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Microwave dielectric properties of $(1 - x)Nd(Co_{1/2}Ti_{1/2})O_3$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ composite ceramics

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Abstract $(1 - x)Nd(Co_{1/2}Ti_{1/2})O_3$(NCT)–$xCa_{0.8}Sr_{0.2}TiO_3$ (CST) composite ceramics were prepared by the conventional solid-state reaction process. From the X-ray diffraction analysis, it indicates that the $Nd(Co_{1/2}Ti_{1/2})O_3$ phase coexists with $Ca_{0.8}Sr_{0.2}TiO_3$ phase, and it is easy for the cobalt volatilization to form second-phase $Nd_2Ti_2O_7$ as $x = 0.5$ and 0.7. As the content of CST increases from 0.1 to 0.9, the dielectric constant of the $(1 - x)Nd(Co_{1/2}Ti_{1/2})O_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ composite ceramics increases from 29.3 to 114.7, the $Q \times f$ value decreases from 60,000 to 8,500 GHz, and the τ_f value varies from −33.8 to 271 ppm/°C. A near zero τ_f could be achieved at 0.5NCT–0.5CST ceramics with $\varepsilon_r = 44.5$ and $Q \times f = 20{,}000$ (GHz) sintered at 1,340 °C for 4 h.

Introduction

With the explosive growth of wireless and mobile communication technology, the performance microwave dielectric ceramics have been widely used for microwave device applications, such as resonators, filters, antennas, and oscillators. Commercial microwave dielectrics with a high dielectric constant (ε_r) from 30 to 45, a high-quality factor ($Q \times f$) more than 10,000 (GHz) and a near-zero temperature coefficient of the resonant frequency (τ_f) are currently fabricated for the applications. A high dielectric constant can reduce the size of resonators because the wavelength in dielectric is inversely proportional to $\sqrt{\varepsilon_r}$ of the wavelength in vacuum. The quality factor ($Q \times f$) is required to be high to enhance the selectivity of the resonators. A near-zero temperature coefficient of the resonant frequency (τ_f) is demanded for achieving the stability required of dielectric resonators for practical use.

Recently, $Nd(Co_{1/2}Ti_{1/2})O_3$ ceramics possessing good dielectric properties have been reported. $Nd(Co_{1/2}Ti_{1/2})O_3$ has a dielectric constant (ε_r) of 27 and a extremely high-quality factor ($Q \times f$) of 140,000 (GHz); however, its rather high negative temperature coefficient of resonant frequency (τ_f) of −46 ppm/°C precludes its practically usage [1]. In experience, the typical way involves mixing two or more compositions, τ_f having coefficients with opposite sign to improve the temperature characteristic of microwave ceramics [2, 3]. Strontium–calcium titanate, $Sr_xCa_{(1-x)}TiO_3$ $(0 \leq x \leq 0.8)$ has been investigated with considerable interest for tunable microwave application. With partial replacement of Ca by Sr, the $Ca_{0.8}Sr_{0.2}TiO_3$ ceramics possess excellent dielectric characteristics. $Ca_{0.8}Sr_{0.2}TiO_3$ ceramics have $\varepsilon_r = 181$, $Q \times f = 8{,}300$ GHz (at 1.36 GHz), and $\tau_f = 991$ ppm/°C as reported by Wise et al. [4]. In the similar cases, employing Sm, La, and Nd substitute for Ca site to form $Ca_{0.8}Sm_{0.4/3}TiO_3$, $Ca_{0.6}La_{0.8/3}TiO_3$, and $Ca_{0.6}Nd_{0.8/3}TiO_3$ ceramics. Yoon et al. [5] investigated the $Ca_{1-x}Sm_{2x/3}TiO_3$ solid-solution system and they found that the $Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic possesses a high dielectric constant value of 119.3, a maximum $Q \times f$ value of 12,000 (GHz), and a positive τ_f of 400 ppm/°C. $Ca_{0.6}La_{0.8/3}TiO_3$ was reported to have a ε_r of 109, a $Q \times f$ of 17,600 GHz, and a τ_f of 213 ppm/°C [6]. In addition, $Ca_{0.6}Nd_{0.8/3}TiO_3$ ceramic has a ε_r of around 98, a $Q \times f$ value higher than 8,600 GHz, and a τ_f of 247 ppm/°C [7]. Comparing these similar ceramic composites, though the $Q \times f$ value of $Ca_{0.8}Sr_{0.2}TiO_3$ ceramic is slightly low, the ε_r and τ_f values are more outstanding

