Different Additives Doped Ca–Nd–Ti Microwave Dielectric Ceramics with Distorted Oxygen Octahedrons and High $Q \times f$ Value

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ABSTRACT: We investigated the structure and antireduction of Ti4+ in orthorhombic perovskite Ca$_{0.61}$Nd$_{0.26}$TiO$_3$ (CNT) ceramic by doping with three different additives (Cr$_2$O$_3$, MnO$_2$, and SnO$_2$). The X-ray diffraction patterns showed that the main phase of orthorhombic perovskite was formed in all the samples. In addition, the substitution of M (M = Cr$^{3+}$, Mn$^{4+}$, Sn$^{4+}$) for Ti$^{4+}$ resulted in the oxygen octahedral distortion and changes of order degree of B-site, which was confirmed by Raman spectra. The $\varepsilon_r$ and $\tau_f$ values were concerned with the average ionicity of B–O bond $f_i$(B-ave) and the linear expansion coefficient $\alpha$, respectively. The X-ray photoelectron spectra indicated that three different additives could restrain the reduction of Ti$^{4+}$, which was beneficial to the improvement of the $Q \times f$ value for CNT ceramic. High Q × f value of 16 123 GHz was obtained in the CNT + 1 mol % Cr$_2$O$_3$ ceramic compared with Q × f value of 11 207 GHz in pure CNT ceramic.

1. INTRODUCTION

Microwave dielectric ceramics (MWDCs) play a key role in electronic components, which are used widely in the communication, including internet of things, software radio, global positioning system, DBS, radio frequency identification, environmental monitoring via satellite, etc.1 For example, a dielectric resonator made of MWDCs is an electromagnetic component that exhibits resonance for a narrow range of frequencies. The key properties of MWDCs required for a dielectric resonator are high relative permittivity ($\varepsilon_r$), high quality factor ($Q \times f$), and a near-zero temperature coefficient of resonant frequency ($\tau_f$). Many specific MWDCs should have high $\varepsilon_r$ value (70–130) and thermal stability to satisfy the miniaturization of microwave devices, such as CaTiO$_3$-based MWDCs.

The Ca$_{0.61}$Nd$_{0.26}$TiO$_3$ (CNT) ceramic with properties of $\varepsilon_r$ ~ 108, $Q \times f$ ~ 17 200 GHz, and $\tau_f$ ~ 270 ppm/°C, originating from CaTiO$_3$ ceramic is thought to be potential and suitable MWDCs applied in the high-frequency circuit.5 For the needs of practical application, many literatures concentrated on tuning the $\tau_f$ value of the CNT ceramic to near zero by substitution of A or B site in perovskite structure3,4 or combining other ceramics with opposite $\tau_f$ value.5–8 Nevertheless, little attention has been attached to the improvement on $Q \times f$ values by preventing reduction of Ti$^{4+}$ to Ti$^{3+}$. Two valence states of Ti exist in many Ti-based MWDCs sintered in an air atmosphere or under low oxygen partial pressure, such as TiO$_2$,9 BaZn$_{0.71}$Ti$_4$O$_{11}$,10 Ba$_{4.2}$Sm$_{0.5}$Ti$_{18}$O$_{34}$,111 Na$_{0.5}$Sm$_{0.5}$TiO$_3$,12 and so on. The reduction of Ti$^{4+}$ can be expressed by following reactions

$$\text{O}_2^- \leftrightarrow \text{O}^- + 2e^- + \frac{1}{2} \text{O}_2$$

(1)

$$\text{Ti}_4^+ + e^- \leftrightarrow \text{Ti}_3^+$$

(2)

As shown in reactions 1 and 2, Ti$^{4+}$ attracted free electrons and was transformed into Ti$^{3+}$. It is reported that the Q × f value of the pure CNT ceramic sintered at high temperature in air was under the value of 17 200 GHz due to the reduction of Ti$^{4+}$ to Ti$^{3+}$.5,8,13,14 Aiming at solving this problem, CNT ceramic samples were prepared by doping with 1 mol % M (M = Cr$_2$O$_3$, MnO$_2$, SnO$_2$) ceramics, CNT + 1 mol % M (M = Cr$_2$O$_3$, MnO$_2$, SnO$_2$) ceramics, CNT + 1 mol % Cr$_2$O$_3$ ceramic, CNT + 1 mol % MnO$_2$ ceramic, and CNT + 1 mol % SnO$_2$ ceramic were shortened as CNTM ceramics, CNT + Cr ceramic, CNT + Mn ceramic, and CNT + Sn ceramic, respectively. The effects of these additives on the structure and microwave dielectric properties of CNTM ceramics were studied in this work.

