

Sintering behaviour and microwave dielectric properties of a new complex perovskite: $(1-x)(\text{Sr}_{0.3}\text{Ca}_{0.427}\text{Nd}_{0.182})\text{TiO}_{3-x}\text{SmAlO}_3$ ceramics

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Abstract. Structural features and microwave dielectric properties of $(1-x)(\text{Sr}_{0.3}\text{Ca}_{0.427}\text{Nd}_{0.182})\text{TiO}_{3-x}\text{SmAlO}_3$ ($0.05 \leq x \leq 0.4$) ceramics were investigated. X-ray diffraction patterns illustrated that solid solutions with the orthorhombic perovskite were shown to be formed in the ranges of $0.05 \leq x \leq 0.4$. Moreover, the dielectric constant (ϵ_r) of sintered ceramics had a quasi-linear decrease with the increase in SmAlO_3 content. A certain amount of Sm and Al substitution for A- and B-sites could substantially improve the quality factor (Qf) of the ceramics. Increasing the oxygen octahedral distortion led to a decrease in the temperature coefficient of the resonant frequency (τ_f) from 216.3 to $-34.8 \text{ ppm } ^\circ\text{C}^{-1}$. Additionally, optimized microwave dielectric properties can be achieved for the specimens using $0.75(\text{Sr}_{0.3}\text{Ca}_{0.427}\text{Nd}_{0.182})\text{TiO}_3-0.25\text{SmAlO}_3$ ceramics [$\epsilon_r \sim 58.3$, $Qf \sim 18800 \text{ GHz}$ (at 4.65 GHz) and $\tau_f \sim 2.3 \text{ ppm } ^\circ\text{C}^{-1}$] after being sintered at 1500°C for 4 h.

Keywords. $(\text{Sr}_{0.3}\text{Ca}_{0.427}\text{Nd}_{0.182})\text{TiO}_3$; SmAlO_3 ; microwave dielectric properties; oxygen octahedral distortion.

1. Introduction

The proliferation of commercial wireless technologies, such as cellular phones, global positioning systems and satellite broadcasting, has placed increasing demands on the performance of dielectric resonators in the microwave frequency range [1,2]. These microwave dielectric ceramics must combine a high dielectric constant (ϵ_r), a high-quality factor (Qf) and a near-zero temperature coefficient of resonant frequency (τ_f). These three parameters are correlated to the resonator size, frequency selectivity and temperature stability of the system, correspondingly. A great many perovskite-type compounds and/or their solid solutions have been investigated and applied in microwave frequency devices [3–12]. Among them, microwave dielectric properties of SrTiO_3 -based and/or CaTiO_3 -based materials have been intensively investigated because of their high ϵ_r . However, their τ_f values are too large to apply those microwave frequency devices, so that much attention has been paid to improve their microwave dielectric properties with La^{3+} , Nd^{3+} and Sm^{3+} substitution for Ca^{2+} [13–15]. Even though such substitution is done, τ_f value is still positive.

It is well known that an effective way to achieve near-zero τ_f is to mix two compounds, one with a positive τ_f and the other with a negative τ_f , to form a solid solution or composite. In our previous work [16], the $(\text{Sr}_{0.3}\text{Ca}_{0.427}\text{Nd}_{0.182})\text{TiO}_3$ specimen sintered at 1400°C for 4 h showed a very high

$\epsilon_r \sim 145$ and moderate Qf value $\sim 7900 \text{ GHz}$. In addition, a relatively low positive $\tau_f \sim 415.6 \text{ ppm } ^\circ\text{C}^{-1}$, compared with that of SrTiO_3 and/or CaTiO_3 [3,7], can also be obtained for this sample. Furthermore, LnAlO_3 ($\text{Ln} = \text{Sm}, \text{Dy}$ and Er) with the same or distorted perovskite structure show a negative value of τ_f . Especially, the SmAlO_3 ceramic exhibits good microwave dielectric properties with $\epsilon_r \sim 20.4$, $Qf \sim 65000 \text{ GHz}$ and a large negative $\tau_f \sim -44 \text{ ppm } ^\circ\text{C}^{-1}$ [17]. Therefore, this work focuses on achieving a high ϵ_r , good Qf and near-zero τ_f by synthesizing $(1-x)(\text{Sr}_{0.3}\text{Ca}_{0.427}\text{Nd}_{0.182})\text{TiO}_{3-x}\text{SmAlO}_3$ ($0.05 \leq x \leq 0.4$) specimens [referred to hereafter as SCNT-SAx]. Moreover, the crystalline phases, microstructures, sintering behaviour and microwave dielectric properties of SCNT-SAx ceramics in the composition range of $x = 0.05-0.4$ are investigated.

