

Dielectric properties of $\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$ and $\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$ ceramics synthesized by semi-wet route

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Abstract. The effect of Co^{+2} doping on Cu^{+2} and Ti^{+4} sites in calcium copper titanate, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, has been examined. The doped compositions, $\text{CaCu}_{3-x}\text{Co}_x\text{Ti}_4\text{O}_{12}$ and $\text{CaCu}_3\text{Ti}_{4-x}\text{Co}_x\text{O}_{12}$ ($x = 0-10$) ceramics, were prepared by novel semi-wet route. In this method, calcium, copper and cobalt salts were taken in solution form and TiO_2 was used in solid form. XRD analysis confirmed the formation of single-phase materials. Structure of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ does not change on doping with cobalt either on Cu-site or Ti-site and it remains cubic. Scanning electron micrographs (SEM) show average grain size of $\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$ to be larger than $\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$ ceramic. Energy dispersive X-ray spectroscopy (EDX) studies confirmed the purity of parent and Co-doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. Dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) of $\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$ is comparatively higher than that of $\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$ ceramic at all measured frequencies and temperatures.

Keywords. Oxides; chemical synthesis; X-ray diffraction; dielectric properties.

1. Introduction

BaTiO_3 is a ferroelectric material exhibiting high dielectric constant. Dielectric properties of ferroelectric materials based on BaTiO_3 are strongly temperature dependent near their transition temperature (Wang *et al* 2001). This property is undesirable from applications point of view in electronic devices. Subramanian and co-workers reported a complex cubic perovskite compound, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) which has high dielectric constant ($\sim 10^4$) and does not show ferroelectric behaviour (Ramirez *et al* 2000; Subramanian *et al* 2000). These unique properties of CCTO make it a promising material for microelectronic applications. But its high dielectric loss restricts its application in miniaturization of electronic devices. Dielectric constant of CCTO is almost constant in the temperature range 100–600 K (Homes *et al* 2001). Neither a phase transition nor a detectable change in the long-range crystal structure was found by high-resolution X-ray and neutron diffraction studies in the temperature range 100–600 K. The intrinsic dielectric responses in CCTO are due to barrier layer capacitance associated with grain boundaries, which results in interfacial polarization (Sinclair *et al* 2002; Fang and Liu 2005). Researchers have been working on CCTO to reduce dielectric loss and maintaining high dielectric constant by doping or modification in the preparation technique (Feng *et al* 2006; Rai *et al* 2010). In recent years, a few reports have been published on the effect of substitution of some transition metal ions on dielectric properties of CCTO ceramic. Partial substitutions for Ca, Cu and Ti

ions of CCTO were also attempted to improve the dielectric properties (Aygün *et al* 2005; Grubbs *et al* 2005; Rai *et al* 2011).

In the present work, we report dielectric properties of cobalt-doped CCTO on titanium site, i.e. $\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$ (CCTCO) and copper site, i.e. $\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$ (CCCTO), synthesized by a semi-wet route. Only a few such methods to make CCTO have been reported in the literature. These include polymerized complex methods (Jha *et al* 2003; Masingboon *et al* 2006) and sol-gel methods (Hassini *et al* 2001; Jin *et al* 2007).

2. Material and methods

$\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$ and $\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$ powders were prepared by semi-wet route. Analytical grade chemicals such as: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.5%, Qualigens, India), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.5%, Merck, India), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.8%, Ranbaxy, India), TiO_2 (99.5%, Merck, India) and citric acid (99.5%, Merck, India) having purity greater than 99.95% were used as starting materials. Standard solution of metal nitrates were prepared by using distilled water. CCTCO and CCCTO were prepared by semi-wet route. Stoichiometric amount of these metallic ions, solid TiO_2 powder and citric acid equivalent to metals ions were mixed in a beaker (Mandal *et al* 2009). The solution was heated on a hot plate magnetic stirrer at 70–80°C to evaporate water and dried at 100–120°C in hot air oven for 12 h to yield a blue gel. The gel was calcined in air at 800°C for 6 h in an electrical furnace. The calcined powder was ground and mixed again with 2% PVA solution as binder. Powder

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was pressed into cylindrical pellets by using hydraulic press. All the pellets were sintered at 900°C for 6 h in air. The structure of the sintered samples was determined using powder X-ray diffractometer (Rich-Siefert, ID-3000) employing Cu K α radiation. The microstructures of the fractured surfaces were examined using a scanning electron microscope (Model JEOL JSM5410). Energy dispersive X-ray analyser (Model KeveX, Sigma KS3) was used for elemental analysis in the sintered samples. Dielectric properties of CCTCO and CCCTO ceramics were measured by using LCR meter (PSM 1735, Newton 4th Ltd, UK) with variation of frequency (10^2 – 10^6 Hz) and temperature (300–500 K).