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RESULTS AND DISCUSSION

Figure 1 presents the X-ray photoelectron spectroscopy (XPS) of O 1s and Ti 2p for CNTM ceramics. As shown in Figure 1a, the asymmetric O 1s XPS spectra of CNTM ceramics were located at about 530.4 eV, which was consistent with previous studies of TiO2.15 The increases in the O 1s binding energy was attributed to the existence of oxygen vacancy in ceramics-based TiO2.16

According to reactions 1 and 2, the generation of oxygen vacancy was accompanied by the generation of free electrons in high-temperature sintering. Then, Ti3+ was formed, which lowered the Ti4+ 2p energy levels. As depicted in Figure 1b, the Ti4+ 2p binding energy increased to different degrees when different additives were doped in CNT ceramic, suggesting the reduction of Ti4+ was suppressed. The mechanism of antirestraint of Ti4+ reduction to Ti3+ could be explained by following equations

\[ \text{NO} \rightarrow \text{N}_2 + \text{V}_O + \text{O}_2 \] (3)

\[ \text{N}_2\text{O}_3 \rightarrow 2\text{N}_2 + \text{V}_O + 3\text{O}_2 \] (4)

where N is a metal cation. Additionally, as shown in Figure 1s, the position for Mn 2p3/2 was at 640.8 eV, and lower than that in literature, suggesting tetravalent Mn was reduced. This could be explained by the fact that the Mn ions in CNT ceramic sintered at high temperature in air showed mixed valence states (2+, 3+, 4+). N is Cr and Mn in this work. So, the substitution of bivalent or trivalent ions for Ti4+ would suppress the generation of the oxygen vacancies and then restrain to produce electrons based on reaction 1.

Figure 2 shows the scanning electron microscopy (SEM) photographs and the bulk density of CNTM ceramics. As illustrated in Figure 2a–d, the large grains of about 100 μm dominated in all compositions, and the small grains were distributed around the large grains. Obviously, the grain size of CNT + Cr ceramic was slightly smaller than of CNT ceramic, which was explained by the inhibition of Cr for the grain growth in CNT + Cr ceramic.19 Compared with the CNT ceramic, less tiny grains were distributed around the large grains in the CNT + Sn ceramic. It is reported that SnO2 addition with few amounts could promote the grain growth in Ca0.6La0.8/3TiO3 ceramics.20 Similarly, the tiny grains became less, and grain distribution was compact for the CNT + Sn ceramic. Furthermore, the variation in bulk density revealed that the large grain microstructure contributed to the densification in CNTM ceramics. The CNT + Sn ceramic
showed the most compact grain distribution compared with other composition, but did not present the highest bulk density value. This discrepancy may be ascribed to the pore in the CNT + Sn ceramic.

The X-ray diffraction (XRD) patterns of the CNTM ceramics are shown in Figure 3a. Pure orthorhombic-perovskite-structured CaTiO$_3$ phase was formed in CNT and CNT + Mn ceramics with a Pnma (62) space group, which is well-indexed to JCPDS #88-0082. However, for CNT + Cr and CNT + Sn ceramics, there was minor amount of TiO$_2$ secondary phase in CNT + Cr ceramic and Ti$_{0.7}$Sn$_{0.3}$O$_2$ secondary phase in CNT + Sn ceramic, which was shown in Figure 3b. To further study the variations in the structural parameters of orthorhombic-perovskite phase, Rietveld refinement was carried out. Figure 4 shows the X-ray patterns for CNTM ceramics after Rietveld refinement, and the crystallographic parameters of CNTM ceramics are shown in Table 1. As presented in Figure 5, the trend of lattice parameters in CNTM ceramics were the result of substitution of Cr$^{3+}$ (0.615 Å, CN = 6), Mn$^{4+}$ (0.53 Å, CN = 6), and Sn$^{4+}$ (0.69 Å, CN = 6) with Ti$^{4+}$ (0.605 Å, CN = 6) at the B-site. In addition, the substitution of M (M = Cr$^{3+}$, Mn$^{4+}$, Sn$^{4+}$) with Ti$^{4+}$ resulted in the shift in the (121) lattice plane peaks based on the Bragg’s law ($2d \sin \theta = n\lambda$), which is illustrated in Figure 3a.

