SYNTHESIS AND CHARACTERIZATION OF MULTIFERROIC COMPOSITE (Barium Titanate-Nickel Ferrite) BY SOLID STATE ROUTE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology

in

Ceramic Engineering

By

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CERTIFICATE

This is to certify that the thesis entitled, "**SYNTHESIS AND CHARACTERIZATION OF MULTIFERROIC COMPOSITE (Barium Titanate-Nickel Ferrite) BY SOLID STATE ROUTE"** submitted by Mr. **ANURAG KUMAR** 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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ACKNOWLEDGEMENT

First of all I express my sincere gratitude to Mr A. Chowdhury for his support, his patience, his guidance, and his acceptance of me as a B.Tech student working under his guidance. I also want to thank my teachers Prof S.Bhattacharya, Prof J.Bera, Prof S.K.Pratihar, Prof B.B.Nayak, Prof R.Mazumdar and Prof S.Pal for their encouragement, teaching and in helping me to successfully complete my B.Tech degree and also all the members of the technical staff of my department. My sincere acknowledgement to the Research Scholars, M. Tech students and the non-teaching staff for the help and cooperation extended to us. And finally, my hearty thanks to all my friends who have constantly helped me.

7th May 2010 ANURAG KUMAR

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ABSTRACT

Conventional ceramic processing method was followed to study 50-50 Barium Titanate and Nickel Ferrite composite. Mixed oxide of $BaCO_3$ and TiO_2 for $BaTiO_3$ and NiO and Fe_2O_3 for $NiFe_2O_4$ were calcined at 1000^o C for four hour and 900^o C for four hour respectively. Phases of particular compounds have been confirmed by XRD. The pellets of composites were sintered at varying temperature (1100, 1150, 1200 ^{o}C for 4 hr). The samples were made ready for required characterization. The observations from XRD were proved to be important for the composite as this is the requirement for making good composite.

INTRODUCTION

With the development of electronic technology, composite materials have been widely used for electronic devices where higher densities, limited space and multifunction are required. Recently the ferroelectric–ferromagnetic composite materials were intensively researched for two uses: the magnetic–electric sensors in radio-electronics, optoelectronics, microwave electronics and transducers and the compact electrical filters for suppressing electromagnetic interference (EMI). As for the magnetic–electric sensors, high ferroelectric content was necessary for the composite materials with sufficient resistivity to generate magnetoelectric effect.

Magneto electric coupling describes the influence of a magnetic field (or an electric field) on the polarization (or magnetization) of a material.

In the past few years, extensive research has been conducted on magneto electric effect in single phase and composite materials. Direct polarization of a material under a magnetic field or an in induced magnetization under an electric field requires the simultaneous presence of long range ordering of magnetic moments and electric dipoles.

Magneto Electric materials are of two types:

- Single Phase
- Composites

In a magnetoelectric (ME) composite the magnetostrictive strain in the magnetic phase creates an electric polarization in the adjacent piezoelectric phase and hence is capable of converting magnetic field into electric field and vice versa. Such product property can be utilized in smart materials used in sensors, processors and feedback systems.

The first magneto electric effect was predicted in Cr_2O_3, but magneto electric materials with a single phase show a weak magneto electric effect , hence the need of composites.

Magneto electric composites on other hand have large magneto electric coefficients of magnitude of magneto electric voltage coefficients. The composites are made exploiting the product property of materials.

Composite materials are engineered materials made from two or more constituent materials with significantly different physical or chemical properties and which remain separate and distinct on a macrospace level within the finished structure.

There are number of physical methods for preparing nano crystalline materials viz inert gas condensation, physical vapour deposition , laser ablatiion, chemical vapour deposition, sputtering, molecular beam epitoxy etc. Among the available solution- chemistryroutes, combustion technique is capable of producing nano crystallline powders of oxide ceramics, at a lower calcination temperature in a surprisingly short time. The solution combustion is a two step process:

- Formation of a precursor
- Auto ignition

The formation of precursor (viscous liquid or gel), is a primary condition for an intimate blending of the starting constituents and preventing the random redox reaction between a fuel and an oxidizer. The very high exothermicity generated during combustion manifests in the form of either a flame or a fire and hence the process is termed as auto ignition process. The nature of the fuel and its amount are some of important process parameters for getting the transparent viscous gel without any phase separation and precipitation. Thus the basic characteristics of a fuel are that it should be able to maintain the compositional homogenity among the constituents also undergo combustion with an oxidizer at low ignition temperature. Commonly used fuels are glycine, urea, citric acid etc.

