Synthesis and Characterization of Sodium Potassium Niobate ($Na_{0.5}K_{0.5}NbO_3$)–Nickel-Zinc Ferrite ($Ni_{0.6}Zn_{0.4}Fe_2O_4$) Composite

A THESIS SUBMITTED IN PARTIAL FULFILLMENT

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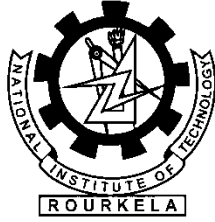
Bachelor of Technology

in

Ceramic Engineering

By

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Under the guidance of

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CERTIFICATE

This is to certify that the thesis entitled, "**Synthesis and Characterization of Sodium Potassium Niobate ($Na_{0.5}K_{0.5}NbO_3$)–Nickel-Zinc Ferrite ($Ni_{0.6}Zn_{0.4}Fe_2O_4$) Composite**" submitted by Mr. **VINAY BANSAL** in partial fulfillments for the requirements for the award of **Bachelor of Technology** Degree in **Ceramic Engineering** at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

Date: 7th may, 2010

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CONTENTS   Page No

ABSTRACT

The present project dealt with the preparation of a multiferroic composite $(Na_{0.5}K_{0.5})NbO_3$-$(Ni_{0.6}Zn_{0.4})Fe_2O_4$ in which the constituent materials $(Na_{0.5}K_{0.5})NbO_3$ [NKN] and $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ [NZFO] were prepared by coating method and combustion method respectively. These were mixed in required proportion and densified by conventional sintering process to form composite. Four compositions were prepared to form composite $(1-x)(Na_{0.5}K_{0.5})NbO3$-$x(Ni_{0.6}Zn_{0.4})Fe_2O_4$ [NKN-NZFO] ceramics, where $x=0.01$, 0.10, 0.15 and 0.20. XRD of the sintered and ground sample showed no reaction between individual phases and no secondary phase formation in the final product. SEM image shows that addition of NZFO significantly modifies the microstructure of the sintered sample. Grain size found to be 10-15 µm for 1% NZFO addition. The grain size reduced to 2-5 µm for higher NZFO addition. The dielectric constant and dissipation factor were studied as a function of frequency for ceramic composites

CHAPTER - 1

GENERAL INTRODUCTION

INTRODUCTION:

1.1 Multiferroics: Multiferroics are materials in which (ferro)magnetism, the spontaneous ordering of orbital and spin magnetic moments, and ferroelectricity, the spontaneous ordering of electric dipole moments can coexist in one material in the absence of external electric and magnetic fields. A third type of ordering, spontaneous deformation, which leads to ferroelasticity can also coexist. Boracites were probably the first known multiferroics [1].
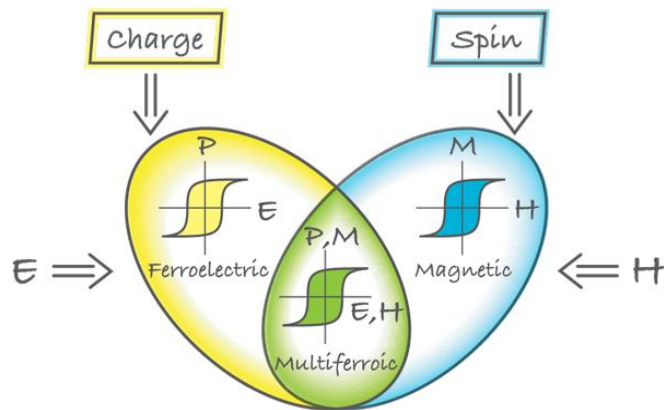
The origin of magnetism is basically the same in all magnets but the situation with ferroelectrics is quite different because there can be several different microscopic sources of ferroelectricity leading to different types of multiferroics. Type-I multiferroics, in these materials ferroelectricity and magnetism have different sources of origin and appear largely independently of one another. Ferroelectricity typically appears at higher temperatures than magnetism, and the spontaneous polarization $\mathbf{P}$ is often rather large. Examples are $BiFeO_3$ (T_{FE}~1100K,T_N=643 K,$\mathbf{P}$~90μC/cm^2). Another category is type-II multiferroics, is the relatively recently discovered materials [2], in which magnetism causes ferroelectricity. However, the polarization in these materials is usually much smaller (~$10^{-2}\mu$C/cm^2). example, in $TbMnO_3$

magnetic ordering appears at T_{N1}=41 K, and at a lower temperature, T_{N2}=28 K, the magnetic structure changes. Magnetoelectric coupling is an independent phenomenon that can, but need not, arise in any of the materials that are both magnetically and electrically polarizable. But in most of the cases ferroelectric or magnetic transition temperature is below room temperature, so it cannot be used in practical application. The conditions for the occurrence of ferroelectric and magnetic order in the same material require: (i) the presence of adequate structural building blocks permitting ferroelectric-type ionic movements, i.e. off-centre displacement associated with the spontaneous polarization in ferroelectrics, (ii) magnetic-interaction pathways for the magnetic order, usually of the super-exchange type and (iii) symmetry conditions [4]. Multiferroic composite structures in bulk form are explored for high-sensitivity ac magnetic field sensors and electrically tunable microwave devices such as filters, oscillators and phase shifters. In multiferroic thin films, the coupled magnetic and ferroelectric order parameters can be exploited for developing magnetoelectronic devices. These include novel spintronic devices such as tunnel magneto resistance (TMR) sensors. One can also explore multiple state memory elements, where data are stored both in the electric and the magnetic polarizations.

A high inherent coupling between multiferroic components has not yet been found in single phase compounds. Example of single phase multiferroic materials are Cr_2O_3. These single phase materials exhibit magnetoelectric behavior only at very low temperature and sometimes at high external field. They have magnitude of ME response very lower as compared to composite materials (around $1/10^{th}$). So they can't be used for potential applications.

Magnetoelectric Composites: They have greater design flexibility, a large magnetoelectric response and can be operated at room temperature. So they can be used as multifunctional

devices such as magnetic-electric transducers, actuators and sensor applications. ME results from the cross interaction between different ordering of the two phases in the composite. Neither the piezoelectric nor magnetic phase has ME effect but the composite have remarkable ME effect, and it is result of magetostrictive effect(magnetic/mechanical effect) in the magnetic phase and the piezoelectric effect (mechanical/electrical effect) in the piezoelectric material. Applying magnetic field will change the magnetostrictive constituent and volume will change so a local stress will be generated, which will pass into the piezoelectric phase, thus producing electric polarization (charge). Our ME composite 0-3 type particulate composite of piezoelectric and magnetic oxide materials. Originally particulate composites were prepared by unidirectional solidification of a eutectic composition of the quinary system Fe-Co-Ti-Ba-O [5]. It helps in the decomposition of the eutectic liquid in to alternate layers of a piezoelectric perovskite phase and a piezomagnetic spinel phase. High ME coefficient of 130mV/cm Oe was obtained in a eutectic composition if $BaTiO_3$-$CoFe_2O_4$ by unidirectional solidification. Sintering processing is much easier and cheaper than directional solidification. Sintered composites have several advantages like freedom in the selection of constituent phase, there starting particle sizes, processing parameters. Sintering temperature has a significant effect on ME coefficient. In spite of the high ME coefficient in these 0-3 particulate composite ceramics, it is difficult to achieve experimentally.