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than that of the others. Hence, the $Ca_{0.8}Sr_{0.2}TiO_3$ ceramic has been introduced to the $Nd(Co_{1/2}Ti_{1/2})O_3$ composite to improve the microwave dielectric properties for meeting commercial requirements. In this present study, the $(1-x)$ $Nd(Co_{1/2}Ti_{1/2})O_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ composites have been synthesized and reported to demonstrate the significant change in microwave dielectric properties by the introduction of $Ca_{0.8}Sr_{0.2}TiO_3$.

Experimental procedure

Samples of $(1-x)Nd(Co_{1/2}Ti_{1/2})O_3-xCa_{0.8}Sr_{0.2}TiO_3$ were synthesized by conventional solid-state method. The starting materials were high-purity oxide powders (>99.9%): Nd_2O_3, CoO, TiO_2, $CaCO_3$, and $SrCO_3$ which were separately prepared according to the desired stoichiometry of $Nd(Co_{1/2}Ti_{1/2})O_3$ and $Ca_{0.8}Sr_{0.2}TiO_3$. The powders were ground in distilled water for 12 h in a ball mill with agate balls and then dried at 80 °C in an oven overnight. After drying, the $Nd(Co_{1/2}Ti_{1/2})O_3$ and $Ca_{0.8}Sr_{0.2}TiO_3$ powder was forced through a 200-mesh sieve, and calcined at 1,250 °C for 2 h and 1,100 °C for 4 h, respectively. After calcinations, the calcined powders were mixed according to the molar fraction and then re-milled for 12 h. The fine powder with 3 wt% of a 10% solution of PVA as a binder was pressed into pellets with dimensions of 11 mm in diameter and 5 mm in thickness under a pressure of 2,000 kg/cm^2. These pellets were sintered at temperatures of 1,310–1,460 °C for 4 h in air. The heating and the cooling rates were both set at 10 °C/min. On the other hand, the X-ray diffraction (XRD, Siemens D5000) data of powder and bulk samples were collected using Cu-Kα radiation and a graphite monochromator in the 2θ range of 20–60°. The microstructural observations and analysis of the sintered surface were performed using a scanning electron microscopy (SEM, Philips XL40FEG, Eindhoven. the Netherlands) and an energy dispersive X-ray spectrometer (EDS). The density of the sintered specimens, as a function of sintering temperature, was measured by the liquid Archimedes method using distilled water as the liquid.

