

Disruptive chemical approach to modify perovskites for chemical and biological sensors

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ABSTRACT

We have been investigating $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ class of perovskites for variety of applications due to its very large dielectric constant. Several mechanisms have been proposed for the existence of the high dielectric constant based on grain boundaries and oxygen deficiencies. We will report the results of the effects of monovalent substitution to replace calcium. This will alter the size to distort the perovskite structure. In addition, we used this system as a sensor for organic agents. There were very large changes in dielectric constant and resistivity indicating this system as a very good sensor material.

Keywords: Dielectric, Capacitor, Resistivity, Grain, Annealing, Coarsening

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1. INTRODUCTION

There is a strong need for low-cost, large volume reusable material-based sensors for variety of applications. After the research of Subramanian et al [1] on existence of a colossal dielectric constant in the class of perovskite calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ or CCTO) materials. Mandal and his coworkers [2-5] have performed a series of experiments to develop electrical and magnetic properties for a variety of systems. They showed that several mechanisms which have been developed for the existence of colossal dielectric constant in the class of perovskite calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ or CCTO) materials. Research indicates that existence of twinning parallel to (100) (001) and (010) planes cause planar defects and causes changes in local electronic structure. This change can cause insulating barriers locally which contribute to the large dielectric values irrespective of processing. However, the goal of this paper is very different. We proposed to evaluate effect of organic and inorganic agents on the properties and hence one can use these materials as sensors. In this study we present the synthesis and characterization of $\text{Na}_2\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (NCTO) material. This provides both distortion due to atomic size difference and defects due to insertion of nitrogen. The morphology of the compound was determined to show that processing has tremendous effect on the dielectric values. We showed that treatments with organics have tremendous effects on the dielectric constant and resistivity of the NCTO material system.

2. EXPERIMENTAL METHOD

2.1 Materials Synthesis: For the synthesis of stoichiometric $\text{Na}_2\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (NCTO), we used Na_2CO_3 , CuO and TiO_2 to prepare the desired stoichiometry. Source materials were listed for 99.99+% purity. Before preparing mixtures, we used Wig-L-bug to prepare the particles of almost uniform sizes of source materials. The particle sizes varied but these were in the range of $100\mu\text{m}$ size. For the processing, powder was pressed to make pellets of cm sizes, using a pressure of 7000 to 8000 lb/inch². We used a temperature range of 600 °C for sintering and 750 °C for the grain growth, and at higher temperatures we observed partial melting and crystallization of the material. The morphology of material was studied by optical microscope and scanning electron microscope.

2.2 Fabrication and measurements of dielectric constant, capacitance and resistance: Details of parameters are described in references [3-5] for cutting, polishing, electrode bonding and other fabrication into capacitors. We were able to achieve good quality polished surfaces on polishers with pads and using several solvents. For the measurements we used silver paste as the electrode source. Parallel-plate capacitors were fabricated from pressed and sintered pellets with thickness from 3 to 4 mm. Dielectric capacitance of bulk samples was inferred from measurement of complex impedance as a function of frequency from 100 Hz to 100 kHz with an Agilent/HP 4284A LCR meter. Resistivity was inferred from two measurements: (a) using a parallel-resistance model of complex-impedance measurements and (b) measuring current from a dc voltage bias.

3.Results and Discussion

Most of the samples prepared in this study were in the range of 0.6 to 1 gram in weight. The diameter of the samples was 13 mm, and a thickness of about 3-4mm. A 10g batch of powder was made using 1.59g Na_2CO_3 , 3.60g CuO , and 4.80g TiO_2 . After crushing and mechanically mixing the powders, smaller samples of about 0.8g were measured out to make the smaller pellets. The powder was placed in a pellet press to condense the samples. The pressure applied in each case was 7000-8000 lb/inch². Pellet samples of NCTO were prepared for sintering and annealed at 750 °C and are shown in **Figure 1**.

