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Dielectric Properties of Sol-gel-derived Calcium Copper Titanate and Calcium Barium Copper Titanate Thin Films

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ABSTRACT

The complex perovskite compound $CaCu_3Ti_4O_{12}$ (CCTO) is of considerable interest because of its anomalously large dielectric response. In this study, the dielectric properties of sol-gel-derived thin films of CCTO prepared at various annealing temperatures; 7000 °C, 7200 °C, and 7500 °C have been reported. The frequency and temperature-dependent dielectric properties of all these samples have been studied in metal-insulator-metal configuration using an impedance analyser. Dielectric measurements at room temperature show that the dielectric constant increases with the increase in annealing temperature from 700 °C–7500 °C. High dielectric constant (varying from 600 to 3000 with the change in annealing temperature) has been observed at room temperature at 100 kHz. The dielectric measurements below room temperature do not show any evidence of structural relaxation in CCTO except a little additional tilting of the TiO_6 octahedra with decreasing temperature. The dielectric response of *Ba*-doped CCTO films has also been reported.

Keywords: Dielectric properties, calcium copper titanate, calcium barium copper titanate, thin films, perovskite compound, CCTO, perovskite structure

1. INTRODUCTION

In the present day technology, high dielectric constant materials are needed for capacitor applications. Such materials should have high dielectric constant, which does not change with temperature. The ferroelectric ceramics like $BaTiO_3$, PZT, etc have a high dielectric constant, but these undergoe large change with temperature. A relatively new ceramic material $CaCu_3Ti_4O_{12}$ (CCTO) shows a very high ($>10^4$) dielectric constant, which remains nearly constant[1] from 100 K to 400 K. This property has generated a significant amount of interest in this material. The boundary layer capacitor model consisting of semiconducting grains and insulating grain boundaries has been invoked to explain high values of the dielectric constant. Existence of microdomains within single crystals, reported recently, makes the mechanism applicable to single crystals also. So far, very little work on thin films of CCTO has been reported.

Usually, a material in thin film form is found to have a considerably lower dielectric constant as compared to its bulk counterpart. But, perovskite $CaCu_3Ti_4O_{12}$ thin films have received significant attention due to their giant dielectric constant ($\varepsilon \geq 2000$). Such high dielectric constants are seen in ferroelectric or relaxor materials, both of which show sharp maxima in dielectric constant as a function of temperature. However, as mentioned above, the dielectric constant of calcium copper titanate is fairly constant from 100 K to 400 K, but drops to approximately 100 without any change in the crystal structure[1] below 100 K. The giant dielectric

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response of $CaCu_3Ti_4O_{12}$ has initiated several studies searching for its origin[2-4].

The $CaCu_3Ti_4O_{12}$ structure type is derived from the cubic perovskite structure, by an octahedral tilting distortion. The *Ca* atoms are at the corners and centre of the cube, the *Cu* atoms are bonded to four oxygen atoms and the *Ti* atoms are at the centres of tilted octahedra. The perovskite structure has a high degree of chemical flexibility, allowing for numerous cation and anion substitutions. It is well known that TiO_2- and ATiO_3-based oxides (where A= *Ca*, *Sr*, and *Ba*) loose small amounts of oxygen and become conductive on firing in reducing atmospheres[6]. Limited reoxidation can produce thin insulating layers on the outer surfaces of pellets or along the grain boundaries and outer regions of individual grains, such devices known as surface and internal barrier layer capacitors (IBLC) respectively possess high effective permittivity values of 10,000-50,000 under appropriate processing conditions.

Although, CCTO shows high dielectric constant but it is associated with high losses too. This factor can restrict its use in several devices. Since the perovskite structure can accommodate a variety of cations and anions that change its structure and dielectric properties, a keen interest in this class of materials has been emerged. In the present study, thin films of CCTO by sol-gel method followed by their structural and electrical characterisations has been prepared. A reduction in dielectric loss has recently been reported in bulk CCTO ceramics doped with *Ba*. Therefore, the effect of *Ba*-doping on the dielectric response of the CCTO films has also been studied

2. EXPERIMENTAL

Calcium copper titanate (CCTO) thin films were deposited on platinised silicon (*Pt*/*Si*) substrates by the sol-gel technique. A sol was first prepared by dissolving titanium butoxide [$Ti(OC_3H_7)_4$] in 2-ethyl heaxanoic acid followed by addition of monohydrated calcium acetate [$Ca(C_2HO_2)_2 \cdot H_2O$] and monohydrated copper acetate [$Cu(OOCCH_3)_2 \cdot H_2O$] at room temperature. This solution was refluxed at 1200 °C for 30 mins.

