



Influence of rare earth ion doping on the dielectric properties of $\text{CaTiO}_3\text{-SmAlO}_3$ ceramics

Yang Hu*

Lam Research Corporation, Fremont, CA 94538, USA

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Abstract

Rare earth ion (Nd, Sm, La and Ce) doped $\text{CaTiO}_3\text{-SmAlO}_3$ ceramics were obtained from corresponding oxides by thermal decomposition method and sintering at different temperatures up to 1370°C . The microstructure, densification and dielectric properties were systematically studied. The relationship between microstructure and dielectric properties was also correlated to understand the key contributor which improves quality factor. Relative dielectric constant of $\epsilon_r \approx 39.3$ and the highest quality factor $Q \times f = 49430\text{ GHz}$ with small temperature coefficient τ_f of -9.4 ppm/K were obtained for the $\text{CaTiO}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$ sample doped with 1.5 at.% Ce.

Keywords: $\text{CaTiO}_3\text{-SmAlO}_3$, microstructure, dielectric properties, energy storage

I. Introduction

The demand for a smaller dielectric resonator with superior frequency selectivity and temperature stability has increased due to the fast development of the wireless communication industry and energy storage applications. However, the early dielectric resonator has very large volume and cannot be applied to the microwave integrated circuits. The fast growth of wireless communication industry drives the demand for smaller dielectric resonators with high quality factor and stable temperature performance [1–3]. Recently, dielectric ceramics have attracted great interests due to their superior performance, including high dielectric constant ϵ_r , high quality factor $Q \times f$ and low temperature coefficient τ_f . Among all the dielectric ceramics, CaTiO_3 system has gained lots of interest due to their wide range of potential applications [4–7].

The typical perovskite CaTiO_3 has a distorted orthorhombic structure and exhibits high dielectric constant ($\epsilon_r > 170$), a moderate quality factor $Q \times f \sim 3600\text{ GHz}$ and high positive temperature coefficient $\tau_f > 800\text{ ppm/K}$ [5]. Obviously, the low quality factor and high temperature coefficient of a single pure CaTiO_3

ceramic makes it difficult to meet the demands of actual production. To lower the high temperature coefficient and increase the quality factor, the rare earth aluminates such as LaAlO_3 , NdAlO_3 and SmAlO_3 are often added to CaTiO_3 to create a solid solution $\text{CaTiO}_3\text{-LnAlO}_3$ ($\text{Ln} = \text{La}, \text{Nd}$ and Sm) [4–6, 8–12]. According to earlier studies, $\text{CaTiO}_3\text{-LnAlO}_3$ ceramics perform exceptionally well in terms of high permittivity, high quality factor and small or near zero temperature coefficient. Suvorov *et al.* [13] investigated dielectric behaviour of $\text{CaTiO}_3\text{-NdAlO}_3$, $\text{CaTiO}_3\text{-LaAlO}_3$ and $\text{CaTiO}_3\text{-SmAlO}_3$ solid solutions and confirmed that $0.65\text{CaTiO}_3\text{-}0.35\text{SmAlO}_3$ ceramics had dielectric constant $\epsilon_r \approx 41$, quality factor $Q \times f \approx 42000\text{ GHz}$ and temperature coefficient $\tau_f \approx 18\text{ ppm/K}$. In addition, it has been shown that $0.7\text{CaTiO}_3\text{-}0.3\text{NdAlO}_3$ specimens also displayed high dielectric performance of $\epsilon_r \approx 45\text{--}47$ and $Q \times f \approx 38000\text{ GHz}$ [5]. Recently, $(1-x)\text{CaTiO}_3\text{-}x\text{La}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$ solid solutions were prepared and achieved $\epsilon_r \approx 23.65$, $Q \times f \approx 33517\text{ GHz}$ [14]. Fan *et al.* [15] studied dense $(1-x)\text{La}[\text{Al}_{0.9}(\text{Mg}_{0.5}\text{Ti}_{0.5})_{0.1}]\text{O}_3\text{-}x\text{CaTiO}_3$ ceramics. When $x = 0.65$, the temperature coefficient is near zero. The optimal microwave dielectric performance was $\epsilon_r \approx 44.6$, $Q \times f \approx 32057\text{ GHz}$. Zhou *et al.* [16] studied $0.695\text{CaTiO}_3\text{-}0.305\text{SmAlO}_3 + x\text{wt.}\% \text{ CeO}_2$ ($x = 0, 0.5, 1.0, 1.5$) ceramics. The addition of CeO_2 effectively improves the sintering be-

*Corresponding authors: tel: +1 510 731 8199,
e-mail: yang.hu@lamresearch.com;
hu_yang1990@hotmail.com

haviour. At $x = 0.5$ wt.%, the material exhibits the best microwave dielectric properties with $\epsilon_r \approx 43.9$ and $Q \times f \approx 48779$ GHz.

