PREFACE

Barium titanate stannate, $Ba(Ti_{1-x}Sn_x)O_3$ is a binary solid solution system composed of ferroelectric barium titanate and non-ferroelectric barium stannate. The both compounds are perovskite oxide. The natural occurring perovskite oxide is $CaTiO_3$.The perovskite structure has general formula ABO_3, where valency of A and B cation varies +1,+2,+3 and +3,+4,+5 respectively.

The ideal perovskite structure has a cubic unit cell, space group Pm3m and contains one formula unit. Due to distortion perovskite structure have different structure depends upon the value of the tolerance factor (t), given by $((r_A + r_O/\sqrt{2}(r_B + r_O)$.

The perovskite oxides have wide technological application in ferroelectricity, anti-ferroelectricity, piezoelectricity, insulating behavior semiconductivity, metallic conductivity, ferromagnetism, anti-ferromagnetism, etc. Due to their dielectric and ferroelectric properties nanosized barium titanate materials have found various technological applications, such as capacitors, sensors with positive temperature coefficients of resistivity, piezoelectric transducers and ferroelectric thin-film memories [Steinhausen R.et al., 2004]. The ionic radius is the main factor that decides the substitution site for the dopants. $SrTiO_3$, $BaTiO_3$, $KNbO_3$, etc., represents a important class of perovskite materials with high potential for future application in microelectronic. Introduction of extrinsic and intrinsic dopants, such as transition metal cations results the formation of cation or oxygen vacancies which enhances the properties dramatically. Relaxor ferroelectrics characterized by their broad dielectric transition, also known as the diffused phase transitions, are important materials for use in non-volatile memory devices. In order to develop environment-friendly materials, efforts are focused on the lead-free materials [Wei Xiao Yong et al., 2005]

To improve the properties of the perovskite oxide, it can be modified by the partial substitution of ions on A and B sites. Substitution in perovskite oxide are classified into three categories (Jaffe and Jaffe, 1972)

1. **Isovalent substitution-**The valency of the substituent ion having same as valency of host ion. This substituent is may be either A site or B-site. For example Ca^{+2}, Sr^{+2} substituted Ba^{+2} and Zr^{+4}, Sn^{+4} on Ti^{+4} in $BaTiO_3$.
2. **Hetrovalent substitution-** The valency of the substituent ion is different valency of host ion. This substituent is may be either A site or B-site. The electrical charge neutrality is maintained by the generation of electrons or cationic vacancies in Ba^{2+} or Ti^{4+}sublattice.
3. **Valence compensated substitution-**Simultaneous substitution of a combination of hetrovalent ions A and b sites, such that electrical charge neutrality in the crystal is maintained internally.

Chapter 1 describes literature review in the present area. The solid solutions of barium titanate stannates system are widely investigated material. A survey of the literature has revealed that the barium titanate stannate has been successfully prepared via solid state reaction method,[Wei X.et al., 2004]and it suggested that this solid solution system is a mutual soluble and the lattice constant increased by increasing the Sn content.[Wei X. and Yao X., 2007] The dielectric relaxation behavior was observed in barium titanate stannate with $0.20 \leq x \leq 0.30$ [Wanga J, 2013]. These make the barium titanate stannate interesting for dielectric amplifiers and switching circuit snubbers [Campbell C.K., 1995].

Composites based on the BTS ferrites like $\gamma - Fe_2O_3$, Fe_3O_4, of Fe-Ni ferrites have been prepared by different methods. These composites enhance the magnetic properties. A significant amount of research has been done on the structural and electrical properties of both elastic and non-elastic CNT-polymer composites. However, very little research is available on the electrical properties of CNT-polymer composites. It is, therefore, proposed that this field of study could benefit from the proposed thesis research. Coal–burning thermal power plants produce large amounts of flyash (FA) as a residue. There have been many experiments on FA for technical studies and possible applications. Electrically insulating nature of FA makes it desirable to regulate conductivity of polymer composite. The wastes FA have been incorporated in polyaniline by in-situ polymerization. The addition of FA results in an enhancement of microwave absorption with an added advantage of industrial waste utilization.

