Perovskite oxides, known for their high dielectric constant, have found significant applications due to this property. Their general formula is ABO_3, where A represents an alkaline earth ion, and B denotes a transition metal ion. These compounds have been extensively studied because of their intriguing properties in the realms of dielectric, electrical, piezoelectric, and optoelectronic phenomena.

Perovskites can be modified through various substitutions on either the A-site or the B-site, resulting in structures like $AA'BO_3$ and $ABB'O_3$. These substitutions may involve isovalent or heterovalent elements. Ferroelectric materials typically exhibit dielectric constants higher than 1,000. However, the dielectric constant demonstrates a peak concerning temperature. The undesirable temperature dependence of the dielectric constant near the peak temperature poses challenges for certain applications. The specific site occupied by an element in the parent compound, as well as the composition range for solid solution formation, depends on parameters such as radius, valency, and coordination number.

We have reported here the results of our investigation on a class of compounds having perovskite related structure. These have dielectric properties very different from those of ferroelectrics or relaxors. Their high dielectric constant shows only a small dependence on temperature.

The $ACu_3Ti_4O_{12}$ family of compounds has been known since 1967, and in 1979, its family was expanded, and more accurate structures were determined. However, it was not until after the year 2000 that the dielectric properties of these compounds were thoroughly studied. Among the oxides in this family, $ACu_3Ti_4O_{12}$ types exhibit remarkably high dielectric constants. Particularly, $CaCu_3Ti_4O_{12}$ stands out with a dielectric constant of about 12,000 at 1 kHz and a low loss tangent ($\sim10^{-1}$), maintaining this behavior in the temperature range of 100-600 K and across frequencies from 10^2 to 10^6 Hz. This exceptional property makes it an ideal thermally stable material with a high dielectric constant. The cubic structure of these compounds is related to that of perovskite, specifically $CaTiO_3$, further supporting their suitability as high dielectric constant materials. However, below 100 K, the dielectric constant value drops dramatically to around 100. Notably, neutron powder diffraction studies indicate no change in the crystal structure within the temperature range of 298-1273 K.

Structure of $CaCu_3Ti_4O_{12}$ is much more constrained than the usual perovskite structure. TiO_6 octahedra have tilted to form a square planar arrangement around Cu^{2+}. If one assumes that both Ti-O and Cu-O distances are 1.96 Å and that the Ti-O octahedron is not distorted, one finds that the unit cell edge must be 7.383 Å and the Ca-O distance should be 2.61 Å. A small deviation of the O-Ti-O angles from 90^0 produces the experimentally determined values of a = 7.391Å and Ca-O = 2.604 Å**.** This Ca-O distance is much less than the 2.72 Å, a value predicted based on the ionic radii. The situation is then similar to that in $BaTiO_3$, where the Ba-O distance of 2.84 Å is much less than the predicted value of 2.99 Å, on the basis of sum of ionic radii. Thus, in both $BaTiO_3$ and $CaCu_3Ti_3O_{12}$, the A^{2+} cation is in a site too small for it. As it pushes out to expand the lattice, it places the Ti-O bonds under tension and increases the polarizability of the TiO_6 octahedra.

In the cubic perovskite structure encountered in $BaTiO_3$ above 393 K, the Ti^{4+} cation is in a site of full cubic symmetry. With decreasing temperature, Ti^{4+} displaces toward one, then two and finally three oxygen anions, to produce, respectively, the tetragonal, orthorhombic, and rhombohedral ferroelectric structures. The site symmetry for Ti^{4+} in $CaCu_3Ti_4O_{12}$ is much lower than that in cubic $BaTiO_3$; this greatly reduces the possibility of a ferroelectric phase transition based on the displacement of Ti^{4+} from the center of its octahedron. For example, the lack of a fourfold axis in the Im3 space group for $CaCu_3Ti_4O_{12}$ eliminates the possibility of a transition to a tetragonal ferroelectric structure. The Ti^{4+} cations could displace off center along their one threefold axis. However, this could not be a pure ferroelectric transition because the displacements would actually occur along four different directions. Thus, we have in $CaCu_3Ti_4O_{12}$, a perovskite-type structure, where polarizability and dielectric constant are enhanced by tension on the Ti-O bonds, but where a transition to a ferroelectric state is frustrated by the TiO_6 octahedra tilt structure that accommodates the square planar coordination of Cu^{2+}. Substitution of Zn^{2+}, Mg^{2+} and Ni^{2+} at Cu^{2+} site and Ge^{4+} at Ti site gives rise to interesting useful properties. Therefore it was considered worthwhile to investigate the effect of their independent substitution as well as simultaneous substitution in equimolar concentration at Cu^{2+} and Ti^{4+} sites. We have also studied the Nickel and Germenium doping at copper and titanium sites and their effect on the crystal structure, microstructure and dielectric properties.

