

CERTIFICATE

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.

Date: 13/09/2021

Place: Varanasi

Vinod Kumar.
(Mr. Vinod Kumar)

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: Synthesis and Characterization of Mn-doped High Dielectric Constant
Material Calcium Copper Titanate Ceramics.

Name of the Student: Mr. Vinod Kumar

Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the abovethesis submitted for the award of the "Doctor of Philosophy".

Date: 13/09/2021

Place: Varanasi

Vinod Kumar.
Signature of the Student

(Mr. Vinod Kumar)

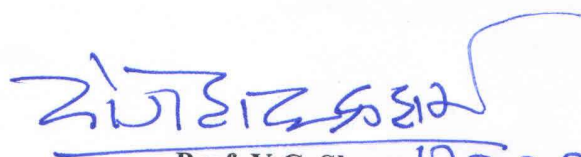
Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for the author's personal use provided that the source and the Institute's copyright notice are indicated.

CERTIFICATE BY THE SUPERVISOR(S)

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


13.9.221

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.)
Indian Institute of Technology (B.H.U.)
वाराणसी-221005/Varanasi-221005



**DEDICATED
TO
MY BELOVED
FAMILY**

ACKNOWLEDGMENTS

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. K. D. 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 her 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) Varanasi and **Dr. Shail Upadhyaya** Department of Physics, Indian Institute of Technology, (B.H.U) for giving valuable suggestions throughout my Ph.D. program.

I also want to acknowledge the In-charge and members of the central instrumentation facility center (CIFIC) and office staff of the Chemistry Department for their help and support, I also thankful to Bhabha Atomic Research Centre (BARC) Mumbai ,Indian Institute of Technology Bombay ,Banaras Hindu University (BHU) Varanasi .

My special thank goes to my senior and good friend **Dr. Laxman Singh**, **Dr. Shiva Sundar Yadava** Department of Chemistry, University of Ulsan, South Korea, **Dr. Sunita Sharma**, **Mr. Arun Kumar**, **Mr. Ajay Kumar**, **Mr. Raj Bali**, **Late Surya Bhan Shen** and **Miss Shashikala Jaiswar**, **Mr. Pradeep Kumar Sharma** , **Late Ram**

ACKNOWLEDGMENTS

Charan (PCS) , Dr. Ram Milan for useful discussions and help throughout my research. I would also like to thank to my lab mates **Dr. Pooja gautam , Mr. Santosh Pandey, Miss Shruti Singh** and **Mr. Manish Kumar Verma, Mr. Vishnu Shankar Rai, Mr. Dinesh Prajapati** for their active support.

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

I heartily thank my best friends **Mr. Nitesh Singh Malan, Mr. Rahul Kumar, Mr. Shashi Kant Verma, Dr. Bharat Kumar, Mr. Ashish Raina (MNIT Allahabad), Miss Priyanka Chaudhary (BBAU Lucknow), Mr. Praveen Kumar Diwakar, Ms. Monika Saroj** for encouraging me to get enrolled for this degree.

Parents are God on earth and I am very lucky to have very caring and loving parents **Shri Ram Bharat** and **Smt. Ram Dulari**. I would like to put in words my gratitude to my family members and special thanks to my siblings **Mr. Neeraj Kumar, Mr. Nagendra Kumar, Ms. Pinky Devi, Ms. Rinki Devi, Mr. Santosh Kumar** for making my life happy with their constant love and moral supports.

I wish to express my special thanks to IIT (BHU) for providing 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.

Place: Varanasi

Date: 09/09/2021

(Mr. Vinod Kumar)

Content	Page No.
Title of Thesis	i
Certificate	ii
Declaration by the Candidate	iii
Certificate by the Supervisor(s)	iv
Copyright Transfer Certificate	v
Dedication	vi
Acknowledgment	vii-viii
Contents	ix-xiv
List of Figures	xv-xviii
List of symbols/ Abbreviation	xix-xxi
Preface	xxii-xxvii
CHAPTER – 1	1-49
Introduction	
1.1History of Perovskite	1
1.2 Classification of Perovskite	3
(a) Calcium Titanate CaTiO_3	5
(b) Barium Titanate (BaTiO_3)	5

(c) SrTiO_3	6
1.3. APPLICATIONS OF PEROVSKITE OXIDES	6-8
1.4. Complex Perovskite	10
1.3. Ceramic Materials	11
1.4. Composite Material	12
1.5. Capacitors	13
1.7. Dielectric Materials	14
1.8. Electronic polarization	16
1.9. Orientation polarization	16
1.10. Space charge polarization	17
1.11. Atomic or ionic polarization	17
1.12. Dielectric Constant	18
1.13. Dielectric loss	19
1.14. Impedance	20
1.15. Magnetic Properties	23
1.15.1. Origine of magnetism	24
1.15.2. Types of Magnetic Materials	27
(I)Paramagnets	27