Sintered composite materials are much easier as well as cheaper to prepare than unidirectional solidified in situ composites. As regard to the ME effect it was found that ME composites made by unidirectional solidification always gave a higher value than those prepared by solid state sintering of the presintered component phases for a given composition.

Nanocrystalline $NiFe_2O_4$ samples can be synthesized by following methods; coprecipitation, combustion, citrate gel and conventional ceramic method. AR grade metal nitrates, $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were used for all three syntheses.

Nanocrystalline $BaTiO_3$ samples can be synthesized by autocombustion, solid oxide route and conventional ceramic method.

Recently auto combustion synthesis method attracted considerable attention in fabricating homogeneous and unagglomerated fine ceramic powder. Availability of comparatively inexpensive precursors, simple calculations, eases in optimizations of process parameters proved to be advantageous in auto combustion synthesis.

Some Magnetoelectric Applications:

- SENSORS

  Magnetoelectric Sensors

  Hall probe sensor

  Electric field detector

- TRANSDUCERS

- MICROWAVE DEVICES

1. Resonator
2. 2. Phase shifter
3. 3. oscillator

LITERATURE REVIEW

Historically $BaTiO_3$- $NiFe_2O_4$ composites were first obtained in 1972 by Van Suchtelen.

Type of materials that undergo ME multiferroic: Single material/ Composite

Theoretically the magneto electric effect came into picture in 1894 when curie discussed correlation of magnetic and electric properties in low symmetry crystals. Another strong footing on ME effect theoretically is by L.D. Landau in 1957. According to him, " The magneto electric effect is odd with respect to time reversal and vanishes in materials without magnetic structure. First experimental observation of the ME effect was in 1960 by Astrov who found the electric field induced magneto electric effect in Cr_2O_3. Conventionally, oxide ceramic powders are made by solid-state reaction method which requires heating at elevated temperatures for long periods of time. In addition to high energy consumption, the production rate is slow. Recently, several wet chemical methods, such as the hydrothermal method, co-precipitation process, and sol–gel technique, have been developed for the synthesis of oxide ceramic powders to improve their properties. These methods may have several drawbacks : high pH sensitivity, stringent drying conditions, complex equipment and expensive precursors, and others. Generally the low temperature environment is mostly preferred for the synthesis of nanoparticles,. Some of the physical and chemical methods widely used in the synthesis of nanoferrites are ball-milling, sol–gel, co-precipitation, spray pyrolysis and hydrothermalmethods . Though the sol–gel route yields more promising results in the synthesis of nanoferrites , several preparation conditions such as dilution, fuel/oxidant ratio, pH and temperature can have an impact on the formation of the ferrites and their properties . As some of the advantageous perspectives are, this method exploits the advantages of cheap precursors, simple preparation and a resulting ultra fine and homogeneous powder .

As reported above solid state reaction or conventional ceramics method is usually followed to prepare $BaTiO_3$- $NiFe_2O_4$ or $BaTiO_3$. Nickel ferrite ($Ni_2Fe_2O_4$) is widely used as a soft ferrite in electronic devices. It is also used in catalysis. Nickel ferrite belongs to inverse spinel structure, in which the tetrahedral sites (A) are occupied by Fe^{3+} ions and the octahedral sites (B) by Fe^{2+} and Ni^{2+} ions. $_3$- $NiFe_2O_4$ based composites. The advantages of this route are: simple, cheap and free choice of composition of the constituents. Using this method various composites have been made such as $NiFe_2O_4$/PZT, $Ni_{0.75}Co_{0.25}Fe_2O_4$ + $Ba_{0.8}Pb_{0.2}TiO_3$ etc. Among these different composites $BaTiO_3$-$NiFe_2O_4$ composite seems to be most promising for applications. We therefore put the effort to study that system. Multiferroic $BaTiO_3$-$NiFe_2O_4$ composite could be regarded as model system illustrating magneto electric effect. $BaTiO_3$ is a typical ferroelectric material which has a large piezoelectricity. $NiFe_2O_4$ is ferromagnetic with large magnetization. Wet chemical methods are coming into this field of particulate composite with a lot of advantages. Firstly the sintering temperature likely to be reduced as that is followed in conventional ceramic method. This will save electrical energy in processing. Playing with the properties with varrying compositions is also possible. Composite properties could be improved by proper mixing of constituents. Wet chemical method is very much helpful.

