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Preparation of high dielectric constant thin films of $CaCu_3Ti_4O_{12}$ by sol–gel

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Abstract. Preparation of sol–gel derived $CaCu_3Ti_4O_{12}$ (CCTO) thin films using two different sols and their characterization including their dielectric response are reported. The properties of CCTO films depend heavily on solvents used to prepare the sols. Dielectric constant as high as ~900 at 100 kHz could be obtained when acetic acid was used to prepare the sol; in contrast, use of hexanoic acid in the sol yielded films with a much lower dielectric constant. The variation in grain and grain boundary conductivities with temperature has been measured. Activation energies of 0·08 eV and 0·68 eV have been found for grain and grain boundary conduction, respectively.

Keywords. Sol–gel preparation; thin film; electrical properties.

1. Introduction

High dielectric constant ceramics are of interest for use in electronic circuits, microwave devices and other applications. The ceramic, $CaCu_3Ti_4O_{12}$ (CCTO), is at present of considerable research interest because of its high dielectric constant (~10^4) which is independent of temperature and frequency over a wide range near room temperature. $CaCu_3Ti_4O_{12}$ (CCTO) has a perovskite-related structure (general formula, ABO_3) in which Ca^{2+} and Cu^{2+} share the A-site (Deschanvres *et al* 1967; Bochu *et al* 1979; Subramanian *et al* 2000). The size difference between Ca^{2+} and Cu^{2+} causes the TiO_6 octahedra to undergo substantial tilting, leading to a body centred cubic supercell of space group *Im*3 in which the Ti^{4+} ions occupy centrosymmetric position in the octahedral sites. The angle of tilt is sufficiently large that the Cu^{2+} ions occupy an essentially square-planer environment (Adams *et al* 2006). High dielectric constant, as shown by CCTO, is usually found in ferroelectric materials; however, no evidence of a phase transition (paraelectric to ferroelectric) in CCTO has so far been found.

The most widely accepted mechanism for the high dielectric constant in CCTO is a grain boundary layer capacitor model invoking semiconducting grains and insulating grain boundaries. Several models have been proposed to explain the difference in the conductivity between the grains and the grain boundaries (Li *et al* 2004, 2006; Zhang and Tang 2004; Fang *et al* 2006; Fang and Mei 2007). Zhang and Tang (2004) found evidence for the existence of Ti^{3+} as well as Ti^{4+} ions in CCTO and attributed the high grain conductivity to polaron transport along Ti^{3+}–O–Ti^{4+} linked path. The observed segregation of Cu ions to grain boundaries led Fang *et al* (2006) and Fang and Mei (2007) to suggest that Cu ions act as acceptors and increase the grain boundary resistivity while the electron hopping between Cu^{3+} and Cu^{2+} is thought to be the origin of the high conductivity of grains.

Considerable amount of work has been done on bulk CCTO ceramics (Subramanian *et al* 2000; Adams *et al* 2006; Fang *et al* 2006; Fang and Mei 2007; Prakash and Varma 2007). However, the reported studies on thin films of CCTO, especially those prepared by chemical solution methods, are scarce (Lu *et al* 2004; Feng *et al* 2006; Jimenez *et al* 2007). Lu *et al* (2004) deposited CCTO films on $LaAlO_3$ substrates using a sol prepared from titanium butoxide and naphthenates of Ca and Cu in toluene solution. A single crystal film was obtained. The same group (Feng *et al* 2006) also reported the deposition of CCTO films on $SrTiO_3$ substrates. They did not report any dielectric measurements on their films. Recently, Jimenez *et al* (2007) used a titanium diol based sol to deposit CCTO films on platinum coated Si substrates. They reported a dielectric constant of 280 at 100 kHz, which is nearly constant between 150 K and 300 K. This is much lower than that reported for CCTO ceramics (Subramanian *et al* 2000). The dielectric properties of sol–gel prepared thin films are known to be very sensitive to the constitution of the sol. In the present work, we report the preparation of CCTO thin films by a sol–gel method using two different sols. It is seen that quite high dielectric constant can be obtained by using acetic acid as the solvent for the precursors.

