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Microwave dielectric properties of $(1-x)Ca_{0.6}La_{0.267}TiO_3 - xCa(Sm_{0.5}Nb_{0.5})O_3$ ceramics

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Abstract

Microstructures and microwave dielectric properties of $(1-x)Ca_{0.6}La_{0.267}TiO_3 - xCa(Sm_{0.5}Nb_{0.5})O_3$ ($0.1 \le x \le 0.7$) ceramics have been investigated. A two-phase system was formed in the given compositional range. The grain morphology exhibited two different types of grain: large circular grain and small square grain. With the increasing x value, the grain morphology of the small square grain became irregular. The microwave dielectric properties were strongly related to the composition. As the x value increased from 0.1 to 0.7, the dielectric constant (ε_r) decreased from 87 to 48.3, the quality factor ($Q \times f$) value from 14390 to 8360 GHz, and the temperature coefficient of resonant frequency (τ_f) value from +130.6 to −24.8 ppm/°C, respectively. For practical application, an ε_r of 74.3, a $Q \times f$ value of 12690 GHz and a τ_f value of +8.8 ppm/°C were obtained for $0.7Ca_{0.6}La_{0.267}TiO_3-0.3Ca(Sm_{0.5}Nb_{0.5})O_3$ ceramics sintered at 1450 °C for 4 h.

Keywords: $Ca_{0.6}La_{0.267}TiO_3$; $Ca(Sm_{0.5}Nb_{0.5})O_3$; Microwave dielectric properties; Microstructure

1. Introduction

With the rapid development of the wireless communication, the demand for microwave components with combined dielectric properties has been increased. For practical application, three key properties of high quality factor ($Q \times f$), high dielectric constant (ε_r) and near-zero temperature coefficient of resonant frequency (τ_f) are required to the microwave dielectric ceramics. High dielectric constant ceramics make it possible to noticeably miniaturize passive microwave components. In the past 30 years, many efforts have been made to develop microwave ceramics with a high dielectric constant. C. Huang et al. [1] reported that the partial substitution of Ca^{2+} ions by La^{3+} ions in $CaTiO_3$ led to the formation of single phase $Ca_{1-x}La_{2x/3}TiO_3$ solid solution. Meanwhile, a decrease in ε_r, τ_f and an increase in $Q \times f$ value with the increasing x value were observed. When $x = 0.4$, $Ca_{0.6}La_{0.267}TiO_3$ ceramics showed a high ε_r of 109 and a maximum $Q \times f$ value of 17,600 GHz. However, complete suppression of the large positive τ_f (τ_f = +213 ppm/°C) to zero was not achieved.

Therefore, it should be an important issue to further adjust the τ_f value of $Ca_{0.6}La_{0.267}TiO_3$ to zero. Practically, two or more compounds having positive and negative τ_f values are used to form a solid solution or mixed phases to adjust τ_f to zero. Several ceramic systems such as $(1-x)Ca_{0.6}La_{0.267}TiO_3 - x(Li_{0.5}Nd_{0.5})TiO_3$ (ε_r = 105, $Q \times f$ = 7000 GHz, τ_f = +4.5 ppm/°C at $x = 0.4$), $(1-x)(Mg_{0.95}Co_{0.05})TiO_3 - xCa_{0.6}La_{0.267}TiO_3$ (ε_r = 21.9, $Q \times f$ = 131,000 GHz, τ_f = −15.5 ppm/°C at $x = 0.1$) and $(1-x)Ca_{0.6}La_{0.267}TiO_3 - xNd(Mg_{0.5}Ti_{0.5})O_3$ (ε_r = 49, $Q \times f$ = 13,000 GHz, τ_f = +1 ppm/°C at $x = 0.4$)with near-zero τ_f values have been developed in recent years [1–3].