According to the crystallographic parameters, the schematic representation of the CNT ceramic and its oxygen octahedron are presented in Figure 6. The CNT crystal constituted of Ti–O octahedrons, and Ca and Nd cations occupied the 4c Wyckoff positions in the octahedral interstice. The bond length between the Ti cation and O anion was nonequivalent in the

Figure 3. (a) XRD patterns of the CNTM ceramics sintered at their optimal temperatures. (b) Characteristic peaks in the 2θ range of 27.1–27.7.

Figure 4. Observed XRD (black circle) and calculated pattern (magenta solid line) along with difference plot (at the bottom) of the CNTM ceramics (allowed Bragg reflections are indicated by vertical bars and goodness-of-fit shown inset).
Table 1. Crystallographic Parameters of Different Additives of CNTM Ceramics Sintered at Their Optimal Temperature

| additives | none | Cr   | Mn   | Sn   |
|-----------|------|------|------|------|
| a (Å)     | 5.3486 | 5.4404 | 5.4381 | 5.4432 |
| b (Å)     | 7.6655 | 7.6696 | 7.6648 | 7.6734 |
| c (Å)     | 5.4079 | 5.4105 | 5.4069 | 5.4131 |
| V (Å³)    | 225.4531 | 225.7559 | 225.3731 | 226.0940 |

![Figure 5](image5.png)

**Figure 5.** Cell parameters variation in the CNTM ceramics.

![Figure 6](image6.png)

**Figure 6.** Schematic of the ABO₃ orthorhombic-perovskite structure (release of distorted oxygen octahedrons in the inset).

same Ti–O octahedron, which resulted in the tilting of the Ti–O octahedrons.

As is known, the spectra of structural variations can be detected by Raman spectrometer. In this work, Raman analysis was performed to confirm the structural evolution of the CNTM ceramics. According to the crystal structure data, the optic modes of CaTiO₃ with orthorhombic Pnma(62) space group can be predicted by the Group theory and represented as: \[ \Gamma_{\text{optic}} = 7A_g (R) + 8A_u (s) + 5B_{1g} (R) + 7B_{1u} (IR) + 7B_{2g} (R) + 7B_{2u} (IR) + 5B_{3g} (R) + 9B_{3u} (IR). \]

Twenty-four Raman-active modes \( (7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}) \) can be expected. Nevertheless, there are 30 Raman-active modes \((9A_g + 6B_{1g} + 9B_{2g} + 6B_{3g})\) in the CNT ceramic. This discrepancy was ascribed to the decrease in crystal symmetry as Nd³⁺ partially substituted for Ca²⁺ at the A-site in the CaTiO₃ crystal. Normally, not all of the Raman modes were identified in this experiment. Some peaks were annihilated due to weak signals.

As shown in **Figure 7a**, seven Raman-active modes of CNTM ceramics were measured, which appear as peaks at 133, 230, 326, 470, 549, 676, and 763 cm⁻¹. Here, seven modes were numbered M1–M7. The M7 at 763 cm⁻¹ represented an A_g mode. The M6 and M5 at approximately 676 and 549 cm⁻¹, respectively, corresponded to the Ti–O stretching mode. The M4 at 470 cm⁻¹ was related to the internal vibration in oxygen cage. The peaks in the range 200–350 cm⁻¹ (M2, M3) were related to the rotations of the oxygen cage and those in less than 200 cm⁻¹ (M1) were associated with the motion of the A-site cations.