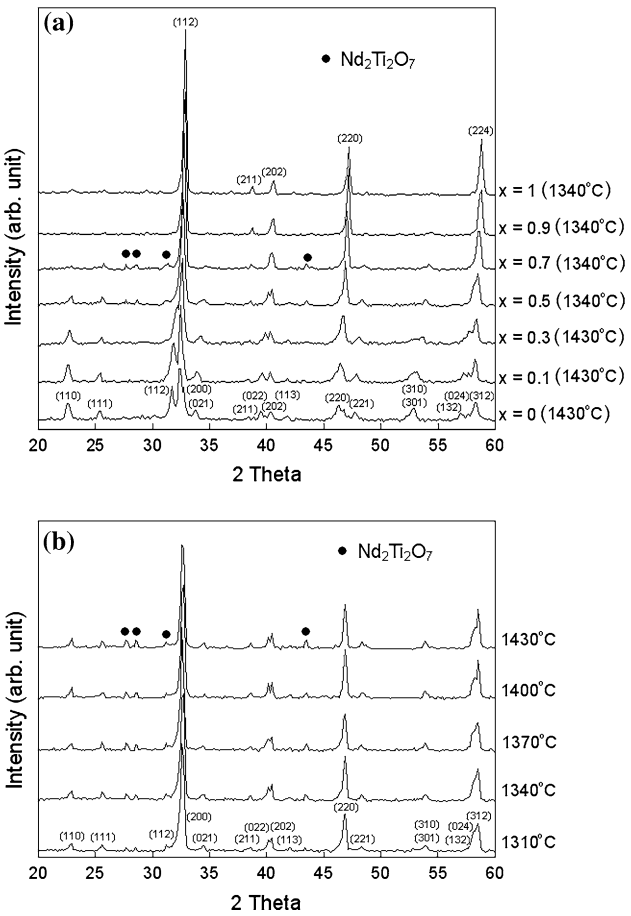


Fig. 1 **a** XRD patterns of the $(1-x)$NCT–xCST composite ceramics sintered at their optimal temperature for 4 h. **b** XRD patterns of the 0.5NCT–0.5CST ceramics at different sintering temperature

Fig. 2 SEM micrographs and EDS analysis of $(1-x)$NCT–xCST composite ceramic samples with **a–e** $x = 0.1$, 0.3, 0.5, 0.7, 0.9, respectively, sintered at their optimal temperature for 4 h; **f–i** $x = 0.5$, sintered at 1,310, 1,370, 1,400 and 1,430 °C ▶

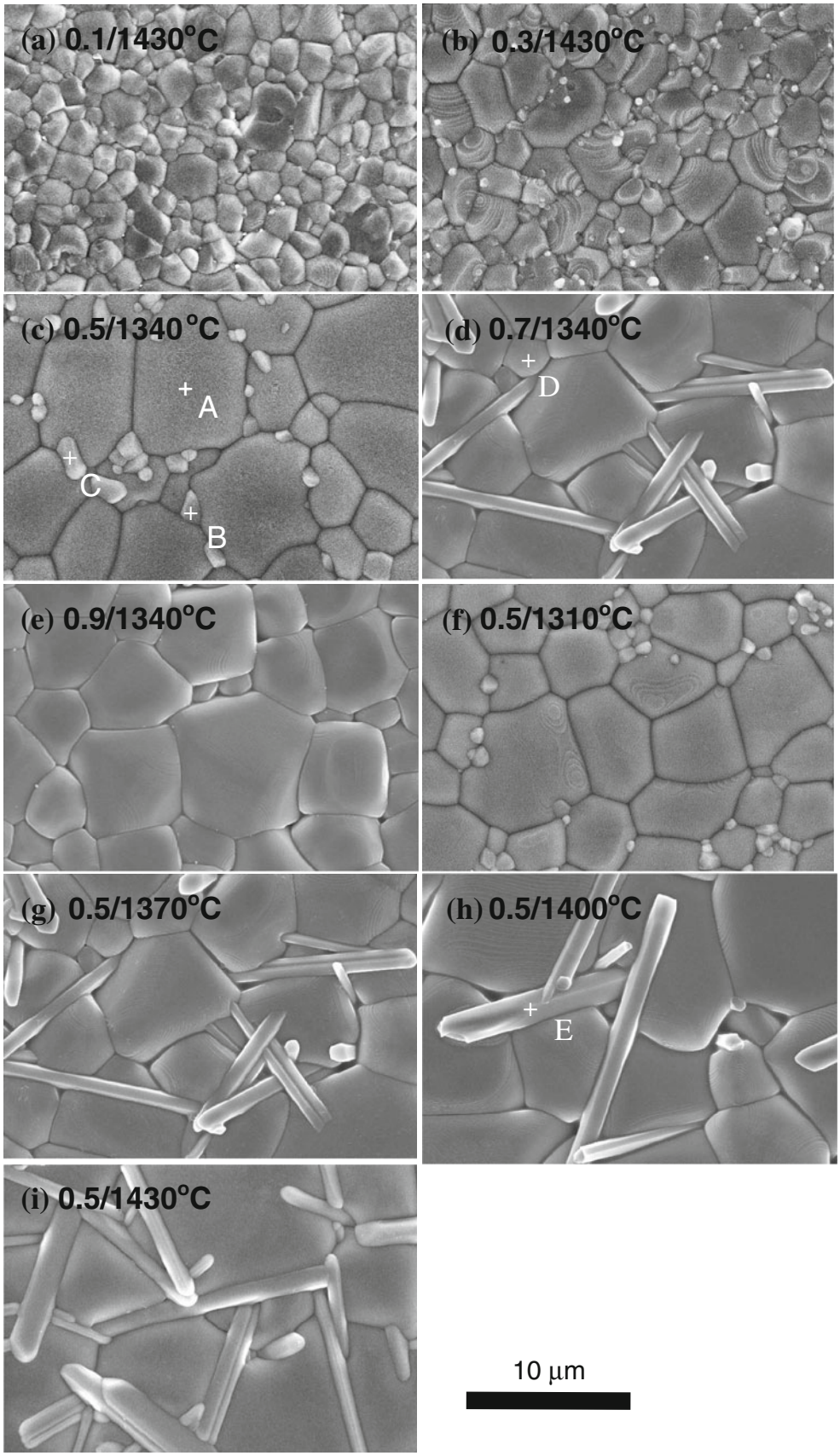
The dielectric constants (ε_r) and $Q \times f$ values at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method, as modified and improved by Courtney [8, 9]. The dielectric resonator was positioned between two brass plates to form a cavity-like structure. The test cavity was placed over a thermostat and the temperature range used was 25–80 °C, with a heating rate of 1 °C/min for heating and the residence time was 10 min at each time. The τ_f (ppm/°C) was calculated by noting the change in the resonant frequency using the formula,

