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It is certified that the work contained in the thesis titled "**Synthesis and Characterization of Mn-doped High Dielectric Constant Material Calcium Copper Titanate Ceramics**" by "**Vinod Kumar**" has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive examination, Candidacy and SOTA for the award of Ph.D. degree.

13/9/2021

Prof. K. D. Mandal
(Supervisor)
Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University)
Varanasi

DECLARATION BY THE CANDIDATE

I, Vinod Kumar , certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of Prof. K. D. Mandal from 2016 to 2021, 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.

13/9/2021

Prof. K. D. Mandal
(Supervisor)
Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University)
Varanasi

13.9.2021

Prof. Y.C. Sharma
(Head)
Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University)
Varanasi

विभागाध्यक्ष/HEAD
रसायन विज्ञान विभाग
Department of Chemistry
भारतीय प्रौद्योगिकी संस्थान (का.हि.वि.वि)
Indian Institute of Technology (B.H.U.)
वाराणसी-२२१००५/Varanasi-221005

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TO

MY BELOVED

FAMILY

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Place: Varanasi

Date: 09/09/2021 (Mr.Vinod Kumar)

LIST OF SYMBOLS/ ABBREVIATION

t	Tolerance factor
E	Electric field
ε_0	Permittivity of free space
P	Electrical dipole moment
χ_e	Dielectric susceptibility
n	Unitless constant
ε_r	Relative permittivity
E_{loc}	Local field
P_{mol}	Moment
α'	Polarizability
N	Molecules per unit volume
k	Relative dielectric constant
ε^*	Complex Quantity of dielectric constant
ε'	Real components of dielectric constant
ε''	Imaginary component of dielectric constant
i	Imaginary number
D_f	Dissipation factor
tan δ	Tangent loss
W	Energy loss
ε_r	Relative dielectric constant
C	Capacitance
F	Farad
σ	Conductivity
f	Frequency

LIST OF SYMBOLS/ ABBREVIATION

$P_{electronic}$	Electronic polarization
P_{ionic}	Ionic polarization
$P_{molecular}$	Molecular polarization
$P_{interfacial}$	Interfacial polarization
Hz	Hertz
λ	Wavelength
θ	Angle theta
°C	Degree centigrade
K	Kelvin
k_B	Boltzmann constant
T_B	Blocking temperature
χ	Magnetic susceptibility
C	Curie constant
M	Magnetization
H	Magnetic field
Oe	Oersted
B	Magnetic flux density
H_r	Remanance
P	Net polarization
ω	Angular frequency
τ	Relaxation time
Å	Angstrom
R	Resistance
C	Capacitance
Z'	Real impedance

LIST OF SYMBOLS/ ABBREVIATION

Z”	Imaginary impedance
M'	Real modulus
M”	Imaginary modulus
m	Magnetic moment
H_c	Coercivity
T_G	Griffith temperature

The general formula of simple perovskite is ABO_3. Perovskites are widely investigated due to their excellent piezoelectric, dielectric, optoelectronic, and electrical properties. Perovskite properties can be modified by doping or substitution either A site or B site or simultaneous. Such substitutions may be represented as $A_{1-x}A'_xBO_3$, $AB_{1-x}B'_xO_3$, and $A_{1-x}A'_xB_{1-x}B'_xO_3$ respectively. These substitutions may be heterovalent, isovalent, or valence compensated perovskite oxide. During the substitution or doing valency, radius, and coordination number are very important parameters to determine the site. The ceramic materials have a high dielectric constant and good thermal stability. These materials are very useful in memory capacitors, devices, humidity sensors, and gas sensors.

It is pointed out that the Calcium Copper Titanate, $CaCu_3Ti_4O_{12}$ (CCTO) ceramic displaying high dielectric constant Subramanian *et. al.* reported the first time. The excellent properties of this ceramic, very dielectric constant ($\sim 10^4$) which is independent of temperature (100 - 600 K) and frequency (10^2 - 10^6 Hz), and no phase transition was observed. This ceramic phase independent of temperature means no phase changes with the temperature. Several studies have been done on CCTO family members since the last few years $ACu_3Ti_4O_{12}$ (A= Ca, $Bi_{2/3}$, $Y_{2/3}$, $Gd_{2/3}$, $La_{2/3}$, $Na_{1/2}$). Ceramic materials are widely used in micro multilayer capacitors (MLCC), electronic devices such as dynamic random access memory (DRAM), microwave devices. Material with high dielectric constant and low dielectric loss is very important in capacitor application. It is pointed out that being the huge dielectric constant slightly high dielectric loss of CCTO ceramic. For reducing tangent loss of ceramic material scientists working by doping or substituting elements to make ideal capacitor materials.