2. Experimental

Samples of $(1-x)(\text{Sr}_{0.3}\text{Ca}_{0.427}\text{Nd}_{0.182})\text{TiO}_{3-x}\text{SmAlO}_3$ with $x = 0.05, 0.1, 0.2, 0.25, 0.3$ and 0.4 are prepared using the conventional solid-state reaction method. The starting materials are CaCO_3 , SrCO_3 , Nd_2O_3 , Sm_2O_3 , Al_2O_3 and TiO_2 powders of reagent grade. These materials are mixed according to the desired compositions and ground in distilled water for 24 h with ZrO_2 balls. The mixtures are dried and calcined at 1150°C for 2 h. The calcined powders are milled again with ZrO_2 balls for 24 h in ethanol and then sieved using a 200 mesh screen. The sieved powders with 5 wt% PVA as a binder are pressed into pellets 11.5 mm in diameter and

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5.5–6.0 mm in thickness under a pressure of 150 MPa. These pellets are preheated at 600°C for 2 h to remove the organic binder and then sintered for 4 h in air at various temperatures in the range of 1400–1550°C.

The crystalline structure of the prepared samples was analysed by an X-ray diffractometer (XRD, D8-Advance, Bruker, Germany) using Cu K α radiation with 40 kV, 35 mA, at a scanning rate of 6° min⁻¹. In addition, the surfaces of the sintered samples were observed using a scanning electron microscope (SEM, S-4800, Hitachi, Japan). The bulk densities of the sintered ceramics were measured by the Archimedes method. Also, the dielectric behaviours at microwave frequency of the samples were measured by the TE₀₁₈ shielded cavity method using a network analyzer and a temperature chamber (Agilent E5230C) [18]. The quality factor was characterized by Qf ($Q = 1/\text{dielectric loss}$, $f = \text{resonant frequency}$) value at 3.5–6.5 GHz. The temperature coefficient of the resonant frequency (τ_f) was calculated by the following formula [19]:

$$\tau_f = \frac{\Delta f_0}{f_0 \Delta T} = \frac{f_{75} - f_{25}}{f_{25} \times 50}, \quad (1)$$

where f_{75} and f_{25} represent the resonant frequencies at 75 and 25°C, respectively.

3. Results and discussion

The room-temperature X-ray diffraction (XRD) patterns recorded from the SCNT-SAx ($0.05 \leq x \leq 0.4$) ceramics

sintered at 1480°C for 4 h are illustrated in figure 1a. It also indicates that the solid solution based on a single orthorhombic perovskite type (JCPDS#42-0423), belonging to the space group Pnma, is identified at $x = 0.05$ –0.4. Furthermore, the (121), (022) and (042) diffraction peaks slightly shift to a higher angle with increasing SmAlO₃ content, as shown in figure 1b–d. This is due to the similarity of ionic radii between Sm³⁺ (1.24 Å, CN = 12) and (Sr_{0.3}Ca_{0.427}Nd_{0.182})²⁺ (1.235 Å, CN = 12) at A-site but the incorporation of the smaller Al³⁺ (0.535 Å, CN = 6) in place of Ti⁴⁺ (0.605 Å, CN = 6) at B-site [20]. This phenomenon obeys the general known Vegard's law as well. The lattice parameters and unit cell volume of the SCNT-SAx ($0.05 \leq x \leq 0.4$) ceramics sintered at 1480°C for 4 h are presented in table 1 and figure 2. It can be seen that the unit cell volume linearly decreases from 228.51 to 222.65 Å³ with the increase in SmAlO₃ content. Similarly, the replacement of a smaller B-site ions causes a decrease in the unit cell volume for the present ceramic systems.

