0.25) ceramics as a function of Co content

ε_r was observed with increase in x value. It is obvious that secondary phases, ionic dielectric polarizability of the constituting ions and density influence the ε_r of a material. The theoretical dielectric polarizability of the ceramics calculated via Eq. 2 was found to increase with an increase in x value, due to the large ionic dielectric polarizability of Co (1.65 $Å^3$) than that of Mg (1.32 $Å^3$) [20]. Since the secondary clinoenstatite $MgSiO_3$ based phase has ε_r in the range of 7 [2, 7, 24]. Therefore, its effect on ε_r cannot be encounter. Similarly, the density decrease for $x > 0.15$, the ε_r showed decrease but here the ratio of the increase in polarizability is more therefore, the increase in the observed ε_r of the ceramics with increasing x value was attributed to the greater ionic dielectric polarizability of Co than Mg. The observed ε_r of the ceramics was found to increase from 7.85 to 8.30 with x value increasing from 0 to 0.25.

$$\alpha_D = (1-x)(\alpha Mg) + x(\alpha Co) + \alpha Si + 3(\alpha O) \qquad (2)$$

Figure 6 demonstrate the increase in the Q_uf_o value of $Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) ceramics as a function of Co content. It has been reported that two factors namely extrinsic and intrinsic factors are responsible for the total dielectric loss of a material [12, 21–23]. The density; pores, grain size, secondary phases, and order–disorder phase transformations are the extrinsic factor, whereas the lattice vibration is included in the intrinsic factor. In this study, the Q_uf_o value was observed to increase first from 103,453 to 145,846 GHz with increase in the x value from 0 to 0.15, but further increase in x content to 0.25 caused a decrease in Q_uf_o value to125086 GHz. The variation in the Q_uf_o value followed the relative density (Fig. 3). This shows that the most possible cause of the enhancement in the Q_uf_o value of the $Mg_{1-x}Co_xSiO_3$ ceramics is not intrinsic but extrinsic factors particularly the grain size, uniform grain growth that led to a decrease in the grain boundaries by Co substitution. The final decrease in the Q_uf_o could be the result of the lower densities for the compositions with $x > 0.15$ (Fig. 3). Co substitution for Mg has also been reported to increase the Q_uf_o value in other compounds [24–26].

Figure 7 demonstrates the variations in the τ_f values of $Mg_{1-x}Co_xSiO_3$ ceramics as a function of Co content. The τ_f value of $Mg_{1-x}Co_xSiO_3$ ceramics initially increased from − 24 to − 12 ppm/°C with increasing the x content from 0 to 0.15 and then decreased to − 20 ppm/°C with further in x content to 0.25. The τ_f value of a material is influenced by the relative density, additives, secondary phases, and composition. In this study, the shift in the τ_f values of the

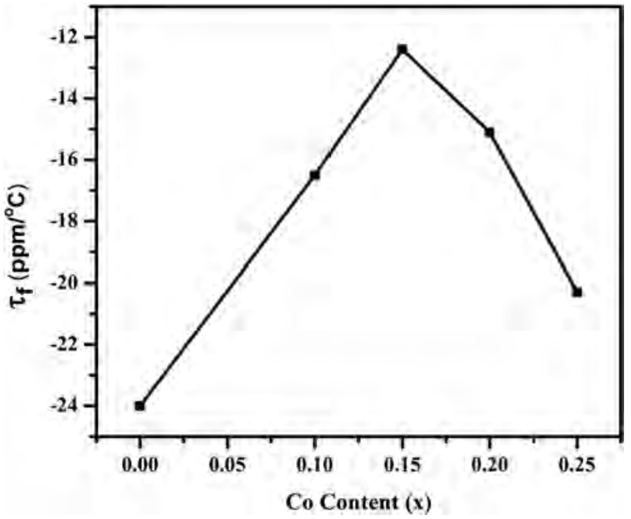

Fig. 7 Variation in the τ_f of $Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) sintered at 1350 °C for 9 h as a function of Co Content

Table 3 Processing temperatures, relative densities, and microwave dielectric properties of $Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) ceramics

(x)	ST(°C)	ρ_r	ε_r	Q_uf_o (GHz)	τ_f (ppm/°C)
0	1450/9 h	96.5	7.85	103,453	− 24
0.1	1350/9 h	94.9	8.06	128,954	− 16
0.15	1350/9 h	97.2	8.11	145,846	− 12
0.2	1350/9 h	95.7	8.25	135,843	− 15
0.25	1350/9 h	93.6	8.30	125,086	− 20

$Mg_{1-x}Co_xSiO_3$ ceramics are attributed to the variations in the density and composition. The highest τ_f value was obtained for the $Mg_{0.85}Co_{0.15}SiO_3$ composition sintered at 1350 °C for 9 h, listed in Table 3.

3 Conclusions

All the $Mg_{1-x}Co_xSiO_3$ (x = 0, 0.1, 0.15, 0.2, 0.25) compositions were prepared using the conventional solid- state sintering route. The Q_uf_o and τ_f values were observed to increase from 103,453 to 145,846 GHz and − 24 to − 12 ppm/°C with increasing x from 0 to 0.15, respectively. Due to the higher ionic dielectric polarizability of Co^{2+} than Mg^{2+}, ε_r of $Mg_{1-x}Co_xSiO_3$ ceramics increased from 7.85 to 8.30 with increasing value of x from 0 to 0.25. For the composition with x = 0.15 (i.e. $Mg_{0.85}Co_{0.15}SiO_3$) outstanding dielectric properties at microwave frequency, (i.e.; $\varepsilon_r \sim 8.11$, $Q_uf_o \sim 145{,}846$ GHz, $\tau_f \sim -12$ ppm/°C) were obtained sintered at 1350 °C for 9 h. This is suggested as a very favorable dielectric material for millimeter wave applications.

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