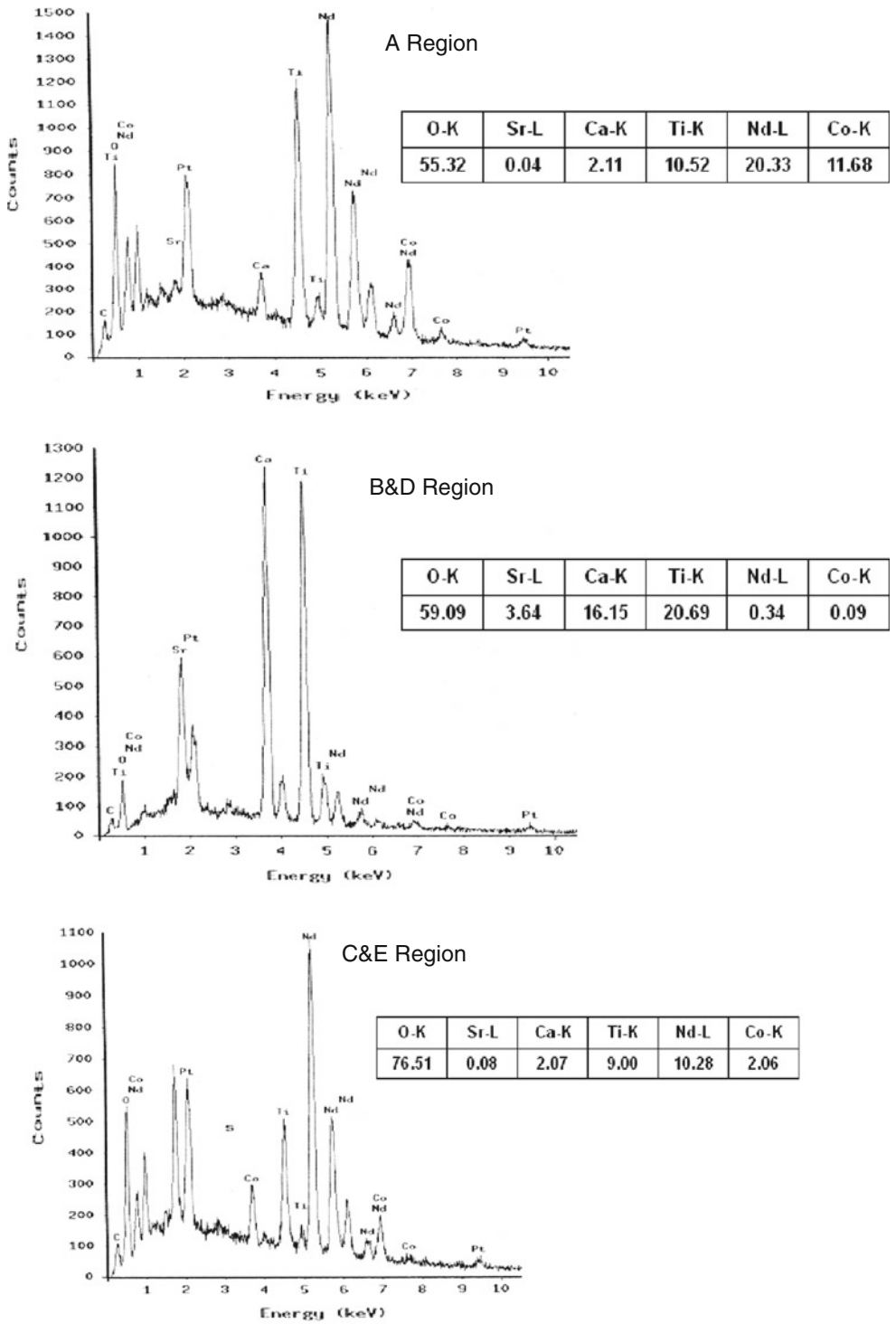
$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 is the resonant frequency at T_1 and f_2 is the resonant frequency at T_2.