In this work, $0.65\text{CaTiO}_3\text{-}0.35\text{Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$ was doped with different rare earth elements (Nd, Sm, La and Ce) to enhance the quality factor and minimize temperature coefficient. The microstructure and its correlation with dielectric performance were systematically studied. The improved quality factor of 49430 GHz and a near zero temperature coefficient of -9.4 ppm/K with Ce doping were observed.

II. Experimental

In this work $\text{CaTi}_{1-x}\text{R}_x\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$ (CT-SNA) systems were investigated, where R represents doping atoms (i.e. Nd, Sm, La and Ce) and x is the doping concentration (Table 1). The doped samples were fabricated by precursor thermal decomposition method. Firstly, CaCO_3 , TiO_2 and rare earth oxide (Sm_2O_3 , Nd_2O_3 , La_2O_3 , CeO_2) with purity $>99\%$ were mechanically milled with ZrO_2 balls in deionized water for 6 h. In the separate batch, Sm_2O_3 , Al_2O_3 and Nd_2O_3 with purity $>99\%$ were also mechanical milled with ZrO_2 balls in deionized water for 6 h. All precursor materials were provided from Wuxi Xishenghuilong Company, China.

Table 1. $\text{CaTi}_{1-x}\text{R}_x\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$ (R = Nd, Sm, La, Ce) sample name and molecular formula

Sample name	Molecular formula
CT1-1	$\text{CaTi}_{0.995}\text{Nd}_{0.005}\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$
CT1-2	$\text{CaTi}_{0.99}\text{Nd}_{0.01}\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$
CT1-3	$\text{CaTi}_{0.985}\text{Nd}_{0.015}\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$
CT2-1	$\text{CaTi}_{0.995}\text{Sm}_{0.005}\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$
CT2-2	$\text{CaTi}_{0.99}\text{Sm}_{0.01}\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$
CT2-3	$\text{CaTi}_{0.985}\text{Sm}_{0.015}\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$
CT3-1	$\text{CaTi}_{0.995}\text{La}_{0.005}\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$
CT3-2	$\text{CaTi}_{0.99}\text{La}_{0.01}\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$
CT3-3	$\text{CaTi}_{0.985}\text{La}_{0.015}\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$
CT4-1	$\text{CaTi}_{0.995}\text{Ce}_{0.005}\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$
CT4-2	$\text{CaTi}_{0.99}\text{Ce}_{0.01}\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$
CT4-3	$\text{CaTi}_{0.985}\text{Ce}_{0.015}\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$

It is well known that contamination from the milling media can affect the crystal structure, grain size and dielectric properties. Contamination can also occur from the milling atmosphere, particularly if the milling is carried out in air. Atmospheric contaminants such as moisture can react with the powder during the milling process, leading to changes in the microstructure and dielectric properties. Thus, to mitigate the impact of contamination from mechanical ball milling, high purity milling media and ZrO_2 balls were used, too long milling time was avoided and lower ball-to-powder ratio was selected. Several measurements by electron dispersion spectroscopy (EDS) were taken to confirm low contamination of the powders during milling process.

After drying, two powders were mixed and calcined at 950°C for 3 h. The calcined powders were mixed with 5 wt.% PVA (polyvinyl alcohol) binder and uniaxially pressed into disks with diameter of 10 mm and thickness of 6 mm under the pressure of 200 MPa. The obtained ceramic disks were first heat treated using $5^\circ\text{C}/\text{min}$ to 600°C , held for 60 min and then sintered at 1370°C for 3 h. The sintering temperature was a critical factor that affects the microstructure and dielectric properties of the prepared materials. Thus, experiments with different sintering temperatures for the doped $\text{CaTiO}_3\text{-SmAlO}_3$ ceramics were conducted to find optimal sintering conditions.

