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Undertaking from the Candidate

I, Mrs. Sunita Sharma, research scholar under the supervision of Prof. K. D. Mandal, Department of Chemistry, Indian Institute of Technology (BHU) Varanasi give undertaking that the thesis entitled "**Dielectric Properties of $Y_{2/3}Cu_3Ti_4O_{12}$ and Effect of Doping at its Different sites**" submitted by me for the degree of **Doctor of Philosophy** is a record of first-hand research work carried out by me during the period of study.

I avail myself to responsibility such as an act will be taken on the behalf of me, mistakes, errors of facts, and misinterpretation are of course entirely my own.

Date……………

Place: Varanasi **(Mrs. Sunita Sharma)**

Candidate's Declaration

*I, **Mrs. Sunita Sharma** certify that the work embodies in this Ph.D. thesis is my own bonafide work carried out by me under the supervision of Prof. K. D. Mandal and co-supervision of Prof. M. M. Singh, Department of Chemistry, Indian Institute of Technology (Banaras Hindu University), Varanasi for a period of approximately 4 years and 10 months from August, 2011 to June, 2016. The matter embodied in this Ph.D. thesis has not been submitted for the award of any other degree / diploma.*

I declare that I have faithfully acknowledged, given credit to and referred to the research workers wherever their works have been cited in the text and the body of the thesis. I further certify that I have not wilfully lifted up some other's works, para, text, data, results, etc. reported in the journals, books, magazines, reports, dissertations, thesis, etc., or available at websites and included them in this Ph.D. thesis and cited as my own work.

Date:

Place : Varanasi *(Mrs. Sunita Sharma)*

Certificate from the Supervisor/Co-supervisor

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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Co-supervisor ***Supervisor***

(Prof. R. B. Rastogi)

Head

Course Work / Comprehensive Examination Certificate

*This is to certify that **Mrs. Sunita Sharma**, a bonafide research scholar of Department of Chemistry, Indian Institute of Technology (Banaras Hindu University), Varanasi has successfully completed the course work / comprehensive examination requirement which is a part of her Ph.D. programme.*

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Place: Varanasi

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Pre Submission Seminar Completion Certificate

This is to certify that ***Mrs. Sunita Sharma****, a bonafide research scholar of Department of Chemistry, Indian Institute of Technology (Banaras Hindu University) Varanasi, has successfully completed the pre-submission seminar requirement on the topic "***Dielectric Properties of*** $Y_{2/3}Cu_3Ti_4O_{12}$ ***and Effect of Doping at its Different sites****" on dated 23-02-2016 which is a part of this Ph.D. programme.*

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Title of the Thesis: ***"Dielectric Properties of $Y_{2/3}Cu_3Ti_4O_{12}$ and Effect of Doping at its Different Sites".***

Candidate's Name: ***Mrs. Sunita Sharma***

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Contents

List of abbreviations

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PREFACE

Electronic industries are in constant search of high performance dielectric materials exhibiting temperature and frequency-stability, colossal permittivity (ε_r > 1000) and sufficiently low dielectric loss. It facilitates miniaturization of high-energy-density storage devices such as Dynamic Random Access Memory (DRAM) devices, Multi Layer Ceramic Capacitors (MLCC) and many other electronic devices in automobile and aircraft. Traditional $Pb(Zr_xTi_{1-x})O_3$ and $BaTiO_3$-based ferroelectric materials exhibit high dielectric properties. However, their dielectric properties are strongly temperature-dependent due to phase transition at Curie temperature (Tc). Furthermore, lead-based materials are eco-unfriendly and harmful to health. Hence, it is necessary to find some non-ferroelectric materials with high dielectric constant to substitute these traditional materials.

