The Effect of $Y^{3+}$ Doping on CaTiO$_3$-LaAlO$_3$ Microwave Dielectric Ceramics

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Abstract. CaTiO$_3$-LaAlO$_3$ solid solution with perovskite structure has suitable relative permittivity ($\varepsilon_r$) and high quality factor ($Q\times f$) for application as dielectric resonators, but the negative value of the temperature coefficient of resonance frequency ($\tau_f$) affects its utilization. To improve dielectric properties and adjust lattice matching, $Y^{3+}$ ion was selected as doping element to prepare the 0.65CaTiO$_3$-0.35(La$_{1-x}$Y$_x$)AlO$_3$ ($x=0, 0.02, 0.04, 0.06, 0.08$) microwave dielectric ceramics by conventional mixed solid method. The effects of $Y^{3+}$ ion doping on the crystal structure and microwave dielectric properties were investigated. The results revealed that a single orthorhombic phase for all the compositions can form and the unit cell volume increases linearly with the doping content $x$. $Y^{3+}$ ion dopant can increase the quality factor and improve the temperature coefficient of resonant frequency of 0.65CaTiO$_3$-0.35LaAlO$_3$ ceramics. When $x=0.02$, the optimal microwave dielectric properties of $\varepsilon_r=45.8$, $Q\times f=38957$ GHz, and $\tau_f=4\times10^{-6}/\circ C$ for the 0.65CaTiO$_3$-0.35(La$_{1-x}$Y$_x$)AlO$_3$ ceramics could be obtained, which sintered at 1500 $\circ C$ for 5 h.

1. Introduction

With the development of mobile communication technology over recent ten years, the communication devices become more miniaturization and more performance-based. Especially, the handheld mobile communication system has entered the cellular program control phase from the manual/automatic phase. And the operating frequency of the communication equipment extends from 4G to 5G high frequency range. In addition, with microwave dielectric ceramics as the core components, the microwave components, such as resonators, filters, dielectric guided wave circuit, antennas, etc. become more and more important [1,2]. In order to further miniaturize microwave device, microwave dielectric ceramics are required to have high relative permittivity ($\varepsilon_r$), high-quality factor ($Q\times f$) value and $(0-10)\times10^{-6}/\circ C$ temperature coefficient of resonant frequency ($\tau_f$ value) [3,4].

At present, a great number of microwave dielectric materials with high quality factor were developed, such as BaTi$_4$O$_9$ ($\varepsilon_r=37$, $Q\times f=22700$ GHz, $\tau_f=15\times10^{-6}/\circ C$) [5], Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ ($\varepsilon_r=29.6$, $Q\times f=96000$ GHz, $\tau_f=0.5\times10^{-6}/\circ C$) [6], (Zr$_{0.8}$Sn$_{0.2}$)TiO$_4$ ($\varepsilon_r=38$, $Q\times f=50000$ GHz, $\tau_f\approx0/\circ C$) [7]. Among of them, the CaTiO$_3$-LnAlO$_3$ (CTLA, Ln = La, Nd, Sm) perovskite solid solutions is a ceramic with excellent dielectric properties. CTLA ceramics have attracted attention as a typical microwave dielectric ceramic with suitable relative permittivity and high quality factor value. Jancar B et al [8]...
systematically studied the microwave dielectric properties of $x$CaTiO$_3$-$(1-x)$LaAlO$_3$ ceramics, it was found that 0.65CaTiO$_3$-0.35LaAlO$_3$ ceramics had the best microwave dielectric properties: $\varepsilon_r = 44$, $Q\times f = 30000$ GHz, $\tau_f = -2\times10^{-6}$/°C. Later, Zheng J S et al [9] carried out research and analysis to 0.65CaTiO$_3$-0.35LaAlO$_3$ ceramics, discovered that the CTLA ceramics sintered densely at 1320 °C, and the $\tau_f$ value could reach $+10\times10^{-6}$/°C by adding 0.75wt% CuO or 0.75wt% MnCO$_3$, meanwhile, $\varepsilon_r = 43$, $Q\times f = 32800$ GHz. But in 5G applications, CTLA ceramics are required to have a quality factor $Q\times f$ as high as possible and $\tau_f=(0~10)\times10^{-6}$/°C. Dielectric properties of CTLA ceramics needs to be systematically modified.