3. Results and discussion

X-ray diffraction patterns of $\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$ (CCTCO) and $\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$ (CCCTO) sintered at 900°C for 6 h

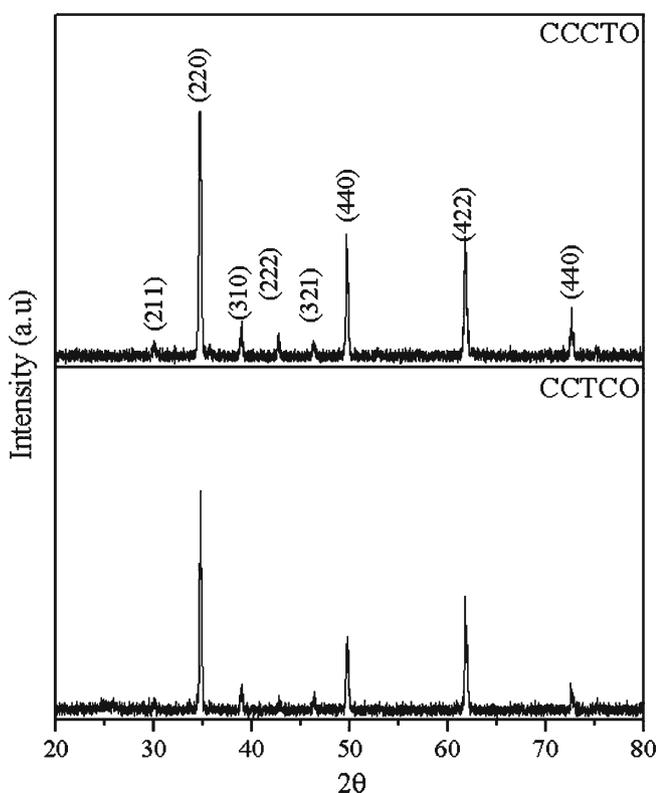


Figure 1. X-ray powder diffraction patterns for system, $\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$ and $\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$ sintered at 900°C for 6 h.

are shown in figure 1. All the peaks in the diffraction pattern were indexed on the basis of cubic unit cell. Position of the peaks in the sintered samples remains almost same as that of undoped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramic (JCPDS Card No. 75-2188). The lattice parameter and unit cell volume were determined by least square refinement method and are given in table 1.

These results show that partial substitution of Co^{+2} in Cu^{+2} or Ti^{+4} sites of CCTO ceramic does not change cubic perovskite structure. Lattice parameter of CCCTO is slightly more than that of CCTCO ceramic. This increase in lattice parameter can be explained on the basis of ionic radius and oxidation state of cobalt ion. If cobalt ions exist in divalent state (Co^{+2}), then these have larger value of ionic radius (0.72 Å) than the host Cu^{+2} (0.71 Å) (Shannon and Prewitt 1970). Cobalt ions may also exist in +3 in high spin (t_{2g}^4, e_g^2) or low spin (t_{2g}^6, e_g^0) oxidation states having ionic radii 0.75 Å or 0.685 Å, respectively (Taguchi *et al* 1996). Co^{+3} ions (HS) and Ti^{+4} ions (0.745 Å) have nearly same ionic radii, hence the lattice parameter of CCTO and CCTCO have same value (7.379 Å). Oxidation state of cobalt is yet to be confirmed by other studies, e.g. X-ray photoelectron spectroscopy. There is no evidence of the presence of secondary phase in the sintered ceramic samples. XRD patterns show the presence of split peaks for the reflections 400, 422 and 440. This may be due to the presence of $\text{Cu K}\alpha_2$ along with $\text{Cu K}\alpha_1$ in the X-ray radiations used for diffraction. This is supported by the fact that in all these reflections, intensity of peaks due to $\text{Cu K}\alpha_2$ is almost 50% of intensity of peak due to $\text{Cu K}\alpha_1$ as expected (Cullity and Stock 2001).