Two different sintering temperatures (1310 and 1370°C) were examined. The sample $\text{CaTiO}_3\text{-SmAlO}_3$ sintered at 1310°C contains larger amount of pores, indicating that the temperature is not high enough to fully densify the materials. Conversely, at 1370°C the sample was fully densified and very few pores were detected. In addition, the sample sintered at 1310°C had the dielectric constant and $Q \times f$ of 39.07 and 20976 GHz, respectively. On the other hand, for the sample sintered at 1370°C , the dielectric constant was 44.50 and $Q \times f$ was 37756 GHz. Two additional sintering temperatures (i.e. 1350 and 1360°C) were checked, and it was observed that the dielectric constant and $Q \times f$ increase and stabilize at around 1370°C . Therefore, 1370°C was selected as optimal sintering temperature for the prepared materials.

Density of the sintered samples was measured by the Archimedes method. X-ray diffraction (D/Max-2500, Rigaku, Tokyo, Japan) was used to characterize the crystal structures. Microstructure was characterized by scanning electron microscopy (SEM, JSM-6301F, JEOL, Tokyo, Japan) and Raman spectroscopy (HR800, Horiba Jobin Yvon, Villeneuve D'ascq, France). Chemical composition of the sintered samples was analysed by electron dispersion spectroscopy (EDS) attached to SEM instrument. The dielectric properties were measured using precision impedance analyser (HP8720ES, Hewlett-Packard, Santa Rosa, CA). The dielectric constant was measured using Hakki-Coleman method and temperature coefficient was calculated by collecting resonance frequency at different temperatures.

III. Results and discussion

Figure 1 shows XRD spectra of all samples. Strong peaks of perovskite phase, such as (121), (022), (040) and (004), are clearly visible in all spectra. Only the CT1-1 sample doped with 0.5 at.% Nd has a small amount of a secondary $\text{Ca}_7\text{Nd}_3\text{Ti}_4\text{O}_{19.5}$ phase with XRD peaks corresponding to $(1\bar{2}0)$ (120), $(4\bar{1}1)$ and (311) planes.

The lattice constant and cell volume based on XRD data were calculated and the results are shown in Table 2. With the increase of Nd-doping concentration (the CT1-1, CT1-2 and CT1-3 samples) the lattice constant also increases. This can be attributed to the higher ionic