As a summary of some of the literatures which came across is tabulated as follows:

<u>TABLE 1:</u>

Serial no.	**Name/group**	**Solid State Route followed to Synthesize $NiFe_2O_4$**	**Conclusions**
1	Vittorio Berbenni , Chiara Milanese, Giovanna Bruni, Amedeo Marini		XRPD patterns of samples of both physical and milled mixture annealed at temperatures between 400 ˚Cand 1100 ˚C show that $NiFe_2O_4$ is obtained by 12 h annealing at temperatures as lowas 400 ˚C while 24 h at 1100 ˚C are needed to yield $NiFe_2O_4$ when starting from the physical mixture.
2	ZHANG Lei,ZHOU Ke-chao, LI Zhi-you,YANG Wen-jie		High temperature has a sintering effect on the composite powder, and the microstructure with high density and fine grain inside the particle is gained.
3	H.G. El-Shobaky, N.R.E. Radwan		Solid interaction between Fe_2O_3 and NiO occurred at temperatures starting from 700 ˚C to produce $NiFe_2O_4$. The degree of reaction propagation was increased as a function of temperature.
4	F. Novel and R Valenzuela		This study contributes to the investigation of reaction kinetics mainly in two aspects: i) the use of a DTA system to perform the reactions in small quantities, thus decreasing the problems of heat transfer, and more important, providing precise reaction conditions (time and temperature); and ii) by using diffraction peak areas instead of peak heights, which leads to a higher regression coefficient.

TABLE 2:

Serial no.	Name/group	Solid State Route followed to Synthesize $BaTiO_3$	Conclusions
1	Sung-Soo Ryu , Sang-Kyun Lee , Dang-Hyok Yoon		Reaction Temperature was decreased by doping Calcium
2	U.Manzoor, D.K.Kim		Enhanced Reaction Rates due to increase in Contact area due to Small particles
3	Maria Teresa Buscaglia1, Vincenzo Buscaglia, Massimo Viviani, Giovanni Dondero, SergeR¨ohrig, Andreas R¨udiger and Paolo Nanni		
4	Teoh Wah Tzu, Ahmad Fauzi Mohd Noor, Zainal Arifin Ahmad		Complete formation of $Ba_{0.7}Sr_{0.3}TiO_3$ happen at 1150^oC and above, several different phases are detected if the calcination is done below 1150^oC.

EXPERIMENTAL WORK:

Synthesis of Nickel ferrite:

- $NiFe_2O_4$ is prepared through dry route using NiO and Fe_2O_3. NiO used was from LOBA CHEMIE with comlexometric Ni 70% and Fe_2O_3 used was from LOBA CHEMIE with 98.5% purity.
- It follows the following reaction:

$$NiO + Fe_2O_3 \rightarrow NiFe_2O_4$$

- NiO and Fe_2O_3 in1:1 molar ratio is taken and mixed using iso-propanol. After homogeneous mixing the mixture is calcined. XRD analysis is done for phase conformation.

