SYNTHESIS AND CHARECTERIZATION OF BARIUM TITANATE-COBALT FERRITE COMPOSITE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology in Ceramic Engineering

BY

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DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA-769008
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National Institute of Technology, Rourkela

CERTIFICATE

This is to certify that the thesis entitled, ***"Synthesis and Characterization of barium titanate-cobalt ferrite composite"*** submitted by MR. ARPIT GUPTA in partial fulfilment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the 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:

Prof. Arun Chowdhury
Dept. of Ceramic Engineering
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Finally, yet importantly, my sincere thanks to all my friends who have patiently extended all sorts of help for accomplishing this undertaking, and the successful completion of this project.

13^{th} may 2013

Thanking you,

Arpit Gupta

CONTENTS

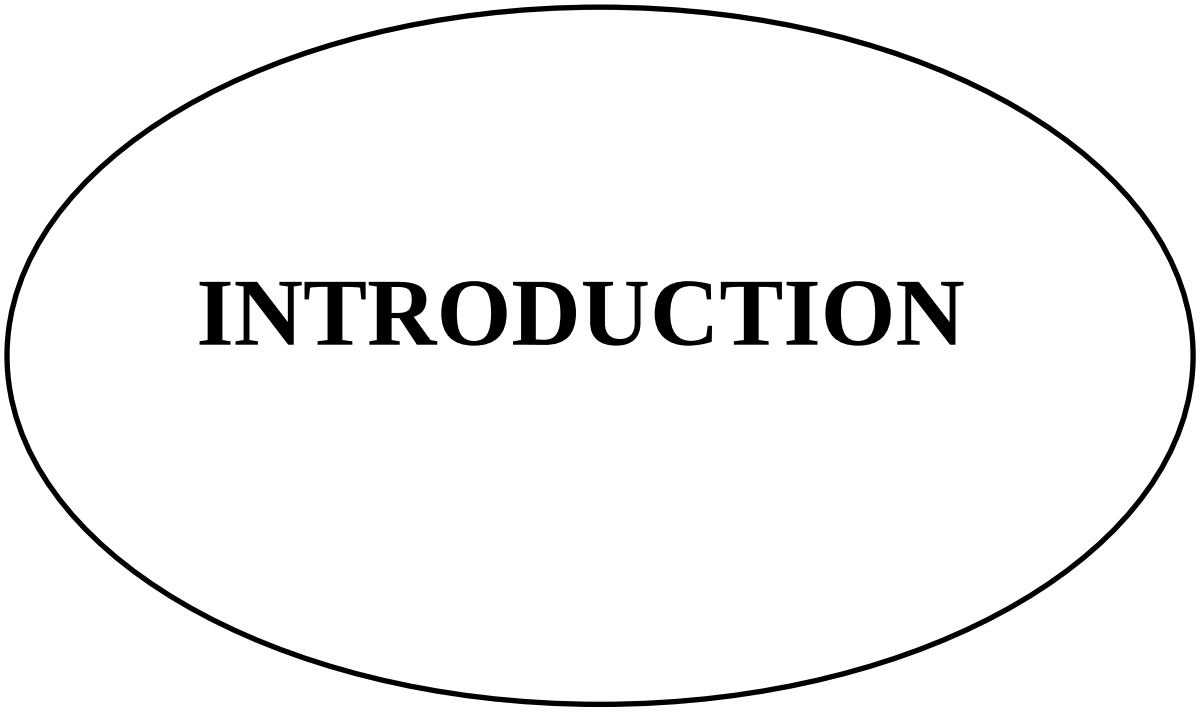
LIST OF FIGURES:

LIST OF TABLES:

ABSTRACT

Barium titanate –cobalt ferrite composite has been prepared by mixing of cobalt ferrite obtained by co-precipitation method and barium titanate synthesized by solid route. Phase formation behavior of the sample has been studied from the XRD pattern of the sintered sample. Microstructure of the sintered sample has been studied by using scanning electron microscopy. Magnetoelectric voltage co-efficient of different composition of composite has also been studied.

Chapter 1



Barium titnate:

Chemical formula: $BaTiO_3$

Compound type: inorganic

Structure: pervoskite

This titanate is a ferroelectric ceramic material, with a photorefractive effect and piezoelectric properties. Barium titanate is a dielectric ceramic used for capacitors. It is a piezoelectric material for microphones and other transducers. The spontaneous polarization of barium titanate is about 0.15 C/m^2 at room temperature and its Curie point is 120 °C. As a piezoelectric material, it was largely replaced by lead zirconate titanate, also known as PZT. Polycrystalline barium titanate displays positive temperature coefficient, making it a useful material for thermistors and self-regulating electric heating system.