Generally CCTO is made by traditional solid-state reaction from the metal oxides at high temperatures. This method needs tedious work, relatively long reaction times, and high calcination temperature. In addition some secondary phases may appear in ceramics. In contrast, synthesis from a solution leads to intimate and homogenous mixing of the metal ions at the atomic scale, thus reducing the diffusion path length required. Shorter diffusion length leads to shorter reaction time and lower temperature. Many researchers have synthesized the undoped and doped $CaCu_3Ti_4O_{12}$ samples at high temperature (around 1123 K for 24 h) by solid-state method. $Bi_{2./3}Cu_3Ti_4O_{12}$(BCTO) is isostructural with CCTO, has been reported in the literature. It indicated the temperature and frequency dependence of dielectric as CCTO.

We have synthesized the high dielectric constant materials based on Bismuth Copper Titanium by new chemical method i.e. known as semi-wet route avoiding the use of expensive titanium iso-propoxide $Ti(OR)_4$. In this method, solutions of metal nitrates and Acetates of Bi, Cu, Zn, Mg, Ge, Ni have been used with TiO_2 powder. Using this method, these materials have been synthesized at lower temperature and in short time. The mixing process is performed in a sol state. Each constituent ion is uniformly dispersed in the resulting mixture after removing organic mater by heating in air.

To the best of our knowledge, no report is available on these substituted materials synthesized by this novel route in the literature so far. The results of these investigations are reported in this thesis. There are seven chapters in this thesis.

Chapter I

This chapter contains the introduction of the present work, describing briefly the scientific and technical investigations carried out in the field of perovskite oxides. This includes the effect of heterovalent substitutions and valency compensated substitutions on the dielectric properties. The aim of the present work is to investigate (a) crystal structure, (b) microstructure, (c) elemental analysis (d) particle size and (e) dielectric behaviour of materials prepared by semi-wet route in the following systems.

(i) BCTO $Bi_{2/3}Cu_3Ti_4O_{12}$ (ii) BCMgTO-0.05 $Bi_{2/3}Cu_{2.95}Mg_{0.05}Ti_4O_{12}$

(iii) BCMgTO-0.1 $Bi_{2/3}Cu_{2.9}Mg_{0.1}Ti_4O_{12}$ (iv) BCMgTO-0.2 $Bi_{2/3}Cu_{2.8}Mg_{0.2}Ti_4O_{12}$

(v) BCNTO-0.05 $Bi_{2/3}Cu_{2.95}Ni_{0.05}Ti_4O_{12}$ (vi) BCNTO-0.1 $Bi_{2/3}Cu_{2.9}Ni_{0.1}Ti_4O_{12}$

(vii) BCNTO-0.2 $Bi_{2/3}Cu_{2.8}Ni_{0.2}Ti_4O_{12}$ (viii) BCZTO-0.05 $Bi_{2/3}Cu_{2.95}Zn_{0.05}Ti_4O_{12}$

(ix) BCZTO-0.1 $Bi_{2/3}Cu_{2.9}Zn_{0.1}Ti_4O_{12}$ (x) BCZTO-0.2 $Bi_{2/3}Cu_{2.8}Zn_{0.2}Ti_4O_{12}$

(xi) BCTGO-0.05 $Bi_{2/3}Cu_3Ti_{3.95}Ge_{0.05}O_{12}$

(xii) BCZTGO-0.05 $Bi_{2/3}Cu_{2.95}Zn_{0.05}Ti_{3.95}Ge_{0.05}O_{12}$

Chapter II describes the experimental techniques used for preparation and characterization of the above perovskite oxide ceramics. The semi-wet route used for preparation of these materials has been described with the help of a flow chart. Powder X-ray diffraction and scanning electron microscopy have been used for study of crystal structure and microstructure of these materials respectively. 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. X- ray Photoelectron Spectroscopy (XPS) has been used to find the oxidation states of the elements present in the ceramics. Dielectric characteristictics and Electrical Conductivity of all the samples were measured as a function of temperature (300-500 K) in the frequency range 100 Hz-10 MHz with the help of PSM 1735 Newton's 4th limited LCR Meter.

