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CuO as sintering additive to $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics

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The effects of CuO addition on the sintering behavior and microwave dielectric properties of $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics were investigated. CuO was selected as a liquid phase sintering aid to lower the sintering temperature of $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics. With CuO addition, the sintering temperature of $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics was effectively reduced from 1550 °C to 1475 °C. The crystalline phase exhibited no phase difference and no second phase was detected at all addition levels. The electric permittivity was not significantly affected by various amounts of CuO addition and ranged from 52 to 54. Small values (<+7 ppm/K) of the temperature coefficient of resonant frequency were obtained for $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics. However, the unloaded quality factor Q_u was strongly dependent upon the CuO concentration. $Q_u f_o \sim 10500$ GHz was obtained for $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics with 0.5 wt.% of CuO addition, sintered at 1475 °C.

Keywords: *CuO; calcination; additive*

1. Introduction

Extensive investigations have been carried out on microwave dielectric ceramics for the use as resonators, oscillators and filters in mobile communication systems such as cellular phones, global positioning systems, and personal communication systems [1]. These systems require ceramic materials having relatively high electric permittivity ($\varepsilon_r > 20$), a near zero temperature coefficient of resonant frequency (τ_f) and a high unloaded quality factor Q_u, generally reported as a product with frequency f_o at which it is measured ($Q_u f_o$) [2–4]. In multilayer structures, the dielectrics with low sintering temperature are needed. There have been several approaches to reduce the sintering temperature of microwave ceramics, for example, addition of glass or low melting point materials, chemical processing, and the use of smaller particles as the sintering materials. In general, the addition of glass or low melting point materials such as B_2O_3, CuO, SiO_2, PbO and Bi_2O_3 is known to be an effective and inexpensive way to obtain dense sintered ceramics [5–8]. CuO has been reported as a good sintering additive to lower the sintering temperature for many materials [9]. Jawahar *et al.* [10] investigated the microwave dielectric properties of $CaLa_4Ti_5O_{17}$ ceramics that were sintered at 1625 °C to be $\varepsilon_r \sim 53$, $\tau_f \sim -20$ ppm/K and $Q_u f_o \sim 17359$ GHz. The microwave dielectric properties of $CaLa_4Ti_5O_{17}$ ceramics were improved by substituting Ca^{2+} ions with Zn^{2+} ions [11]. 0.5 wt.% CuO additive to $Ca_{0.99}Zn_{0.01}La_4Ti_5O_{17}$ ceramics sintered at 1450 °C for 4 h resulted in $\varepsilon_r \sim 57$, $Q_u f_o \sim 15{,}000$ GHz, $\tau_f \sim -8.16$ ppm/K [12]. More recently, Yaseen *et al.* [13] reported $\varepsilon_r \sim 53.7$, $Q_u f_o \sim 11532$ GHz and $\tau_f \sim -1.4$ ppm/K for $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics and suggested its application as a dielectrically loaded antenna core, but the optimum sintering temperature of this ceramics was as high as 1550 °C. No one has attempted yet to lower the sintering temperature of $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics.

This paper is aimed at lowering the sintering temperature of $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics and obtain high microwave dielectric performance using CuO as a sintering aid.

2. Materials and methods

$Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics was prepared via solid state sintering route. The starting raw materials of $SrCO_3$ (Aldrich, 99+%) and $CaCO_3$ (Aldrich,

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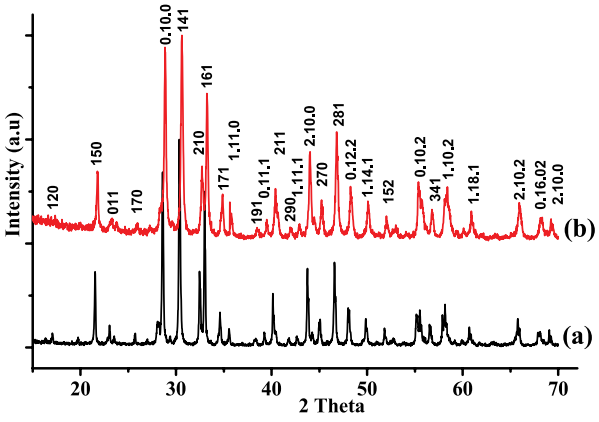

Fig. 1. XRD patterns from $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics with a) 0 wt.% and b) 0.5 wt.% CuO, showing single phase formation for each composition within the in-house XRD detection limit.

