American Journal of Materials Synthesis and Processing
2017; 2(6): 90-93
http://www.sciencepublishinggroup.com/j/ajmsp
doi: 10.11648/j.ajmsp.20170206.13
ISSN: 2575-2154 (Print); ISSN: 2575-1530 (Online)

Structural and Dielectric Properties of Lanthanum Doped $CaCu_3Ti_4O_{12}$ for Capacitor Application

Anshuman Srivastava[1], Om Parkash[2], Devendra Kumar[2], Pralay Maiti[3]

[1]Mechanical Engineering Department, SIET, Allahabad, India

[2]Department of Ceramic Engineering, Indian Institute of Technologym, Banaras Hindu University, Varanasi, India

[3]School of Material Science & Technology, Indian Institute of Technology, Banaras Hindu University, Varanasi, India

Email address:

anshuman0203@gmail.com (A. Srivastava)

To cite this article:

Anshuman Srivastava, Om Parkash, Devendra Kumar, Pralay Maiti. Structural and Dielectric Properties of Lanthanum Doped $CaCu_3Ti_4O_{12}$ for Capacitor Application. *American Journal of Materials Synthesis and Processing*. Vol. 2, No. 6, 2017, pp. 90-93. doi: 10.11648/j.ajmsp.20170206.13

Received: September 24, 2017; **Accepted**: October 26, 2017; **Published**: November 15, 2017

Abstract: $CaCu_3Ti_4O_{12}$ (CCTO) is a novel material with high relative dielectric constant and low loss tangent, CCTO belongs to a family of oxides of the type $ACu_3Ti_4O_{12}$ (A=Ca, Cd, Sr, Na, Th). $CaCu_3Ti_4O_{12}$ was first reported by Subramanian et al., to have an unusually high dielectric constant (~10,000) at 1 kHz. It is well known that dielectric properties of CCTO are strongly dependent upon the processing conditions as well as on doping. Semi-wet route was used to synthesise samples of $CaCu_3Ti_4O_{12}$ and $Ca_{(1-3x/2)}La_xCu_3Ti_4O_{12}$ (x=0.01). Analytical grade chemicals, $Ca(NO_3)_2.4H_2O$, $La(NO_3)_3.6H_2O$, $Cu(NO_3)_2.3H_2O$, titanium dioxide and citric acid having purity better than 99.95% were used as starting materials. The formation of single-phase solid solutions was confirmed by the absence characteristic lines of constituent's oxides in the XRD patterns. Dielectric measurement of undoped and La doped CCTO has been performed using four probe novocontrol set up (ZG4) in a wide range of temperature starting from the room temperature. With La doping in CCTO there is an increase in the value of dielectric constant in comparison to undoped CCTO.

Keywords: $CaCu_3Ti_4O_{12}$, XRD, Dielectric Constant, Dielectric Loss

1. Introduction

$CaCu_3Ti_4O_{12}$ (CCTO) is a novel material with high relative dielectric constant and low loss tangent, CCTO belongs to a family of oxides of the type $ACu_3Ti_4O_{12}$ (A=Ca, Cd, Sr, Na, Th) [1-3]. $CaCu_3Ti_4O_{12}$ was first reported by Subramanian et al., to have an unusually high dielectric constant (~10,000) at 1 kHz [1]. These types of materials are widely used in technological applications such as capacitors, resonators, and filters. Compared to the high-K ferroelectric materials including $BaTiO_3$, CCTO has advantageous features for the potential applications to the electronic devices. First, its dielectric constant (K≈12,000) is independent of temperature between 100 and 400 K. Also, the structure with its cubic unit cell (a=7.391 Å) remains unchanged, indicating that no phase transition occurs.

