Synthesis and characterizations of lead free KNNT & Ni doped KNNT ceramics

A thesis submitted in partial fulfilment

FOR THE DEGREE OF MASTERS OF SCIENCE IN PHYSICS

by

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Certificate

This is to certify that the thesis entitled "Synthesis and characterizations of KNNT and Ni-doped KNNT ceramics" submitted by Meeta Ashok Kamde(410PH2128) in the partial fulfilments for the requirement for the award of Master of Science Degree in Physics Department at NIT, Rourkela, is an authentic work carried out by her under my supervision and guidance.

The work incorporated in this thesis has not been submitted elsewhere, in part for the fulfilment of any other award or degree or diploma at any institute or any university.

Date: 12.05.2012   Prof.Pawan Kumar

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<u>Acknowledgement</u>

I would like to express my deep and sincere thanks to the people whose help made the present project work a success. I express my deep sense of gratitude to my supervisor Prof. Pawan Kumar, Department of Physics, NIT, Rourkela, for his valuable guidance, motivation and full attention at all stages in my project work.

I am extremely thankful to Prof. S. Jena, Head, Department of Physics and all the faculty members of Physics department for providing all kinds of possible help and advice during the course of this work.

I would like to thank Mr. S. Naresh, Mr. Prakash Palei, Ms. Sridevi Swain and Mr. Subrat Kar with immense pleasure for their valuable guidance and co-operation which I have received during last one year.

I wish to thank my lab partners and other friends for their help and suggestions throughout my project work.

Lastly, a heartily thanks to my parents for their blessings, inspiring thoughts and moral support.

Contents:

ABSTRACT

In order to replace the lead based ceramics with the same properties of piezoelectricity and other electrical properties, lead free ceramics like KNNT perovskites were developed.. The samples with KNNT and Ni-doped KNNT ceramics were prepared. KNNT-Ni was prepared by doping 1% Ni in KNNT:. Both types of samples were calcined and sintered in microwave furnace. Different characterization techniques like XRD, SEM etc were used to characterize these ceramics. Single perovskite phase formation was confirmed by the XRD study. Electrical properties such as dielectric constant and dielectric loss were studied as a function of temperature and frequency.

Chapter-1

1. Introduction:

The dielectric materials which make use of very high dielectric constants and low dielectric losses are generally used in applications such as capacitor [1]. These solid capacitors are compact in size and rugged and are utilized widely in the devices such as computers, cell phones, micro-electronic devices, etc. The dielectric ceramics are usually the basis of ceramic capacitors. With the polarizability of the material, its dielectric constant is usually determined. The word "dielectric" is being derived from a Greek word, which means "across" or "through". Hence, the dielectric can be referred to a material which permits the passage or flow of the electric field or electric flux. Dielectric materials have some interesting properties because here the electric field has the ability to polarise the material to create an electric dipole. The dipole is an entity where the equal number of positive and negative charges is separated by a small distance and the electric dipole moment is given by

$$\mu = q \cdot dl$$

where, q can be either of the two point charges of opposite signs i.e. positive or negative, which are separated by distance dl [2]. The electric dipole is a vector quantity. From the discovery by Faraday's experiment, the result was concluded that the capacitance of any condenser can be increased if the space between the conductors is filled with a dielectric material. If the capacitance of the condenser with the region between the conductors evacuated be C_0 and C be its capacitance when the region is filled with any dielectric, then the ratio

$$\frac{C}{Co} = \varepsilon_r$$

which is independent of the shape or dimension of the conductor. Here, ε_r is called the relative permittivity or the dielectric constant of the medium. The dielectric constant of the material is a macroscopic quantity which measures how effective the electric field is in polarising the material [3].

1.1. <u>Polarizability and susceptibility:</u>

When a dielectric material is placed in an external magnetic field E_0, the charges i.e. positive and negative charges gets displaced from their equilibrium positions by some atomic diameter distance, which results in the formation of large number of dipoles, each having some dipole moment in the direction of field. The material thus gets polarised with a polarisation P, which is defined as the dipole moment per unit volume of the material. The effect of polarisation is to reduce the magnitude of the external electric field. Thus the resultant field becomes less as compared to the applied field E_0, i.e.

$$E = E_0 + E_P$$

The field E_P is called as the polarisation field since it tends to oppose the applied electric field E_0 in the material. For any dielectric fields, the polarisation is directly proportional to the field E. It can be expressed as

$$P = \varepsilon_0 \, \chi_e \, E$$

where, ε_0 is the permittivity of the free space,

χ_e is the electric susceptibility.

Thus it can be concluded that the electric susceptibility is the measure of the polarisation per unit electric field of the material [4].

1.2 <u>Local electric field:</u>

The electric field of an atom or molecule, acting on the site is significantly different from the macroscopic electric field E and it is called the *local field.* This is the field which is responsible for the polarisation of each atom of a solid. The local field is given by the *Lorentz relation* as,

$$E_{LOC} = E_O + E_{dep} + E_L + E_{dip}$$

where, E_O is the field owing to fixed charges external to the dielectric body.

E_{dep} is the depolarisation field caused by the uniform polarisation of the dielectric.

E_L is the field at centre of cavity created by the charges induced on the imaginary surface bounding the fictitious cavity.

E_{dip} is the field at the centre of the cavity contributed by dipoles within the cavity.

1.3 <u>Dielectric constant and polarizability:</u>

The electric displacement vector for an isotropic can be defined as:

$$D = \varepsilon_0 \varepsilon_r E = \varepsilon_0 + P$$

where, ε_r is the relative permittivity or dielectric constant of the dielectric. It is a scalar quantity and dimensionless. It can also be used to define the dielectric constant as

$$\varepsilon_r = \frac{\epsilon_0 E + P}{\epsilon_0 E}$$

$$= 1 + \chi_e$$

Thus dielectric constant is also a measure of the polarisation of the material, like susceptibility. Hence, for larger polarisation per unit resultant field, greater will be the dielectric constant of the dielectric.

Polarizability α for an atom can be defined as the dipole moment per unit local field of the atom, i.e.,

$$p = \alpha \, E_{LOC}$$

Thus the polarizability is an atomic property and dielectric constant is a macroscopic property that depends on the arrangement of atoms within the crystal. The polarizability for N number of atoms per unit volume can be expressed as

$$P = N \, p$$

$$= N \, \alpha \, E_{LOC}$$

The expression for Clausius-Mossotti relation is given by

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N \, \alpha}{3 \, \epsilon_0}$$

This relation relates the dielectric constant with the atomic polarizability, if the condition of cubic symmetry holds [5].

1.4 Sources of polarizability:

The resultant polarizability of the dielectric crystal is due to the following three types of contributions:

1. Electronic polarizability
2. Ionic polarizability
3. Dipolar polarizability
4. Space charge polarizability

1.4.1 Electronic Polarizability:

The electronic polarizability is due to the displacement of the electron cloud of an atom relative to its nucleus in the presence of an applied electric field as shown below:
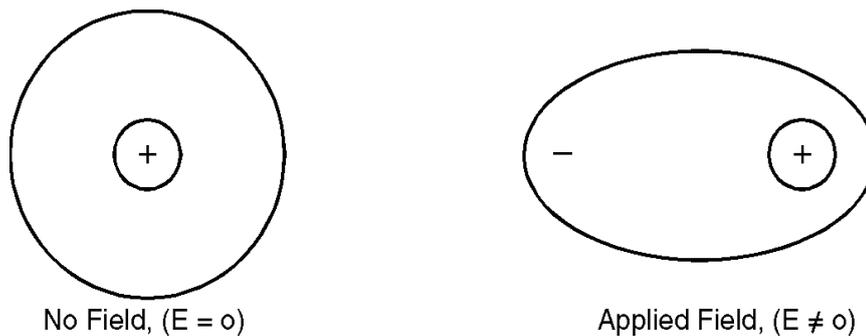

No Field, (E = o)   Applied Field, (E ≠ o)

Fig. 1(a) shows unpolarized atom & 1(b) shows polarized atom in applied field.

This type of polarization is produced by the opposite displacement of positive nuclei and negative electrons within the same atom. The polarization as well as the dielectric constant of the material, at optical frequency results mainly from the electronic polarizability. At optical frequency, the *Clausius-Mossotti* relation can be modified as:

$$\frac{n^2-1}{n^2-1} = \frac{1}{3\epsilon_0} \Sigma N_j \alpha_j$$

where, n is the refractive index and ϵ_r has been replaced by refractive index. It is independent of temperature.