99+%) were dried at ∼185 °C and La_2O_3 (Aldrich, 99.95 %) and TiO_2 (Aldrich, Anatase, 99+%) at 900 °C, over a night prior to the weighing, to remove the moisture and assure the correct initial stoichiometry. The dried carbonates and oxides were then weighted in stoichiomatric ratios and ball-milled for 24 h in disposable polyethylene mill-jars using Y-toughened ZrO_2 balls as grinding medium and isopropanol as lubricant to make slurry. The slurry was dried for over a night in an oven at ∼95 °C. The mixed batch was sieved and calcined at 1350 °C for 6 h at heating/cooling rates of 5 °C/min. The calcined powder was reground in a pestle and mortar with different amounts of CuO as sintering aid for about 45 min. The powder was then pressed into 4 mm to 5 mm high and 10 mm in diameter pellets at 80 MPa. The pellets were placed on platinum foil and sintered at 1425 °C to 1575 °C for 4 h at heating/cooling rates of 5 °C/min. The dimensions of the ceramic compacts were controlled in such way that the sintered body had an aspect ratio (D/L) of 1 to 1.3 or 2 to 2.3 to obtain maximum mode separation during measurements. Apparent densities of the sintered pellets were measured using Archimedes method. The sintered samples were crushed into fine powders and phase analysis was performed using x-ray diffractometer (D500) operating at 30 kV and 40 mA at a scan rate of 1 °/min from $2\theta = 10°$ to 70° at the step size of 0.02°. For scanning electron microscopy (SEM), optimally sintered pellets were cut into pieces and finely polished prior to thermal etching for 30 min at the temperatures by 10 % lower than their corresponding sintering temperatures, at a heating/cooling rate of 5 °C/min. The etched surfaces were gold-coated to avoid charging effect and examined in a JEOL 6400 SEM operating at 20 kV.

Microwave dielectric properties were measured using Agilent network analyzer (R3767CH) by cavity method proposed by Krupka [14]. The cylindrical samples were placed on a low-loss quartz single crystal at the centre of the Au-coated 20 mm high and 24 mm in diameter brass cavity. τ_f values were measured by noting the variation in the resonant frequency of $TE_{01\delta}$ resonant mode over the temperature range of 20 °C to 80 °C.

3. Results and discussion

Fig. 1 illustrates the x-ray diffraction patterns (XRD) recorded at room temperature for the pulverized pellets of $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ specimens with 0 wt.% and 0.5 wt.% CuO additive. The reflections could be indexed according to the orthorhombic (*Pnnm*) $CaLa_4Ti_5O_{17}$ unit cell (PDF# 27-1059) but with the peaks positions shifted towards larger d-values due to the presence of bigger Sr^{2+} (1.44 Å) instead of smaller Ca^{2+} (1.33 Å) at the A-site of the perovskite structure [15]. There was no evidence of any second phase formation within the in-house XRD detection limits. The crystal structure of $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ was reported to be orthorhombic (*Pnnm*) with the unit cell parameters a = 5.5595 (6) Å, b = 31.526 (3) Å, c = 3.9239 (5) Å, $Z = 2$, ρ_{th} =5.54 g/cm^3 and V = 687.74 Å^3 refined by the least squares method [13].

Bulk density of sintered $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ samples with different amounts of CuO as a function of sintering temperature is illustrated in Fig. 2. The results demonstrate that the bulk density of the samples steadily increases with increasing the sintering temperature. The density increased at 0.5 wt.% CuO addition, then decreased with more CuO addition. The densification might be caused by the liquid phase effect of CuO. At higher temperature, the decrease in density might be due to the low density of liquid phase and the vaporization of CuO.

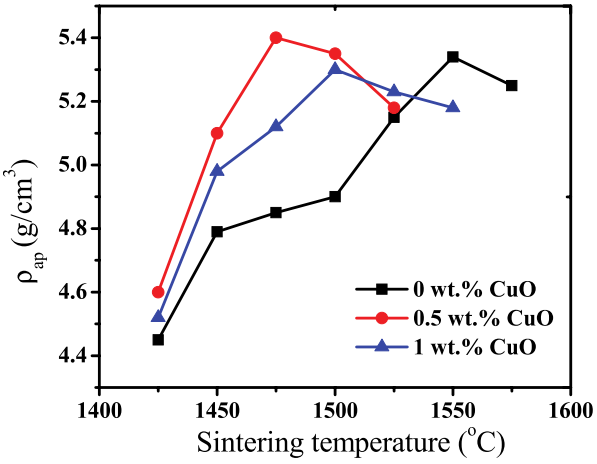

Fig. 2. Variation in ρ_{ap} of $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics with different amounts of CuO addition as a function of increasing sintering temperature, showing optimum density for 0.5 wt.% CuO added composition at 1475 °C.

Table 1. Preparation conditions, relative density and microwave dielectric properties of $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics with different amount of CuO addition.

CuO wt.%	S.T (°C)	ρ_{rel}	ε_r	$Q_u f_o$ (GHz)	τ_f (ppm/K)
0	1550/4 h	96.3	53.7	11532	−1.4
0.5	1475/4 h	97.4	54.3	10500	2.5
1.0	1500/4 h	96.0	52.8	10080	5.3