In order to achieve a near-zero τ_f value, $Ca(Sm_{0.5}Nb_{0.5})O_3$ ceramics ($\varepsilon_r \sim 24.7$, $Q \times f \sim 33{,}200$ GHz, $\tau_f \sim -34.3$ ppm/°C) [4] were chosen as a τ_f compensator and added to $Ca_{0.6}La_{0.267}TiO_3$ ceramics to form a new ceramic system $(1-x)Ca_{0.6}La_{0.267}TiO_3 - xCa(Sm_{0.5}Nb_{0.5})O_3$ in this paper. Based on phase composition and the microstructure of the present ceramics, the resultant microwave dielectric properties were studied.

2. Experimental procedures

The starting materials were high-purity grade (≥99.9%) powders of $CaCO_3$, La_2O_3, TiO_2, Sm_2O_3 and Nb_2O_5. The

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powders were individually prepared according to the desired stoichiometry $Ca_{0.6}La_{0.267}TiO_3$ and $Ca(Sm_{0.5}Nb_{0.5})O_3$, and ground in ethanol for 24 h in a ball mill with zirconia balls. $Ca_{0.6}La_{0.267}TiO_3$ and $Ca(Sm_{0.5}Nb_{0.5})O_3$ powders were calcined at 1100 °C for 3 h and 1200 °C for 4 h, respectively. The calcined powders were weighed according to the composition of $(1-x)Ca_{0.6}La_{0.267}TiO_3 - xCa(Sm_{0.5}Nb_{0.5})O_3$ and remilled 24 h. After dried, these powders with 7 wt.% PVA solution as a binder were pressed into pellets with dimensions of 12 mm diameter and 6 mm thickness under a pressure of 300 MPa. These pellets were finally sintered at 1400–1550 °C for 4 h in air.

The bulk densities of the sintered pellets were measured by the Archimedes method. The crystalline phases of the ceramics were identified by using an X-ray diffractionmeter (XRD) using Cu Kα radiation (40 kV and 20 mA, XRD, D8 Advance, Bruker, Germany). The microstructural observations and analysis of the sintered surfaces were performed by using scanning electron microscopy (SEM, JEOL JSM 6490, Japan) coupled with energy dispersive spectroscopy (EDS). The dielectric constant (ε_r) and unloaded Q values at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method, as modified and improved by Courtney [5,6]. The τ_f was measured in a temperature range from 25 to 80 °C. The τ_f value was calculated by the following equation:

$$\tau_f = \frac{f_{80} - f_{25}}{f_{25} \cdot 55} \times 10^6 (\text{ppm}/^\circ\text{C}) \quad (1)$$

where f_{25} and f_{80} are the $TE_{01\delta}$ resonant frequencies at 25 and 80 °C, respectively.

3. Results and discussion

The XRD patterns of $(1-x)Ca_{0.6}La_{0.267}TiO_3 - xCa(Sm_{0.5}Nb_{0.5})O_3$ (hereafter referred to as $(1-x)$CLT $- x$CSN) ceramics with different x values are shown in Fig. 1. No second phase is detected and the pattern exhibits a two-phase system that includes CLT phase and CSN phase through the entire compositional range. With the increase of the x value in the system, the relative intensities of CLT reflection lines decrease gradually, implying that the content of CSN phase in the $(1-x)$CLT $- x$CSN ceramics increases. When the x value increases to 0.5, the main crystal phase changes from CLT to CSN phase. Table 1 lists the lattice parameters of the CLT phase. The values of a axis, b axis, c axis and unit cell volume almost do not change with the increase of CSN content as seen from Table 1. This result is similar to the $(K_{0.5x}Bi_{1-0.5x})(Mo_xV_{1-x})O_4$ ceramics reported by D. Zhou et al. [7]. The reason is that the phase composition and structure of the two end members shall not change with the different ratio between them in a stable composite system.