Synthesis of Barium Titanate:

- $BaTiO_3$ is prepared through solid state reaction method. The precursors were $BaCO_3$ and TiO_2. $BaCO_3$ used was of Qualigens with 98% purity and TiO_2 used was of LOBA chemie with 99% purity.
- $BaCO_3$ and TiO_2 were taken in 1:1 mole ratio into a small agate mortar. To achieve a homogeneous mixture convenient amount of iso-propanol was used as wet mixing media. After homogeneous mixing it is calcined. During calcinations CO_2 gas is evolved. It follows the following reaction :

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2$$

- Considering the molecular weights of $BaTiO_3$ and $NiFe_2O_4$ the amount of $BaCO_3$, TiO_2, NiO and Fe_2O_3 required is calculated.

Preparation of the (50:50) Composite of Barium Titanate and Nickel Ferrite:

In the next step calcined $NiFe_2O_4$ and $BaTiO_3$ are mixed using iso-propanol in required proportion (1:1 molar weight ratio). After preparation of all the batches 3% PVA (binder) is added to each batch and mixed uniformly.

- The PVA mixed mixture was used to make several pellets. Each pellet being formed from around 0.75gm mixture.

Pressing

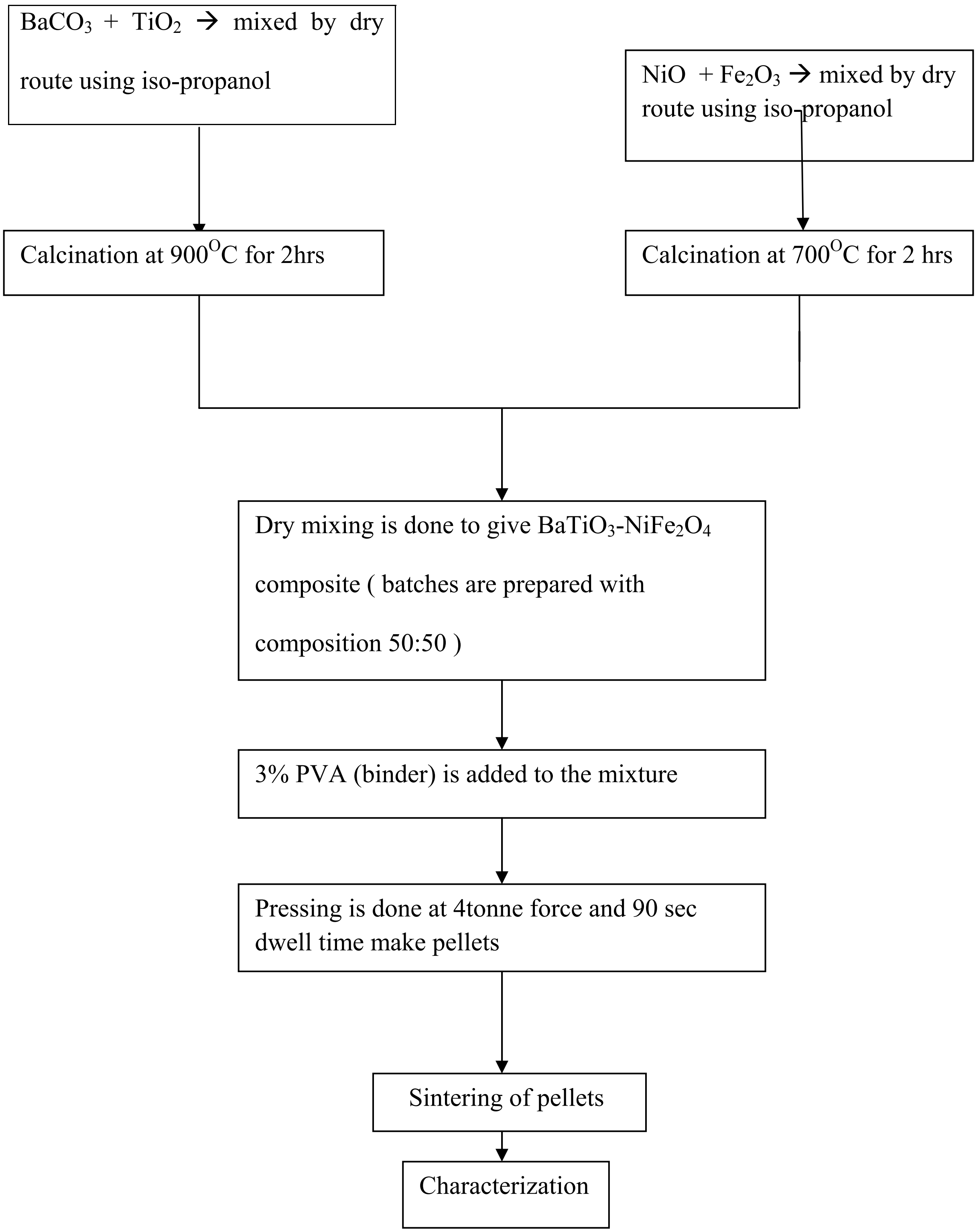
- The powder was pressed using CARVER PRESS USA and circular die.
- For the preparation of pellets 4 Ton force and dwell time of 90 sec was set.

