Highly enhanced $Q \times f$ value of Ca$_{0.61}$Nd$_{0.26}$TiO$_3$ ceramics with SnO$_2$ additive

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Abstract. The microstructure and microwave dielectric properties of Ca$_{0.61}$Nd$_{0.26}$TiO$_3 + x$ mol SnO$_2$ (0 ≤ $x$ ≤ 0.05) ceramics (CNTS$_x$) were investigated by Field Emission Scanning Electron Microscope, Hakki-Coleman dielectric resonator, network analyser and X-ray Diffractometer. The XRD results indicated that all CNTS$_x$ samples were formed as orthorhombic-perovskite-structured CaTiO$_3$ phase. There were second phase Ti$_{0.7}$Sn$_{0.3}$O$_2$ in range of 0.02 ≤ $x$ ≤ 0.05. The SnO$_2$ additive promoted the grain size of CNT ceramic, which was conducive to the promotion of $Q \times f$ value. Although the $\varepsilon_r$ value declined as contents of SnO$_2$ increased, the SnO$_2$ additive had a little of amelioration for $\tau_f$ value. Finally, the CNTS0.01 ceramic sintered at 1400 °C had stable comprehensive dielectric characteristic: $\varepsilon_r$ ~ 105.2, $Q \times f$ ~ 14,369 GHz, $\tau_f$ ~ +262.3 ppm/º C.

1. Introduction

With the advent of the era of 5G, the rapid development of mobile communication technology has vigorously promoted the research of dielectric materials. It is well known that microwave ceramic with perovskite structure has been used widely in radio communications with super high frequency electromagnetic wave, including CaO-Nd$_2$O$_3$-TiO$_2$ solid system. A number of researchers have reported the microwave dielectric properties ($\varepsilon_r$ ~ 82 – 175, $Q \times f$ ~ 250 – 17,200 GHz) of the Ca$_{1-x}$Nd$_{2x/3}$TiO$_3$ ceramic [1-3]. Here, $\varepsilon_r$, $Q \times f$ and $\tau_f$ indicate relative permittivity, quality factor and temperature coefficient of resonant frequency, respectively. The dielectric resonator (DR) applied in super high frequency radio communications is made of microwave dielectric ceramics (MWDCs), which requires high $\varepsilon_r$ and $Q \times f$ ($Q = 1/\tan \delta$) value and near-zero $\tau_f$ value[4, 5].

As noted above, the Ca$_{0.61}$Nd$_{0.26}$TiO$_3$ (CNT) ceramic, as a member in Ca$_{1-x}$Nd$_{2x/3}$TiO$_3$ solid system, with adjustable and comprehensive properties ($\varepsilon_r$ ~ 106, $Q \times f$ ~ 17,200 GHz, $\tau_f$ ~ +270 ppm/º C) [1] is thought to be a potential and suitable MWDCs applied in the high frequency circuit. Most of these studies[2, 3, 6-8] have only concentrated on tuning the $\tau_f$ value of the CNT ceramic to near zero by substitution of A or B site in perovskite structure or combining other ceramics with opposite $\tau_f$ value. However, many researchers failed to obtain the pure CNT ceramic with high $Q \times f$ value of 17,200 GHz, which is shown in Table 1. In these works, the pure CNT ceramic has a low $Q \times f$ value under 17,200 GHz, which is interpreted to be due to oxygen deficiency[9, 10]. Lowndes et al. added moderate amounts of Mn$_2$O$_3$ in CNT ceramic to restrain the generation of oxygen deficiency at high sintering
temperature (≥1300 ºC). Analogously, this phenomenon also exists in other ceramics, such as 
Na_{0.5}Sm_{0.5}TiO_3 [11], BaZn_2Ti_4O_11 [12], Ba_{4.2}Sm_{3.8}Ti_{18}O_{54} [13], and so on. Aiming at solving this 
problem, doping with stable divalent and trivalent cations, such as Mg, Cu, Cr and Al is an appropriate 
method to prevent Ti^{4+} reduction. Furthermore, tetravalent cations Sn has been made valid by 
improvement of Q× f value for Ca_{0.6}La_{0.8/3}TiO_3 ceramic [14]. Hence, CNT ceramic samples were 
prepared by doping with different contents of SnO_2 in this study. Ca_{0.61}Nd_{0.26}TiO_3 + x mol SnO_2 (0 ≤ x 
≤ 0.05) ceramics were shorted as CNTS_x ceramic.

