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Rationalization of dielectric properties of nano-sized iron doped yttrium copper titanate using impedance and modulus studies

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ABSTRACT

Iron doped Yttrium Copper Titanate nano-ceramic with composition, $Y_{2/3}Cu_3Ti_{3.90}Fe_{0.10}O_{12}$ (YCTFO) was prepared by semi-wet route. It displays all normal XRD peaks of $Y_{2/3}Cu_3Ti_4O_{12}$ (YCTO) along with a few secondary peaks of CuO. Stoichiometric purity of the composition was ascertained by EDX spectral analysis. The distribution of bimodal spherical grains confirms 0.5–1.5 μm size limit along with a few irregular shaped large grains with size 1.5–2.8 μm. The impacts of acceptor type of hetero-valent substitution of Ti^{4+} by Fe^{3+} in $Y_{2/3}Cu_3Ti_4O_{12}$ (YCTO) were reflected as decrease in grain size and broadening of ε_r–T peak with simultaneous decrease in ε_r value. The presence of temperature dependent relaxation was also rationalized by impedance and modulus spectroscopic studies which confirm ferroelectric to paraelectric phase transition at 348 K.

1. Introduction

With an ever growing demand of microelectronic products in miniaturized versions along with high performance, enhanced functionality and low cost, researchers, from all over the world, have shown potential attention to develop a material ideally suitable for capacitors, resonators and filler applications. For such applications, the most important prerequisites are materials with high dielectric constant and low dielectric loss at certain operating frequency with a wide range of thermal stability [1–2]. Recently $CaCu_3Ti_4O_{12}$ (CCTO) has gained considerable interest both scientifically and technologically due to its extraordinary high static dielectric constant ($\varepsilon_r \sim 10^4$–10^5) which is independent of temperature (100–600 K) and frequency (10^2–10^6 Hz). Although a number of research articles have been published on CCTO ceramic [3–5], structural analogue of $ACu_3Ti_4O_{12}$ (A = $Bi_{2/3}$, $La_{2/3}$, $Y_{2/3}$) with complex perovskite structure are quite interesting. However, till date, no available material satisfies all these prerequisites, and therefore immense interest for synthesis of some new material has been developed. A critical scanning of the existing literature reveals that very few works have been reported on YCTO [6]. In our previous communication, we have reported the dielectric properties of $Y_{2/3}Cu_3Ti_4O_{12}$ (YCTO) which is structurally analogous to $CaCu_3Ti_4O_{12}$ (CCTO) ceramic. Undoped YCTO nano-sized material, prepared by semi-wet route, exhibits high dielectric constant ($\varepsilon_r \sim 8434$) at room temperature and at 100 Hz. However, the most challenging factor is its dielectric loss. Undoped YCTO shows quite high dielectric loss ($\tan\delta \sim 1.5$–2.04) in the temperature range 308–428 K which needs further improvement by lowering this value within the acceptable ranges for device applications [7]. It is reported in literature that the partial isovalent substitution of metal cations at different sites of perovskite can improve properties associated with ferroelectricity and

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dielectric response in ceramic. Further, structural flexibility and chemical versatility of the materials make them more suitable for device applications [8–11].

With a view to develop YCTO and its isomorphs with high dielectric constant and low dielectric loss, doping of Fe^{3+} at Ti^{4+}-site was studied. For this purpose $Y_{2/3}Cu_3Ti_{3.90}Fe_{0.10}O_{12}$ (YCTFO) was synthesized by the semi-wet route and it was characterized by the XRD, SEM, TEM methods. Through this communication, we are reporting microstructure of YCTFO ceramic synthesized by semi-wet route. We are also reporting its dielectric properties and dielectric loss under different frequency and temperature conditions along with the rationalization of dielectric relaxation phenomena with the help of impedance and modulus spectroscopic studies. This paper discusses most recent developments pertaining to the YCTFO system and its application as a nano-ceramic. It aims to present these aspects of YCTFO in a format such that researchers of various disciplines can understand and utilize it for further research.