1.2 Sodium Potassium Niobate ($Na_{0.5}K_{0.5}NbO_3$): Piezoelectric materials play an important role in actuators and sensors applications. Lead oxide based ferroelectrics, for example lead zirconate titanate (Pb(Zr,Ti)O_3) or (PZT) , are widely used for piezoelectric actuators, sensors and transducers due to their excellent piezoelectric properties [6 and 7]. But due to the toxicity of lead oxide and its high vapor pressure during processing, we will use environmental friendly

materials. Potassium sodium niobate $Na_{1-x}K_xNbO_3$ (abbreviated as NKN) ceramics are one of the candidates as the alternative systems. $Na_{1-x}K_xNbO_3$ is a combination of ferroelectric $KNbO_3$ or KN and antiferroelectric $NaNbO_3$ or NN, and forms a morphotropic phase boundary (MPB) near 50/50 composition (x=0.50) separating two orthorhombic phases [8]. NKN is an attractive material that has been thoroughly investigated as a result of its high electromechanical coupling coefficient (k^2) and high phase transition temperature (Tc $\sim$ 420 °C), especially near the morphotropic phase boundary (MPB). However, the difficulty of sintering NKN ceramics under atmosphere is a serious drawback. The main problem is the volatilization of potassium oxide (K_2O) at 800 °C which makes it difficult to control stoichiometry [9] and [10]. Another problem is oxygen deficiency during preparation resulting from high-temperature processing and giving rise to electronic conductivity [10]. At present, the best densities reported for $Na_{0.5}K_{0.5}NbO_3$ are 90–95% of the theoretical density. Nevertheless, dense NKN ceramics are difficultly obtained since their phase stability is limited to 1140 °C close to the melting point [11]. The crystal phase of the $Na_{0.5}K_{0.5}NbO_3$ has an orthorhombic structure. It has a general formula ABO_3 and may be described as a simple cubic unit cell with the corners occupied by a large cation ("A", such as Pb, Ba, Ca, K, Na, etc.), a smaller cation ("B", such as Ti, Nb, Mg, Zr, etc.) and oxygens in the face centers. sodium potassium niobate (NKN), has both Na and K at the A site. Piezoelectric performance evidently is the ultimate criteria to judge how good a piezoelectric is, a high Curie temperature is also strongly desired in order to provide a wide temperature range of operation and ensure the stability of the material performance. $Na_{0.5}K_{0.5}NbO_3$-based materials present a clear-cut advantage in possessing high piezoelectric performance while maintaining high Curie temperature.
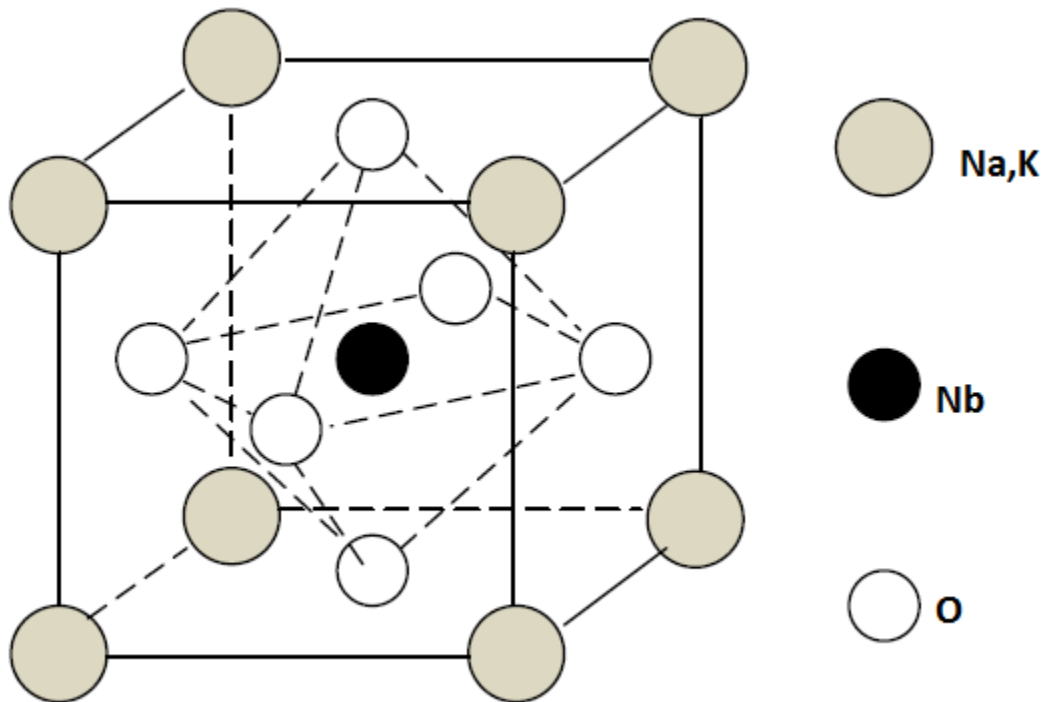
Figure.1.2.1 Schematic Representation of Perovskite structure of Sodium Potassium Niobate

1.3 Nickel–Zinc Ferrites (Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$) : Oxides having spinel structure (AB$_2$O$_4$), are found to be technological and commercial applications in electric and magnetic fields. These properties are depending upon the nature, oxidation state and distribution of metal ions over tetrahedral and octahedral sites of spinel lattice. Spinel ferrites have been widely studied due to their interesting properties like high resistivity, mechanical hardness, remarkable stability and promising memory storage capacity. They have a wide range of applications in microwave absorbance, number of electronic devices as, radio, TV sets, integrated non-reciprocal circuits, high frequency transformers, memory cores devices, rod antennas, read-write heads for high-speed digital tape

or disk recording [12],[13],[14],[15]. The change of the Ni molar ratio content (x) from 0.2 to 0.9 had strongly affected the properties of the formed ferrites powders. The lattice parameters found to decline gradually with increasing nickel content and the crystallite size was in the range between 27 and 155 nm. The crystal structure of Ni–Zn ferrites spinel configuration is based on a face centered cubic lattice of oxygen ions. The unit cell consists of eight formula units of the type $[ZnFe_{1-x}]_A[Ni_{1-x}Fe_{1+x}]_B O_4$, where A represents tetrahedral site and B octahedral site [16].

Oxygen

B-atoms
octahedral sites

A-atoms
tetrahedral sites

AB_2O_4 spinel The red cubes are also contained in the
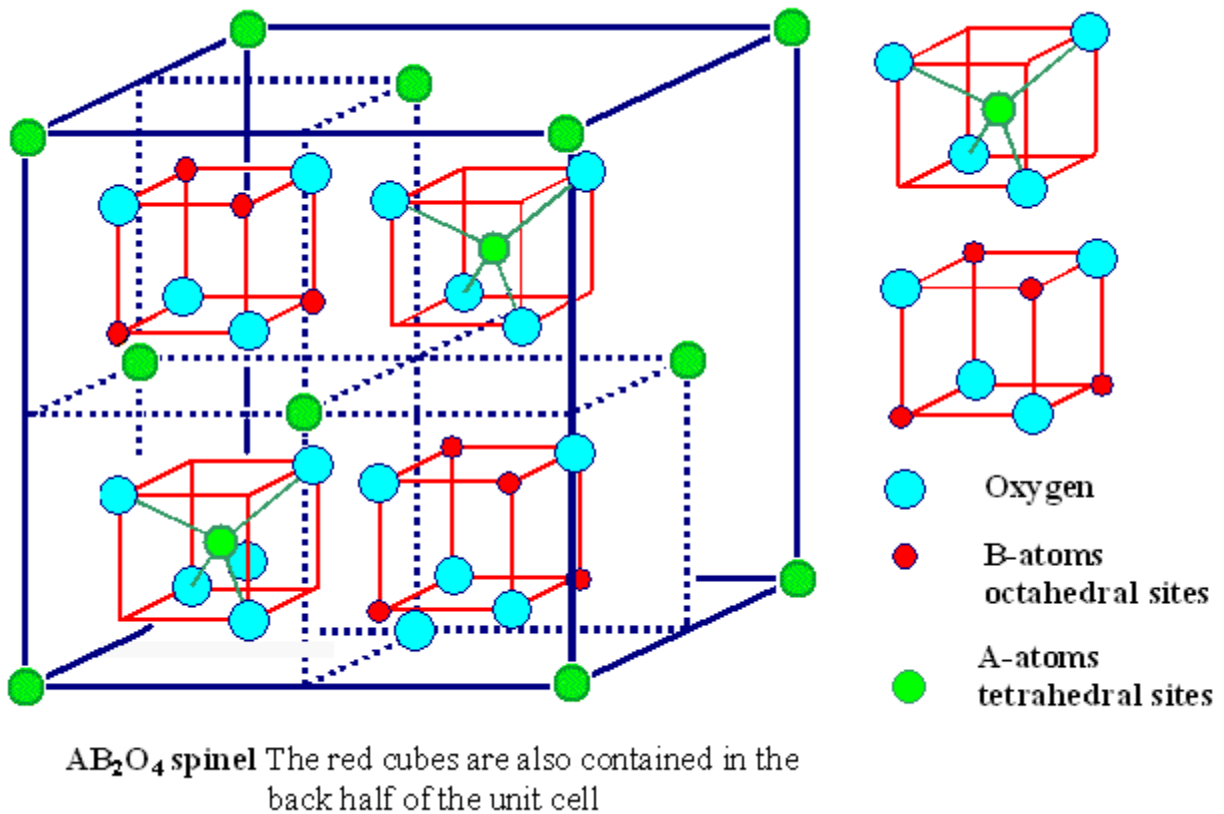back half of the unit cell

Figure1.3.1 [17] spinel structure

The properties of Ni–Zn ferrites are strongly depending on their chemical composition and microstructure. Selection of the appropriate process is, therefore, a key factor to obtain the

desired ferrite quality especially for low loss and high frequency [18]. The saturation magnetization (M_s) of the Ni–Zn ferrites is 52.97 emu/g.