$CaCu_3Mn_4O_{12}$ (CCMO) is a member of the $CaCu_3Ti_4O_{12}$ (CCTO) family that display similar high dielectric as well as similar structure. The dielectric study on

CCMO was not reported on this system. Many research groups have been working on this system. Manganese doped or substituted CCTO ceramic shows a very low tangent loss as well as a high dielectric constant. This material is very useful in microelectronic devices such as non-volatile random access memories.

The non –volatile random access memories application is mainly based on the existence of two opposite polarization states. In the practice, materials have to satisfy several requirements e.g., a low coercive field, a low processing temperature, and a large remnant polarization which is compatible with Si-based IC technology.

Particle size, morphology, and composition of material directly affected on magnetic properties of the ceramic. The material which shows magnetic properties are very useful in several applications has some special properties such as high electrical resistivity, low loss, and magnetic coupling. Many research groups have to work on magnetic materials by doping or substitution of metal in CCTO are simple perovskite. When two or more ceramics of different compositions are mixed, the properties of the materials become great the called composite material. The application of composite material like glass fiber, automobile bodies to particulate composites for aerospace and other applications Most of the composite materials contain fiber of one material tightly bound into another material called a matrix. The matrixes bind the fiber together a bit like on adhesive and make them more resistant to external damage, whereas the fiber makes the matrix stiffer, stronger, and helps it resist cracks.

Presently, many research groups have been working on polymers based and metal composites but perovskite oxide Manganese (Mn) doped or substituted CCTO ceramic very few studied available which excellent high dielectric constant as well as very low tangent loss. When Titanium of CCTO ceramic completely replaced with Mn shows unusual Griffith’s phase behavior .

The aim of the present work is to be synthesize CCTO, CCMTO, CCTMO, CCMTMO, and some of their composites and described the crystal structure, microstructure, elemental analysis, Oxidation state, surface roughness, dielectric and magnetic behavior of the following systems:

- $CaCu_3Ti_4O_{12}$ (CCTO)
- $CaCu_3Mn_4O_{12}$ (CCMO)
- $CaMn_1Cu_2Ti_4O_{12}$ (CCMTO)
- $CaCu_{2.9}Mn_{0.1}Ti_{3.9}Mn_{0.1}O_{12}$ (CCMTMO)
- $CaCu_3Ti_{3.9}Mn_{0.1}O_{12}$ (CCTMO)

A brief description of the research work presented in the thesis divided into seven chapters have been given as follows:

Chapter I contains a general introduction of complex perovskite, ceramic and composite materials. Ceramic and composite materials have received great interest in ferroelectrics, ionic conductors, superconductors, multiferroic, and magneto resistant materials result from their mutual interaction. The details of complex perovskite and composite materials considered in the current study and the purpose of the thesis is mentioned in this chapter.

Chapter II described the experimental procedure used for the preparation and characterization of the perovskite oxides and its composites. The semi-wet route and the chemical route was used for the preparation of materials. X-ray diffraction and transmission electron microscope (TEM) have been studied for the determination of crystalline size and particle size respectively. Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) analysis have been used for microstructural studies and elemental analysis of materials respectively. The oxidation state of the ceramics was to be examined by X-ray photoelectron spectroscopy, Study of

surface roughness and the maximum peak height of the materials have been determined by atomic force microscopy (AFM). Magnetic properties of the materials were measured by a superconducting quantum interference device with the temperature and applied field. Dielectric properties of materials were measured on a LCR meter with the variation of temperature and frequency.

