

# 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**

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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**” is submitted by Mr. **ALOK PATEL** 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: 7<sup>th</sup> May, 2010

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ALOK PATEL

## CONTENTS

## PAGE NO.

A. ABSTRACT	5
B.	
1. INTRODUCTION	6
2. LITERATURE REVIEW	11
3. EXPERIMENTAL WORK	14
4. RESULTS AND DISCUSSIONS	20
5. CONCLUSIONS	25
C. LIST OF TABLES	
Table 1	15
Table2	16
D.LIST OF DIAGRAMS	
Fig.1-XRD graph of BaTiO <sub>3</sub> prepared by solid state reaction method (calcination temperature = 900 °C)	21
Fig.2- XRD graph of BaTiO <sub>3</sub> prepared by solid state reaction method (calcination temperature = 1000 °C)	22
Fig.3- XRD graph of NiFe <sub>2</sub> O <sub>4</sub> prepared by solid state reaction method (Calcination temperature = 900 °C )	23
E. REFERENCES	26

## **ABSTRACT**

Both Barium titanate and Nickel ferrite were synthesized by Conventional ceramic processing method. Mixed oxide of  $\text{BaCO}_3$  and  $\text{TiO}_2$  for  $\text{BaTiO}_3$  and  $\text{NiO}$  and  $\text{Fe}_2\text{O}_3$  for  $\text{NiFe}_2\text{O}_4$  were calcined at  $1000^\circ\text{C}$  for four hour and  $900^\circ\text{C}$  for four hour respectively. Phases of particular compounds have been confirmed by XRD. For preparing multi ferroic composites the two separate powders are proved to be suitable. Composite (Four batches were prepared with composition 50:50, 60:40,70:30 and 80:20 ).

# **CHAPTER 1:**

## **INTRODUCTION**

## **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 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  $\text{Cr}_2\text{O}_3$ , 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 epitaxy etc. Among the available solution- chemistry routes, combustion technique is capable of producing nano crystalline 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 homogeneity 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  $\text{NiFe}_2\text{O}_4$  samples can be synthesized by following methods; coprecipitation, combustion, citrate gel and conventional ceramic method. AR grade metal nitrates,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were used for all three syntheses.

Nanocrystalline  $\text{BaTiO}_3$  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.

## **Other Magnetolectric Applications:**

- **SENSORS**

  - Magnetolectric Sensors

    - Hall probe sensor

    - Electric field detector

- **TRANSDUCERS**

- **MICROWAVE DEVICES**

1. Resonator
2. Phase shifter
3. oscillator

# **CHAPTER 2:**

# **LITERATURE REVIEW**

## **LITERATURE REVIEW**

Historically BaTiO<sub>3</sub>- NiFe<sub>2</sub>O<sub>4</sub> 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<sub>2</sub>O<sub>3</sub>. 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 hydrothermal methods . 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<sub>3</sub>- NiFe<sub>2</sub>O<sub>4</sub> or BaTiO<sub>3</sub>. Nickel ferrite (Ni<sub>2</sub>Fe<sub>2</sub>O<sub>4</sub>) 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<sup>3+</sup> ions and the octahedral sites (B) by Fe<sup>2+</sup> and Ni<sup>2+</sup> ions. <sub>3</sub>- NiFe<sub>2</sub>O<sub>4</sub> 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<sub>2</sub>O<sub>4</sub>/PZT, Ni<sub>0.75</sub>Co<sub>0.25</sub>Fe<sub>2</sub>O<sub>4</sub> + Ba<sub>0.8</sub>Pb<sub>0.2</sub>TiO<sub>3</sub> etc. Among these different composites BaTiO<sub>3</sub>-NiFe<sub>2</sub>O<sub>4</sub> composite seems to be most promising for applications. We therefore put the effort to study that system. Multiferroic BaTiO<sub>3</sub>-NiFe<sub>2</sub>O<sub>4</sub> composite could be regarded as model system illustrating magneto electric effect. BaTiO<sub>3</sub> is a typical ferroelectric material which has a large piezoelectricity. NiFe<sub>2</sub>O<sub>4</sub> 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 varying compositions is also possible. Composite properties could be improved by proper mixing of constituents. Wet chemical method is very much helpful.

