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Low temperature sintering and microwave dielectric properties of $CaSiO_3$–Al_2O_3 ceramics for LTCC applications

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Abstract

The effects of CuO, Li_2CO_3 and $CaTiO_3$ additives on the densification, microstructure and microwave dielectric properties of $CaSiO_3$–1 wt% Al_2O_3 ceramics for low-temperature co-fired applications were investigated. With a single addition of 1 wt% Li_2CO_3, the $CaSiO_3$–1 wt% Al_2O_3 ceramic required a temperature of at least 975 °C to be dense enough. Large amount addition of Li_2CO_3 into the $CaSiO_3$–1 wt% Al_2O_3 ceramics led to the visible presence of $Li_2Ca_3Si_6O_{16}$ and $Li_2Ca_4Si_4O_{13}$ second phases. Fixing the Li_2CO_3 content at 1 wt%, a small amount of CuO addition significantly promoted the sintering process and lowered the densification temperature to 900 °C whereas its addition deteriorated the microwave dielectric properties of $CaSiO_3$–1 wt% Al_2O_3 ceramics. Based on 10 wt% $CaTiO_3$ compensation in temperature coefficient, good microwave dielectric properties of $\varepsilon_r = 8.92$, $Q \times f = 19{,}763$ GHz and $\tau_f = -1.22$ ppm/°C could be obtained for the 0.2 wt% CuO and 1.5 wt% Li_2CO_3 doped $CaSiO_3$–1 wt% Al_2O_3 ceramics sintered at 900 °C. The chemical compatibility of the above ceramics with silver during the cofiring process has also been investigated, and the result showed that there was no chemical reaction between silver and ceramics, indicating that the as-prepared composite ceramics were suitable for low-temperature co-fired ceramics applications.

Keywords: Microwave dielectric properties; $CaSiO_3$ ceramic; Al_2O_3 ceramic; LTCC

1. Introduction

The rapid growth of the telecommunication and satellite broadcasting industry has created a high demand for microwave ceramic components. Multi-layer devices, which consist of alternating microwave dielectric ceramics and internal metallic electrode layers, enable the microwave components to be miniaturized and hybridized. As a metallic electrode, Ag has been widely used because of its high conductivity and low cost. Compared with the melting temperature of Ag, which is about 961 °C, the sintering temperature of the microwave dielectric ceramics is generally high, above 1300 °C. Therefore, from the point view of the fabrication of multi-layer devices, it is important to develop low temperature co-fired ceramics (LTCC) [1]. Several LTCC systems such as (Mg, Ca) TiO_3, $Ba_5Nb_4O_{15}$, $Li_2ATi_3O_8$ (A=Mg, Zn), $Ba_2Ti_9O_{20}$ and $ZnTiNb_2O_8$ have been investigated for microwave applications [2–8]. However, most of the reported LTCC microwave dielectric ceramics show a relatively high dielectric constant, which could be applied only in low frequency ranges such as 1.89 and 2.45 GHz. Comparatively, LTCC microwave dielectric ceramics with low-permittivity, which can work at a high frequency such as millimeter-wave range and are required for multilayer components particularly antennas and baluns, have not been extensively studied [9].

$CaSiO_3$ ceramic has been proved to be an excellent dielectric material with a low dielectric constant and a low dielectric loss, and it might be regarded as a suitable candidate for antennas and baluns. However, the sintering temperature range of neat $CaSiO_3$ ceramic is very narrow. Chakradhar et al. pointed out that it was difficult to obtain dense $CaSiO_3$ ceramic since its grains grew exceptionally and the bulk $CaSiO_3$ ceramic became more porous with the increase of the calcination temperature [10]. In our previous work, the sintering behavior and microwave dielectric properties of $CaSiO_3$ ceramics have been investigated by a traditional solid-state

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process and a sol–gel method, respectively [11]. The maximum bulk density of $CaSiO_3$ ceramic sintered at 1340 °C prepared by the conventional solid-state process was 2.439 g/cm^3, and the microwave dielectric properties were $\varepsilon_r=6.59$ and $Q \times f=13{,}109$ GHz. Whereas for $CaSiO_3$ ceramic obtained by the sol–gel method, the maximum bulk density was 2.505 g/cm^3 and the microwave dielectric properties were $\varepsilon_r=6.69$ and $Q \times f=25{,}398$ GHz. The density value of the above two samples synthesized either by the traditional solid-state method or by the sol–gel method is much smaller than that of the theoretical density of the $CaSiO_3$ ceramic, which is 2.91 g/cm^3, indicating that it is difficult to obtain dense $CaSiO_3$ ceramic.

In order to improve the sintering characteristic and microwave dielectric properties, Sun and co-workers have used Mg^{2+} to substitute Ca^{2+} in the $CaSiO_3$ host to prepare the CaO–MgO–SiO_2 ceramics for LTCC applications [9,12]. In our previous work, we have found that the Al_2O_3 addition can restrict the growth of $CaSiO_3$ grains by surrounding their boundaries and also improve the bulk density of $CaSiO_3$–Al_2O_3 ceramics [13]. The optimum amount of Al_2O_3 addition was found to be 1 wt%, and the derived $CaSiO_3$–1 wt% Al_2O_3 ceramic presented improved microwave dielectric properties of $\varepsilon_r=6.66$ and $Q \times f=24{,}626$ GHz. However, the sintering temperature is high, which is about 1250 °C, so the $CaSiO_3$–Al_2O_3 ceramics cannot be co-fired with the Ag electrode.