Table 1. The microwave dielectric properties of pure Ca_{0.61}Nd_{0.26}TiO_3 (CNT) ceramic.

| S.T (ºC) | ε_r | Q× f (GHz) | τ_f (ppm/ºC) | References |
|----------|-----|------------|--------------|------------|
| 1400     | 106 | 17,200     | 270          | [1]        |
| 1450     | 87.5| 12,400     | 242          | [2]        |
| 1400     | 102.8| 8,560     | 247          | [15]       |
| 1350     | 103 | 15,340     | 247          | [16]       |
| 1400     | 98  | 8,560      | 247          | [3]        |
| 1400     | 94.4| 7,800      | 160          | [17]       |
| 1400     | 106.5| 10,159    | 271          | This work  |

As listed in Table 1, the ε_r and τ_f values reported in this work were in accord with the results in Ref. 1. The biggest difference was the Q×f value. The reasons for this should be complex and diverse. Not only did oxygen deficiency have effects on the Q×f value of CNT ceramic, the difference in the purity of the raw materials, the preparing technique, the sintering condition (temperature, time and atmosphere) and so on all could influence the Q×f value seriously. Although the level of the Q×f value in our paper was lower than that in Ref. 1, all CNTS_x (0 ≤ x ≤ 0.05) samples were prepared under same conditions (raw materials, the preparing technique, the sintering condition, etc). So it did not influence our discussion on the effects of Sn additive on the microwave dielectric properties of CNT ceramic.

2. Experimental

2.1. Preparation
The Ca_{0.61}Nd_{0.26}TiO_3 + x mol SnO_2 (0 ≤ x ≤ 0.05) ceramics (CNTS_x) mixed raw powder was 
synthesized by solid-state reaction method. Starting materials (CaCO_3 (≥99.5%), Nd_2O_3 (≥99.9%), 
TiO_2 (>99.5%) and SnO_2 (≥99.9%)) were analytical reagent. Then these raw powders in the 
stoichiometric ratio were high-energy ball milled for 8 h at the speed of 280 rpm with the ball to 
powder weight ratio of 5:1 by planetary mill (Nanjing Machine Factory, China), followed by calcining 
at 1100 ºC for 5 h. And the heating rate of calcining procedure was 3ºC/min. The calcined powders 
were re-milled with the same parameters. Then the calcined mixtures were uniaxially pressed into 
pellets directly with dimension of 15mm in diameter and 7mm in thickness using PVA solution as 
binder. After removing the binder at 600 ºC, the samples were sintered at 1350 ºC ~ 1450 ºC for 4 h. 
The heating rate was set to 5 ºC /min.

2.2. Characterization
After sintering, Archimedes method was used to calculate the bulk density of the ceramics. The 
microstructure and the phase components were characterized by Field Emission Scanning Electron 
Microscope (SEM, Electron Optics B.V, FEI, USA) and X-ray Diffractometer (XRD, 7000s,
Shimadzu, Japan), respectively. The relative permittivity ($\varepsilon_r$) and quality factor (Q×f) at microwave frequency were measured by the Hakki-Coleman method with a network analyzer (N5230A, Agilent, USA). The $\tau_f$ value was measured from difference between the resonant frequency at 25 ºC and 85 ºC.

3. Results and discussion

Figure 1. (a) XRD patterns of CNTS$\_x$ (0 ≤ $x$ ≤ 0.05) ceramics sintered at 1400 ºC; (b) the shifts in Ti$_{0.7}$Sn$_{0.3}$O$_2$ phase peak.

Figure 1(a) shows the crystal structure and phase constituent of CNTS$\_x$ (0 ≤ $x$ ≤ 0.05) ceramics sintered at 1400 ºC. As illustrated in Figure 1(a), all CNTS$\_x$ ceramics samples were formed as orthorhombic-perovskite-structured CaTiO$_3$ phase with a Pnma(62) space group, which is well-indexed to JCPDS # 88-0082. The second phase Ti$_{0.7}$Sn$_{0.3}$O$_2$ was detected at $x$ ≥ 0.02, which was explained by the partial substitution of Sn for Ti at B-site in CNT crystal. Figure 1(b) indicated the content of Ti$_{0.7}$Sn$_{0.3}$O$_2$ phase increased with increase of Sn additive. On the other hand, the substitution of Sn$^{4+}$ for Ti$^{4+}$ may result in the crystal lattice mismatch. Hence, it is difficult to crystallize a solid solution as extra SnO$_2$ additive.

Figure 2. SEM images of CNTS$\_x$ (0 ≤ $x$ ≤ 0.05) as-sintered ceramics sintered at 1400 ºC with (a) $x$ = 0; (b) $x$ = 0.01; (c) $x$ = 0.02; (d) $x$ = 0.03; (e) $x$ = 0.04; (f) $x$ = 0.05.
The microstructure of CNTS\(_x\) (0 \leq x \leq 0.05) as-sintered ceramics sintered at 1400 °C are presented in Figure 2. When SnO\(_2\) molar concentration is \(x = 0.01\), the average grain size of ceramic sample is 112.4 μm, which is larger than that of pure CNT sample. The big grains became more at \(x = 0.01\). Then the average grain size of CNTS\(_x\) ceramics declined as \(x\) increased. Nevertheless, the average grain size of CNTS\(_x\) ceramics increased again when \(x\) value exceeded 0.04.