(II) Diamagnets	29
(III) Ferromagnets	30
(IV) Anti-ferromagnets	31
(V) Ferrimagnetism	32
(VI) Griffith's Phase (T_G)	32
(VII) Super-paramagnets	34
1.15.3.Hysteresis loop	35
1.15.4. Aim of the present study	38
References of chapter 1	40-49
CHAPTER – 2	50-62
Experimental Procedure	
2.1. Experiment	50
2.2. Synthesis of Materials	51
(a) Semi wet Route	51
(b) Chemical method	51
2.3. Calcination Process	51

2.4. Sintering Process	51-53
2.5. X-Ray diffraction Pattern	53-55
2.6. FTIR spectroscopy	55
2.7. Scanning Electron Microscopy (SEM) Analysis	55
2.8. Energy Dispersive X-ray Analysis (EDX)	56
2.9. Transmission Electron Microscopy (TEM) Analysis	57
2.10. X-ray Photoelectron Spectroscopy (XPS)	58
2.11. Raman spectroscopy	59
2.12. Atomic Force Microscopy (AFM) Analysis	60
2.13. Superconducting quantum interference device (SQUID)	60
2.14. Electric and Dielectric Measurement:	60-62
CHAPTER – 3	63-87
Studies on $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ Ceramic	
3.1. Introduction	63
3.2. Experimental	64
3.3. Results and discussion	64
3.3.1 Microstructural studies	70
3.3.2 Magnetic measurements	76
3.3.3. Dielectric studies	80
3.4. Conclusions	82
References	82-87

CHAPTER – 4	88-110
Studies on $\text{CaCu}_{2.9}\text{Mn}_{0.1}\text{Ti}_{3.9}\text{Mn}_{0.1}\text{O}_{12}$ Ceramic	
4.1. Introduction	88
4.2. Experimental	90
4.3. Results and discussion	91
4.3.1. Microstructural studies	95
4.3.2. Magnetic studies	100
4.3.3. Dielectric studies	102
4.4. Conclusions	104
4.5. References	106-110
CHAPTER – 5	111-126
Studies on $\text{CaCu}_3\text{Ti}_3\text{O}_{12}$ and $\text{CaCu}_3\text{Ti}_{3.9}\text{Mn}_{0.1}\text{O}_{12}$ ceramics	
5.1. Introduction	111
5.2. Experimental	112
5.3. Results and discussion	113
5.3.1. Microstructural studies	117
5.3.2. Magnetic properties	119
5.3.3. Dielectric behavior	120
5.4. Conclusions	122
5.5. References	124-126

CHAPTER – 6	127-149
Studies on $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and $\text{CaCu}_2\text{Mn}_1\text{Ti}_4\text{O}_{12}$ ceramics	
6.1. Introduction	127
6.2. Experimental	129
6.3. Results and discussion	130
6.3.1. Microstructural studies	131
6.3.2. Dielectric behavior	141
6.4. Conclusions	145
References	146-149
List of Publication	150-151

	Page No.
Figure 1.1. Classification of Perovskite.	1
Figure 1.2. The structure of complex Perovskite.	3
Figure 1.3. Structure of dielectric capacitor.	9
Figure 1.4. Shows parallel plate capacitors in circuit, including the alignment of charges in the dielectric material [Mark Howard (2015)] .	13
Figure 1.5. Depict the polarized and nonpolarized plates of an applied electric field (Saint Jude (2012)).	14
Figure 1.6. Flow chart for the origin of magnetism in the materials.	24
Figure 1.7. Shows the Paramagnetic nature of the material in the absence of applied magnetic field and in the presence of the magnetic field.	27
Figure 1.8. Paramagnetic structure of the materials.	28
Figure 1.9. Displays the diamagnetic materials disperse the line of force a magnetic field.	29
Figure 1.10. Diamagnetic structure .	30
Figure 1.11. Ferromagnetism non-magnetized material and Magnetized material with the corresponding magnetic field .	31
Figure 1.12. Anti-ferromagnetic structure	31
Figure 1.13. Ferromagnetism structure	32
Figure 1.14. Griffith's phase.	33
Figure 1.15. M-H hysteresis loop	35
Figure 1.16. Hysteresis loop or B-H curve	36
Figure 1.17. Applications of magnetic materials	37
Figure 2.1. Flow chart for the synthesis of complex perovskite by the semi-wet route.	53
Figure 2.2. shows the basic concept of X-ray diffraction pattern.	54
Figure 2.3. Powder X-ray diffract meter, Rigaku Miniflex600 (Japan).	54
Figure 2.4. Scanning Electron Microscope (ZEISS, model EVO-18 Research) used for microstructure of the surface of the ceramics.	56
Figure 2.5. Transmission Electron Microscope (TEM, FEI TECANI G ² 20 TWIN, USA) used to determine particle structure.	58
Figure 2.6. The basic principle of Raman spectroscopy	59
Figure 2.7. LCR meter (PSM 1735, Newton 4th Ltd, U.K.) used for dielectric properties measurement.	61

