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Low temperature sintering of CCTO using P_2O_5 as a sintering aid

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Abstract

Recent work on CCTO is directed towards decreasing its dissipation factor and further raising its dielectric constant by using different dopants. Also attempts have been made to lower its sintering temperature by adding different sintering aids so as to save energy and use low-cost electrodes (Ag–Pd or base metal) for making multilayer capacitors. Normally, CCTO needs a processing temperature of 1100 °C and above for densification. We report the formation of dense CCTO ceramics at a temperature as low as 1000 °C by adding P_2O_5 as a sintering aid. The samples showed dielectric constant value as high as 40,000, though the dissipation factor values remained high like those reported for pure CCTO.

Keywords: A. Sintering; C. Dielectric properties; Calcium copper titanate

1. Introduction

There is a renewed interest in developing dielectric materials with high permittivity due to a continuous demand for miniaturization in electronics. $CaCu_3Ti_4O_{12}$ (CCTO) is known to have a giant dielectric permittivity [1–4] of $>10^4$ over a wide temperature range from ≈100 to 400 K. The possible origin of such a high dielectric constant is still controversial [1,2,5] though the generally accepted mechanism is an internal barrier layer capacitor model, which consists of semiconducting grains and insulating domain or grain boundaries. Presently, the work on CCTO is mostly directed towards decreasing its dissipation factor and further raising its dielectric constant by using different dopants [6–9] and also lowering its sintering temperature (by adding different sintering aids) [4,10–12] so that, other than energy saving, low-cost electrodes (Ag–Pd or base metal) can be used for making multilayer capacitors using CCTO. Normally, CCTO needs a processing temperature of 1100 °C and above for densification [13]. So far, by adding sintering aids [10–12] like B_2O_3 and SiO_2 or by CIP [14,15], the densification could be achieved at around 1050 °C. In the present work we show that by adding a small amount of P_2O_5 (as ammonium dihydrogen phosphate), the densification can be achieved even at a lower temperature of 1000 °C without sacrificing the giant permittivity, though the dissipation factor remained high like that of pure CCTO.

2. Experimental

CCTO powder was synthesized by conventional mixed oxide route. Raw materials used were reagent grades $CaCO_3$, CuO and TiO_2. Stoichiometric amounts of raw materials were mixed thoroughly by ball milling in ethanol medium for 24 h. The mixture was calcined at 1000 °C for 10 h, followed by planetary milling for a cumulative period of 1 h. The phase purity of the powder was examined by XRD analysis. The powder was then mixed with 0–5 wt% P_2O_5 (as ammonium dihydrogen phosphate), palletized by uniaxial pressing followed by sintering at 1000 °C for 15 h. The density of the sintered pellets was measured geometrically. The microstructure of the sintered pellets was studied on a SEM (Leo 430i). For dielectric measurements the samples were polished and coated with conducting silver paste and cured at 550 °C for 20 min. The impedance and dielectric measurements were made on a Hioki 3532-50 LCR Hitester in the frequency range of 100 Hz–1 MHz.

3. Results and discussion

The X-ray diffraction peaks of CCTO (Fig. 1) are indexed based on body centered cubic lattice with space group Im3. No

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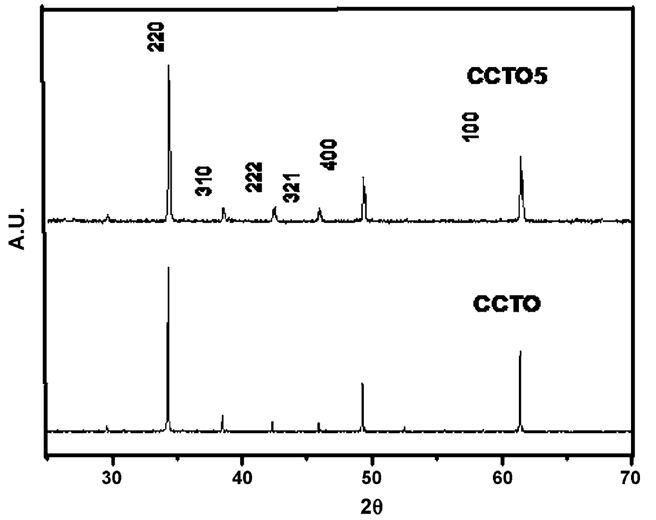

Fig. 1. XRD plots of pure (CCTO) and 5% P_2O_5 doped (CCTO5) CCTO ceramics.