Films were deposited by spin coating at 4000 rpm for 30 s. Each coating was dried at 500 °C for 5 min followed by firing at T $\geq$ 700 °C for 10 min. This process of coating and firing was repeated several times to get the desired film thickness and the final annealing were also done at 700 °C, 720 °C, and 7500 °C for 2 h. Furthermore, *Ca* was substituted with different atom fractions *x* of barium (x = 0.05, 0.1, 1.0, 5.0 and 10). To measure the electrical properties, circular *Pt* electrodes of 0.2 mm dia were deposited on CCT films by dc magnetron sputtering. All the dielectric properties were studied in metal-insulator-metal configuration using an impedance analyser (HP 4192 A).

3. RESULTS AND DISCUSSION

3.1 Structural Characterisation

Figure 1 shows room temperature XRD pattern of CCTO film annealed at temperatures 7000 °C, 7200 °C and 7500 °C. Single perovskite cubic phase of CCTO has been obtained. Films annealed at 7200 °C, and 7500 °C show more intense peak as compared to the film annealed at 7000 °C, suggesting the sample annealed at higher temperature is well crystallised. With barium substitution, any structural change or secondary phase was not observed.

3.2 Dielectric Characterisation

3.2.1 Dielectric Properties at Room Temperature

Figures 2(a) and 2(b) show dielectric constant and loss variation with frequency at room temperature for all three annealing temperatures. Dielectric constant was found to be increased as annealing temperature increases from 7000 °C to 7500 °C. Film annealed at 7500 °C showed the highest dielectric constant. Also dielectric constant decreased slightly as frequency increased from 100 kHz to 1 MHz. Similar trend was observed for loss variation with annealing temperature. Loss values increased with annealing temperature.

3.2.2 Temperature Dependence of Dielectric Properties

The temperature dependence (100 K–470 K) of the dielectric parameters has been measured for

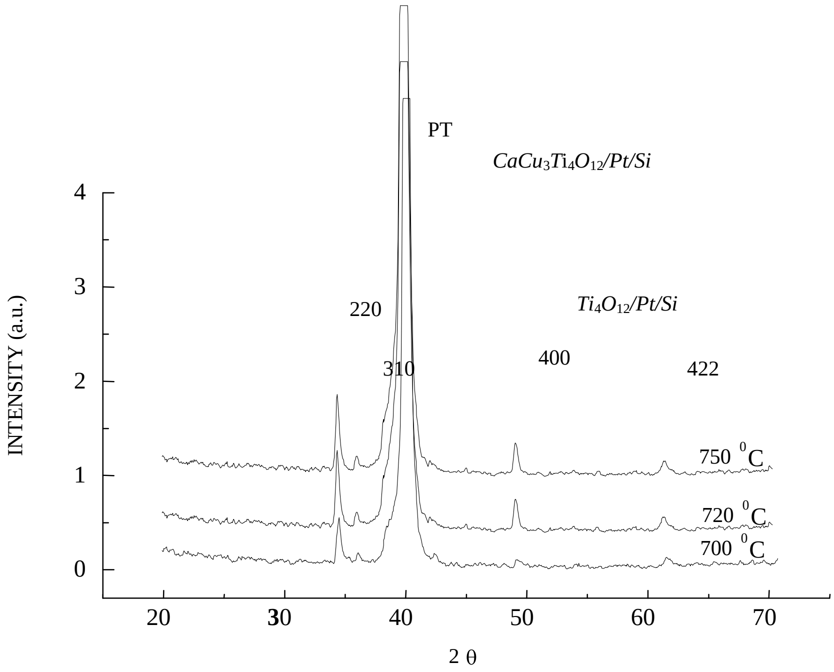


Figure 1. X-ray diffraction pattern of films annealed at different temperatures.

