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Chemical and biological sensing using polarity of materials

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ABSTRACT

Polarity is very important in developing materials with colossal dielectric. To meet the demands for the tunable devices and high dielectric parallel plate capacitors, several perovskites such as $CaCu_3Ti_4O_{12}$ (CCTO), $La_{2/3}Cu_3Ti_4O_{12}$ (LCTO) $Pr_{2/3}Cu_3Ti_4O_{12}$ (PCTO) and several other materials of this class have been studied all over the world. Detailed studies showed that results vary a lot based on processing methods, such as powder vs. multi crystals and single crystals. In spite of great progress in processing, low resistivity and process driven variables in properties remain a big hurdle for its applications as a dielectric capacitor. We observed that dielectric values are significantly changed when these materials are exposed to chemicals and biological agents. We used parallel plate capacitor design for making chemical and biological sensors from CCTO member of this group. The data indicated huge difference in the dielectric and resistivity of the exposed samples.

Keywords: Calcium copper titanate, Perovskite, Chemical sensor, Electrical resistivity, Synthesis, Dielectric properties, Ionic characteristics

1. INTRODUCTION

Since past few decades Barium strontium titanate (BST) perovskites have been proven to be very important materials for variety of applications and technology has been transferred for several applications. With a continuous demand for the tunable devices and very high dielectric parallel plate capacitors, perovskites such as $CaCu_3Ti_4O_{12}$ (CCTO), $La_{2/3}$ $Cu_3Ti_4O_{12}$ $Pr_{2/3}Cu_3Ti_4O_{12}$ and many other systems of this class of compounds have been studied by investigators [1-5] all over the world. In the early stage of investigation of this class of ternary perovskites it was observed that their electrical properties were very dependent on the processing methods, crystalline states such as powder vs. multi crystals and single crystals. Despite intensive research in the area there is no any source of literature to give all the possible relevant information regarding various synthetic methods, characterizations, effect of sintering parameters such as temperature, time and atmosphere of sintering. However, it was observed that this class of materials have colossal dielectric constant in KHz and MHz frequency range. In addition, it was also observed that trace of chemical impurities affected the dielectric constant and resistivity significantly. This provided the basis for chemical sing by using this class of materials. CCTO is a very important member of this very important perovskite family and has been investigate by various researchers [4-6] and has been found to show dielectric constant of the order of 10^4-10^5. It shows ability to undergo a series of cationic exchange reactions which results into corresponding isomorphs. Although several mechanisms have been put forward to explain large dielectric constant, it has been suggested that colossal dielectric constant in this class of materials are associated with the presence of re-oxidized grain boundary regions on the outer surfaces of the large semiconducting grains or to a secondary phase at the grain boundaries which confirm the internal barrier layer capacitor (IBLC) mechanism present in these ceramics. Some results of impedance spectroscopy demonstrated that there are electrically heterogeneous semiconducting grains with insulating grain boundaries. It was also observed that significant transition occurs in morphologies due to impurities as well as intentional doping. Slight lead oxide doping showed even transition from nonfaceted to faceted morphology and huge decrease in dielectric constant. With these goals, we used the parallel plate capacitors as chemical and biological sensors. The data indicated huge difference in the dielectric and resistivity of the exposed samples. This indicates that perovskites can be used for chemical and biological sensors at very low cost. Also, preliminary data indicates that after exposing in atmosphere, there materials can recover to original characteristics. Although we have used variety of processes for preparing this class of materials including wet and semiwet methods, results presented in this article are based on annealing method of compacted powder material.