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2. Experimental

Two different sols were prepared for the deposition of CCTO films. To prepare sol-1, titanium butoxide [Ti $(OC_4H_9)_4$, 97%] was mixed with acetic acid and stirred for 30 min inside a glove box with controlled humidity. Calculated amounts of precursors (calcium acetate, $Ca(OOCCH_3)_2{\cdot}H_2O$, 99% and monohydrated copper acetate, $Cu(OOCCH_3)_2{\cdot}H_2O$, 99%) were mixed with 15 ml of acetic acid and 15 ml of ethanol and stirred for 30 min. Both the above solutions were then mixed and to this about 10 ml of 2-methoxy ethanol was added. This solution was stirred at 100°C on a hot plate for 30 min and then cooled to room temperature. To this 10 ml of diethanolamine (DEA) was added and the solution was again stirred for 30 min. A light blue transparent sol was obtained.

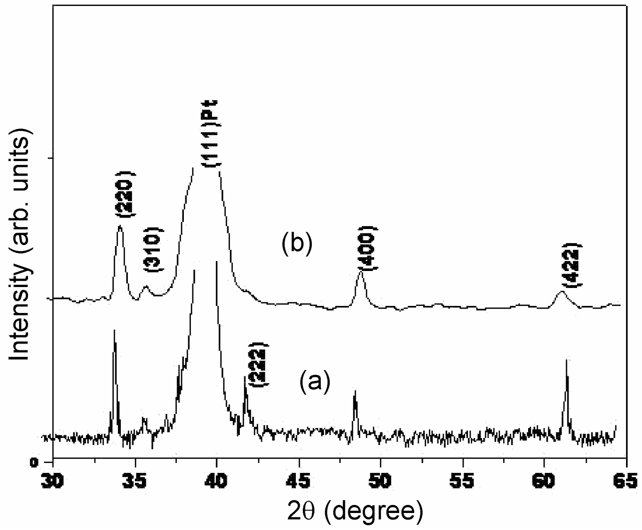

Figure 1. Room temperature X-ray diffractograms for CCTO thin films prepared by (a) sol-1 and (b) sol-2.

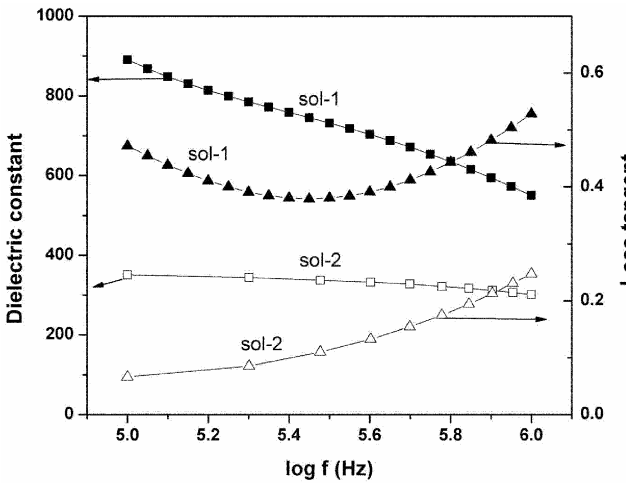

Figure 2. The dielectric response as a function of frequency for CCTO films prepared by using different sols.

Sol-2 was prepared by dissolving titanium butoxide in 2-ethyl hexanoic acid. The calculated stoichiometric amounts of monohydrated calcium acetate and monohydrated copper acetate were then mixed into the solution at room temperature. The solution was refluxed at 120°C for 30 min.

The sols as prepared above were filtered through a 0·2 μm syringe filter and were used for film preparation by spin coating at 5000 rpm for 30 s on (111) oriented $Pt/Ti/SiO_2/Si$ substrates. After each coating, the films were fired at 500°C for 5 min followed by annealing at 750°C for 10 min. The final annealing was performed at 750°C for 2 h. The thickness of the films was measured by a profilometer (Tencor Instruments Alfa-step 500).

To measure the electrical properties, circular Pt electrodes of 0·2 mm diameter were deposited on these films through a shadow mask by d.c. magnetron sputtering. All the dielectric properties were studied in metal–insulator–metal configuration using an impedance analyser (HP 4192 A).

3. Results and discussion

Figure 1 shows X-ray diffractograms of the CCTO films prepared using the two sols. In both cases, the perovskite phase formation occurred as revealed by comparing with standard X-ray data [JCPDF File No. 21-0140]. The films have no preferred orientation, though the (220) line is the strongest of all.

