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Investigation on the anti-reduction mechanism of Ti^{4+} in high dielectric constant system $Ca_{0.9}La_{0.067}TiO_3$ by doping with Al_2O_3

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ABSTRACT

$Ca_{0.9}La_{0.067}TiO_3$ (abbreviated as CLT) ceramics doped with different amount of Al_2O_3 were prepared via the solid state reaction method. The anti-reduction mechanism of Ti^{4+} in CLT ceramics was carefully investigated. X-ray diffraction (XRD) was used to analyze the phase composition and lattice structure. Meanwhile, the Rietveld method was taken to calculate the lattice parameters. X-ray photoelectron spectroscopy (XPS) was employed to study the valence variation of Ti ions in CLT ceramics without and with Al_2O_3. The results showed that Al^{3+} substituted for Ti^{4+} to form solid solution and the solid solubility limit of Al^{3+} is near 1.11 mol%. Furthermore, the reduction of Ti^{4+} in CLT ceramics was restrained by acceptor doping process and the Q × f values of CLT ceramics were improved significantly. The CLT ceramic doped with 1.11 mol% Al_2O_3 exhibited good microwave dielectric properties: ε_r = 141, Q × f = 6848 GHz, τ_f = 576 ppm/°C.

1. Introduction

The modern information revolutions, such as 5G mobile communication, large capacity satellite, wearable electronics, etc. demand billions of microwave devices with small size, light weight and good microwave dielectric properties. As we all know, the dimensions of the electronic devices are inversely proportional to the square roots of dielectric constants ($\sqrt{\varepsilon_r}$) of the ceramics. Thus, we need high dielectric constant ceramics to minimize the size of the microwave devices. Meanwhile, to ensure high SNR values of the electronic devices, the ceramics should also possess high quality factor (Q × f) values. Therefore, fabricating dielectric ceramics with high ε_r (usually ≥ 100) and high Q × f values has attracted much attention of the global researchers in the past few decades [1–4].

Fortunately, there had been several high ε_r ceramic systems reported by researchers, such as: CaO-Li_2O-Ln_2O_3-TiO_2 (ε_r = 100–120, Ln = La, Nd, Sm) [5–8], lead based perovskite (ε_r = 60–110) [9,10] and BaO-Ln_2O_3-TiO_2 (ε_r = 80–95, Ln = La, Sm, Nd) [11,12]. However, compared with those high dielectric constant systems, $CaTiO_3$ is the naturally occurring perovskite structure which possesses a higher dielectric constant ($\varepsilon_r \sim 162$) [13]. Moreover, substituting the Ca^{2+} at A site in perovskite structure by La^{3+} to form $Ca_{1-x}La_{2x/3}TiO_3$ solid solution was beneficial to improve the Q × f value which was attributed to the formation of Ca^{2+} vacancies at A site in the double-perovkite structure [14,15]. Nevertheless, dark core was founded in the CLT ceramic which sintered at a high temperature above 1300 °C but unfortunately, deteriorated the Q × f value. As reported by Templeton and Pullar [16,17], the dark core was attributed to the reduction of Ti^{4+} to Ti^{3+} caused by the oxygen vacancies formed at the high temperature. Actually, the Ti^{3+} is formed by Ti^{4+} weakly bounding an electron. And those weakly bound electrons would exacerbate the conductive loss which deteriorates the Q × f values. As reported by Yao [18], doping with Al_2O_3 as an acceptor was beneficial to restrain the reduction of Ti^{4+} in $Ba_{4.2}Sm_{9.2}Ti_{18}O_{54}$ system. To further investigate whether this anti-reduction mechanism is also true for the CLT system or not is of great significance to the improvement of Q × f value.

In this paper, CLT ceramic ($\varepsilon_r \sim 150$) is chosen as the basic composition and Al_2O_3 as an acceptor. The influences of Al_2O_3 on the sintering behavior, micro-structure and microwave dielectric properties have been fully studied. Above all, the anti-reduction mechanism of Ti^{4+} in Al_2O_3 doped CLT ceramics has been carefully investigated.

2. Experimental procedure

CLT ceramic powders were prepared by the conventional solid state reaction method. The raw materials $CaCO_3$ (99.9%), La_2O_3 (99.9%) and TiO_2 (99.9%) were weighed according to the desired stoichiometry of CLT. The powders were ball milled by ZrO_2 balls in deionized water medium for 24 h. The slurry was dried at 150 °C for 5 h and then the powders were calcined at 1150 °C for 4 h. The calcined powders were mixed with 0 wt%, 0.2 wt%, 0.4 wt%, 0.6 wt%, 0.8 wt%, 1 wt% Al_2O_3 (For better understanding, the mass percents were converted into mole

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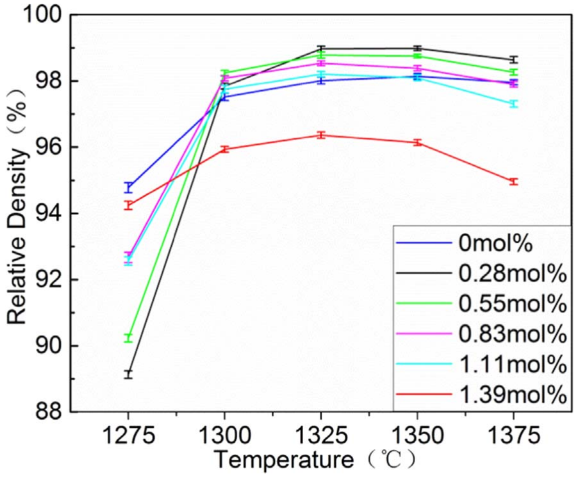

Fig. 1. Relative densities of $Ca_{0.9}La_{0.067}TiO_3$-xAl_2O_3 (x = 0–1.39 mol%) ceramics sintered at different temperatures for 4 h.

percents, corresponding to 0 mol%, 0.28 mol%, 0.55 mol%, 0.83 mol%, 1.11 mol% and 1.39 mol%, respectively). Afterwards, the mixtures were ball milled by ZrO_2 balls in deionized water medium for 24 h. The slurry was dried at 120 °C for 5 h and then granulated with polyvinyl alcohol (PVA). The granules were preformed under uniaxial pressure of 100 MPa. Finally, the green compacts were sintered at 1275–1375 °C in air for 4 h with a heating rate of 5 °C/min.