**Figure 7c** shows the Raman shift of modes in the CNTM ceramics. As different additives were doped in CNT ceramic, the Raman shifts of M2, M4, M5, and M6 indicated the changed trend in the unit cell volume, which conformed to the shift of diffraction peaks in the XRD patterns. As shown in **Figure 7a**, the intensity of M7 in CNT + Cr ceramic was significantly distinct from other compositions, and the position of M7 dramatically moved from 763 to 773 cm⁻¹ compared with that in CNT ceramic. Zheng et al. proposed that M7 was related to the B-site ordering in complex perovskites. In our compositions, the M7 was generated on account of difference in the B-site ordering influenced by the distribution of cation (Ca, Nd) and vacancy at the A-site. Besides, their distribution would be affected by the valence of the substitutional cation for Ti⁴⁺ in CNT + Cr ceramic, which may play a key role in the M7 mode intensity.

The Mo–O bond structural information can be presented by the Raman spectra in the metal oxide molecule, which was expressed by eq 5

![Ti-O octahedron](image7.png)

\[
s (\text{cm}^{-1}) = 32895 \times \exp(-2.073R_{\text{Mo–O}}) \quad (5)
\]

where \( s \) is the Raman shift and \( R_{\text{Mo–O}} \) is the Mo–O bond length. Therefore, we have made a guess, and eq 5 could show the relationship between Raman shift and bond length for the B-site bonds in CNT + Mn ceramics. As shown in **Figure 7bc**, it is clear that the Raman shifts of M5 and M6 were in accordance with the trend of B–O1 and B–O2¹ bond length based on eq 5. However, the different changing tendency of bond length was observed between the B–O1 and B–O2¹ bond length. In CNTM ceramics, Ti⁴⁺ and Cr³⁺, Ti⁴⁺ and Mn⁴⁺, or Ti⁴⁺ and Sn⁴⁺ were occupied randomly at the B-site. Two adjacent oxygen octahedrons may become nonequivalent and the state of stabilization of two adjacent oxygen octahedrons was broken because of the differences of ionic sizes between Ti⁴⁺ and Cr³⁺, Mn⁴⁺ or Sn⁴⁺, which led to the structural distortion of oxygen octahedrons. The variation in oxygen octahedron with different additives for CNTM ceramics is shown in **Figure 7e**. The octahedral distortion \( (\delta_{\text{oct}}) \) was calculated from eq 6 based on the individual bond distance of the B-site.

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\[ \delta_{\text{oct}} = \frac{1}{6} \sum \left( \frac{R_i - \bar{R}}{\bar{R}} \right)^2 \]

where \( R_i \) is an individual bond distance and \( \bar{R} \) is the average bond distance at the B-site. As presented in Figure 7c, different additives have different impact on the oxygen octahedron, especially the B–O\(^{2-} \) bond. The \( \delta_{\text{oct}} \) reflected the differences in bond length between three B–O bonds in the oxygen octahedron. Therefore, CNT + Sn ceramic presented a more distorted oxygen octahedron with the highest \( \delta_{\text{oct}} \) value (as shown in Figure 7d) in all compositions. In addition, electronegativity of the B-site cations may affect the A\(_g\) mode (M7) frequency and the lineshape through B–O bond lengths. Nowadays, complex chemical bond theory has been applied in discussing the relationships of crystal structure, properties, and chemical bonds such as ATiNb\(_2\)O\(_8\) (A = Mg, Zn)\(^{30}\) and LnNbO\(_4\) (Ln = La, Nd)\(^{31,32}\). However, few studies were reported about this aspect for CNT ceramic. In this article, the bond ionicity \( f_i \) and the coefficient of thermal expansion \( \alpha \) of CNTM ceramics were calculated based on this theory.