Properties of $BaTiO_3$:

- Ferroelectric

- By implication, para-electric and also piezoelectric material

- Hysteresis loop for polycrystalline $BaTiO_3$ ceramic has a higher coercive field (E_c) and lower remnant polarization (P_r) than the single crystal.

- Melting point is 1625 °C.

 Density is 6.02 gm/cc.

 Behaves as Relaxor dielectric, dielectric susceptibility (κ) and dielectric loss factor (tanδ) changes with frequency.

Cobalt ferrite:

Chemical formulae: $CoFe_2O_4$

This is a cubic ferrite and is magnetically hard. These ferrites has a spinel structure and are sometimes called Ferro-spinel, because its crystal structure is closely related to that of the mineral spinel, $MgO.Al_2O_3$.The structure is complex, in that there are eight formula units or a total of 8*7=56 ions, per unit cell. The large oxygen ion is packed quite close together in a face centered cubic arrangement, and the much smaller metal ions occupy the spaces between them. These spaces are of two kinds.one is called a tetrahedral or A site, because it located at the center of a tetrahedron whose corners are occupied by oxygen ions. The other is called octahedral or B site, because the oxygen ions around it occupy the corners of an octahedron

Properties of $CoFe_2O_4$:

Piezomagnetic material

Lattice Parameter : 0.838 nm

Density : 5.29 g/cm3

Barium titanate-cobalt ferrite composite

In the past few decades, extensive research has been conducted on the magnetoelectric (ME) effect in single phase and composite materials. Dielectric 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. Single phase materials suffer from the drawback that the ME effect is considerably weak even at low temperatures, limiting their applicability in practical devices. Better alternatives are ME composites that have large magnitudes of the ME voltage coefficient. The composites exploit the product property of the materials.

The ME effect can be realized using composites consisting of individual piezomagnetic and piezoelectric phases or individual magnetostrictive and piezoelectric phases.

One way is to use the product property of the piezoelectric and magnetostrictive effect. A composite material of magnetostrictive and piezoelectric materials can be explained as follows. When a magnetic field is applied to the composite the magnetostrictive material is strained. This strain induces a stress on the piezoelectric, which generates the electric field. The converse effect is also possible, in which the electric field applied to the piezoelectric material produces strain, which is transferred as stress to the

magnetostrictive material. This causes the change in magnetic permeability of the material.

In both case, the product properly resulting in such composites is the magnetoelectric effect in which an applied magnetic field induces an electric field, and an applied electric field induces the change in magnetic permeability in the composite. .

ME Effect = (Magnetic／mechanical) × (mechanical／electrical)

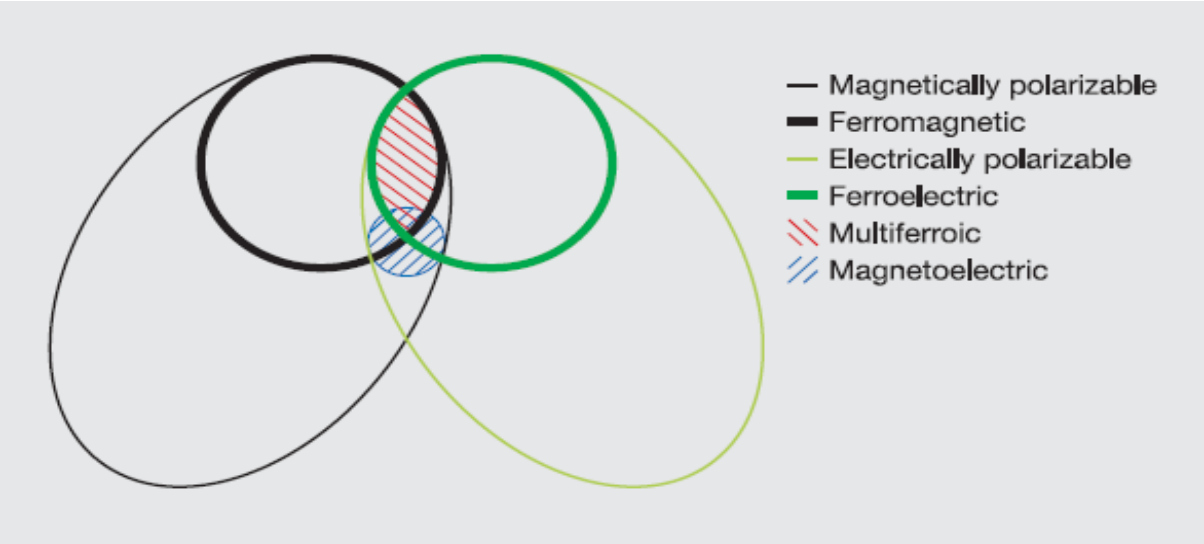


Fig1-The relationship between multiferroic and magnetoelectric materials.