# **CHAPTER 3:**

## **EXPERIMENTAL**

## **WORK**

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

**TABLE 1:**

<b>Serial no.</b>	<b>Name/group</b>	<b>Solid State</b>	<b>Conclusions</b>
1	Sung-Soo Ryu , Sang-Kyun Lee , Dang-Hyok Yoon	<b>Route followed</b>	Reaction Temperature was decreased by doping Calcium
2	U.Manzoor, D.K.Kim	<b>to Synthesize</b>	Enhanced Reaction Rates due to increase in Contact area due to Small particles
3	Maria Teresa Buscaglia1, Vincenzo Buscaglia, Massimo Viviani, Giovanni Dondero, Serge Röhrig, Andreas Rüdiger and Paolo Nanni	<b>BaTiO<sub>3</sub></b>	
4	Teoh Wah Tzu, Ahmad Fauzi Mohd Noor, Zainal Arifin Ahmad		Complete formation of Ba <sub>0.7</sub> Sr <sub>0.3</sub> TiO <sub>3</sub> happen at 1150°C and above, several different phases are detected if the calcination is done below 1150°C.

**TABLE 2:**

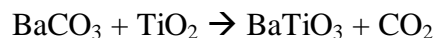
<b>Serial no.</b>	<b>Name/group</b>	<b>Solid State</b>	<b>Conclusions</b>
1	Vittorio Berbenni , Chiara Milanese, Giovanna Bruni, Amedeo Marini	<b>Route</b>	XRPD patterns of samples of both physical and milled mixture annealed at temperatures between 400 °C and 1100 °C show that NiFe <sup>2+</sup> O <sub>4</sub> is obtained by 12 h annealing at temperatures as low as 400 °C while 24 h at 1100 °C are needed to yield NiFe <sub>2</sub> O <sub>4</sub> when starting from the physical mixture.
2	ZHANG Lei,ZH OU Ke-chao, LI Zhi-you, Y ANG Wen-jie	<b>to</b>	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	<b>Synthesize</b>	Solid interaction between α-Fe <sub>2</sub> O <sub>3</sub> and NiO occurred at temperatures starting from 700 °C to produce NiFe <sub>2</sub> O <sub>4</sub> . The degree of reaction propagation was increased as a function of temperature.
4	F. Novel0 and R Valenzuela	<b>NiFe<sub>2</sub>O<sub>4</sub></b>	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.



## **EXPERIMENTAL WORK:**

### **Synthesis of Barium Titanate:**

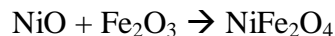
- BaTiO<sub>3</sub> is prepared through solid state reaction method. The precursors were BaCO<sub>3</sub> and TiO<sub>2</sub>. BaCO<sub>3</sub> used was of Qualigens with 98% purity and TiO<sub>2</sub> used was of LOBA chemie with 99% purity.
- BaCO<sub>3</sub> and TiO<sub>2</sub> were taken in 1:1 mole 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<sub>2</sub> gas is evolved. It follows the following reaction :



- Considering the molecular weights of BaTiO<sub>3</sub> and NiFe<sub>2</sub>O<sub>4</sub> the amount of BaCO<sub>3</sub>, TiO<sub>2</sub>, NiO and Fe<sub>2</sub>O<sub>3</sub> required is calculated.

### **Synthesis of Nickel ferrite:**

- NiFe<sub>2</sub>O<sub>4</sub> is prepared through dry route using NiO and Fe<sub>2</sub>O<sub>3</sub>. NiO used was of LOBA CHEMIE with complexometric Ni 70% and Fe<sub>2</sub>O<sub>3</sub> used was of LOBA CHEMIE with 98.5% purity.
- It follows the following reaction:



- NiO and Fe<sub>2</sub>O<sub>3</sub> in 1:1 molar ratio is taken and mixed using iso-propanol. After homogeneous mixing the mixture is calcined. XRD analysis is done for phase conformation.