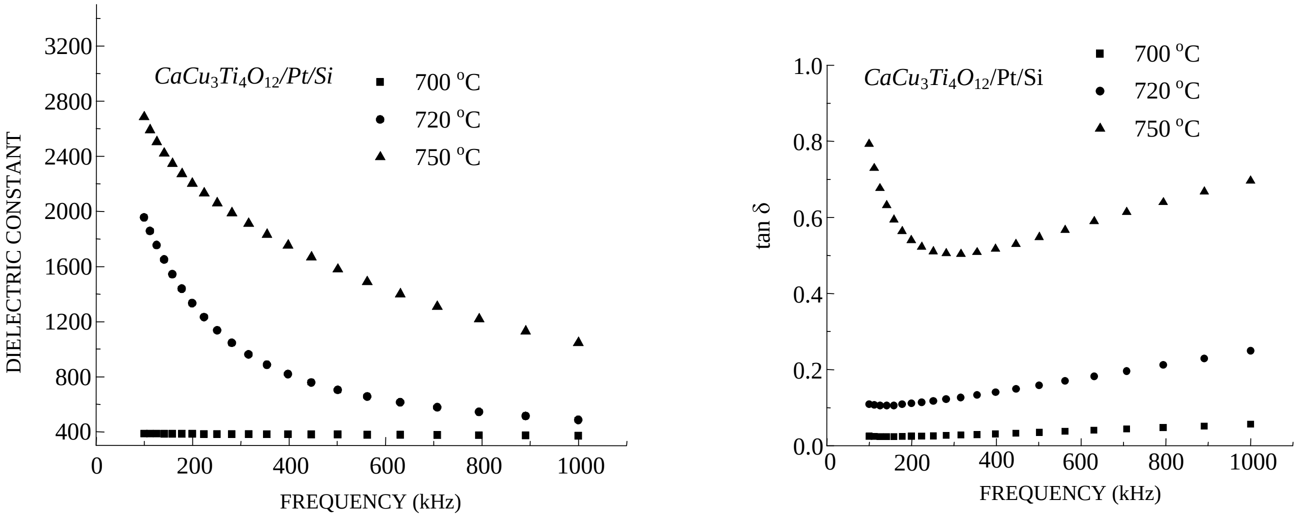


Figure 2. Frequency-dependent dielectric constant at different annealing temperatures.

pure CCTO film (annealed at 7500 °C) as a function of frequency [Figs 3(a) and 3(b)]. No evidence of any structural transition in this temperature range was found which is in contrast with $BaTiO_3$. In the cubic perovskite structure encountered in $BaTiO_3$ above 1200 °C, the Ti^{4+} cation is in a site of full cubic symmetry and with decreasing temperature Ti^{4+} displaces towards one, then two, and finally three oxygen anions, to produce the tetragonal, orthorhombic and ferroelectric phases, respectively.

The site symmetry in CCTO is much lower than in cubic $BaTiO_3$: this generally reduces the possibility of ferroelectric phase transition based on displacement of Ti^{4+} from the centre of octahedron[7]. Dielectric constant remains invariant in temperature range 100–450 K. Loss tangent variation with temperature at different frequencies shows similar characteristics.

Figure 4 shows a frequency versus dielectric constant response at different temperatures. Dielectric

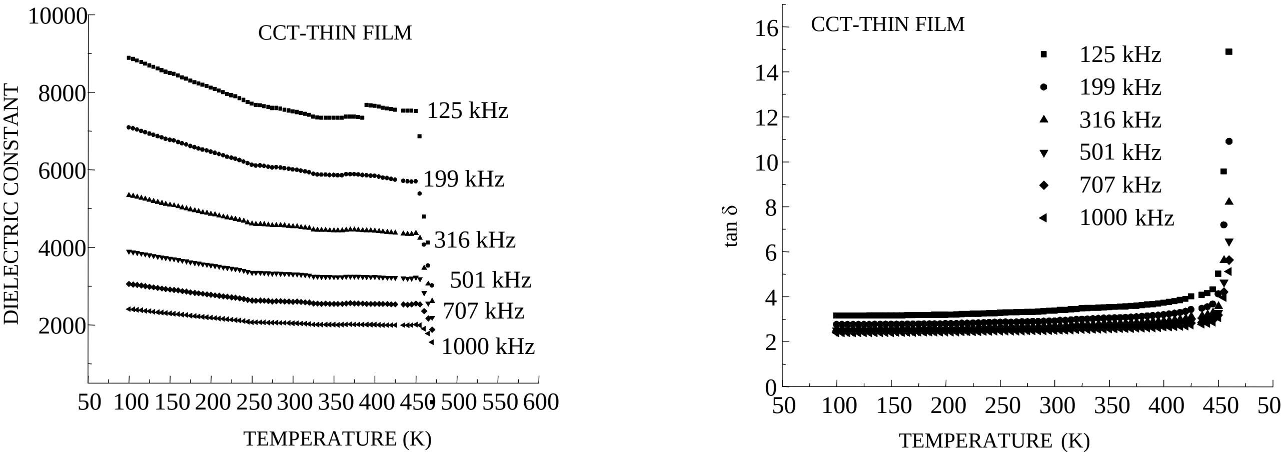


Figure 3. (a) Temperature-dependent dielectric constant at different frequencies; the break at about 400 K at 125 kHz is an artifact (b) Temperature-dependent dielectric loss at different frequencies.

constant shows dispersion with frequencies. In the frequency range of measurements for bulk, the dielectric constant of CCTO is found to remain nearly invariant at temperatures above 140 K; however, a significant drop was found in the dielectric constant with increasing frequency in the thin films of CCTO.