APPLICATIONS:

1. Composite structures in bulk form are explored for high-sensitivity ac magnetic field sensors (1).
2. Electrically tunable microwave devices such as filters (2), oscillators and phase shifters.

3. Novel spintronic devices such as tunnel magnetoresistance (TMR) sensors.
4. One can also explore multiple state memory elements, where data are stored both in the electric and the magnetic polarizations.

(1) (2)

High-sensitive ac magnetic field sensor; microwave filter

Chapter 2

Studies by Van den Boomgaard et al**.** [1] have first demonstrated that the effective magnetoelectric coupling effect in the composite materials relies on optimal composition, favourable microstructure and non-slip contact between different phases. Among various magnetoelectric composite systems, $BaTiO_3/CoFe_2O_4$ composite materials are the first investigated. The $BaTiO_3$ and $CoFe_2O_4$ phases are found to be separated from each other by cooling the eutectic liquid in a unidirectional solidification process, which produces the $BaTiO_3/CoFe_2O_4$ composites with a lamellar morphology.

The directional solidification and the interface structure of $BaTiO_3$-$CoFe_2O_4$ eutectic were investigated by J. ECHIGOYA [2] using the floating zone melting method and following result was obtained.

The micro structure of the eutectic consisted of grains of lamellar or fibrous morphology.

The magnetoelectric sensitivity of these materials was usually poor due to the undesirable $CoFe_2O_4$ phase distribution and the lack of control to the microstructure of the composites. To overcome these difficulties,S.Q .Ren reports a novel approach [3] of preparing multiferroic $BaTiO_3/CoFe_2O_4$ composites through a one-pot process. The $BaTiO_3/CoFe_2O_4$ particulate composites are synthesized by a one-pot process. Particulate $CoFe_2O_4$ phase is embedded in the $BaTiO_3$ matrix homogeneously with 3-0 connectivity via a phase segregation mechanism, leading to an excellent interface contact between the $BaTiO_3/CoFe_2O_4$ phases and the high insulation. Consequently, the

particulate Composite exhibits high ME sensitivity, and the maximum α_{ME} at the optimal magnetic bias.

Haimei Zheng created vertically aligned multiferroic $BaTiO_3$-$CoFe_2O_4$ thin film [4] nanostructures using pulsed laser deposition. Spinel $CoFe_2O_4$ and perovskite $BaTiO_3$ spontaneously separated during the film growth. $CoFe_2O_4$ forms nano-pillar arrays embedded in a $BaTiO_3$ matrix, which show three-dimensional heteroepitaxy. $CoFe_2O_4$ pillars have uniform size and spacing. As the growth temperature increases the lateral size of the pillars also increases. The size of the $CoFe_2O_4$ pillars as a function of growth temperature at a constant growth rate follows an Arrhenius behaviour. The formation of the $BaTiO_3$-$CoFe_2O_4$ nanostructures is a process directed by both thermodynamic equilibrium and kinetic diffusion.

R. P. Mahajan studied $CoFe_2O_4$–$BaTiO_3$ composites prepared by conventional ceramic double sintering process with various compositions [5]. Presence of two phases in the composites was confirmed using X-ray diffraction. The dc resistivity and thermo-emf as a function of temperature in the temperature range 300 K to 600 K were measured. Variation of dielectric constant (ε) with frequency in the range 100 Hz to 1 MHz and also with temperature at a fixed frequency of 1 kHz was studied. The ac conductivity was derived from dielectric constant (ε) and loss tangent (tan δ). The nature of conduction is discussed on the basis of small polaron hopping model. The static value of magnetoelectric conversion factor has been studied as a function of magnetic

field. He showed that the conduction in the present composites is due to thermally activated polaron hopping. This is also confirmed from variation of ac conductivity with frequency. The maximum magnetoelectric coefficient is observed for 75 mole % of $BaTiO_3$.