Sintering

- Two pellets were sintered at 1200 ^oC for 8 hrs. Other pellets were sintered at 1100, 1150 and 1200 ^oC for 2 hrs.
- From above each sample two pellets were taken and their dry weight was measured. Then suspended weight and soaked weight of the sample was measured. From these measurement of bulk density of the pellets was calculated. The calculated density was compared to that of theoretical density of $BaTiO_3$-$NiFe_2O_4$ (50:50) i.e. =5.69.
  The average bulk density was found to be 96.5%.

- The sintered pellets were polished and XRD analysis was done.

FLOW CHART FOR SYNTHESIS OF BARIUM TITANATE-NICKEL FERITE COMPOSITE



RESULTS AND DISCUSSION

After Calcination the samples were characterized by XRD.

XRD Results of Nickel Ferrite

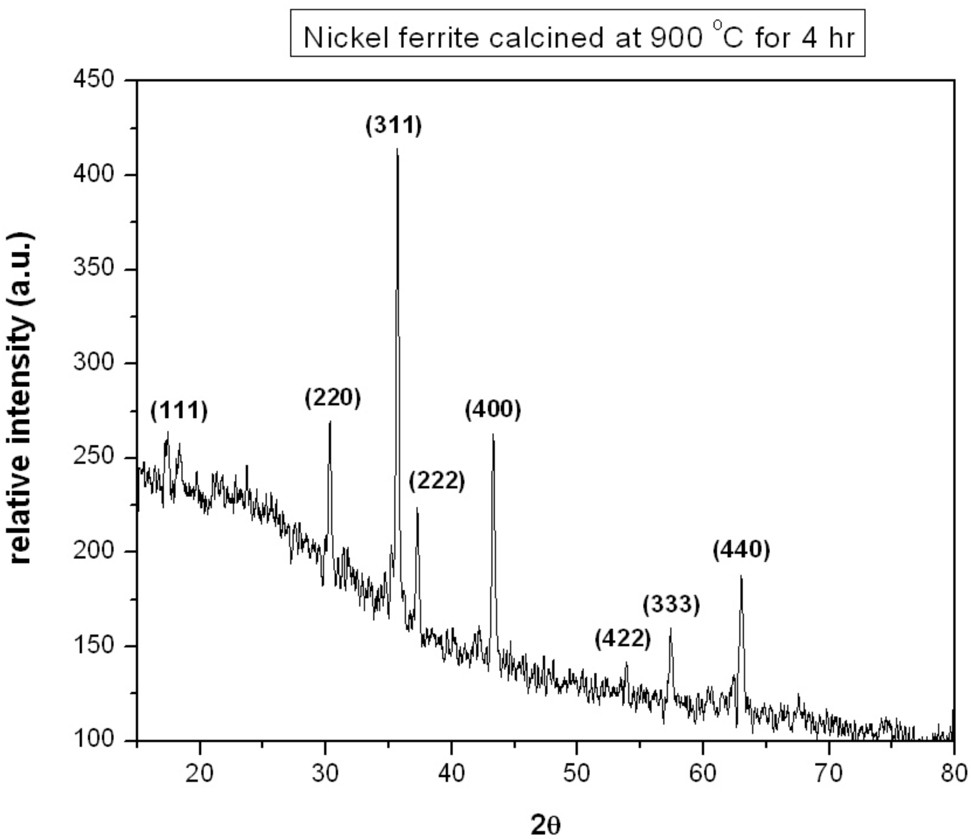


Fig.1- XRD graph of $NiFe_2O_4$ prepared by solid state reaction method (Calcination temperature = 900 ^oC)