Ion substitution is an effective way to modify the dielectric properties of CTLA ceramics. Rare earth cations, such as $\mathrm{Y}^{3+}$ (0.1019 nm), have the same chemical valence and similar ionic radii to $\mathrm{La}^{3+}$ (0.1160 nm), so solid solutions might be easily formed in the $0.65\mathrm{CaTiO}_3\cdot0.35(\mathrm{La}_{1-x}\mathrm{Y}_x)\mathrm{AlO}_3$ (CTLYA) system, which is conducive to improving the microwave dielectric properties of materials [10]. There is a significant effect of the doping of rare earth oxide on particle size, in that it is useful in CTLA ceramics grain growth control. As such, the doping element chosen in this case was $\mathrm{Y}$, where the purpose of the study is to better the quality factor and temperature coefficient of resonant frequency, along with maintain relative permittivity. In this study, the CTLYA ceramics were made through the CSSR process, and among the things being investigated were dielectric properties, microstructure and sintering behavior.

2. Experimental

Proportionate amounts of high-purity CaCO$_3$ (99.3%), TiO$_2$ (99.9%), La$_2$O$_3$(99.99%), Al$_2$O$_3$ (94%) and Y$_2$O$_3$ (99.99%)were prepared according to the stoichiometric compound formulation of $0.65\mathrm{CaTiO}_3\cdot0.35(\mathrm{La}_{1-x}\mathrm{Y}_x)\mathrm{AlO}_3$ ($x$ =0, 0.02, 0.04, 0.06, 0.08). The stoichiometrically weighed raw materials were mixed and ball milled with zirconia media in deionized water for 12 h. The mixtures were dried and calcined at 1260 °C for 3 h. The calcined powders were ball milled again for 12 h, after drying and sieving, the dried powders were pressed into cylinders 13 mm in diameter and 6-7 mm in height)in a steel die with 4 wt% PVA binder addition under a uniaxial pressure of 100MPa. Samples were sintered at different temperatures for 5 h, and then cooled down to room temperature in the furnace.

The D8-Advance X-ray diffractometer was used to analyse the crystal structure and phase composition of the samples. The JSM-6700F field emission scanning electron microscope was used to observe the micro-structures of the samples such as grains’ size and morphology. The Archimedes drainage method was applied to measure the volume density of the samples at room temperature. The HP8720 network analyser was used to measure the relative permittivity $\varepsilon_r$ and the quality factor $Q\times f$ of the ceramic samples at microwave frequency. The cavity method was applied to measure the temperature coefficient of resonant frequency $\tau_f$ of the samples at 20°C to 80°C, and the resonant frequency at 20 °C was used as the standard frequency, the formula of which is equation (1):

$$\tau_f = \frac{1}{f(20)} \times \frac{f(80) - f(20)}{80 - 20}$$

The $f_{(20)}$ and $f_{(80)}$ are temperature coefficient of resonant frequency of CTLYA ceramics at 20 °C and 80 °C, respectively.

3. Results and discussion

Figure 1 shows the bulk density and relative density curve of CTLYA ceramics at different sintering temperatures. As can be seen from Figure 1, with the increase of temperature, the bulk density of ceramics first increases to the maximum and then decreases. For different doping amount, sintering temperatures are different when the bulk density reaches saturation. $\mathrm{Y}^{3+}$-doping can increase the densification of CTLYA ceramics. When the size of grain increases, the pore decreases, the number of grain boundaries decrease gradually, and the densification of ceramics increase. However, the
introduction of $Y^{3+}$ will also increase the optimal sintering temperature. When $x = 0.02$ and the sintering temperature is 1500 °C, the bulk density of the sample reaches maximum value.

**Figure 1.** Bulk densities and relative densities of the 0.65CaTiO$_3$-0.35(La$_{1-x}$Y$_x$)AlO$_3$.

**Figure 2.** XRD patterns of 0.65CaTiO$_3$-0.35(La$_{1-x}$Y$_x$)AlO$_3$. 

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Figure 2 shows the present X-ray diffraction patterns of the CTLYA ceramics. The results reveal that a single tetragonal perovskite structure for all the compositions could be formed, and there are no impurities. This indicates that Y$^{3+}$ enters the A site of ABO$_3$ perovskite structure and forms a solid solution. Diffraction peak turned to high angle with increasing $x$ value, because the Y$^{3+}$ crystal radius (0.1019nm) is smaller than La$^{3+}$ (0.1160 nm), the lattice constant decreases when Y$^{3+}$ substitutes La$^{3+}$ into the lattice.

In order to further study the crystal cell parameters of CTLYA ceramics, the different Y$^{3+}$ doping amount in Figure 2 XRD patterns were refined by using Rietveld simulations under the GSAS. The structure refinement is shown in Figure 3. According to the calculation of crystal cell parameters based on the finished XRD data, the results are shown in Table 1. The $R_{wp}$ of the CTLYA ceramic refinement results is close to 10%, and the goodness of fit $\chi$ is $1 < \chi < 1.5$, suggesting that the refinement results are reliable.

