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Effect of Al_2O_3 Nanoparticles Doping on the Microwave Dielectric Properties of CTLA Ceramics

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Abstract

$CaTiO_3$-$LaAlO_3$ (CTLA) ceramics with Al_2O_3 nanoparticles were prepared by conventional two-step solid-state reaction, and the sintering behavior and the microwave dielectric proprieties were investigated. The results show that the doping of Al_2O_3 nanoparticles can promote the growth of uniform grain, increase the density and $Q\times f$ value, while it has no obvious influence on the dielectric constant (~45). CTLA ceramics with 0.05 wt% Al_2O_3 nanoparticles doping, sintered at 1420°C for 4h exhibited the optimal microwave dielectric properties, and CTLA ceramics with 0.2 wt% Al_2O_3 nanoparticles doping sintered at 1380°C for 4h exhibited the optimal microwave dielectric properties, respectively. A proper increase of Al_2O_3 nanoparticles content can reduce the sintering temperature.

Keywords: CTLA ceramics; Al_2O_3 nanoparticles doping; Sintering behavior; Microwave dielectric proprieties

Introduction

With the development of telecommunication technology, microwave dielectric ceramics with light mass, miniaturization, integration and thermal stability have been intensively studied in the field of telecommunication materials during the last several years [1,2]. Medium dielectric constant microwave ceramics, which have the properties including moderate dielectric constant, low dielectric loss and near-zero temperature coefficients of the resonant frequencies, have been applied in wireless microwave devices in a wide range such as resonator, filter, dielectric antenna and dielectric guided wave circuit. $CaTiO_3$ ceramics with orthorhombic perovskite structure have the microwave dielectric properties of $\varepsilon_r = 170$, $Q\times f = 3500$ GHz and $\tau_f = 800$ ppm/°C, while $LaAlO_3$ ceramics with rhombohedral perovskite structure have the microwave dielectric properties of $\varepsilon_r = 23.4$, $Q\times f = 68{,}000$ GHz and $\tau_f = -44$ ppm/°C. $CaTiO_3$-$LaAlO_3$ ceramics (CTLA) prepared from calcined $CaTiO_3$ and $LaAlO_3$ were considered as the typical microwave dielectric ceramics with the middle dielectric constant.

Previous studies have demonstrated that the crystal structure of CTLA ceramics transformed from orthorhombic to rhombohedral as the increase of $LaAlO_3$ content [3]. Hou et al. [4] have reported the sintering behavior of CTLA microwave dielectric ceramics heavily depends on the preparation temperature. Jiang et al. [2] investigated the solid-state reaction mechanisms of CTLA ceramics by X-ray diffraction and thermogravimetric/differential scanning calorimetric analysis techniques. Modified perovskite ceramics by replacing the A/B-site of CTLA were reported, such as $0.7CaTiO_3$-$0.3[La_xNd_{(1-x)}]AlO_3$ [5] and $xCaTiO_3$-$(1-x)La[Ga_{(1-\delta)}Al_\delta]O_3$ [6]. However, both the dielectric loss and sintering temperature of CTLA ceramics cannot meet the requirement of application.

Al_2O_3 showed most considerable microwave dielectric properties of $\varepsilon_r = 10$, $Q\times f = 500{,}000$ GHz, $\tau_f = -60$ ppm/°C, thus the microwave dielectric properties of CTLA ceramics may be enhanced by the Al_2O_3 doping. Ravi et al. [7] studied the densification, structure, and microwave dielectric properties of $0.7CaTiO_3$-$0.3LaAlO_3$ ceramics doped with 0.25 wt% Al_2O_3 and sintered at 1500°C, and the ceramics exhibited better dielectric properties of $\varepsilon_r = 46$, $Q\times f = 38{,}289$ GHz, and $\tau_f = 12$ ppm/°C compared with those of the non-doped sample ($\varepsilon_r = 41$ and $Q\times f = 26{,}618$ GHz). In the work of Yao et al. [8], the dielectric property test revealed that the $Q\times f$ value of the BNT ceramics with Al_2O_3 additive has been improved by 47%, compared with that of the undoped BNT ceramics. Meanwhile, Al_2O_3 were added to suppress the reduction of Ti^{4+} ions so as to improve the microwave dielectric properties of $Ba_{4.2}Sm_{9.2}Ti_{18}O_{54}$ ceramics by Yao et al. [9] reported. So, Al_2O_3 is considered as a candidate to improve the microwave dielectric properties of CTLA ceramics.