In this work, CuO and Li_2CO_3 were added to the $CaSiO_3$–1 wt% Al_2O_3 ceramics to decrease the sintering temperature for LTCC applications, and $CaTiO_3$ was selected as compensation for a zero temperature coefficient. Furthermore, microstructure, microwave dielectric properties, green tape and co-firing with silver electrode of the CuO, Li_2CO_3 and $CaTiO_3$ added $CaSiO_3$–1 wt% Al_2O_3 ceramics were also investigated.

2. Experimental procedure

Specimen powders were prepared by a conventional solid-state method using commercial oxide powders (> 99.5%) of $CaCO_3$, SiO_2, Al_2O_3, CuO, Li_2CO_3 and TiO_2 as raw materials. Stoichiometric $CaCO_3$ and SiO_2 (TiO_2) powders were weighed and ground in ethanol for 24 h in a balling mill with ZrO_2 balls. Prepared powders were dried and calcined at 1200 °C for 2 h in air to obtain $CaSiO_3$ ($CaTiO_3$). The calcined powders were mixed as desired composition $CaSiO_3$ with 1 wt% Al_2O_3 and different amounts of CuO, Li_2CO_3 and $CaTiO_3$ additives and re-milled for 24 h. After drying and sieving, the as-prepared powders together with the organic binder (5 wt% polyvinyl alcohol) were uniaxially pressed under a pressure of 135 MPa into cylinders of 15 mm in diameter and 7–8 mm in thickness. These samples were then sintered at 875–1000 °C for 2 h in air with a heating rate of 5 °C/min.

The bulk densities of the sintered pellets were measured by the Archimedes method using distilled water as medium. The sintered bulks were broken up and ground to powders using an agate mortar. Crystal structures of the powders were performed by the X-ray diffraction (XRD, ARL XTRA) with Cu K_α radiation (36 kV, 30 mA, $2\theta=10$–80°). The polished surfaces of the ceramics were investigated by scanning electron microscopy (SEM, S-4800) after thermal etching. The microstructure observation of the green tape and the interface of ceramic and silver were performed by scanning electron microscopy (SEM, TM3000). The dielectric constants ε_r and the quality values $Q \times f$ at microwave frequencies were measured by Hakki–Coleman dielectric resonator method [14,15] using an Agilent 8719ET (50 MHz to 13.5 GHz) Network Analyzer. The temperature coefficient of the resonant frequency τ_f was also measured by the same method in the temperature range from 25 °C to 80 °C and calculated by the following equation:

$$\tau_f = \frac{f_{80}-f_{25}}{f_{25} \times 55} \times 10^6 \ (\text{ppm}/^\circ C)$$

where f_{80} and f_{25} represent the resonant frequency at 80 °C and 25 °C, respectively.

3. Results and discussion

3.1. Effects of the CuO addition on $CaSiO_3$–1 wt% Al_2O_3 ceramics

Fig. 1 shows the bulk densities of $CaSiO_3$–1 wt% Al_2O_3 ceramics sintered at different temperatures with 1 wt% Li_2CO_3 and different amounts of CuO additions. It is firstly evidenced that ceramics with the addition of CuO and Li_2CO_3 could be sintered at temperatures in the range of 900–925 °C whereas the ceramic without CuO addition requires a higher temperature, which is at least 975 °C, to be dense enough. The effect of CuO addition on crystal structure is investigated by the XRD analysis. Due to the small quantity of Al_2O_3, Li_2CO_3 and CuO, only the phase of $CaSiO_3$ (PDF 27-0088) is observed, as is shown in Fig. 2.

The SEM photographs of $CaSiO_3$–1 wt% Al_2O_3 ceramics incorporated with 1 wt% Li_2CO_3 and different amounts of CuO sintered at 900 °C for 2 h are illustrated in Fig. 3(a)–(d).

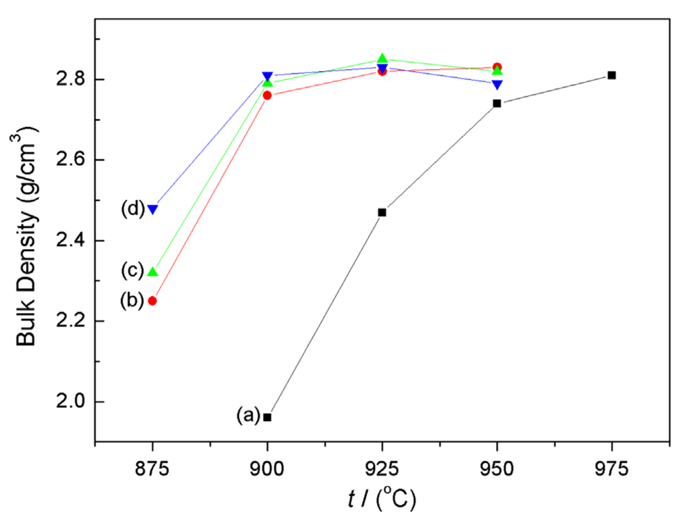

Fig. 1. Bulk densities of $CaSiO_3$–1 wt% Al_2O_3 ceramics sintered at different temperatures with 1 wt% Li_2CO_3 and (a) 0 wt%, (b) 0.2 wt%, (c) 0.4 wt% and (d) 0.8 wt% CuO additions.