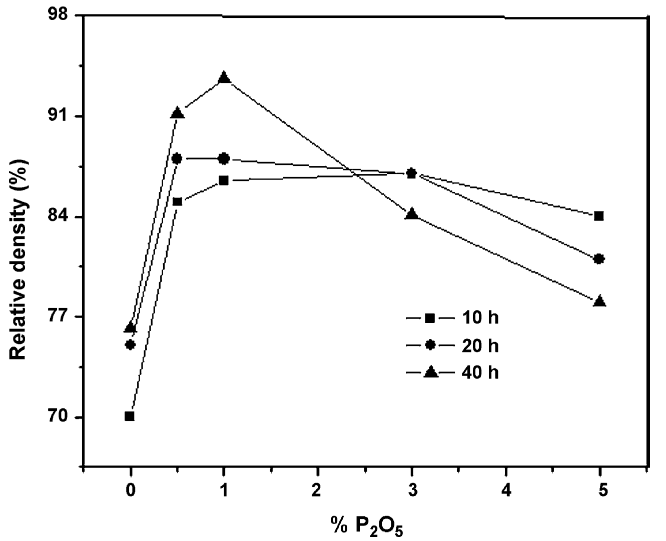

Fig. 2. Variation of sintered density with P_2O_5 content after sintering at 1000 °C for different soaking times.

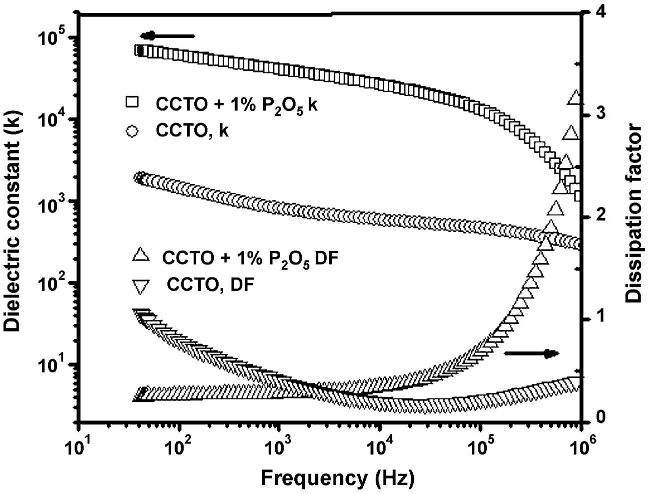

Fig. 4. Dielectric constant and dissipation factor of pure and 1% P_2O_5 incorporated CCTO ceramics (sintered at 1000 °C for 40 h) measured at room temperature.

secondary phase is observed up to 5 wt% P_2O_5 addition. It is also found that the lattice parameter remains almost the same for pure CCTO (7.39389 Å) and 5 wt% P_2O_5 added CCTO (7.39378 Å), which means that practically no P^{5+} substitution takes place in CCTO inside the grains.

Fig. 2 represents the variation of bulk density of CCTO with P_2O_5 addition after sintering at 1000 °C for 40 h. It can be seen that the density is maximum for 1% P_2O_5 incorporated sample and the density increases with soaking time. It is expected that P_2O_5 forms a glassy phase [4] and helps in liquid phase sintering of CCTO. For liquid phase sintering there is an optimum amount of liquid phase [11] above which the densification decreases as has been found in the present case. The increased densification of P_2O_5 incorporated CCTO is evident from the microstructures (Fig. 3).

The frequency dependence of dielectric constant (k) and dissipation factor (DF) of pure and 1% P_2O_5 incorporated samples (optimally sintered) is depicted in Fig. 4. A low frequency dispersion of dielectric constant is observed. The dielectric loss increases without any peak at high frequency. This is a signature of stray inductance of the contacts and leads [4]. Incidentally, increasing the P_2O_5 concentration beyond 1%

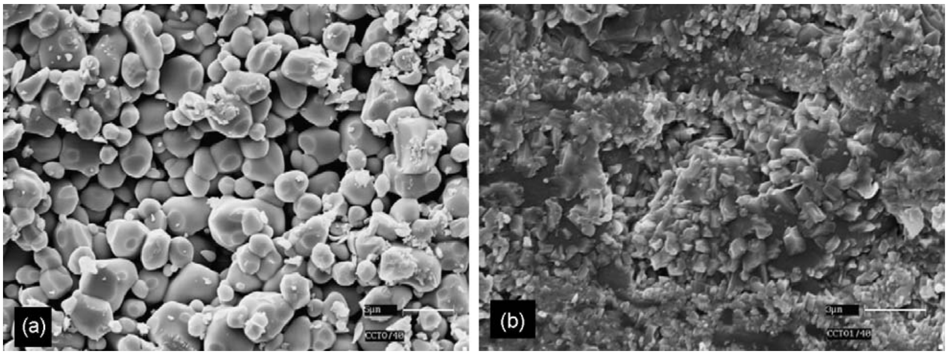

Fig. 3. SEM image of (a) pure and (b) 1% P_2O_5 incorporated CCTO ceramics sintered at 1000 °C for 40 h.