Chapter III contains synthesis, characterization, and application of $CaCu_3Mn_4O_{12}$ (CCMO) ceramic synthesized through chemical route. The phase formation was confirmed by the X-ray diffraction pattern. Thermogravimetric (TGA), FT-IR, SEM, TEM, EDX, and XPS analysis were performed for investigation of the thermal behavior, phase identification, microstructural analysis, elemental analysis and oxidation state of the CCMO ceramic respectively. FT-IR spectra confirmed the existence of MnO_6 octahedral in body-centered cubic (BCC) complex perovskite oxide that resembles the $CaCu_3Ti_4O_{12}$ structure. The average particle size was observed by TEMin the range between 100 to 200 nm. AFM shows the average roughness of the surface was found to be in the range of 30 ±5 nm. XPS and EDX studies confirmed the purity and oxidation state of the CCMO ceramic.The synthesized material shows unique Griffith's phase which arises due to disorded of magnetic succeptibiliy .The dielectric constant and dielectric loss of the ceramic was found to to be 330 and 1.2 at 100 Hz and at 313 K ,respectively.

Chapter IV described the synthesis, characterization of manganese (Mn) doping in $CaCu_3Ti_4O_{12}$(CCTO) ceramic (simultaneously doping copper and titanium site) with the help of X-ray Photoelectron Spectroscopy (XPS), High Resolution - Scanning Electron Microscopy (HR-SEM), High Resolution- Transmission Electron Microscopy(HR-TEM) and Raman spectra. The doping of manganese in CCTO ceramic, the dielectric constant was largely decreased due to Mn existing in variable oxidation state like Mn^{+2},

$Mn^{+3}$and Mn^{+4} . Due to this reason the grains (g) and grain boundaries (g_b) slightly behave conducting in nature. Raman spectra show the existence of copper oxide and manganese oxide presence in the grain and grain boundary of $CaCu_{2.9}Mn_{0.1}Ti_{3.9}Mn_{0.1}O_{12}$ (CCMTMO) ceramic. The novelty of Mn-doped CCTO ceramic is that the tangent loss also decreases largely as compared to CCTO ceramic. The dielectric constant and tangent loss of CCMTMO ceramic 375 and 0.3 at 10 Hz temperature, respectively. CCMTMO ceramic is very useful for microelectronic devices. The polycrystalline nature of CCMTMO was to be studied with the help of X-ray diffraction(XRD), HR-SEM, HR-TEM, and Magnetic Property Measurement System (MPMS, Quantum Design). The elemental analysis and oxidation state were confirmed by (Energy Diffraction X-ray) EDX and XPS respectively. The elements were found to be their required stoichiometric and oxidation state. The impedance and modulus spectroscopy also studied.

Chapter V describe the syhthesis of undoped and Mn-doped CCTO ceramics . The synthesized ceramics were characterized by TGA, FT-IR, XRD, HR-SEM, HR-TEM MPMS, and dielectric studied. The thermal behavior of CCTO and CCTMO ceramic were to be studied by Thermogravimetric analysis (TGA). The metal-oxygen bond was to be analyzed by Fourier Transform- Infrared spectroscopy (FT-IR). The phase formation of CCTO and CCTMO ceramic were to be analyzed by the X-ray diffraction pattern. In the CCTO ceramic, there is a minor phase TiO_2 peak also recorded. The Microstructural studies of CCTO and CCTMO were to be analyzed by HR-SEM and HR-TEM. The metal ions were found to be their required stoichiometric ratio, examined by EDX. The magnetic properties were to be examined by DC SQUID magnetization. The maximum dielectric constant of CCTMO ceramic was found to be 5×10^2 at 308 K and the minimum tangent was to be recorded at 0.8 at 100 Hz frequency.

Chapter VI described the synthesis, characterization of the effect of manganese doped and non-doped CCTO ceramic ($CaCu_{3-x}Mn_xTi_4O_{12}$, x = 0, 1) synthesized through semi-wet route. The phase formation of both ceramic were confirmed by the XRD pattern. The Microstructural studies (CCTO and CCMTO) were performed through HR-SEM, TEM, and AFM. Both the sample were characterized by dielectric properties, cyclic voltammetry and Electrochemical Impedance spectroscopy. The dielectric properties (ε') were observed to be $\varepsilon' \sim 10^4$ and 5×10^3 over the wide range of frequency 10 Hz to 100 kHz of CCTO and CCMTO ceramic respectively. The tangent loss ($\tan\delta$ =0.75) had observed for CCMTO ceramic which is less than that observed for CCTO ceramic ($\tan\delta$ = 3.2). The high value of the dielectric constant of both CCTO and CCMTO ceramic may be attributed to the internal barrier layer capacitance (IBLC) mechanism of semiconducting grains with insulating grain boundaries. The oxidation state of the elements was confirmed by X-ray photoelectron spectroscopy.