Figure 3.1. shows TGA graph of $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ as- prepared powder.	66
Figure 3.2. FTIR spectra of CCMO calcined powder at 600 °C for 6 h and sintered at 800 °C for 6 h different temperature.	67
Figure 3.3. XRD pattern for $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ (CCMO) calcined at 600°C and sintered at 800°C 6 h respectively.	68
Figure 3.4. Raman spectra of $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ Perovskite oxides sintered at 800°C for 6 h.	69
Figure 3.5.(a) SEM micrographs of calcined at 600°C for 6 h (b) SEM micrographs of sintered at 800°C 6 h showing the needle-like structure and (c) shows the elemental analysis of CCMO ceramic.	72
Figure 3.6. (a) Shows particle size of CCMO, (b) Shows cubical structure of CCMO, (c) Shows the histogram plot Of CCMO particle size and (d) Shows SEAD pattern of CCMO ceramic.	73
Figure 3.7. (a) AFM images of CCMO Ceramic sintered at 800°C for 6 h two-dimensional image showing grains and grain boundaries (b) Three-dimensional image of surface roughness of CCMO (c) Histogram of three-dimensional particle roughness.	74
Figure 3.8 (a) XPS graph of Calcium oxidation state peak recorded at 347.3 eV and 350.7 eV.	76
(b) Shows the Copper oxidation state peak recorded at 934.54 eV and 954.23 eV.	
(c) Shows the Manganese binding energy peak recorded at 641.4 eV and 652.4eV.	
(d) Shows the Oxygen binding energy peak recorded at 529.7 and 531.6 eV.	
Figure 3.9. (a) Temperature dependence of ZFC and FC magnetization plot, top insert indicates dM/dT vs T (b) depicts the M-H hysteresis loop recorded at 5 and 300 k. (C) Shows inverse magnetic susceptibility $1/\chi$ (T) for CCMO measured in the range of 0 to 300 K. The onset temperature T_G , where $1/\chi$ (T) deviates from the linear temperature dependence (solid green line) are indicated by the arrows, showing the signature of Griffith's Phase behavior.	80
Figure 3.10. (a) and (b) display dielectric constant, the tangent loss against	82

frequencies of CCMO ceramic, (c) and (d) tangent loss against temperature at few selected frequencies.

Figure 4.1. TGA plot of dry powder ($\text{CaCu}_{2.90}\text{Mn}_{0.10}\text{Ti}_{3.90}\text{Mn}_{0.10}\text{O}_{12}$ (CCMTMO) as-prepared powder.	92
Figure 4.2. FT-IR spectra of CCMTMO ceramic sintered 900°C for 12 h.	92
Figure 4.3. displays the XRD patterns of the sintered CCMTMO ceramic sintered at 900°C for 12 h.	94
Figure 4.4. displays the Raman shift of CCMTMO ceramic sintered at 900°C for 12 h.	95
Figure 4.5. (a) displays the morphology and microstructure of sintered CCMTMO ceramic and (b) displays Energy Disperse X-ray (EDX) .	96
Figure 4.6. (a) displays the HR-TEM image of sintered CCMTMO ceramic (b) displays the SEAD pattern.	97
Figure 4.7. (a) to (e) display the XPS spectrum of Ca, Cu, Mn, Ti and oxygen respectively.	99
Figure 4.8. (a) displays the magnetization versus magnetic field (b) magnetization versus temperature CCMTMO.	101
Figure 4.9. show (a) and (b) the dielectric constant of CCMTMO ceramic versus temperature and frequency, respectively. (c) and (d) depicts the tangent loss of CCMTMO ceramic versus temperature and frequency respectively.	103
Figure 5.1. (a) and (b) display the TGA graph of CCTO and CCTMO respectively.	114
Figure 5.2. (a) and (b) display the XRD graph of CCTO and CCTMO respectively.	115
Figure 5.3. depict the FT-IR spectra of CCTO and CCTMO sintered 900°C for 12 h.	116
Figure 5.4. shows the Raman spectra of CCTMO ceramic .	117
Figure 5.5. display (a) and (b) the HR-SEM of CCTO and CCTMO ceramic sintered 900°C respectively. (c) and (d) EDX spectrum of CCTO and CCTMO ceramic respectively .	118
Figure 5.6. display (a) The HR-SEM image of CCTMO ceramic (cubical structure), (b) the SEAD pattern of CCTMO ceramic .	119
Figure 5.7. display (a) the magnetization versus magnetic field (b) magnetization versus temperature of CCTO and CCTMO.	120
Figure 5.8. (a) and (c) show the dielectric constant versus frequency and temperature respectively, figure (b) and (d) depicts the tangent loss versus frequency and temperature respectively.	121
Figure 6.1. XRD patterns of (a) CCTO and (b) CCMTO sintered at 1100 °C for 8 h.	131
Figure 6.2. SEM micrographs of (a) CCTO and (b) CCMTO sintered at 1100 °C for 8 h. EDX spectra of (c) CCTO and (b) CCMTO sintered at 1100 °C for 8 h.	133
Figure 6.3. HR-TEM images of the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and $\text{CaCu}_2\text{Mn}_1\text{Ti}_4\text{O}_{12}$ (a) and (C) at sintered at 1100°C for 8 h and (b) and (d) Indexed SAED patterns of the sintered at 1100 °C for 8 h.	134
Figure 6.4. (a) and (c) AFM images of CCMTO Ceramic sintered at 1100°C for 8 h two-dimensional image showing grains and grain	135