### **Preparation of the Composite of Barium Titanate and Nickel Ferrite:**

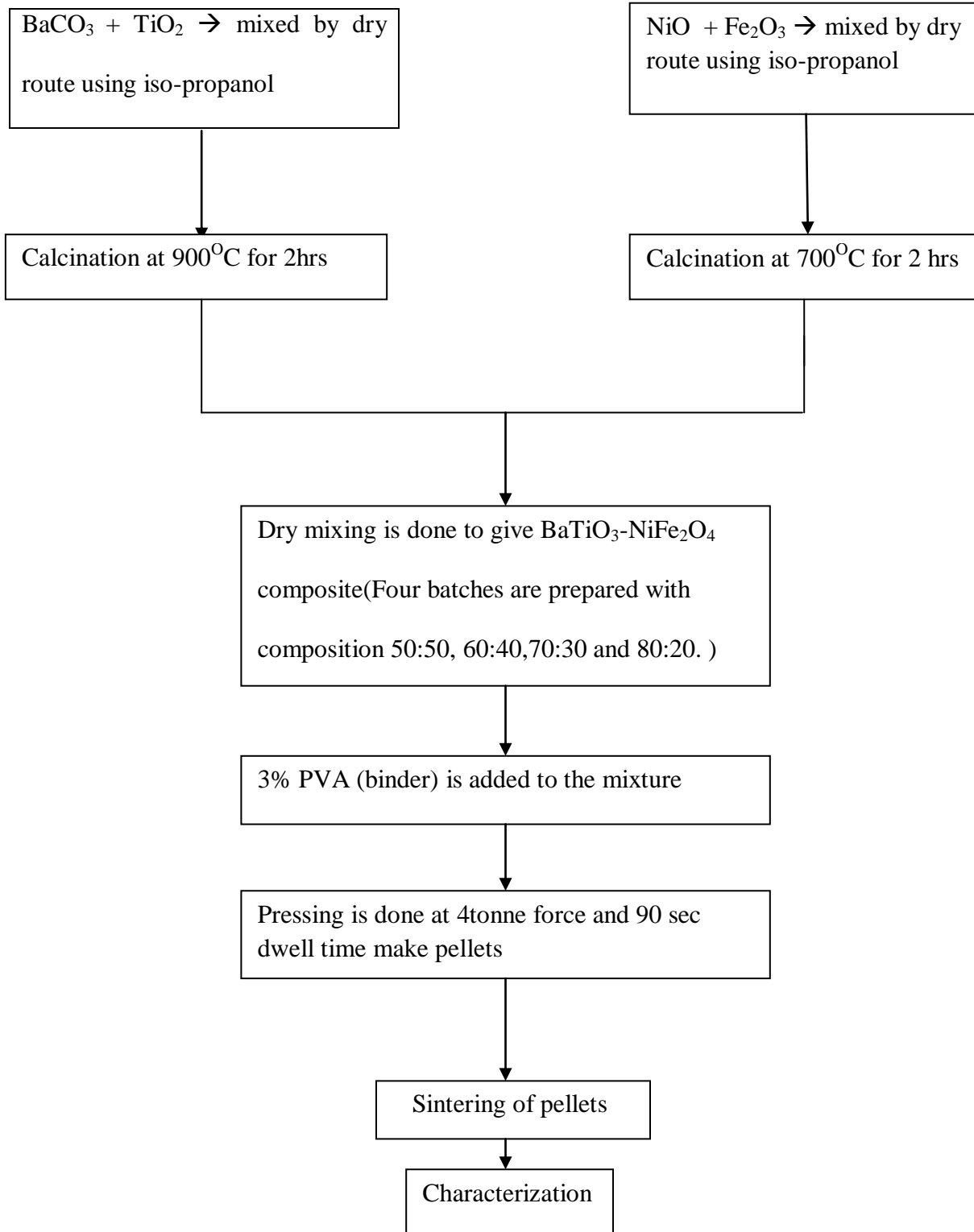
In the next step calcined  $\text{NiFe}_2\text{O}_4$  and  $\text{BaTiO}_3$  are mixed using iso-propanol in required proportion. Four batches of  $\text{BaTiO}_3$ - $\text{NiFe}_2\text{O}_4$  with composition ratio 50:50, 60:40, 70:30 and 80:20 are prepared.

