Microwave dielectric properties of CaO–La$_2$O$_3$–Nb$_2$O$_5$–TiO$_2$ ceramics

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Abstract A series of ceramics with a general formula Ca$_{1+x}$La$_{4-x}$Nb$_x$Ti$_{5-x}$O$_{17}$ ($0 \leq x \leq 4$) were fabricated using the solid-state ceramic route. The phase, microstructure, and microwave dielectric properties varied distinctly with composition or the value of x. X-ray diffraction results showed that the two end member phases, CaLa$_4$Ti$_5$O$_{17}$ and Ca$_5$Nb$_4$TiO$_{17}$, crystallized into single phases with orthorhombic and monoclinic crystal structure, respectively. For intermediate compounds with $x = 1$, 2, and 3, mixture phases CaLa$_4$Ti$_5$O$_{17}$ and Ca$_5$Nb$_4$TiO$_{17}$ coexisted and a trace amount of second phase was detected. The ceramics showed high ε_r in the range of 45–52, relatively high quality factors with $Q \times f$ in the range of 9,870–15,680 GHz and τ_f value in the range between -38 and -126.4 ppm/°C. τ_f of CaLa$_4$Ti$_5$O$_{17}$ can be tuned to a near-zero value by addition of suitable amount of TiO$_2$.

1 Introduction

Dielectric ceramics with general formula A$_n$B$_n$O$_{3n+2}$ have recently drawn considerable attention because of their high Curie temperatures, low dielectric loss and thermal stability [1–3], making them promising materials being used as high temperature piezoelectrics and microwave dielectrics [4–8]. The diverse properties of A$_n$B$_n$O$_{3n+2}$ are related to their unique layered structure composed of corner-shared BO$_6$ octahedra with A cations within the perovskite-like slabs, where n is the number of octahedral layers in the perovskite slab [1, 2]. Specifically, the microwave dielectric properties of such materials has been a subject of various investigations in the last years because of the excellent observed properties, which makes these materials good candidates for many practical applications, specially viewing the possibility to be used in highly miniaturized electronic devices.

More recently, several $n = 5$ members in the A$_n$B$_n$O$_{3n+2}$ series have been investigated for possible use as dielectric resonators [9–16]. Most of them exhibited favorable microwave dielectric properties, especially those in the CaO–La$_2$O$_3$–TiO$_2$–M$_2$O$_5$ (M = Nb, Ta) system. Joseph et al. [9] reported Ca$_5$Nb$_4$TiO$_{17}$ and Ca$_5$Ta$_4$TiO$_{17}$ to have $\varepsilon_r = 44.9$, $Q \times f = 17,600$ GHz and $\tau_f \sim -112.9$ ppm/°C, and $\varepsilon_r = 40.1$ $Q \times f = 16,450$ GHz and $\tau_f \sim -53.6$ ppm/°C, respectively. CaLa$_4$Ti$_5$O$_{17}$ was characterized with excellent microwave dielectric properties with a ε_r value of 55.2, a $Q \times f$ value of 17,359 GHz and a lower τ_f value of -20 ppm/°C [10]. Fei Zhao et al. [11] reported an improvement in temperature coefficient of resonant frequency and relative permittivity ($\tau_f \sim 3.7$ ppm/°C, $\varepsilon_r \sim 56.5$) with a relative lower quality factor ($Q \times f \sim 12,500$ GHz) for CaLa$_4$Ti$_5$O$_{17}$. Moreover, a great deal of emphasis has been put on the adjustment of microwave properties of these ceramics, especially the optimizing of temperature coefficient of resonant frequency [11–14]. For example, a near-zero τ_f value was achieved by partial Sr substitution for Ca in CaLa$_4$Ti$_5$O$_{17}$ without obviously deteriorating the quality

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factor [13]. Generally, there are two methods to obtain a near-zero τ_f value [17–19]: forming a solid solution or composite created of two materials, each having opposite signs of τ_f. Therefore, some perovskite-like structured materials with a general formula $Ca_{1+x}La_{4-x}Nb_xTi_{5-x}O_{17}$ ($0 \leq x \leq 4$) were prepared and their microwave dielectric properties were characterized.