1.4.2 Ionic Polarizability:

The ionic polarizability arises due to displacement of a charged ion relative to other ions in the solid. In case of ions, the applied electric field tends to displace the positive and

negative ions in opposite direction, causing a change in length of the ionic bond. The effect of this change in length is to produce a net dipole moment in the unit cell. Since this polarization is due to relative displacements of ions, it is called as ionic polarizability. Assuming the forces near equilibrium as simple harmonic in the presence of electric field, the displacement Δx is given by

$$\beta \Delta x \cong e E$$

where β is the force constant. Thus the ionic polarizability is determined as

$$\alpha_i = \frac{P}{E} = \frac{e \Delta x}{E} = \frac{e^2}{\beta}$$

The ionic contribution is important at low frequencies. It is also temperature independent.

1.4.3 <u>Dipolar Polarizability:</u>

The molecule having a permanent dipole moment is called a dipolar or polar molecule and a substance comprising such molecule is called a dipolar substance. The dipolar polarizability is the property of dipolar substance. In the absence of electric field the dipoles have random orientations and hence there is no net polarization. But when the field is applied, the dipoles orient themselves along the field and produce orientational or dipolar polarizability. But the orientations along the field direction are continuously disturbed by the thermal agitation. Therefore an equilibrium is attained in which the dipoles make zero to π angles with the field directions. The potential energy of such a molecule of dipole moment **p** oriented at an angle θ with the field direction is given by

$$U = -\textbf{p}. \text{E} = -pE \cos \theta$$

The dipolar polarizability per molecule is given by

$$\alpha_d = \frac{p^2}{3kT}$$

Thus the existence of dipolar polarizability depends on whether the molecules possess a permanent dipole moment. This polarizability depends on the temperature [6].

1.4.4 Space charge polarizability:

This is the polarizability of the dielectric which occurs when charge carriers are present, which can migrate an appreciable distance through dielectric material but which become trapped or cannot discharge at an electrode. It is also called as interfacial polarization. Its contribution towards the net polarizability is very low.

1.5 Frequency dependence on net polarizability:

The net polarizability of a dielectric is given by

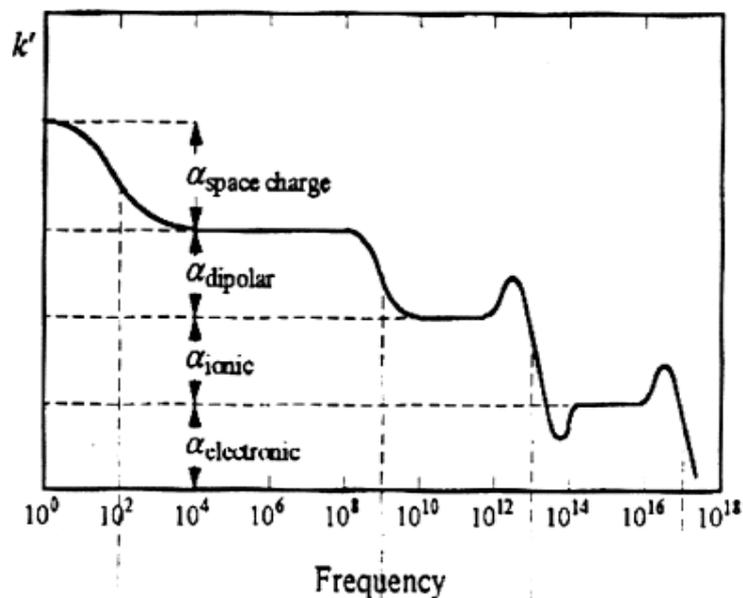$$\alpha = \alpha_e + \alpha_i + \alpha_d + \alpha_s$$

Fig.2 shows frequency dependence of various contributions to polarizability

As it is shown in the above figure, the polarizability decreases with increase in temperature. This type of polarizability can be explained on the basis of the relaxation times of the various contributing polarization processes. When the frequency of the applied field is quite large as compared to the inverse of the relaxation time for a particular polarization process, the contribution of that process to polarizability is negligible. As the dipolar contribution is maximum for the space charge process and then the dipolar process and minimum for the electronic process, the space charge contribution and dipolar contribution disappears first followed by the ionic and electronic contributions [7].

Chapter-2

Literature survey and material selected:

The most important and widely used materials for the piezoelectric transducers, buzzers, sensors, actuators, transformers and other electronic devices, is the piezoelectric ceramic, because of their excellent electrical property. But these piezoelectric ceramics contain mostly lead based ceramics which contain more than 60 weight percentage of lead [8]. Lead based ferroelectric materials are the most commonly used piezoelectric [9]. Lead based ceramics have excellent electrochemical properties also [10]. Since the lead is a toxic material to the human health and environment. Hence, the lead free piezoelectric ceramic have attracted great attention from the recent few years.

Lead based ceramics also involves the issues of restoring and recycling the materials as the lead maintains in the environment for a large time and it also damages the brain, nervous system and also accumulates in living tissue causing a lot of health problems. Also, its improper disposing causes environmental issues in the eco-system and also causes acid rain. Hence the lead free ceramics are mostly preferred these days as they don't involve such problems as like that of lead based-ceramics which causes the environmental and health hazard problems.

The classification of lead free materials is done in four categories:

1. Bismuth layered structure
2. Tungsten-bronze structure
3. Pyrochlore structure
4. Perovskite structure

Among all the above mentioned structures, perovskite structure gets special attention because of its simple structure as compared to other structures and also it is very easy to prepare. Perovskite structure is any material with the same type of crystal structure as that of Calcium Titanium Oxide ($CaTiO_3$), known as the perovskite structure. The perovskite compounds have a general formula of ABX_3, where 'A' and 'B' are the two cations of different sizes and 'X' is an anion that is bonded to both of them. Here atom 'A' is usually larger than that of 'B' atom. Complex perovskite structure has two different B-site

cations[11]. The main advantage of perovskite structure is that, here many different types of anions and cations can be substituted on both A and B sites without any change in the overall structure. These compounds are used as sensors and catalyst electrodes in certain types of fuel cells and also for the memory devices and spintronic applications. These structures contains properties like ferroelectricity, colossal magnetoresistance, spin dependent transport, superconductivity, charge ordering, high thermo power and other structural, magnetic and transport properties. Ceramic materials have perovskite like structure.

In order to replace the lead based ceramics with the materials of same properties various experiments were being performed. The KNN-based ceramics showed relatively high piezoelectric properties as because of the formation of Morphotropic Phase Boundary (MPB) [12]. MPB plays a vital role in PZT ceramics as they show a maximum of piezoelectric and dielectric property around the MPB. MPB is independent of the temperature and MPB in KNN ceramics is an orthorhombic tetragonal polymorphic phase transition [13].

KNN showed its lead free piezoelectric properties and has high curie temperature~420^0C with large electromechanical coupling factors [14]. It is a combination of both ferroelectric ($KNbO_3$) and anti-ferroelectric ($NaNbO_3$). To enhance its piezoelectric properties KNN ceramics were studied with Tantalum. The substitution of the element Tantalum in the compound KNN makes the ceramic more relaxor, which as a result exhibited a broadening transition peak [15]. KNNT ceramics contain quadrate grains [16]. Tantalum has effect of suppressing the growth of the grain during the sintering process. Tantalum compound in KNN ceramics, on XRD characterisation showed orthorhombic symmetry without any secondary phases which suggests that Ta in KNNT ceramics incorporates well in the B-sites [17]. With increased concentration of Tantalum, single phase pattern were observed in XRD data which indicated that Ta is beneficial for the preparation of single phase powders. The XRD pattern of this compound was found same as that of $K(Nb,Ta)O_3$, except that the 2θ values shifted towards the high angle, which indicated that Na^+ ions were doped into this crystal lattice. Here, sodium and potassium volatilizes easily during high temperature sintering [18]. The dielectric properties were found better for the samples for a sintering temperature greater than 1000^0C as compared to those ceramics which were sintered at a temperature less than 1000^0C. Enhanced dielectric properties were also observed, which were due to the dense structure and high density of the ceramic sample [19].

KNNT ceramics also showed higher values for d_{33} and d_{31} as compared to that of KNN [20]. These ceramics also have good thermal stability as compared to that of KNN-ceramics [21]. Lv. Et al. proved that the composition of KNNT as $(K_{0.5}Na_{0.5})(Nb_{0.7}Ta_{0.3})O_3$ ceramics have the highest value of the piezoelectric coefficient [22]. The ceramic KNNT is very difficult to sinter at high temperature and it is also difficult to obtain dense and well sintered ceramic of this compound using ordinary sintering process due to the deviation in stoichiometric proportion caused by the volatility of the alkaline elements present. Various processing methods such as hot press and spark plasma are used to improve the sintering parameters [23].

2.1 <u>Objectives:</u>

- To synthesis the ceramic material consisting of KNNT and Ni-doped KNNT and calcinating it by using the microwave furnace.

- Sintering the sample using the microwave furnace.