SEM images of CCTCO and CCCTO samples are shown in figures 2(a) and (b). Grain size of CCTCO ceramic is found to be in the range of 2–10 μm , further the grains of CCTCO have smooth surfaces associated with a squarish appearance. It has a duplex microstructure consisting of a few large grains isolated by regions consisting of fine grains. Larger grains are present because of abnormal grain growth. Average grain size of these is $\sim 50 \mu\text{m}$ in CCCTO ceramic. The size of these particles synthesized by semi-wet route is relatively smaller than those prepared by ceramic method. Interfaces between grains are straight in CCTCO while those in CCCTO are clearly separated by a liquid phase. The light coloured exfoliated sheets observed at grain boundaries are identified as Cu-rich phases and deficient in Ca and Ti. This is confirmed by EDX studies. It is known that the liquid phase formed during sintering could assist the densification through particle rearrangement, solution reprecipitation and

Table 1. Crystal system, lattice parameter, unit cell volume, theoretical density and porosity for electroceramics, $\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$ and $\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$.

System	Crystal system	Lattice parameter (Å)	Unit cell volume (Å ³)	Theoretical density (%)	Porosity
$\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$	Cubic	7.379	401.79	96.1	3.9
$\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$	Cubic	7.381	402.25	96.5	3.5

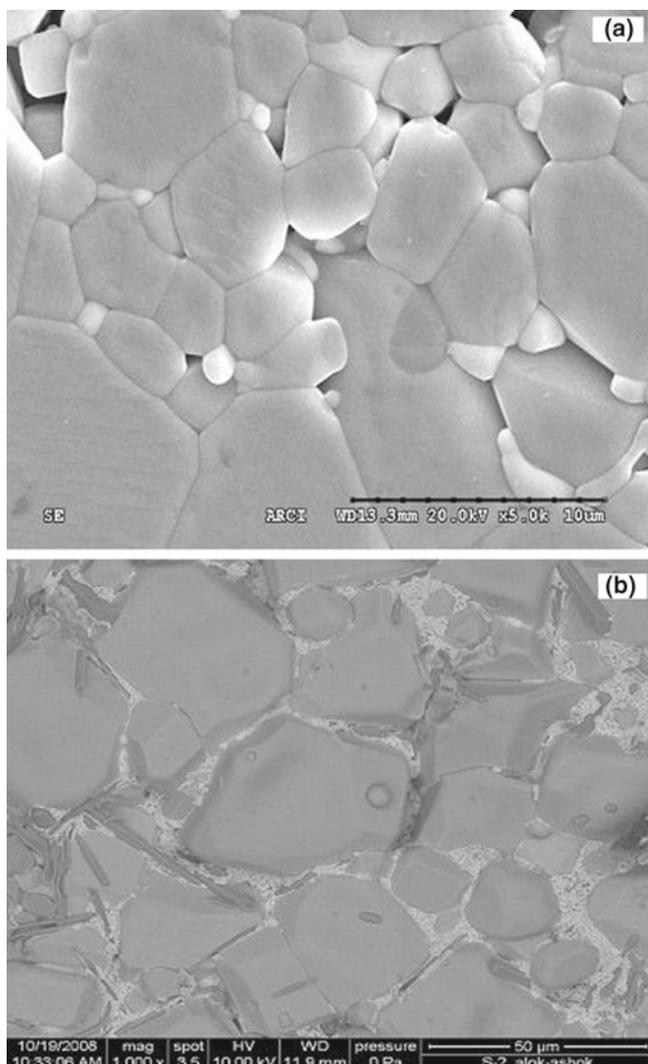


Figure 2. SEM micrographs of (a) $\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$ and (b) $\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$.

solid skeleton processes. These results are similar to those reported in the literature (Kim *et al* 1999, 2008; Huang *et al* 2001; Huang and Chen 2002). It was also reported that CuO segregates at the grain boundaries even at the stoichiometric composition, $\text{Cu}/\text{Ca} = 3$. It melts during sintering, leading to abnormal grain growth (Fang and Shiau 2004). The above explanation is also confirmed by EDX studies. It is clearly seen that the microstructure of CCTO ceramics changed slightly on partial substitution of Cu or Ti by Co ions.