![Figure 3. The XRD patterns obtained from Rietveld refinement of 0.65CaTiO$_3$-0.35(La$_{1-x}$Y$_x$)AlO$_3$.](image)

| Table 1. Lattice parameters and cell volumes of the 0.65CaTiO$_3$-0.35(La$_{1-x}$Y$_x$)AlO$_3$. |
|---------------------------------|-----------|-----------|-----------|-----------|
| $x$   | 0         | 0.02      | 0.04      | 0.06      |
| a (nm) | 0.54114   | 0.54109   | 0.5411    | 0.54099   |
| b (nm) | 0.76444   | 0.7643    | 0.76412   | 0.76418   |
| c (nm) | 0.54079   | 0.54057   | 0.54056   | 0.54061   |
| V ($10^3$nm$^3$) | 223.708   | 223.555   | 223.503   | 223.496   |
| $R_{wp}$ (%) | 12.2      | 10.0      | 10.1      | 10.3      |
| $\chi^2$ | 1.83      | 1.50      | 1.47      | 1.54      |
Figure 4. SEM images of 0.65CaTiO\(_3\)-0.35(La\(_{1-x}\)Y\(_x\))AlO\(_3\): (a) \(x = 0/1480^\circ C\); (b) \(x = 0.02/1500^\circ C\); (c) \(x = 0.04/1520^\circ C\); (d) \(x = 0.06/1540^\circ C\).

Figure 4 shows the SEM photos of CTLYA ceramics at optimal sintering temperature. As can be seen from Fig. 4, all the grain morphology is granular crystal with clear grain boundary and no heterogeneous phase. Dense two-mode grown grains were obtained within the range of all sample components. This two-mode distribution is mainly caused by the rapid discontinuity of some small grains. With the increase of Y\(^{3+}\) doping content, the grain boundary of sintered samples narrows and the grain size increases gradually. Among them, the size of small grains increases from about 3 \(\mu m\) to about 8 \(\mu m\). The large grain size increases from about 10 \(\mu m\) to about 15 \(\mu m\). When \(x = 0.02\), the optimal tightness and uniformity could be obtained. It can be seen that proper doping of Y\(^{3+}\) is beneficial to obtain ceramics with uniform grain size and good compactness. With the increase of the doping amount of Y\(^{3+}\), pores appear at the edge of the grain boundary of the ceramic, which decreases the densification of the ceramic sample.

Figure 5 shows the relative permittivity change curve of CTLYA (\(x=0\sim0.08\)) at different sintering temperatures with 5 h soaking time. It can be seen from Figure 5 that the change rule of the relative permittivity and bulk density are roughly the same. With the increase of temperature, the relative permittivity of ceramics first increases and then decreases. This is because the increase of sintering temperature is conducive to the diffusion of ions, and the pores of the ceramic sample gradually decrease, resulting in a gradual increase in densification, so that the relative permittivity of the material increases. When the sintering temperature is too high, some grains will grow abnormally and the densification of the material will decrease, thus the relative permittivity will decrease. The relative permittivity of CTLYA ceramics is affected not only by sintering temperature, but also by the doping amount of Y\(^{3+}\). The doping of Y\(^{3+}\) changes the microstructure of the material. Generally speaking, the more uniform the grain size distribution is, and the higher the degree of densification is, then the higher the corresponding relative permittivity will be. However, the relative permittivity \(\varepsilon_r\) of the sintered ceramics decreases under the same sintering temperature. The relative permittivity was calculated by equation (2):
The relative permittivity is proportional to dielectric polarizability $\alpha$ and inversely proportional to molar volume $V_m$. The polarizability of $Y^{3+}$ ($\alpha=3.81$) is less than that of $La^{3+}$ ($\alpha=6.07$). With the increase of doping amount of $Y^{3+}$, the decrease of polarizability is more advantageous than the decrease of cell volume. Therefore, as the doping amount of $Y^{3+}$ increases, the relative permittivity of ceramics decreases. On the other hand, with the change of lattice constant, it can be shown that with the increase of $Y^{3+}$ substitution amount, the lattice constant becomes smaller, the cell volume decreases, and the polarization space of B-site ions in the center of the oxygen octahedron decreases, which also leads to the decrease of the relative permittivity of CTLYA ceramics.