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2. EXPERIMENTAL METHODS

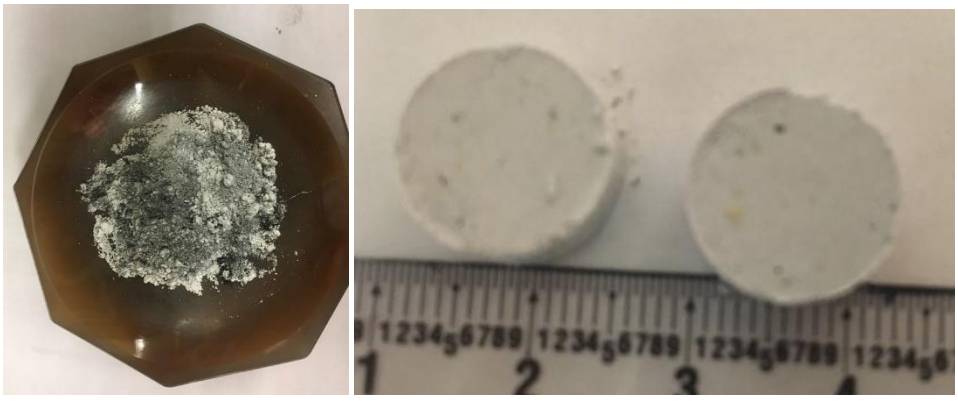
2.1 Stoichiometric $CaCu_3Ti_4O_{12}$ (CCTO) Materials Synthesis: For the synthesis of $CaCu_3Ti_4O_{12}$, material we used $CaCO_3$, CuO and TiO_2 source materials in stoichiometric composition. Source materials were listed for 99.99+% purity. Before mixing, we grinded the powder and used Wig-L-bug to prepare the particles of uniform sizes of source materials. The particles sizes varied a lot, but microscopic studies indicated that these were in the range of 50 to 100μm size. For the processing, powder was pressed to make pellets of cm sizes, using a pressure of 5000 to 8000 lb/inch^2. A temperature range of 600C for sintering and 950 ^{0}C for the grain growth was used in this study. When temperature was increased in range of 1000$^+$C, slight trace of Cu-rich melted phase material was observed. The morphology of material was studied by optical microscope and scanning electron microscope.

2.2 Fabrication and measurements of dielectric constant, capacitance and resistance: The detailed methods for cutting, polishing, electrode bonding and other fabrication into parallel plate capacitors are described in references [**6-8**]. Parallel-plate capacitors were fabricated from pressed and sintered pellets with thicknesses from 0.5 to 2 mm (thinned and polished). We used pads and ethylene glycol solvent to achieve good quality polished surfaces Silver dots were used for electrode on both sides of the pellets. The material does not react with silver or indicating long-term stability very good at room temperature. Dielectric capacitance of bulk ceramic samples was inferred from measurement of complex impedance as a function of frequency from 1 to 1000KHz with an Agilent/HP 4284A LCR meter. Resistivity was inferred measuring current from a dc voltage bias and size and thickness of the sample and electrode.

2.3 Chemical Sensing: Chemical sensing tests were performed using acetone of the pellets. The acetone treated pellets were characterized for the dielectric constant and resistivity and compared with the untreated samples. In this case only a very small drop of the acetone was used on the pellet. In order to evaluate effect of bias voltage and frequency, the data was determined for a range of more than an order of magnitude as described in section 2.2 using LCR meter.

3. RESULTS AND DISCUSSION

All samples for this study were prepared in this study using well mixed powder (**Figure 1a**) were in the range of 2.0 to 5 grams. The powder was pressed, and the diameter was in the range of 7 to 10 mm. To prepare samples in this diameter range with few mm thickness had weight of $CaCO_3$, CuO and TiO_2 was approximately 5g. To ensure homogeneity, after crushing and mechanically mixing powder was crushed repeatedly to make smaller size particles. The pressure applied in each case an identical pressure for pressing the samples. Typical as prepared samples of CCTP for sintering and grain growth are shown in **Figure 1b.** The sintering temperature of 600C showed significant shrinking and sintering. Grain growth was more visible above 900^{o}C. We did not observe much change in the morphology above a temperature of 1050^{0}C. In the growth runs where we used excess copper oxide, we observed few drops liquid rich in copper on the surface of pellet.