The X-Ray Diffraction pattern of synthesized nickel ferrite matched exactly with reference number 44-1485 (JCPDS) . It was evident that the prepared ferrite belongs to cubic spinel and the space group as Fd3m. the value of lattice parameter = 8.3393 A^o .

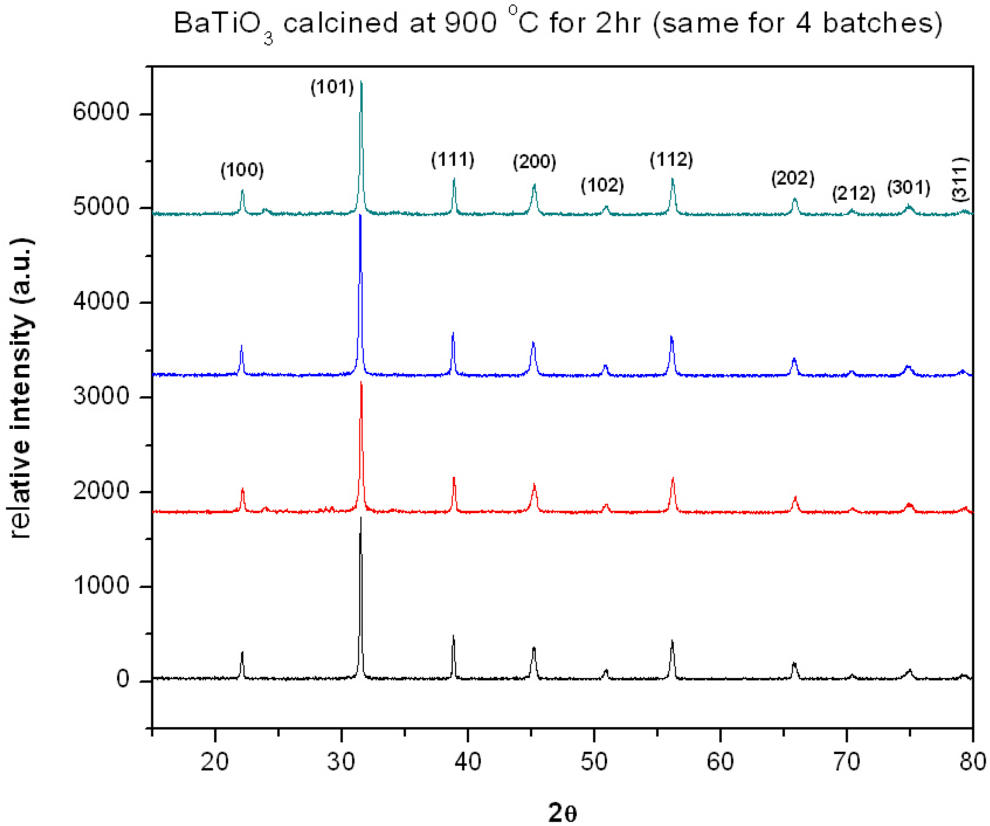


Fig.2- XRD graph of $BaTiO_3$ prepared by solid state reaction method (Calcination temperature = 900 ^oC for each)

It was found that all the batches of $BaTiO_3$ had some impurity phases near the 2θ value of 23 except bottom most sample. Those were identified as some intermediate phases of Ba-Ti-O system as $BaTi_2O_5$, $BaTi_3O_7$ and so on. As phase pure $BaTiO_3$ was the requirement, mixed powder of $BaCO_3$ and TiO_2 was calcined further for higher temperature. The report of the samples which were calcined at 1000 ^oC has been given below.