- 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 4T force and dwell time of 90 sec was set.
- Each pellet prepared is sintered at  $1250^\circ\text{C}$  for 2 hrs.
- The pellets prepared with 50:50 composition of  $\text{BaTiO}_3$  and  $\text{NiFe}_2\text{O}_4$  are divided into three categories:
  1.  $\text{BaTiO}_3$  fired at  $1000^\circ\text{C}$  and  $\text{NiFe}_2\text{O}_4$  fired at  $900^\circ\text{C}$ .
  2.  $\text{BaTiO}_3$  fired at  $1000^\circ\text{C}$  and  $\text{NiFe}_2\text{O}_4$  fired at  $800^\circ\text{C}$ .
  3.  $\text{BaTiO}_3$  fired at  $1100^\circ\text{C}$  and  $\text{NiFe}_2\text{O}_4$  fired at  $800^\circ\text{C}$ .
- 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 density of the pellets was calculated. The calculated density was compared to that of theoretical density of  $\text{BaTiO}_3$ - $\text{NiFe}_2\text{O}_4$  (50:50).
- The sintered pellets were polished and XRD analysis was done.

**FLOW CHART FOR SYNTHESIS OF BARIUM TITANATE-NICKEL FERITE COMPOSITE**



# **CHAPTER 4:**

**RESULTS**

**AND**

**DISCUSSION**

## **RESULTS AND DISCUSSION**

After calcination the samples were characterized by XRD.