2 Experimental procedure

$Ca_{5-x}La_xNb_{4-x}Ti_{1+x}O_{17}$ samples with compositions varying from $x = 0$ to $x = 4$ were synthesized by solid-state reactions of $CaCO_3$ (99.0 %), La_2O_3 (99.95 %), Nb_2O_5 (99.5 %) and TiO_2 (98.0 %). La_2O_3 and TiO_2 were dried at 900 °C to remove the moisture prior to weighing. The oxides were weighed in stoichiometric amounts and fully mixed through ball milling for 4 h. The calcination took place in air at 1,300 °C for 4 h. After calcination, the samples were thoroughly reground and mixed with a 3 wt% solution of polyvinyl alcohol (PVA) as a binder. The resultant slurries were then dried and pressed into cylindrical compacts of different thickness in the range 4–6 and 11 mm in diameter under a pressure of 100 MPa. The samples were fired at 600 °C for 4 h to remove the organic binder and then sintered in the range 1,400–1,520 °C for 4 h to approach the maximum densities. The sintered samples were typically annealed at 1,300–1,350 °C for 10 h to minimize the reduction of titanium ions.

The phase purity of the samples were performed on the well-polished ceramics using a Rigaku DMAX-RB X-ray diffractometer (XRD) with $CuK_{\alpha 1}$ (1.54059 Å) radiation over a range of $2\theta = 20$–$60°$. The apparent densities of the sintered ceramics were measured by Archimedes method. Scanning electron microscopy (SEM; JEOL JSM-5610LV) was employed to examine the microstructures of the specimens. The microwave dielectric properties were measured by the post-resonator method developed by Hakki and Coleman [20] using a network analyzer (8720ES, Agilent, USA.) and a temperature chamber (DELTA 9023, Delta Design, USA.). The temperature coefficients of resonant frequency τ_f values were measured by noting the temperature variation of the TE_{011} resonance in the temperature range 25–85 °C.

3 Results and discussion

$Ca_{1+x}La_{4-x}Ti_{5-x}Nb_xO_{17}$ ($x = 0, 1, 2, 3, 4$) ceramics were sintered at temperature range of 1,400–1,520 °C to optimize the sintering condition. Figure 1 shows the bulk densities of $Ca_{1+x}La_{4-x}Ti_{5-x}Nb_xO_{17}$ ($x = 0, 1, 2, 3, 4$) ceramics as a function of sintering temperature. For each sample, the bulk density was found to increase steadily

with increasing sintering temperature, reach a maximum and thereafter decrease slightly with further increase in temperature. Maximum densities of 5.203 g/cm^3 (95.1 %) and 4.262 g/cm^3 (97.7 %) were obtained for $CaLa_4Ti_5O_{17}$ and $Ca_5Nb_4TiO_{17}$ respectively. The optimum sintering temperature for each sample was taken as the temperature at which the maximum density was achieved. As shown in the inset of Fig. 1, the optimum sintering temperature firstly decreases remarkably from 1,520 °C for $x = 0$ to 1,420 °C for $x = 2$ and then increases to 1,480 °C for $x = 4$. It has been previously reported that the sintering temperature of a solid solution mainly depends on the refractory nature, the size relationship of the ions and the lattice vacancies, etc. [21]. The compositional dependent optimum sintering temperature may also due to the difference in the melting temperature of the oxides.

XRD patterns performed on the $Ca_{1+x}La_{4-x}Ti_{5-x}Nb_xO_{17}$ ceramics sintered at their optimum temperatures are shown in Fig. 2. Within the limit of XRD analysis, all the observed peaks of the end member with $x = 0$ could be indexed according to the orthorhombic $CaLa_4Ti_5O_{17}$ with *Pnnm* symmetry (JCPDS No. 27-1059) except for the difference in relative intensity. Similarly, the end member with $x = 4$, $Ca_5TiNb_4O_{17}$, crystallized into a single phase, being isostructural with $Ca_5Nb_5O_{17}$ (JCPDS No. 51-0412). When $x = 1$, the orthorhombic reflections according to $CaLa_4Ti_5O_{17}$ phase dominated the diffraction pattern but for $x = 3$ the major phase was $Ca_5TiNb_4O_{17}$ with monoclinic structure. With reference to Fig. 2 (b), we can see that for sample with $x = 2$ both $CaLa_4Ti_5O_{17}$ and $Ca_5TiNb_4O_{17}$ were observed. Furthermore, apparent secondary phase(s) was detected in the XRD patterns of sample with $x = 2$, as indicated by hollow squares in Fig. 2.