- To characterise the samples of KNNT and Ni-doped KNNT by various techniques like X-Ray Diffraction (XRD) for formation of phase and to determine the crystallite size, etc., Scanning Electron Microscope (SEM) for the surface morphology, density and electrical study for dielectric constant and transition temperature.

Chapter-3

Synthesis Process and Experimental Technique:

The synthesis of the ceramic samples involves a number of steps to get the desired samples which are described below:

Raw material:

The raw materials used for the synthesis of the $K_{0.5}Na_{0.5}Nb_{0.5}Ta_{0.5}O_3$ were first weighed according to their stoichiometric ratio as per required in the desired ceramic. The size of the particles should be in the sub-micron range for the reaction to occur by atomic diffusion.

Mixing:

The constituents were then accomplished using an agate mortar and pestle. Here the mechanical mixing is done which can be done either by ball milling or by attrition milling for a short time. The mixed ceramic compounds were then ball milled for about 8 hours for proper mixing of the powders in acetone medium by using the zirconia balls.

Calcination:

Calcination is a thermal treatment process to ores or other materials to bring about a thermal decomposition, phase transition or removal of a volatile fraction. This process of calcination is done as the phase reaction of the constituents take place by the inter-diffusion of the ions, giving the ferroelectric phase. In other words, by using this thermal decomposition process, the phase transition of ceramic materials takes place. The calcination process normally takes place at a temperature below the melting point of the product materials. Calcination reaction usually takes place at or above the thermal decomposition temperature or the transition temperature (for phase transition). The homogeneity and density of the final ceramic product depends on the calcinations temperature. Calcination is done mainly to remove the water and carbon dioxide components from the compound to get the desired product.

Grinding:

After calcinations, the powder was grinded in the mortar and pestle in order to remove the lumps which were produced from calcinations of the sample.

Binder addition:

Binder is a liquid i.e. Poly Vinyl Alcohol (2 mol%) added with distilled water that is added to the dry ceramic powder in order to draw the grain particulates together in such a way that they aid the granulation of the powder and provides the strength to the sample. In other words, it provides bridges between the particles.

Shaping:

Shaping is done by the powder compaction method. In this process, a high pressure is applied to a weighed quantity of the calcined powder to give it the desired shape.

Binder burnout:

This is a processing step which is being performed before the sintering of the samples. The pellets are heated at a temperature of about 600^0 C with the soaked time for about two hours in which the binder is burnt out of the ceramic sample.

Sintering:

It is the thermal treatment of the powder at a temperature below the melting point of its main constituents and higher than that of calcinations temperature. It is done for the purpose to increase the strength by bonding together of the particles. It is a kind of firing process. With the increase in sintering temperature, the density of ceramics increases. Sintering temperature is that temperature at which the grains of the solid formed from the powder starts connecting with one another through their boundaries and merges to form a larger grain. By reducing the particle size, sintering can be improved as the driving force is inversely proportional to the particle size [24].

Electroding:

A thin layer of metallic silver is dispersed in a liquid solution to form a paste. This paste of silver is then applied as a layer on the surface of the sintered pellets. The coated layer is very thin, having zero resistance practically with a nice chemical and physical durability. The silver pasted pellets are then heated to form a continuous conducting layer to get properly bonded with the surface of the ceramic pellet.
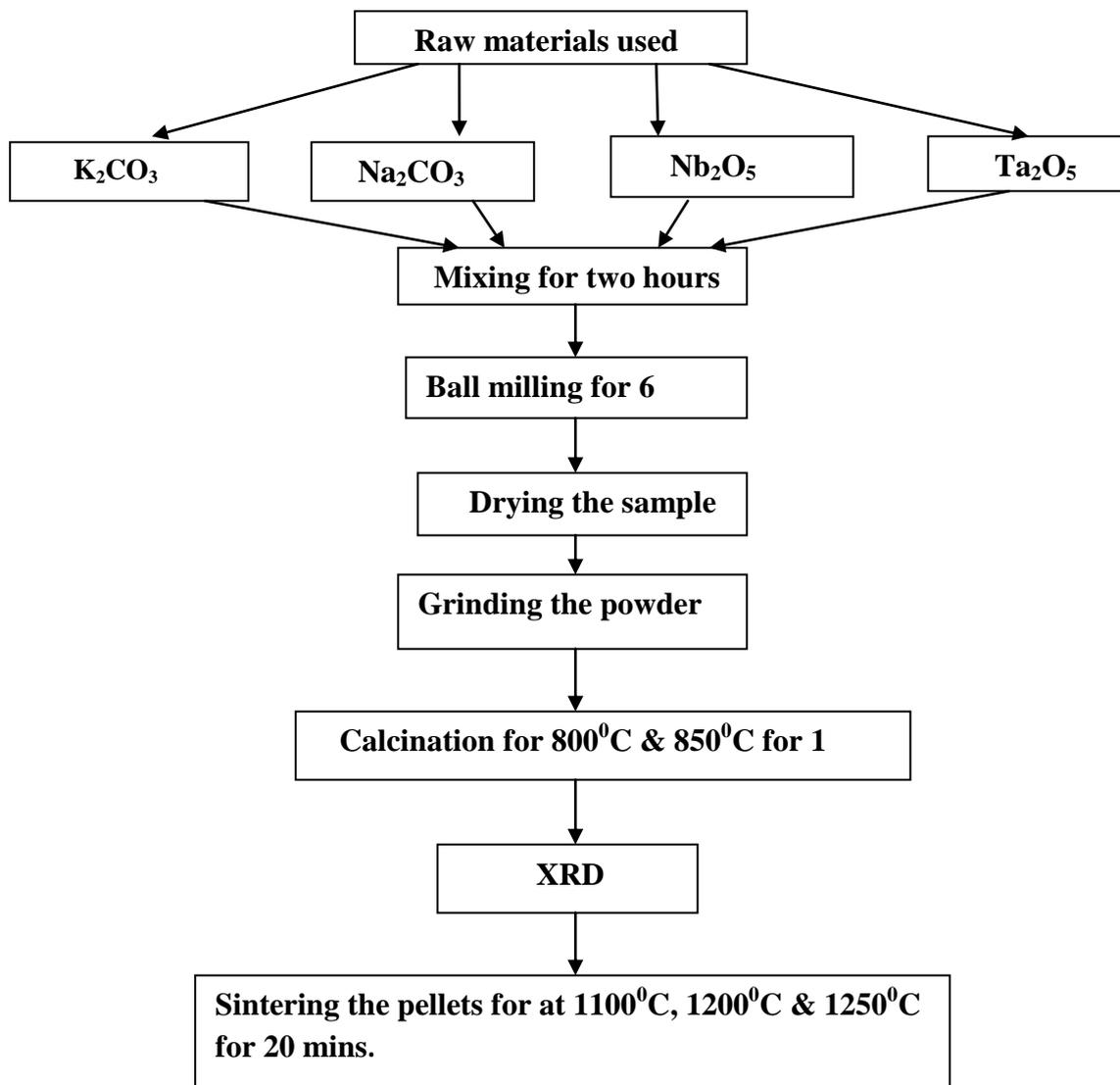
Flow chart for the synthesis of KNNT:

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                    ┌─────────────────────┐
                    │  Raw materials used │
                    └─────────────────────┘
        ┌──────────┬───────────┴───────────┬──────────┐
        ▼          ▼                       ▼          ▼
   ┌─────────┐ ┌─────────┐          ┌─────────┐ ┌─────────┐
   │ K₂CO₃   │ │ Na₂CO₃  │          │ Nb₂O₅   │ │ Ta₂O₅   │
   └─────────┘ └─────────┘          └─────────┘ └─────────┘
        └──────────┴───────────┬───────────┴──────────┘
                               ▼
                    ┌─────────────────────┐
                    │ Mixing for two hours│
                    └─────────────────────┘
                               ▼
                    ┌─────────────────────┐
                    │  Ball milling for 6 │
                    └─────────────────────┘
                               ▼
                    ┌─────────────────────┐
                    │  Drying the sample  │
                    └─────────────────────┘
                               ▼
                    ┌─────────────────────┐
                    │ Grinding the powder │
                    └─────────────────────┘
                               ▼
               ┌──────────────────────────────┐
               │ Calcination for 800°C &      │
               │ 850°C for 1                  │
               └──────────────────────────────┘
                               ▼
                    ┌─────────────────────┐
                    │        XRD          │
                    └─────────────────────┘
                               ▼
         ┌──────────────────────────────────────────┐
         │ Sintering the pellets for at 1100°C,     │
         │ 1200°C & 1250°C for 20 mins.             │
         └──────────────────────────────────────────┘
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Raw materials used → K_2CO_3, Na_2CO_3, Nb_2O_5, Ta_2O_5 → Mixing for two hours → Ball milling for 6 → Drying the sample → Grinding the powder → Calcination for 800^0C & 850^0C for 1 → XRD → Sintering the pellets for at 1100^0C, 1200^0C & 1250^0C for 20 mins.