2. Materials and methods

2.1. Material synthesis

$Y_{2/3}Cu_3Ti_{3.90}Fe_{0.10}O_{12}$ (YCTFO) was synthesized by semi-wet route using analytical grade chemicals $Y(NO_3)_3 \cdot 6H_2O$ [99%, HiMedia, India], $Cu(NO_3)_2 \cdot 3H_2O$ [99.5%, Merk, India], $Fe(NO_3)_3 \cdot 9H_2O$ [99.8%, Merk, India], TiO_2 [99.5%, Merk, India] and glycine [99.5%, Merk, India], as starting materials. Standard solutions of these metal nitrates were prepared using double distilled water. Solutions of metal nitrates in stoichiometric amount of these metallic ions were mixed in a beaker and a calculated amount of TiO_2 and glycine, equivalent to metal ions, were added to the solution. The solution was heated on a hot plate with constant stirring using a magnetic stirrer at 70–80 °C to evaporate water until a blue coloured gel was obtained. After the combustion of the blue gel, dry powder was obtained. Thermal studies were carried out for the dry powder using TG/DTA (Pyris Diamond TG/DTA, Perkin Elmer Instrument, USA) with heating rate 10 °C per minute from ambient to 1000 °C. The dry powder was calcined in air at 500 °C and 800 °C for 5 h and 8 h, respectively, in a muffle furnace. The calcined powder was ground into fine powder using 1–2 drops of poly vinyl alcohol (PVA) as a binder, and cylindrical pellets of thickness 1.5 mm and diameter 9.5 mm were made using hydraulic press applying uniaxial pressure of 3.5 tonn. The pellets were sintered at 950 °C for 12 h in air for different physiochemical characterizations.

2.2. Material characterization

The crystalline phase structure of the sintered YCTFO was identified using an X-ray diffractometer (D/max-2550/PC, Rigaku, Tokyo, Japan) employing Cu-K_α radiation (λ= 1.5414 Å). The morphology of the fractured surfaces of sintered YCTFO ceramic were characterized by scanning electron microscopy (SEM, Model JEOL JSM5410) and transmission electron microscopy (TEM, FEI Tecnai-20G^2) with an accelerating voltage of 200 kV. For TEM analysis, powder form of sintered ceramic was dispersed in acetone and 1–2 drops were mounted on a carbon coated copper grid. The solvent was subsequently allowed to escape in air at room temperature. For dielectric measurements, the pellets were polished and then coated by silver paste on both sides. The pellets were treated at 200 °C for 30 min to form the electrodes for electrical characterization. Dielectric measurement data were taken by LCR meter (PSM1735-NumetriQ, Newton 4th Ltd., U.K.) with variation of temperature and frequency from room temperature to 500 K and 100 Hz to 5 MHz respectively. The value of dielectric constant was evaluated using the standard relation, $\varepsilon_r = C_d/\varepsilon_0 A$, where C is capacitance, d is the thickness of the pellet, A is the effective cross sectional area of the pellet and $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m.

2.3. Determination of density and porosity

Data concerning density measurement of sintered YCTFO sample were recorded employing Archimedes Principle. First, the weight of dry pellet and the weight of wet pellet were recorded. The pellet was suspended in distilled water and then weighed again. The bulk density (d_B) [12] was calculated using equation:

$$d_B = \frac{W_d}{W_w - W_s} \tag{1}$$

where W_d is the weight of dry pellet, W_w is the weight of wet pellet; and W_s is the weight of sample suspended in water. At the same time, theoretical density (d_T) was also calculated using solid-state density equation:

$$d_T = \frac{ZM}{a^3 N_A} \tag{2}$$

where Z is the effective number of atoms in the unit cell; M is the molar mass of $Y_{2/3}Cu_3Ti_{3.90}$ $Fe_{0.10}O_{12}$ ceramic corresponding to the chemical formula (g mol^{-1}), a^3 is the unit cell volume (Å^3) while N_A is the Avogadro's number (6.0221×10^{23} mol^{-1}). The values of cell parameters i.e. lattice constant (a) and volume of unit cell (V) were obtained for YCTFO ceramic (BCC arrangement, Z=2). Apparent Porosity [12] of YCTFO ceramic was calculated from the equation:

$$\varphi = \frac{W_{sat.} - W_{dry}}{W_{sat.} - W_{susp.}} \tag{3}$$

where the terms, φ is the apparent Porosity, $W_{sat.}$ is the weight of pellet when it is assumed that all pores are completely saturated with water, $W_{susp.}$ is the weight of pellet immersed in water (by water displacement method) and W_{dry} is the weight of dry pellet.

3. Results and discussion

3.1. TGA/DTA studies

To ascertain the ideal temperature required for the thermal decomposition of precursor dry powder of YCTFO ceramic, TG/DTA was carried out. Fig. 1 shows simultaneous TG/DTA/DTG plots of precursor powder of YCTFO ceramic. Two major stages of weight loss in the temperature range from 100 °C to 1000 °C were observed in TGA plot, the first major weight loss at 250 °C is due to an exothermic reaction