$ACu_3Ti_4O_{12}$ family of compounds, discovered in 1967 and their crystal structure well established in 1979, could be considered as a substitute. In the tear 2000, it was reported for the first time that that $CaCu_3Ti_4O_{12}$ (CCTO) ceramic exhibits giant dielectric response. CCTO has a body-centred cubic perovskite-related structure having lattice parameter a =7.391Å. It shows typically high static dielectric constant value (ε ~10^4 for bulk and 10^5 for single crystals) and moderately low dielectric loss (~ 0.10). This property remains practically independent of frequency (10^2-10^6Hz) and shows good thermal stability without any phase transition in a wide range of temperature (100-600K) well as noteworthy nonlinear characteristics. These properties make it applicable in the fields of varistor devices, especially for miniaturized components. However, compared to commercial varistor ceramics, for e.g. ZnO varistors which is widely used, the nonlinear coefficient of CCTO is too low and the dielectric loss is too high for miniaturized components. So far, the internal barrier layer capacitor (IBLC) model of Schottky-type potential barriers has been widely accepted to explain its admirable properties. Recently, the scientists have been carrying out researches to improve the performance of CCTO ceramics via tuning the microstructure, especially the grain boundary structure and its effective contribution towards the admirable response. The secondary phase addition has been established to be an effective method to control grain growth and grain boundary barrier of CCTO ceramics.

During the last decade, the studies on CCTO were focused mainly on two aspects: to optimize the dielectric properties and lower the dielectric loss of CCTO ceramics to realize practical application through doping as the first one and introducing a binary phase, using new preparation methods and so on as the second. The stoichiometry of constituents plays an important role in obtaining giant permittivity. Deviation from stoichiometry can result in the decrease of dielectric constant at lower frequencies. To discuss the effect of stoichiometry on dielectric properties, some dopants have been introduced into the CCTO structure. The B-site doping with donors like Nb^{5+} or acceptors like Fe^{3+} cations could decrease the value of the dielectric plateau due to an increase in grain boundary layer thickness, resulting in a lower grain boundary capacitance. The other aspect is to study the origin of giant dielectric properties. To explain the nature of the giant dielectric permittivity for CCTO, several interpretations have been proposed so far from both intrinsic and extrinsic viewpoints, and there still remain some controversies. The interpretations include fluctuations of lattice-distortion-induced dipoles in nanosize domains, electrode polarization effects due to different work functions of electrode and the sample, inhomogeneous conduction within the crystal due to the occurrence of defects in the grains, internal barrier layer capacitor (IBLC) effects originating from the insulating grain boundaries surrounding semiconducting grains, and intragrain insulating barrier effects. Among these, the IBLC effect has been widely used to interpret the giant dielectric constant of CCTO ceramics. The oxygen vacancies, CuO segregation and aliovalences of Ti and Cu ions were suggested to play important roles in the IBLC formation in CCTO ceramics.

In recent years, $Y_{2/3}Cu_3Ti_4O_{12}$ (YCTO) ceramics, as a member of the $ACu_3Ti_4O_{12}$ family, have been reported to exhibit a giant dielectric constant (ε_r > 1000) with a relatively low dielectric loss (0.033 at 1 kHz) and a good temperature stability. It seems that this material could be a promising candidate for commercial application in the future. Furthermore, it is quite interesting that YCTO with 1/3 vacancy at Y site represents a unique type of $CaCu_3Ti_4O_{12}$ (CCTO)-like oxides. Owing to the occurrence of 1/3 vacancy at Y site, the electrical properties of YCTO ceramics can be modulated more easily by impurity substitution. Based on the electrical neutrality, this 1/3 vacancy at Y site is suppressed gradually through the low valence ions doping. This will substantially affect the dielectric and electric behavior, rendering the study of this system more interesting. Unfortunately, till date, there are very few works concentrated on impurity substitution effects on the dielectric properties of YCTO ceramics. On the basis of the IBLC model, without the semiconducting grains there would be no high dielectric constant, and the increase of grain boundary resistance will induce an obvious decrease in the low-frequency dielectric loss. The insulating grain boundary and semiconducting grain of CCTO ceramics have been verified to be Cu-rich and Cu-deficient phase, respectively. As CCTO-like oxides, YCTO ceramics should also exhibit similar composition at grain and grain boundary. An elemental substitution could effectively modify the electric properties both in grain and at grain boundary. The lattice distortion caused by the substitution ions with larger radius may improve the formation of Cu-rich and Ti-poor grain-boundary layer which can enhance the resistance of the grain boundaries. It is anticipated that the introduction of the doping of desired ions on different Y sites in YCTO ceramics would tune the resistance of grain and grain boundary at the same time it may decrease the dielectric loss. In fact, studies on YCTO system regarding methods of processing, sintering times, sintering temperatures, doping schemes as well as nature of dopants and their stoichiometric variations and its impact on various material properties has yet to be disclosed.

