

A capacitor material with high dielectric constant and low dielectric loss is highly applicable in microelectronics. It is widely used as multilayer capacitor (MLCC), dynamic random access memory (DRAMs), microwave devices, electronic devices in automobiles and aircrafts.  $ACu_3Ti_4O_{12}$  ( $A = Ca, Bi, Sr$ ) type oxides consist of complex Perovskite structure. It exhibits a high dielectric constant ( $\epsilon_r \sim 10^4$ ) and moderately low dielectric loss ( $\tan \delta \sim 0.10$ ). This property remains practically constant in a wide temperature range (100–600K). The display of dielectric loss  $> 0.05$  at 1 kHz, is still a serious issue as its capacitive applications. Presently, the Perovskite  $BaTiO_3$  is mostly used as a capacitor material which is also environmental friendly. The problem persisting with  $BaTiO_3$  is its unstable nature at higher temperature with phase transitions which makes it is unsuitable for applications at high temperature. Therefore, search of an excellent dielectric material with good thermal stability over wide temperature and frequency ranges is highly demanding.

The modern technology needs for the development of composite material with some excellent properties at a time which can't be in a single component material. Composites play an 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 a composite, a novel set of physical and chemical properties may be obtained that would be completely different from that of the individual constituent material. A collection of properties can be tailored in a composite by combining two or more components.

The electrical and dielectric properties of composite are also interesting in high-density energy storage and capacitor applications. With the smaller sizes of nanoparticle  $< 100$  nm, surface to volume ratio increases, the number of atoms on the surface of

nanocrystal increases, an alteration in electrical properties with required change in structure within nanoscale region is observed. The electrical and dielectric properties of nanoparticles are affected by its particle size, morphology, and chemical composition.

In the thesis, the synthesis of  $x\text{BaTiO}_3-(1-x)\text{ACu}_3\text{Ti}_4\text{O}_{12}$  ( $A = \text{Bi}_{2/3}, \text{Ca}$ ) composite perovskite with different stoichiometry of  $x$  by the solid-state method is reported. All the synthesized composites were characterized by various physicochemical techniques to investigate (a) crystal structure (b) microstructure (c) elemental analysis (d) particle size (e) electrical and dielectric properties of these composites, and (f) effect of sintering duration on properties (a-e) in detail.

In brief, the present work aims of the following composites were prepared by the solid state route:

<b>S. No.</b>	<b>Composite</b>	<b>Abbreviation</b>
1.	$0.9 \text{BaTiO}_3-0.1 \text{CaCu}_3\text{Ti}_4\text{O}_{12}$	BTC
2.	$0.9\text{CaCu}_3\text{Ti}_4\text{O}_{12}-0.1\text{BaTiO}_3$	CC-BT
3.	$0.5\text{BaTiO}_3-0.5\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$	BT-BCT 5
4.	$0.6\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}-0.4\text{BaTiO}_3$	BC-BT

The present thesis discusses the results of investigation on the above system and it has been divided in to seven chapters.

**Chapter 1** contains an introduction of composite materials. It describes briefly the investigations reported in the field of Perovskites, its different types and their technical applications in different fields. It also includes some high dielectric constant materials structurally based on complex Perovskites describing the polarization mechanism related to dielectric properties as well as some basic knowledge of impedance spectroscopy and its applications in investigation of dielectric phenomena.

**Chapter 2** describes the experimental procedure in the synthesis of different composites by solid state method. Different samples were characterized by X-ray diffraction analysis (Rigaku, miniflex-600, Japan) to examine the crystalline phases of sintered samples, Scanning electron microscopy to investigate the microstructure including grains and grain boundaries. Transmission electron microscopy was also employed for determination of size and shape of the particle and atomic force microscopy was used to analyze the surface morphology of different composite samples. Electrical and dielectric properties of different composites were also studied as a function of temperature (300-500 K) and frequency (100Hz-5 MHz) using PSM 1735 (NumetriQ 4<sup>th</sup> U.K Limited) LCR Meter.