Figure 3 shows EDX spectrum of CCCTO and CCTCO ceramics. Atomic percentage of the constituent elements in CCTCO and CCCTO ceramics is obtained by EDX studies and given in table 2. It clearly shows the presence of Ca, Cu, Ti and O as per expected stoichiometry of the ceramics, which confirm purity of the materials. A representative EDX spectrum of grain boundary of CCCTO is also shown in figure 3(c). Grain boundaries of CCCTO contain a liquid phase, which is mainly copper oxide. This liquid phase is also seen in SEM micrograph. These results are similar to

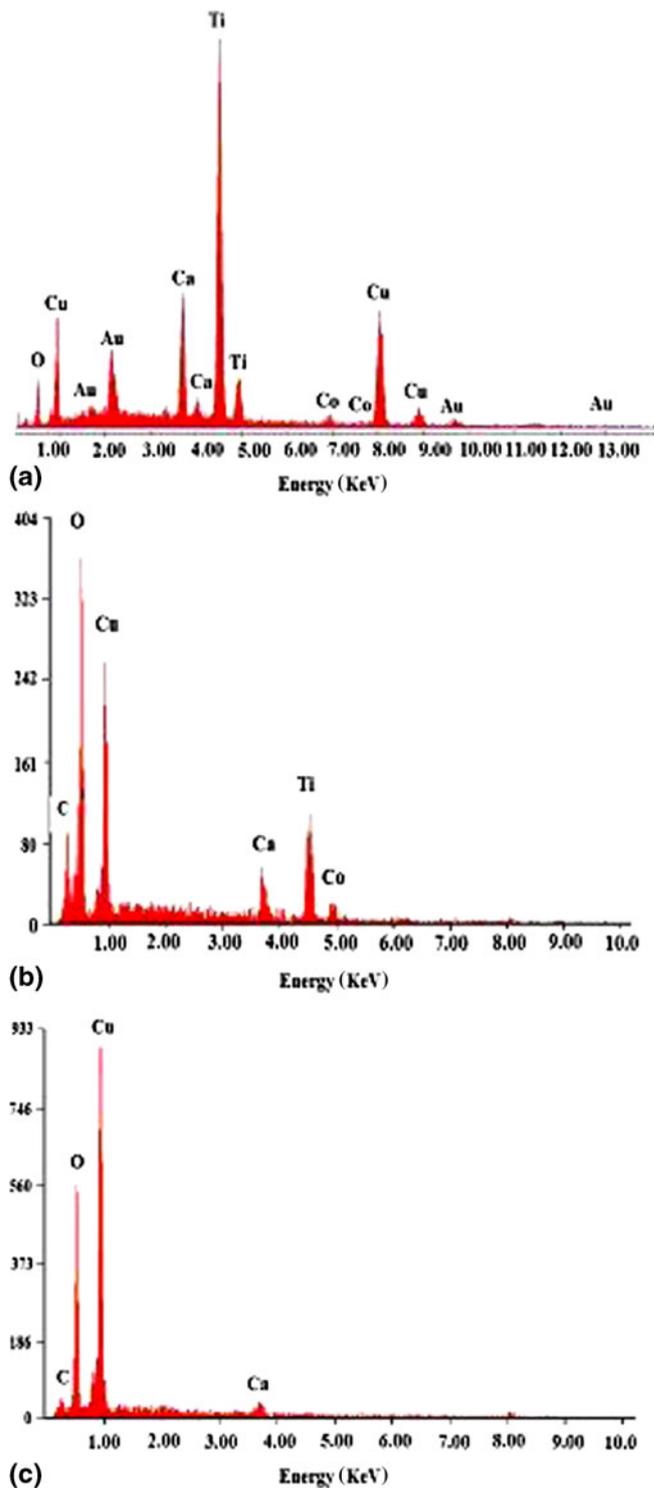


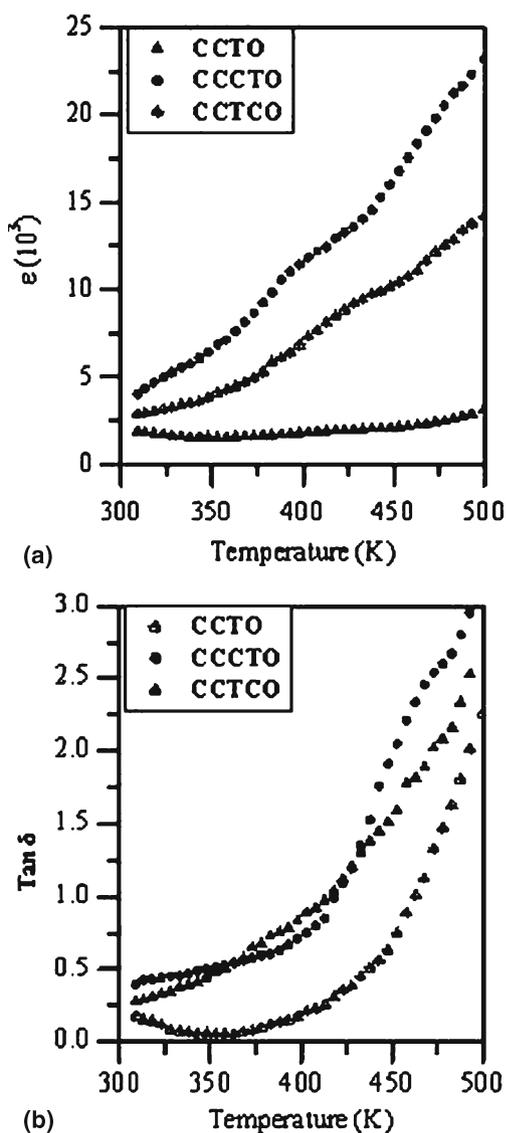
Figure 3. EDX spectra for grain of (a) $\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$, (b) $\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$ and (c) EDX spectra for grain boundary of $\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$.