The nanoparticles ratio of surface area is larger, compared with the bulk ratio of surface area. With the reduction of dimensions, nanoparticles provide a tremendous driving force during the sintering, particularly at elevated temperatures and hence the surface energy of the nanoparticles substantially affects the interior bulk properties of the host materials [10].

With doping of these smaller particles, the ceramics can be sintered at lower temperatures over shorter time than ceramics doping with larger particles [11]. Thus, nanoparticles doped can increase the density, and reduce the sintering temperature. For example, it is found that the addition of CeO_2 nanoparticles to the $MgTiO_3$ ceramics leads to improvement of the relative density, reduction in sintering temperature [10].

In a word, Al_2O_3 nanoparticles are an excellent additive with excellent dielectric properties. In this work, the addition of Al_2O_3 nanoparticles was used to improve the sintering behavior and the microwave dielectric properties of CTLA ceramics, and the effects of Al_2O_3 nanoparticles addition on the sintering behavior and microwave dielectric properties of CTLA ceramics were investigated and discussed in detail.

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Experimental Procedures

Specimen preparation

Al_2O_3 nanoparticles doped 0.67$CaTiO_3$-0.33$LaAlO_3$ ceramics, CTLA-$x$$Al_2O_3$ (x = 0 wt%, 0.05 wt%, 0.1 wt%, 0.2 wt%, 0.4 wt%, 0.8 wt%), were prepared using a conventional two-step solid-state reaction from high-purity $CaCO_3$ (99.3%), TiO_2 (99.9%), La_2O_3 (99.99%), micron Al_2O_3 (94%) and nano-size Al_2O_3 (99.999%). $CaTiO_3$ was calcined at 1090°C for 6h and $LaAlO_3$ was calcined at 1200°C for 5h. The fully calcined powders ($CaTiO_3$, $LaAlO_3$) and nano-size Al_2O_3 were weighed stoichiometrically and ground using ball milling for 8h, dried at 120°C for 12h, and then mixed with a 5 wt% polyvinyl alcohol solution as a binder. The final particles were uniaxial pressed 12 mm diameter and 6 mm in high pellets. The pellets were debindered at 650°C and then sintered at the temperature of 1360°C ~1450°C for 4h in air. Pellets were cooled from the sintering temperature to 1000°C at a rate of 2°C/min, and then the ceramics were allowed to cool inside the furnace naturally.

Property characterization and theoretical analysis

The crystal structure of the sintered samples was characterized using X-ray powder diffraction (XRD) using a Bruker advanced X-ray powder diffractometer and Cu Kα radiation. The apparent densities of the ceramics were measured using the Archimedes method. The microstructures of the ceramics were examined with a JEOL JSM-7100F scanning electron microscope (SEM). The microwave dielectric properties of the ceramic samples were measured with an Agilent E5071C network analyzer using the cavity reflection method, and τ_f was measured between -20°C and 65°C and was defined as

$$\tau_f = \frac{f_{(T_2)} - f_{(T_1)}}{f_{(T_1)}\left(T_2 - T_1\right)} \quad (1)$$

Where,

$f_{(T_1)}$ is the resonant frequency at -20°C.

$f_{(T_2)}$ is the resonant frequency at 65°C.