Figure 3a presents the relative densities of the SCNT-SAx ($0.05 \leq x \leq 0.4$) ceramics at different sintering temperatures (T_s) for 4 h. It can be observed that, with increasing T_s , the relative densities first increase and then reach a saturation value and in the end decrease with further increasing T_s . As a general rule, this is because the grain size increases with the increase of T_s . However, a small number of large grains occur if the T_s increases further, which leads to the existence of a certain amount of pores (as shown in figure 6). Thus, for all the SCNT-SAx ($0.05 \leq x \leq 0.4$) ceramics, the relative

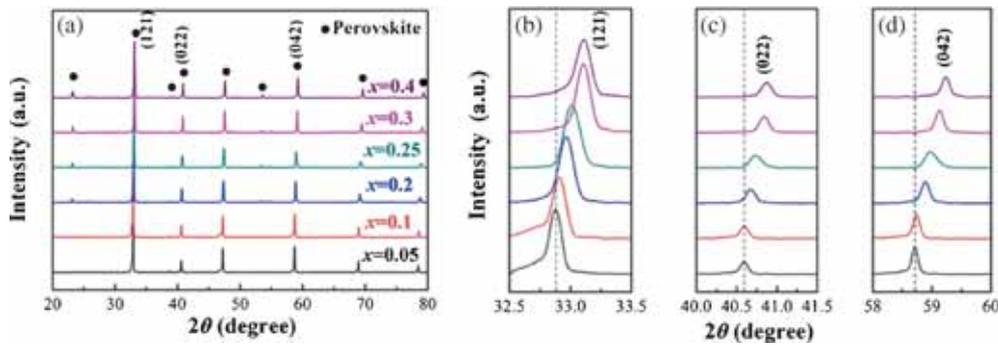


Figure 1. (a) X-ray diffraction patterns of the SCNT-SAx ($0.05 \leq x \leq 0.4$) specimens sintered at 1480°C for 4 h and the magnified figures of (b) the (121) peak, (c) (022) peak and (d) (042) peak.

Table 1. The lattice parameters, unit cell volume, octahedral distortion and τ_f value of SCNT-SAx ($0.05 \leq x \leq 0.4$) ceramics sintered at 1480°C for 4 h.

Composition (x)	a (Å)	b (Å)	c (Å)	Unit cell volume (Å ³)	R _x , R _y (Å)	R _z (Å)	\bar{R} (Å)	Δ ($\times 10^{-6}$)	τ_f (ppm °C ⁻¹)
0.05	5.4455	7.7026	5.4481	228.51	3.8515	3.8513	1.807	0.6401	216.3
0.1	5.4375	7.7044	5.4430	228.02	3.8468	3.8522	1.799	0.6490	127.1
0.2	5.4261	7.6765	5.4290	226.14	3.8378	3.8382	1.782	0.6655	38.1
0.25	5.4127	7.6584	5.4197	224.66	3.8298	3.8292	1.774	0.6713	2.7
0.3	5.4093	7.6468	5.4061	223.62	3.8238	3.8234	1.766	0.6787	-15.6
0.4	5.4038	7.6371	5.3951	222.65	3.8179	3.8185	1.749	0.6997	-34.8

densities first increase and then decrease with increasing T_s . Obviously, the T_s that reached the saturation value gradually increases with increasing x -value because SmAlO_3 requires the high T_s of $\sim 1650^\circ\text{C}$ as shown in the previous report [17]. Notice that the specimen with SCNT-SA0.4 ($T_s = 1520^\circ\text{C}$) also possesses the highest relative density of 97.1%, compared with those with other compositions.

The dielectric constants (ϵ_r) of SCNT-SAx ($0.05 \leq x \leq 0.4$) ceramics as a function of sintering temperature for 4 h are shown in figure 3b. As the T_s increases, the ϵ_r of all the compositions increases to a maximum value,

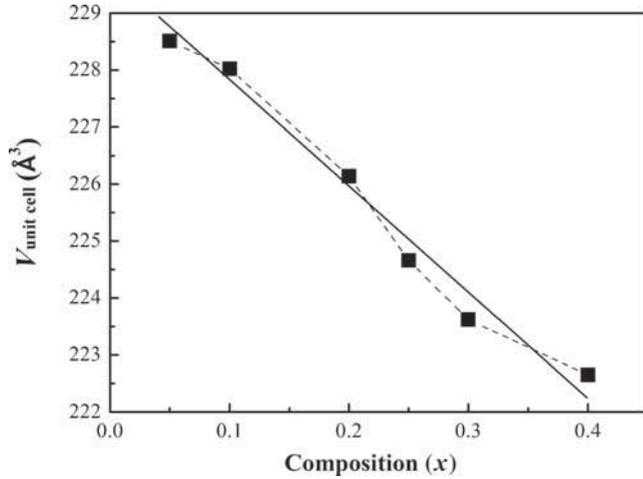


Figure 2. Unit cell volume of the SCNT-SAx ceramics sintered at 1480°C for 4 h as a function of x -value.