(a) **(b)**

Figure 1 (a) Grinded mixture of powder of and (b) pellets for annealing and grain growth of CCTO

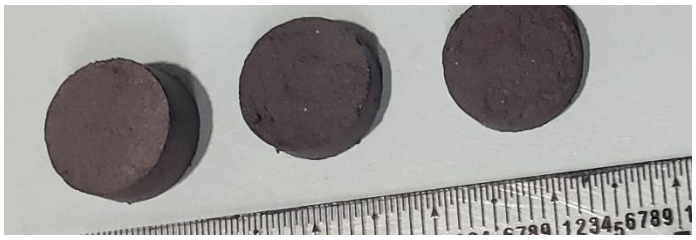


Figure 2. Annealed at 900oC samples of CCTO

As prepared samples of CCTO were placed in horizontal furnace in ceramic crucibles. The sintering temperature of 600-650 was maintained for 24 hours. After annealing temperature was raised to 900^0C for a period of 70^+ hours. **Figure 2 s**hows treated samples. The color of reacted sample was dark brown compared to white mixed CCTO powder. Silver dots were used as electrodes and were stable at room temperature. **Figure 3** shows a typical morphology of grains with copper rich phases. There is some region where one can see liquidus region and copper rich phases. In addition, in copper rich samples we observed more voids compared to stoichiometric samples. When the sample was cooled down, copper rich material seggregated between the grains and appeared as smooth**.** At some places, in the sample a thin layer covering the grains also appeared.