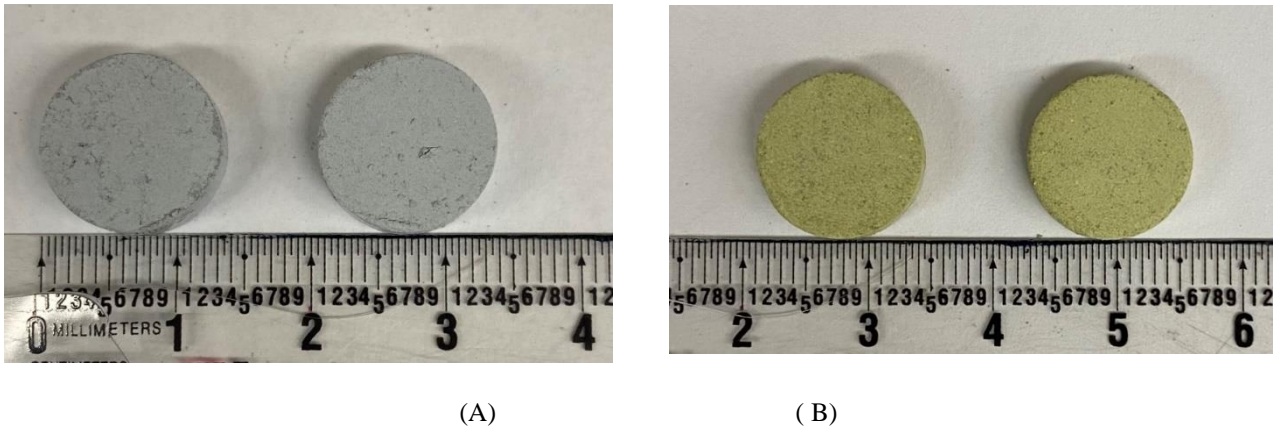


Figure 1 (A) as prepared and (B) annealed at 750 °C samples of NCTO

Samples were annealed for about 100 hours at 750 °C and some samples were annealed for an additional 165 hours to study any changes in the morphology of the samples using the scanning electron micrograph (SEM). Figures 2-5 show the morphology of samples and the changes that that occurred due to the annealing.

In addition to pure samples of NCTO as described above, samples were also prepared by doping with sodium nitrite. In a 1.0g sample of NCTO powder, 0.20g of sodium nitrite was added and combined in using a mortar and pestle. Samples were annealed for 100 hours at 750 °C as well. We used this dopant to examine changes to NCTO's electrical properties. Electrical properties were also examined when the pure NCTO was exposed to acetone to test the effects of carbon-based materials on this substance and assess its ability as a chemical sensor. These properties were evaluated by measuring the samples' dielectric constant and resistivity.