$BaTiO_3$-based ferroelectric materials exhibit high dielectric constant, but here is a problem with these materials as they exhibit strong temperature dependence of their dielectric constants near ferro- to para-electric transition. Therefore, $CaCu_3Ti_4O_{12}$ (CCTO) has attracted increasing scientific and technological interest because of its giant dielectric constant (ε_r ~10^4) with weak temperature/frequency dependence in a wide range of temperature (100–600 K) and frequency. It is well known that dielectric properties of CCTO are strongly dependent upon the processing conditions as well as on doping [4-7]. Now a days lot of work is being done on doping such as substitution of Mn for Cu and Zr for Ti [7-10]. CCTO is generally prepared by the conventional solid-state method. It suffers from the disadvantages of chemical in homogeneity leading to coarse particle size for the product [8]. Semi-wet route has advantages over the conventional solid-state method such as multi component system can possible with high homogeneity. In attempts to find out the origin of the anomalous dielectric behavior of CCTO, several explanations were initially proposed to explain such colossal dielectric constant (CDC). Nowadays it is widely accepted that the nature of the CDC phenomenon is extrinsic: it is due to the presence of internal-barrier-layer capacitances (IBLC) which arise at the interface between semiconducting and insulating regions [10-15]. Moreover, the internal barrier layer capacitor (IBLC) model representing semiconducting grains and insulating grain boundaries confirmed the electrical heterogeneities in the microstructure of CCTO, and has been widely accepted as the most likely explanation for the abnormal dielectric response in CCTO [9]. In the case of polycrystalline ceramics, impedance spectroscopy (IS) studies have revealed that the grains of CCTO have a core–shell structure in which the semiconducting bulk is enclosed by insulating boundaries, and the very high dielectric constant arises due to the Maxwell–Wagner effect [16-23]. These high dielectric constant ceramics can also be used as dispersion in polymer matrix to develop polymer ceramic composites for embedded capacitor applications.

2. Experimental

Semi-wet route was used to synthesise samples of $CaCu_3Ti_4O_{12}$ and $Ca_{(1-3x/2)}La_xCu_3Ti_4O_{12}$ (x= 0.01). Analytical grade chemicals, $Ca(NO_3)_2.4H_2O$, $La(NO_3)_3.6H_2O$, $Cu(NO_3)_2.3H_2O$, titanium dioxide and citric acid having purity better than 99.95% were used as starting materials. Distilled water was used for making standard solutions of metal nitrates. Solutions of metal nitrates in stoichiometric amount of these metallic ions were mixed in a beaker. Calculated amount of TiO_2 and citric acid equivalent to metal ions were added to the solutions. The mixture was heated at 70–80°C on a hot plate to evaporate water and then dried at 100–120°C in hot air oven for 12 h to yield a blue dry powder. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the powder was done from 30 to 1000°C at a heating rate of 10°C/min in air using TGA/DTA Analyser, Perkin-Elmer, USA. Calcination was done at 800°C in an electrical furnace for 6h. Pellets of well mixed calcined powder were made using hydraulic press and sintered at 900°C for 6h. X ray diffraction patterns of sintered pellets confirmed the formation of single phase solid solution.

3. Results and Discussion

3.1. XRD Analysis

X-ray diffraction patterns for CCTO and 1%LaCCTO were recorded in a X-ray diffractometer employing Cu-K_α radiation with a Ni-filter shown in figure 1. A scanning rate of 2^0/min was used for recording. The formation of single-phase solid solutions was confirmed by the absence characteristic lines of constituent's oxides in the XRD patterns. The XRD patterns were indexed using standard procedure. The XRD pattern obtained was compared with the available XRD pattern of CCTO using JCPDS file. The XRD pattern obtained was in accordance with the available CCTO XRD pattern.