Figure 8a presents the \( \varepsilon_r \) values and the bulk density in the CNTM ceramics sintered at their optimal temperatures. (b) The \( \tau_f \) values, \( \alpha \) values, and octahedron distortion \( \delta_{\text{oct}} \) in the CNTM ceramics sintered at their optimal temperatures.
and bulk density variation with different additives showed the same trend in the CNTM ceramics, which revealed that $\varepsilon_r$ was closely related to the bulk density for CNTM ceramics. Additionally, Batsanov et al.\textsuperscript{34} proposed that the relationship between permittivity and bond ionicity could be expressed as

$$
\varepsilon_r = -\frac{n^2 - 1}{1 - f_i(B-ave)} + 1
$$

(7)

where $n$ is the refractive index. According to the previous structure analysis, the additives primarily affected oxygen octahedrons at the B-site. Therefore, the average bond ionicity at the B-site ($f_i(B-ave)$) was calculated. As shown in Figure 8a, the $\varepsilon_r$ and $f_i(B-ave)$ values showed the same changing tendency with different additives, which confirmed the bond ionicity has a close relationship with the relative permittivity. Although the second phases were formed in CNT + Cr and CNT + Sn ceramics, the $\varepsilon_r$ values of TiO$_2$ and Ti$_{0.7}$Sn$_{0.3}$O$_2$ were both higher than that of CNT ceramic,\textsuperscript{9} implying that the second phase was not a factor of decreasing $\varepsilon_r$ value in CNT + Cr and CNT + Sn ceramics.

There have been many researches on the relationship among $\tau_f$ and distorted oxygen octahedrons,\textsuperscript{21,25,35} which indicated that positive $\tau_f$ value decreased due to more tilted and distorted oxygen octahedrons. Although CNT + Sn ceramic presented the highest $\delta_{oct}$ value, its $\tau_f$ value was not the lowest, as shown in Figure 8b. As is well known, the $\tau_f$ value has a close relationship with the thermal expansion coefficient ($\alpha$) and temperature coefficient of the relative permittivity ($\tau_{r}$): $\tau_f = -\tau_r/2 - \alpha$. Hence, the $\alpha$ values of CNTM ceramics were calculated by the complex chemical bond theory. As shown in Figure 8b, $\alpha$ and $\tau_f$ present two contradictory trends with different additives, indicating an important role of $\alpha$ in $\tau_f$.

Figure 9. (a) Fitting curves of XPS spectra of the Ti 2p core level line for CNTM ceramics. (b) The $Q \times f$ values, binding energy shifts of O 1s and Ti 2p, and $A$ values in the CNTM ceramics sintered at their optimal temperatures.
As shown in reactions 1 and 2, most perovskite ceramics easily formed a large number of oxygen vacancies sintered in low oxygen tension such as reducing atmosphere or at high sintering temperature. The Q × f microwave properties of CNT ceramic were deteriorated by excessive oxygen vacancies. Thus, the Ti 2p XPS spectra of CNTM ceramics were fitted, and fitting curves are shown in Figure 9a. For the CNT ceramic sintered in air, two valence states of Ti element could be detected, and the Ti\(^{3+}\) 2p\(_{3/2}\) and Ti\(^{4+}\) 2p\(_{3/2}\) peaks were observed at ~457.8 and ~458.7 eV, respectively. The Ti\(^{3+}\) content ratio in total Ti content can be calculated by eq 8 using the area of the t e peaks (Ti\(^{3+}\) 2p\(_{3/2}\) and Ti\(^{4+}\) 2p\(_{3/2}\)).

\[
A = \frac{A(Ti^{3+} 2p_{3/2}) + A(Ti^{3+} 2p_{1/2})}{A(Ti^{4+} 2p_{3/2}) + A(Ti^{4+} 2p_{1/2}) + A(Ti^{3+} 2p_{1/2})} \times 100\%
\]

\(A(Ti^{3+} 2p_{3/2}), A(Ti^{4+} 2p_{3/2}), A(Ti^{4+} 2p_{1/2}), \) and \(A(Ti^{3+} 2p_{1/2})\) refer to their individual peaks area. The calculated A values are shown in Table 2. The mechanism of antireduction of Ti\(^{4+}\) could be explained by eq 3 in CNT + Cr and CNT + Mn ceramics. For CNT + Sn ceramic, tetravalent Sn ion substituted for tetravalent Ti ion and the second phase Ti\(_{0.7}\)Sn\(_{0.3}\)O\(_2\) was formed, which decreased the Ti content. This may be a cause of antireduction of Ti\(^{4+}\). The A value of the CNT + Cr ceramic is zero, which implied there was no Ti\(^{3+}\) in ceramic, and the Q × f value was highest among all the samples. Besides, more research was needed into the different suppression force of Ti\(^{3+}\) in CNT ceramic doped with different additives (Cr\(_2\)O\(_3\), MnO\(_2\), SnO\(_2\)).