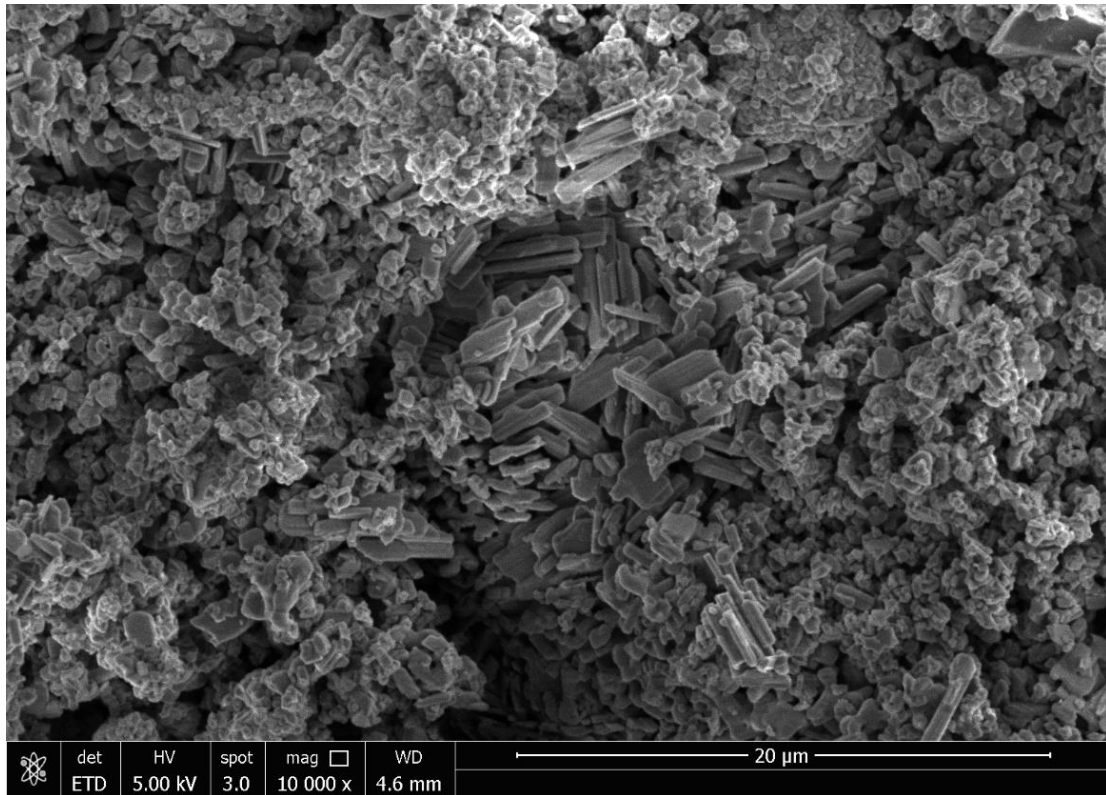


Figure 2. Morphology of NCTO annealed for 100 hours. SEM shows irregular crystal growth at 20 um scale.

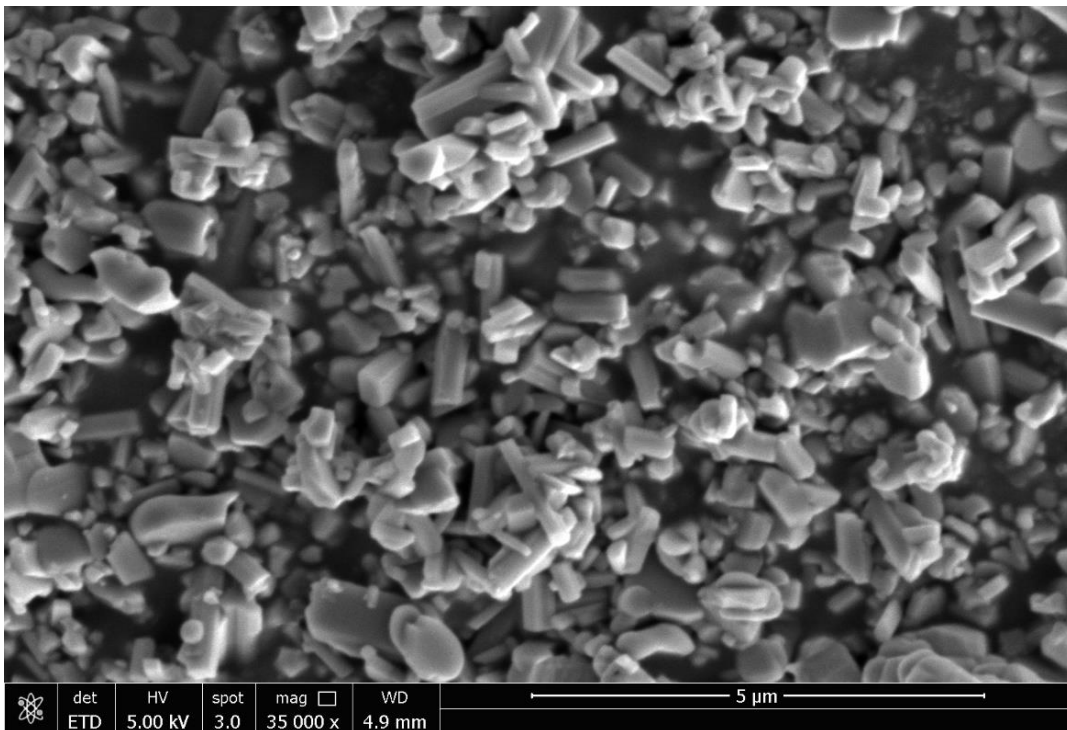


Figure 3. Morphology of NCTO annealed for 100 hours. SEM 5 um scale showing cell growth of sample.