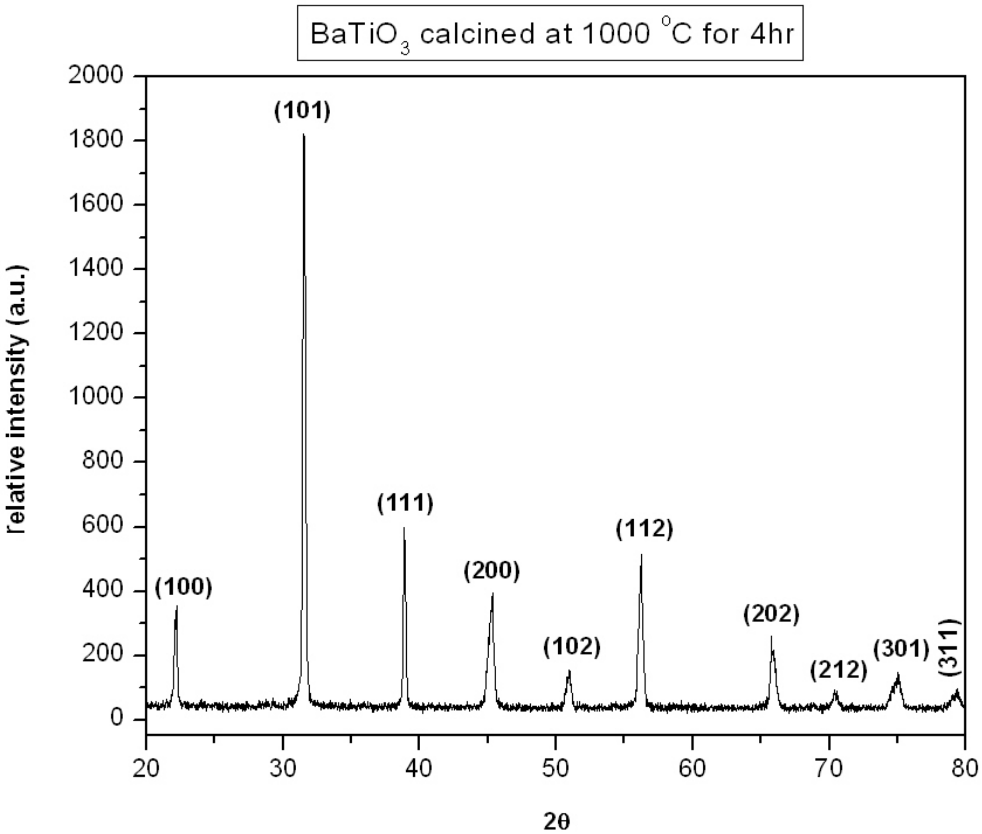


Fig.3- XRD graph of $BaTiO_3$ prepared by solid state reaction method (Calcination temperature = 1000 ^oC)

The XRD peaks were found to be matched with reference sample 75-0461. It was also confirmed that cubic Barium Titanate was formed after calcination. It belongs to the space group Pm-3m. Lattice parameter was observed as 4.0119 A^o .

It has been proved that 1200 ^oC for sintering pellets was not favourable. It was evident from the following XRD result which depicted that there are some impurity phases along with the individual constituent phases.