Figure 2 shows the dielectric constant and loss for the two types of films. The films prepared using sol-1 show a high dielectric constant (~900 at 100 kHz). This is much higher than the dielectric constant of chemical solution deposited thin film reported earlier (Jimenez *et al* 2007). The dielectric constant of the films prepared using sol-2 was much lower (350 at 100 kHz) although they had a lower dielectric loss (figure 2). As the thickness of the films in the two cases was nearly the same (~500 nm), these differences can be attributed to the microstructures of the films (Ni *et al* 2006). The porosity and fine details of the microstructure in the sol–gel films depend in a complex way upon the relative rates of drying and gelation and the ease of removal of the organics (Brinker and Scherrer 1990). The microstructures of the two films are shown in figures 3(a) and (b), respectively. From the SEM micrographs, the grain size distributions of the two films were determined. This is shown in figure 4. The distribution in case of sol-2 is much wider, with there being significant number of grains, > 500 nm. Moreover, this film (sol-2) has a considerable number of large pores with size extending up to ~ 260 nm whereas the film from sol-1 has much less porosity and the pores are also smaller. The difference in the electrical properties of the two films can be attributed to these differences in grain size distribution and porosity (Adams *et al* 2006). The films prepared us-

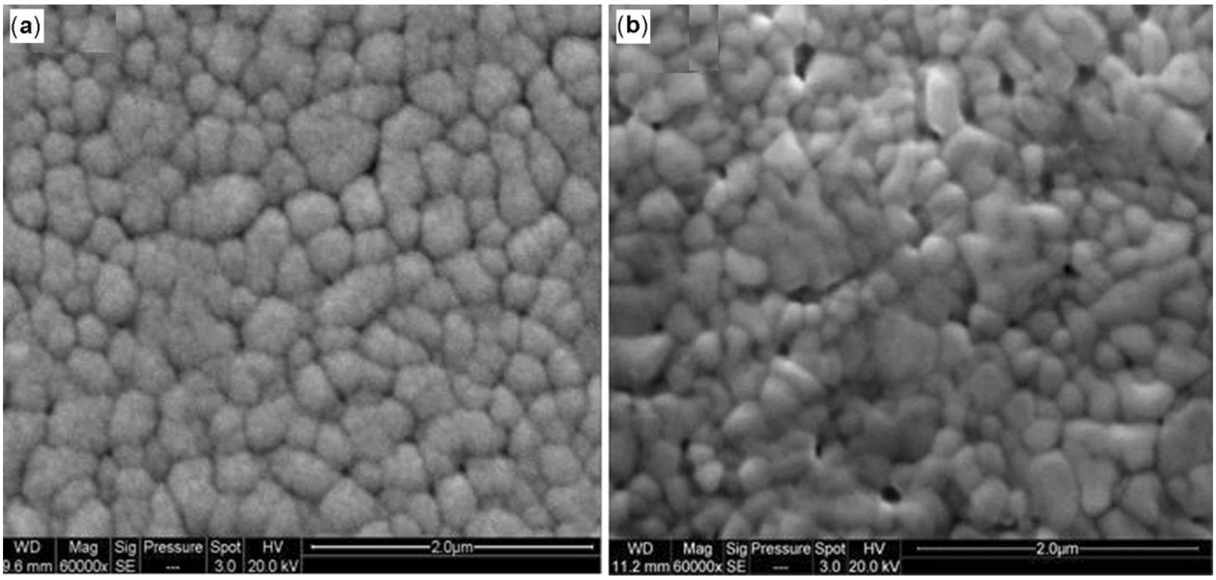

Figure 3. SEM micrographs for CCTO thin films prepared by (**a**) sol-1 and (**b**) sol-2.