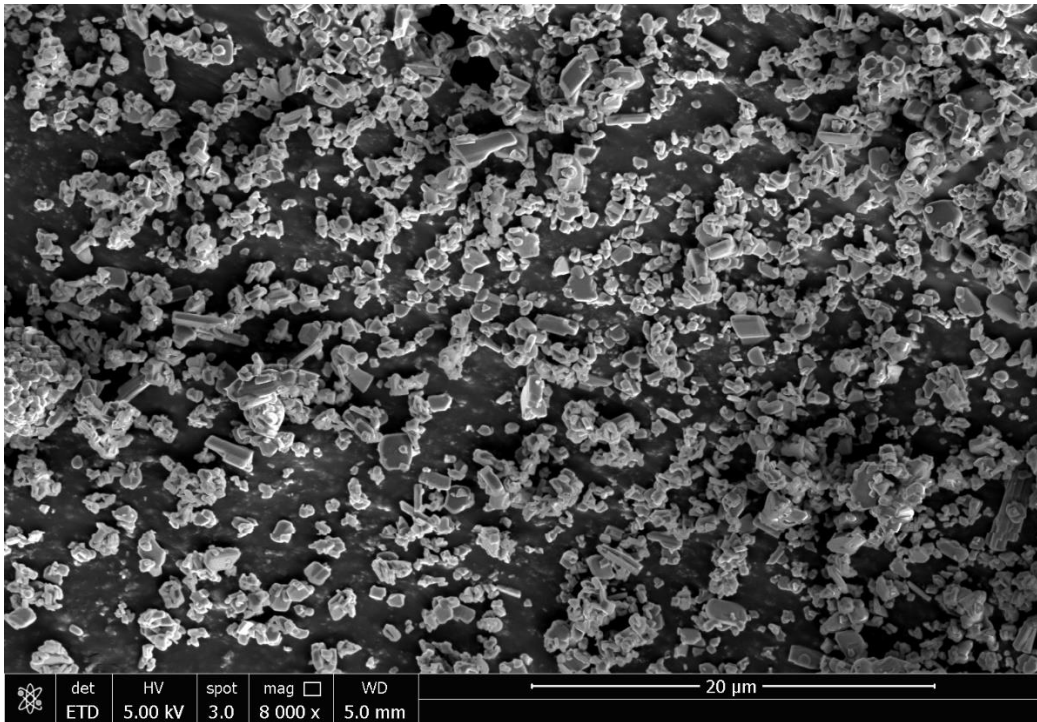


Figure 4. Morphology of NCTO annealed for 265 hours. SEM image of 20 um scale.