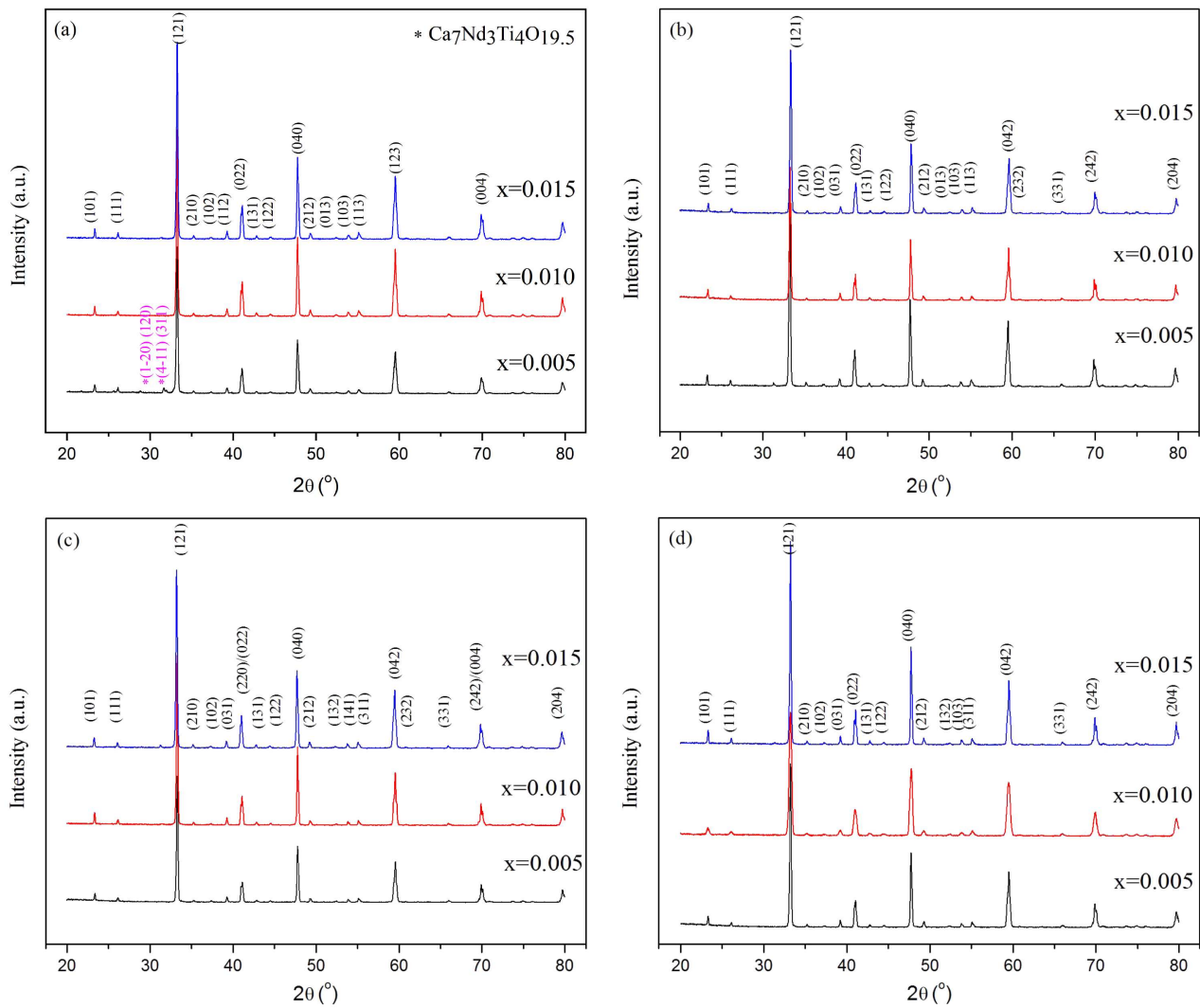


Figure 1. XRD spectra of: a) $\text{CaTi}_{1-x}\text{Nd}_x\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$ (secondary phase $\text{Ca}_7\text{Nd}_3\text{Ti}_4\text{O}_{19.5}$ diffraction peaks are marked in pink colour with * mark), b) $\text{CaTi}_{1-x}\text{Sm}_x\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$, c) $\text{CaTi}_{1-x}\text{La}_x\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$ and d) $\text{CaTi}_{1-x}\text{Ce}_x\text{O}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$ (where $x = 0.005, 0.010, 0.015$)

Table 2. Cell volume, theoretical density and relative density of sintered $0.65\text{CaTi}_{1-x}\text{R}_x\text{O}_3\text{-}0.35\text{Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$ ($\text{R} = \text{Nd, Sm, La, Ce}$) samples

Sample	$V_m [\text{\AA}^3]$	XRD volume mass density $[\text{g}/\text{cm}^3]$	Measured sample density $[\text{g}/\text{cm}^3]$	Relative density [%TD]
CT1-1	220.72	5.0332	5.00	99.3
CT1-2	221.00	5.0362	4.95	98.3
CT1-3	221.15	5.0422	4.98	98.8
CT2-1	220.38	5.0415	4.95	98.1
CT2-2	222.72	4.9985	4.95	99.0
CT2-3	220.15	5.0669	5.02	99.1
CT3-1	221.15	5.0228	4.93	98.2
CT3-2	220.86	5.0383	4.93	97.8
CT3-3	221.43	5.0343	4.99	99.2
CT4-1	221.11	5.0239	4.92	98.0
CT4-2	223.78	4.9728	4.91	98.7
CT4-3	221.16	5.0407	4.96	98.4