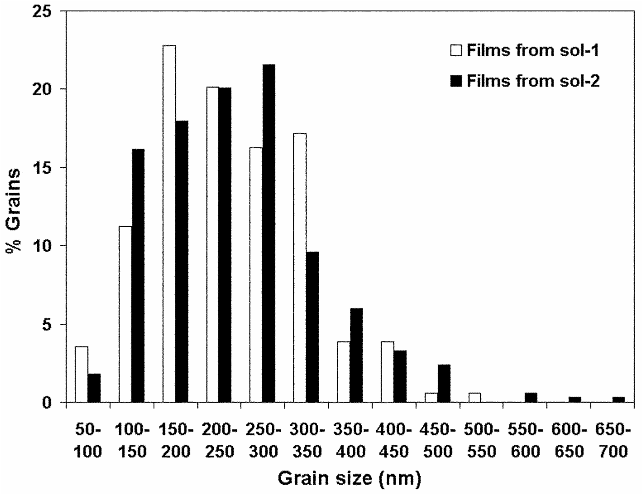

Figure 4. Grain size distribution of CCTO films prepared by using different sols.

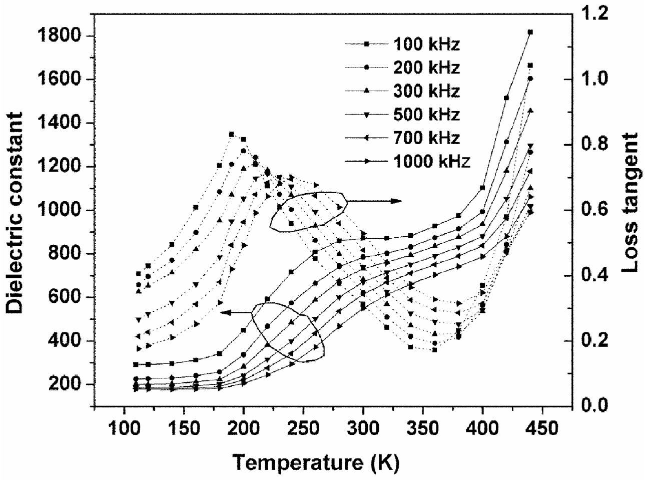

Figure 5. Temperature dependence of dielectric response for CCTO thin film prepared by using sol-1.

ing sol-2 also showed a large variation in properties and were difficult to reproduce; hence, further measurements were carried out on the films prepared using sol-1.

The variation with temperature of the dielectric constant and loss tangent for CCTO films (from sol-1) is shown in figure 5. The dielectric constant shows a nearly constant value from 100 K to about 180 K. It then increases rapidly from ~ 180 K to ~ 300 K similar to the bulk CCTO. However, the films show a slowly increasing dielectric constant from 300 K to 400 K unlike the bulk ceramics, which show a plateau near room temperature (Ramirez *et al* 2000). Above 400 K, the dielectric constant again increases rapidly as in the case for bulk CCTO. The dielectric loss data shows a peak between about 175 K and 250 K which lies in the temperature range in which there is a relaxation in dielectric constant below the room temperature. Activation energy for this relaxation was obtained by plotting reciprocal of the peak temperature against log of frequency. An excellent straight line fit was obtained giving an activation energy of 0·18 eV. This is similar to the activation energy of 0·18–0·2 eV reported by others (Jimenez *et al* 2007) for the first relaxation. A Debye relaxation model has also been used to analyse the data for CCTO ceramics in this temperature range.

The values of the grain and grain boundary resistances can be obtained using the Cole–Cole formulation (Sinclair and West 1989). Figures 6(a) and (b) show Cole–Cole plots for CCTO films (from sol-1) at 380 K and