Multiferroic composites are made because they yield high magnetoelectric coupling response above room temperature, so they can be easily used in technological applications. An electric polarization is induced by a weak ac magnetic field and magnetization polarization appears upon applying an electric field. [19]. In such composites electromechanical coupling occurs and magnetostriction in the ferrite phase give rise to mechanical stress that transfer to the ferroelectric phase , resulting in the electric polarization of ferroelectric phase and account an excellent magnetoelectric effect[20],[21,[22],[23]. There are very less number of reports available on dielectric properties of these composites.

CHAPTER 2

LITERATURE REVIEW

2.1 Literature Review:

Kapse at al. formed Nickel–zinc ferrites ($Ni_{0.6}Zn_{0.4}Fe_2O_4$). Transition metal ferites are a family of oxides that plays a vital role in wide range of fields and is related to the variety of transition metal metal cations that can be incorporated in to the lattice of parent magnetic structure. Most ferrites are produced by conventional process having downsides like chemical inhomogeneity, poor compositional control, coarser particle size. The stoichiometric molar amount of ferric nitrate, nickel nitrate,, zinc nitrate were dissolved in distilled water and then adding them to the warm solution of citric acid monohydrate/ethylene glycol. Continuous magnetic stirring of the resultant solution for 2 hours will give homogeneous mixture. this solution is transferred to Teflon lined stainless steel autoclave and the autoclave temperature was slowly raised to 120°c and maintained for 12 hours to get gel precursor. Autoclave was allowed to cool to RT and the resulting product further heated for 4h to 350°c and calcined for 6h at 700°c to improve the crystallinity of the prepared material. XRD analysis confirmed the formation of cubic spinel strucuture. Usually ferrites preparedby chemical routes show presence of α-Fe_2O_3. Here extra peaks are found due corresponding to α-Fe_2O_3 are found for x=0, indicating considerable loss of Ni^{+2} ions, and for other x values cubic spinel structure is formed.

Rupesh et al. formed (Ni–Co–Cu)ferrite/BTO composites. These electroceramic composites of ferrite and ferroelectric phases have the ability to show product and sum properties [24]. The development of such multiferroics facilitate the conversion of energies between electric and magnetic fields and are potential candidates as memory elements. The distortion of the ferrite lattice due to the Jahn-Teller ions (i.e. Ni^{2+} and Cu^{2+}) induces a stress in the nearby ferroelectric lattice, which may results in improvement of electric properties. The individual

phases and their composites having the general formula $(x)BaTiO_3 + (1 − x)Ni_{0.93}Co_{0.02}Cu_{0.05}Fe_2O_4$ were prepared by double sintering ceramic technique. The BTO was presintered at 900 °C and $Ni_{0.93}Co_{0.02}Cu_{0.05}Fe_2O_4$ was presintered at 800 °C for 10 h. Milling for 3–4 h after mixing 85 mol%, 70 mol% and 55 mol% ferroelectric phase with 15 mol%, 30 mol% and 45 mol% ferrite phase, respectively was done and pressed into pellets. Finally sintering at 1150 °C for 12 h was done. The ferrite phase shows the cubic spinel structure and ferroelectric phase crystallizes into tetragonal perovskite structure which is evidenced from the splitting of peaks. Absence of unidentified peak confirms no chemical reaction has taken place during the final sintering. The dielectric constant increases with temperature up to Curie temperature (T_c) and then decreases, which is normally expected behavior in most of the ferrites and ME composites [25]. The dielectric constant reduced with increase in ferrite content.

Singh et al. made $LaFeO_3$-$PbTiO_3$ multiferroic. The composition $[(Pb_{0.8}La_{0.2})(Ti_{0.8}Fe_{0.2})O_3]$ originates by combining A-site ferroelectricity with B-site magnetic order. Solid solutions are prepared by conventional solid state reaction route. Raw materials La_2O_3, PbO, Fe_2O_3, TiO_2 are weighed in stoichiometric proportion. XRD confirms single phase tetragonal structure at room temperature at room temperature. The unit cell has lattice parameters a=3.924 Å and c=3.980 Å with c/a ratio approx. 1.014. two peaks in permittivity versus temperature graph are observed at all frequencies. The first sharp peak at 434 K is independent of frequencies shows ferroelectric to paraelectric transition. Dielectric losses also increase with temperature

Kambale et al. formed 25% Co-Mn ferrite (CMFO) and 75% Ba-Zr Titnate(BZT) ferroelectric multiferroic composite. The product property is of technical importance as the composite can be used as an magnetic field sensor, electric generator, switches, waveguides etc. The sum properties like dielectric properties, electrical conductivity and density are also equally

important because they affect the product property and hence its application in various practical devices. The ferrite i.e. CMFO phase is synthesized by an autocombustion. AR grade $BaCO_3$, ZrO_2 and TiO_2 were milled for 2–3 h and pre-sintered at 1000 °C for 10 h to synthesize $BaZr_{0.08}Ti_{0.92}O_3$ phase and then the individual phases were ground to fine powder and the ME composites were prepared by mixing 25 wt.% ferrite phase and 75 wt.% ferroelectric phase using an agate mortar. 2% polyvinyl alcohol as a binder is added and pressed into pellets. The pellets were finally sintered at 1250 °C for 10 h with heating rate 5 °C/min. XRD shows all the peaks confirms constituent phasesof the spinel cubic and tetragonal perovskite crystal structure. For spinel ferrite a (311) peak and for ferroelectric a (110) peak is more intense. No impurity peaks are observed. So no chemical reaction between the constituent phases during final sintering of composite. The lattice constant of the ferrite phase increases with increasing Mn content, in the cobalt ferrite, from 8.38 Å to 8.42 Å. The average grain sizes for CMFO0 + BZT, CMFO1 + BZT, CMFO2 + BZT, CMFO3 + BZT and CMFO4 + BZT composites are 0.62 µm, 0.83 µm, 1.10 µm, 0.71 µm and 0.65 µm respectively. Dielectric constant decreases with increasing frequency, due to dipoles resulting from changes in valence states of cations and space charge polarization.

Corral-Flores at al. prepared $CoFe_2O_4$–$BaTiO_3$ multiferroic core–shell-type nanostructures. $CoFe_2O_4$ was synthesized by chemical co-precipitation. A 0.2 M solution was prepared by dissolving $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ in deionized water. The precipitating agent was a 5 M NaOH solution with 100% molar excess. Both solutions were heated separately to 65 °C and then mixed under constant stirring. The temperature was raised to 80 °C for 20 min, causing completely crystallization of the spinel phase. The precipitate was centrifuged and washed with distilled water. The $CoFe_2O_4$ was kept in a water suspension. One

small portion of it was dried at 80 °C for characterization. Cobalt ferrite/water suspension was heated to 80 °C with gentle stirring. Oleic acid was added to the suspension at 30 wt.% with respect to the cobalt ferrite. The temperature was raised to 90 °C for 30 min and then cooled to 60 °C. Adding Octane and further stirring for another 30 min. The sample was dried at 80 °C from room temperature to 700 °C at $5°$ min^{-1}.Core–shell-like nanostructures of $CoFe_2O_4$–$BaTiO_3$ were synthesized by the sol–gel technique. $Ba(C_2H_3O_2)_2$ was mixed with titanium (IV) n-butoxide stearic acid and glacial acetic acid at 90 °C to form a sol. The ferrofluid was added to the sol at an adequate amount. Anhydrous 2-methoxyethanol will promote the gel formation. The obtained gels were dried overnight at 80 °C and sintered at 700 °C for 2 h under some conditions to prevent BTO cracking. No secondary phases were detected by this technique during XRD. The structure corresponds to a spinel type cubic crystal with an average crystallite size of 14.6 nm. The degree of tetragonality increased with the ferrite content. Taking into account that the crystallite size of the barium titanate decreased with the content of ferrite.

