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Calcium Copper Titanate $CaCu_3Ti_4O_{12}$ (CCTO): A Substantial Substitute for Energy Storage Applications

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Abstract

Calcium copper titanate (CCTO) is a high dielectric constant material of cubic perovskite structure with low dielectric losses. The material is attractive in many areas such as; electronics, solid-state etc. because of high dielectric permittivity. This review of CCTO has explored the possibilities of CCTO bulk ceramics in energy storage applications. The synthesized material has properties which can be used for fabricating an efficient energy storage device (EDS). Because of high breakdown voltage, it is also found that permittivity of CCTO is higher than barium titanate (BT) and tangent loss is low at 1 MHz. It is compatible for class II capacitors.

Keywords: CCTO, Ceramic, XRD, Colossal dielectric constant, Perovskite.

1. Introduction

In the last few years CCTO has been explored due to extensively high dielectric permittivity (ε), from 10^5 to 10^4 for single crystal and bulk material, respectively. After the discovery of colossal dielectric constant, its applications to resonator, sensors and energy storage has been of great interest. The structure of this type belongs to the family of $ACu_3Ti_4O_{12}$ (A= Ca, Sr, Ba, $Bi_{2/3}$, $Y_{2/3}$, $La_{2/3}$) oxide of cubic perovskite related structure (space group: Im3) with a lattice parameter of 7.391 Å [1]. The dielectric properties of CCTO are mainly related to its microstructure. CCTO has an electrically heterogeneous ABO_3 type perovskite structure in which grain boundaries are believed to be the origin of giant dielectric constant. The origin of its huge dielectric response has been the subject of some controversy. An internal barrier layer capacitor model (IBLC) has been used to explain the origin of an abnormally high dielectric constant in CCTO. In IBLC model, the dielectric properties of CCTO are treated as heterogeneous structures composed of semi-conducting grains and insulating grain boundaries.

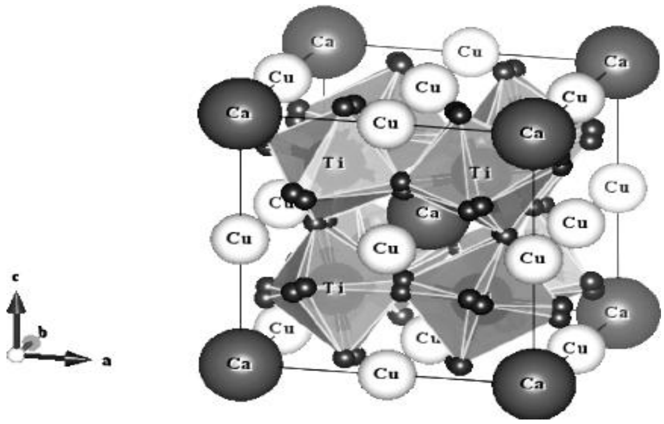

Fig.1 Crystal structure of CCTO compound

The high dielectric loss in CCTO prevents its use as a capacitor. So far, a dielectric constant as high as $3.5x10^4$ and tan δ (dielectric loss) as low as 0.014 at 1 kHz at room temperature were found for pure CCTO synthesized by sol-gel process. The processing conditions such as sintering, calcination cause change in microstructure, which ultimately changes dielectric constant and tangent loss [2-3]. The low dielectric loss and low dielectric constant are useful in insulator. However, high dielectric constant, low tangent loss are desirable for capacitor application. Therefore, many studies have been mainly focusses to minimize the dielectric loss as well as change the structure of insulating grain boundaries by enhance the processing conditions such as sintering and doping element. Much work have been done in the past years on substitution of Ti sites by cations such as Al [3], Fe [4], Mn [5], Ni[6].

In the present review, application of CCTO as energy storage has been discussed. Many researches have resulted in devices with high energy-density storage capacities which are called as supercapacitors. A supercapacitor is different from other capacitors by its orders-of-magnitude advantage in energy density.

2. Experimental Techniques

Many researchers have done the synthesis of CCTO by physical and chemical method such as conventional solid-state route, sol-gel process, wet-chemistry route, chemical assisted route etc. Xin Ouyang et al. [7], Ravikiran Late et al. [8], Romy Lohnert et al. [9], Mohsen Ahmadipour et al. [10] have been synthesized CCTO by conventional solid state reaction route from the raw materials of calcium carbonate calcium carbonate ($CaCO_3$) copper oxide (CuO) and titanium dioxide (TiO_2) powders in proper stoichiometric ratio. The materials were mixed in ethanol by ball milling process using zirconia balls for 24 h. After the suitable calcination and sintering process they found the pure CCTO material.

$$CaCO_3+3CuO+4TiO_2 \rightarrow CaCu_3Ti_4O_{12}+CO_2\uparrow$$

The phase of the synthesized material was determined by XRD analysis with Cu Kα (λ=1.5406Å) over the 2θ range of 2º to 80° with a step size of 0.04° and a scan speed of 0.25°/min.[11].