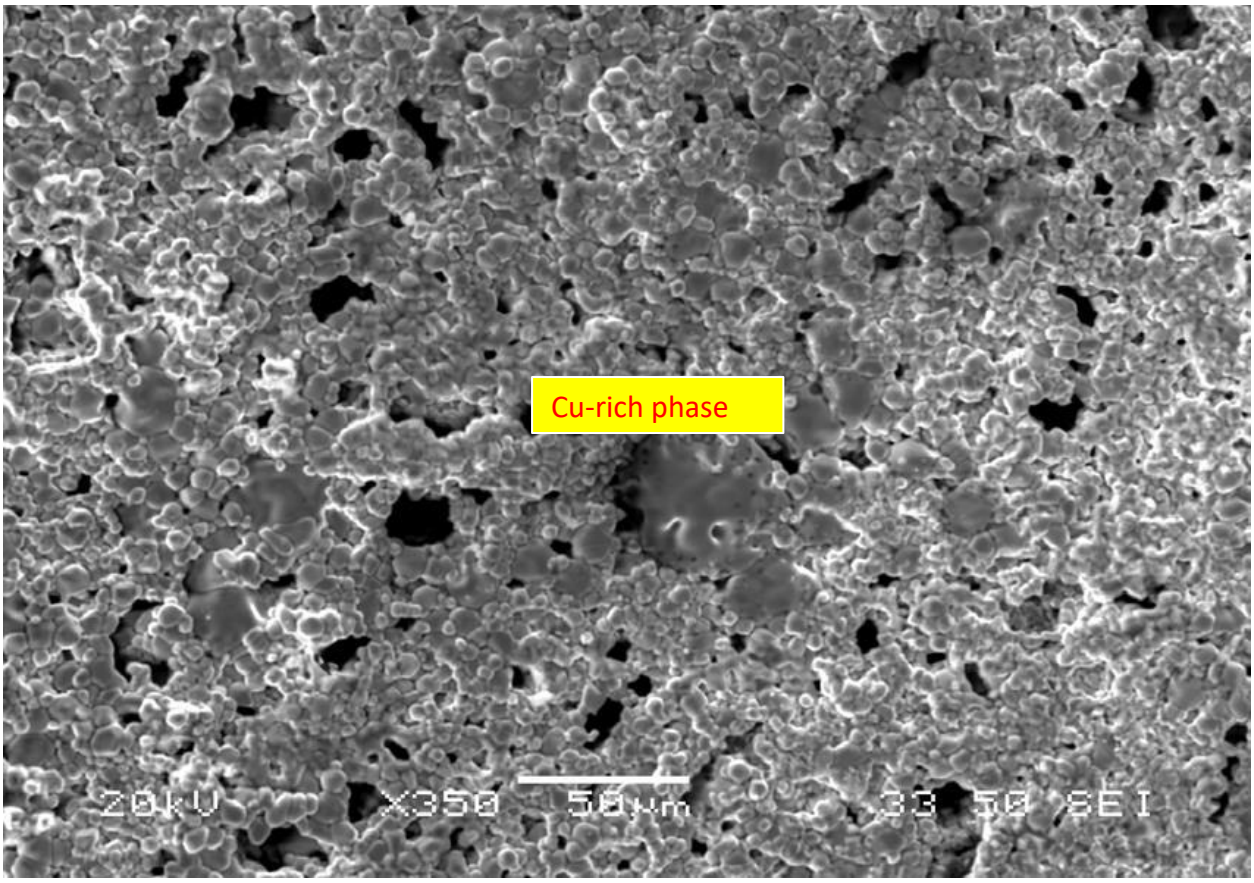
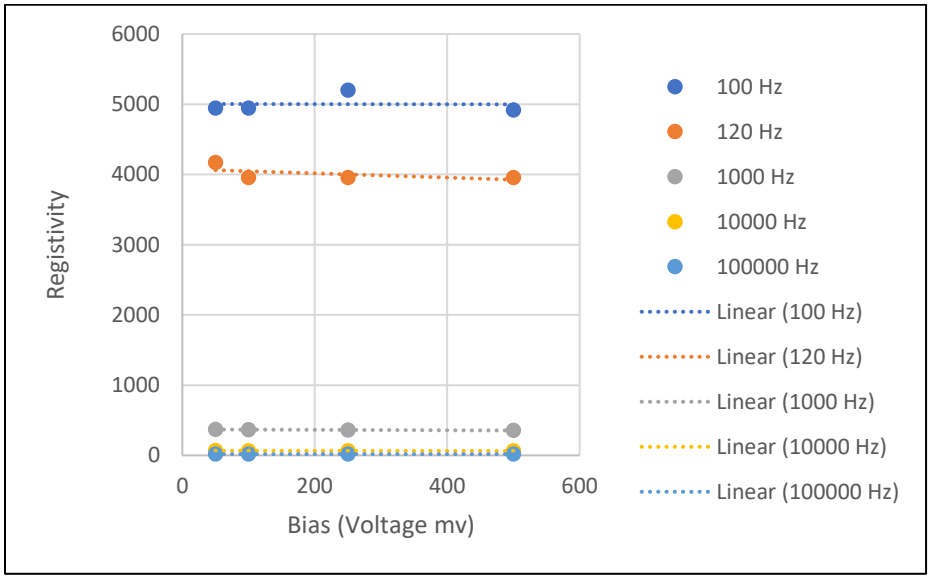
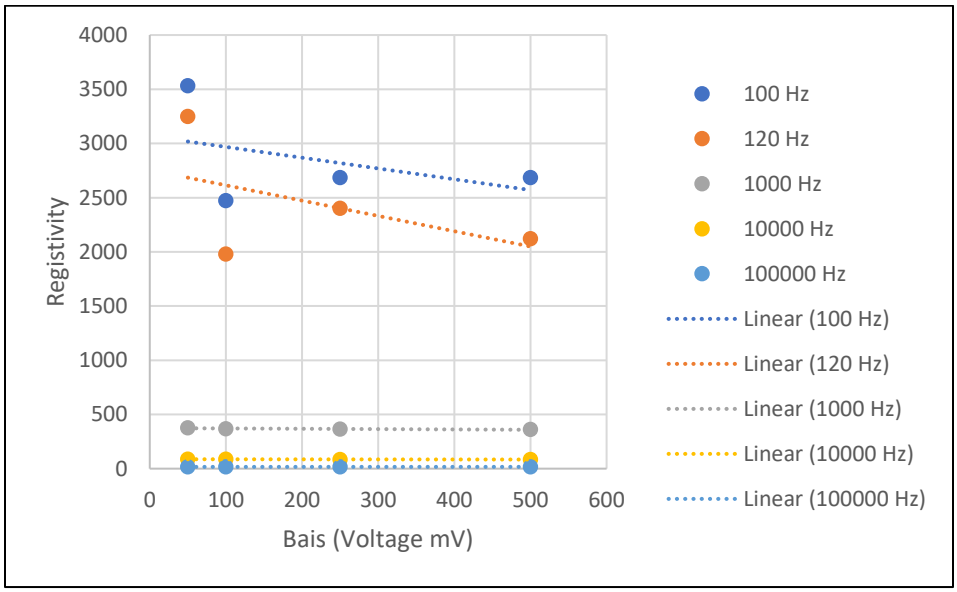


Figure 3. Morphology of CCTO showing effect of cu-rich phases.