Junwu Nie prepared magnetoelectric nano-composites powders and Ceramics by the molten-salt synthesis method and standard sintering ceramic method, respectively **[**6]. The XRD patterns of the powder and ceramics exhibit both ferrite and ferroelectric phases. The perfect interface of the two phases was presented by SEM images. The dielectric behaviour was explained in terms of dielectric constant patterns and electric hysteresis loops, suggesting that polarization in these composites was similar to that of conduction in ferrite. The magnetic hysteresis loops show good magnetic characteristics in all the composites. A maximum value of magnetoelectric coefficient (E =17.04mVcm^{-1} Oe^{-1}) was obtained in the case of $0.5CoFe_2O_4$ + $0.5BaTiO_3$ composite. We think that the high magnetoelectric coefficient is due to the larger nano-level interface connection and interaction area in x = 0.5 ME ceramic than that x = 0.65 ME, which lead to good piezoelectricity/piezomagneticity behaviours and the effective magnetic-mechanical electric interaction between the magnetostrictive and ferroelectric phases.

Atchara Khamkongkaeo prepared $CoFe_2O_4$−$BaTiO_3$ particulate composites by wet ball milling method, their magnetoelectric (ME) effect was

studied as a function of their constituents and modulation frequency [7]. The results show that the ME coefficient increases as a function of modulation frequency from 400 to 1000 Hz and the ME characteristics of ME curves are also modified because the electrical conductivity of the $CoFe_2O_4$ phase is sensitive to the increase in frequency between 400 and 1 000 Hz. The third phase $Ba_2Fe_2O_5$ formed during the sintering tends to reduce the ME effect.