![Figure 3. Relative permittivity (\(\varepsilon_r\)) of CNTS\(_x\) (0 \leq x \leq 0.05) ceramics sintered at different temperature.](image)

Figure 3 depicts the relative permittivity (\(\varepsilon_r\)) of CNTS\(_x\) (0 \leq x \leq 0.05) ceramics sintered at different temperature. Results in Figure 1 manifested the second phase Ti\(_{0.7}\)Sn\(_{0.3}\)O\(_2\) was observed in range of 0.02 \leq x \leq 0.05, which is a significant factor of declined \(\varepsilon_r\) value. On the other hand, the decrease of \(\varepsilon_r\) values with increase of SnO\(_2\) contents can be attributed to the decline of molar polarizability. It is well known that ionic polarizability has an impact on the molar polarizability. When Sn\(^{4+}\) with lower ionic polarizability value of (2.83 Å\(^3\)) substituted for the Ti\(^{4+}\) (2.93 Å\(^3\)), the molar polarizability of CNTS\(_x\) ceramics decreased, then \(\varepsilon_r\) values decreased as \(x\) value increased. Furthermore, results in Figure 3 imply the \(\varepsilon_r\) values of samples sintered at 1400 °C are higher than that of samples sintered at the other sintering temperatures, suggesting the optimized sintering temperature is 1400 °C.

![Figure 4 shows the \(\tau_f\) values and unit cell volume of CNTS\(_x\) (0 \leq x \leq 0.05) ceramics sintered at different temperature.](image)

Figure 4 shows the \(\tau_f\) values and unit cell volume of CNTS\(_x\) (0 \leq x \leq 0.05) ceramics sintered at different temperature. As presented in Figure 4, the sintering temperature has less impact for \(\tau_f\) values. As \(x\) increased, the \(\tau_f\) value decreased from 270 ppm/°C to 206 ppm/°C. It is reported that the \(\tau_f\) value is affected by the many factors, such as second phase, tilting of oxygen octahedrons, compactness, and so on[18-20]. In this paper, the unit cell volumes of CNTS\(_x\) ceramics sintered at 1400 °C were obtained by refined XRD data, and results are shown in Figure 4. The tendency of unit cell volume was accordance with Vegard's law. According to the data of ionic radius[21], the unit cell volume of CNTS\(_x\) ceramics increased and the oxygen octahedrons became more tilted when Sn\(^{4+}\) (0.69 Å, CN = 6) substituted for Ti\(^{4+}\) (0.605 Å, CN = 6). As discussed above, the \(\tau_f\) value of CNT ceramic decreased as contents of SnO\(_2\) increased.

As well known, the \(Q\times f\) value of MWDCs was influenced by the compactness, density, second phase, grain size, porosity and so on [22]. As shown in Figure 5, the change of \(Q\times f\) value was consistent with bulk density for CNTS\(_x\) ceramics when SnO\(_2\) concentration increased. The CNTS0.01 ceramic has the largest \(Q\times f\) value and bulk density. High bulk density means low porosity, which
implies that external loss decreased, and had less impact on the Q×f value. In addition, the Q×f value of samples sintered at 1400 °C presented a rising trend in range of 0.03 ≤ x ≤ 0.05. This was accordance with the trend of grain size of samples sintered at 1400 °C. The big grain size promoted the compactness of ceramics, and bulk density would increase. The substitution of Sn for Ti would suppress reduction of Ti$^{4+}$ because of the generation of the second phase Ti$_{0.7}$Sn$_{0.3}$O$_2$ [23]. The results in Figure 5 reveal 1400 °C was the optimized sintering temperature, which was in accord with results in Figure 3.

Taken together, this work revealed that SnO$_2$ was conducive to the promotion of Q×f value in moderate amounts for CNT ceramic.

![Figure 4](image-url)  
**Figure 4.** τ$_f$ values and unit cell volume of CNTS$_x$ (0 ≤ x ≤ 0.05) ceramics sintered at different temperature.

![Figure 5](image-url)  
**Figure 5.** Q×f values and bulk densities of CNTS$_x$ (0 ≤ x ≤ 0.05) ceramics sintered at different temperature.
4. Conclusions
The CNTSx \((0 \leq x \leq 0.05)\) ceramics were obtained via solid-state method. The XRD results indicated that all CNTSx samples were formed as orthorhombic-perovskite-structured CaTiO\(_3\) phase. There were second phase Ti\(_{0.7}\)Sn\(_{0.3}\)O\(_2\) in range of \(0.02 \leq x \leq 0.05\). The SnO\(_2\) additive promoted the grain size of CNT ceramic, which was conducive to the promotion of \(Q \times f\) value. Although the \(\varepsilon_r\) value declined as contents of SnO\(_2\) increased, the SnO\(_2\) additive had a little of amelioration for \(\tau_f\) value. Finally, CNTS0.01 ceramic sintered at 1400 °C possessed stable comprehensive microwave dielectric characteristic of \(\varepsilon_r = 105.2, Q \times f = 14,369\) GHz, \(\tau_f = +262.3\) ppm/°C.

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