Chapter 6

Thesis Summary and Future Scope

Perovskite oxides are thought of to be most extensively studied and important for their technological applications among all the ABO\(_3\) phase forms with A- and B- sites could remarkably be occupied with almost every element from the periodic table. This led to charismatic range of properties to ferroelectricity, multiferrocity, ferromagnetism, piezoelectricity, metal-insulator transitions etc. Perhaps these properties existed by virtue of amusing structural phase diagrams due to instability of cubic perovskites to energy lowering structural distortions.

Extensive studies on obtainability of several electrical and dielectric properties of ABO\(_3\) type compounds been of great interest for years. For instance; the technique of doping foreign elements was introduced and materialized to improve upon the electrical and optical properties of BaTiO\(_3\). Furthermore, the selection of sites for dopants itself determined modifications in properties of the resultant materials.

To summarize; chapter-wise summary on historical background of ceramics, literature review, objectives of study, points of observation, instrumentation, results, discussion and conclusions so drawn are discussed in detail below:

In first chapter, history of ceramic materials is revealed especially changes in ceramics, their constituent’s compositions, quality of ceramic materials by various civilizations according to their needs. How in an ancient era the ceramics were home to pottery items and with times the ceramic forms for insulating materials in modern use for
electrical and electronic purposes, viz; at least two new positions, one at electric poles and others as heat resistant materials. The second world war brought in use of ceramics for controlled electrical properties through formation of dielectrics from ceramics. It happened to be of paramount importance as to how the ceramic materials like barium titanate displaced mica and proved to be the best ceramics for use as dielectric materials. ABO$_3$ compounds as ceramics, such as; Calcium titanate, basically known to be from one of the ores of titanium reduced to give titanium metal or ferro-titanium alloy. It had lower dielectric values and its dielectric properties changed irregularly with temperature and frequency. Hence this compound was of less importance as far as studies on permittivity of ceramics were concerned, though some derivatives of CaTiO$_3$ proved to be suitable for minimizing the radiation effects.

Barium Titanate has been established to be the most important among the family of perovskites. It is a ferroelectric material existing in the multilayer form and is the most widely used material since its discovery of around 60 years ago. The mixed oxides of barium and titanium did wonders as the material so formed was found to have as high values of dielectric constant as ten times to that of any of the ceramics known of that time. Thernaurer et al. (1941). The material became so important at that time because only TiO$_2$ had its permittivity of $\varepsilon_r =110$ among all the known ceramics, while the permittivity of BaTiO$_3$ was found to be very high with its dielectric constant value of around 1000 which was ten times greater than that of any other ceramic materials of those times. Methods of ore extraction of TiO$_2$, their anomalous behaviors, crystal structure etc. were of tremendous significance.

The basic perovskite structure of BaTiO$_3$ remained point of study for decades. As the availability of this ceramic saw tremendous increase due to its large crystals, there used to be
extensive research and experiments to explore anomalous behavior and charismatic properties of BaTiO$_3$ ceramic like extent of polarization and permittivity. Experiments on improving structural understandings at different temperatures and the transitional phases by considering the size and low energy structural effects were taken up. The difficulties in observing structural transitions at lower temperatures (i.e. orthorhombic) and need to set up labs outdoors for chilling temperatures as low as 4 °C are discussed. The modern era of electron microscope and atomic force microscopy have changed the scenario to precision measurements.

Basic interrelationships in single domain BaTiO$_3$ in terms of free energy $G$ described through general form of the Devonshire theory were established. The equation, its solution for calculating energy function using coefficients from experimental gave way to theoretical models. The free energy so obtained as used in thermodynamic relations to obtain thermodynamic quantities like; temperature, stress, dependence on electric field etc. The development of theoretical microscopic models was made to explaining structural and dielectric properties of the ferroelectric oxides, dipole moments in BaTiO$_3$ ceramic above Curie temperature and application of instrumentation like diffuse x-ray scattering, inelastic neutron scattering and Raman spectroscopy were explained. BaTiO$_3$, as of now, has been accepted to be of soft-mode phonons that requires deep understanding of its microscopy and therefore the phase transitions of this compound remained a topic of investigation.

Finally, the history of doping, the doping techniques from ancient times through Vedic times to modern era are discussed in detail in this chapter. In modern science, its importance has been recognized while formation of semiconductor materials. How the trivalent, pentavalent impurities (dopants) largely modified the properties as semiconducting materials.
This process became very popular to increase the conductivity and decrease the forbidden gap energy in semiconductors. In today’s times, successive selective counter doping methods are in use to prepare semiconductors with the specific areas of p- and n-types.