The resistivity and dielectric measurements were made similar to methods described earlier (**References**). The resistivity data deduced from the resistance measurements are shown in **Figure 4 a and b** for comparison. It was observed that pure CCTO showed resistivity unaffected by bias voltage and was constant for a particular frequency. While as resistivity of acetone treated CCTO was much lower than pure CCTO and showed significant variation due to bias at a particular frequency. At higher frequency it showed some linearity and was constant. The biggest effect on resistivity due to chemical presence was observed at lower frequency (100Hz) range. It was almost 45% lower. The details of mechanism are still under discussion. However, Mandal at al [6, 7] have shown that oxidation state and polarity both contribute to this difference.

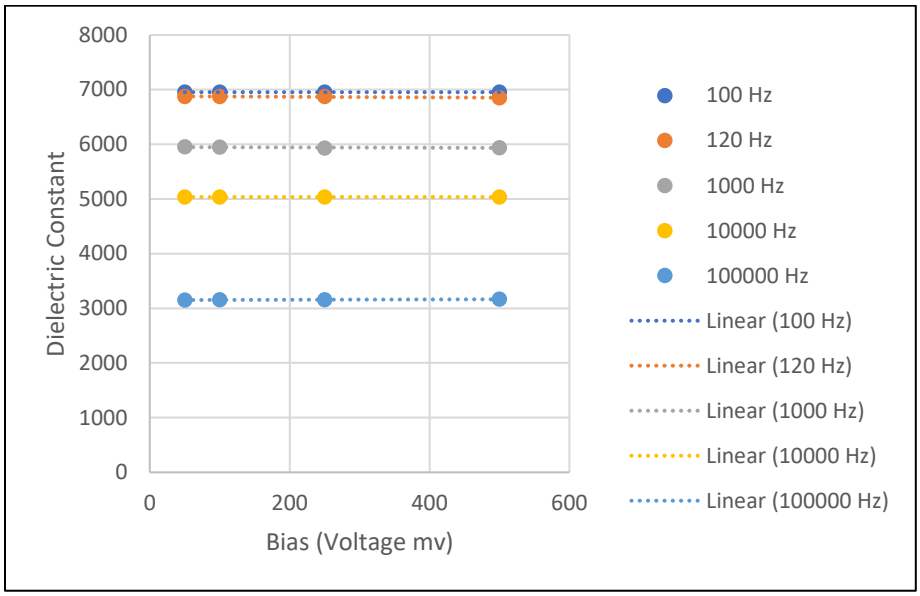


(a)