Table 1
Lattice parameters of the CLT phase.

x	a (Å)	b (Å)	c (Å)	V_m (Å^3)
0.1	5.53713	5.43587	7.75206	233.33
0.3	5.53785	5.43558	7.75212	233.35
0.5	5.53898	5.43332	7.75210	233.30
0.7	5.53926	5.43446	7.75208	233.36

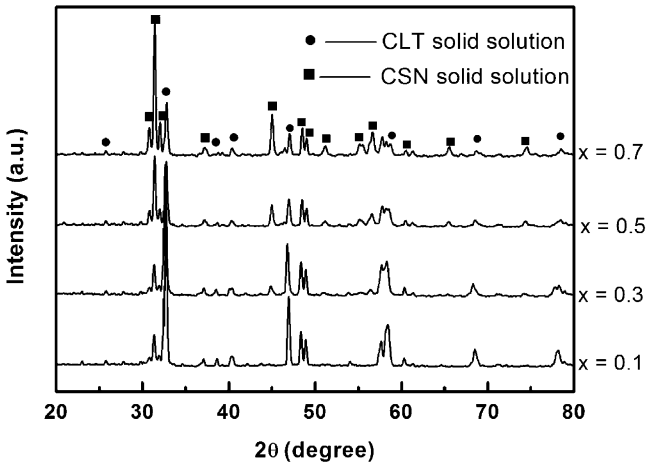

Fig. 1. XRD patterns of $(1-x)Ca_{0.6}La_{0.267}TiO_3 - xCa(Sm_{0.5}Nb_{0.5})O_3$ ceramics with different x values.

However, compared with the diffraction peaks of CLT phase reported by C. Huang et al. [1], the diffraction peaks of the CLT phase in the present composite system slightly shift to lower angles with the increasing x value, indicating that the unit cell volume is enlarged. It is mainly attributed to a larger effective radius of $(SmNb)^{4+}$ (0.799 Å) than that of Ti^{4+} (0.605 Å). This phenomenon means that a limited solid solution might be formed by element substitution between CLT phase and CSN phase.

Fig. 2 shows the variation of bulk density for the $(1-x)$CLT $- x$CSN ceramics as a function of sintering temperature. It is obviously seen that the density steadily increases first with the increase of sintering temperature and then saturates for all compositions. The density saturation with sintering temperature implies the densification. However, the densification temperature is different for different compositions.

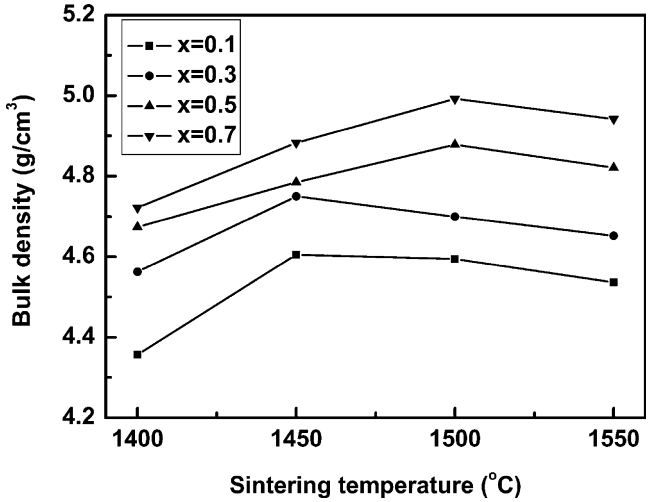

Fig. 2. Variation of bulk density for $(1-x)Ca_{0.6}La_{0.267}TiO_3 - xCa(Sm_{0.5}Nb_{0.5})O_3$ ceramics as a function of sintering temperature.