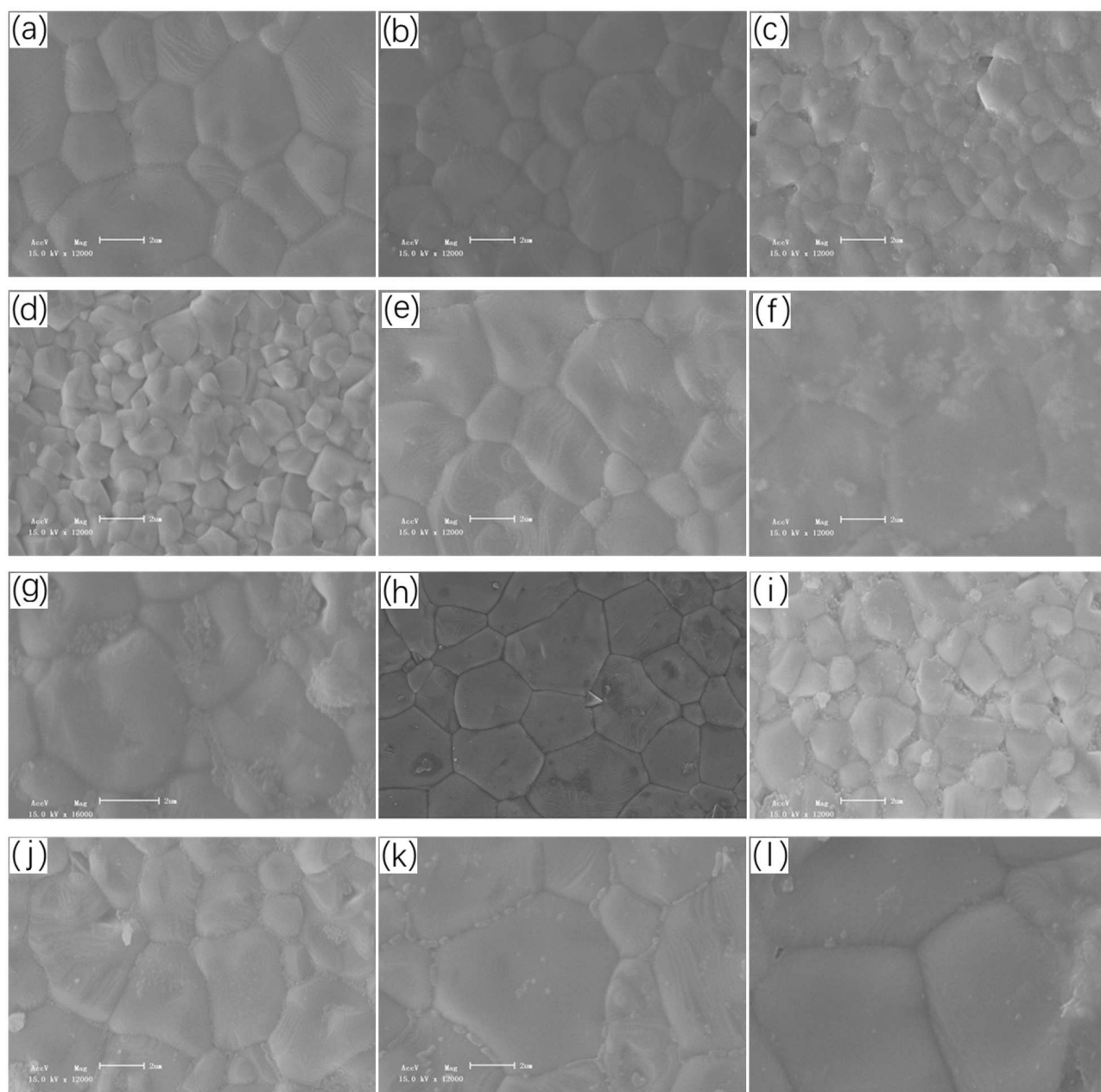


Figure 2. SEM images of: (a-c) Nd-doped CT-SNA (d-f) Sm-doped CT-SNA, (g-i) La-doped CT-SNA and (j-l) Ce-CT-SNA samples with different doping concentrations (0.005, 0.010, 0.015)

radius of Nd ($0.983 \text{ \AA}$) in comparison to Ti ionic radius.

The sample density was measured by the Archimedes method and compared with density calculated from X-ray diffraction. The relative sample density was calculated by the ratio of measured sample density vs. XRD volume mass density. All samples have a relative density $>97\% \text{TD}$ which shows that the sample is highly dense after sintering. The La-doped and Ce-doped samples have somewhat lower relative density (Table 2) and the existence of a small amount of pores is confirmed in corresponding SEM images (Fig. 2). On the other hand, improved sinterability was obtained by Sm-doping. With the increase of Nd-doping concentration, the density and grain size are reduced. Similar behaviour was visible for the La-doped samples. In addition,

doping with Sm and Ce causes the considerable grain growth (Fig. 2).