those reported earlier (Mohamed *et al* 2007). The large grain size of CCCTO, containing copper oxide rich phase at grain boundaries has been reported earlier (Fritsch *et al* 2006).

Plots of dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) vs temperature at 1 kHz of CCTO, CCCTO and CCTCO

Table 2. Atomic percentage of elements in electroceramics, $\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$ and $\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$.

System	At% of elements				
	Ca	Cu	Ti	Co	O
$\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$	8.67	28.61	33.34	1.51	27.87
$\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$	5.30	10.30	16.87	0.70	45.65

**Figure 4.** Plots of (a) dielectric constant (ϵ_r) and (b) dielectric loss ($\tan \delta$) vs temperature at 1 kHz for undoped CCTO and cobalt-doped CCTO.

ceramics are shown in figure 4. It is observed from figure 4(a) that the dielectric constant of undoped CCTO is around 1850 at room temperature and it is almost temperature independent in the range 300–500 K. The dielectric constant of CCTCO and CCCTO ceramic at room temperature and at 1 kHz is around 2900 and 4000, respectively. It is observed that

dielectric constant of cobalt-doped CCTO increases rapidly with increase in temperature.

Figure 4(b) shows that the dielectric loss ($\tan \delta$) of undoped CCTO is temperature independent up to 375 K and then it increases rapidly. It is observed that the dielectric loss of CCTCO and CCCTO is 0.20 and 0.30, respectively at room temperature. It is also observed that the dielectric loss of CCCTO is temperature independent in the range 300–400 K while for CCTCO, it increases gradually with temperature up to 430 K and then it increases rapidly. In CCTCO, the rapid increase in $\tan \delta$ for CCTCO ceramic at higher temperature is due to exponential increase in conductivity of the sample. This may be due to replacement of Ti^{+4} having $3d^0$ configuration by Co^{+2} or Co^{+3} ion having $3d^7$ or $3d^6$ configuration, respectively. This leads to increase in the conductivity, which increases dielectric loss in doped CCTO ceramics.

Figure 5(a,b) shows plots of dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) vs log frequency at a few different selected temperatures of undoped CCTO ceramic. It is noted from the figures that at higher temperature, the dielectric constant and dielectric loss of undoped CCTO ceramic decreases with increasing frequency up to 10 kHz and thereafter, it shows frequency independent behaviour. At low temperature, dielectric loss of CCTO ceramic is almost frequency independent up to 1 MHz.

Figure 5(c,d) shows the variation of dielectric constant and dielectric loss with frequency for CCCTO ceramic. Dielectric constant and dielectric loss decrease with increasing frequency up to 10 kHz. It is also observed that the dielectric constant is frequency independent in the frequency range 10 kHz–1 MHz. At room temperature and at 100 Hz, dielectric loss of CCCTO ceramics is found to be 0.70, which is comparatively less than that of undoped CCTO ceramic.

Figures 5(e) and (f) show the variation of dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) of CCTCO ceramic as a function of log frequency at a few selected temperatures. Dielectric constant of this ceramic decreases with increasing temperature and frequency. It is also observed that the value of dielectric constant of CCCTO is more than that of CCTCO ceramics. Dielectric loss of CCTCO sample is less than that of CCCTO sample at all temperatures in the frequency range 10^2 – 10^4 Hz. Dielectric constant increases with decreasing frequency suggesting the presence of interfacial polarization in these materials which plays an important role for enhancement of dielectric constant in the low-frequency region. Interfacial polarization arises due to