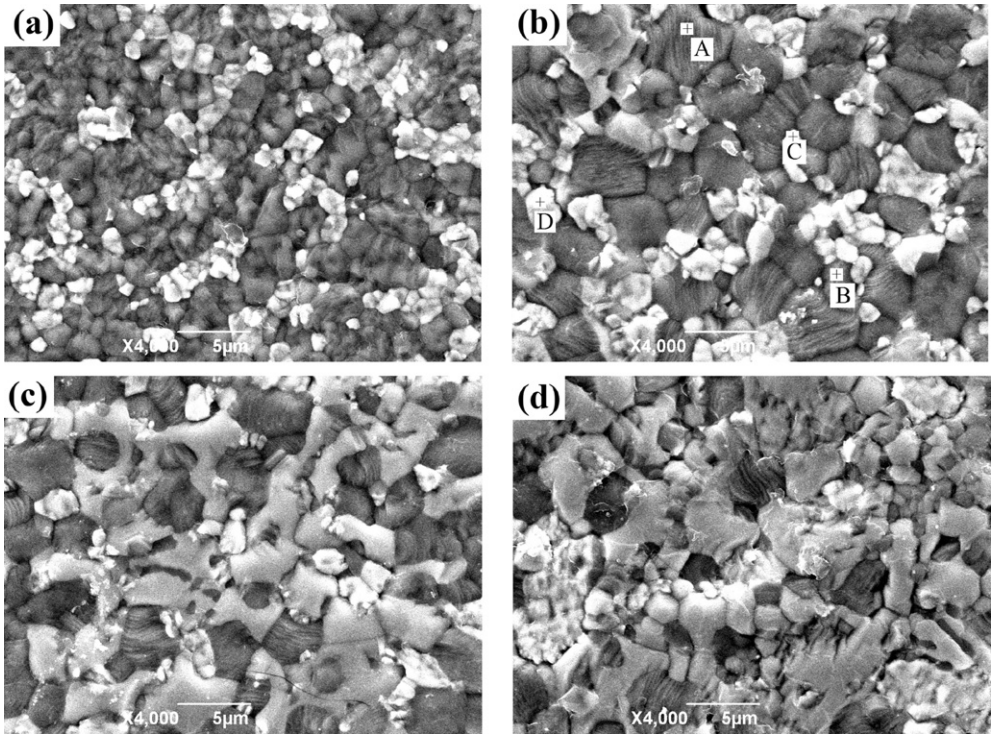

Fig. 3. SEM micrographs of $(1-x)Ca_{0.6}La_{0.267}TiO_3 - xCa(Sm_{0.5}Nb_{0.5})O_3$ ceramics sintered at 1500 °C for 4 h: (a) $x = 0.1$; (b) $x = 0.3$; (c) $x = 0.5$; (d) $x = 0.7$.

For compositions of $x = 0.1$ and 0.3, the maximum bulk density appears at about 1450 °C. In contrast, the bulk density maximum occurs at about 1500 °C for compositions with $x = 0.5$ and 0.7. These results indicate that the addition of CSN significantly retards the sintering of the system owing to its higher sintering temperature (∼1550 °C) than that of CLT(∼1400 °C) [1,4]. In addition, the bulk density increases with the increasing x value for a given sintering temperature due to the larger density (5.20 g/cm^3) of CSN ceramics than that (4.60 g/cm^3) of CLT ceramics [1,4].