It can be also seen in Fig. 2 that the diffraction peaks of $CaLa_4Ti_5O_{17}$ phase shifted towards higher angle region

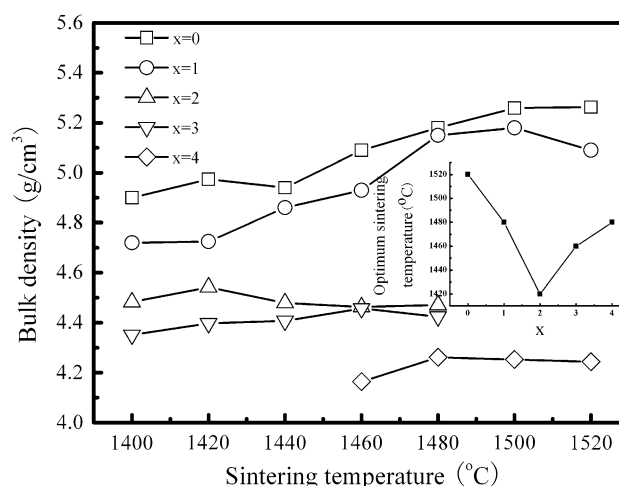**Fig. 1** The bulk densities of $Ca_{1+x}La_{4-x}Ti_{5-x}Nb_xO_{17}$ (x = 0, 1, 2, 3, 4) ceramics as a function of sintering temperature

Fig. 2 a XRD patterns performed on the $Ca_{1+x}La_{4-x}Ti_{5-x}Nb_xO_{17}$ ceramics sintered at their optimum temperatures and b detailed XRD patterns between 26° and 34°: (filled square) $CaLa_4Ti_5O_{17}$ phase; (filled inverted triangle) $Ca_5Nb_4TiO_{17}$ phase; (open square) unknown second phases
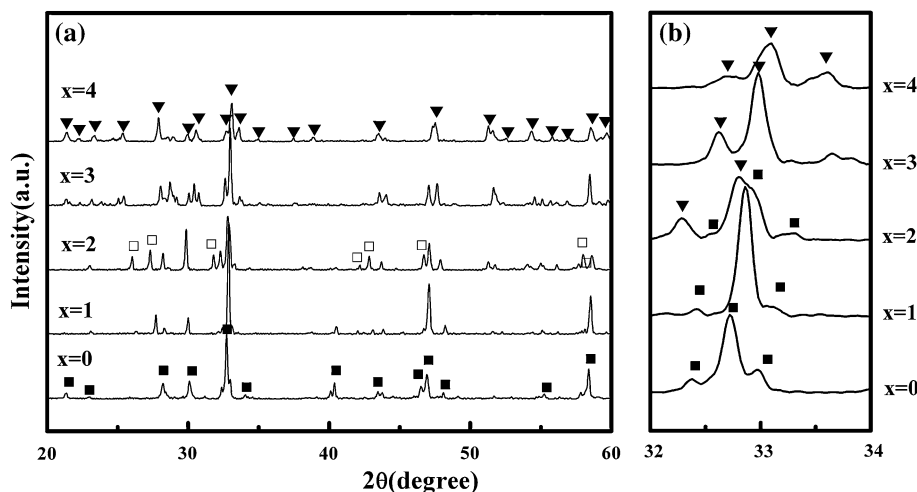
with increasing x from 0 to 2, while a shift of diffraction peaks of $Ca_5TiNb_4O_{17}$ phase towards lower angle region occurred when x decreased from 4 to 2. This led to the overlap of diffraction peaks of $CaLa_4Ti_5O_{17}$ and $Ca_5TiNb_4O_{17}$ phase and explained the broadening XRD peaks in the vicinity of $2\theta \sim 33°$ of sample with $x = 2$. The shift of XRD peaks to higher angle region with increasing Ca/Nb contents indicates the lattice contraction, which may be due to the different ionic radii of Ca^{2+} (1.34 Å) and Nb^{5+} (0.64 Å) compared with those of La^{3+} (1.36 Å) and Ti^{4+} (0.605 Å). Surprisingly, it is observed that the ionic radius of Nb^{5+} is larger than that of Ti^{4+} at B sites, which generally leads to the lattice expansion. Moreover, the difference of radius between Ca^{2+} and La^{3+} (1.47 %) is much smaller than that (5.79 %) of B-site cations. Therefore, it is proposed that the A-site modification is more obvious than B-site modification in stabling the perovskite-like structure, which may de related to the special structure of $A_nB_nO_{3n+2}$ since the neighboring perovskite layers are linked by A-site cations.

SEM images recorded from the thermally etched surfaces of $Ca_{1+x}La_{4-x}Ti_{5-x}Nb_xO_{17}$ ceramics are shown in Fig .3a–e. It is observed that the grain morphology and size changed clearly with composition. Obviously, the typical plate-like grains were observed in $Ca_5Nb_4TiO_{17}$ sample. For $1 \leq x \leq 3$, the presence of two distinct types of dark rod-like grains and bright plate-like grains was clearly found indicating that the ceramic specimens showed the formation of a mixture phase. Figure 4 presents the Energy-dispersive X-ray analysis (EDS) of the markers 1, 2, 3, 4, 5, 6, and 7 in Fig. 3. EDS analysis suggests that the dark grains (indicated as 1, 4, and 6) are rich in La/Ti and deficient in Ca/Nb, compared with the bright grains (indicated as 2, 3, 5, and 7). These results were consistent with the XRD results.