The doping technique has also proved to enhance the properties of some ceramic compounds. Using this technique, the morphology, electric properties and magnetic properties could be easily modified. The various types of doping, the methods of doping like; using single dopant in semiconductors, doping in organic conductors, magnetic doping, neutron transmutation doping, doping in polymers are discussed in addition to doping procedures, viz; doping by weight percentage, doping by atomic weight percent, doping using stoichiometric proportions.

The formation of materials of interest to present research work, viz; barium zinc titanate, zirconium doped ceramics, rare-earths’ doping, neodymium doped barium zinc titanate, neodymium doped barium zirconium titanate, barium ferrites, titanium doped barium ferrites and application of time differential perturbed angular correlation technique are discussed under.

Chapter 2 enlists and explains various materials used for present research and methods of sample preparations and techniques employed to investigate the properties of materials under external effects. Sample preparation and sample characterizations are the backbone of experimental research work. Stress has been mainly laid on predominant methods of sample preparation, viz; sol-gel, co-precipitation and solid state sintering methods. Solid state sintering method, employed in present research work has been explained its vital importance and its edge over methods limited to present work. Various steps taken to sample preparation
through solid state route are also discussed in detail. Besides, spectroscopic Instrumentation, viz; Scanning Electron Microscopy, Transmission electron microscopy, Energy-dispersive X-ray spectroscopy \((EDS)\), X-ray Photoelectron Spectroscopy, IR and FT- Raman Spectroscopy, X-Ray diffraction, Normal Zeeman Spectroscopy, LCR meter, time differential perturbed angular correlation Technique are discussed from the angle of their use to carry structure investigations and properties of materials of research.

**Chapter 3** is about study of a well-known ceramic, barium zinc titanate. A dopant, neodymium has been substituted in the molecular configuration of barium zinc titanate \((\text{BaZn}_2\text{Ti}_4\text{O}_{11})\). The resultant complex of ceramic, ‘neodymium doped Barium Zinc Titanate \((\text{Ba}_{1-x}\text{Nd}_x\text{Zn}_2\text{Ti}_4\text{O}_{11})\)’ has been prepared using solid state method and characterized using conventional instrumentation as explained in chapter 2. Neodymium metal has quickly oxidizing nature in ordinary air. The oxide layer then peels off exposing the metal to further oxidation. For sample preparation, \(\text{BaCO}_3\), \(\text{ZnO}_2\), \(\text{TiO}_2\) and \(\text{Nd}_2\text{O}_3\) powders in ultra-pure form from Sigma Aldrich Co. were taken in stoichiometric proportions. The addition of \(\text{Nd}_2\text{O}_3\) was carried out in right proportions to synthesize the complexes so formed with concentration of \(\text{Nd}^{3+}\) while \(x\) was taken to be 0.000, 0.001, 0.002 and 0.003 respectively in the order of increase in doping amounts. The pre-sintered heating, sintering and grinding to at each stage to uniformity, pellet press diameter and thicknesses of the pellets etc. are explained in this chapter. Doping of neodymium at barium site affects the cubic symmetry of the molecules crystal and made the ceramic precious. For TDPAC measurements the sample preparation using Stock solution of \(^{181}\text{Hf}/^{181}\text{Ta}\) tracer in \(\text{HfCl}_4\) form obtained from Bhabha Atomic Research Centre, Trombay, Mumbai, India was made available by labs at Bhabha Atomic Rsearch Center (VECC) Kolkata. The \(^{181}\text{Hf}\) tracer was prepared through neutron activation in
reaction $^{180}\text{Hf} \ (n,\gamma) \ ^{181}\text{Hf}$ with thermal neutron flux of $\sim 5 \times 10^{13} \ n/cm^2$. The stock solution of $^{181}\text{Hf}$ tracer with 0.1572 mg/ml hafnium was prepared by dissolving neutron irradiated HfCl$_4$ in dilute HCl. 300$\mu$l of stock $^{181}\text{Hf}$ solution was taken in 10ml of 3(N) HCl and 7ml of Ti-doped barium zinc titanate solution was added to it dropwise resulting in the formation of white lump. It was stirred until the lump was dissolved and a clear solution was obtained. To this solution, ammonia solution was added dropwise to obtain a white precipitate doped with $^{181}\text{Hf}$. The white precipitate was filtered off and washed with water several times. The precipitate was then dried and crushed to have TiO2 matrix doped with $^{181}\text{Hf}$. The sample got an activity of 11000 Bq/gm with respect to $^{181}\text{Hf}$ tracer. The samples so prepared were placed in sample holder of angular correlation table and coincidence data were recorded with three planar LaBr3(Ce) detectors.