Therefore in the present investigation we aimed to prepare following system.

(1) $BaTi_{1-x}Sn_xO_3$ (x=0.00, 0.05, 0.15, 0.30 and 0.40) using $BaCO_3$ TiO_2 and SnO_2 raw materials

(2) $BaTi_{1-x}Sn_xO_3$(x=0.00, 0.15, 0.20, 0.30 and 0.40) using $BaNO_3$, TiO_2 and $SnCl_4.5H_2O$ raw materials

And also the investigations of composites of optimum composition are-

(3)1-x ($BaTi_{0.85}Sn_{0.15}O_3$) - x ($NiFe_2O_4$) (x=5%,10% 15% and 20%)

(4) 1-x ($BaTi_{0.85}Sn_{0.15}O_3$) - x (CNT) (x=5%,10% 15% and 20%)

(5) 1-x ($BaTi_{0.85}Sn_{0.15}O_3$) - x (Fly ash) (x=5%,10% 15% and 20%)

We aimed to determine the range of solubility limit of solid solution of barium titanate stannate and study the properties of composites of optimum composition. The crystal structure, dielectric properties for relaxor characteristic, electrical and magnetic characteristic of different composition and their composites have to be investigated to build up an understanding between different composition and their composites.

Chapter 2 deals experimental techniques, which have been used to study preparation and characterization of materials. Barium titanate stannate system has been successfully prepared via solid state reaction method. Further, we synthesized the Ceramics of composites and their constituent phases in a planetary ball mill (Retsch, Germany) for 6 hrs using acetone as a milling medium.

Thermal analysis (TG and DSC) of samples powders was carried out using simultaneous TG-DSC (Mettler Toledo). Crystal structure, microstructure and chemical composition in was observed by XRD (Rigaku Miniflex II), and scanning electron micrographs (Zeiss Evo18 Research). The dielectric and electrical properties were observed by a computer-controlled LCR meter (Wayne Kerr 6500 P.)

The investigation on the preparation and characterization of barium titanate stannate using $BaCO_3$ are described in Chapter 3. The thermal analysis has been studied and investigated the calcination temperature is above the 1000^0C. Analysis of the X-ray diffraction studies of calcined powder of BTS5 and BTS15 confirmed that formation of single phase solid solution $BaTi_{0.95}Sn_{0.05}O_3$and $BaTi_{0.95}Sn_{0.05}O_3$ proceeds through the formation of $BaTiO_3$ and $BaSnO_3$ phases and reaction between them at temperatures > 1100 °C . The solubility of Sn in the $BaTiO_3$ lattice is a function of heat treatment temperature. The percent of the single phase solid solution and the lattice parameter were increased with increasing calcination temperatures. At room temperature samples BTS0, BTS5 have tetragonal crystal structure whereas sample BTS15, BTS30 and BTS40 have acubic crystal structure. Dissolution of Sn ion at the lattice of $BaTiO_3$ has been probed by Fourier transform infrared spectroscopy (FTIR) technique. Scanning electron micrographs of these samples clearly exhibited well-crystalized microstructure and grain size is 3 -5 µm. Energy dispersive x-ray analysis (EDXA) studies confirmed the presence of elements Ba, Ti, Sn and O. The value of dielectric constant and phase transition temperature is Sn concentration dependent. At room temperature dissipation factor of the samples is approximately varies 0.1-0.90.