Figure 3 and Table 3 show the quality factor, dielectric constant and temperature coefficient of the samples with different doping concentrations of Nd, Sm, La and Ce. The highest quality factor $Q \times f$ of 49430 GHz with a small temperature coefficient (-9.4 ppm/K) was observed for the CT-SNA doped with $1.5 \text{ at.}\% \text{ Ce}$ (Fig. 3). This could be related to sample microstructure characterized by high density and coarse grain size.

To further understand why higher Ce doping concentration gives high quality factor and its correlation with the structure of solid solution, Raman spectroscopy was carried out as shown in Fig. 4d. Since there are two or more cations at the B-site of perovskite structure, it is of

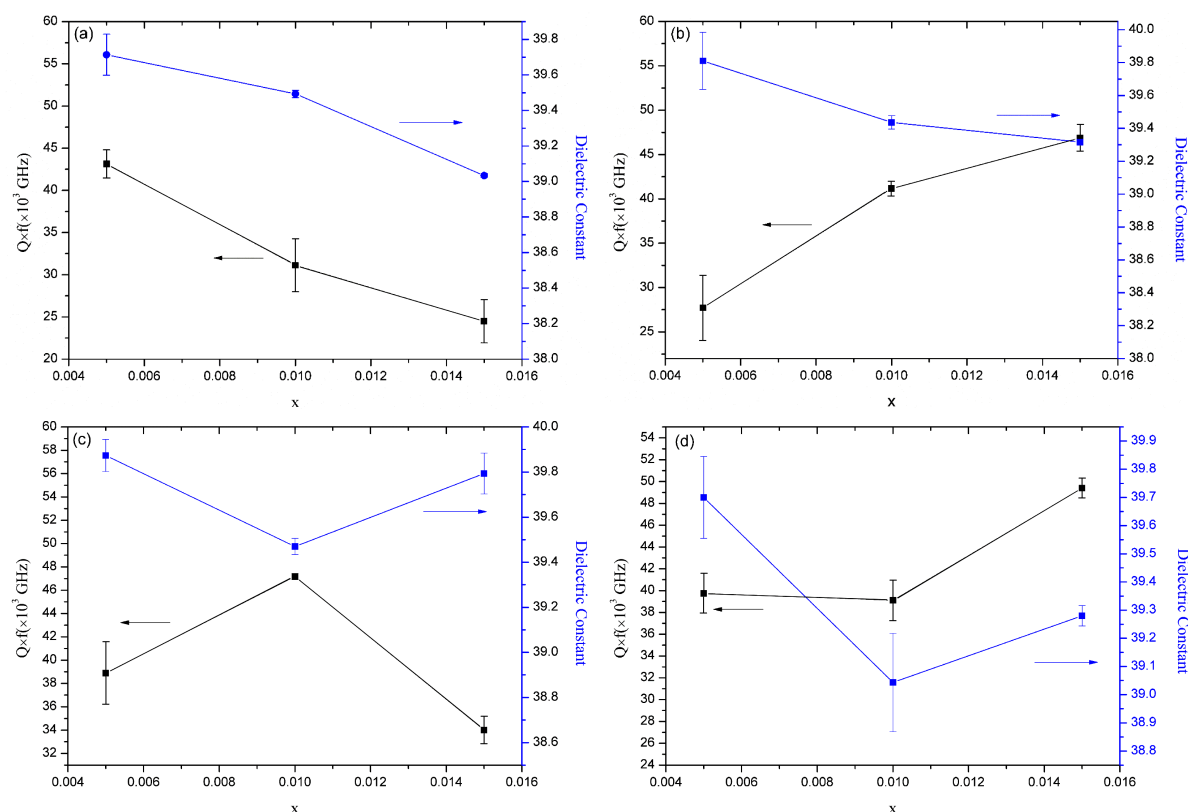


Figure 3. Dielectric constant and quality factor $Q \times f$ of: a) Nd-doped CT-SNA, b) Sm-doped CT-SNA, c) La-doped CT-SNA and d) Ce-doped CT-SNA samples (black and blue data points correspond to quality factor and dielectric constant, respectively)

Table 3. $0.65\text{CaTi}_{1-x}\text{R}_x\text{O}_3-0.35\text{Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$ (R = Nd, Sm, La, Ce) temperature coefficients