All samples of BZnT have been characterized in first stage using X-ray diffraction technique, scanning electron microscopy, dielectric properties have been studied at different temperature and frequencies, and some other parameter related to it. At the end of these observation specially prepared samples for PAC measurements have been uploaded in holder of PAC table for correlation coefficients.

The XRD data revealed formation of single phase perovskite tetragonal structure. The observed main peaks of low intensity are found for undoped compound while the intensities for doped compound have shown upward trend with Nd$^{3+}$ ion concentration. Some abnormal growth in peaks between angles of 56.60° and 56.66° have been noticed.

SEM images show expansion of lattice and fine agglomerates developed causing the material, a porous. The surface activity has shown uprising trend in electron concentration on
traces of neodymium substitution. At higher concentrations, the spheroidization sets in which enhances the charge retention capacity.

Dielectric behavior of all the samples has been observed in the frequency range of 20 to 2.0MHz. The dielectric constants have been found to be in close vicinity at lower frequencies while better at higher frequencies. Remanent polarization exists in all samples although sharp rise is observed with highest doped sample. Dielectric observations also indicate change of phase from ferroelectric to paraelectric state at a temperature of 350 °C. Beyond this temperature, the material starts loosing electrical permittivity. Curie temperature values of all the four samples with x = 0.000 to x=0.003 are observed respectively as 350°C, 355°C, 360°C and 370°C. It indicates the dopant concentration improves the performance of neodymium doped barium zinc titanate ceramic over a wider range of temperature and frequency. Tan-loss is found to be predominantly higher at lower frequency but makes the samples possibly better ceramics for higher frequency values. The consistent decline in tangent loss beyond 100 KHz and quality factor is improved dopant concentration.

The samples were subjected to electric stress to study effects of electric field on any change in dipole orientations and net polarization of the sample materials. Saturation polarization for each sample Nd, 0.000 to Nd, 0.003 has been observed to be 7.772, 7.910, 8.252 and 8.59 µC/cm² respectively. The continuous horizontal stretch in P-E graph refers to rise in electric coercivity.

TDPAC measurements were carried out on the 133-482 keV cascade where the intermediate 482 keV, 5/2+ level has a half-life of 10.8 ns in order to study the variations in charge distribution around the neighbourhood of the probe atom. For surface studies, the
nuclear quadrupole interaction (NQI) parameters identify the atomic configuration around the probe nucleus. The potential use of PAC is understood from the fact that the distinctively different parameters for different complexes provide varying information of correlation coefficients. The higher values of EFG are indicative of highly charged state around nuclear probe. The doping of neodymium by virtue of 4f-shell effects is responsible for accumulation of charge around the probe.

At the end of the chapter it has been summarized that consistent improvement in dielectric constant values corresponds to dopant concentration. Deduced from non-linearity of polarization with electric field, the compounds also show improvements in both their Remanent polarization and ferroelectricity tendencies with dopant presence.\textsuperscript{181}Hf nuclear probe is employed for analyzing effects of dopant concentrations and consequently the dielectric properties of the sample materials.

\textbf{Chapter 4} provides detailed investigation of Barium Zirconium Titanate compound. has been presented. Pure form of Barium Zirconium Titanate (BZrT) has been widely studied by different researchers. Doping technique has been found to be of tremendous importance for enhancing electrical properties of the compound. In addition to pure form of BZrT, synthesis has been carried out on formation of neodymium doped complexes of molecular formula (Ba\textsubscript{1-x}Nd\textsubscript{x}Zr\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{3}) for x=0.00, 0.05, x= 0.1, x= 0.2 values.

XRD data revealed single phase perovskite cubic structure with Pm\textsuperscript{3}m space group. A real negative peak shift surfaces which is attributed to enormous strain in the lattice as a result of doping concentration.
SEM imagery shows grain size growth through all samples with the surface showing asymmetric with fine agglomerates seen in the patterns. Particle size, as obtained from Scherrer formula are obtained respectively for all samples as 10.12, 10.15, 10.20 and 10.25 nano meters. Increase in porosity with dopant concentration is in line with earlier findings. However, it looks that even with marginal increase of Nd$^{3+}$ ions the constituents realign to acquire closely packed position which in turn perturbs the conditions necessary for resonant bonding. The excess dopant presence sets in impurity or imperfections in the lattice which causes outward stress that appears at face centred sites with Nd$^{3+}$ presence. The presence of impurities expands grain boundaries by virtue of enhanced of grain size further leading to consistent decline in sample density.