Fig.3 Flow chart showing the synthesis process of KNNT

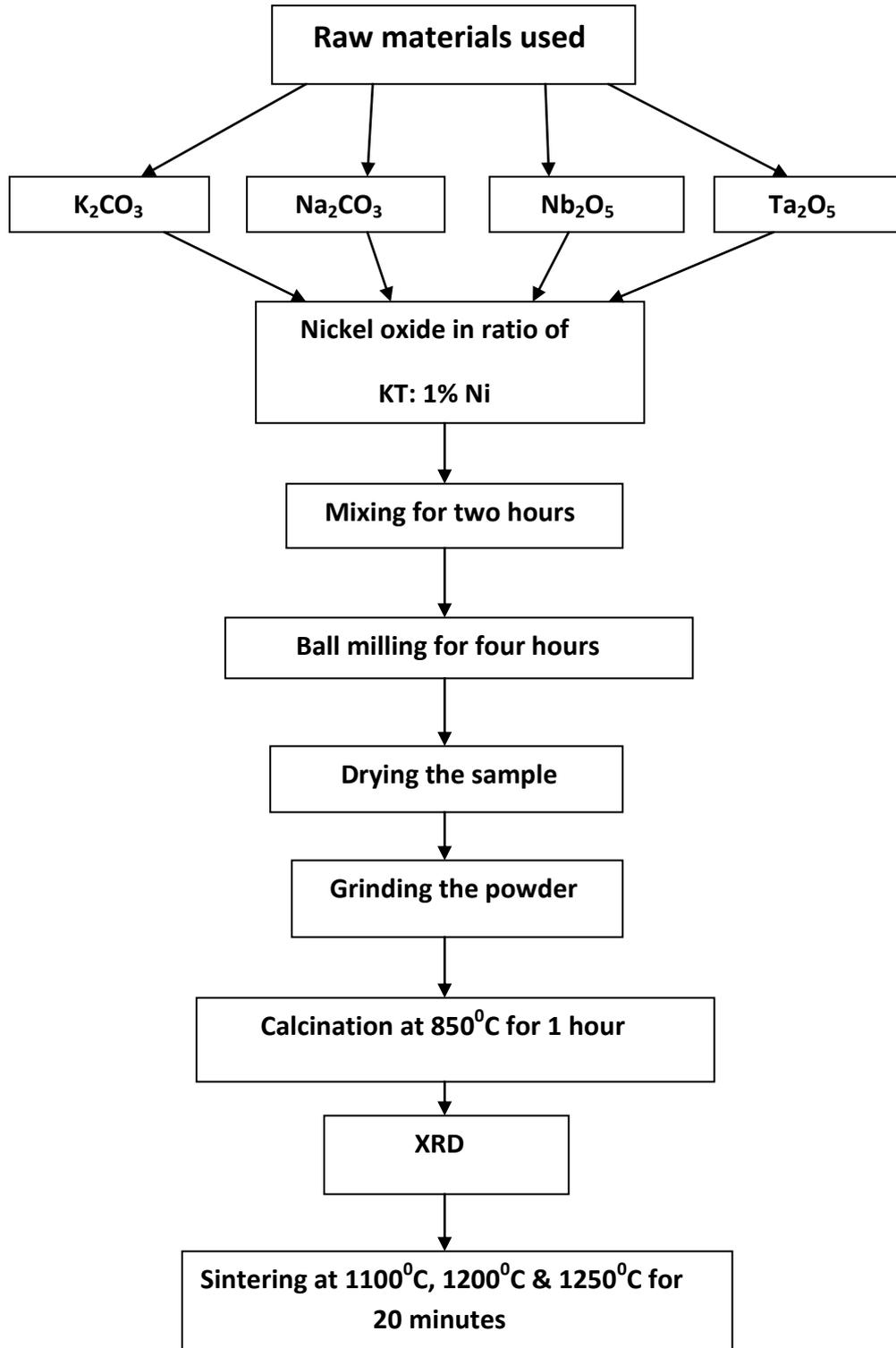## Flow chart for synthesis of KNNT-Ni:

Fig.4 Flow chart showing the synthesis process for KNNT-Ni

3.1 <u>Experimental procedure:</u>

Lead free $K_{0.5}Na_{0.5}Nb_{0.5}Ta_{0.5}$ and Ni-doped $K_{0.5}Na_{0.5}Nb_{0.5}Ta_{0.5}$ ceramics were prepared using the microwave reaction route. The starting materials that were used are K_2CO_3, Na_2CO_3, Nb_2O_5 and Ta_2O_5 with 99% purity, for KNNT ceramic. For Ni-doped KNNT ceramic, in addition to the above compounds NiO was also taken. The stoichiometric weights of all the compounds were calculated and as per the calculation, the compounds were mixed with the acetone in mortar and piston. The mixture of the ceramic was then mixed with the zirconia balls were taken out of the slurry ceramic and it was again grinded in the mortar and piston till the time all the acetone was removed from the ceramic compound. After the ceramic compound turns into powder, the powder was carried out for the calcinations in a microwave furnace at 800^0C and 850^0C for the KNNT ceramics and 850^0C for Ni-doped KNNT ceramics for 1 hour each. The X-ray diffraction technique was used then to confirm the single phase formation of the ceramic compound. The X-ray diffraction analysis of the sample was performed by the PHILIPS X-RAY DIFFRACTOMETER using CuK_α with wavelength λ=0.0154 nm radiation to examine the phases present there in the system.

The powder formed after the calcinations were then mixed thoroughly with 2 wt% of polyvinyl alcohol (i.e. PVA) binder solution and then again a fine powder was formed from the mixed compound of ceramic and binder. This powder was then pressed within a diameter of about 10mm and thickness about 1.4mm to 2mm under a pressure of about 60 MPa using the mechanical cold press.

The pellets formed were then sintered at temperature greater than that of calcinations temperature. The temperature used for sintering the samples were 1100 K, 1200K and 1250 K for 20 minutes for both the samples formed by the KNNT and Ni-doped KNNT ceramics. Sintering was also done by the microwave furnace with a heating rate of $30^0C/minute$. Sintered samples have good dimensional accuracy with excellent surface finishing and its porosity inherent is useful for specialized applications like filters, etc. By the reduction in initial particle size, sintering of the sample can be improved as the driving force is inversely proportional to the particle size [24]. The pellets after sintering were observed under a JSM-6480LV JEOL, Japan, SEM (Scanning Electron Microscope). The grain sizes of the samples were then observed from the images of the SEM. Also, using Archimedes principle, the bulk densities of the samples of KNNT and KNNT-Ni were measured by observing their dry

weights, soaked weights and suspended weights. Metallic silver with solution forming a silver paste was then applied on both sides of the samples for their electrical measurements. Using a computer interfaced HI0KI 3532-50 LCR-HITESTER, dielectric constant (ε_r) and dielectric loss (tanδ) were measured as a function of temperature.

3.2 <u>Route for synthesis:</u>

Microwave Route for calcinations and sintering of the sample:

Microwave heating is difficult from the conventional heating. The microwaves have electromagnetic radiations with their wavelengths ranging from 1 mm to 1 m in the free space with a frequency between 300 GHz to 300 MHz respectively. Now a day, microwaves are generally used for industrial and scientific applications at the frequency of 2.45 GHz. In this process, the heat is generated internally. Here, the heat is generated internally within the material instead of originating it from any external sources, hence there is an inverse heating profile created here [25]. The material is heated by the energy conversion. Hence the heating process is very rapid here. Conventional technique uses the energy transfer mechanism. In microwave heating, there is almost 100 % conversion of the electromagnetic energy into the heat i.e. the energy gets largely within the sample itself, unlike the conventional heating, where there occurs significant thermal energy losses. Microwave heating is the function of material which is being processed when the material itself is microwave sensitive (i.e. material with permanent electric dipoles). In this route, the energy losses are much lesser than as compared to those processed with the samples or materials by the conventional heating. It gives the homogeneous and fast heating of the ceramics which can avoid micro-cracks, Kirkendall effect, internal stresses, etc. [26] This route of heating has many significant advantages over the conventional heating methods [1-5], which includes time and energy saving, heating rates are very rapid i.e. greater than 400^0 C/min, also have reduced processing time and temperature, fine microstructures and hence improved mechanical properties, enhancement in sintering and most important, it is an environmental friendly processing and so on.

In the microwave processing of ceramics, there occurs an interaction between microwaves and matter that take place through the electric field vector and magnetic field vector of the electromagnetic field of the microwaves and involves the polarisation and conduction processes. The objective of obtaining the finer microstructures in the microwave

processed products has also led its applications for the development of transparent and translucent ceramics for a variety of applications [26].