### 3. CONCLUSIONS

In the present work, CNT ceramics doped with different additives were explored. The XRD patterns and Raman spectra demonstrated that Cr, Mn, and Sn ions partially substituted Ti ions in the B-site, and the structural distortion of oxygen octahedrons became stronger in CNTM ceramics. Also, CNT + Sn ceramic presented the shortest bond length of B–O2\(^{-}\). The \(\varepsilon_i\) and \(\tau_i\) values were dependent on the average B-site bond ionicity \(f(B-ave)\) and the linear expansion coefficient \(\alpha\) respectively. The XPS spectra indicated that Ti\(^{3+}\) existed on account of the generation of oxygen vacancy in pure CNT ceramic sintered at high temperature. Furthermore, and Cr\(_2\)O\(_3\), MnO\(_2\), and SnO\(_2\) were verified to effectively suppress Ti\(^{3+}\) generation, contributing to the improvement of the Q × f value in CNT ceramic.

### 4. EXPERIMENTAL SECTION

The Reagent-grade raw materials—CaCO\(_3\), Nd\(_2\)O\(_3\), TiO\(_2\), Cr\(_2\)O\(_3\), MnO\(_2\), and SnO\(_2\) powders—were proportionately weighed in accordance with Ca\(_{0.25}\)Nd\(_{0.25}\)TiO\(_3\) + 1 mol % M (M = Cr\(_2\)O\(_3\), MnO\(_2\), SnO\(_2\)) (CNTM) chemical formula. Like traditional solid-state reaction method, the raw materials need to be ball mixed with deionized water using planetary. After drying, the resulting mixtures were calcined at 1130 °C for 5 h in alumina crucibles with an intermediate grinding to avoid the impurity phase. Then, the calcined mixtures were uniaxially pressed into pellets directly with dimension of 15 mm diameter and 7 mm thickness PVA. After removing the binder at 600 °C, the samples sintered at 1350–1450 °C for 4 h in air. The heating rate was set to 5 °C/min. The cooling rate were controlled at 2 °C/min until the 1000 °C and then naturally cooled to room temperature.

Archimedes method was used to calculate the bulk density of the ceramics. The XRD data were obtained using X-ray diffraction (XRD, XRD-7000, Shimadzu, Kyoto, Japan) using Cu Kα radiation over a 2θ range of 10–80° with a step of 0.013°. And, the phase analysis was performed by Rietveld refinement using GSAS and EXPGUI software. The microstructure was observed by scanning electron microscope (SEM, Sirion 200, Netherlands). The Raman signal of samples with different preparation process and doping content was collected at room temperature and recorded by a DXR microscope Raman spectrometer (LabRAM HR Evolution). The 10 mW output of the 532 nm line of He–Ne laser was used as the excitation source. The obtained Raman spectra exhibited a resolution of approximately 2 cm\(^{-1}\). The dielectric constant was measured by the Hakki–Coleman method, and the unload Q × f value was measured by the cavity method using a network analyzer (E8362B, Agilent Technologies). The \(\tau_i\) value was measured from the difference between the resonant frequency at 25 and 85 °C. An X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) was used to identify the valency of Ti and O ions with Al Kα (monochromatic) radiation. And, the XPS spectra were calibrated by positions of the C 1s peaks compared with the binding energy of 284.8 eV.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01311.

Fitting procedure for the XPS spectra and fitting curve of XPS spectra for CNTM ceramics with Cr 2p, Mn 2p, and Sn 3d core level line (PDF)

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#### Notes

The authors declare no competing financial interest.
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