The Archimedes' method was used to measure the apparent densities (ρ_{ap}) of ceramics. And the theoretical densities (ρ_{theo}) and relative densities (ρ_{rela}) of ceramics were calculated by following equations [19]:

$$\rho_{theo} = ZM/N_A V \tag{1}$$

$$\rho_{rela} = (\rho_{ap}/\rho_{theo})\times 100\% \tag{2}$$

where *Z*, *M* and N_A represented the number of unit cell per crystal cell, molar mass of unit cell and Avogadro constant, respectively. And *V* represented cell volume obtained by XRD refinement. The crystalline phase was identified by using a Rigaku D/max 2550 V X-ray diffractometer with a conventional Cu-Kα radiation in the range of 10–80° with a step size of 0.02°. The micro-structure and elemental composition of CLT ceramics were examined by a Magellan 400 field emission scanning electron microscope with an energy dispersive spectroscopy (EDS). And ESCALAB250 X-ray photoelectron spectroscopy was used to determine the valence states of atoms. The method developed by Hakki and Coleman was used to measure the microwave dielectric properties of the samples. All the microwave measurements were used in the TE_{011} mode of an Agilent E8363A PNA series network analyzer. The temperature coefficient of resonant frequency (τ_f) was measured using the same method by varying the temperature from 20 °C to 60 °C and was calculated by the following equation:

$$\tau_f = (f_{60} - f_{20})/(60 - 20)f_{60} \tag{3}$$

where f_{60} and f_{20} represented the resonant frequency at 60 °C and 20 °C respectively.

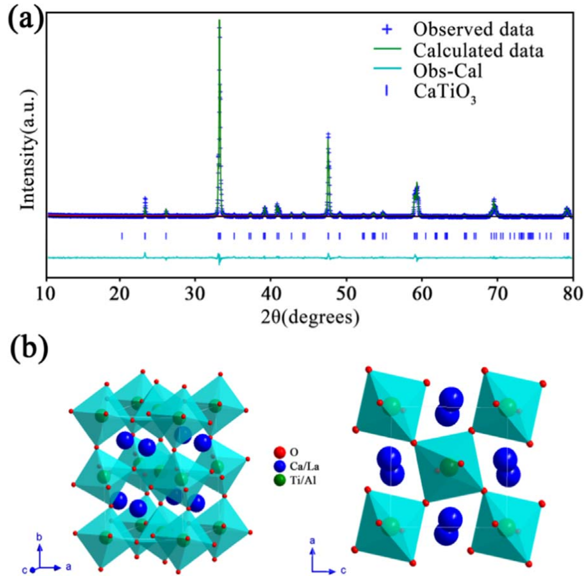

Fig. 3. the representative (a) plots of the experimental (blue cross) and calculated (green line) XRD data and (b) structure model of $Ca_{0.9}La_{0.067}TiO_3$-xAl_2O_3 (x = 1.11 mol%) ceramic sintered at 1325 °C for 4 h. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

3. Results and discussions

Fig. 1 shows the relative densities of CLT-xAl_2O_3 (x = 0 mol%,

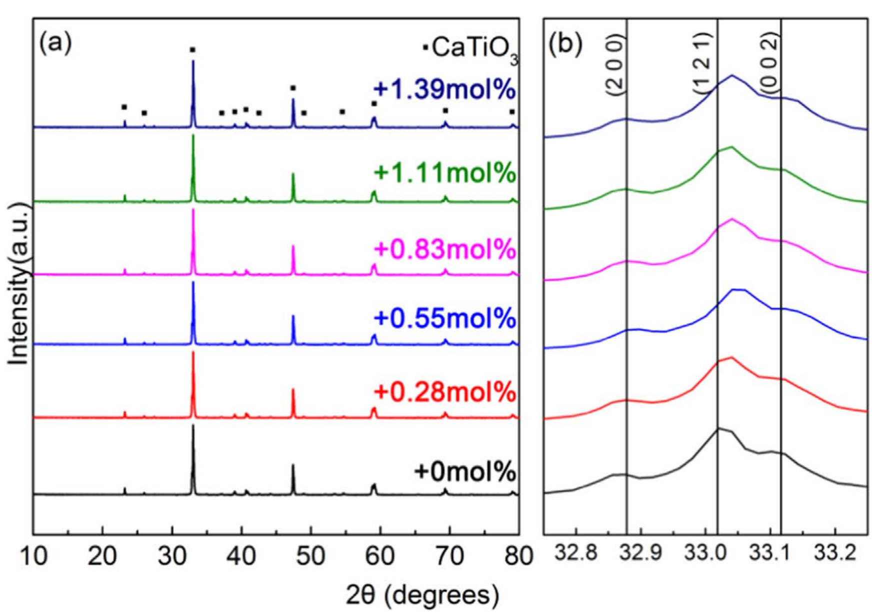

Fig. 2. X-ray diffraction patterns of $Ca_{0.9}La_{0.067}TiO_3$-xAl_2O_3 (x = 0–1.39 mol%) ceramics sintered at the optimal temperatures for 4 h: (a) full diffraction range; (b) enlarged diffraction peaks.