Figure 5 shows the $Q\times f$ value of CTLYA ceramics at different sintering temperatures with 5 h soaking time. It can be seen from figure 6 that with the increase of sintering temperature, the $Q\times f$ value first increases and then decreases, and presents a decreasing trend with the increase of $x$, which is consistent with the change of bulk density with sintering temperature. When the sintering temperature is 1500 °C and $x = 0.02$, the maximum $Q\times f$ value is $Q\times f = 38957$ GHz. It is generally considered that the loss of materials at microwave frequency can be divided into intrinsic dielectric loss and extrinsic dielectric loss. The intrinsic dielectric loss is mainly controlled by lattice vibration mode and is related to the properties of the material itself [11]. The extrinsic dielectric loss is mainly related to the microstructure of the material. The fewer defects and pores there are, the higher the quality value will be. The increase of sintering temperature is conducive to the diffusion of ions, the reduction of lattice defects and the increase of the densification of the material, so that the $Q\times f$ value of the material increases accordingly. When the sintering temperature is too high, the ions can obtain enough energy to break away from the lattice, resulting in structural defects and reducing the $Q\times f$ value of the material [12]. As can be seen from the SEM photos of the ceramic sample in Fig.4, with the increase of the doping amount of $Y^{3+}$, the grain size increases and the number of grain boundaries decreases, while the defects tend to accumulate at the grain boundaries, and a greater $Q\times f$ value is obtained. When $x=0.02$, the ceramic grains have the best densification and uniformity, the result is a high $Q\times f$ value. For CTLYA ceramics, the densification is the main reason affecting the material $Q\times f$ value.
value. The higher the densification is, the higher the $Q \times f$ value is. On the other hand, when a small number of positive ions with small mass are doped, the ion conversion mass can be reduced under the condition that the cell volume is basically not affected [13]. Therefore, the dielectric constant of the material does not change obviously while the $Q \times f$ value is improved.

Figure 6. $Q \times f$ of 0.65CaTiO$_3$-0.35(La$_{1-x}$Y$_x$)AlO$_3$ ceramics at different sintering temperatures.

Figure 7. The relation between $\tau_f$ and bond Value of 0.65CaTiO$_3$-0.35(La$_{1-x}$Y$_x$)AlO$_3$ ceramics.

Figure 7 shows the temperature coefficient of resonant frequency of CTLY ceramics sintered at different sintering temperatures for 5 h and the bond strength value of each component at the optimum sintering temperature. Table 2 is the tolerance factors and the distortion results of the oxygen octahedron of CTLYA ceramics. There are many factors that can affect the temperature coefficient of resonant frequency, and there is no unified theory in current research. In this study, the effects of Y$^{3+}$
doping on the temperature coefficient of resonant frequency of CTLA ceramics are studied from the aspects of structural features and factors such as tolerance factors, the incline and distortion of the oxygen octahedron, ionic bond valence, etc. The concept of tolerance factor is proposed to judge the stability of perovskite structure. The closer its value is to 1, the more stable the perovskite structure is. When the tolerance factor is close to 1, the resonant temperature frequency coefficient moves towards the positive direction, and the closer to 1 it is, the more stable the perovskite structure is [14]. The expression of tolerance factor for the composite perovskite structure \((A_1^{x}, A_2^{1-x})(B_1^{Ce}, B_2^{1-Ce})_3\) can be calculated from equation (3):

\[
 t = \frac{x r_{A1} + (1 - x) r_{A2} + r_D}{\sqrt{2} (y r_{B1} + (1 - y) r_{B2} + r_O)}
\]

(3)

Wherein \(r_A\), \(r_B\) and \(r_O\) are the radius of the A site ion, B site ion, and \(O^{2-}\) ion, respectively. The incline and distortion of the oxygen octahedron changes as the doping amount of \(Y^{3+}\) increases. Research finds that as the radius of A site ion decreases, the dip angle of the oxygen octahedron increases, and the restoring force of the positive ion having anharmonic vibration is weakened, which makes the stability of the resonant temperature frequency decrease. Meanwhile, as the doping amount increases, the crystal structure changes and affects the distortion of the oxygen octahedron, and the temperature coefficient of resonant frequency moves towards the negative direction as the distortion of the oxygen octahedron increases [15]. The oxygen octahedral distortion of the perovskite structure \(ABO_3\) is calculated as equation (4), and the tolerance factor and the oxygen octahedral distortion results obtained are shown in Table 2.

\[
 \Delta_{\text{octahedral aberration}} = \frac{B_{O_{max}} - B_{O_{min}}}{B_{O_{avg}}}
\]

(4)