The chapter 4 demonstrated that the single phase powders nano-sized powders of solid solutions, $BaTi_{1-x}Sn_xO_3$synthesized by the solid state route using $Ba(NO_3)_2$, TiO_2 and

$SnCl_4.5H_2O$. Thermal analysis (simultaneous TGA/DSC) of the raw materials as well as of a mixture of these raw materials has confirmed that the formation of reliable solid solutions in this method takes place between 600-700°C. The formation of BTS system proceeds while heating up in three steps : (i) formation of SnO_2 from $SnCl_4$ $5H_2O$, (ii) melting of $Ba(NO_3)_2$ and (iii) reaction among molten $Ba(NO_3)_2$ and TiO_2 and SnO_2 (solid form). Therefore, we can conclude that replacement of $BaCO_3$ by $Ba(NO_2)_3$ as raw materials for the mass production of nanopowders of BTS for industrial applications is a cost-efficient and straightforward method as compared to other methods reported in the literature

X-ray diffraction technique has confirmed that synthesized powders of composition x=0.0 and 0.10 have tetragonal whereas x=0.20, 0.30 and 0.40 have a cubic crystal structure. Transmission electron microscopic studies confirmed that particles of calcined powders have a spherical shape with diameter 30-50 nm. The microstructure of BTS ceramics is small and uniform grain size as compared to same ceramics synthesized by conventional solid state route using oxide or carbonate as starting materials. The dielectric constant, dissipation factor and diffusivity are increases with increasing concentration of Sn in $BaTi_{1-x}Sn_xO_3$ systems. The remnant polarization (P_r) and coercive field (E_c) values for the samples BTS0, BTS10 and BTS20, determined from hysteresis loop are 5.54, 7.65 and 0.32 and 9.49, 9.63 and 0.47 respectively.

The chapter 5 studied that the single phase powders of $BaTi_{0.85}Sn_{0.15}O_3$ and $NiFe_2O_4$ were synthesized by solid state and Gel-combustion methods, respectively. Dense and homogeneous composites of $BaTi_{0.85}Sn_{0.15}O_3$ and $NiFe_2O_4$ were synthesized by solid state method. The formation of the composites and their constituents was confirmed by X-ray diffraction, FTIR and SEM analyses. Conduction in the samples is governed by hopping of electrons among the different ions of the elements Sn, Ti, Ni and Fe present in the BTS and composites. Variation of dielectric constant with respect to frequency shows a dispersive behavior due to Maxwell-Wagner effect. The interfacial polarization has a significant contribution for composites as compared to BTS. A relaxation phenomenon in the high-frequency range was observed in the composites which are intrinsic properties of the composites. AC conductivity, dielectric constant and dissipation factor of the composites are smaller than that of BTS. BTS and composite BTS+NF15 exhibits ferroelectric hysteresis loop at room temperature. For the composite flattened P-E loops with smaller values of the saturation polarization and larger value of coercive electric field were obtained as compared to BTS. Synthesized Nickel ferrite is in superparamagnetic state at room temperature. Composites are also magnetically ordered system. The value of saturation magnetization increases linearly with increasing concentration of ferrite phase in the composite. However, the coercive field (H_c) and remnant magnetization (M_r) for all the composite samples is larger than that of pure $NiFe_2O_4$ phase. The value of saturation magnetization and coercive field indicates that composites are soft magnetic materials. The composite may be used in transformer, inductor cores, recording heads, microwave devices and magnetic shielding.

The chapter 6 dedicated to focus on the composite of barium titanate and carbon nanotube which improve the microstructural and electrical properties of the composites. The present work on ferroelectric composites reveals that the effect of the CNT on the ferroelectric in the composites is to shift the ferroelectric–non ferroelectric phase transition to the higher-temperature side with a broad Curie temperature transition. The AC electrical conductivity is found to vary linearly with frequency in these composites within the frequency range studied. The conduction mechanism in these ferroelectric composites is found to obey polaron hopping in the high-temperature region.

The chapter 7 concluded that the fly-ash generally which waste material enhance the dielectric properties of the barium titanate stannate. The thermal analysis of composites was studied by TG-DSC, which results shows that the composite behaves thermal stability. The morphology of new composite materials was studied by scanning electron microscopy (SEM) and analysis of grain size of composites varies from 1-3μm. Dielectric constant and dissipation decrease with increasing the fly ash contents.

Chapter 8 gives conclusions derived from the present investigation. Suggestion for future work is also given in this chapter.