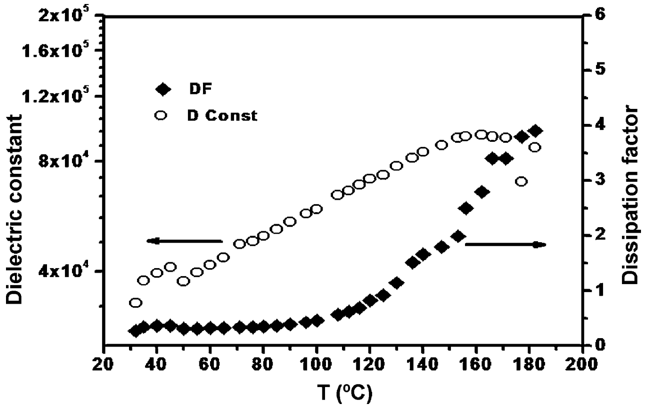

Fig. 5. Temperature variation of dielectric constant and dissipation factor (at1 kHz) of 1% P_2O_5 incorporated CCTO ceramics sintered at 1000 °C for 40 h.

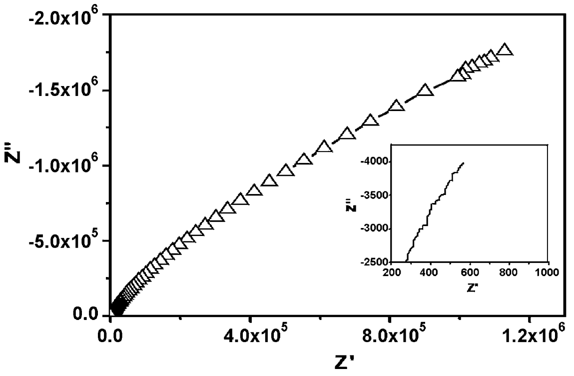

Fig. 6. Complex impedance spectrum of 1% P_2O_5 incorporated CCTO ceramics (inset shows an expanded view of the high frequency data close to the origin).

deteriorates the dielectric properties of the material (k value for 3% and 5% P_2O_5 incorporated samples are 870 and 470 at 1 kHz, respectively) which is in agreement with the decreasing trend of bulk density with P_2O_5 content. The 1% P_2O_5 incorporated samples sintered at 1000 °C for 40 h show very high dielectric constant value (≈40,000) at 1 kHz at room temperature, which is comparable to or better than higher temperature (>1000 °C) sintered CCTO with additives like SiO_2, [10] B_2O_3, [11] BaO–B_2O_3–SiO_2 glass [4]. Longer soaking time produces more oxygen vacancies and space charge [16] leading to a very high dielectric constant value. The temperature variation of k and DF of 1% P_2O_5 incorporated samples are shown in Fig. 5 and thermally activated dissipation is observed from the figure.

Fig. 6 shows the complex impedance plot of 1% P_2O_5 incorporated CCTO ceramics measured at room temperature. Only an incomplete semicircular arc was observed with a non-zero intercept on the real axis at a high frequency. By zooming the high frequency region further (inset Fig. 6), it is found that the intercept on Z'-axis for the high frequency limit is not zero and another semicircle should exist outside our measuring frequency band. Here the less resistive phase is the bulk phase and the more resistive phase is the grain boundary phase [5]. The impedance spectroscopy data can be modeled by an equivalent circuit consisting of two parallel RC elements connected in series, one corresponding to semiconducting grains, another for insulating barrier layer. The grain and grain boundary resistance values for 1 wt% P_2O_5 incorporated samples were found to be 2.19×10^3 and $133.30 \times 10^3\ \Omega$, respectively. However, the DC resistivity value of the 1% P_2O_5 incorporated samples was 50 MΩ cm and that of the pure CCTO is around 500 MΩ cm.

4. Conclusion

Highly dense CCTO ceramics can be obtained at a low sintering temperature of 1000 °C by using P_2O_5 as a sintering aid. The optimum amount of P_2O_5 was found to be 1%. The samples showed a very high dielectric constant values comparable to or better than the reported values. However, the dissipation factor values remained high like most of the reported values for pure and doped CCTO.

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