The variations in relative permittivity (ε_r) and quality factor ($Q \times f$) with sintering temperature for $Ca_{1+x}La_{4-x}Ti_{5-x}Nb_xO_{17}$ ceramics are shown in Fig. 4. It can be

seen that with increasing sintering temperature, the relative permittivity increased to a maximum value and thereafter decreased, showing the same relation as that between the bulk densities and sintering temperature. Similarly, the quality factor exhibited a distinct dependence on the sintering temperature: the higher the density, the larger the quality factor. Therefore, it was concluded that the improvement in microwave dielectric properties with sintering temperature were mainly attributed to the high densities of the ceramics.

Figure 5 shows the compositional dependence of relative permittivity (ε_r), quality factor ($Q \times f$) and temperature coefficient of resonant frequency (τ_f) of $Ca_{1+x}La_{4-x}Ti_{5-x}Nb_xO_{17}$ ceramics sintered at their optimum temperatures. The permittivity exhibited a monotonous decrease from 51.2 for $CaLa_4Ti_5O_{17}$ to 45.8 for $Ca_5Nb_4TiO_{17}$ with $x = 4$. The variation of permittivity could be partially explained by the average ionic polarizability (α_D^T/V_m) that is proportional to ε_r, as given in the modified Clausius–Mossotti equation [22]: $\varepsilon_r = \frac{1+2b\alpha_D^T/V_m}{1-b\alpha_D^T/V_m}$ (where, α_D^T is the sum of ionic polarizability of individual ions, V_m is the molar volume and $b = 4\pi/3$). The average ionic polarizability (α_D^T/V_m) was calculated using the ion polarizability given by Shannon [23] and the results were 0.1133 and 0.1012 for $CaLa_4Ti_5O_{17}$ and $Ca_5Nb_4TiO_{17}$, respectively. Thus, the smaller (α_D^T/V_m) value of $Ca_5Nb_4TiO_{17}$ compared with $CaLa_4Ti_5O_{17}$ can explain its lower relative permittivity.

$Q \times f$ value decreased from 14,010 GHz for $x = 0$ to 9,875 GHz for $x = 2$, then it increased to 15,680 GHz for $x = 4$. It is well known that there are many factors affecting the microwave dielectric loss including intrinsic loss caused by the lattice vibration modes and extrinsic loss induced by the impurities, grain boundaries, porosity, microstructure defects, order–disorder etc. [24]. Based on the XRD analysis, it was suggested that the extremely lower $Q \times f$ value for $x = 2$ was ascribed to the formation
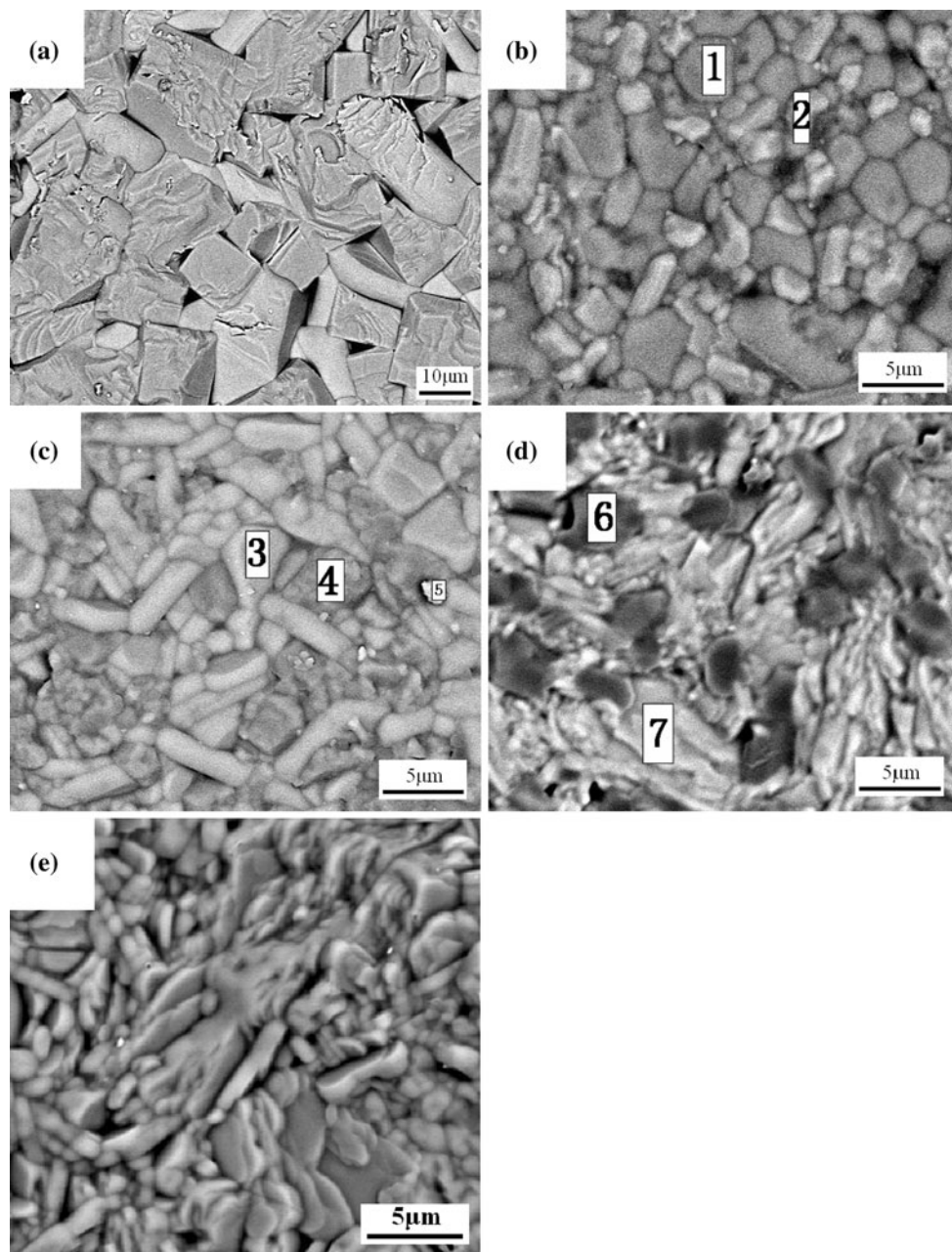
Fig. 3 SEM imagines recorded from the thermally etched surfaces of $Ca_{1+x}La_{4-x}Ti_{5-x}Nb_xO_{17}$ ceramics: (**a**) x = 0; (**b**) x = 1; (**c**) x = 2; (**d**) x = 3; (**e**) x = 4