From literature review we found that there are no reports on formation of composite of lead free piezoelectric NKN with other ferrimagnetic material. It is mentioned that NZFO has very high saturation magnetization and also insulating in nature. It will be interesting to synthesize and characterize the NKN and NZFO composite.

2.2 Objective of present work:

No work have been there for the dielectric measurement of $(Na_{0.5}K_{0.5})NbO_3$-$(Ni_{0.6}Zn_{0.4})Fe_2O_4$ composite , so our main objective here will be

1) To find the interaction between the magnetic phase and piezoelectric phase during sintering and phase analysis in the sintered composite.

2) To study the microstructure of the composite with NZFO addition

3) To study the dielectric behaviour of the composite with NZFO addition.

CHAPTER 3

EXPERIMENTAL WORK

3.1 Preparation of NKN in coating method:

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┌─────────────────────┐
│   NaNO₃, KNO₃        │
└─────────────────────┘
          │                    ┌──────────────────────────────┐
          │    ◄───────────────│  Dissolved in ethylene glycol │
          ▼                    └──────────────────────────────┘
┌─────────────────────┐
│   Clear solution     │
└─────────────────────┘
          │                    ┌──────────────────────────────┐
          │    ◄───────────────│       Nb₂O₃ added             │
          ▼                    └──────────────────────────────┘
┌─────────────────────┐
│      Stirred         │
└─────────────────────┘
          │
          ▼
┌─────────────────────────────┐
│  Nb₂O₅ (in NaNO₃ + NaNO₃)   │
└─────────────────────────────┘
          │
          ▼
┌─────────────────────┐
│      Drying          │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│  NKN precursor powder│
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│  Calcinations and ball│
│  milling             │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│    NKN powder        │
└─────────────────────┘
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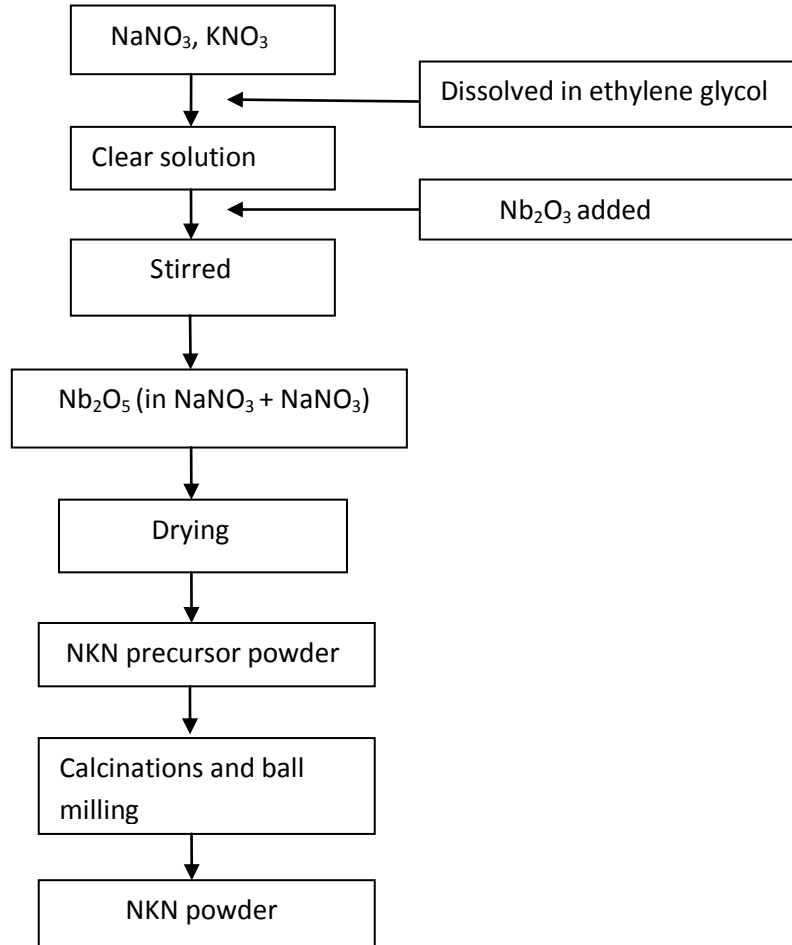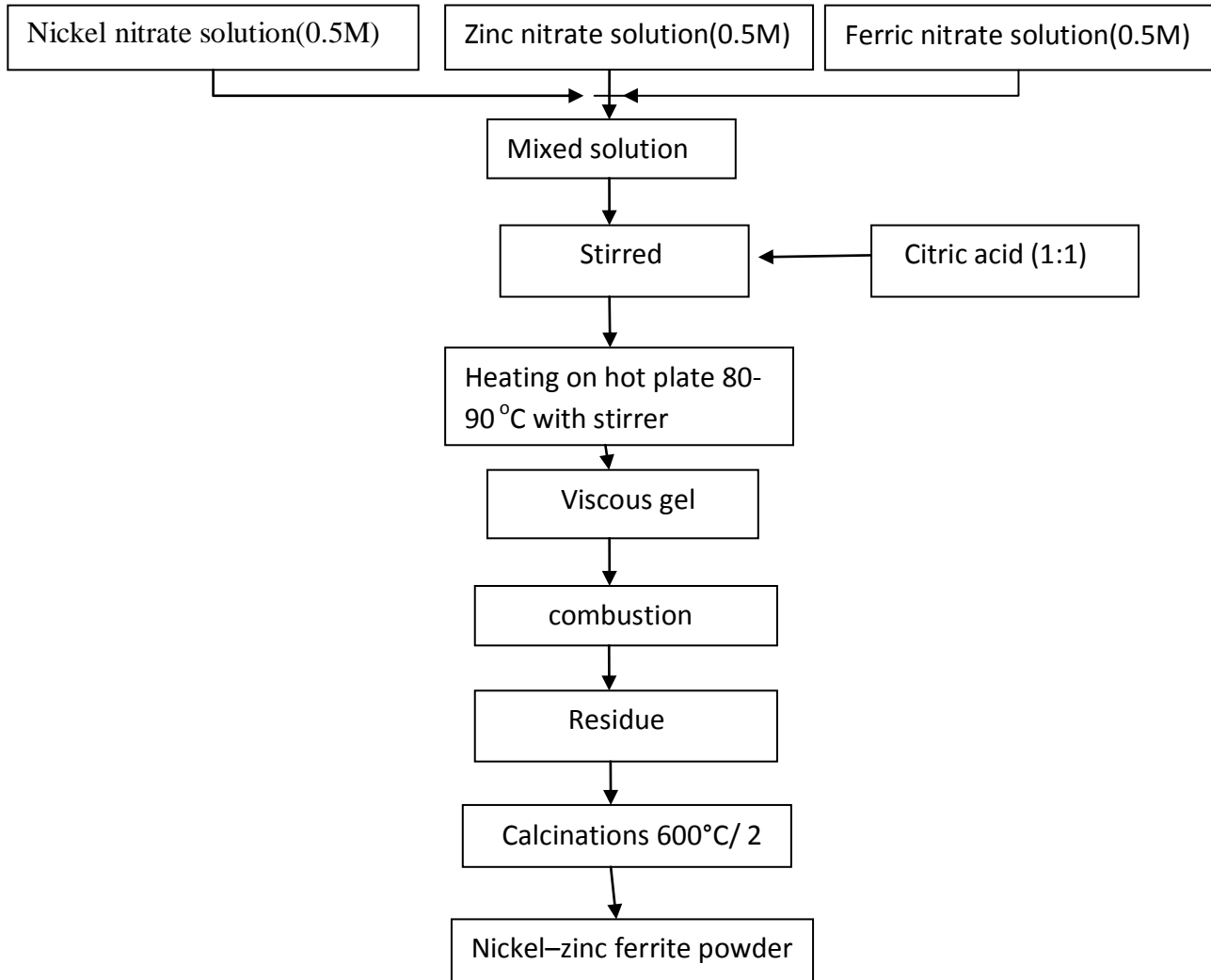
As prepared powder is calcined at $750\ ^{\circ}C/2$ hr in chamber furnace. After that powder is kept at room temperature to cool it down , mixed in agate mortar and 3%PVA is added and then pellets are prepared at pressure of 4 ton and dwelling time 120 sec . pellets were sintered at $1100\ ^{\circ}C$ for 4 hr and then the XRD of the pellet.