### **XRD Results of Barium Titanate**

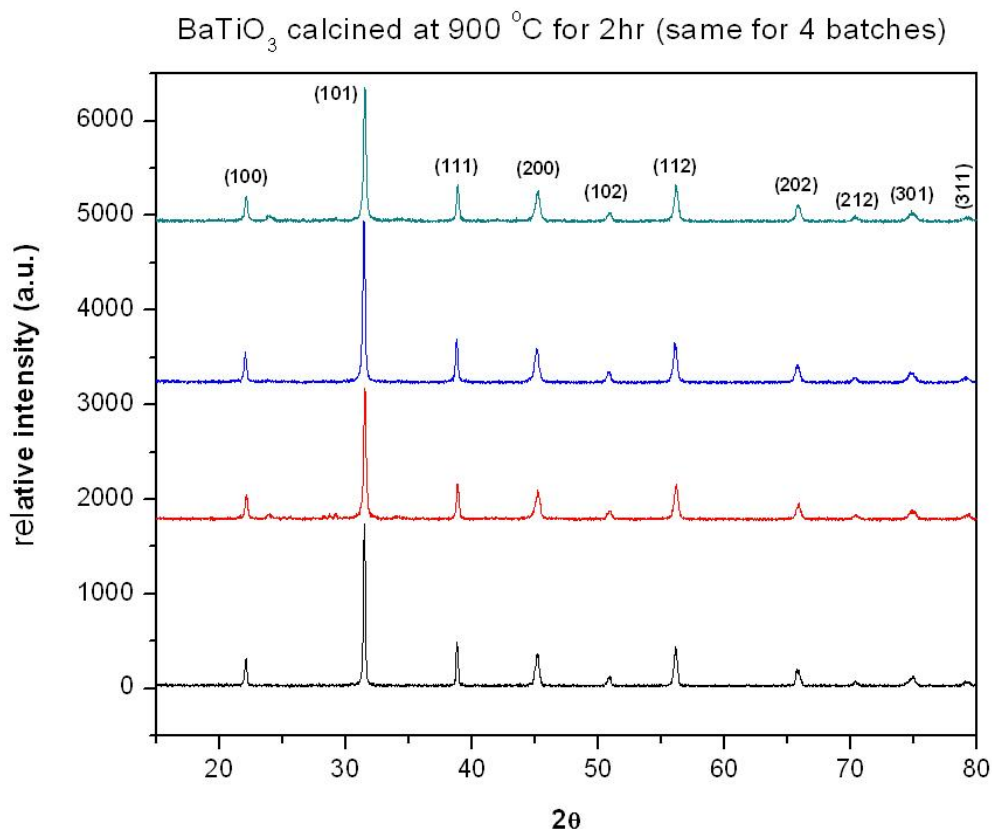


Fig.1- XRD graph of BaTiO<sub>3</sub> prepared by solid state reaction method (Calcination temperature = 900 °C for each)

It was found that all the batches of BaTiO<sub>3</sub> 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<sub>2</sub>O<sub>5</sub>, BaTi<sub>3</sub>O<sub>7</sub> and so on. As phase pure BaTiO<sub>3</sub> was the requirement, mixed powder of BaCO<sub>3</sub> and TiO<sub>2</sub> was calcined further for higher temperature. The report of the samples which were calcined at 1000 °C has been given below.

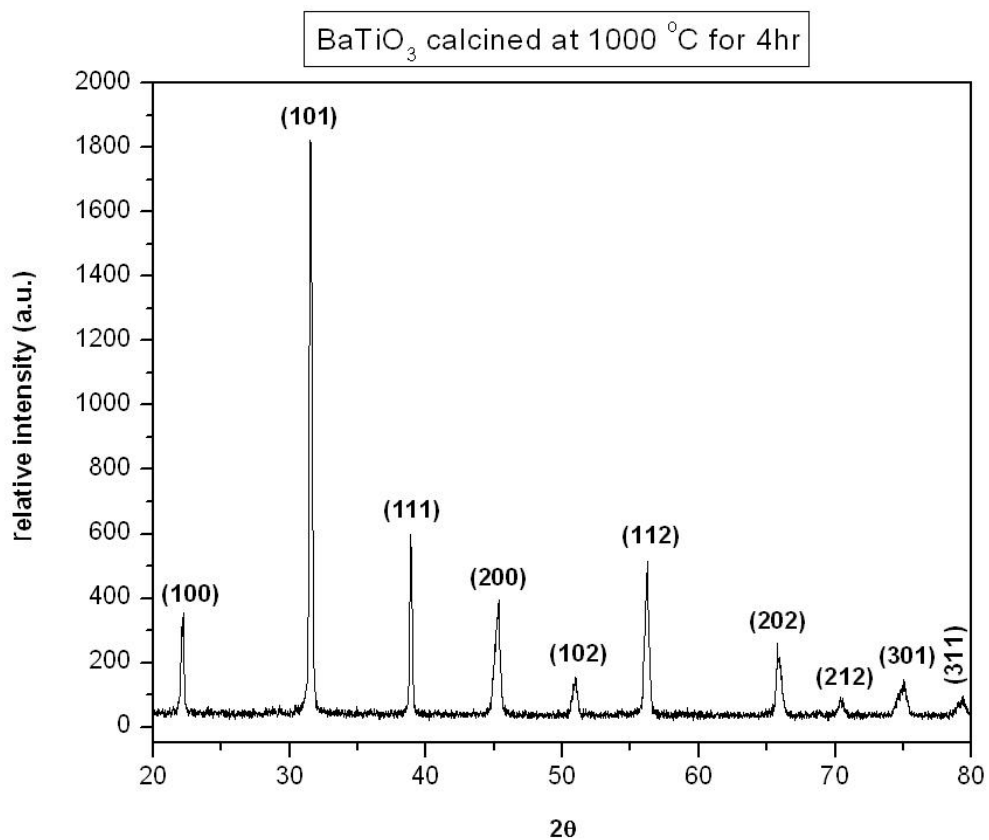


Fig.2- XRD graph of BaTiO<sub>3</sub> prepared by solid state reaction method (Calcination temperature = 1000 °C )

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 Å .

