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It is certified that the work contained in the thesis titled *"**Studies on Magnetic and Dielectric Properties of Mn-doped $CaCu_3Ti_4O_{12}$ synthesized through semi-wet route**"* by *"**Santosh Pandey**"* has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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8/3/2022

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DECLARATION BY THE CANDIDATE

I, *"**Santosh Pandey**"*, certify that the work embodied in this thesis is my own bona fide work and carried out by me under the supervision of *"**Prof. K. D. Mandal**"* from *"2017" to "2022"*, at the *"Department of Chemistry"*, Indian Institute of Technology (Banaras Hindu University),Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not will fully copied any other's work, paragraphs, text, data, results, *etc*., reported in journals, books, magazines, reports dissertations, theses, *etc*., or available at websites and have not included them in this thesis and have not cited as my own work.

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It is certified that the above statement made by the student is correct to the best of my knowledge.

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Dedicated

To

My Beloved family

It's my great pleasure to thank my *supervisor* ***Prof. K. D. Mandal***, Department of Chemistry, Indian Institute of Technology, (B.H.U) for allowing me to join his research group, and for providing the knowledge base for my future. *Prof. Mandal* is an excellent advisor and good friend. He was always available for discussions and regularly took the time to answer my many questions. As a supervisor, he was very active in my continuing education and scientific growth, allowing me to explore different aspects of materials science independently and with guidance. In addition, he continually provided opportunities for collaborations with other scientists, which allowed me to learn more about related fields.

My sincere gratitude is also expressed to **Prof. Y.C. Sharma,** Head, Department of Chemistry, Indian Institute of Technology, (B.H.U) Varanasi, for his fruitful suggestions and providing research facilities available in the Department.

It's my great pleasure to thanks my RPEC members **Prof. D.Tiwary,** Department of Chemistry, Indian Institute of Technology, (B.H.U) and Prof. **V. L. Yadav,** Department of chemical engineering, Indian Institute of Technology, (B.H.U) for helping me and giving valuable suggestions throughout my Ph.D program.

I also want to acknowledge the members of central instrumentation facility center (CIFC) and office staff of the chemistry department for their help and support.

I would also like to thank to my lab mates Vinod Kumar and Manish Kumar Verma, shruti singh, Vishnu shankar rai and Dinesh parajapati for their active support.

I am very much thankful and grateful to all faculty members of the Department for their encouragement and support.

I take great pleasure in thanking my friend Manish kr. Tirpathi, Suresh kumar Pandey, Himanshu kr.singh. Department of Chemistry BHU for sharing with me all the happiness and difficulties throughout my research work.

Parents are the God on earth and I am very lucky to have very caring and loving parents Mr. Swaminath Pandey, and Mrs. Kesh kumari I would like to put in words my gratitude to my family members for making my life happy with their constant love.

I wish to express my special thanks to the funding agency, IIT(BHU) for providing the financial support to carry out this work.

Last but not least, I thank almighty God for providing me strength and courage to do this work.

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E	Permittivity or dielectric constant
ε^*	Complex Quantity of dielectric constant
ε’	real components of dielectric constant
ε’’	Imaginary component of dielectric constant
i	Imaginary number
ε_0	Permittivity of free space
ε_r	relative dielectric constant
C	Capacitance
F	Farad
tan δ	tangent loss
σ	conductivity
f	frequency
λ	Wavelength
θ	Angle theta
°C	Degree centigrade
K	Kelvin
k_B	Boltzmann constant
T_B	Blocking temperature
X	Magnetic susceptibility
C	Curie constant
M	Magnetization
H	Magnetic field
Oe	Oersted
P	Density
B	Induced magnetic field
E	Electric field

P	Net polarization
$P_{electronic}$	Electronic polarization
P_{ionic}	Ionic polarization
$P_{molecular}$	Molecular polarization
$P_{interfacial}$	Interfacial polarization
Hz	hertz
ω	angular frequency
τ	Relaxation time
t	tolerance factor
Å	angstrom
R	Resistance
C	Capacitance
R_b	Resistance of bulk
C_b	Capacitance of bulk
R_{gb}	Resistance of grain boundary
C_{gb}	Capacitance of grain boundary
eV	electron Volt