3.2 Preparation of Nickel–Zinc Ferrites:

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┌─────────────────────────┐ ┌─────────────────────────┐ ┌──────────────────────────┐
│ Nickel nitrate          │ │ Zinc nitrate            │ │ Ferric nitrate           │
│ solution(0.5M)          │ │ solution(0.5M)          │ │ solution(0.5M)           │
└─────────────────────────┘ └─────────────────────────┘ └──────────────────────────┘
                          │            │            │
                          └────────►  ◄┘◄───────────┘
                               ┌──────────────────┐
                               │  Mixed solution  │
                               └──────────────────┘
                                        │
                               ┌──────────────────┐      ┌─────────────────────┐
                               │     Stirred      │◄─────│  Citric acid (1:1)  │
                               └──────────────────┘      └─────────────────────┘
                                        │
                         ┌─────────────────────────────┐
                         │  Heating on hot plate 80-    │
                         │  90 °C with stirrer          │
                         └─────────────────────────────┘
                                        │
                               ┌──────────────────┐
                               │   Viscous gel    │
                               └──────────────────┘
                                        │
                               ┌──────────────────┐
                               │    combustion    │
                               └──────────────────┘
                                        │
                               ┌──────────────────┐
                               │     Residue      │
                               └──────────────────┘
                                        │
                         ┌─────────────────────────────┐
                         │   Calcinations 600°C/ 2      │
                         └─────────────────────────────┘
                                        │
                         ┌─────────────────────────────┐
                         │  Nickel–zinc ferrite powder  │
                         └─────────────────────────────┘
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Now this powder is mixed in agate mortar and 3%PVA is added as binder to form pellets under 4 ton pressure and 120 sec dwelling time. The pellet formed is sintered at 1000°C for 4 hr, then XRD of this sample is performed. Particle size measurement was done here and the size is approximately 196 nm. Now both the powder materials are mixed together in different weight % composition.   There are four weight % composition which are 0.99NKN + 0.01NZFO, 0.90NKN + 0.10NZFO, 0.85NKN + 0.15NZFO, 0.80NKN + 0.20NZFO. The XRD

measurement of these four types of compositions is done. The pellets are polished and then silver electroding is done for the measurement of dielectric properties.

3.3 General Characterization

All the samples were characterized using the room temperature powder X-ray diffraction ((Philips PAN analytical, Netherland) with filtered 0.154056 nm Cu Kα radiation. Samples are scanned in a continuous mode from $15° - 70°$ with a scanning rate of 0.04^{o} / (sec).

Microstructural features were studied using Scanning Electron Microscope (JSM 6480 LV JEOL, Japan) on surface of sintered sample. Density of sintered samples was determined by Archimedes principle.

Particle size distribution measurements have been carried out on powder samples by ZETASIZERS Nanoseries (Malvern Instruments) while electrical measurements have been carried out on sintered pellets after firing. For dielectric measurements the silver electrodes were cured at 500°C/30 min in air. The low frequency (100 Hz–1 MHz) dielectric measurements have been carried out on an HIOKI 3532-50 LCR   Hi tester.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 XRD Analysis:

NKN powder prepared by coating method and calcined at 750°C for 2 h and then the pellete is sintered at 1100°C for 4 hr. Fig4.1.1 shows the XRD pattern of the both powder and pellete sample of NKN. It was found that the powders Calcined at 750°C shows complete phase formation without any impurity phase. The crystal structure is orthorhombic and it was matched with JCPDS card no.77-0038. The crystal structure should not change at high temperature, it is because the property get changed with the crystal structure.
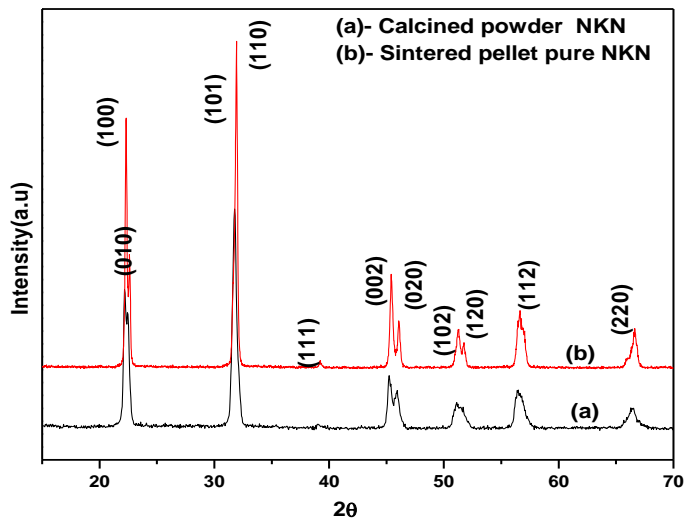
FIG 4.1.1 XRD pattern of both Calcined powder and Sintered pellet of pure NKN

Fig 4.1.2 shows the XRD pattern of $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ prepared by combustion method, the powder was Calcined at 600°C /2hr.There was no impurity phase found in the Calcined powder.

The crystal structure was found to be cubic and was found to be matched with JCPDS card no.08-0234.
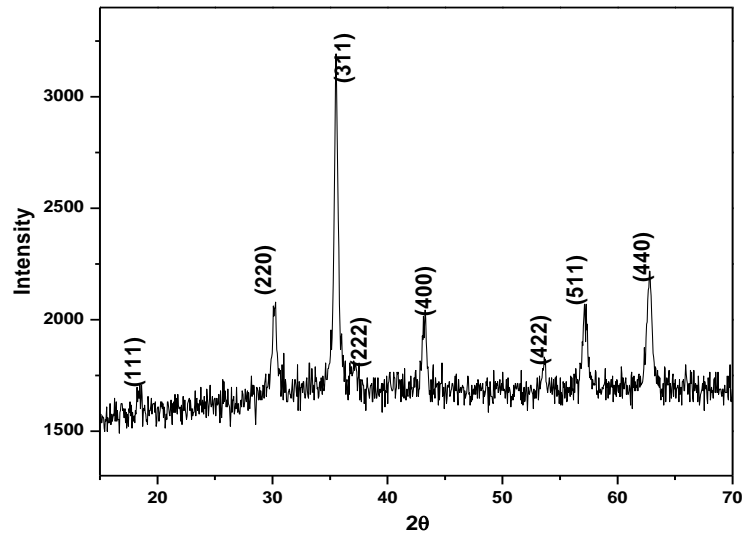
FIG4.1.2 XRD pattern of $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ powder Calcined at 600°C for 2h
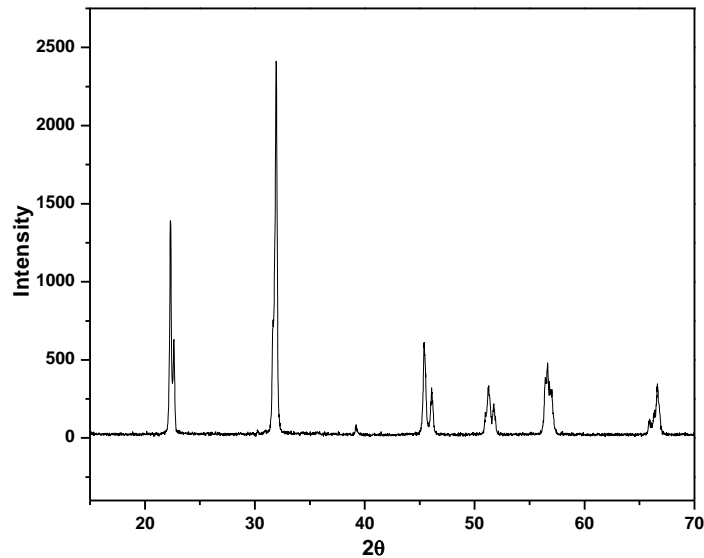
FIG 4.1.3 XRD pattern of $0.99(Na_{0.5}K_{0.5})NbO_3$-$0.01(Ni_{0.6}Zn_{0.4})Fe_2O_4$ pellet sintered at 1090°C for 4h