In the present exploratory work an attempt has been made to synthesize undoped and a few doped samples of $Y_{2/3}Cu_3Ti_4O_{12}$ (YCTO) material by semi-wet route which is in fact auto-combustion glycine-nitrate route. In semi wet route, solution of nitrates of all ions is taken except titanium which is used in solid form as TiO_2. The calculated amount of glycine, equivalent to metal ions, was added to the solution and heated. This method facilitates the synthesis of ceramic at relatively lower temperature and short duration. The mixing process is performed in a sol state. Each constituent ion is uniformly dispersed in the resulting mixture after removing organic matter by heating in air.

The aim of the present exploratory research work is to investigate (a) crystal structure (b) microstructure, (c) elemental analysis, (d) particle size and (e) dielectric characteristic of materials prepared by the semi-wet route in the following systems:

(i) $Y_{2/3}Cu_3Ti_4O_{12}$ (YCTO)

(ii) $Y_{1/3}La_{1/3}Cu_3Ti_4O_{12}$ (YLCTO)

(iii) $Y_{2/3}Cu_{3-x}Zn_xTi_4O_{12}$ (YCZTO) (x = 0.10, 0.20, 0.30)

(iv) $Y_{2/3}Cu_3Ti_{4-x}Fe_xO_{12}$ (YCTFO) (x = 0.05, 0.10, 0.15, 0.20)

The present thesis discusses the results of investigation on the above systems and it has been divided in to six chapters

Chapter I contains a brief introduction of the subject describing technical investigations reported in the field of perovskite oxides. This includes the effect of isovalent, heterovalent and valence compensated substitutions on the dielectric properties.

Chapter II describes the experimental techniques used for preparation and characterization of these perovskite oxide ceramics. The semi-wet route used for preparation of these materials has been described with the help of a flow chart. DTA/TGA has been used to characterize the materials that exhibit a weight change due to decomposition or dehydration. Thermo-grams of the precursor powder materials carried out in static air from room temperature to 1000 °C at a heating rate of 10 °C min^{-1} are given. Powder X-ray diffraction and scanning electron microscopy have been used for study of crystal structure and microstructure of these materials respectively. Methods for density and porosity measurements have been described. Energy Dispersive X-ray spectroscopy (EDX) technique has been used for elemental analysis of the materials. Transmission Electron Microscopy (TEM) has been used for determination of particle size in the samples. Dielectric characteristics of all the samples were measured as a function of temperature (300-500 K) in the frequency range 100Hz-1MHz with the help of PSM 1735 (Newton's 4th limited U.K.) LCR Meter.

Chapter III contains the synthesis and characterization of the parent composition $Y_{2/3}Cu_3Ti_4O_{12}$ (YCTO). Pellets have been sintered at 950 °C for 12 hrs. Single-phase formation along with CuO as a minor secondary phase was confirmed by XRD. SEM micrograph exhibited the presence of bimodal grains of size ranging from 1-2 μm. The stoichiometry of synthesized samples was confirmed by EDX studies. Bright field TEM image clearly displays nano-crystalline particle which is supported by the presence of a few clear rings in the corresponding selected area electron diffraction pattern. The dielectric study of pure $Y_{2/3}Cu_3Ti_4O_{12}$ ceramic has been described in this chapter along with its rationalization with help of Impedance and modulus studies.