Sample name	Temperature coefficient, τ_f [ppm/K]
CT1-1	-3.9
CT1-2	-4.0
CT1-3	-3.6
CT2-1	-1.6
CT2-2	-2.0
CT2-3	-3.0
CT3-1	-4.5
CT3-2	-18.7
CT3-3	-10.3
CT4-1	-6.2
CT4-2	-4.5
CT4-3	-9.4

great importance to understand the ordering degree of B-site. The degree of ordering, including disordered distribution, short-range ordering and long-range ordering depends mainly on size difference of B-site ions. Raman spectroscopy offers the possibility of probing the ordering degree within small volumes, as shown for perovskite structure such as CaTiO_3 and NdAlO_3 [7]. In the Raman spectra, A_{1g} peak reflects the degree of short-range ordering at B-site. In all prepared samples clear

signature of A_{1g} peak can be seen, which indicates the presence of short-range ordering, while F_{2g} peak which represents long range ordering was not observed. This also could be indication that Ce ions (as well as Nd, Sm and La ions) are incorporated in the structure by replacing the cation at B-sites. The full width at half maximum of A_{1g} peak (inset in Fig. 4d) was measured too. The full width at half maximum (FWHM) is an indication of the degree of ordering at B-sites. Smaller FWHM means better ordering which will result in higher $Q \times f$ value. The observed decrease of FWHM for the sample with 1.5 at.% Ce (Fig. 4d) is consistent with the measurement of $Q \times f$ (Fig. 3d) and confirmed that Ce-doping helps to increase the quality factor.

The sintering performance of the CT-SNA system improves after the doping with small amounts of Nd (i.e. 5 at.%) and relative high quality factor was obtained. However, the density and quality factor decrease with the increase of Nd content. Thus, it is not advisable to over-dope, as it may lead to insufficient sintering and a decrease in the quality factor. In order to gain deeper insights into the relationship between a higher Nd doping concentration and the resulting worse quality factor, we conducted Raman spectroscopy, as illustrated in Fig. 4a. We also determined the FWHM of A_{1g} peak, as shown in the inset of Fig. 4a. The observed increase in FWHM for the sample with higher Nd doping aligns with the $Q \times f$ results and corroborates that higher Nd doping deteriorates the quality factor.