The composite was prepared by mixing the powders of NKN and NZFO by solid state technique. Then the pellets were prepared and conventionally sintered at 1090°C/4hrs in air. The phase of the sintered pellet was checked by XRD. There was no Ferrite phase found in this composition .But with the increase in the NZFO concentration, the Ferrite phase was found. It has been shown in fig 4.1.4-4.1.6.
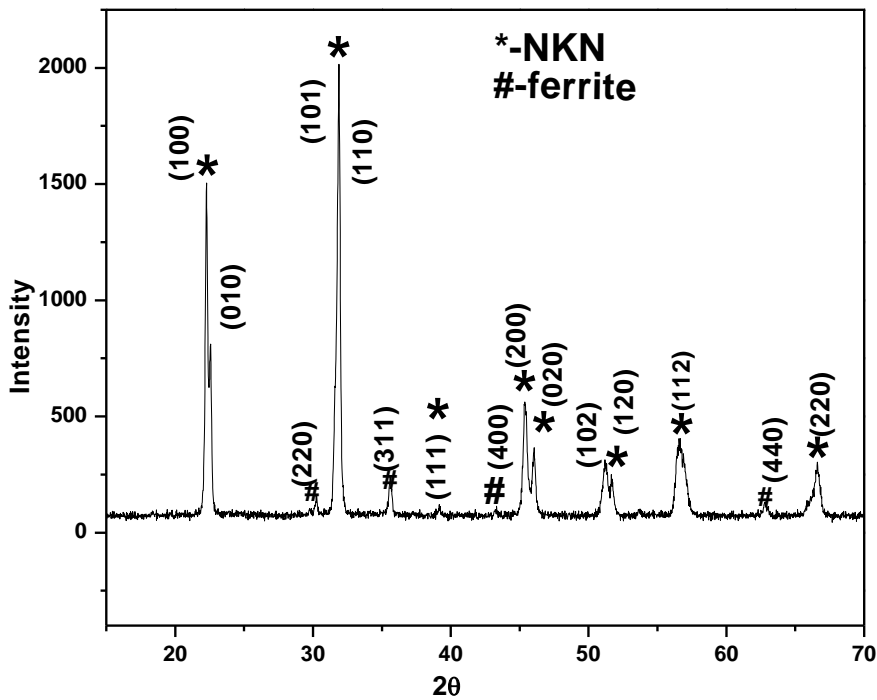
FIG 4.1.4 XRD pattern of 0.90(Na$_{0.5}$K$_{0.5}$)NbO$_3$-0.10(Ni$_{0.6}$Zn$_{0.4}$)Fe$_2$O$_4$ pellet sintered at1070°C for 4h

The pronounced diffraction peaks were indexed. The ferrite phase shows that cubic spinel structure and ferroelectric phase crystallizes into tetragonal perovskite structure which was evident from the splitting of (200)/(002). The intensity of the peaks (100)/(010) found to be

increasing with the addition of NZFO content but the intensity of peaks (101)/(110) found to be

decreasing with the addition of NZFO content.
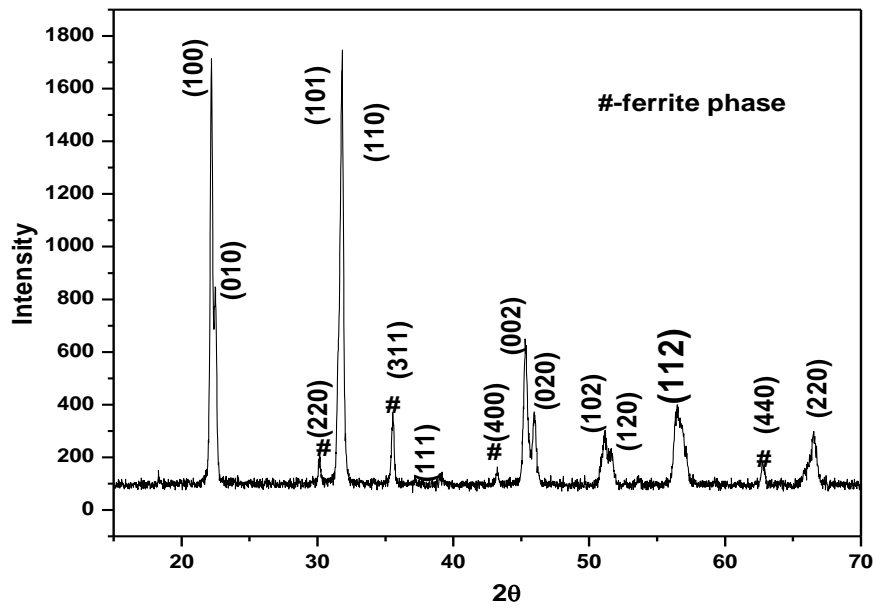
FIG 4.1.5 XRD pattern of 0.85(Na$_{0.5}$K$_{0.5}$)NbO$_3$-0.15(Ni$_{0.6}$Zn$_{0.4}$)Fe$_2$O$_4$ pellet sintered at1050°C for 4h
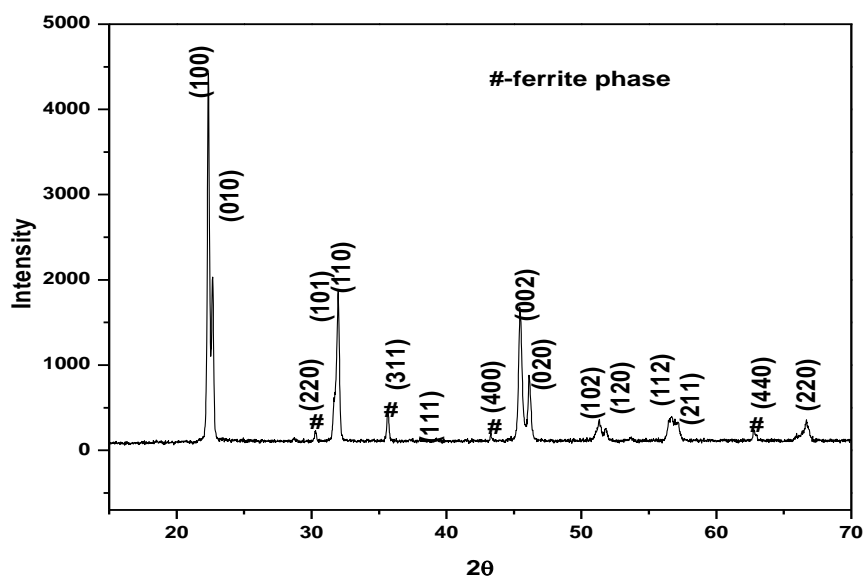
FIG 4.1.6 XRD pattern of $0.80(Na_{0.5}K_{0.5})NbO3-0.20(Ni._6Zn_{0.4})Fe_2O_4$ pellet sintered at1030°C for 4h
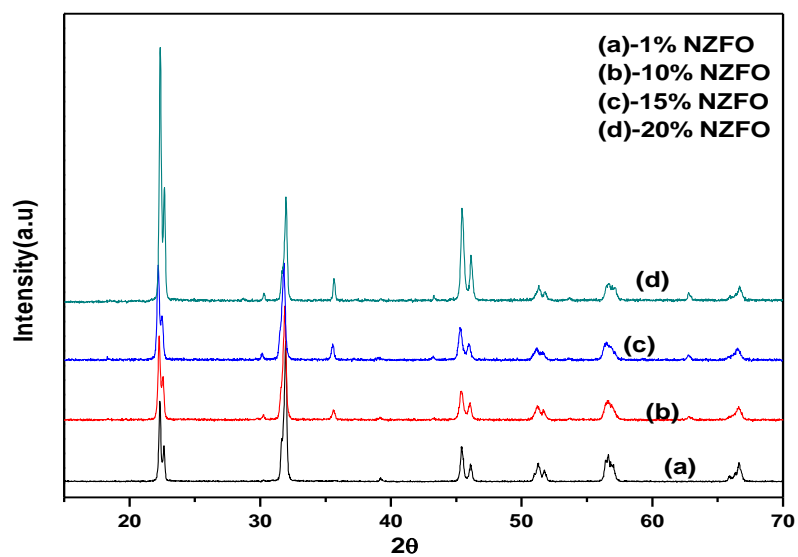
FIG 4.1.7

The composite does not contain any other phases and this composite confirms that no any chemical reaction has taken place at the interface of constituent grain during the final stage of sintering.