boundaries (b) Three-dimensional image of surface roughness of CCTO
(d) Histogram of three-dimensional particle roughness.

Figure 6.5. (a) and (c) AFM images of CCMTO Ceramic sintered at 1100°C for 8 h two-dimensional image showing grains and grain boundaries (b) Three-dimensional image of surface roughness of CCTO (D) Histogram of three-dimensional particle roughness.	136
Figure 6.6. (a) to (d) XPS images of the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and at sintered at 1100°C for 8 h.	138
Figure 6.6. (e) to (i) XPS images of the $\text{CaCu}_2\text{Mn}_1\text{Ti}_4\text{O}_{12}$ and at sintered at 1100°C for 8 h .	139
Figure 6.7. (a) displays to cyclic voltammetry and (b) displays Electrochemical Impedance spectroscopy of the $\text{CaCu}_2\text{Mn}_1\text{Ti}_4\text{O}_{12}$ and $\text{CaCu}_2\text{Mn}_1\text{Ti}_4\text{O}_{12}$ at sintered at 1100°C for 8 h .	141
Figure 6.8. (a) and (b) shows the Variations of dielectric constant (ϵ_r) against frequency at few selected frequency as well as at few selected. (c) and (d) dielectric loss ($\tan \delta$) versus frequency of CCTO ceramic .	153 142
Figure 6.9. (a) and (b) show the variations of dielectric constant (ϵ_r) against temperature, (c) and (d) dielectric loss ($\tan \delta$) versus temperature of CCTO ceramic.	144

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
$\tan \delta$	Tangent loss
W	Energy loss
ϵ_r	Relative dielectric constant
C	Capacitance
F	Farad
σ	Conductivity
f	Frequency

LIST OF SYMBOLS/ ABBREVIATION

$P_{\text{electronic}}$	Electronic polarization
P_{ionic}	Ionic polarization
$P_{\text{molecular}}$	Molecular polarization
$P_{\text{interfacial}}$	Interfacial polarization
Hz	Hertz
λ	Wavelength
θ	Angle theta
$^{\circ}\text{C}$	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
$\text{\AA}$	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:

- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO)
- $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ (CCMO)
- $\text{CaMn}_1\text{Cu}_2\text{Ti}_4\text{O}_{12}$ (CCMTO)
- $\text{CaCu}_{2.9}\text{Mn}_{0.1}\text{Ti}_{3.9}\text{Mn}_{0.1}\text{O}_{12}$ (CCMTMO)
- $\text{CaCu}_3\text{Ti}_{3.9}\text{Mn}_{0.1}\text{O}_{12}$ (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 $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ (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 $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ structure. The average particle size was observed by TEM in 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 disordered of magnetic susceptibility. The dielectric constant and dielectric loss of the ceramic was found 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 $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (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 $\text{CaCu}_{2.9}\text{Mn}_{0.1}\text{Ti}_{3.9}\text{Mn}_{0.1}\text{O}_{12}$ (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 synthesis 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 ($\text{CaCu}_{3-x}\text{Mn}_x\text{Ti}_4\text{O}_{12}$, $x = 0, 1$) 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 $\epsilon' \sim 10^4$ 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.