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Sintering behavior and microwave dielectric properties of $0.67CaTiO_3$–$0.33LaAlO_3$ ceramics modified by B_2O_3–Li_2O–Al_2O_3 and CeO_2

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ABSTRACT

A low temperature sintering method was used to avoid the relatively high sintering temperatures typically required to prepare $0.67CaTiO_3$–$0.33LaAlO_3$ (CTLA) ceramics. Additionally, CeO_2 was introduced into the CTLA ceramics as an oxygen-storage material to improve their microwave dielectric properties. $0.67CaTiO_3$–$0.33LaAlO_3$ ceramics co-doped with B_2O_3–Li_2O–Al_2O_3 and CeO_2 were prepared by a conventional two-step solid-state reaction process. The sintering behavior, crystal structure, surface morphology, and microwave dielectric proprieties of the prepared ceramic samples were studied, and the reaction mechanism of CeO_2 was elucidated. CTLA+0.05 wt% BLA+3 wt% CeO_2 ceramics sintered at 1360 °C for 4 h exhibited the optimal microwave dielectric properties: dielectric constant (ε_r)=45.02, quality factor ($Q\times f$)=43102 GHz, and temperature coefficient of resonant frequency (τ_f)=2.1 ppm/°C. The successful preparation of high-performance microwave dielectric ceramics provides a direction for the future development and commercialization of CTLA ceramics.

1. Introduction

To satisfy the high requirements of microwave devices relating to miniaturization, integration, reliability, and low cost, microwave dielectric ceramics, a new type of functional electronic material, have become important materials in the field of electronic communications [1].

For medium-frequency dielectric filters, one of the most important aims is to develop a dielectric material with intermediate dielectric constant (ε_r), low dielectric loss (high Q-values), and tunable temperature coefficient of resonant frequency (τ_f) [2]. Ceramic materials based on the $CaTiO_3$–$LaAlO_3$ (CTLA) system, one of the most competitive material systems, have attracted great interest, as evidenced by the numerous research works studies [1–4]. For instance, Moon et al. [5] studied the dielectric properties and sintering behavior of $(1-x)CaTiO_3$–$xLaAlO_3$ ceramics and reported microwave dielectric properties of $\varepsilon_r\approx 43$, quality factor $(Q\times f)\approx 32500$ GHz, and $\tau_f\approx 10$ ppm/°C for non-doped $0.7CaTiO_3$–$0.3LaAlO_3$ ceramic. To obtain dense ceramics, calcination and sintering temperatures as high as 1400 °C and 1600 °C, respectively, were employed the addition of a mixture of Bi_2O_3 and Al_2O_3 or NiO slightly reduced the sintering temperature to 1450 °C. However, unfortunately, the additives caused the $Q\times f$ value to drop by at least 15%. In a more recent study, Suvorov [6] reported $\varepsilon_r=44$, $Q\times f=30{,}000$ GHz, and $\tau_f=-3$ ppm/°C for $0.7CaTiO_3$–$0.3LaAlO_3$ ceramics prepared with calcination temperatures ranging between 1350 and 1450 °C for 40 h and sintering temperatures as high as 1450 °C for 12 h. Similarly, Ravi et al. [3] 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 $\varepsilon_r=46$, $Q\times f=38289$ 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 brief, the above results indicate that the high preparation temperatures involved and resultant relatively low microwave dielectric properties hinder the development and commercial application of $(1-x)CaTiO_3$–$xLaAlO_3$ ceramics.

Many attempts have been made to improve the sintering behavior and consequently enhance the microwave dielectric properties of CTLA ceramics. Doping with glass additives to reduce the sintering temperature is one of the most effective methods. B_2O_3–Li_2O–Al_2O_3 (BLA) is a glass system that has been reported to decrease the sintering temperature remarkably [7–9]. However, the introduction of BLA inevitably leads to the decrease of $Q\times f$, as reported by Li et al. [9]. In their study, a secondary phase (an

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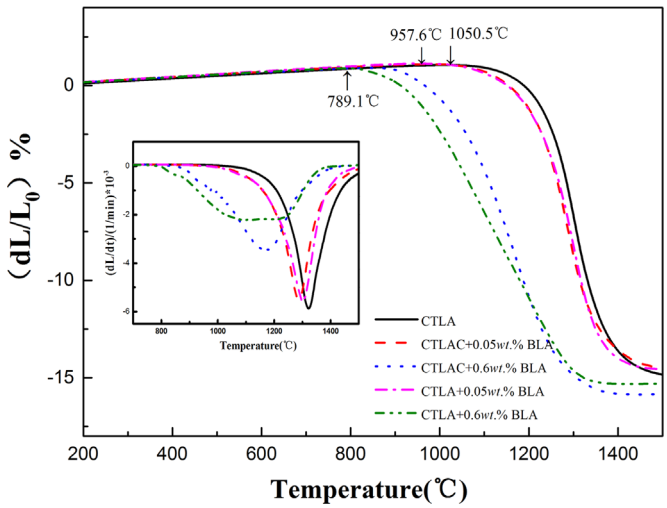

Fig. 1. Shrinkage curves and shrinkage rates (inset) of CTLA+*x* wt% BLA and CTLA+*x* wt% BLA+*y* wt% CeO_2 powders.

aluminum-containing compound) formed after the introduction of BLA. To prevent the formation of this secondary phase, the introduction of CeO_2 was considered for combining with Al^{3+} to form $CeAlO_3$, which has a tetragonal perovskite structure similar to that of $LaAlO_3$ [10–12]. During the sintering process, the following reaction was expected to occur:

$$2CeO_2+Al_2O_3 \rightarrow 2CeAlO_3+\frac{1}{2}O_2 \quad (1)$$

Furthermore, as an oxygen-storage material, CeO_2 could considerably enhance the microwave dielectric properties of CTLA ceramics [13–15]. In this paper, the effects of BLA and CeO_2 addition on the sintering behavior, microstructure, and microwave dielectric properties of CTLA ceramics were investigated in detail.