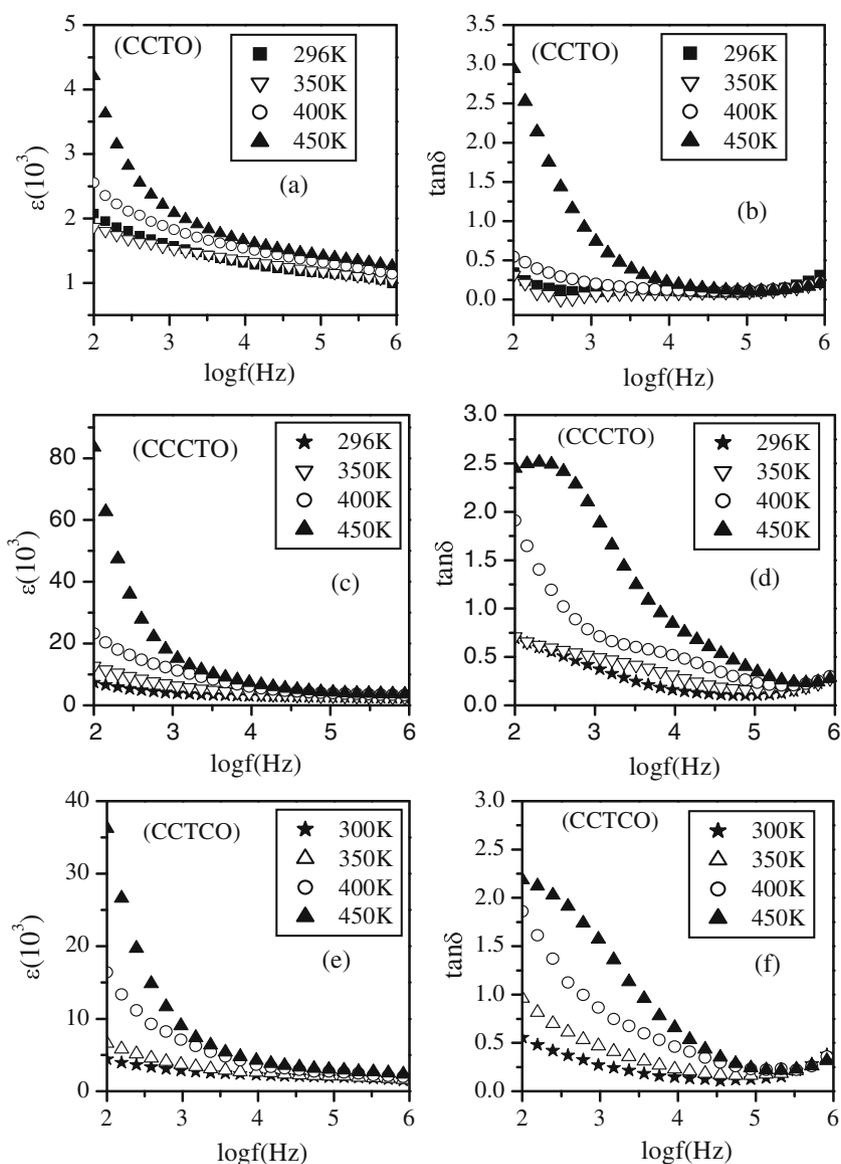


Figure 5. Plots of dielectric constant (ϵ_r) and dielectric loss vs $\log f$ at different temperatures for (a, b) undoped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, (c, d) $\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$ and (e, f) $\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$.

the presence of microheterogeneities in these ceramics. The presence of microheterogeneities in these ceramics is due to slow diffusion controlled thermochemical process used for their preparation.

4. Conclusions

Cobalt-doped CCTO such as $\text{CaCu}_{2.9}\text{Co}_{0.1}\text{Ti}_4\text{O}_{12}$ and $\text{CaCu}_3\text{Ti}_{3.9}\text{Co}_{0.1}\text{O}_{12}$ were synthesized by semi-wet route using TiO_2 powder and metal nitrate solution. The grain size of CCCTO and CCTCO ceramics sintered at 900°C for 6 h are found in the range of 30–50 μm and 2–10 μm , respectively. EDX studies confirm the presence of copper oxide

rich phase at grain boundaries in CCCTO ceramic. Dielectric measurement carried out on CCTO, CCTCO and CCCTO samples shows slight increase of dielectric loss on cobalt doping. Dielectric constant of CCCTO is higher than that of CCTCO samples. The high value of ϵ_r and ($\tan \delta$) of CCCTO ceramic can be explained on the basis of high resistivity due to presence of copper oxide rich phase at grain boundaries.

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