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Effect of Al_2O_3 on the structure and microwave dielectric properties of $Ca_{0.7}Ti_{0.7}La_{0.3}Al_{0.3}O_3$

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Abstract

The effect of excess Al_2O_3 on the densification, structure and microwave dielectric properties of $Ca_{0.7}Ti_{0.7}La_{0.3}Al_{0.3}O_3$ (CTLA) was investigated. CTLA ceramics were prepared using the conventional mixed oxide route. Excess Al_2O_3 in the range of 0.1–0.5 wt% was added. It was found that Al_2O_3 improved the densification. A phase rich in Ca and Al was found in the microstructure of Al_2O_3 doped samples. Additions of Al_2O_3 coupled with the slow cooling after sintering improved the microwave dielectric properties. CTLA ceramics with 0.25 wt% Al_2O_3 cooled at 5 °C/h showed high density and a uniform grain structure with $\varepsilon_r = 46$, $Q \times f = 38{,}289$ and $\tau_f = +12$ ppm/°C at 4 GHz. XRD and TEM examinations showed the presence of (1 1 2) and (1 1 0) type twins arising from $a^-a^-c^+$ tilt system with the presence of anti-phase domain boundaries from the displacement of A-site cations of the orthorhombic perovskite structure.

Keyword: Microwave dielectrics

1. Introduction

Materials with the perovskite structure are widely employed as dielectric resonators, because of their high dielectric constants and high quality factors. Perovskites are characterised by the chemical formula ABO_3, and a structure which is very tolerant to substitution of ions of various sizes on both A and B cation sublattices.[1] At room temperature many of these perovskites compounds are distorted from the ideal structure through rotation or tilting of the BO_6 octahedra accompanied by displacement of the A-site cations. As a result, most of the perovskites at room temperature exhibit sub-grain features. Such as twining domains and ordering anti-phase boundaries due to the structural phase transitions, which are encountered during cooling from the sintering temperature.[2–4]

$CaTiO_3$ is an orthorhombic distorted perovskite[5] at room temperature with high relative permittivity ($\varepsilon_r = 170$), modest quality factor ($Q \times f = 3500$ GHz) and a very high positive temperature coefficient of resonant frequency ($\tau_f = +800$ ppm/°C).[4,6] In contrast $LaAlO_3$ is a rhombohedral perovskite at room temperature[7] with low relative permittivity ($\varepsilon_r = 23.4$), high quality factor ($Q \times f = 68{,}000$ GHz) and a negative temperature coefficient of resonant frequency ($\tau_f = -44$ ppm/°C).[7] The high positive τ_f of $CaTiO_3$ can be suppressed to small or zero τ_f by addition of $LaAlO_3$, which make it a suitable candidate for microwave applications. Ceramic material based on $CaTiO_3$–$LaAlO_3$ solid solution[8] is a promising candidate for microwave frequencies because of its high dielectric constant ($\varepsilon_r \approx 45$–47) with high quality factor ($Q \times f \approx 38{,}000$) and small or zero temperature coefficient of resonant frequency (τ_f).

Suvorov et al.[6] reported dielectric properties of $\varepsilon_r = 44$, $Q \times f = 30{,}000$ and $\tau_f = -3$ ppm/°C for $0.7CaTiO_3$–$0.3LaAlO_3$. High calcination temperature in the range of 1350–1450 °C for 40 h with intermediate grinding was reported. The sintering temperature was 1450 °C for 12 h. They reported the existence of a significant amount of closed porosity. The densification of the CTLA ceramic was improved by increasing the LA ($LaAlO_3$) content or substitution of 1 at% Sr for Ca. Moon et al.[9] also studied the dielectric and sintering properties of $(1-x)CaTiO_3$–$xLaAlO_3$ ceramics. A high calcinations temperature of 1400 °C and high sintering temperature of 1600 °C were required to obtain dense ceramics. Additions of combinations of Bi_2O_3 with Al_2O_3 or NiO lowered the sintering temperature to 1450 °C. However, the additives reduced the $Q \times f$ value by at least 15%. The microwave dielectric properties of $\varepsilon_r \approx 45$, $Q \times f \approx 22{,}500$ GHz and $\tau_f \approx +10$ ppm/°C were reported for the undoped $0.7CaTiO_3$–$0.3LaAlO_3$.[9]

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In the present study, the effect of excess Al_2O_3 and the change of cooling rate on the sintering behaviour, microstructure and microwave dielectric properties of $0.7CaTiO_3$–$0.3LaAlO_3$ ceramics have been investigated.

2. Experimental

Samples were prepared by conventional mixed oxide route. High purity (>99.9%) $CaCO_3$, TiO_2, La_2O_3 and Al_2O_3 were used as raw materials. The powders were weighed according to the stoichiometry ($Ca_{0.7}Ti_{0.7}La_{0.3}Al_{0.3}O_3$) and mixed for 20 h using propan-2-ol and zirconia media. La_2O_3 was dried at 900 °C for 6 h before weighing. The mixed powders were calcined at 1250 °C for 4 h then 0.25 wt% Al_2O_3 was added and wet milled for 20 h and dried. Pellets were prepared by pressing powders in steel die 20 mm diameter at 100 MPa. The pellets were sintered at 1500 °C for 4 h in air with a heating rate of 180 °C/h and cooling rate of 180 °C/h. Selected samples were also cooled at 60, 15 and 5 °C/h.