**Chapter 3** discusses the synthesis, characterization and application of the  $0.9\text{BaTiO}_3\text{-}0.1\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (BTC) composite. It was synthesized by solid state method and sintered at 950 °C for different durations 3, 6, 9 and 12 h. Microstructural details were studied by XRD, SEM, TEM and AFM. XRD confirmed the existence of  $\text{BaTiO}_3$  (BTO) and  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) as the primary phases along with CuO and  $\text{CaTiO}_3$  as the minor phases. The average grain sizes obtained by SEM analysis were found to be around 269 nm, 309 nm, 342 nm, and 734 nm for sintering durations 3, 6, 9 & 12 h respectively. TEM analysis showed the particle size in the range of  $30 \pm 10$  nm. The surface morphology was

analyzed by AFM. The composite sample sintered for 3 h exhibited very high dielectric constant ( $\epsilon_r \sim 3.19 \times 10^5$ ) at 1 kHz. The presence of semiconducting grains with insulating grain boundaries significantly contribute to such a high dielectric constant value, supporting thus, the internal barrier layer capacitance (IBLC) mechanism operative in BTC nanocomposite.

**Chapter 4** describes the synthesis of  $0.9\text{CaCu}_3\text{Ti}_4\text{O}_{12} - 0.1\text{BaTiO}_3$  (CC-BT) composite by the solid-state reaction method at 950 °C for 12 h. X-ray diffraction analysis confirmed the presence of both phases,  $\text{BaTiO}_3$  and  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  in CC-BT composite. Transmission electron microscope showed the formation of nanoparticles with average size  $40 \pm 5$  nm. The surface morphology demonstrated the formation of large and small grains with bimodal structure. The average and root mean square roughness was found to be 1.41 nm and 2.24 nm respectively by atomic force microscopy study. The dielectric constant of CC-BT composite was found to be  $6.23 \times 10^3$  at 100 Hz. The presence of semiconducting grains and insulating grain boundaries in the composite supported the IBLC mechanism is also operative in it.

**Chapter 5** refers the synthesis and characterization of  $0.5\text{BaTiO}_3-0.5\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$  (BT-BCT5) nanocomposite by a solid-state reaction method at 870 °C for different sintering durations (4, 8, 12 and 16 h). X-ray diffraction analysis confirmed the presence of  $\text{BaTiO}_3$  and  $\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$  phases in BT-BCT5 composite. Transmission electron microscope demonstrated the formation of nano-particles in the range  $90 \pm 10$  nm. Further, scanning electron microscope (SEM) images showed that the morphology consists of bimodal distribution of large and small grains (1.0–2.5  $\mu\text{m}$ ). The surface morphology of composite was studied by atomic force microscope in tapping mode of measurement also validated the

results obtained by SEM. The sample sintered for 12 h exhibited very high dielectric constant ( $\epsilon_r \sim 4.34 \times 10^4$ ) at 100 Hz. The presence of semiconducting grains with insulating grain boundaries significantly attributed high dielectric constant for BT-BCT 5 nanocomposite.

**Chapter 6** describes  $0.6\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}-0.4\text{BaTiO}_3$  (BC-BT) nanocomposite synthesized successfully by solid state route. XRD confirmed the formation of  $\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$  and  $\text{BaTiO}_3$  phases in BC-BT composite at 870 °C for different sintering durations (4, 8, 12 and 16 h). Particles in the range  $70 \pm 10$  nm were observed by TEM. AFM showed statistically significant changes in the surface roughness. The BC-BT nanocomposite exhibited an improvement in the dielectric loss ( $\tan \delta \sim 0.09$ ) at 1 kHz and 50 °C. The grains resistance ( $R_g$ ) was found to be 37.30  $\Omega$ . The complex impedance spectroscopic study revealed temperature dependent electrical relaxation. The AC conductance obeyed Jonscher power law. The exponent factor (s-value) was found to be 0.40-0.51. Magnetic behavior of the composite indicated a weak ferromagnetic phenomenon in M-T and M-H curve with display of ferromagnetic to paramagnetic transition.

**Chapter 7** describes the key finding 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'.