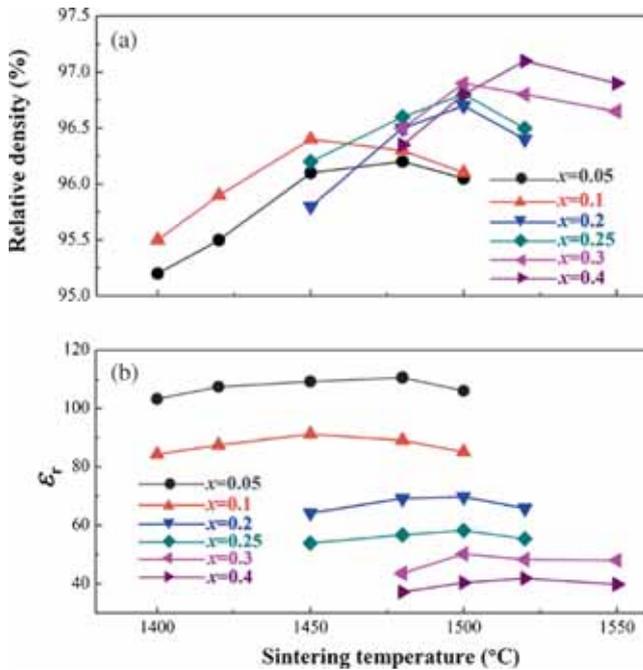


Figure 3. (a) Relative density and (b) ϵ_r of the SCNT-SAx ($0.05 \leq x \leq 0.4$) ceramics as functions of various sintering temperatures for 4 h.

corresponding to the optimum densification temperature, and decreases thereafter. The variation of ϵ_r is consistent with that of the densities. As expected, a maximum ϵ_r value of 58.3 can be obtained for the specimen using SCNT-SA0.25 sintered at 1500°C for 4 h; meanwhile, the specimen's relative density also reaches a peak value ($\sim 96.8\%$). On the other hand, in addition to the relative density, the variance in ϵ_r can be attributed to the change in dielectric polarizability. With the increase in the Sm substitution for (Sr, Ca, Nd) site and the Al in place of Ti site, the dielectric polarizability calculated with additivity rule for SCNT-SAx ($0.05 \leq x \leq 0.4$) ceramics slowly decreases due to the smaller dielectric polarizability of SmAlO_3 (11.56 \AA^3) than that of $(\text{Sr}_{0.3}\text{Ca}_{0.427}\text{Nd}_{0.182})\text{TiO}_3$ (12.49 \AA^3) [21]. Thus, for the samples sintered at 1480°C for 4 h, the ϵ_r decreases from 110.6 to 37.3. This result is identical to the change of previous reports of $(1-x)\text{Ca}_{0.85}\text{Nd}_{0.1}\text{TiO}_{3-x}\text{LnAlO}_3$ ($\text{Ln} = \text{Sm, Er and Dy}$) ceramic systems [22].

Figure 4 shows the room-temperature Qf values of the SCNT-SAx ceramics sintered at 1480°C for 4 h as functions of x -value. In the figure, the Qf value shows a monotonic increase with a rise of SmAlO_3 content. This can be explained by the fact that the SCNT ceramics possess lower Qf value ($\sim 7900 \text{ GHz}$) [16] than that of SA ceramics ($\sim 65000 \text{ GHz}$) [17], which leads to increasing Qf value of SCNT-SAx ceramics with increasing x -value. Moreover, in general, Qf value of the specimens is also dependent on secondary phase, grain size and density [23,24]. In these ceramic systems, the effects of secondary phase can be neglected because the secondary phase is not detected in the composition range from $x = 0.05$ to 0.4, as confirmed in figure 1. Therefore, as a function of the x -value, Qf value is most likely controlled by the relative density and grain size. For example, figure 5 shows the room-temperature Qf values for the SCNT-SAx ($x = 0.25$) specimens sintered at different sintering temperatures for 4 h. It is shown in this figure that the Qf value increases from 16050 GHz (at 4.77 GHz) to 18800 GHz (at 4.65 GHz) as the T_s increases from 1450 to 1500°C , then decreases up to 16270 GHz (at 4.81 GHz) at