A capacitor material which has high dielectric constant and low dielectric loss is an interesting topic in materials science. It may be used as multilayer capacitor (MLCC), dynamic random access memory (DRAMs), microwave devices, electronic devices in automobiles andaircrafts.$ACu_3Ti_4O_{12}$ (A = Ca, Bi, Sr) type oxides had complex perovskite structure and discovered in 1967 by Subramanian *et al*. It produces a high dielectric constant ($\varepsilon_r \sim 10^4$) and nearly constant in the temperature range of 100–600 K. which has led to many important applications. The high dielectric loss of CCTO ceramics (tan $\delta > 0.05$ at 1 kHz) is still the most serious problem for applications requiring capacitive components. Presently we use simple perovskite $BaTiO_3$, which are not environmentally friendly as capacitor materials. The problem with $BaTiO_3$ is that it is quite unstable at higher and shows phase transition. Therefore, it is not suitable for use at high temperature. Therefore, Development of excellent dielectric materials with good stability over wide temperature and frequency ranges are highly desired.

The modern age technology needs for the development of electrical composite, that properties are not available in individual single component materials. The required combination properties are possible to tailor composite by combining two or more components. Composites perovskite play a very important role in various areas of chemistry, physics, biology and materials science because of their interesting properties. When two or more perovskites are mixed together either by physical or by chemical methods to fabricate composite, a novel set of physical and chemical properties may be obtained that would be completely different from that of the individual constituents.

Electrical and dielectric properties of the composite are also very important. Which leads to data storage, tunnel junction, and spin valves. The composite has also been increasing interest in flexible, high dielectric constant and a polymer for use in

high-density energy storage and capacitor applications. With the smaller sizes of nanoparticle less than 100 nm surfaces to volume ratio increases resulting in the number of atoms on the surface of nanocrystals, therefore variation in electrical properties with change in structure in the nanoscale region is observed in comparison to the bulk material. The electrical and dielectric properties of nanoparticle are affected by particle size, morphology, and chemical composition.

In the present work synthesis of composite perovskite with different composition using semi-wet route. All the synthesized composites were characterized by various physicochemical techniques to study the crystal structure, particle size and shape whereas electrical and dielectric, properties of materials were studied in detail. And it also studied the effect of sintering duration of these composite.

The present work aims to investigate (a) crystal structure (b) microstructure (c) elemental analysis (d) particle size (e) electrical and dielectric behavior of the following compound prepared by semi-wet route.

1. $CaCu_3Ti_3MnO_{12}$

2. $CaCu_3Ti_{3.5}Mn_{0.5}O_{12}$

3. $CaCu_3Ti_{3.75}Mn_{0.25}O_{12}$

4. $CaCu_3Ti_{3.5}W_{0.5}O_{12}$

5. $CaCu_3Ti_{3.5}Nb_{0.5}O_{12}$

Chapter I This chapter contains a brief introduction of the subject describing briefly the technical investigations reported in the field of perovskite oxides and composite materials. Polarization also describes which related to dielectric properties as well as the

frequency of perovskite. It contains basic knowledge of Impedance spectroscopy which separates the contributions of the grains and grain boundaries, and electrode specimen interface observed RC elements of the composite. This includes the effect of isovalent, heterovalent and valence compensated substitutions on the electrical and dielectric properties.

Chapter II This chapter describes the details of experimental procedure used for the synthesis, characterization, and application of composite materials. The crystalline phases of composite sintered samples were identified by using the X-ray diffraction analysis (Rigaku, miniflex-600, Japan) employing Cu-kα radiation.Scanning Electron Microscopy gives an idea of formation of the microstructure of these materials. Transmission Electron Microscopy (TEM) has been used for determination of their size and shape of the particle. Atomic force microscopy analyzed the surface morphology. Electrical and dielectric properties which are characteristic of all the composite were measured as a function of temperature (300-500 K) in the frequency range 100Hz-5 MHz with the help of PSM 1735 (NumetriQ 4th U.K Limited) LCR Meter.