Results and Discussion

Figure 1 presents the XRD patterns of CTLA-$x$$Al_2O_3$ ceramics sintered at 1420°C for 4h. A single phase of perovskite structure was confirmed over the entire compositional range. It can be seen that pure orthorhombic perovskite phase with space group *P*nma (62) (PDF#52-1773) were identified. At the range of 0~0.4 wt%, the diffraction peaks didn't shift almost. But at the doping level of x = 0.8 wt% the diffraction peaks slight shifted towards higher angles, because the Al^{3+} ions with smaller ionic radius ($R_{Al^{3+}}$ = 0.535 Å) substituted Ti^{4+} ionic with larger ionic radius (RTi4+ = 0.605 Å) in the CTLA ceramics.

Figure 2 shown the densities of CTLA-$x$$Al_2O_3$ ceramics at different sintering temperatures. As is shown, the density of CTLA-$x$$Al_2O_3$ ceramics increased firstly. The density of ceramics with low Al_2O_3 nanoparticles doping amount (x < 0.1 wt%) reached a maximum value at the temperature of 1420°C, while the density of ceramics with high content (x ≥ 0.2 wt%) reached the maximum value at a lower temperature (1380°C). After that the densities decreased as the sintering temperature continues to rise. At x = 0.05 wt%, the CTLA ceramics sintered at 1420°C obtained the maximum density of 4.669 g/cm^3. And at x = 0.2 wt%, the CTLA ceramics sintered at 1380°C also obtained a higher density of 4.663 g/cm^3. It is well known that the nanoparticles have large ratio of surface area, high surface energy, low melting point, and the smaller the particle size, the faster the sintering rate [10,12,13]. When the Al_2O_3 nanoparticles dispersed in the grain boundaries, it can promote mass transfer in the sintering process, reduce the surface energy of the system, accelerate the reaction, and then lead to the increase of the density. Similar, to previous reports [10,11], when the sintering temperature is higher than the certain value, the grains appeared abnormal growth and resulted in the lower density. Therefore, adding appropriate Al_2O_3 nanoparticles can increase CTLA ceramic density effectively, and reduce the sintering temperature.

The SEM of Al_2O_3 nanoparticles modified CTLA ceramics sintered at 1420°C was given in Figure 3. As shown in the Figure 3, the surface of CTLA ceramics modified by Al_2O_3 nanoparticles was smooth and densification with the pores in the grain and there was no obvious secondary phase for the composition. The SEM images of the CTLA ceramics with smooth grain and uniform size was shown in Figure 3a. By adding a small amount of nanoparticles (Figure 3b), the surface energy of the grain boundary can be improved, and the material transfer can be accelerated, which promote the uniformity growth of grain size. With the increase of the content of Al_2O_3 nanoparticles, the decline of onset sintering temperature and higher sintering temperature makes the grain abnormal growth due to two times recrystallization in the Figures 3c-3f. At the same time, with the increase of Al_2O_3 nanoparticles content, the grain boundary becomes vague, this is due to the excess introduction of Al_2O_3 nanoparticles particles, for nanoparticles cannot completely diffuse, forming aggregate in the grain boundary surface. Therefore, Al_2O_3 nanoparticles can accelerate the mass transfer rate of CTLA system and promote the grain size more uniform. But the excess addition cause grains abnormal growth and resultantly affects the density of CTLA ceramics.

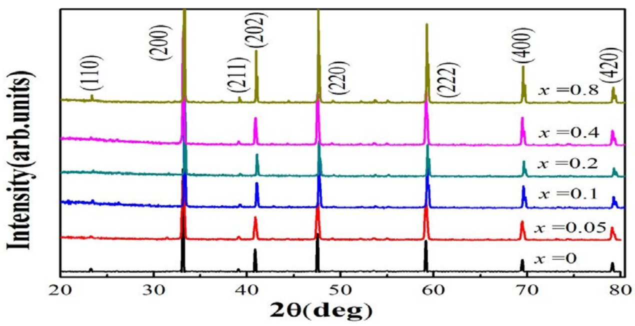

Figure 1: XRD patterns of CTLA-$x$$Al_2O_3$ ceramics sintered at 1420°C for 4 h.