of second phase. It is noted that the temperature coefficient of resonant frequency of $Ca_{1+x}La_{4-x}Ti_{5-x}Nb_xO_{17}$ monotonously decreased from −38.3 to −126.4 ppm/°C as x increased from 0 to 4.

Table 1 summarizes the microwave dielectric properties of the present ceramics, compared with the previous reported results [9–13]. For $Ca_5Nb_4TiO_{17}$, ε_r and τ_f are consistent with those previously reported. The microwave dielectric properties of $CaLa_4Ti_5O_{17}$ are similar to those reported by I.N. Jawahar et al., but there are difference in

$Q \times f$ and τ_f values from the previously reported values by Fei Zhao et al. ($Q \times f$ = 17,359 GHz, τ_f = −20 ppm/°C). The difference may be due to the different processing conditions and raw materials used. Comparing with some alternative materials with permittivity of 45–50 [25–27], as shown in Table 1, $Ca_{1+x}La_{4-x}Ti_{5-x}Nb_xO_{17}$ ceramics possess reasonable temperatures and microwave dielectric properties. However, the τ_f values are higher than that of some alternative materials and the $Q \times f$ values are too low, which precludes their application as dielectric
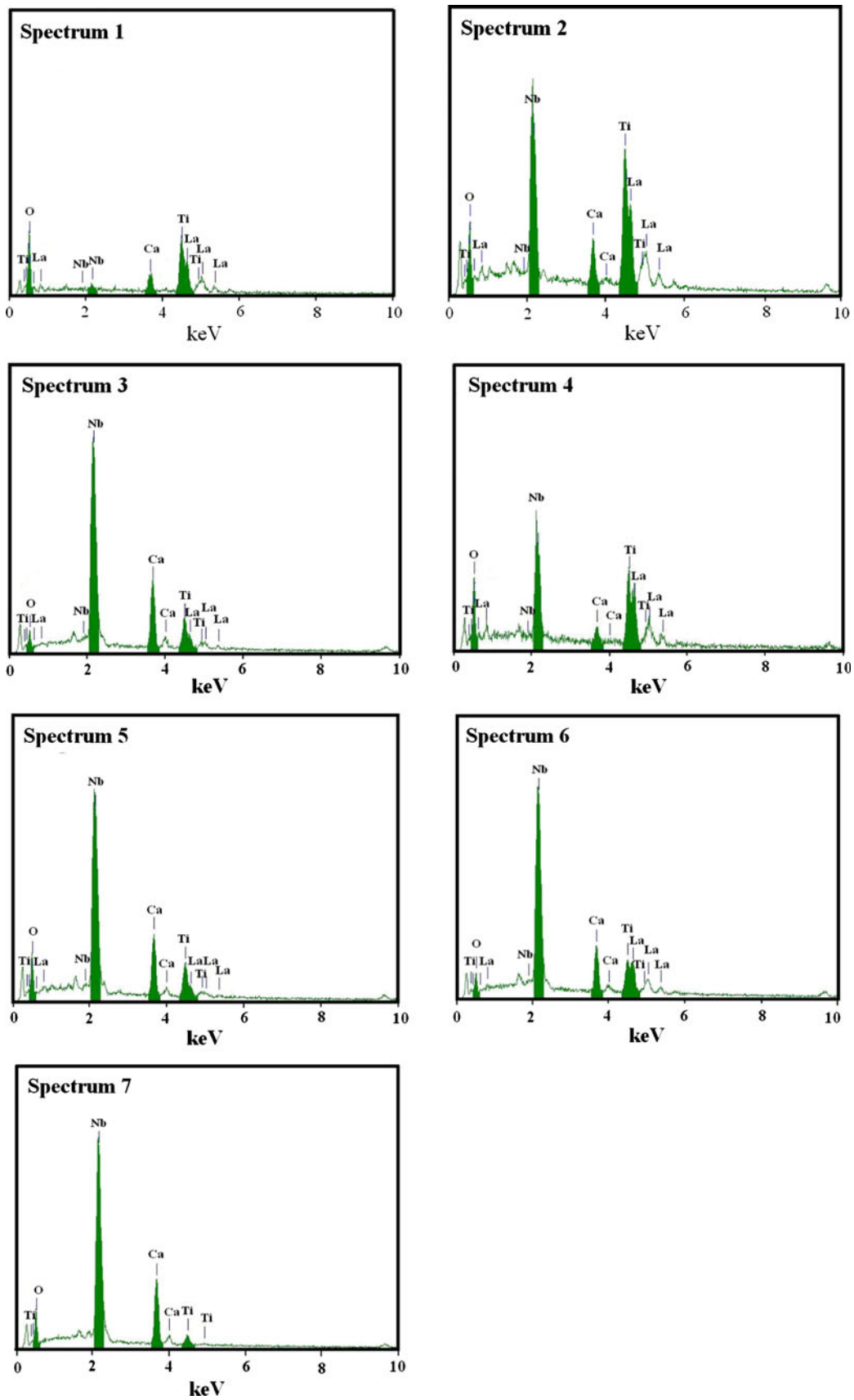
Fig. 4 Energy dispersive spectroscopy spectra of markers 1, 2, 3, 4, 5, 6, and 7 in Fig. 3
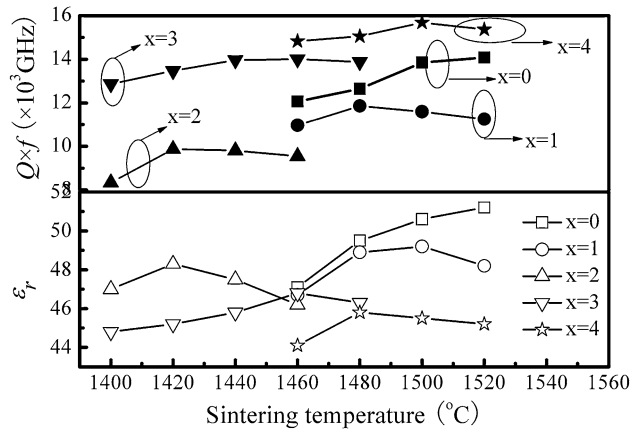
Fig. 5 The variations in relative permittivity (ε_r) and quality factor ($Q \times f$) with sintering temperature

Table 1 Sintering temperatures and microwave dielectric properties of CaO-La$_2$O$_3$-Nb$_2$O$_5$-TiO$_2$ ceramics (compared with some previous reported ceramics)