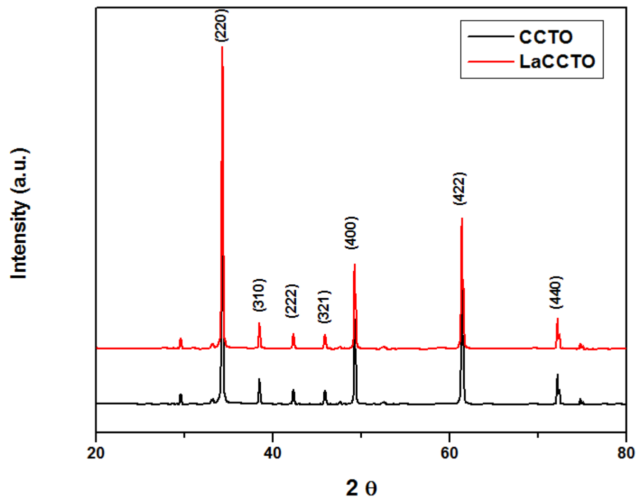


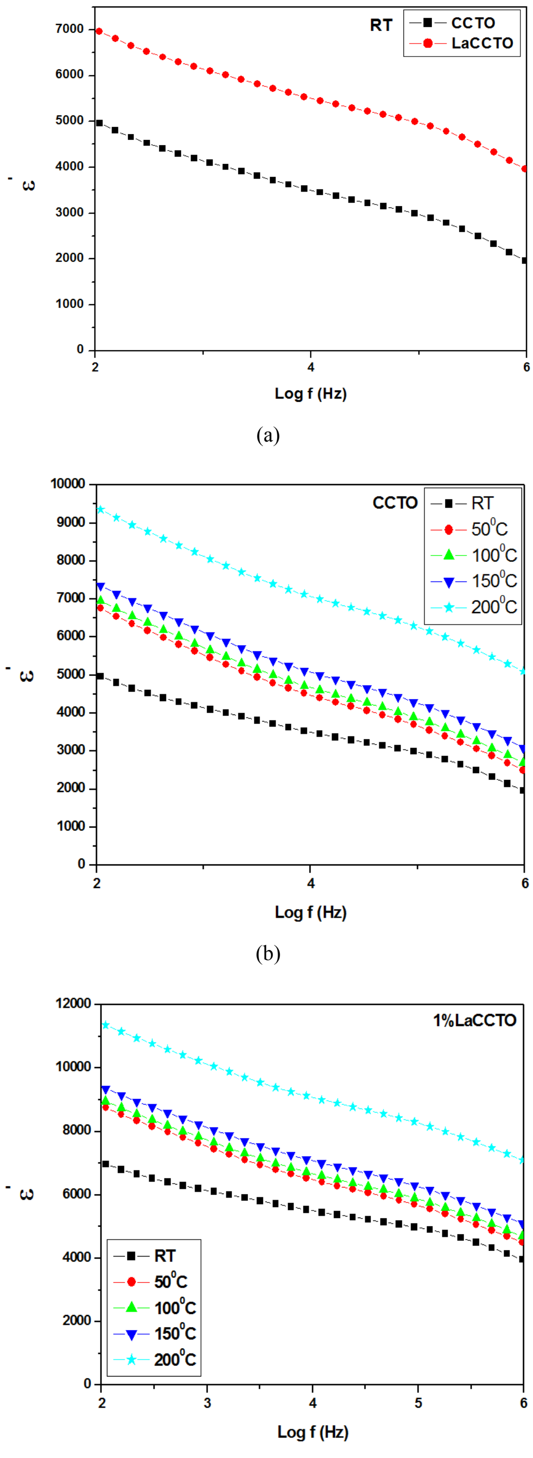
Figure 1. *X-ray Diffraction pattern for the CCTO and 1% Ladoped CCTO.*

3.2. Dielectric Properties

Dielectric measurement of undoped and La doped CCTO has been performed using four probe novocontrol set up (ZG4) in a wide range of temperature starting from the room temperature. Sintered pellets were first polished by the help of different grades of emery paper and then silver coated which is known as electroding. Then the sample was fixed in the sample holder. Sample has diameter of 15 mm and thickness 2.383 mm and measurement was done in the frequency range of 10^2 to 2×10^7. Graph of frequency versus loss factor (tan δ) and frequency versus ε' were recorded.

Figure 2. *Novo control ZG4 Setup.*

Frequency dependence of dielectric constant of CCTO and La doped CCTO are shown in Figure 3a-c at different temperature in the frequency range 10^2 to 2×10^7. The dielectric constant decreases as the frequency increases. The effective dielectric constant increases with the increase in temperature at all the frequencies under study. At 40°C and 100 Hz the value of dielectric constant for CCTO is 5000, which increases to 7000 in case of 1% La doped CCTO. With the temperature there is sharp increase in the value of dielectric constant in case of undoped CCTO as well as La doped CCTO. In case of CCTO the value of dielectric constant of CCTO increases from 5000 to 9400 when temperature increases from room temperature to 200°C. Whereas in case of LaCCTO dielectric constant value increases from 7000 to 11300 when temperature increases from room temperature to 200°C.