3. Discussions

3.1 Structural Properties

Subramanian et al. (2000) reported lattice constant of CCTO as 7.391 Å with dielectric constant of 10,286 and tangent loss 0.067 form the XRD measurement. The cubic structure of this material is related to perovskite type with no structural phase change has been examined below 35K, however melting temperature of Cu is approxmately 1084º C. So, the CuO compound has melt at high temperature (1040º C) compared to the lower sintering temperature. The presence of secondary phase in the pure CCTO sample was reported by Hu et al. [13]. By sintering the CCTO sample at 1200º C for 8 h, they detected the minor peak of TiO_2 present in their sample after the sample was analyzed by XRD. Suman Rani et al. [14] have reported no secondary phase in sintering process of CCTO and confirmed that all material reacts during calcination and sintering process. The relationship between the permittivity and loss tangent for CCTO is represented in fig 2. We can say that a strong coupling exists between these two parameters and they increase or decrease with each other. The dependence of these two parameters follows the empirical relationship of $\tan\delta = a \ln(\varepsilon_r) - c$. Here a≈0.057and c=0.36. This coupling appears the intrinsic nature of CCTO and is indicate that it is almost impossible to produce CCTO with giant dielectric constant but very low loss tangent [12].

3.2. Applications

3.2.1. Electronics

CCTO is a cubic perovskite structure with giant dielectric constant occurs to be a good material for microelectronics technology as a high k-oxides. As a wide band gap n-type semiconductors of good temperature of resistivity are good materials for high temperature electronics. CCTO in general used in the stream of IC (Integrated Technology) technology as protective devices.

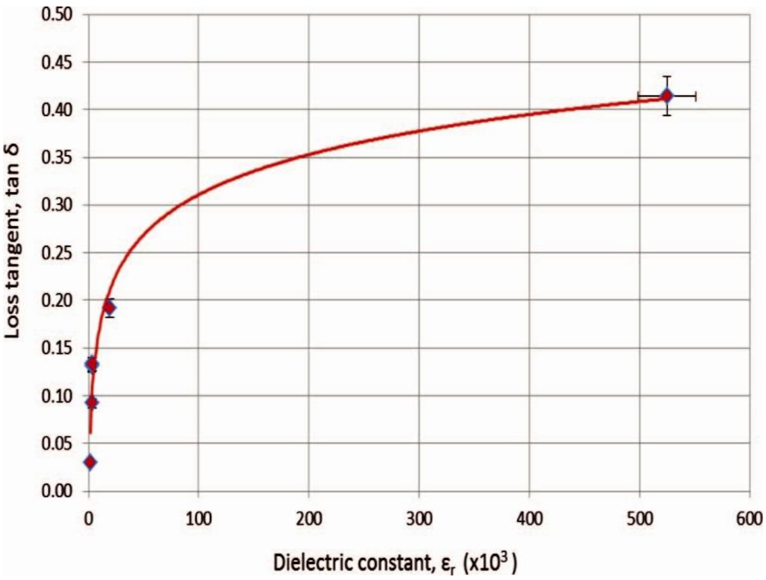

Fig 2. Interdependence of loss tangent and permittivity at 1 kHz for ABO_3 type [12]

3.2.2. Energy storage

Energy storage devices (ESD) are characterized by two parameters: the energy density and the power density. Some ESD devices are batteries, supercapacitors, flywheels, electrolytic capacitors. Their power density and energy density covers a broad range of spectrum, but in general, a device of high energy density shows low power density. Batteries and capacitors are important ESD, which are used in all sorts of applications. Batteries have high energy density and low power density while, capacitors have high power density and low energy density. There are many things in favor of supercapacitors used as an ESD with respect to batteries. They are of high power density, good charge-discharge time, wide temperature range (-40ºC to +300ºC) and long life. It is well known that charge is directly proportional to the energy density from the parallel plate capacitor device. So, increasing the charge, increases the energy density of capacitor. CCTO meet the requirements of class II capacitor, and much more comparable with BT, which is used in current state of solid state capacitors.

R.K. Pandey et al. [12] presented the permittivity of three samples of CCTO in comparison with barium titanate ($BaTiO_3$). They reported that all the permittivity of CCTO samples are higher than BT (barium titanate). The materials requirement for class II capacitor is: they should have very high breakdown voltage. These three samples lies in the range for class II capacitor. According to Y. Li et al. [15] In spite of the high dielectric constant, high dielectric loss in CCTO prevents its use as a capacitor. So far, a dielectric constant as high as $3.5x10^4$ and tan δ (dielectric loss) as low as 0.014 were achieved by sol-gel synthesis of pure-CCTO at 1 KHz.

4. Conclusion

From the XRD analysis it can be concluded that the CCTO is cubic perovskite material with dielectric constant of 100,000 to 10,000 for single crystal and bulk material resp. Dielectric constant of CCTO material sintered at different temperature show different variation in dielectric constant. It is the challenge for researchers to minimize the loss while remaining its giant permittivity. In this short review, we visualize, CCTO is widely used for energy storage and rise to phenomena class II capacitors for high temperature electronics and microelectronics. CCTO has high temperature stability, high permittivity and wide band gap favorable for the many areas of technology. The major drawback of CCTO is tangent loss, due to which it cannot be used for practical applications.

Acknowledgements

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