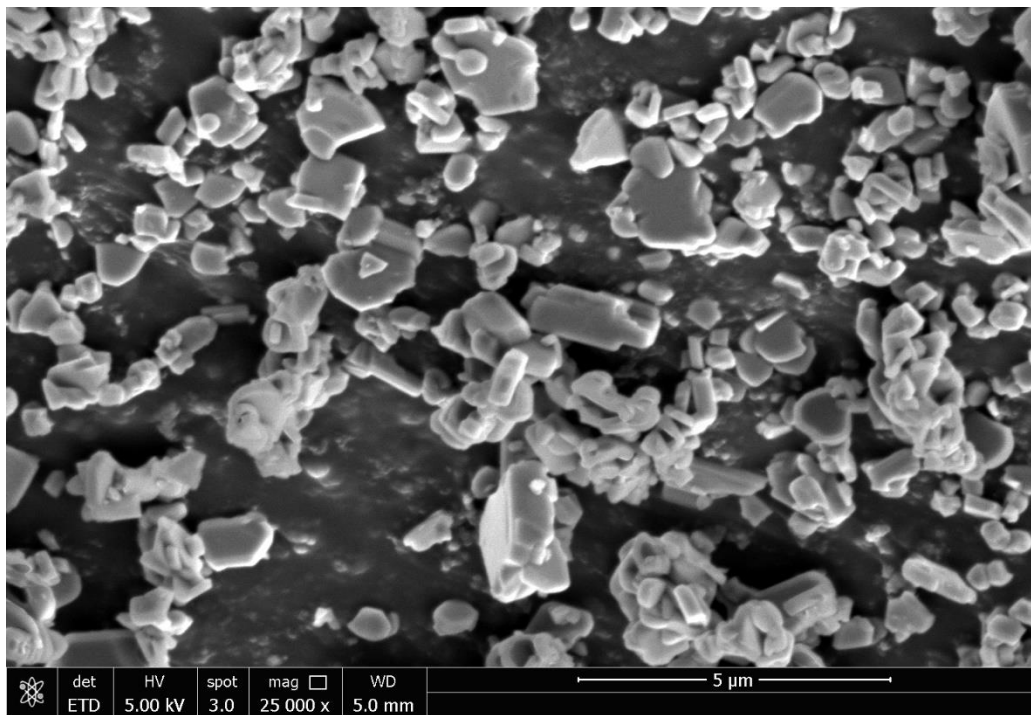


Figure 5. Morphology of NCTO annealed for 265 hours. SEM image of 5 um scale.

These images taken on the SEM show the different growing patterns of NCTO when left to anneal for longer periods of time. The crystalline structure of the sample changes and shows a more uniform pattern with longer time.

The dielectric constants of pure, doped, and acetone tested NCTO were measured by painting a silver electrode on each side of the surface with an area of about $5.03 \times 10^{-5} \text{ m}^2$, and measuring the sample's capacitance values in the LCR meter at varying frequencies and biases. Dielectric was calculated using the formula: $(\text{Capacitance} / 8.854 \times 10^{-12}) * (\text{thickness} / \text{area})$. NCTO showed its highest dielectric at about 10,000 as shown in Figure 6. Resistivity was tested the same way, but the sample's resistance was measured with the LCR meter. Resistivity was calculated using the formula: $\text{Resistance} * (\text{diameter} / \text{area})$. NCTO's highest resistivity value was about $4.5 \times 10^7 \text{ Ohm/m}$ as shown in Figure 7.

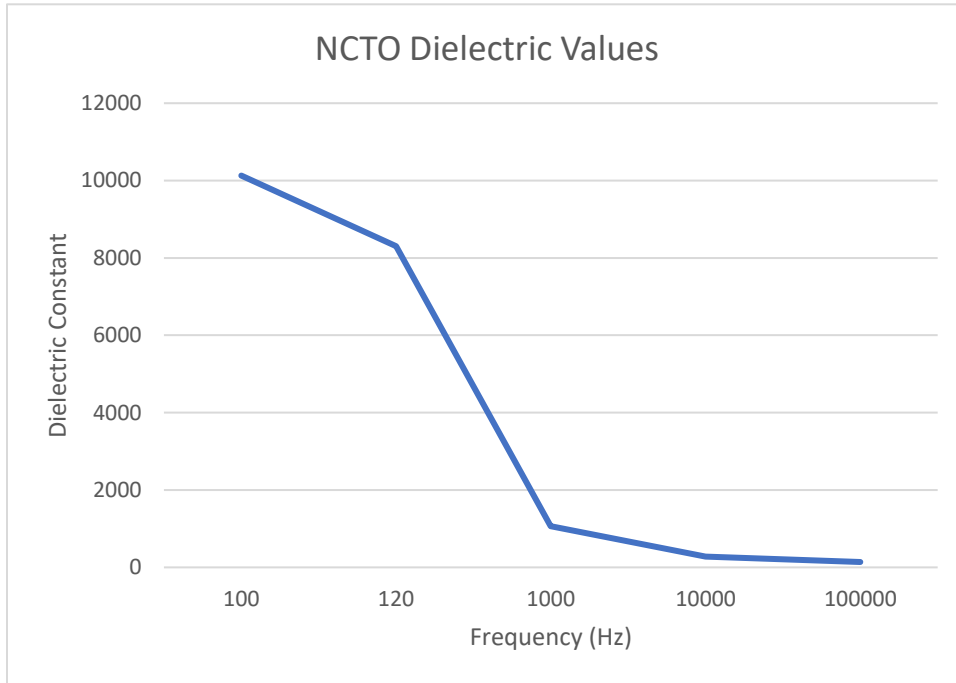


Figure 6. Dielectric Constant values of pure NCTO measured at different frequencies using average value for biases.