Chapter III The detailed synthesis, characterization and application of the $CaCu_3Ti_4MnO_{12}$ (CCTMO) perovskite were described in this chapter. CCTMO was synthesized using a semi-wet method through sintering at 1223 K for 8 h. The structural and microstructural details were studied by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) techniques. XRD analysis confirmed the existence of $CaCu_3Ti_4O_{12}$ (CCTO) as the primary phases along with TiO_2 as the minor aspects. The average grain sizes obtained by SEM analysis were found to be around 1.46 μm sintering for 8 h, respectively. TEM analysis showed the particle size in the range of 43.76 ± 10 nm. The surface morphology was analyzed by

atomic force microscopy (AFM). The sample sintered for 8 h exhibited very high dielectric constant (ε_r ~ 100) at 1 kHz and 303 K. The presence of semiconducting grains with the insulating grain boundaries significantly attributes to such a high dielectric constant value, supporting the internal barrier layer capacitance (IBLC) mechanism operative in CCTMO perovskite.

Chapter IV In this chapter, the $CaCu_3Ti_{(4-x)}Mn_xO_{12}$ (CCTMO) was synthesized by a semi-wet method at 1223 K for 8 h. X-ray diffraction (XRD) analysis confirms the presence of CCTMO and $CaCu_3Ti_4O_{12}$ both phases in the perovskite ceramic. Transmission electron microscope (TEM) analysis of the composite demonstrates the formation of nanoparticles with average particle size 23 ± 10 nm, 31 ± 10 nm and 24 ± 10 nm at a different doping concentration of Mn (x= 0.25, 0.50 and 1.00) in $CaCu_3Ti_{4-x}Mn_xO_{12}$ ceramic.. The surface morphology of the composite sintered at 1223 K for 8 h obtained by SEM analysis indicate the formation of large and small grains with bimodal structure. The average and root mean square roughness is found to be 72 nm and 90 nm, respectively by Atomic force microscopy studies of the ceramic. The dielectric constant of CCTMO ceramic is found to be 150 at 100 Hz and 500 K respectively. The presence of semiconducting grains and insulating grain boundaries in the composite supporting the internal barrier layer capacitance (IBLC) mechanism operative in Mn-doped CCTO type of perovskites of different composition.

Chapter V The synthesis, characterization and application of the $CaCu_3Ti_{3.5}Mn_{0.5}O_{12}$ ceramic were discussed in this chapter. A nano-composite ceramic with the chemical composition $CaCu_3Ti_{3.5}Mn_{0.5}O_{12}$ was synthesized by a semi-wet method at CCTMO sintered at 950 ºC, 1050 ºC, and 1100 ºC, respectively for 8 h. X-ray diffraction analysis confirms the presence of CCTO and TiO_2 phases in the composite ceramic.

Transmission electron microscope analysis of the formation of nano-particles (98.49 ± 10 nm, 92.95 ± 10 nm and 145.50 ± 10 nm at 950 ºC, 1050 ºC, and 1100 ºC, respectively. Further, scanning electron microscope (SEM) images show that the morphology consists of large and small grains (1.0–10 μm) with a bimodal distribution. The surface morphology of composite was studied by atomic force microscope using tapping mode of measurement also substantiates the results obtained by SEM analysis. The sample sintered for 8 h exhibits very high dielectric constant ($\varepsilon_r \approx 130$) at 100 Hz and room temperature. The presence of semiconducting grains with insulating grain boundaries significantly attributes to such a high dielectric constant value, supporting the internal barrier layer capacitance mechanism operative in Mn-doped CCTO of different composition.

Chapter VI the CCTMO, CCTWO and CCTNO perovskites were successfully synthesized by semi-wet route. Powder X-Ray Diffraction confirms the formation of CCTO as main phase along with minor TiO_2 phase in CCTMO, CCTWO and CCTNO at sintered at 950ºC, 1050ºC, and 1100ºC, for 8 h. Particle size observed by TEM is 44 nm, 101 nm, and 51 nm, respectively. Atomic force microscopy shows statistically significant changes in the surface roughness. The nano-composite exhibits improvement in dielectric loss ($\tan \delta \approx 0.9$) at 1 kHz. The low-frequency performance of the doped CCTO was estimated by measuring the frequency dispersion of the dielectric constant (ε') and dielectric loss ($\tan \delta$).