3.2.3 Barium-doped CCTO Films

The dielectric properties were also measured of CCTO films having *Ca* replaced by *Ba* (0.0 %, 0.05 %, 0.10 %, 1.0 % and 10.0 %) [Figs 5(a) and 5(b)]. It was observed that compounds having 0 and 0.05 % *Ba* content show high dielectric constant (~2000) at 200 kHz; on further addition of *Ba*, i.e., for 0.1 per cent and 1.0 per cent of *Ba*, the dielectric constant drastically decreased.

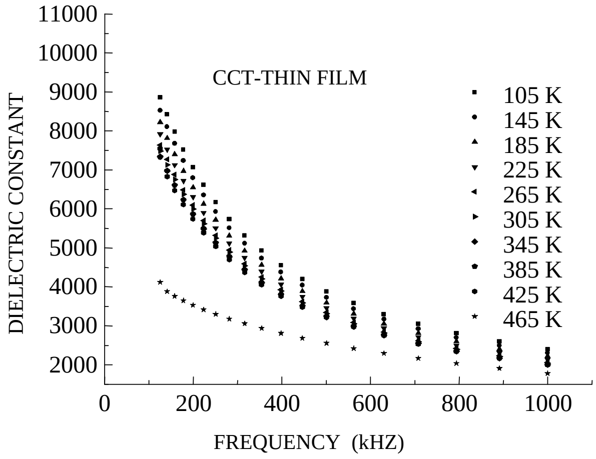
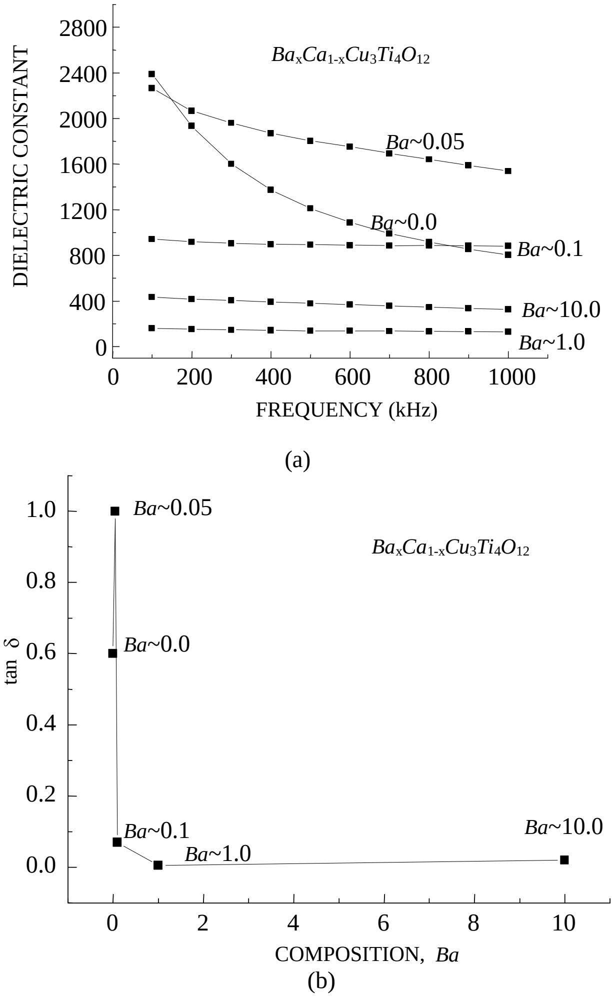


Figure 4. Frequency-dependent dielectric constant at different temperatures.



(a)

(b)

Figure 5. (a) Frequency-dependent dielectric constant at different *Ba* compositions, (b) variation in dielectric loss with different *Ba* compositions at 200 kHz.

On further addition of *Ba*, the dielectric constant again increases slightly followed by decrease in dielectric loss for compounds having 10 per cent *Ba*. The lower dielectric constant observed in *Ba*-substituted $CaCu_3Ti_4O_{12}$ is due to the lower concentration of insulating grain boundaries in the compound. Therefore, it can be suggested that the decrease in the dielectric constant for *Ba* compositions could be due to removal of the IBLC effect. An appreciable decrease in the dielectric loss upon addition of *Ba* can also be seen [Fig. 5(b)].

4. CONCLUSIONS

In this study, thin films of $Ba_xCa_{1-x}Cu_3Ti_4O_{12}$ (x = 0.0, 0.05, 0.1, 1.0, 10.0) were synthesised by sol-gel method. The dependence of dielectric properties with temperature and frequency have been investigated. Calcium copper titanate thin films show almost constant dielectric constant in wide temperature range at all frequencies without showing any structural transition. These films have strong dependence on annealing temperature. It is evidenced that films annealed at higher temperature (7500 °C) show higher dielectric constant. Dielectric loss in CCTO is found to decrease with addition of *Ba*. Further development of films with high dielectric constant and low loss offers the possibility of their applications in novel barrier layer capacitors.

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