## XRD Results of Nickel Ferrite

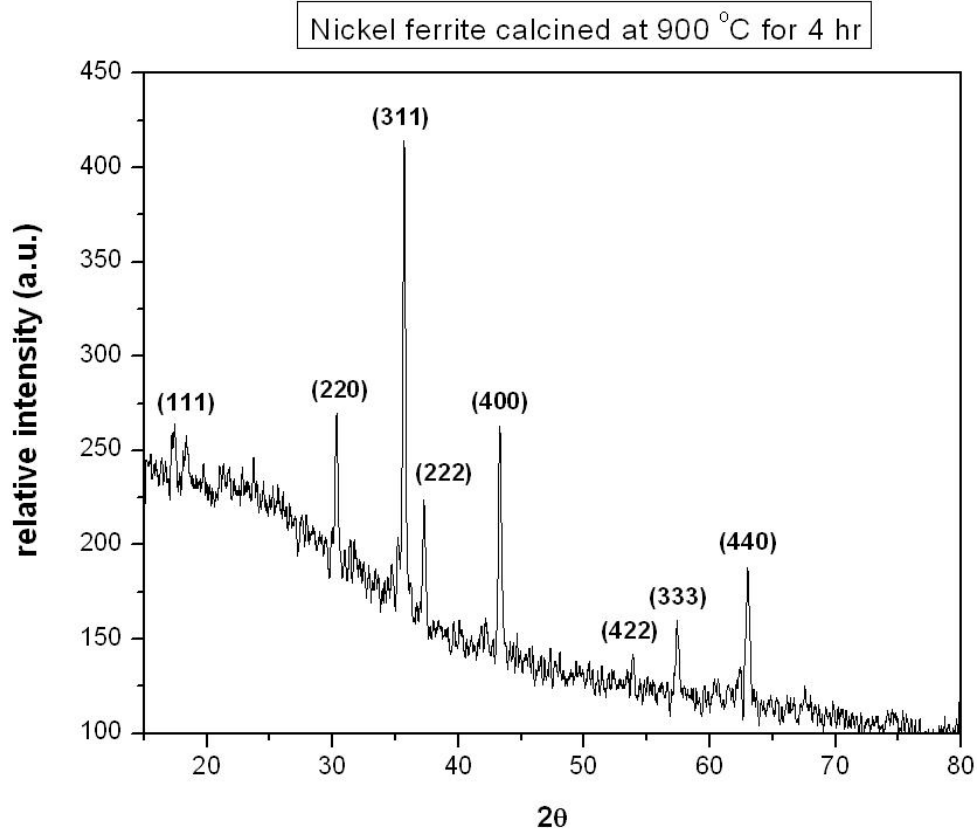


Fig.3- XRD graph of  $\text{NiFe}_2\text{O}_4$  prepared by solid state reaction method (Calcination temperature = 900 °C )

The nickel ferrite X-Ray Diffraction pattern matched exactly with reference number 44-1485 (JCPDS) . It was evident that the prepared ferrite belongs to cubic spinel and the space group as  $Fd\bar{3}m$ . the value of lattice parameter = 8.3393 Å .

After mixing in different compositions, XRD of the samples were taken to see the individual peak positions of the constituent phases. Starting from 50-50, 60-40, 70-30 and 80-20.

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

# **CONCLUSIONS AND FUTURE WORK**



## **CONCLUSIONS AND FUTURE WORK**

1. Phase pure Barium Titanate and Nickel ferrite were prepared.
2. Composites of 50-50, 60-40, 70-30 and 80-20 were prepared where 50, 60 70 and 80 denotes the mole percentage of BaTiO<sub>3</sub> and rest is NiFe<sub>2</sub>O<sub>4</sub>
3. Sintered pellets were prepared as per the requirement of further characterization (like XRD SEM and Dielectric measurement)
4. In future work the followings are to be done
  - i) Ensuring no reaction of constituent phases
  - ii) Optimization of the composition for the highest magnetoelectric voltage co-efficient
  - iii) Modification of particle morphology of the constituent phase to enhance composite characteristics.

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