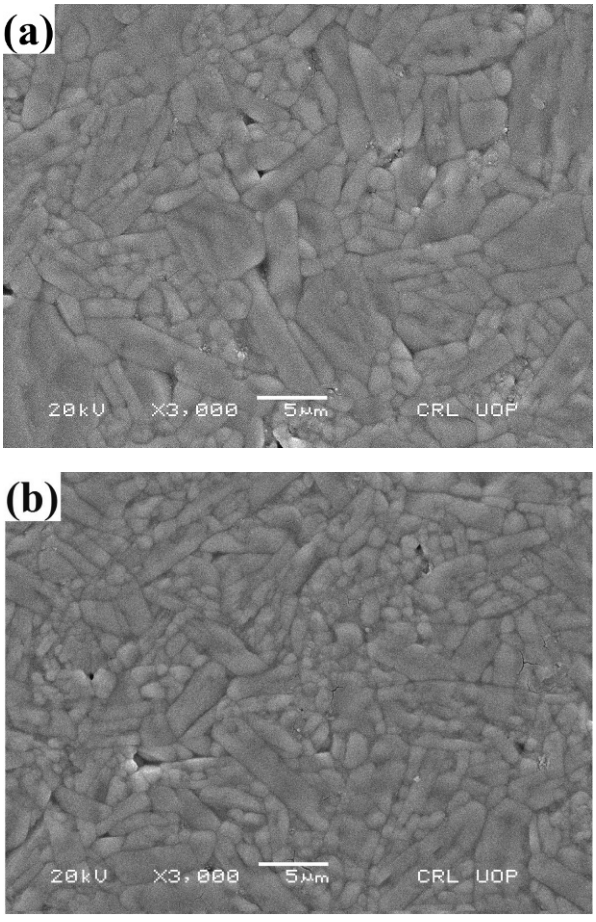

Fig. 3. SEIs recorded from thermally etched, gold-coated sintered $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics with a) 0 wt.% b) 0.5 wt.% CuO addition.

Maximum density was found to be 5.40 g/cm^3 with 0.5 wt.% CuO addition at 1475 °C/4 h.

The microstructure of the optimally sintered $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics with 0 wt.% and 0.5 wt.% CuO additive is shown in Fig. 3. The microstructure of the CuO free composition consists of elongated and needle shaped grains with an average grain size of 4 μm × 7 μm (Fig. 3a). Some abnormal grain growth with the size of ∼20 μm × 25 μm has also been observed in the microstructure of the CuO free composition. The addition of CuO resulted in a decrease in the grain size. The average grain size in the microstructure of $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics with the addition of 0.5 wt.% CuO is 3 μm × 5 μm (Fig. 3b).

The microwave dielectric properties of the optimally sintered $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics with different amounts of CuO addition are compared in Table 1. The electric permittivity (ε_r) was not significantly affected by the addition of various amounts of CuO and was in the range of 52–54 with the increase in the CuO concentration from 0 to 1 wt.%. A maximum $\varepsilon_r \sim 54.3$ was obtained for $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ with 0.5 wt.% of CuO addition, sintered at 1475 °C for 4 h. The slight increase in ε_r may be attributed to the higher density of the composition with 0.5 wt.% CuO addition. The $Q_u f_o$ value is an important factor for the applications of dielectric ceramics at microwave frequencies since higher $Q_u f_o$ value means lower loss for microwave devices. In general, $Q_u f_o$ values are known to be affected by the morphology of the samples, such as grain size and porosity or density. Yang

et al. [16] reported that the loss tangent ($\tan\delta$) increases with an increase in the amount of sintering aid. $Q_u f_o$ value decreased from 11532 GHz of pure $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics sintered at 1550 °C for 4 h to 10080 GHz with CuO concentration increased to 1 wt.%, as illustrated in Table 1. The decrease in $Q_u f_o$ value may be attributed to the presence of CuO as a secondary phase and also to the increase in the number of grain boundaries.

The τ_f value of $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics with different amounts of CuO additives sintered at different temperatures for 4 h are given in Table 1. In general, τ_f is related to the composition, the type of additive, the amount of additive, and the second phases that occurred in the ceramics. τ_f was measured as a function of the amount of CuO additive in this experiment. As the amount of CuO additive increased from 0 to 1 wt.%, the τ_f increased from -1.4 to 5.3 ppm/K. It was observed that the τ_f values shifted to the positive direction as the amount of CuO additive increased. A near-zero τ_f of 2.5 ppm/K was measured for $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics with 0.5 wt.% CuO, sintered at 1475 °C for 4 h. With CuO addition, $\sim$75 °C reduction in the sintering temperature could be achieved for $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics.

4. Conclusions

The effects of CuO addition on the sintering behavior and microwave dielectric properties of $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics were investigated. The sintering temperature of the optimally sintered $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics was effectively reduced from 1550 °C to 1475 °C with 0.5 wt.% CuO addition. The electric permittivity was not significantly affected by the various amounts of CuO addition and was in a range of 52 – 54. Small values (<+7 ppm/K) of the temperature coefficient of resonant frequency were obtained for the $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics. However, the unloaded quality factor $Q_u f_o$ was strongly dependent upon the CuO concentration. $Q_u f_o \sim 10500$ GHz was obtained for the $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics with 0.5 wt.% of CuO addition. CuO addition resulted in 75 °C reduction of the sintering temperature for the $Sr_{0.4}Ca_{0.6}La_4Ti_5O_{17}$ ceramics.

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