The SEM micrographs of the $(1-x)$CLT $- x$CSN ceramics sintered at 1500 °C for 4 h are illustrated in Fig. 3. It can be found that the dense ceramics are obtained and few pores are observed for all compositions. There are two kinds of grains in the present ceramic system, the circular ones with bigger grain size of 3–5 μm and the square ones with smaller grain size of 0.5–4 μm. In order to identify the compositional difference between the two types of grains, the element analysis was performed by means of EDS. According to the EDS analysis showed in Table 2, the square grains such as C and D have much more Nb, Sm and La element contents than the circular grains such as A and B, but they do not contain Ti element. Associating with the XRD analysis in Fig. 1, it can be concluded that the circular and the square grains were the CLT and the CSN grains, respectively. Both of the pure $Ca_{0.6}La_{0.267}TiO_3$ and $Ca(Sm_{0.5}Nb_{0.5})O_3$ composition belong to the perovskite structure. The La and Sm have similar ionic radius and maybe some of the Sm can substitute for the La in $Ca_{0.6}La_{0.267}TiO_3$ to form a limited solid solution. Similarly, the La can also substitute for the Sm in $Ca(Sm_{0.5}Nb_{0.5})O_3$ to form another solid solution to achieve a more stable system. Combining these EDS results (shown in Table 2) with the XRD and SEM analysis of the $(1-x)$CLT $- x$CSN ceramics, the real composition might not be $(1-x)Ca_{0.6}La_{0.267}TiO_3 - xCa(Sm_{0.5}Nb_{0.5})O_3$, might be $(1-x)Ca_{0.6}(La,Sm)_{0.267}TiO_{3-x}Ca((Sm,La)_{0.5}Nb_{0.5})O_3$. Furthermore, the grain size of the CSN grain increases and the grain morphology becomes irregular with the increasing x value. This phenomenon indicates that the CLT solid solution can inhibit the grain growth of the CSN solid solution, which may affect the dielectric properties.

Table 2
EDS data of 0.7CLT-0.3CSN ceramics for spots A–D.

Spot	Atom (%)					
	Ca–K	Ti–K	Nb–L	Sm–L	La–L	O–K
A	12.70	19.18	1.47	1.67	2.41	62.57
B	12.21	21.31	1.07	0.94	2.41	62.06
C	13.11	0	10.04	6.56	4.97	65.32
D	13.94	0	9.63	7.14	3.59	65.7

Fig. 4 shows the dielectric constant (ε_r) and $Q \times f$ value of the $(1-x)$CLT $- x$CSN ceramics as a function of x value. It is clearly seen that the ε_r value decreases almost linearly with the increasing x value, which is attributed to the fact that CLT ($\varepsilon_r = 109$) has a much higher dielectric constant than CSN ($\varepsilon_r = 24.7$) does. As the x value increases from 0.1 to 0.7, the ε_r value decreases from 87 to 48.3. However, an anomalous behavior is found that the $Q \times f$ value of the $(1-x)$CLT $- x$CSN ceramics is outside the range exhibited by the end members CLT with a $Q \times f$ value 17600 GHz of and CSN with a $Q \times f$ value of 33200 GHz. With x increasing from

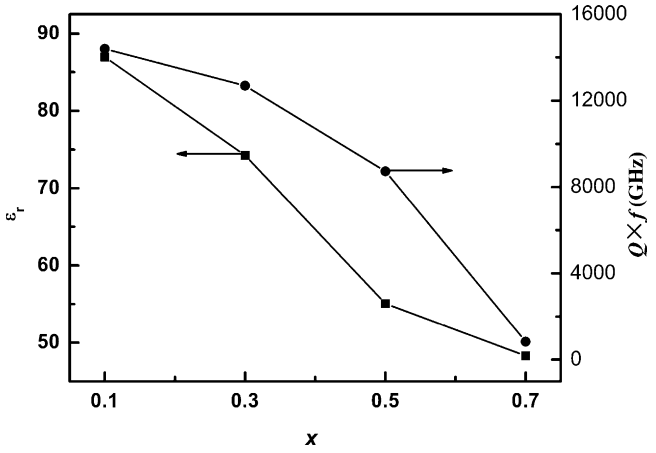

Fig. 4. Dielectric constant and $Q \times f$ value of the $(1-x)Ca_{0.6}La_{0.267}TiO_3 - x\,Ca(Sm_{0.5}Nb_{0.5})O_3$ ceramics as a function of x value.

0.1 to 0.7, the $Q \times f$ value decreases from 14390 to 8360 GHz. It is well known that many factors such as densification or porosity, microstructure and secondary phase affect microwave dielectric loss. However, the $Q \times f$ value is independent of the density for highly densified ceramics [8]. As a result, the $Q \times f$ value is mainly controlled by the microstructure in the present ceramics. As observed in Fig. 3, an irregular grain morphology appears in the ceramics, producing an increase in lattice imperfection and increasing dielectric loss. Consequently, the decrease in the $Q \times f$ value might be a result of the grain morphology.