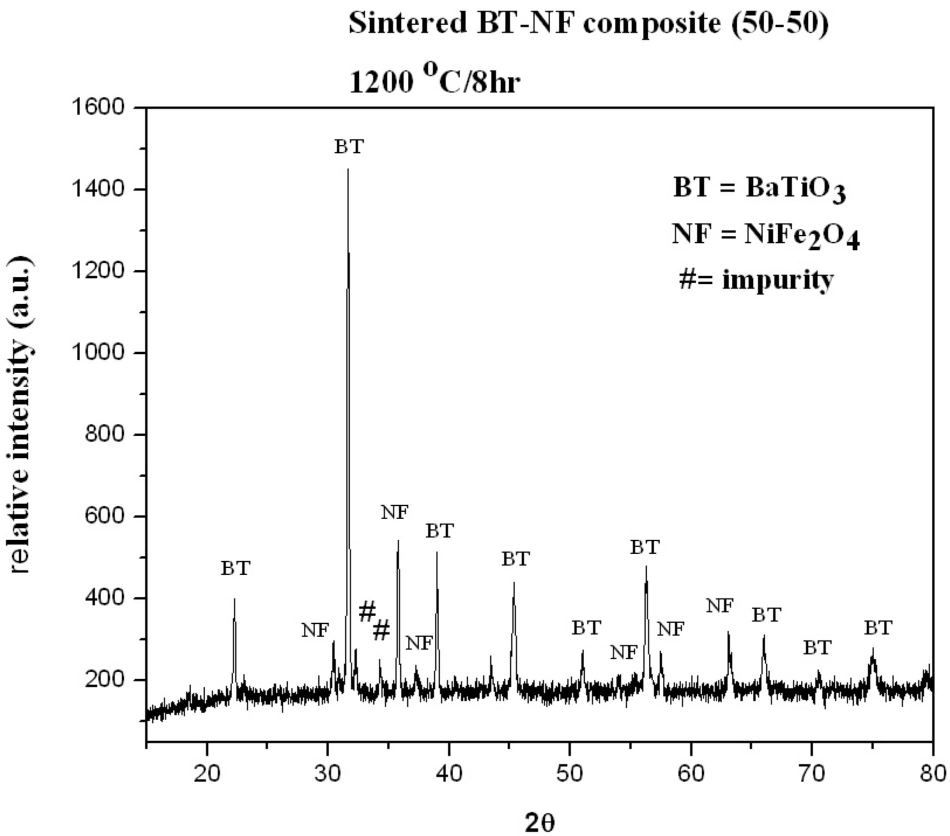


Fig.4- XRD graph of composite (sintered at 1200 oC for 8 hr)

The sintered samples were made (by polishing) ready for further characterization.

CONCLUSIONS AND FUTURE WORK

1. Phase pure Barium Titanate and Nickel ferrite were prepared.
2. Composites of were prepared where the each composites consists of 50 mole percentage of $BaTiO_3$ and mole percentage of $NiFe_2O_4$.
3. Sintered pellets were prepared as par the requirement of further characterization (like XRD SEM and Dielectric measurement)
4. In future work the followings are to be done
   i) Getting ensured of no reaction between constituent phases
   ii) Modification of particle morphology of the constituent phase for the highest magnetoelectric voltage co-efficient.

REFERENCES

1. R. Grossinger, Giap V. Duong and R. Sato-Turtelli, Journal of Magnetism and magnetic materials 320 (2008) 1972-1977.
2. Jungho Ryu, Shashank Priya, Kenji Uchino and Hyoun-EE Kim, Journal of electroceramics, 8, 107-119, 2002.
3. W. Eerenstein, N.D. Mathur and J.F. Scott, nature05023.
4. Vittorio Berbenni , Chiara Milanese, Giovanna Bruni, Amedeo Marini, Thermochimica Acta 469 (2008) 86–90.
5. ZHANG Lei**,**ZH OU Ke-chao, LI Zhi-you,Y ANG Wen-jie, Thermochimica Acta 469 (2008) 86–90.
6. H.G. El-Shobaky, N.R.E. Radwan, Trans. Nonferrous Met. SOC. China 16(2006) 1076-1079.
7. Sung-Soo Ryu , Sang-Kyun Lee , Dang-Hyok Yoon, J Electroceram (2007) 18:243–250 .
8. Maria Teresa Buscaglia1, Vincenzo Buscaglia, Massimo Viviani, Giovanni Dondero, SergeR¨ohrig, Andreas R¨udiger and Paolo Nanni, Nanotechnology **19** (2008) 225602 (7pp).
9. U.Manzoor and D.K.Kim, J. Mater. Sci. Technol., Vol.23 No.5, 2007.
10. Teoh Wah Tzu, Ahmad Fauzi Mohd Noor and Zainal Arifin Ahmad, formation of barium strontium titanate powder by solid state reaction using different calcinations temperatures.
11. F. Novel and R Valenzuela, Materials Research Bulletin, Vol. 30, No. 3, pp. 33X340.1995.