4.2 Density Measurement by the Archimedes principle:
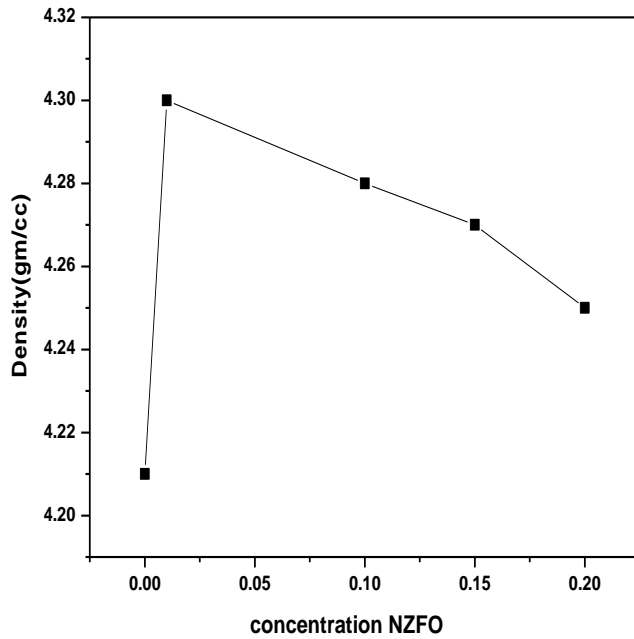
COMPOSITION	DENSITY(g/cc)
NKN	4.21
NKN:NZF(99:01)	4.32
NKN:NZF(90:10)	4.28
NKN:NZF(85:15)	4.26
NKN:NZF(80:20)	4.25

FIG 4.2.1 Variation of sintered density with addition of NZFO

This figure shows the variation of density with the increase in $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ content and it was found that with the increase in content the density was found to be decreasing.

4.3 SEM Analysis:

Fig. shows dense Microstructure with grain size around 10-15 μm for 1% addition of $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ (NZFO). Interestingly, solid solution with $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ drastically reduces the grain size in the range of 1- 3 μm. It was observed that presence of NZFO phase reduces the sintering temperature of the final composite. These are the SEM of image of four different compositions sintered at 1090°C, 1070°C, 1050°C,1030°C each for four hour.
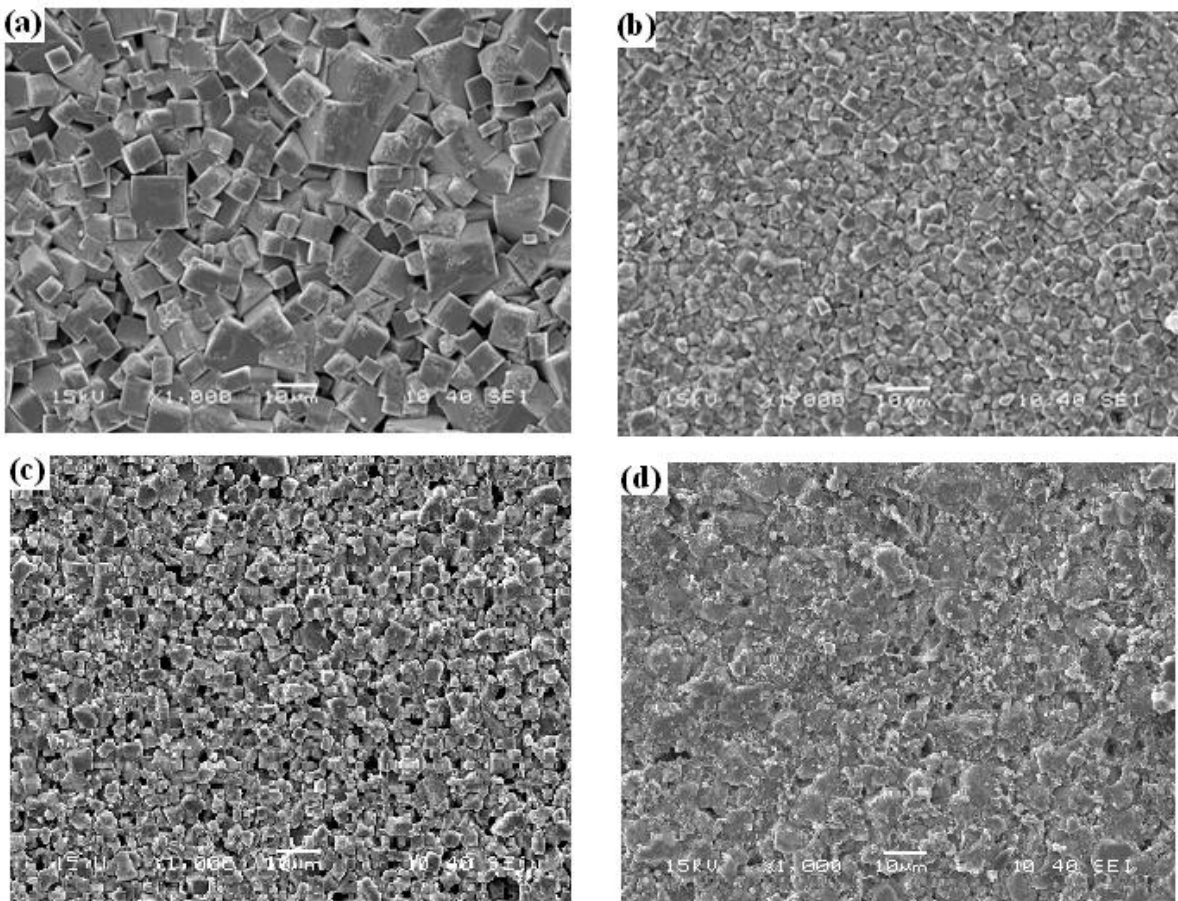

FIG 4.3.1 SEM micrographs of surfaces of sintered $(1-x)(Na_{0.5}K_{0.5})NbO3-x(Ni_{.6}Zn_{0.4})Fe_2O_4$ ceramics, where a) x=0.01 b) x=0.10 c) x=0.15 and d) x=0.20

4.4 Dielectric Measurement:
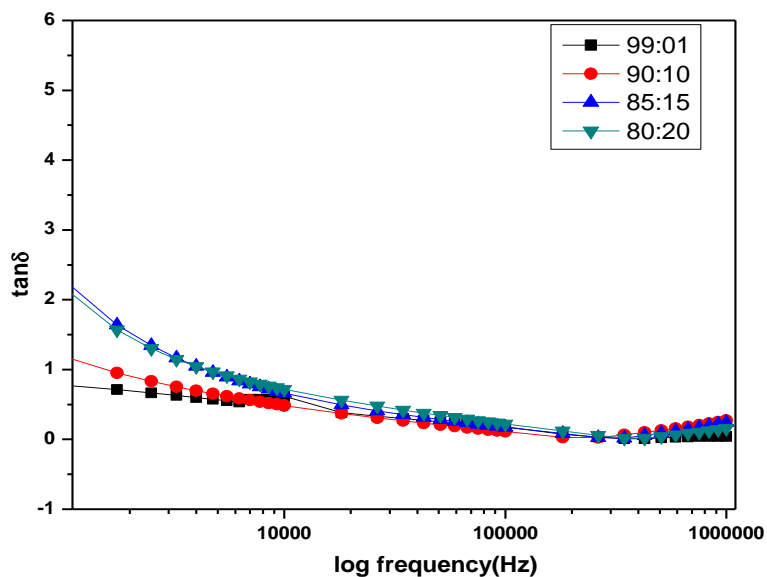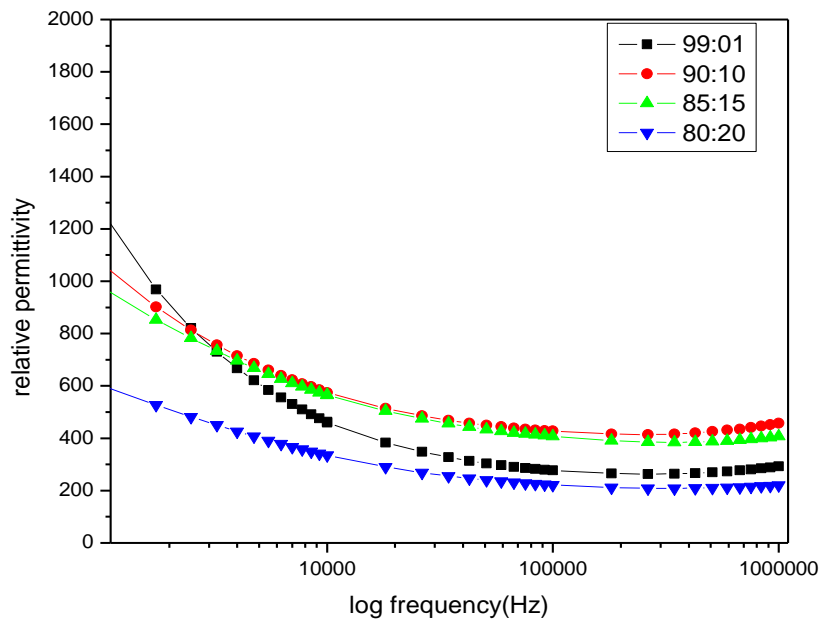
FIG 4.4.1 **Variation of (a) Relative permittivity (ε) (b) dissipation factor with frequency for**