Chapter III contains the synthesis and characterization of the parent composition $Bi_{2/3}Cu_3Ti_4O_{12}$ (BCTO) and Mg doped $Bi_{2/3}Cu_{3-x}Mg_xTi_4O_{12}$ (BCMgTO) ($x = 0.05$, 0.1 and 0.2) compositions Pellets have been calcined at 1073 K for 6 h and sintered at 1123 K for 8 h. Single-phase formation was confirmed by XRD. Average grain size in undoped (BCTO) and Mg doped (BCMgTO) samples is 0.70 µm and 0.63-0.56 µm respectively which is shown by Scanning Electron Micrographs. The stoichiometry of synthesized samples was confirmed by EDX studies. XPS spectroscopy confirmed the oxidation state of the elements present in the ceramic. On doping of Mg^{2+} concentration in CCTO, dielectric constant as well as dielectric loss of the samples decreases. Dielectric constant reduces due to decrease in concentration of oxygen vacancies which give rise to orientation polarization. A comparative dielectric study of BCTO and BCMgTO has been described in this chapter. The internal Barrier Layer Capacitance (IBLC) mechanism was responsible for the high value of the dielectric constant.

Effect of Nickel doping in $Bi_{2/3}Cu_{3-x}Ni_x Ti_4O_{12}$ (x = 0.05, 0.1 and 0.2) (BCNTO) system has been described in **Chapter IV**. Compositions are synthesized by a low-temperature chemical route of the synthesis and formation of single-phase solid solution was confirmed by X-ray diffraction. Pellets were calcined at 1073 K for 6 h and sintered at 1123 K for 8 h. Scanning electron micrographs show polygonal grains morphology having grain size in the range of 0.41-0.43 µm. Anomalous grain growth is observed in these samples. Elemental analysis is performed by EDX studies, which show the presence of Bi, Cu, Ni, Ti, and O. Particle size is determined by TEM technique. In this chapter, we have described the compartive study of structure, microstructure and dielectric properties of different doping concentration of BCNTO ceramics.

Chapter V contains the doping of Zn^{2+} at copper site in BCTO Ceramic. Samples of $Bi_{2/3}Cu_{3-x}Zn_xTi_4O_{12}$ (x = 0, 0.05, 0.1, 0.2) (BCZTO) were synthesized by semi-wet route. X-ray diffraction studies confirmed the single-phase formation at 1123 K for 8 h. Scanning electron microscopy show the grain size is in the range of 0.53-0.70 µm. Particle size is calculated by TEM analysis. The stoichiometry of the samples is confirmed by EDX studies. The oxidation states of the elements present in the ceramics, is confirmed by XPS. In this chapter we have also described the comparison between dielectric properties of undoped (BCTO) and doped BCZTO ceramics. The Impedance studies show the existence of Maxwell - Wagner type of relaxation phenomena in ceramics. The conductivity variation of $Bi_{2/3}Cu_{3-x}Zn_xTi_4O_{12}$ ceramics (where x= 0, 0.05, 0.1, and 0.2), with the inverse of temperature follows the Arrhenius equation, with a major temperature range of 300-500 K.

Chapter VI describes the effect of Ge doping at titanium site in BCTO ceramic as well as Zn and Ge simultaneous doping at copper and titanium site in BCTO ceramic respectively on the dielectric properties. $Bi_{2/3}Cu_3Ti_{3.95}Ge_{0.05}O_{12}$ (BCTGO-0.05) and $Bi_{2/3}Cu_{2.95}Zn_{0.05}Ti_{3.95}Ge_{0.05}O_{12}$ (BCZTGO-0.05) were synthesized by semi-wet route using TiO_2 powder and metal nitrate and acetate solutions. X-ray confirmed the formation of single-phase. The microstructural analysis of the samples were done by SEM and TEM analysis. Average grain size, obtained by SEM, is 0.62 μm and 0.68 μm for BCTGO-0.05 and BCZTGO-0.05 respectively. Elemental analysis was performed by EDX. XPS suggests that all elements present in these ceramics are in proper oxidation states. The dielectric constant was found high for BCTGO-0.05 ceramic.

Summary and future Scope are described in **Chapter VII.**