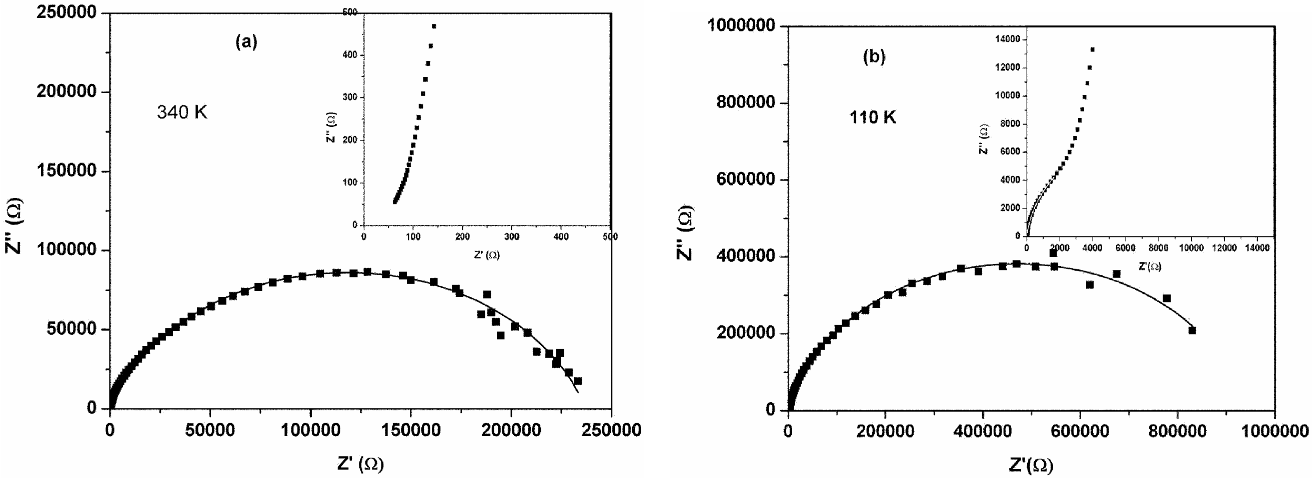

Figure 6. Cole–Cole plots for CCTO thin film (from sol-1) at (**a**) 340 K and (**b**) 110 K. Inset shows high frequency tails of these plots.

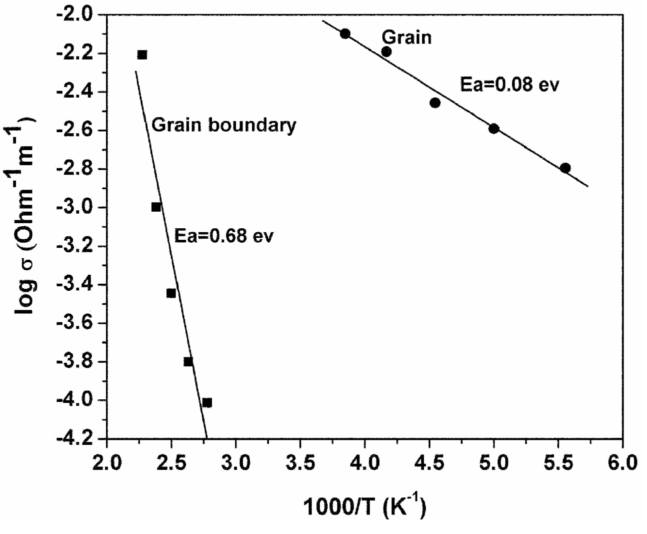

Figure 7. Plots of log (conductivity) vs 1000/*T* (K^{-1}) for CCTO thin film (from sol-1).

110 K, respectively. The dots on the plots are the experimental points and the lines show their fit to semicircles. The insets of figure 5 show the magnified view of high frequency tail of these plots, which represent the bulk contribution to the resistance. The main semi-circles in these plots correspond to the grain boundary resistance. The semi-circles are depressed (e.g. have their centre below the *x*-axis), which is taken to represent the existence of a distribution of relaxation times. The data in the high frequency tail can be fitted to semicircles at low temperatures only.

The activation energies for grain and grain boundary conduction were determined by plotting the respective conductivities as determined from the Cole–Cole plots vs reciprocal of temperature for CCTO films (from sol-1) (figure 7). The activation energies of 0·08 eV and 0·68 eV for grain and grain boundary conduction are in agreement with the values obtained for CCTO ceramics (0·084 eV and 0·678 eV, respectively) (Zhang *et al* 2005) and also with the activation energy for grain conduction in thin films and single crystals i.e. 0·06 eV and 0·08 eV (Si *et al* 2002), respectively.

4. Conclusions

The properties of sol–gel prepared films are heavily dependent on the precursors including the solvent used. We have found that the films prepared using acetic acid and methoxyethanol sol have much higher dielectric constant and are more reproducible as compared to those prepared using hexanoic acid. Dielectric constant as high as 900 at 100 kHz can be obtained which is much higher than about 280 reported in the only work on the properties of chemical solution prepared CCTO films (Jimenez *et al* 2007). Instead of a plateau in the dielectric constant near room temperature, as in the case for the bulk CCTO, the dielectric constant is found to increase slowly just above room temperature. The activation energy for the relaxation below the room temperature is found to be 0·18 eV.

Acknowledgement

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