The theoretical and measured τ_f values of the $(1-x)$CLT $- x$CSN ceramics with various x values are illustrated in Fig. 5. When the x value increases from 0.1 to 0.7, the measured τ_f value decreases from +130.6 to −24.8 ppm/°C, and the theoretical τ_f value decreases from +184 to +31.5 ppm/°C. At $x = 0.3$, a near-zero τ_f value (τ_f = +8.8 ppm/°C) was achieved for the present system. As is well known, the relationship between temperature coefficient of

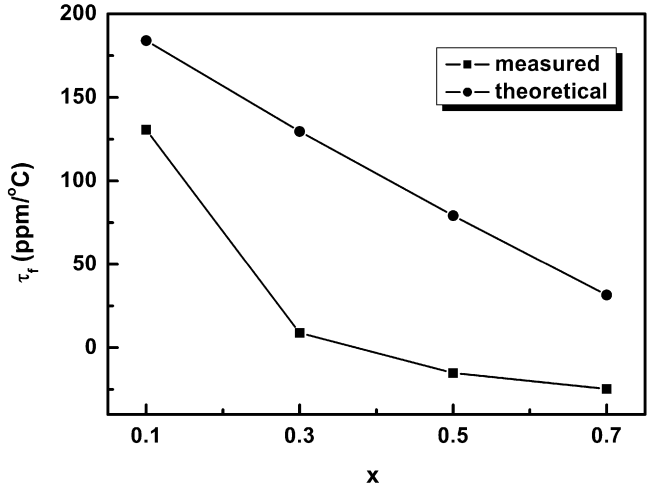

Fig. 5. Theoretical and measured τ_f values of the $(1-x)$CLT $- x$CSN ceramics with various x values.

dieletric constant (τ_ε) and τ_f is defined as the following equation [9,10]:

$$\tau_\varepsilon = \frac{1}{\varepsilon_r}\frac{d\varepsilon_r}{dT} = \frac{d(\lg \varepsilon_r)}{dT} = y_1 \frac{1}{\varepsilon_{r1}}\frac{d\varepsilon_{r1}}{dT} + y_2 \frac{1}{\varepsilon_{r2}}\frac{d\varepsilon_{r2}}{dT}$$
$$= y_1\tau_{\varepsilon_{r1}} + y_2\tau_{\varepsilon_{r2}} \quad (2)$$

where y_1 and y_2 are the volume fractions; $\tau_{\varepsilon_{r1}}$ and $\tau_{\varepsilon_{r2}}$ are the τ_ε values of the CLT and CSN ceramics, respectively. Hence, the mixing rule of the τ_f value can be described as the following:

$$\tau_f = y_1\tau_{f1} + y_2\tau_{f2} \quad (3)$$

The theoretical τ_f values of the $(1-x)$CLT $- x$CSN ceramics were calculated using Eq. (3). Comparing the measured τ_f value with the theoretical τ_f value, it is seen that the measured τ_f is much more negative, which might result from the formation of solid solution in the $(1-x)$CLT $- x$CSN ceramic system. Similar result in the Bi_2MoO_6–TiO_2 composite ceramics was reported by L. Pang et al. [9].

4. Conclusions

The microstructures and microwave dielectric properties of the two-phase system $(1-x)Ca_{0.6}La_{0.267}TiO_3 - xCa(Sm_{0.5}Nb_{0.5})O_3$ $(0.1 \le x \le 0.7)$ ceramics were investigated. The microwave dielectric properties were strongly related to the composition. The dielectric constant, $Q \times f$ value and τ_f value decreased with an increase of x value. A dielectric material with an ε_r of 74.3, a $Q \times f$ value of 12690 GHz and a τ_f value of +8.8 ppm/°C was obtained at $x = 0.3$, which is a promising candidate for communication components.

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