Chapter IV describes the microstructure and dielectric properties of the valence compensated YCTO ceramic obtained by partial substitution of lanthanum at yttrium site. A sample with composition $Y_{1/3}La_{1/3}Cu_3Ti_4O_{12}$(YLCTO) was synthesized by the semi-wet route as the ionic radius of lanthanum (1.15 Å) is very close to that of ionic radius Y^{3+} (1.04 Å). X-ray diffraction studies confirmed the single-phase formation at 950 °C for 12 h. Scanning electron microscopy showed the grain size in the range of 1-2 μm. The particle size was also established by TEM analysis. The stoichiometry of the samples is confirmed by EDX studies. With increasing La^{3+} concentration in YCTO, dielectric constant of the samples decreases. A comparative dielectric study of YCTO and YLCTO has been described in this chapter.

Chapter V discusses the synthesis and characterization of valence compensated zinc doped $Y_{2/3}Cu_{3-x}Zn_xTi_4O_{12}$ (YCZTO) with x = 0.10, 0.20, 0.30 compositions as ionic radius of Zn^{2+} (0.74 Å) is very close to that of ionic radius of Cu^{2+} (0.73 Å). Intrinsic dielectric properties of this unusual cubic perovskite ceramic was rationalised with the help of impedance and modulus spectroscopic measurements. A logical correlation of dependence of dielectric properties on microstructure of YCZTO ceramic was investigated. TG/DTA, XRD, SEM, TEM were employed to disclose its microstructural details. YCZTO ceramic exhibits high dielectric constant (**ε**~18522) at

308 K. Dielectric loss (tan δ) decreases exponentially with increases in temperature due to the thermally activated grain boundary electrical conduction. Grain and grain boundary resistance of YCZTO ceramic at room temperature was found to be 347 Ω and 1.70 MΩ, respectively. The grain boundary resistance decreases with temperature while grain resistance is almost independent of temperature.

Chapter VI focuses on the study of effect of iron doping on Ti^{4+} site in YCTO ceramic. A few samples with composition $Y_{2/3}Cu_3Ti_{4-x}Fe_xO_{12}$ (where x = 0.00, 0.05, 0.10, 0.15, 0.20) were synthesized by semi-wet route. Scanning electron micrographs shows bimodal non-uniform grain size distribution consisting of small smooth surfaced grains with some pores. Anomalous grain growth is observed in these samples. This is due to partial melting of CuO, which promotes anomalous grain growth. The stoichiometry of the samples is confirmed by EDX studies. The particle sizes were determined by TEM technique. The dielectric behaviour of these materials was systematically studied as a function of temperature and frequency. Its rationalization with the help of impedance analysis has been discussed in detail. The effects of concentration of heterovalent dopent on microstructure, dielectric properties and conduction behaviour of $Y_{2/3}Cu_3Ti_{4-x}Fe_xO_{12}$ ceramics have been studied over the frequency range 2Hz-5MHz. The impact of acceptor type of hetero-valent doping of Ti^{4+} site by Fe^{3+} on $Y_{2/3}Cu_3Ti_4O_{12}$ (YCTO) ceramic is reflected in a decrease in the grain size with a significant lowering of dielectric loss as compared with the pure YCTO ceramic. The origin of high dielectric constant in different samples of Fe^{3+}-doped YCTO ceramics along with its rationalization with the help of impedance analysis has been discussed in detail. All compositions were found to be electrically heterogeneous with semiconducting grains and insulating grain boundaries, supporting IBLC mechanism.

Chapter VII describes the key findings as summary of the present work and suggestions for the future Scope.

A consolidated list of books and journals consulted during the present study has been given at the end of the thesis under the heading ‘References’.

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I would like to thank from the bottom of my heart to my Co-Supervisor ***Prof. M. M. Singh,*** *Department of Chemistry, IIT, (B.H.U.) for his keen interest in research and guiding me in a very systematic way. Also, I extend my heartfelt thanks to him for his noble behavior towards me and also towards other students. This thesis wouldn't have taken its present shape without his co-operation and support.*

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Date:

Place: Varanasi *(Mrs. Sunita Sharma)*