Results and discussions

Figure 1a shows the X-ray diffraction patterns of $(1-x)$ $Nd(Co_{1/2}Ti_{1/2})O_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ mixed phases and Fig. 1b shows the XRD patterns of $0.5Nd(Co_{1/2}Ti_{1/2})O_3$–$0.5Ca_{0.8}Sr_{0.2}TiO_3$ composites sintered at different temperatures. All composites formed mixed phase ceramics with their diffraction peaks being indexed according to $Nd(Co_{1/2}Ti_{1/2})O_3$ phase (abbreviated as NCT) and $Ca_{0.8}Sr_{0.2}TiO_3$ phase (abbreviated


(a) 0.1/1430°C
(b) 0.3/1430°C
(c) 0.5/1340°C
A
C
B
(d) 0.7/1340°C
D
(e) 0.9/1340°C
(f) 0.5/1310°C
(g) 0.5/1370°C
(h) 0.5/1400°C
E
(i) 0.5/1430°C
10 μm



O-K	Sr-L	Ca-K	Ti-K	Nd-L	Co-K
55.32	0.04	2.11	10.52	20.33	11.68

O-K	Sr-L	Ca-K	Ti-K	Nd-L	Co-K
59.09	3.64	16.15	20.69	0.34	0.09

O-K	Sr-L	Ca-K	Ti-K	Nd-L	Co-K
76.51	0.08	2.07	9.00	10.28	2.06

Fig. 2 continued

as CST). The XRD patterns suggest that $Nd(Co_{1/2}Ti_{1/2})O_3$ will not form a solid solution with $Ca_{0.8}Sr_{0.2}TiO_3$. From Fig. 1a, it can be found that the intensity of the reflections of $Ca_{0.8}Sr_{0.2}TiO_3$ increases greatly as the content of x increases. Compared with pure NCT phase, the reflection peaks shift systematically toward higher angle with increasing CST content, indicating a cell volume contraction of $(1 - x)$NCT–xCST. In addition to the primary phase, there is clear evidence of additional phases for sample with $x = 0.5$ and 0.7, as shown in Fig. 1a. The minor peaks are observed at about $2\theta = 27.71$, 28.63, and 43.6°. The peaks occur at similar 2θ values as those for $Nd_2Ti_2O_7$ in NCT ceramics [1], and are inferred to be