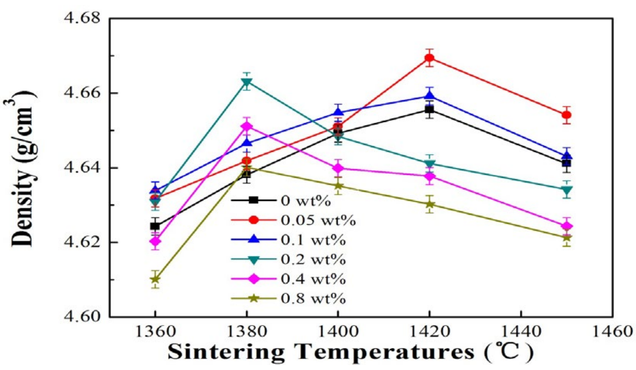

Figure 2: The densities of CTLA-$x$$Al_2O_3$ ceramics at different sintering temperatures.

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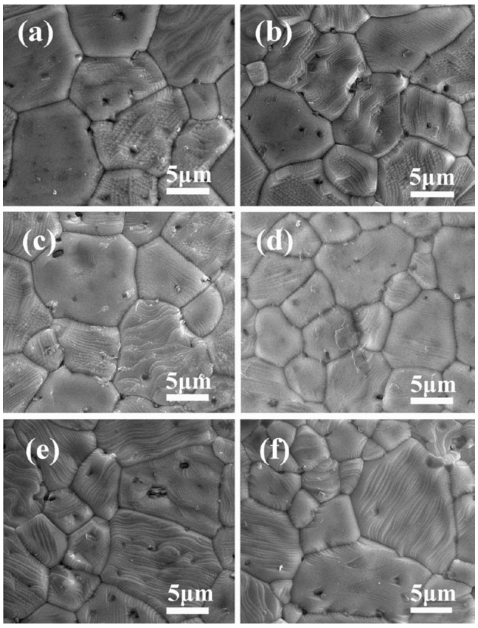

Figure 3: SEM images of CTLA-$x$$Al_2O_3$ ceramics sintered at 1420°C for 4 h (a) x = 0wt%, (b) x = 0.05 wt%, (c) x = 0.1 wt%, (d) x = 0.2 wt%, (e) x = 0.4 wt%, (f) x = 0.8 wt%.

Figure 4 shows the dielectric constant (ε_r) of CTLA-$x$$Al_2O_3$ ceramics sintered at different temperatures ranged from 1360 to 1450°C. For a given composition, the dielectric constant of CTLA ceramics increased with the increase of the sintering temperatures. When the sintering temperature is higher, the ion polarization ability of ionic crystal is stronger than at the lower temperature. At the same sintering temperatures, the dielectric constant increases first and then decreases as the increase amount of Al_2O_3 nanoparticles. At x = 0.05 wt%, the dielectric constant reaches the maximum. It was known that the dielectric constant depended significantly on the relative density at microwave frequencies [14], therefore, the dielectric constant increases first and then decreases, following the change of the density. With the increase of Al_2O_3 nanoparticles amount, the dielectric constant fluctuated slightly around 45.

The $Q\times f$ values of the CTLA-$x$$Al_2O_3$ ceramics sintered at different temperatures are shown in Figure 5. With the increase of the sintering temperature, $Q\times f$ values of CTLA-$x$$Al_2O_3$ ceramics showed the same trend with the density. The $Q\times f$ values first increased and then decreased, but $Q\times f$ values of different Al_2O_3 nanoparticles content ceramics reached maximums at different sintering temperature. The $Q\times f$ of CTLA ceramics with 0.05 wt% Al_2O_3 content reached the maximum value (38,215 GHz) at the sintering temperature of 1420°C, while the $Q\times f$ of CTLA ceramics with 0.2 wt% Al_2O_3 content reached the maximum value (37,346 GHz) at the sintering temperature of 1380°C. This indicates that doping Al_2O_3 nanoparticles can reduce the sintering temperature, while the influence on the dielectric loss is subtle. The trend of the $Q\times f$ values as a function of Al_2O_3 nanoparticles content (Figure 6) was similar to the trend of the density, which illustrates that the $Q\times f$ values of CTLA-$x$$Al_2O_3$ ceramics were affected significantly by the relative density.