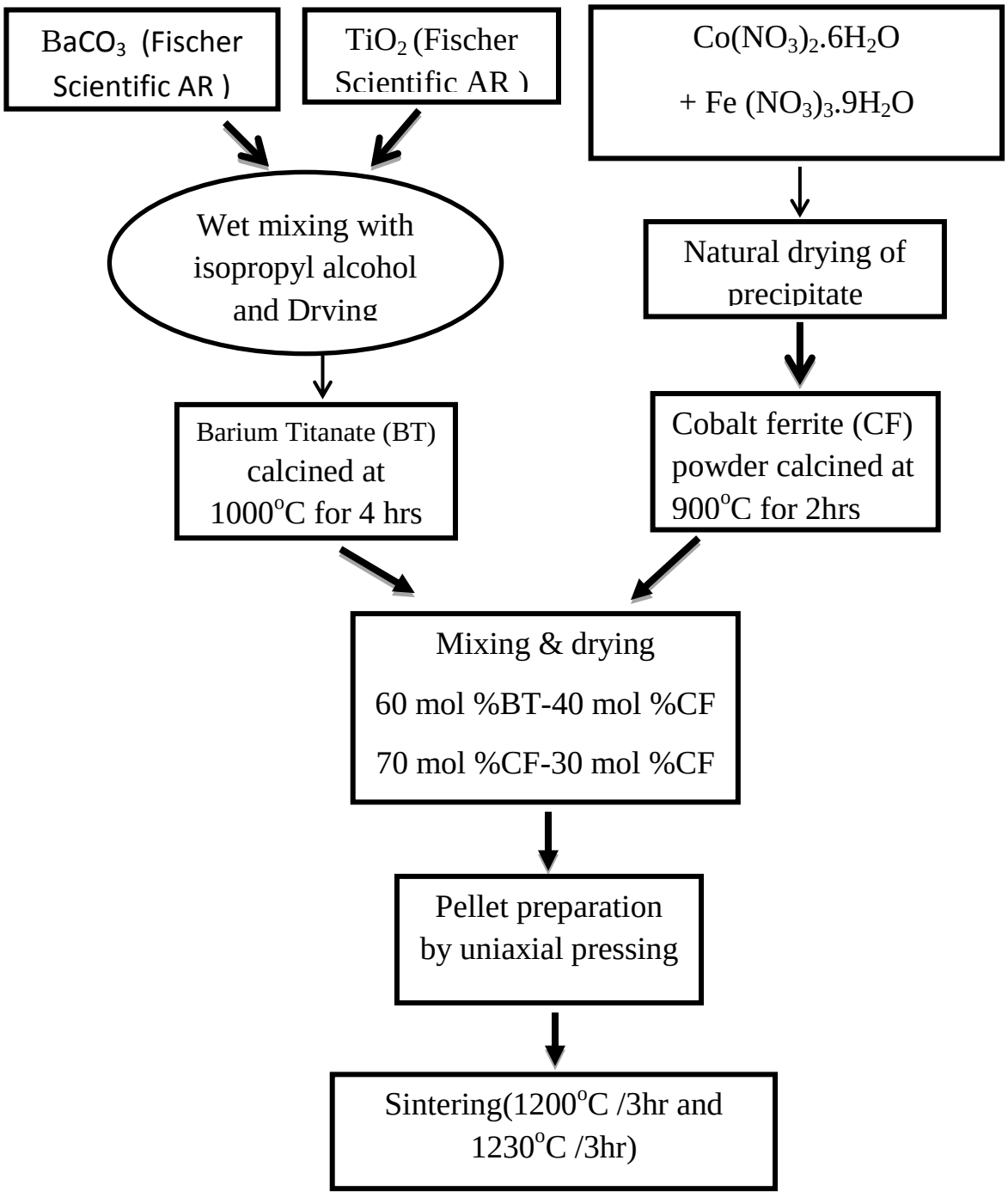
3. OBJECTIVE

- ✓ SYNTHESIS OF BARIUM TITANATE POWDER BY SOLID ROUTE.
- ✓ SYNTHESIS OF COBALT FERRITE POWDER BY CO-PRECIPITATION
- ✓ SYNTHESIS OF BARIUM TITANATE-COBALT FERRITE COMPOSITE OF DIFFERENT COMPOSITIONS.
- ✓ STUDY OF MAGNETOELECTRIC BEHAVIOUR OF SINTERED COMPOSITE

Chapter 4

EXPERIMENTAL WORK

FLOWCHART OF THE COMPOSITE SYNTHESIS



A. SYNTHESIS OF BARIUM TITANATE POWDER

$BaTiO_3$ was prepared by the solid oxide route in which $BaCO_3$ and TiO_2 was taken from Fischer Scientific (AR grade, assuming 100 % purity) in 1:1 mole ratio by corresponding weight and it was milled for 12 hours with isopropyl alcohol as the grinding medium. Then the powder was calcined at 1000 ^oC for 4 hrs and XRD was done to determine its phase.

B. SYNTHESIS OF COBALT FERRITE POWDER

Cobalt ferrite powder was synthesized by co-precipitation of iron nitrate and cobalt nitrate. Obtained powder was first dried naturally in open atmosphere and then calcined at 900 ^oC for 2 hours. The samples of calcined powder were subjected to X-Ray Diffraction experimental to determine the phase.

Batch preparation

I. Barium titanate (BT) and Cobalt ferrite (CF) were taken in 70:30; 60:40; and 80:20 mole percent ratios respectively. The required amounts of BT and CF in weight were calculated by knowing their individual molar weight. Around 10 gram batch of each composition were made in an agate morter back to back by thorough mixing. The composite powder was allowed to dry in air. In each mixed powder, 2% PVA was added and then pressed at 4 tonnes of pressure in the Carver Press.

II. Pellets preparation – as the pellets had to be sintered at different temperatures, therefore 3 pellets of 0.7g were made for each temperature, hence 9 pellets for each composition.

III. Sintering – then the pellets were sintered at different temperatures, 1200 ^{0}C, 1250 ^{o}C,1230 ^{o}C.

X-ray diffraction

The X-ray diffraction of the pellets sintered at 1230 ^{0}C was performed in PW1830 diffractometer, (Phillips, Netherland) at a 0.04 scan rate from 20-80^{o} for 25 minutes**.** This is done to know the different phases present in the pellets.

Bulk Density and Porosity of sintered pellets

The bulk density and apparent porosity of the sintered pellets were determined by Archimedes principle using kerosene. Dry Weight is measured and then the pellets were put in desiccator to create vacuum for about 30 min-45 mins. After that suspended weight is measured using apparatus in which pellet is suspended in kerosene and weight is measured. After taking suspended weight, soaked weight is taken. Hence the dry weight, soaked weight and suspended weight were measured. The bulk density and apparent porosity were calculated by the formulas: Bulk Density = dry weight / (soaked weight – suspended weight)

Apparent porosity= (soaked weight-dry weight) / (soaked weight – suspended weight)

Scanning Electron Microscope (SEM):

Microstructural features along with chemical compositions were studied using Scanning Electron Microscope (JSM 6480 LV JEOL, Japan). Through which

the chemical purity was analysed and even the distinction between different phases were analysed.