$Nd_2Ti_2O_7$ secondary phase by analogy in this case. Tseng et al. [1] showed a secondary phase $Nd_2Ti_2O_7$ had been formed in pure NCT ceramics after high sintering and this phase was formed due to cobalt volatilization. From Bain et al. [10] reported, it can also be observed that the $Nd_2Ti_2O_7$ secondary phase can be formed easily from Nd_2O_3–TiO_2 materials. These results are in good accord with our study result. However, the $Nd_2Ti_2O_7$ secondary phase does not appear for sample with $x = 0.9$. The reason for no clear $Nd_2Ti_2O_7$ peaks in the $x = 0.9$ might be that it is difficult to observe in XRD because of the extremely less amount of $Nd_2Ti_2O_7$ and a tendency toward CST component. In addition, a phenomenon can be observed in Fig. 1b; the intensities of diffraction peaks related to the $Nd_2Ti_2O_7$ phase increase gradually with increasing sintering temperature.

Figure 2 presents SEM photographs and EDS analysis of the $(1 - x)$NCT–xCST ceramics sintered at different temperatures for 4 h. The grain size increases significantly with increasing x, which is consistent with the XRD patterns exhibiting weak and wide peak for 0.9NCT–0.1CST specimens. From the micrograph, it is seen that there are three types of grains in the specimens. To clarify, the composition of the grains, the EDS analysis is performed for $(1 - x)$NCT–xCST ceramics. The EDS analysis shows that the large grain as A belongs to CST phase and small grains as B and D belong to NCT. For the sample with $x = 0.5$ and 0.7, noodle-shaped phase (C and E) exists, which is identified as $Nd_2Ti_2O_7$ compound by EDS analysis. These results are in agreement with the XRD patterns presented in Fig. 1. Figure 2f, c, g, h, i shows the 0.5NCT–0.5CST specimens sintered from 1,310 to 1,430 °C for 4 h, respectively. It depicts the amount of $Nd_2Ti_2O_7$ secondary-phase increase with increasing sintering temperature. The $Nd_2Ti_2O_7$ secondary phase is not observed in Fig. 2f. Nevertheless, it can be found, the phase in XRD reflection pattern for the 0.5NCT–0.5CST specimens sintered at 1,310 °C. It might be that the grain size of $Nd_2Ti_2O_7$ secondary phase is too small to be observed from the SEM photograph.

The microwave dielectric properties related with various amounts of CST content in $(1 - x)$NCT–xCST ceramics sintered at their optimal temperatures are shown in Fig. 3. As indicated with the increasing content of CST, the ε_r and τ_f values increase because CST possesses a high ε_r (181) and a large positive τ_f value (991 ppm/°C). The dielectric constant ε_r changes from 29.3 to 114.7 while the τ_f values range from negative value of −33.8 ppm/°C to positive value of 271 ppm/°C as CST ranged from 0.1 to 0.9. It can be seen that a near-zero τ_f value is obtained as $x = 0.5$. The effect of $Nd_2Ti_2O_7$ secondary phase in dielectric constant and τ_f value can be observed as shown in Fig. 3. As $x = 0.5$ and 0.7, the trend of ε_r is slightly low because the ε_r of $Nd_2Ti_2O_7$ ($\varepsilon_r = 33$) is similar to NCT ($\varepsilon_r = 27$). Owing to $Nd_2Ti_2O_7$