3.3 <u>Characterisation technique:</u>

3.3.1 XRD (X-Ray Diffraction):

      X-rays are a form of electromagnetic radiation. These rays have a wavelength in between 0.01 nm to 10 nm range and have energy of about 120 eV to 120 KeV. X-rays have shorter wavelengths than ultra-violet rays but longer than gamma radiations. X-ray diffraction technique is an analytical technique that gives information about the chemical composition, crystal structure, phase formation, crystallite size, unit cell lattice parameter, Bravais lattice symmetry, texture and other physical properties of the sample material or specimen [27].
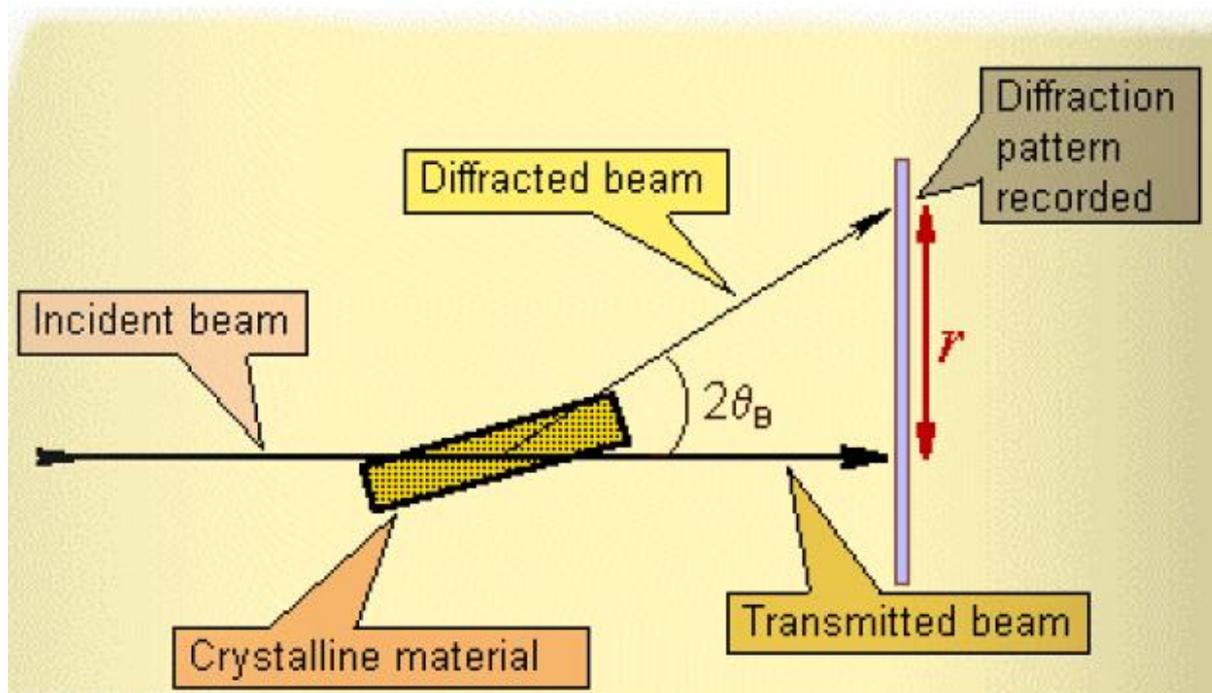
Fig.5 shows the phenomenon of XRD

3.3.2 SEM (Scanning Electron Microscope):

      It is a type of electron microscope. SEM captures the images of the sample by scanning it with a beam of electrons in a rectangular pattern (Raster scan). Scanning Electron

Microscope reveals the information about the surface topography, composition and electrical conductivity of the specimen used. SEM includes signals of the secondary electrons, back scattered electrons, etc. Back scattered electrons are the electrons which get reflected from the sample by elastic scattering. Intensity of the back scattered electrons is strongly related to the atomic number of the specimen. Hence, back scattered electrons can provide good information about the distribution of the different elements present in the sample. Tungsten is usually used in SEM as thermionic element guns as they have highest melting point, lowest vapour pressure of all metals and has low cost.

3.3.3 Density measurement:

The density measurement of the samples is done by using the Archimedes principle. Using this principle, the bulk density of the sample can be calculated as:

Density of the sample = Dry weight / (Soaked weight - Suspended weight) * ρ_l

where, ρ_l is the density of the liquid medium used. Here, kerosene is used.

3.3.4 Dielectric measurement:

The pellets coated with the silver paste were used to make the measurements. Using the computer interfaced HIOKI 3532-50 LCR-HITSTER. The data was collected for dielectric constant (ε_r) and dielectric loss (tan δ) at different temperatures.

Chapter-4

Results and discussions:

4.1 XRD (X-Ray Diffraction):

__For KNNT:__
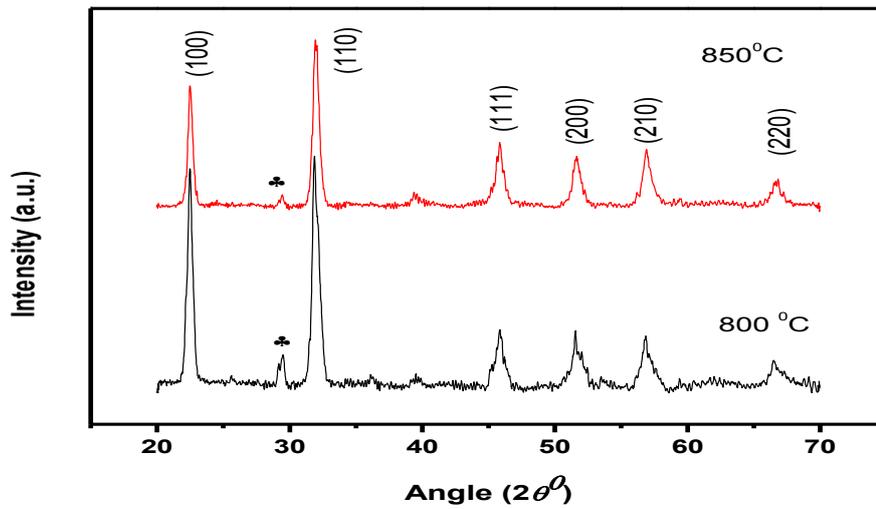
Fig. 6 shows XRD pattern for KNNT

__For KNNT-Ni:__
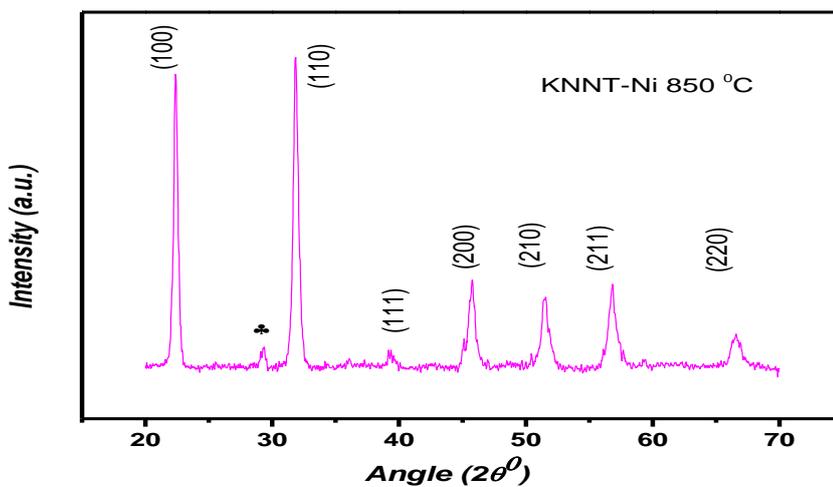
Fig7 shows the XRD pattern for KNNT-Ni

The peaks were found to be distinct and sharp, which indicated good homogeneity and crystallinity of the synthesized ceramic samples . Both the samples KNNT and KNNT-Ni gave the peaks at same values of (hkl). A small peak before 30^0 was obtained which may be due to the impurity present in the sample. Both the ceramic samples showed an orthorhombic perovskite phase. The characteristic peaks at 2θ was obtained for ~45.5^0 [28]. No secondary peaks were obtained from the XRD patterns.