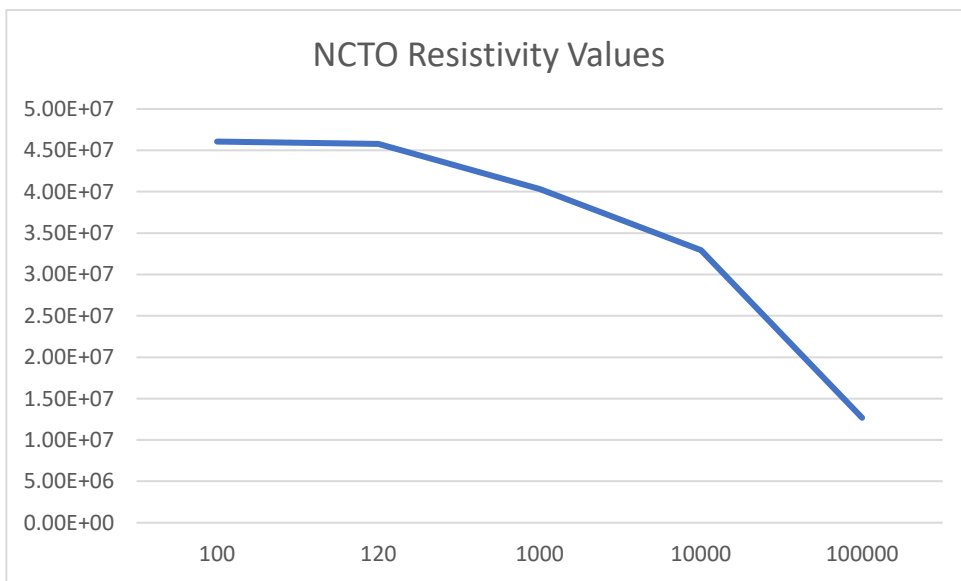


Figure 7. Resistivity values of pure NCTO measured at different frequencies using average value for biases.

Figures 8 and 9 illustrate the affect that different chemical additives had on the dielectric constant and resistivity of pure NCTO. Doping with the nitrate increased both the dielectric and the resistivity of the compound. Acetone did not have much of an effect on the dielectric constant, but it lowered the resistivity of the sample.