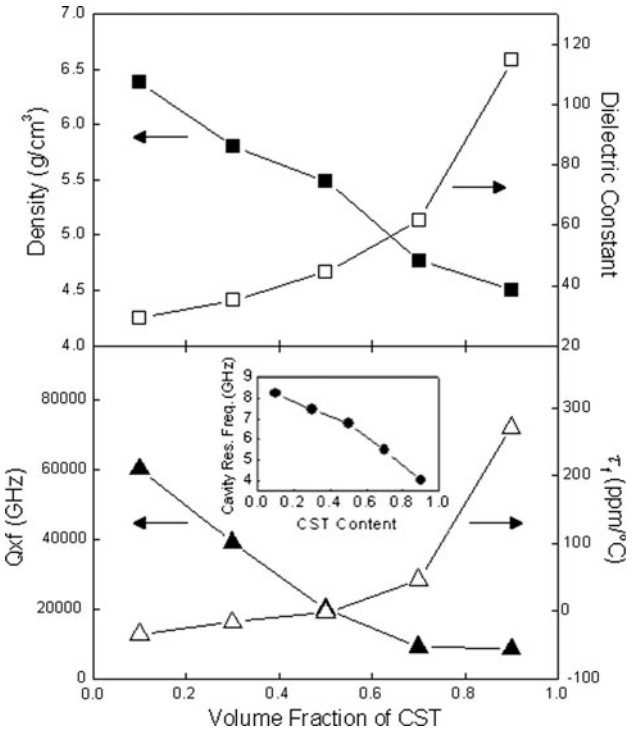


Fig. 3 Microwave dielectric properties of $(1 - x)$NCT–xCST composite ceramics sintered at their optimal temperatures for 4 h

secondary phase not existing at $x = 0.9$, the dielectric constant and τ_f value increase substantially. On the contrary, the densities and $Q \times f$ values decrease with increasing CST. This behavior can be expected because the decrease in the densities and $Q \times f$ values is mainly related to the much lower densities and $Q \times f$ value of CST (density<3.78 g/cm^3, $Q \times f \sim$ 8,300 GHz) than that of NCT (density ~6.6 g/cm^3, $Q \times f =$ 140,000 GHz). In addition, the resonant frequency of dielectric ceramics in the mixed phase measured using a microwave cavity was plotted in Fig. 3 with respect to the content of CST. The resonant frequency of samples with the same dimensions decreases near-linearly from NCT to CST rich composites, which have larger dielectric constant.

Figure 4a and b shows the variation of density and dielectric constant of $(1 - x)$NCT–xCST ceramics as function of sintering temperature. The densities increase with increasing sintering temperature and reach maximum value, and then reduce with further increasing sintering temperature. The decrease in densities at higher sintering temperature is due to the rapid grain growth as observed in Fig. 2. For $x \geq 0.5$, the ceramics achieve clearly the maximum densities at 1,340 °C while the others obtain the values sintered at 1,430 °C. The relationships between ε_r values and sintering temperatures reveal the same trend with those between densities and sintering temperatures. However, the variation of ε_r values is too small to be observed.