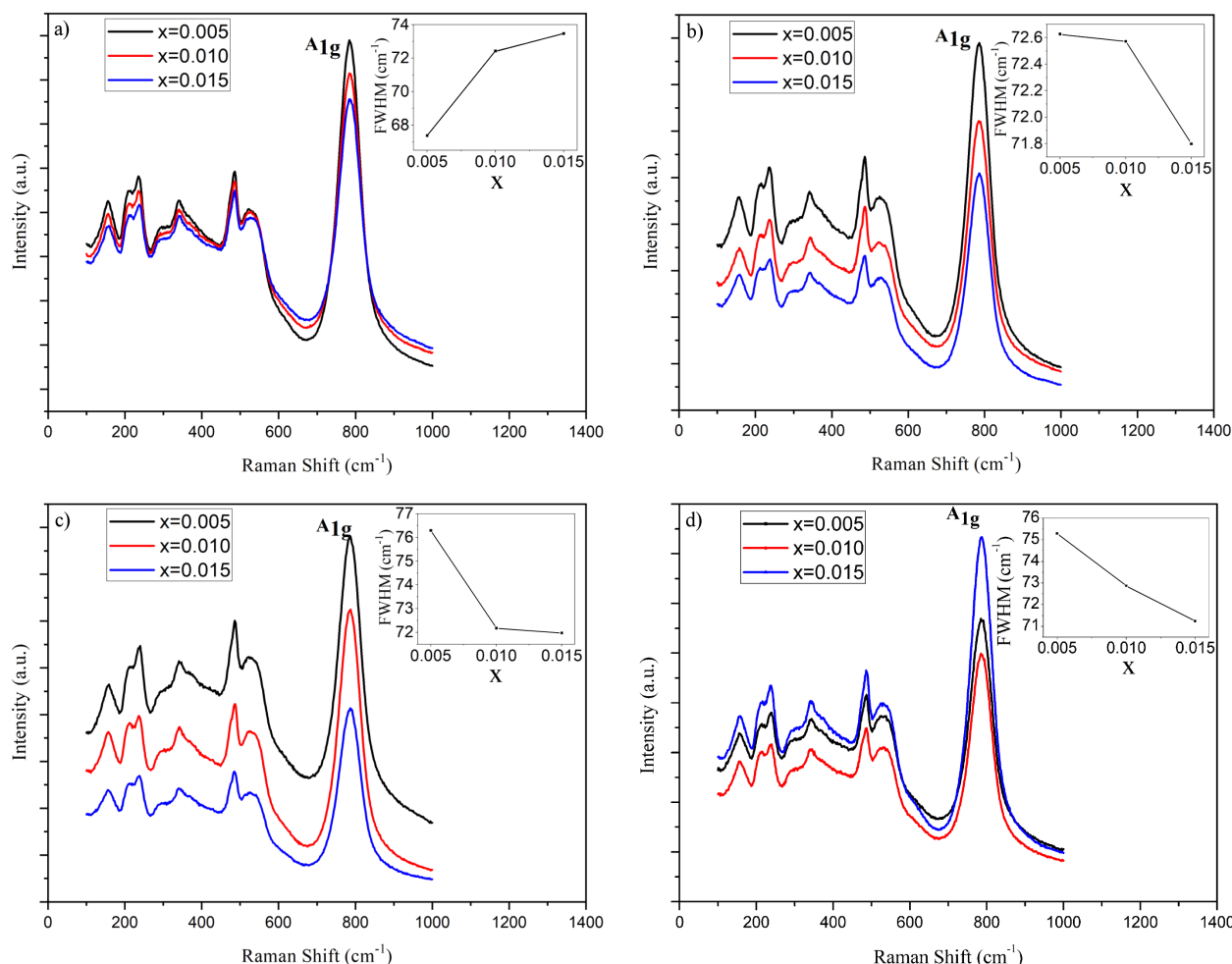


Figure 4. Raman spectra of: a) Nd-doped CT-SNA, b) Sm-doped CT-SNA, c) La-doped CT-SNA and d) Ce-doped CT-SNA samples (inset shows the FWHM for A_{1g} peak)

The Sm-doped CT2-1 sample shows relatively small grains. As a result, the quality factor is the worst among the Sm-doped samples. With the increase of Sm doping, the sintering density is higher and pores are not observed in the SEM images (Fig. 2). This is the reason for the increase of quality factor with Sm doping (Fig. 3). The optimal doping amount was 1.5 at.%, as the grain growth reduces the loss at the grain boundaries. It was also observed that the doping with Sm was beneficial for the enhancement of B-site ion ordering. These effects contributed to the improvement of the sintering performance and quality factor. The Raman spectroscopy data for Sm-doped samples are shown in Fig. 4b. The reduction in FWHM indicates a high degree of B-site ordering with higher Sm doping. This is in agreement with measured higher quality factor with higher Sm doping.

The highest quality factor of the CT-SNA system doped with La ions was obtained for 1.0 at.% La (Fig. 3). Among the La-doped samples, the CT3-2 ceramics has the best sintering performance, while the B-site ion ordering also contributed to the quality factor as shown by the Raman spectroscopy in Fig. 4c.

The effects of Ce-doping on CT-SNA are reflected on

grain structure (i.e. the grains became relatively larger, reaching about $5\ \mu\text{m}$, Fig. 2) and Raman response (i.e. A_{1g} vibrational peak is sharp and FWHM is small, Fig. 4d). These effects contributed to the improvement of the quality factor. The highest quality factor $Q \times f = 49430\ \text{GHz}$ with a small temperature coefficient was observed for the CT-SNA doped with 1.5 at.% Ce (Fig. 3).

IV. Conclusions

The impact of rare earth ions doping in the $\text{CaTiO}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$ system was investigated in detail in this article. The study focused on analysing the microstructure, densification and dielectric properties of the doped ceramics. Based on the experimental results, it was found that the introduction of Nd, Sm, La and Ce into the $\text{CaTiO}_3\text{-Sm}_{0.85}\text{Nd}_{0.15}\text{AlO}_3$ structure significantly improved its sintering performance, densification and dielectric properties. The results indicated that the doping of rare earth ions led to changes in the microstructure, such as an increase in grain size and a decrease in porosity, which in turn improved the quality factor. Specifically, the addition of Ce resulted in

the highest performance, with a dielectric constant of $\epsilon_r \approx 39.3$, a quality factor of $Q \times f \approx 49430$ GHz and a small temperature coefficient of $\tau_f \approx -9.4$ ppm/K.

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