Energy dispersive x-ray spectroscopy has been performed on the samples for elemental analysis and chemical characterization purposes where all constituents of the complex compound are represented by their corresponding peaks. The EDS analysis has shown elemental compositions in stoichiometric proportions. Presence of gold peak from gold contacts for taking SEM images is also noticed.

Dielectric behaviour of the samples has been studied along frequency range of 20 Hz to 2 MHz at normal temperature as shown in Fig. 4.5. Within experimental errors, the values of dielectric constants with dopant concentration for 1 KHz frequency have been measured to be 1065, 1153 and 1525. The dielectric properties of Nd-doped compounds have shown considerable improvement with increase in dopant concentration indicating better frequency stability. The internal stress due to increase in dopant concentration becomes more pronounced and significant enough to shift the Curie temperatures to values of around 50°C. The dopant concentration is in conformation to better quality ceramic for higher frequency
operations requiring reasonable potentials at disposal. There appears to be change from ferro-
to para-electric behaviour in first sample (x = 0.05) at Curie temperature value of 390°C.

The Curie temperature of second sample (x = 0.1) has fallen to 395°C as also the
electrical permittivity at its maximum is low whereas the value of Curie temperature stands at
400°C for the third sample (x = 0.2). It appears that due to enhanced ionicity with Nd\textsuperscript{3+} doping
reduces resonant bonding as also the charge localizes at ion cores. It is the dopant
concentration that drives poor charge transport as well as loss of Curie value. There is no
indication of any significant phase change though temperature dependence of dielectric
constant has been drastically effected.

Tangent loss is found to be quite less prevalent in the first sample which improves for
higher doping concentration and makes the material better and more durable for electrical
permittivity even at higher frequencies.

Optical absorption spectra show absorption troughs for the three samples respectively
at 559.255 cm\textsuperscript{-1}, 586.253 cm\textsuperscript{-1} and 592.153 cm\textsuperscript{-1} wave numbers. Absorption at 543.9 cm\textsuperscript{-1} wave
number has been seen as a finger print of pure BZrT powder. The shift however reveals the
involvement of polarizing effect due to larger Nd\textsuperscript{3+} ions. It also infers that neodymium, having
larger ionic radius (164 pm) substitutes titanium (132 pm) in BZrT ceramic due to which the
vacancies are created at the B-site causing dramatic stress on Metal-Oxygen bond in
perovskite octahedral geometry. It develops stretching of metal oxygen (M–O) vibration band
at the B-site that is the reason of shift from its finger print value.

\textbf{In nut-shell}, neodymium doped barium zirconium titanate has been probed for dopant
concentration effects on morphology and electrical properties of the materials. The Nd\textsuperscript{3+} ion
dopant concentration governs stability of BZrT ceramic. The electrical permittivity is in its
most acceptable form as also its stability over wide ranging frequency and temperature dependence. The curie temperature improves showing upward trend with doping. The tangent loss is also in its lowest form. The dominance of dopant of higher ionic radius replaces titanium, as is also evident from its intensity counts under XRD-patterns, immobilizes charge movements by causing undue outward stress at face centered Zr\(^{3+}\)/ Ti\(^{3+}\) locations thereby lowering the specific electrical permittivity. SEM microgram for first sample shows fine grain formation paving the modest route through Ti-Nd pairing. The Ti-Nd pairing with doping monitors trend of grain growth that vindicates agglomerates and uneven cluster formations. The dielectric constant over a wide frequency range thus makes the material suitable for devices operating under wider frequency bands. Tangent loss is small over a desired frequency range. Conditions of resonant bonding proactively influence electrical permittivity of the material. Dopant caused porosity triggers drastic change in dielectric behaviour of the material as well as its temperature and frequency dependence. The Curie temperature shows significant change with grain size and optical absorption marginally shifted to lower wave number, probably due to formation of new Nd\(^{3+}\) dopant arrangement. The absorption spectrum indicates M-O absorption of IR light at 559.255 cm\(^{-1}\) wave number and appreciable change in dipole moment is observed due to new arrangements with intense IR absorption band. The shuffling between vacancies and distortions may however account for numerous other properties of the ceramic. The dielectric and ferroelectric materials and their microstructure characteristics find strong correlation by virtue of grain size. These correlations reveal possibility of further improvements in dielectric properties of this family of ceramics.