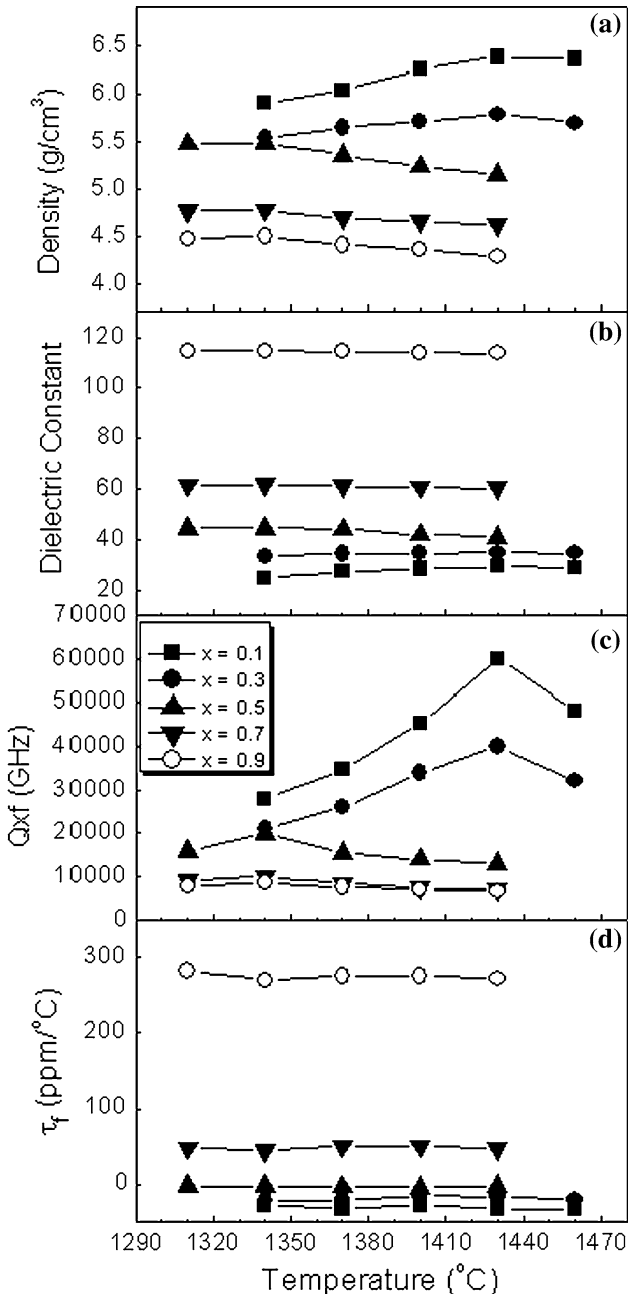


Fig. 4 Microwave dielectric properties of $(1 - x)$NCT–xCST composite ceramics sintered at different temperatures

Figure 4c and d illustrates the $Q \times f$ and τ_f values dependence of sintering temperature for $(1 - x)$NCT–xCST ceramics. For a given x value, the $Q \times f$ values initially increase to a maximum value and decrease thereafter. The correlations between $Q \times f$ values and sintering temperature nearly reveal the same trend as those between densities and sintering temperatures, as observed in Fig. 4a. It is believed that the densification of the ceramics plays an important role in controlling the dielectric loss. Furthermore, it has been noted that the microwave dielectric loss is mainly caused not only by the lattice vibrational modes, but also by the pore, density, and second phase [11]. The further increase in sintering temperature will result in the appearance of rapid grain growth and lead to the degradation of $Q \times f$ values. When x value reaches 0.5 and 0.7, cobalt volatilization results in Nd_2O_3–TiO_2 materials to form $Nd_2Ti_2O_7$ phase which indicates that $Nd_2Ti_2O_7$ phase has a $Q \times f$ value of about 3,000 GHz. Hence, it can be seen that the $Q \times f$ values decrease substantially for $x = 0.5$ and 0.7. Figure 4d shows the τ_f value of $(1 - x)$NCT–xCST ceramics sintered at different temperatures. The τ_f value of the ceramics does not alter with the sintering temperature. As mentioned above, the τ_f values of the ceramics for $x = 0.5$ and 0.7 are inhibited because of the existence of $Nd_2Ti_2O_7$ phase. A near-zero τ_f can be obtained for 0.5NCT–0.5CST ceramics at different sintering temperatures for 4 h. In summary, $0.5Nd(Co_{1/2}Ti_{1/2})O_3$–$0.5Ca_{0.8}Sr_{0.2}TiO_3$ ceramics sintered at 1,340 °C for 4 h have good dielectric properties; these properties are a dielectric constant (ε_r) of 44.5, a quality factor ($Q \times f$) of 20,000 GHz, and a τ_f of -2 ppm/°C.

Conclusion

The microwave dielectric properties of $(1 - x)Nd(Co_{1/2}Ti_{1/2})O_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ceramics have been studied. As expected, the dielectric constant and τ_f increases with increasing the amount of CST, but the $Q \times f$ value decreases. The X-ray analysis and SEM reveal that the $Nd_2Ti_2O_7$ secondary phase appears for $x = 0.5$ and 0.7. $Nd_2Ti_2O_7$ secondary phase degrades the microwave dielectric properties. Under the same content of CST, the densities, ε_r and $Q \times f$ values increase initially and then decrease with increasing sintering temperature; meanwhile, no significant change of the τ_f is observed. The $(1 - x)Nd(Co_{1/2}Ti_{1/2})O_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ($x = 0.5$) ceramics sintered at 1,340 °C for 4 h exhibit microwave dielectric properties with ε_r of 44.5, $Q \times f$ value of 20,000 GHz, and τ_f of -2 ppm/°C, respectively.

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