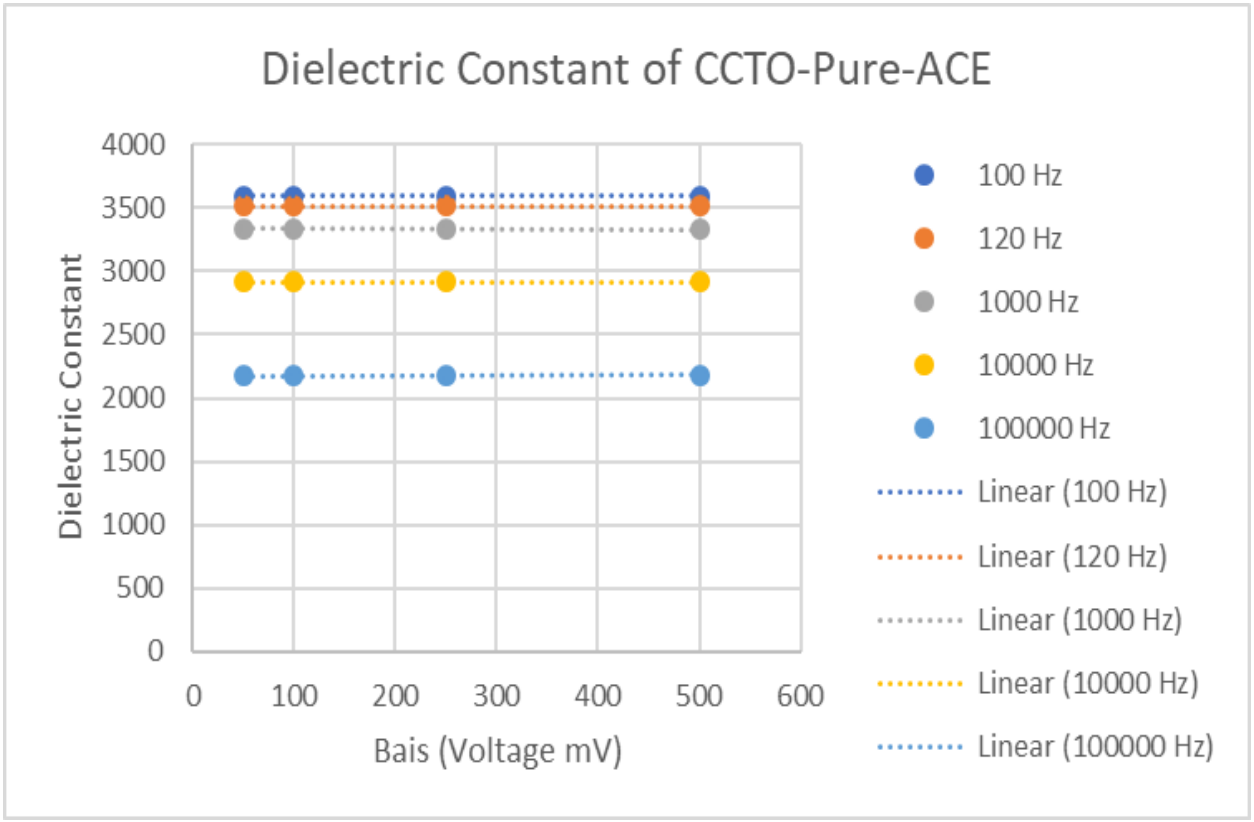


(b)

Figure 4. Resistivity of (a) pure and (b) chemically treated CCTO at different frequency and bias voltage



(a)



(b)

Figure 5. Dielectric constant of (a) pure and (b) chemically treated CCTO at different frequency and bias voltage

Figure 5 shows effect of frequency and bias on the dielectric constant. In the case of CCTO material processed in this case at a particular frequency, the material showed constant value for both pure and chemically treated samples. Samples showed that effect of chemicals (in this case acetone) on CCTO sample was very significant. Again, similar to the resistivity, dielectric values are much lower than that of pure sample. From the data of **Figures 4** and **5** it is clear that both values decreased as result of chemical sensing. The mechanism of variation in dielectric, resistivity and magnetic properties are discussed by Mandal et al. in this class of materials in details. Previous results [4, 5] indicated that carbon impurities decreased the dielectric constant. The resistivity was observed to be higher when significant amount of carbon impurities was intensively added. In this case, amount of acetone was extremely small, and it is not clear if carbon impurities are large enough to be incorporated in matrix. However, it was enough to change the oxidation state and polarity and decrease and dielectric constant and resistivity both. Further investigation in this direction is required.

4. SUMMARY

Perovskites with stoichiometry $Ca_3Cu_3Ti_4O_{12}$ (CCTO) was synthesized and used for chemical sensing. The powder material was treated with trace of acetone to determine detectivity of this material for sensing. Our results indicate that dielectric constant and resistivity was very different for chemically treated sample. Further studies are underway to determine the mechanism of decrease in values. Effect of chemical vapors on the electrical characteristics of CCTO and hence sensing is continuing.

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