Composition	Sintering temperature (°C)	ε_r	Q × f (GHz)	τ_f (ppm/°C)
CaLa$_4$Ti$_5$O$_{17}$	1,520	51.2	14,080	−38.1
CaLa$_4$Ti$_5$O$_{17}$ [9]		55.2	17,359	−20
CaLa$_4$Ti$_5$O$_{17}$ [10]	1,500	56.5	12,500	3.7
Ca$_2$La$_3$Ti$_4$NbO$_{17}$	1,480	49.5	11,865	−52.4
Ca$_3$La$_2$Ti$_3$Nb$_2$O$_{17}$	1,420	48.3	9,875	−74.2
Ca$_4$LaTi$_2$Nb$_3$O$_{17}$	1,460	46.8	14,003	−97.7
Ca$_5$Nb$_4$TiO$_{17}$	1,480	45.6	15,680	−126.4
Ca$_5$Nb$_4$TiO$_{17}$ [7]	1,475	44.9	17,600	−112.9
0.7CaTiO$_3$-0.3NdAlO$_3$ [25]	1,450	45	44,000	0
PrTiTaO$_6$ [26]	1,500	45.8	32,300	33
0.5La(Mg$_{1/2}$Ti$_{1/2}$)O$_3$ −0.5La$_{2/3}$TiO$_3$ [27]	1,400	50	10,000	5

resonators, but the high relative permittivity makes Ca$_{1+x}$La$_{4-x}$Ti$_{5-x}$Nb$_x$O$_{17}$ ceramics possible candidates for application as cores in dielectrically loaded antennas.

From a practical point of view, the temperature coefficient of resonant frequency should be no larger than ±10 ppm/°C to satisfy thermal stability. Generally, two main approaches have been used to tune τ_f of microwave dielectric ceramics including partial cation substitution to form a solid solution and formation of composite materials with opposite sign of τ_f. TiO$_2$ with rutile structure shows ε_r of 104, $Q \times f$ of 26,900 GHz, and a high positive τ_f value of +411 ppm/°C [28] and it is commonly used to tune τ_f of microwave dielectric ceramics having a negative τ_f value [29]. Therefore, it is assumed that it is possible to tune the τ_f of CaLa$_4$Ti$_5$O$_{17}$ ceramics by addition of suitable amount of TiO$_2$ (Fig. 6).
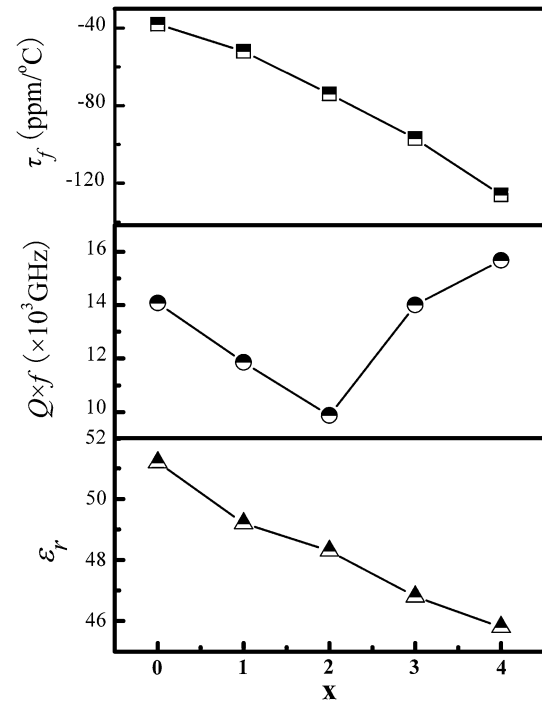

Fig. 6 The compositional dependence of microwave dielectric properties of Ca$_{1+x}$La$_{4-x}$Ti$_{5-x}$Nb$_x$O$_{17}$ ceramics
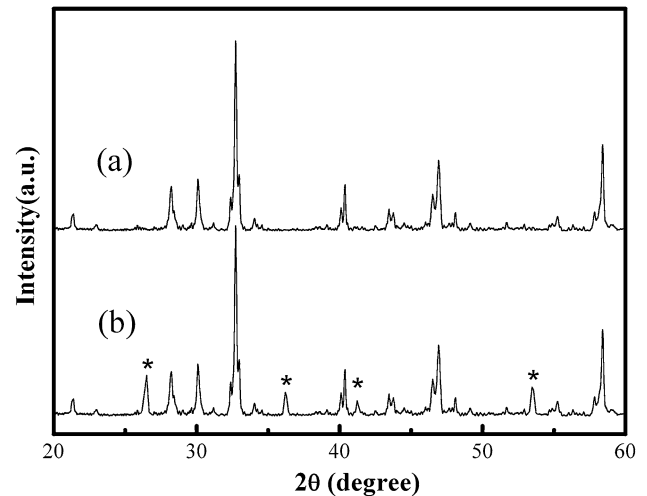
Fig. 7 XRD patterns of **a** CaLa$_4$Ti$_5$O$_{17}$ sintered at 1,520 °C and **b** CaLa$_4$Ti$_5$O$_{17}$ + 8 at% TiO$_2$ sintered at 1,400 °C (The *asterisk* represents the diffraction patterns of rutile phase)