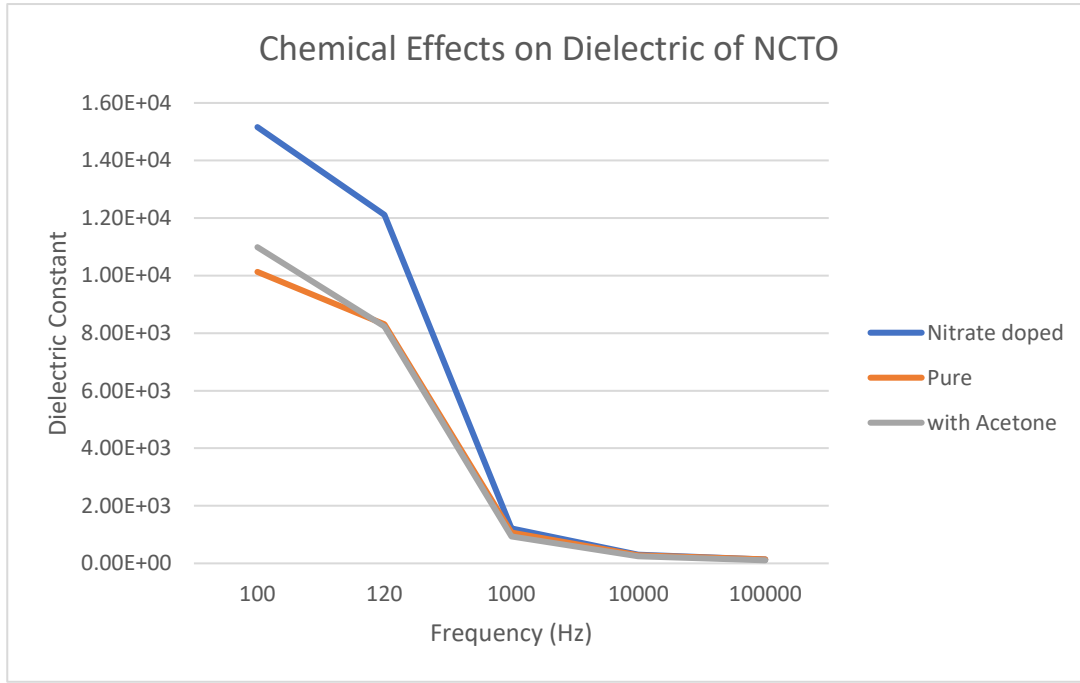


Figure 8. Dielectric Constant values of NCTO and how it is affected by chemical dopants measured at different frequencies using average value for biases.

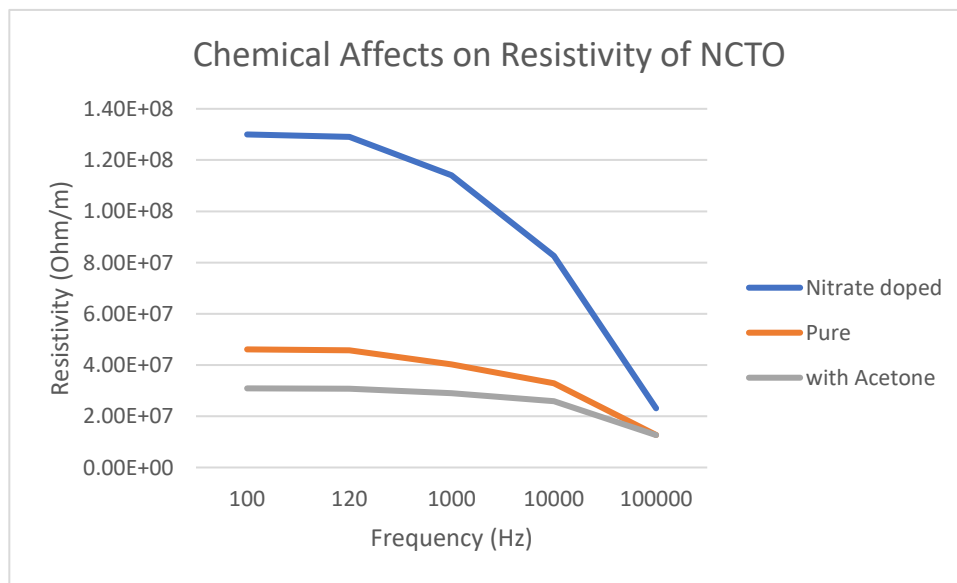


Figure 9. Resistivity values of NCTO and how it is affected by chemical dopants measured at different frequencies using average values for biases.

4. SUMMARY

This overviews the use of $\text{Na}_2\text{Cu}_3\text{Ti}_4\text{O}_{12}$ material system as a chemical capacitor and sensor. There were very large changes in dielectric constant and resistivity indicating the system can be used as a sensor and energy storage material. In addition, results showed that in spite of the distorted structure, $\text{Na}_2\text{Cu}_3\text{Ti}_4\text{O}_{12+d}$ showed high dielectric constant and higher resistivity than well studied material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. This provides both distortion due to the atomic size difference and defects due to insertion of a monovalent vs. bivalent ion affects the properties of the material. In order to keep identical processing parameters, we used nitrates, carbonates, and titanium oxide as parent components and used direct synthesis by sintering and grain growth. In addition to dielectric capacitance, chemical sensing capability will also be presented.

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