4.2 SEM Analysis (Scanning Electron Microscope):

For KNNT
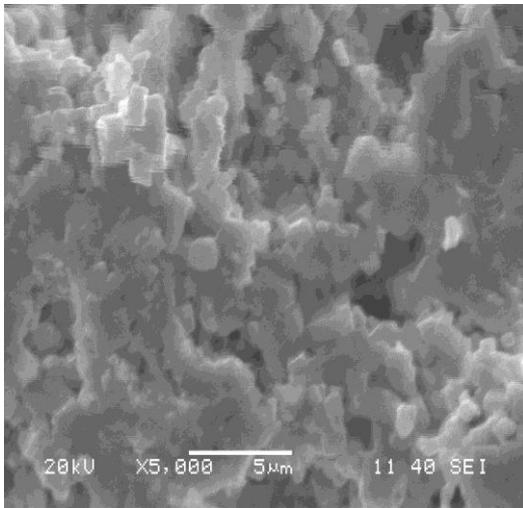
(8-a) KNNT-1100^{0}C
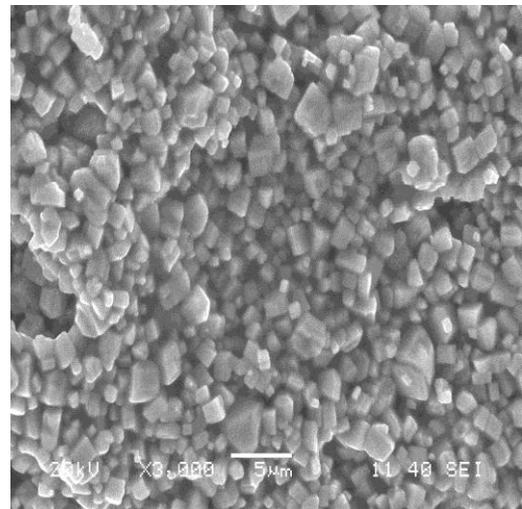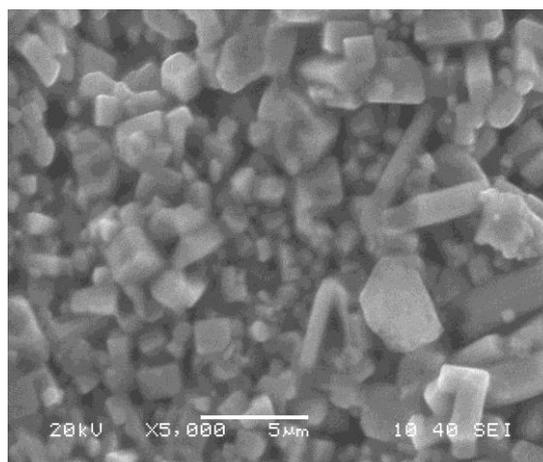
(8-b) KNNT-1200^{0}C

(8-c) KNNT-1250^{0}C

Fig. 8a, 8b & 8c shows the SEM micrographs for KNNT at 1100^{0}C,1200^{0}C & 1250^{0}C

Ni-doped KNNT:
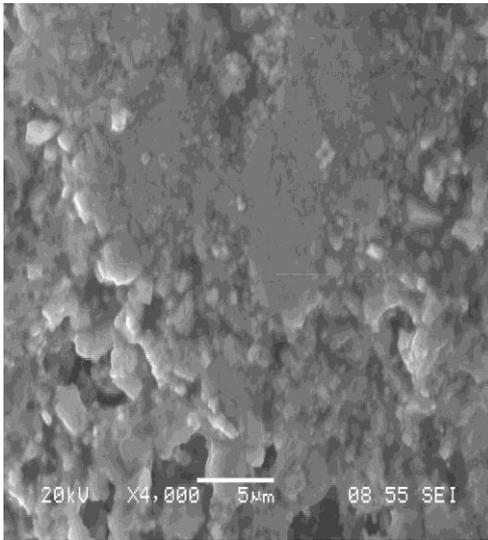
(9 a) KNNT-Ni at1100^{0}C
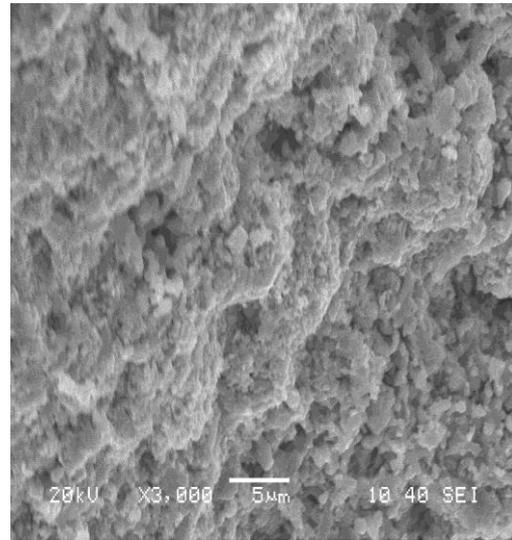
(9 b) KNNT-Ni at 1200^{0}C
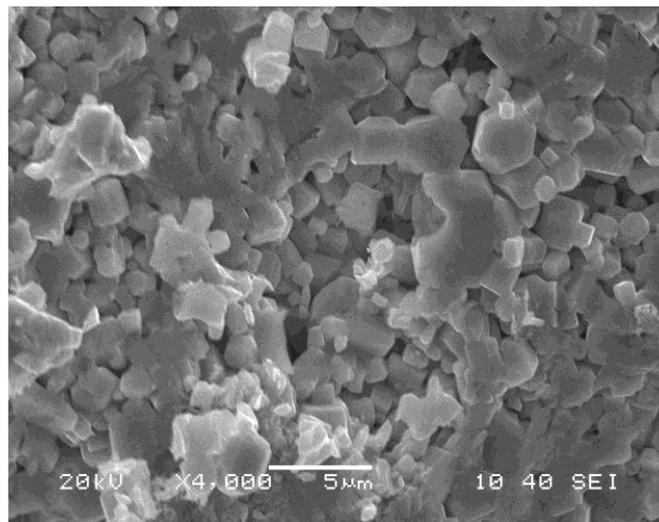
(9 c) KNNT-Ni at1250^{0}C

The SEM images represent the micrographs for KNNT and KNNT-Ni at different sintering temperatures of 1100^{0}C, 1200^{0}C and 1250^{0}C. From these images the grain sizes were calculated which are listed in the table below. From the table it can be observed that with the increasing temperature the grain size increases in both the ceramic samples of KNNT and KNNT-Ni. But the grain growth in KNNT-Ni is less than the grain growth in KNNT. So it can be concluded that the addition of Nickel in KNNT reduced the growth of the grain size.

Sintering temperature	KNNT	KNNT-Ni
1100^0C	1.58μm	1.41μm
1200^0C	1.96μm	1.57μm
1250^0C	2.05μm	1.82μm

Table 1 shows the grain size of KNNT & KNNT-Ni at different temperatures.

4.3 Density Measurement:
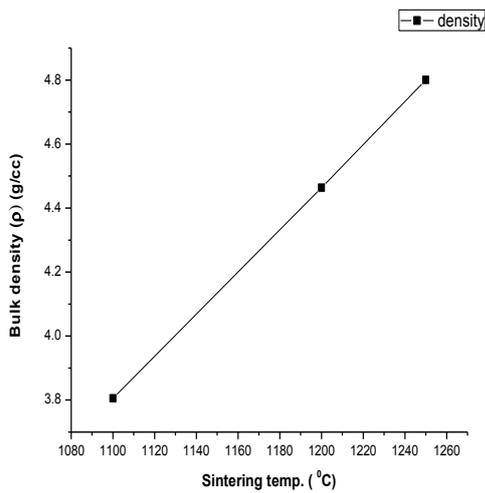
1. <u>**KNNT:**</u>   2. <u>**KNNT-Ni:**</u>
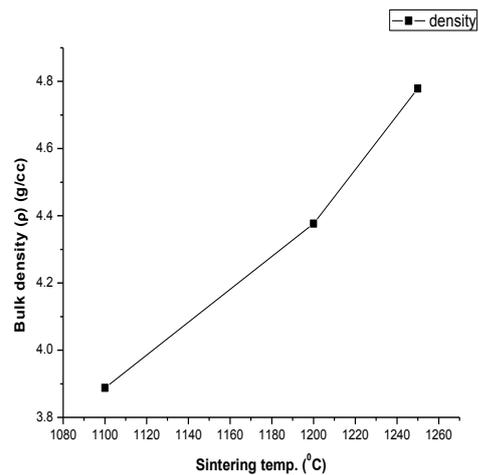
**fig.10 Bulk density of KNNT & KNNT-Ni as a function of temperature**

From the above figure, it is clear that with increase in sintering temperature of both KNNT and KNNT-Ni, the bulk density increases. For KNNT, the graph gives is linear relation but for KNNT-Ni, it is slightly bent. At 1250^0C, the density of KNNT was observed to be 4.81 g/cc whereas for KNNT-Ni, it was observed to be 4.78g/cc. Thus the density of KNNT is more as compared to that of KKNT-Ni, at high temperature.