2. Experimental procedure

BLA sintering additives were synthesized at the appropriate stoichiometric ratios by ball milling with zirconia media and ethanol for 8 h. After drying, the BLA mixture was calcined at 650–800 °C for 1 h, and the obtained large sintering additive particles were then pulverized into powders.

The CTLA ceramics were prepared by a conventional two-step solid-state reaction from high-purity $CaCO_3$ (99.3%), TiO_2 (99.9%), La_2O_3 (99.99%), and Al_2O_3 (94%). Firstly, stoichiometric ratios of $CaCO_3$ and TiO_2, and La_2O_3 and Al_2O_3 were respectively mixed in nylon jars using deionized water and ball milled using zirconia balls for 5 h. After drying, $CaTiO_3$ was calcined at 1090 °C for 6 h and $LaAlO_3$ was calcined at 1230 °C for 6 h. The calcined powders were mixed with 1–5 wt% CeO_2 and 0.05–0.6 wt% BLA, ground by ball milling for 8 h, dried, and then mixed with 8 wt% polymer solution (vinyl alcohol, 5%) as a binder. The final powders were uniaxially pressed into pellets of 12 mm in diameter and 7 mm in height. The cylinders were debindered and then sintered at the temperature range of 1280–1480 °C for 4 h in air. After cooling to 1000 °C at a rate of 2 °C/min, the ceramics were allowed to cool naturally inside the furnace.

Temperature- and time-dependent sintering behavior was investigated using a dilatometer (DIL 402PC, Netzsch Instruments, Germany). The crystal structures of the sintered samples were examined by X-ray powder diffraction (XRD) on a Bruker D8 Advance X-ray powder diffractometer using Cu Kα radiation. The microstructures of the ceramics were observed by scanning electron microscopy (SEM) on a JEOL JSM-7100F equipped with an

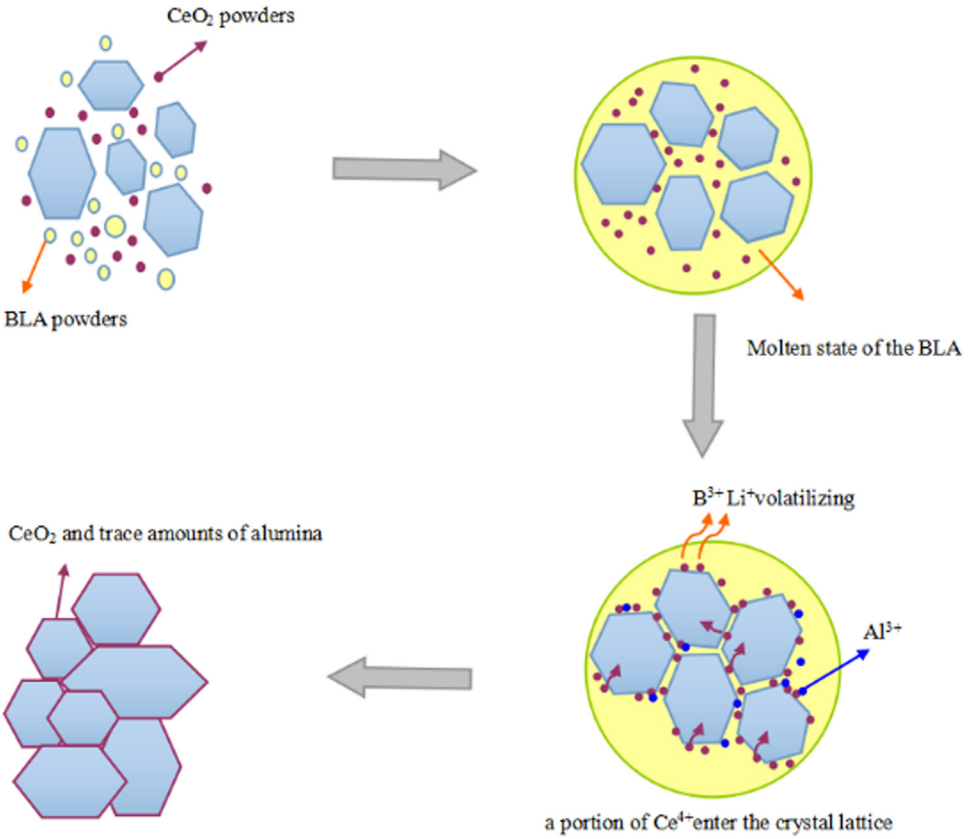

Fig. 2. Sintering mechanism of CTLA+*x* wt% BLA+3 wt% CeO_2.