The relationship between the temperature coefficient of resonant frequency (τ_f) and ε_r of the CTLA-$x$$Al_2O_3$ ceramics sintered at 1420°C are shown in Figure 6. As is shown in Figure 6, both τ_f and ε_r increase and then decrease with the increase of the content of the Al_2O_3 nanoparticles. Because the τ_f of Al_2O_3 is -60 ppm/°C, the τ_f of the CTLA-$x$$Al_2O_3$ ceramics should be increased to the negative direction. However, at x = 0.05 wt%, τ_f reached a maximum value of 3.65 ppm/°C. So there are other reasons for this situation. Harrop [15] differentiated the Clausius-Mossotti equation to justify physically the following empirical relationship

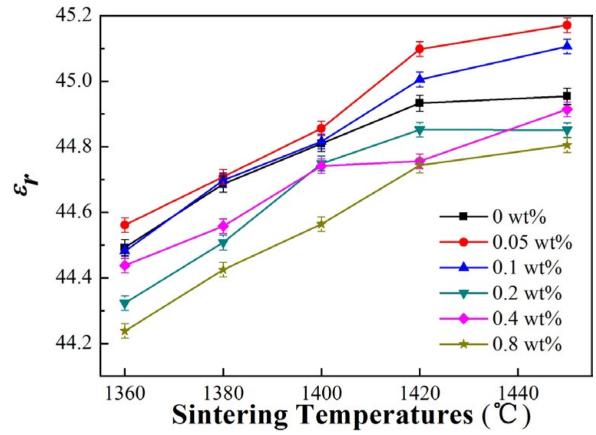

Figure 4: ε_r of CTLA-$x$$Al_2O_3$ ceramics sintered at different temperatures.

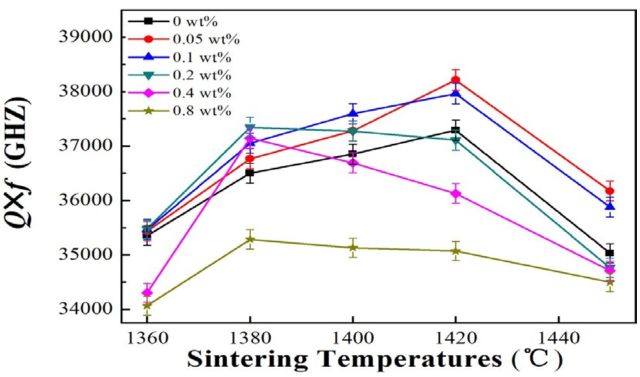

Figure 5: $Q \times f$ values of CTLA-$x$$Al_2O_3$ ceramics sintered at different temperatures.

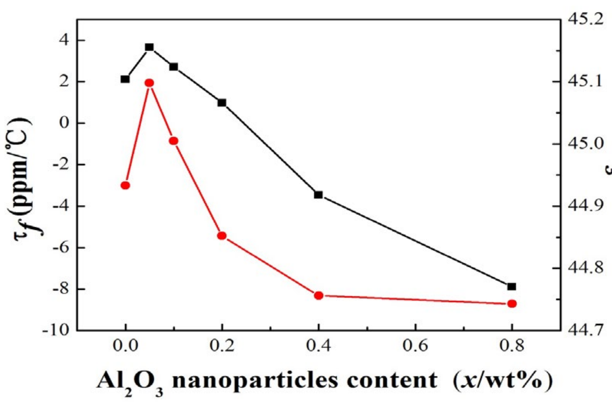

Figure 6: τ_f of CTLA ceramics with different Al_2O_3 nanoparticles content sintered at 1420°C.