**Chapter 5** deals with titanium doped barium ferrite. The composite electric and magnetic properties of these complexes have been discussed in detail in this chapter. The
synthesis process of M-type barium hexaferrite with titanium substitution is explained. Further, after a clue over ferroelectric behavior response while making dielectric measurements it was decided to investigate the compound by applying electric field to view electric hysteresis pattern. BaTi$_x$Fe$_{12-x}$O$_{19}$ for $x = 0.005, 0.01, 0.02$ and $0.03$ are synthesized from mixtures containing stoichiometric proportions of barium carbonate (99.9%), titanium oxide (99.9%) and ferric oxide (99.9%) chemicals from Sigma Aldrich Inc., USA. A pure BaFe$_{12}$O$_{19}$ was also prepared for comparison purposes.

XRD patterns from un-doped and Ti-doped barium hexaferrite depict single phase hexagonal structure with space group P6$_3$/mmc as per JCPDS records. SEM images reveal morphological and topographical information of prepared samples. Though consistent expansion in lattice parameter ‘a’ with neodymium doping prevailed but sharp rise is experienced with highest doping concentration studied. Besides the grain gap has also widened.

Magnetic hysteresis plots show consistently varying trend and remanence properties. The molecular magnets become more and more aligned with applied field strength that provides net flux density and thereby saturation magnetization is arrived at such that the induced magnetic field due to charge flowing through a coil has no or minimal effect on remanence. The coercivity falls due to loss in density of domains.

The resistivity shows gradual increase with titanium substitution perhaps due to the fact that titanium occupancy triggers the formation of Fe$^{2+}$ ions which causes decrease in resistivity of the material. However, with higher titanium concentration, the Ti$^{4+}$ - Fe$^{2+}$ ion pairs expand the lattice (which is obvious from XRD patterns), thus, reduce the hopping
probabilities between Fe$^{2+}$ and Fe$^{3+}$ ions. The separations among B-sites increase due to which the resistivity shows increasing trend at higher titanium substitutions.

The dielectric constant indicates modification which explores the possibility of the compound as a better material for devices requiring high permittivity. The relative permittivity is also found to be of higher order at lower frequencies. The doping effects prove the material for manufacturing devices that require good dielectric values at higher frequencies. The doping however had lowered Curie temperatures consistently for observed samples. The P-E graph also shows expansion of area under the loop with Ti-ion substitution. The net electric dipole polarization has improved with dopant concentration.

**Applications of studied ceramics**

Neodymium doped barium zinc titanate (BZnT) barium zirconium titanate (BZrT) and titanium doped barium ferrite (BTF) materials are synthesized and investigated. Nd doped BZnT has shown moderate dielectric constant value. Such materials are suitable for manufacturing of multi-layer ceramic capacitors. Nd doped BZrT has higher dielectric constant value in comparison to BZnT and has also shown relaxor behavior. Such materials may prove useful for tape casting purposes in addition to capacitor formation. Particularly Neodymium doped BZrT is best material for miniaturization of volatile memory devices, which is the main parts of semiconductor and communication systems. The graph 4.5 depicted the static behavior of sample of Nd doped BZrT between long frequency range 1 KHz to 1 MHz. Such a material is most suitable for long life dynamic access memory (DRAM) and static random access memory (SRAM). The positive temperature coefficient studied doped ceramics makes them a fit candidate for switching device thermistor. For fixed
curietemperature value, the ceramic can be used for automatic switch devices operatable at high temperatures.

The titanium doped barium ferrite (BTF) with doping concentration x = 0.000 to x = 0.03 have proven as best quality dielectrics as well as ferromagnetic material. They can be applied in creation of all ferroelectric devices. But the sample in the present work with highest doping concentration proves to be the fittest candidate both for ferroelectric and magnetic operations and for manufacturing data recording devices. The inculcation of titanium ion is capable of maximizing the remanent polarization and coercive field as required for non-volatile memory devices e.g. ferroelectric random access memory (FRAM). Increased coercive field gap, as observed in the present work, between gaussing and degaussing of the doped samples is further able to make this material appropriate for long life data storage device. The data storage device which are in practice have not been capable of tolerating external electric field while the material under study has its importance in memory devices to be used in space explorations and even under high temperature zones.

**Future scope of work**

During the entire study as explained above, doping of single rare earth material has shown charismatic results. Doping other elements from this class or doping additional elements may yield unexpected results. Substitution of rare earth material at zinc site in barium zinc titanate, at barium site in barium zirconium titanate and at barium site in barium hexaferrrite may be tried for better direction. Nano particles synthesis can be carried out over these materials for more varied information.