Figure 7 shows XRD patterns of CaLa$_4$Ti$_5$O$_{17}$ mixed with 8 at % TiO$_2$ sintered at 1,400 °C compared with the pure CaLa$_4$Ti$_5$O$_{17}$. The rutile phase can be indexed based on the JCPDS file number 76–1,934. This result indicates that the nonreactivity of CaLa$_4$Ti$_5$O$_{17}$ with TiO$_2$. The variation of bulk density and microwave dielectric properties of CaLa$_4$Ti$_5$O$_{17}$ as a function of amount of TiO$_2$ are shown in Fig. 8. With increasing of TiO$_2$ addition, the density shows a linear decrease because of the lower theory density of TiO$_2$ (4 g/cm^3)
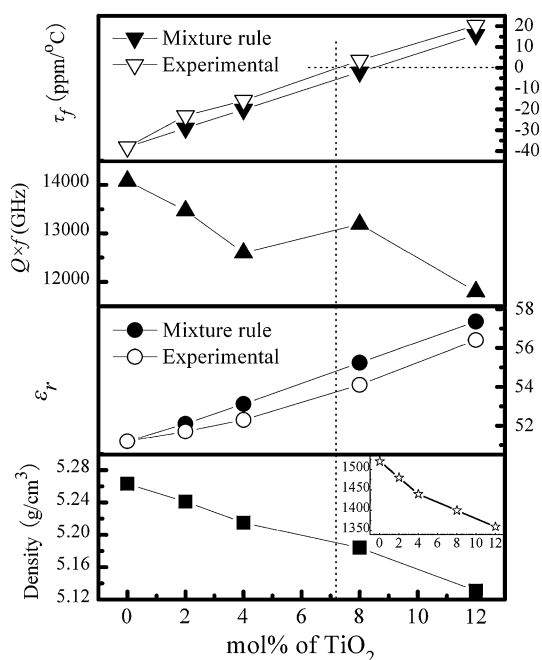
Fig. 8 Variation of bulk density and microwave dielectric properties (ε_r, $Q \times f$, and τ_f) of $CaLa_4Ti_5O_{17}$ as a function of TiO_2 content

compared with that of $CaLa_4Ti_5O_{17}$ (5.48 g/cm^3). Further, it is interesting to note that the sintering temperature of $CaLa_4Ti_5O_{17}$ was significantly lowered from 1,520 to 1,360 °C by TiO_2 addition due to the lower sintering temperature of TiO_2, as shown in the inset of Fig. 8.

Both relative permittivity and temperature coefficient of resonant frequency were found to increase monotonously with increasing TiO_2 content. This is expected since rutile TiO_2 has ε_r of 104 and a high positive τ_f value of +411 ppm/°C [26], much lager than those of the parent $CaLa_4Ti_5O_{17}$ phase. The variation of ε_r and τ_f of the composite of two different phases can be expressed by the general mixture rule, given as $y_{mixture} = V_1 y_1 + V_2 y_2$, where V_1, y_1 and V_2, y_2 are the volume fraction and the properties of the different phases, respectively. The calculated relative permittivity and temperature coefficient of resonant frequency as a function of the amount of TiO_2 are also presented in Fig. 8. It is found that the measured ε_r and τ_f are in accordance with the calculated values. In contrast, the variation of quality factor with increasing TiO_2 content is nonlinear and do not follow the mixture rule. A noteworthy change in τ_f from −38.1 to +20.3 ppm/°C with increasing TiO2 content up to 12 at % was observed. As deduced from the cures, a near-zero τ_f can be obtained when the amount of TiO_2 is around 7 at %.

4 Conclusions

A series of materials in $Ca_{1+x}La_{4-x}Nb_xTi_{5-x}O_{17}$ ($0 \leq x \leq 4$) system were prepared and the microwave

dielectric properties were investigated. XRD, SEM and EDS results showed that the two end member phases were $CaLa_4Ti_5O_{17}$ and $Ca_5Nb_4TiO_{17}$ with intermediate compounds with $x = 1$, 2, and 3. A trace amount of second phase was detected when $x = 2$. It is found that the A-site modification is more obvious than B-site modification in stabling the perovskite-like structure. With x increasing from 0 to 4, the relative permittivity decreased from 51.2 to 45.6 and temperature coefficient of resonant frequency decreased from −38.1 to −126.4 ppm/°C, while the quality factor initially decreased from 14,080 to 9,875 GHz and then increased to 15,680 GHz. τ_f of $CaLa_4Ti_5O_{17}$ can be tuned to a near-zero value by addition of suitable amount of TiO_2.

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