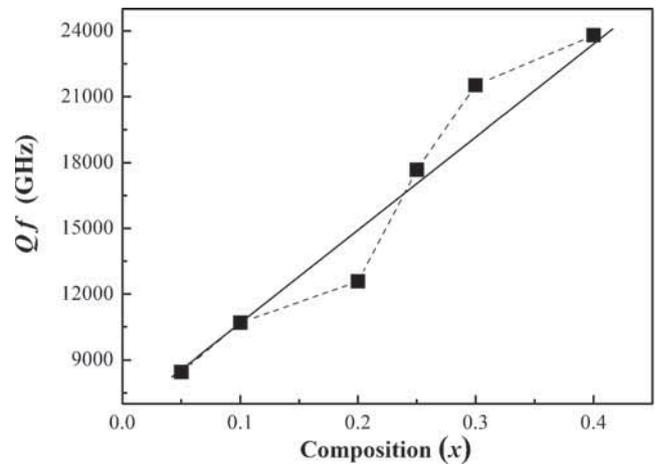


Figure 4. The Qf values of SCNT-SAx ceramics sintered at 1480°C for 4 h as functions of x -value.

$T_s = 1520^\circ\text{C}$. This is consistent with the variation of the relative density, and the higher density means lower porosity, as shown in figure 3a. Furthermore, the typical microstructures of BEIs (back-scattered electron images) for the SCNT-SAx ($x = 0.25$) ceramics sintered at 1450 – 1520°C for 4 h in air are shown in figure 6. As shown in figure 6a, a certain amount of small grains of 2 – $3\ \mu\text{m}$ size are observed at $T_s = 1450^\circ\text{C}$. As the T_s increases, a well-developed and uniform microstructure can be achieved by sintering the specimen at 1500°C (see figure 6c). However, T_s further increasing to 1520°C results in a small number of large grains, as illustrated in figure 6d, which also means that the Qf values of the SCNT-SAx ceramics are largely dependent on the relative density and grain size of the ceramics.

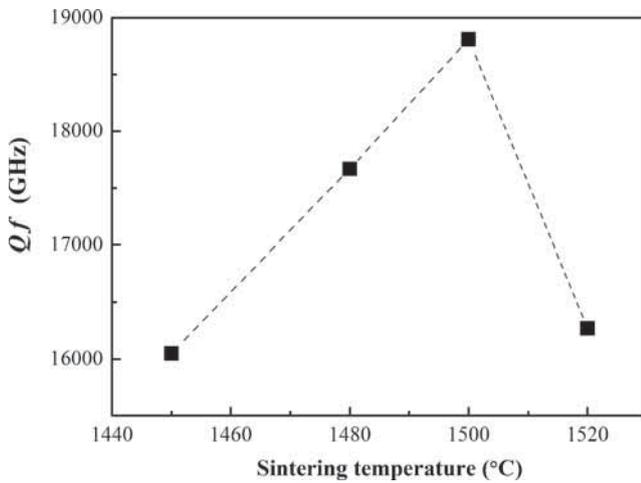


Figure 5. The Qf values of SCNT-SAx ($x = 0.25$) ceramics as functions of various sintering temperatures for 4 h.

From the lattice parameters of orthorhombic perovskite-like structure, the individual bond length of BO_6 octahedra can be obtained as shown in the following equations [20]:

$$R_x = R_y = \frac{\sqrt{a^2 + c^2}}{2}, \quad (2)$$

$$R_z = \frac{b}{2}, \quad (3)$$

where R_x , R_y and R_z are the individual bond length along x -, y - and z -axes in the single BO_6 octahedra, and a , b and c are the lattice parameters in ABO_3 perovskites, respectively. In addition, the octahedral distortion (Δ) can be expected from the individual bond length of BO_6 octahedra [20]:

$$\Delta = \frac{1}{6} \sum \left\{ \frac{R_i - \bar{R}}{\bar{R}} \right\}^2, \quad (4)$$

where R_i is the individual bond length and \bar{R} is the average bond length of BO_6 octahedral. For the SCNT-SAx ($0.05 \leq x \leq 0.4$) ceramics sintered at 1480°C for 4 h, the octahedral distortion obtained from equations (2)–(4) and τ_f values measured by using equation (1) are summarized in table 1. Besides, the \bar{R} is calculated according to the bond-valence parameters (table 1) [25]. It has been reported that the τ_f values are closely related to the structural characteristics of BO_6 oxygen octahedra in ABO_3 perovskite [26]. With an increase in the degree of oxygen octahedral tilting, the restoring force for the tilting recovery increases, which leads to a weakening of the rattling effect. As shown in figure 7, τ_f value is decreased from 216.3 to $-34.8\ \text{ppm}\ ^\circ\text{C}^{-1}$ with increasing x -value. Therefore, τ_f of perovskite compound can be evaluated and predicted by the degree of octahedral