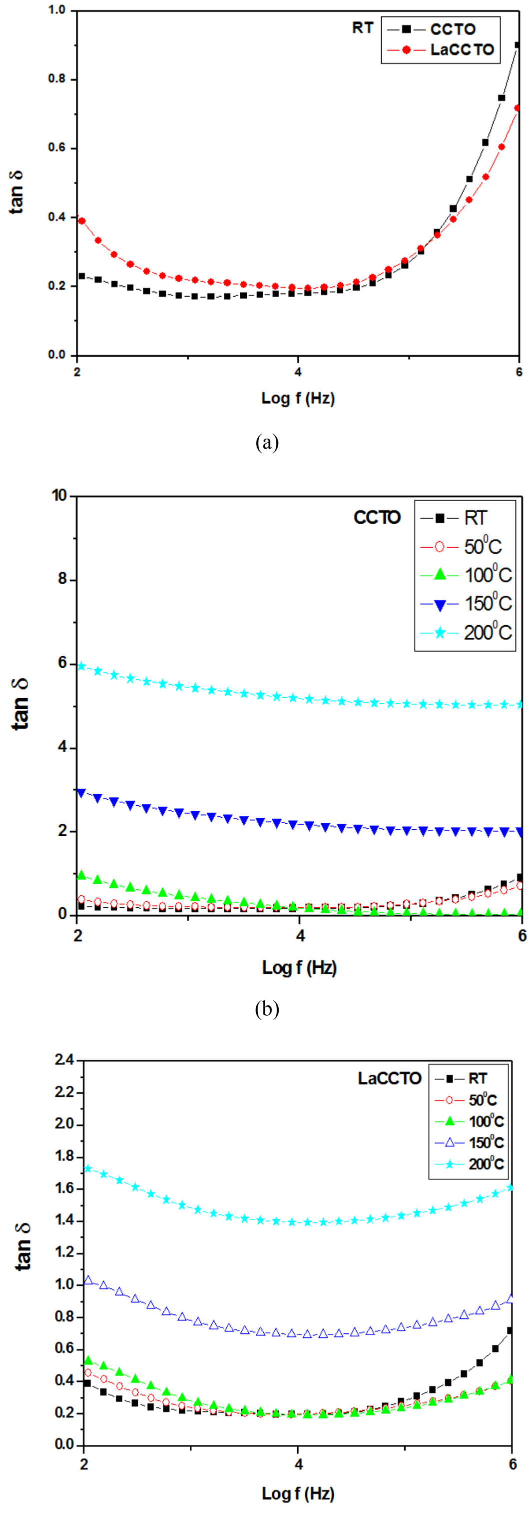
(a)

(b)

(c)

Figure 3. *Dependence of dielectric properties on frequency for La doped CCTO and undoped CCTO at different temperatures.*

Frequency dependence of the dielectric loss for CCTO and La doped CCTO is shown in Figure 4a-c at different temperature in the frequency range 10^2 to 2×10^7. Dielectric loss is increasing with the increase in temperature for both the compositions. The value of dielectric loss at room temperature and at 100 Hz is 0.20 for undoped CCTO which increased to 5.9 when temperature increased to 200°C. Whereas in case of LaCCTO dielectric loss value is 0.39 at room temperature and at 100 Hz, which increased to 1.7 when temperature increased to 200°C. It can be seen that though slight increase in dielectric loss has taken place from 0.20 in CCTO to 0.39 in case of LaCCTO, but with temperature, increase in the value of dielectric loss is less in LaCCTO in comparison to CCTO.



(a)

(b)

(c)

Figure 4. *Dependence of dielectric loss on frequency for La doped CCTO and undoped CCTO at different temperatures.*

4. Conclusion

Undoped CCTO and La doped CCTO ceramics were successfully prepared by Semi wet route. The formation of single-phase solid solutions was confirmed by the absence characteristic lines of constituent's oxides in the XRD patterns. The XRD patterns showed absence of any secondary phase in LaCCTO. With La doping in CCTO there is an increase in the value of dielectric constant in comparison to undoped CCTO. Dielectric constant increases with the increase in temperature and decrease in frequency. It can be concluded that dielectric constant increases with La doping. Whereas dielectric loss slightly increases with La doping.

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