Crystal structures were examined by X-ray diffraction (Philips Analytical, X'pert-MPD) employing Cu Kα1 radiation under the conditions 50 kV and 40 mA. The samples were scanned at 0.03° intervals of 2θ in the range 10–85°; the scan rate was $0.01° \, 2\theta \, s^{-1}$.

Microstructural examination of the sintered ceramics was performed by means of scanning electron microscopy (SEM) (JEOL 6300 and PHILIPS XL30). The sintered surfaces of ceramics were ground (to 1200 grade SiC) and polished (to 1 μm diamond paste). Then, samples were thermally etched at 1320° for 12 min and coated with carbon prior to SEM analysis.

TEM specimens were prepared from the sintered ceramics, after lapping and polishing to form 3 mm diameter discs. The discs were dimpled to reduce the sample to 30 μm thickness in the centre and then thinned to electron transparency with a Gatan Precision Ion Polishing System (PIPS). The specimens were investigated using a Philips CM200 operating at 200 kV and a Tecnai G2 TEM operating at 300 kV. The dielectric properties (ε_r and $Q \times f$) were determined by the parallel plate method.[10] The τ_f values were determined using a silver-plated, aluminium cavity at temperatures between −10 and +60 °C.

3. Results and discussion

3.1. Densification

The density of undoped $Ca_{0.7}Ti_{0.7}La_{0.3}Al_{0.3}O_3$ sample was only 90% theoretical after sintering at 1500 °C for 4 h. Addition of 0.15 wt% Al_2O_3 improved the densification to 93%, whereas 0.25 wt% Al_2O_3 increased density to 96%. Addition of alumina in excess of 0.25–0.3 and 0.5 wt% decreased density to 92 and 90%, respectively. Addition of the excess alumina did not affect the sintering temperature or sintering time.

3.2. X-ray diffraction (XRD) analysis

Fig. 1 shows the X-ray diffraction spectra for the stoichiometric CTLA powders calcined at various temperatures. Powders calcined at 1150 °C contained $La(OH)_3$ as intermediate phase. The amount of intermediate phase reduced as the calcination temperature was increased to 1250 °C. The powders calcined at 1350 °C were single phase but very hard, making it difficult to reduce them to fine powders. Therefore, 1250 °C was chosen as the calcinations temperature for the CTLA ceramics.

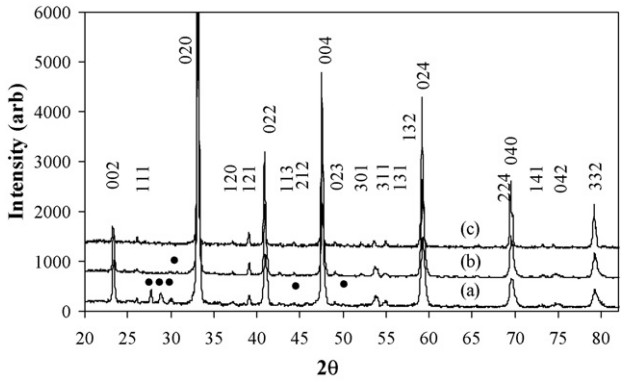

Fig. 1. X-ray diffraction spectra for CTLA powder calcined at: (a) 1150 °C, (b) 1250 °C and (c) 1350 °C, (●) the intermediate phase $La(OH)_3$ identified.

Fig. 2 shows the X-ray diffraction spectrum for CTLA ceramics prepared with different levels of Al_2O_3. The reflections are consistent with that for a tilted perovskite structure. The pattern can be interpreted as an orthorhombic structured perovskite phase containing of both in-phase and anti-phase tilting of BO_6 octahedral in association with anti-parallel shifting of A-site cations. From the reflections, there was no evidence of a secondary phase.

The addition of Al_2O_3 did not change the lattice parameters significantly. Samples doped with 0.25 wt% Al_2O_3 had lattice parameters of $a = 5.4072$ (3) Å, $b = 5.4192$ (4) Å and $c = 7.6467$ (4) Å. The unit cell values obtained are consistent with the results found by Kalyavin et al.[11] since *Pnma* space group assigned in the above refinement doubling of the unit cell with respect to *b*-axis is observed ($a^-b^+a^-$). From this study, it was learnt that the CTLA XRD can be better described with orthorhombic *Pbnm* space group and $a^-a^-c^+$ tilt system, which is consistent with CTNA[12] structure at room temperature.

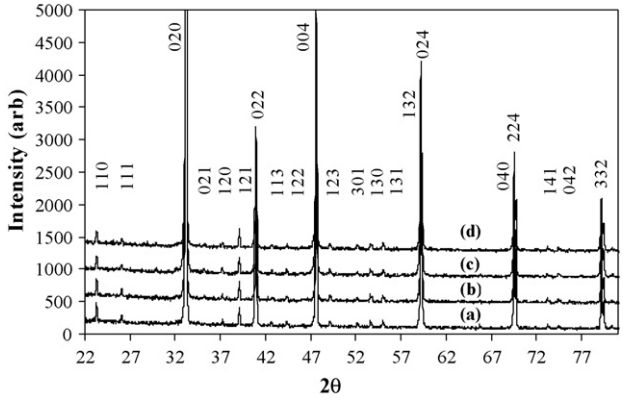

Fig. 2. X-ray diffraction spectra of CTLA prepared with the addition of: (a) 0.15% Al_2O_3, (b) 0.25% Al_2O_3, (c) 0.3% Al_2O_3 and (d) 0.5% Al_2O_3. The samples were sintered at 1500 °C for 4 h and cooled at 180 °C/h.