$(1-x)(Na_{0.5}K_{0.5})NbO3-x(Ni_{0.6}Zn_{0.4})Fe_2O_4$ ceramics .

In all the samples relative permittivity (ε_r) is decreasing with increase in frequency. It is also observed that ε_r value initially increases with NZFO addition. But at higher NZFO content (20%) ε_r value again reducing. It is clear from the figure that NZFO addition increases the low frequency dispersion in tanδ vs frequency plot. That may be due to the comparatively conductive nature of the magnetic phase. But the tanδ value is not changing significantly with NZFO addition at high frequency.

CONCLUSION: $(1-x)(Na_{0.5}K_{0.5})NbO_3-x(Ni_{0.6}Zn_{0.4})Fe_2O_4$ ceramics (where x=0.01, 0.10, 0.15, 0.20) have been prepared by conventional sintering process . Phase pure $(Na_{0.5}K_{0.5})NbO_3$ powder can be prepared at calcination temperature 750^oC for period of 2 h by coating method and $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ prepared at calcination temperature 600^oC by combustion method. XRD analysis of composite have shown that there were no impurity phases and no chemical reaction taking place during final stages of sintering. Density of the composite slightly decreases with the increasing concentration of $(Ni_{0.6}Zn_{0.4})Fe_2O_4$. Introduction of more amount of $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ modify the microstructure remarkably and the grain size decreases significantly with addition. Relative permittivity increases with the increase in $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ concentration but at very high concentration NZFO, again permittivity value decreasing. Loss factor shows no change for higher frequency range.

FUTURE WORK:

➤ To measure the variation of dielectric properties with change in temperature.

➤ To prepare $(Na_{0.5}K_{0.5})NbO_3$-$(Ni0._6Zn_{0.4})Fe_2O_4$ composite having higher amount of NZFO.

REFERENCES:

[1]   E. Asher, H. Rieder, H. Schmid, and H. Stossel, J. Appl. Phys. 37, 1404 (1966).

[2]   T. Kimura et al.,Nature 426, 55 (2003).

[3]   N. Hur et al., Nature 429, 392 (2004).

[4]   T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima and Y. Tokura, Nature, 426, 55 (2003).

[5]   Ce-Wen Nan, M.I.Bichurin, Shuxiang Dong, D.Viehland, Srinivasan, J. Appl. Phys. 103, 031101 (2008).

[6]   J.W. Waanders, Piezoelectric Ceramics-properties and Applications. , Philips Components, Eindhoven (1991).

[7]   B. Jaffe, W.R. Cook and H. Jaffe, Piezoelectric Ceramics. , Academic, New York (1971).
[8]   G. Shirane, R. Newnham and R. Pepinsky. Phys. Rev. 96 (1954), p. 581

[9]   Y. Guo, K. Kakimoto and H. Ohsato, Solid State Commun. 129 (2004), pp. 279–284.

[10]   S.Y. Chu, W. Water, Y.D. Juang, J.T. Liaw and S.B. Dai, Ferroelectrics 297 (2003), pp. 11–17.

[11]   Yiping Guo, Ken-ichi Kakimoto and Hitoshi Ohsato, Solid State Communications, Volume 129, Issue 5, (2004), p. 279-284.

[12]   U. Ghazanfar, PhD Thesis, Punjab University, Pakistan, 2005.
[13]   A.C.F.M. Costa, A.P. Diniz, V.J. Silva, R.H.G.A. Kiminami, D.R. Cornejo, A.M. Gama, M.C. Rezende and L. Gama, J. Alloys Compd. (2008) .
[14]   U.R. Lima, M.C. Nasar, R.S. Nasar, M.C. Rezende and J.H. Araújo, J. Magn. Magn. Mater. 320 (2008), p. 1666.
[15]   D.-L. Zhao, Q. Lv and Z.-M. Shen, J. Alloys Compd. 480 (2009), p. 634. |
[16]   M.M. Mallapur, P.A. Shaikh, R.C. Kambale, H.V. Jamadar, P.U. Mahamuni and B.K. Chougule, J. Alloys Compd. 479 (2009), p. 797.

[17]   irm.umn.edu

[18]   X. Li and G. Wang, J. Magn. Magn. Mater. 321 (2009), p. 1276.

[19]   Rupesh S. Devan, Yuan-Ron Ma and B.K. Chougule, Effective dielectric and magnetic properties of (Ni–Co–Cu)ferrite/BTO composites

[20]   R.S. Devan and B.K. Chougule, Physica B 393 (2007) .

[21]   G. Srinivasan, E. T. Rasmussen, B.J. Levin and R. Hayes, Phys. Rev. B 65 (2002), p.1 34402.

[22]   M.I. Bichurin, D.A. Filippov, V.M. Petrov, V.M. Laletsin, N. Paddubnaya and G. Srinivasan, Phys. Rev. B 68 (2003), p. 132408.

[23]   J. Zhai, J. Li, D. Viehland and M.I. Bichurin, J. Appl. Phys. 101 (2007), p. 014102.

[24]   K. Uchino, Ferroelectric Devices, Marcel Dekker, New York (2000) p. 25.

[25]   N. Sivakumar, A. Narayanasamy, N. Ponpandian and G. Govindaraj, J. Appl. Phys. 101 (2007), p. 084116.

[26]   Yiping Guo, Ken-ichi Kakimoto and Hitoshi Ohsato, Solid State Communications, Volume 129, Issue 5, (2004), p. 279-284.

[27]   Ming-Ru Yang, Cheng-Shong Hong, Cheng-Che Tsai and Sheng-Yuan Chu, Journal of Alloys and Compounds, Volume 488, Issue 1, (2009), p.169-173.

[28]   M.M. Rashad, E.M. Elsayed, M.M. Moharam, R.M. Abou-Shahba and A.E. Saba, Journal of Alloys and Compounds, Volume 488, Issues 1-2, (2009), p.759-767.

[29]   Daniel Khomskii Physics 2, 20 (2009) Physics.2.20.

[30]   Rupesh S. Devan, Yuan-Ron Ma and B.K. Chougule, Materials Chemistry and Physics, Volume 115, Issue 1 (2009), p.263-268.

[31]   Anupinder Singh and Ratnamala Chatterjee, Applied Physics Letter 93, 182908 (2008).

[32]   R.C. Kambale ,P.A. Shaikh, Y.D. Kolekar, C.H. Bhosale and K.Y. Rajpure, Materials Letters, Volume 64, Issue 4 (2010), p.520-523.

[33]   V. Corral-Flores, D. Bueno-Baqués and R.F. Ziolo, Acta Materialia, Volume 58, Issue 3(2010), p.764-769.

[34]   V.D.Kapse, S.A.Ghosh, F.C.Raghuwanshi, S.D.Kapse , Materials Chemistry and Physics, Volume 113, Issues 2-3 (2009), p. 638-644.

[35]   W.Eerenstein, N.D.Mathur and J.F.Scott, Volume 442, 759-765 (2006).