4.4 Dielectric measurement:

KNNT sintered at 1100^{0}C:
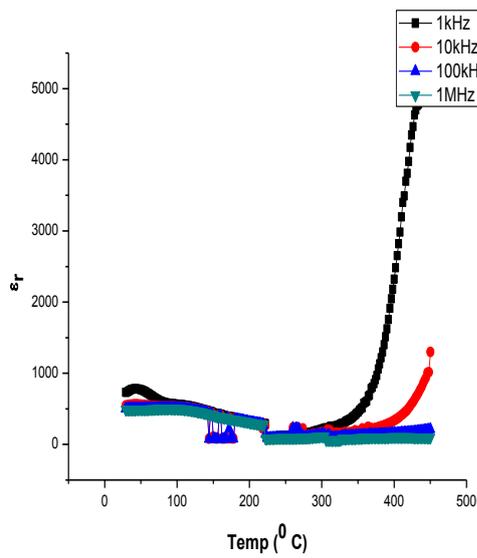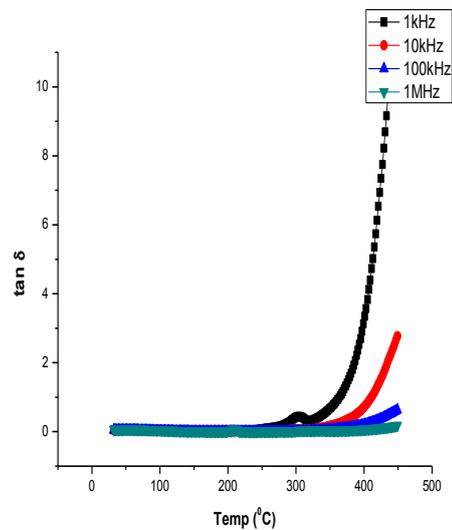

11(a)
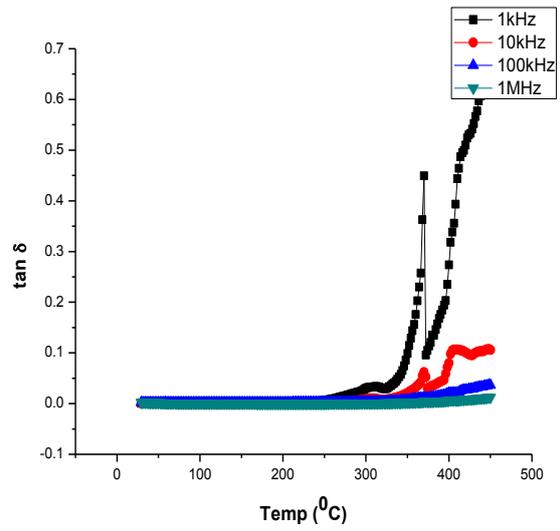
11(b)

Fig.11(a) & 11(b) gives the dielectric constant & loss at 1100^{0}C for KNNT
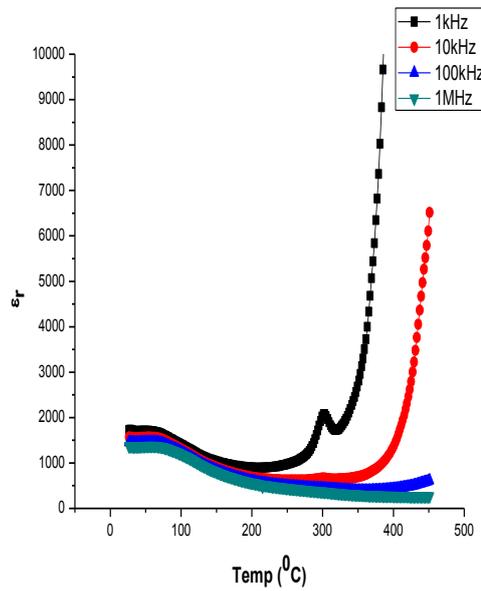
KNNT sintered at 1200^{0}C:
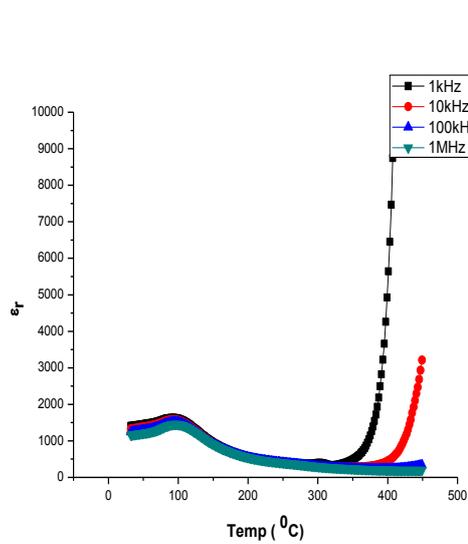
12(a)

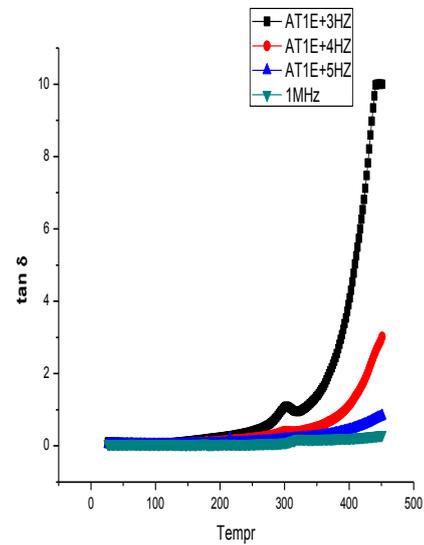

12(b)

Fig.12(a) & 12(b) gives the dielectric constant & loss at 1200⁰C for KNNT

KNNT sintered at 1250⁰C:

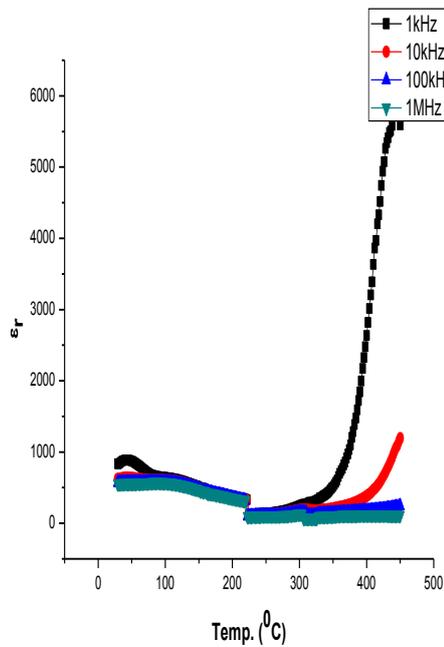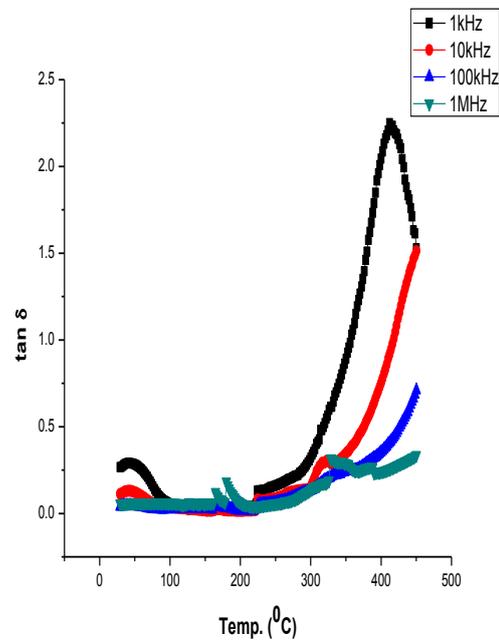**13(a)**   **13(b)**

Fig.13 (a) & 13 (b) gives the dielectric constant & loss at 1250⁰C for KNNT

KNNT-Ni sintered at 1200⁰C:

14(a)   **14(b)**
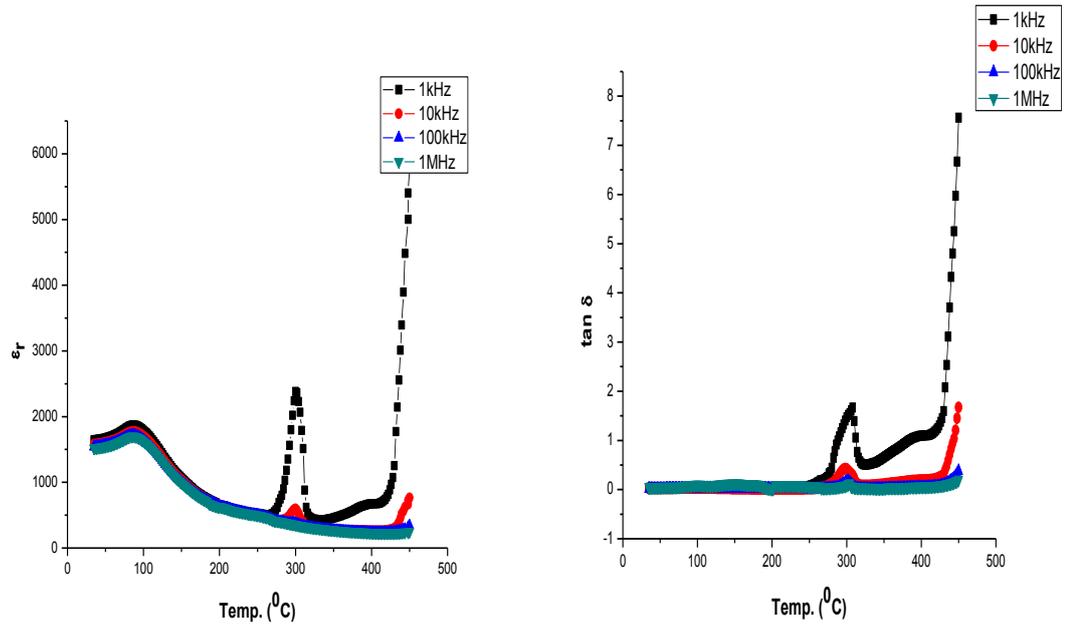
Fig.14 (a) & 14 (b) gives the dielectric constant & loss at 1200⁰C for KNNT-Ni

KNNT-Ni sintered at 1250⁰C:

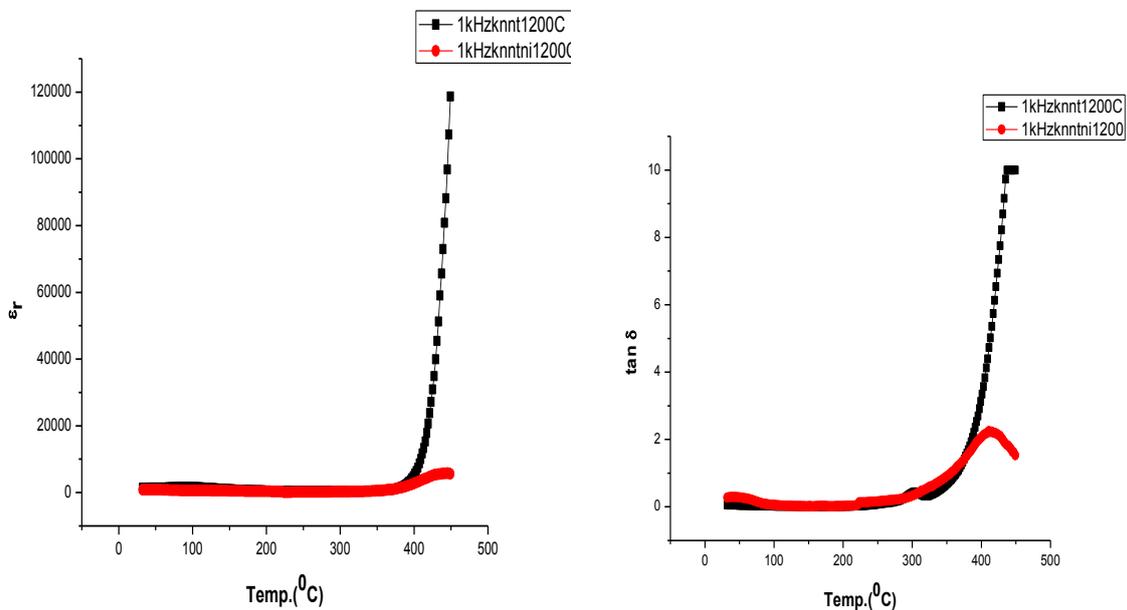15(a)   15(b)

Fig.15 (a) & 15 (b) gives the dielectric constant & loss at 1250⁰C for KNNT-Ni

Comparison between the plots of KNNT & KNNT-Ni for 1200⁰C at 1 kHz:

15(a)   15(b)

fig.15(a) & 15(b) shows the dielectric constant & dielectric loss for KNNT & KNNT-Ni at 1200⁰C

Comparison between the plots of KNNT & KNNT-Ni for 1250^{0}C at 1 kHz:

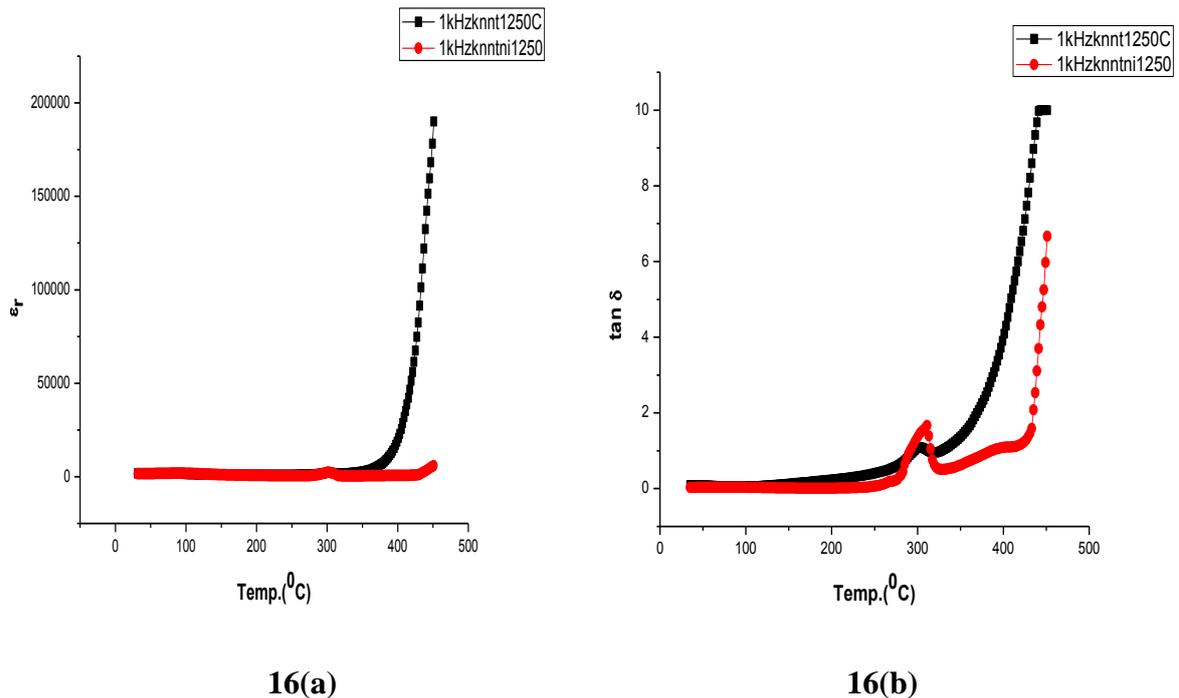**16(a)**   **16(b)**

fig.16(a) & 16(b) shows the dielectric constant & dielectric loss for KNNT & KNNT-Ni at 1250^{0}C

The graphs were plotted for dielectric constant vs. temperature and dielectric loss vs. temperature at 1 kHz, for both KNNT and KNNT-Ni which were sintered at different temperatures. From the comparison of the graphs for KNNT and KNNT-Ni at 1200^{0}C and 1250^{0}C, it is observed that the dielectric constant is almost same for both ceramics till 340^{0}C but after that temperature, it increases gradually for KNNT.

From the graphs of tan δ vs. temperature, it is also observed that the dielectric loss is more in case of KNNT as compared to that of KNNT-Ni ceramics. So, KNNT-Ni leads to less loss of dielectric as compared to KNNT.

Chapter-5

Conclusions:

The lead free ceramics $K_{0.5}Na_{0.5}Nb_{0.5}Ta_{0.5}O_3$ and $K_{0.5}Na_{0.5}Nb_{0.5}Ta_{0.5}O_3$ + 1mol.% of Nickel, were prepared by the microwave processing tecnique. The XRD patterns confirmed the single perovskite phase formation for both types of ceramics. It also confirmed the orthorhombic perovskite phase for the ceramics. The SEM micrographs showed the dense microstructures for KNNT and KNNT-Ni ceramics sintered at different temperatures. The grain size increased with increasing sintering temperature. The growth of grain size for KNNT-Ni is lower as compared to that of KNNT ceramics. The grain size lies in the range of 1.5-2μm. The density measurement was done for both the samples. The bulk density increased with increasing sintering temperature of the ceramics. At 1250^0C, the density for KNNT was observed to be 4.81 g/cc whereas KNNT-Ni it is 4.78 g/cc. The dielectric study was carried out of KNNT and KNNT-Ni ceramics. KNNT ceramics showed higher values of ϵ_r as compared to that of KNNT-Ni ceramics.

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