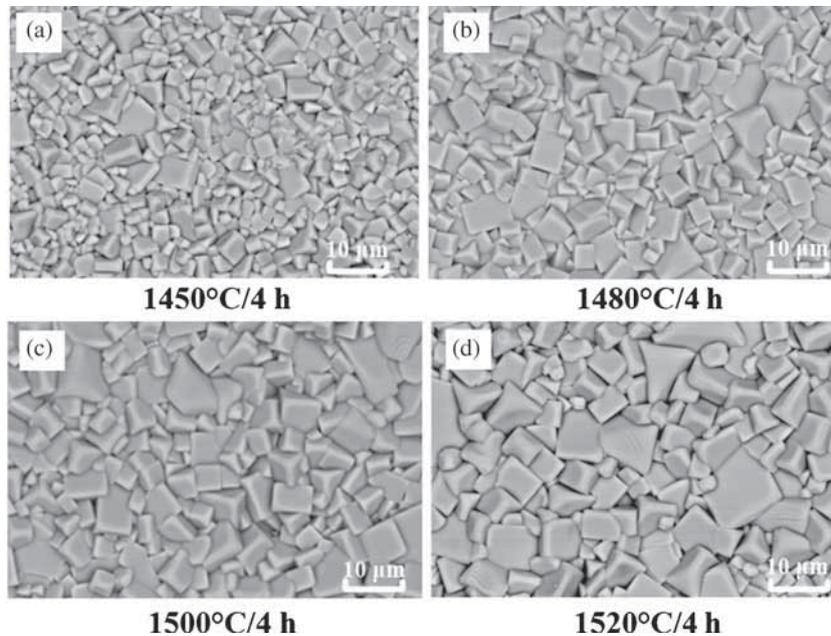


Figure 6. Back-scattered electron images of as-sintered surfaces of the SCNT-SAx ($x = 0.25$) ceramics at (a) 1450°C , (b) 1480°C , (c) 1500°C and (d) 1520°C for 4 h.

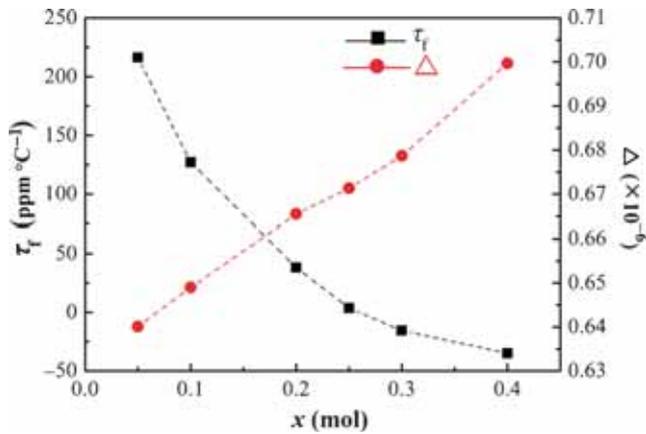


Figure 7. Octahedral distortion and τ_f values of the SCNT-SAx ceramics sintered at 1480°C for 4 h as functions of x -value.

distortions if the perovskite compound has the tilted oxygen octahedral [26].

4. Conclusion

The crystal structures and microwave dielectric properties of $(1-x)(\text{Sr}_{0.3}\text{Ca}_{0.427}\text{Nd}_{0.182})\text{TiO}_{3-x}\text{SmAlO}_3$ ceramics ($0.05 \leq x \leq 0.4$) have been investigated in this paper. The XRD results show that a single phase of orthorhombic perovskite structure is detected with the compositional range of $x = 0.05-0.4$. Dielectric constant (ϵ_r) decreases with increasing x due to the smaller dielectric polarizability of SmAlO_3 than that of $(\text{Sr}_{0.3}\text{Ca}_{0.427}\text{Nd}_{0.182})\text{TiO}_3$. The Qf values of the specimens are strongly dependent on grain size and density. Furthermore, the τ_f values can be adjusted by controlling the degree of octahedral distortions of the perovskite compound. Optimized microwave dielectric properties with $\epsilon_r \sim 58.3$, $Qf \sim 18800$ GHz (at 4.65 GHz) and $\tau_f \sim 2.3$ ppm °C⁻¹ can be obtained for the SCNT-SAx ($x = 0.25$) ceramics after being sintered at 1500°C for 4 h.

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