It can be seen from Table 2 that as the doping amount of \(Y^{3+}\) increases, the dip angle of the oxygen octahedron becomes larger, and the tolerance factor decreases and stays away from 1, indicating that the perovskite structure becomes less stable, and the value of \(|\tau_f|\) becomes larger and stays away from zero. At the same time, as \(x\) increases, the distortion of the oxygen octahedron decreases, and \(\tau_f\) moves towards the direction of positive value. The variation of the value of \(\tau_f\) conforms to the theory of the dip angle and distortion of the oxygen octahedron, indicating that the value of \(\tau_f\) will stay away from zero and increase to positive value. However, the incline and distortion of the oxygen octahedron do not give a clear explanation for the change of the temperature coefficient resonant frequency. In order to fully explain the changing nature of the temperature coefficient of resonant frequency, based on the incline and distortion of the oxygen octahedron, further study is carried out to the influence of the ion bond valence on the temperature coefficient of resonant frequency. \(\tau_f\) is closely related to the bond valence of positive ion. When the bond valence increases, the bond energy increases accordingly, the restoring force required to restore the lattice distortion of the oxygen octahedron increases, and the temperature coefficient of resonant frequency decreases accordingly. On the contrary, when the bond price decreases, the temperature coefficient of resonant frequency increases [16]. For each given ion \(i\), its bond strength value \(I_i\) is defined as the sum of all bond strength values of such ion, the formula of which is as follows equation (5) and equation (6):

\[
 I_{ij} = \sum V_{ij}
\]

(5)

\[
 V_{ij} = \exp \left[ \frac{(R_{ij} - d_{ij})}{b'} \right]
\]

(6)

Wherein \(R_{ij}\) is the parameter of bond strength, \(d_{ij}\) is the bond length between ion \(i\) and ion \(j\), and \(b'\) is a universal constant with a value equal to 0.37. It can be seen from Figure 7 that as the doping amount of \(Y^{3+}\) increases, the bond strength value of A site ion decreases, and the value of \(\tau_f\) increases towards the positive value due to the structural characteristics of the CTLA ceramic [17]. The value of \(\tau_f\) moves
from a negative value to a positive value, indicating that the doping of Y$^{3+}$ can improve the resonant temperature frequency coefficient of CTLA ceramics.

Table 2. Tolerance factor ($t$) and octahedral distortion ($\Delta$) of the 0.65CaTiO$_3$-0.35(La$_{1-x}$Y$_x$)AlO$_3$.

| $x$ value | Tolerance factor $t$ | Octahedral distortion $\Delta$ | $\tau_f$ (10$^{-6}$/°C) |
|-----------|---------------------|-------------------------------|---------------------|
| $x=0$     | 0.904443            | 0.01638                       | -2.3                |
| $x=0.02$  | 0.904093            | 0.006768                      | 4.07                |
| $x=0.04$  | 0.903744            | 0.006011                      | 7.79                |
| $x=0.06$  | 0.903394            | 0.005663                      | 8.2                 |

4. Conclusions

(1) All 0.65CaTiO$_3$-0.35(La$_{1-x}$Y$_x$)AlO$_3$ ceramics doped with Y$^{3+}$ ($x=0, 0.02, 0.04, 0.06, 0.08$) formed a single phase solid solution, and the unit cell volume and cell parameters decreased with the increase of $x$.

(2) With the increase of Y$^{3+}$ doping content, the dielectric constant of 0.65CaTiO$_3$-0.35(La$_{1-x}$Y$_x$)AlO$_3$ ceramics decreases slightly with the decrease of ion polarizability. The quality factor is affected by the density, and the proper doping of Y$^{3+}$ can increase the density of ceramics, so that the quality factor value can be improved.

(3) $\tau_f$ of the 0.65CaTiO$_3$-0.35(La$_{1-x}$Y$_x$)AlO$_3$ ceramic increase from the doping amount of -2.3×10$^{-6}$/°C with $x=0$ up to 8.2×10$^{-6}$/°C with $x=0.06$. With the increase of Y$^{3+}$ doping, the dip angle of the oxygen octahedron increased, the structural stability weakened, the tolerance factor $t$ decreased and $t < 1$, which made the value of $|\tau_f|$ increase and move away from zero. At the same time, the distortion degree of the oxygen octahedron decreases, making the value of $\tau_f$ move to a positive value. The bond strength of A position cations decreases, which shows that the temperature coefficient of resonant frequency increases to a positive value on the other hand.

(4) When the doping amount of Y$^{3+}$ is $x=0.02$, the sintering temperature is 1500 °C, 0.65CaTiO$_3$-0.35(La$_{1-x}$Y$_x$)AlO$_3$ ceramics has the best performance on microwave dielectric: $\varepsilon_r=45.8$, $Q\times f=38957$ GHz, $\tau_f=4\times10^{-6}$/°C.

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