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$$\tau_c = -\alpha_L \varepsilon_r \tag{2}$$

Where,

τ_c is the temperature coefficient of capacitance, and

α_L is the linear expansion coefficient of the dielectric materials.

It is related to the temperature coefficient of permittivity (τ_ε) by [16]

$$\tau_\varepsilon = \tau_c - \alpha_L \tag{3}$$

τ_f is identified as

$$\tau_f = -\left(\frac{1}{2}\tau_\varepsilon + \alpha_L\right) \tag{4}$$

Furthermore, α_L is the linear expansion coefficient of the CTLA ceramics, and it is known to be approximately constant. It follows that:

$$\tau_f \propto -\alpha_L \varepsilon_r \tag{5}$$

It illustrated that τ_f mainly depends on ε_r in the case of CTLA-$x$$Al_2O_3$ ceramic system, so the τ_f increases firstly and then decreases with the change of dielectric constant (ε_r).

The microwave dielectric properties of the 0.67$CaTiO_3$-0.33$LaAlO_3$ ceramics doped with x wt% Al_2O_3 nanoparticles are shown in Table 1. It can be seen that CTLA ceramics with 0.05 wt% Al_2O_3 nanoparticles doping sintered at 1420°C for 4h exhibited the optimal microwave dielectric properties of εr = 45.10, $Q\times f$ = 38,215 GHz, and τf = 3.65 ppm/°C, and at x= 0.2 wt%, the sintering temperature of CTLA ceramics was decreased from 1420°C to 1380°C, and the ceramics exhibited the optimal microwave dielectric properties of εr = 44.51, $Q\times f$ = 37,346 GHz, and τ_f = 4.87 ppm/°C.

Conclusions

Al_2O_3 nanoparticles were adopted to modify the CTLA ceramics. The sintering behavior and microwave dielectric proprieties of the CTLA ceramic samples were studied. The results show that the doping of Al_2O_3 nanoparticles has no obvious influence on the dielectric constant (~45). The Al_2O_3 nanoparticles, as a mass transfer media, promoted the growth of uniform grain, and reduced dielectric loss availably. The temperature coefficient of resonant frequency of the ceramics showed the same dependence on Al_2O_3 nanoparticles content as the dielectric constant. CTLA ceramics with 0.05 wt% Al_2O_3 nanoparticles doping sintered at 1420°C for 4h exhibited the optimal microwave dielectric properties of ε_r = 45.10, $Q\times f$ = 38,215 GHz, and τ_f = 3.65 ppm/°C. Compared with the undoped CTLA ceramics, the $Q\times f$ value has been improved by 2.5 %. At x= 0.2 wt%, the sintering temperature of CTLA ceramics was decreased from 1420°C to 1380°C, and the ceramics exhibited the optimal microwave dielectric properties of ε_r = 44.51, $Q\times f$ = 37,346 GHz, and τ_f = 4.87 ppm/°C. The results showed that the proper amount of Al_2O_3 nanoparticles content reduced the sintering temperature and slightly improved the $Q\times f$ value.

T (℃)	Q×f (GHz)		εr		τf (ppm/℃)	
	1380	1420	1380	1420	1380	1420
0 wt%	36,500	37,291	44.69	44.93	4.38	2.12
0.05 wt%	36,766	38,215	44.71	45.1	6.78	3.65
0.1 wt%	37,054	37,964	44.7	45.01	4.96	2.71
0.2 wt%	37,346	37,110	44.51	44.85	4.87	0.98
0.4 wt%	37,144	36,127	44.56	44.76	0.36	-3.47
0.8 wt%	35,285	35,072	44.43	44.74	-4.7	-7.89

Table 1: The microwave dielectric properties of the CTLA ceramics doped with x wt% Al_2O_3 nanoparticles.

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