Measurement of ME voltage co-efficient:

A. Sample preparation:

i) **Electroding:** first the surface is polished with abrasive paper and alfa-aesar silver conductive paste is applied on specimen surfaces**.** After fired at about 5000c, electrodes of silver are formed on surfaces**.**

ii) **Electrical poling:** electric field (field direction perpendicular to the surface of the sample) is applied in silicon oil where the temperature is decreased from 150^0C down to room temperature.

iii) **Magnetic poling:** The magnetic poling was done at a constant dc magnetic field at about 30 min by mounting a sample centrally between the poles of a horseshoe type electromagnet.

B. ME voltage co-efficient set-up

The ME effect in composites was measured by a set-up as shown in Fig. A DC-field is applied defining a certain working point. Additionally, a small AC-field produced by Helmholtz coils is superimposed.

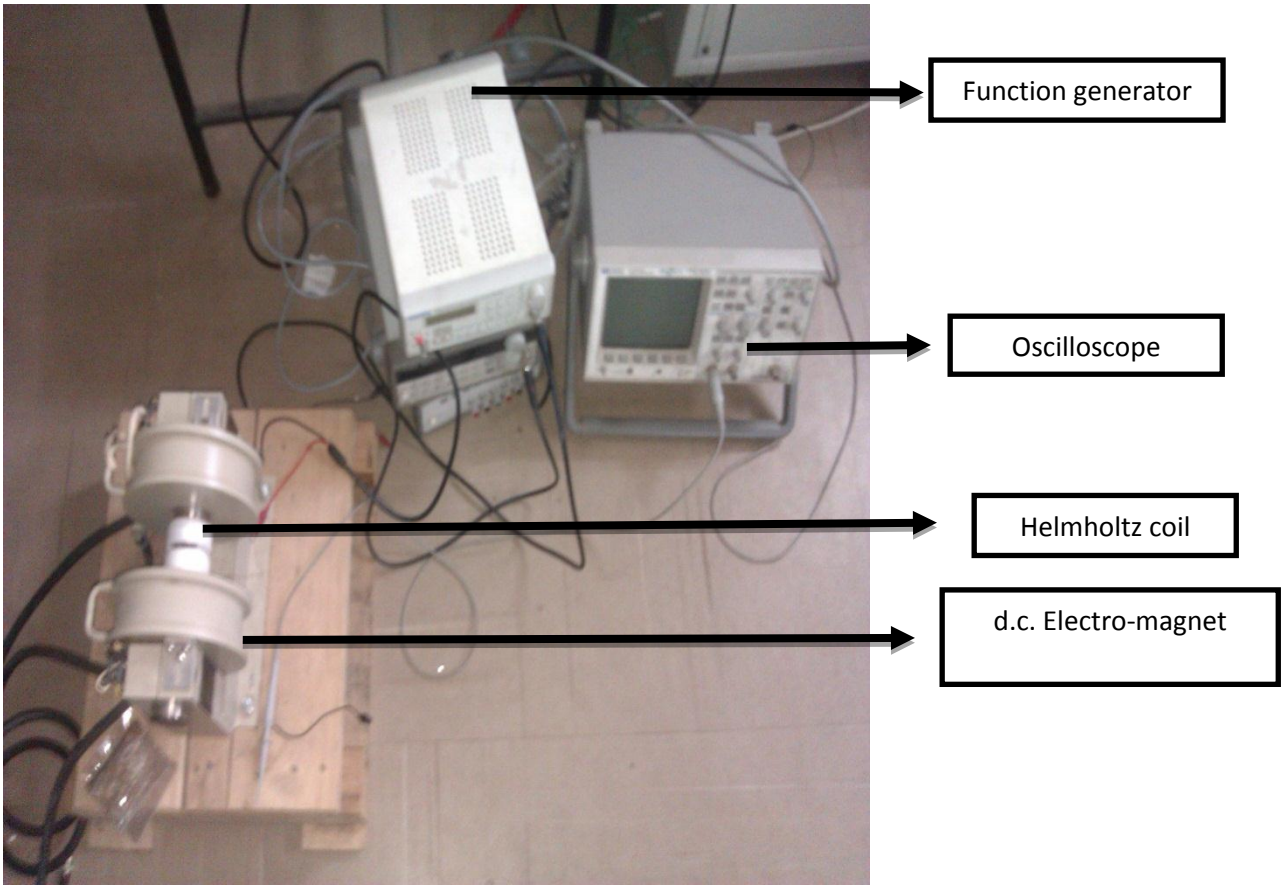


Fig 2. set-up for the measurement of magnetoelectric voltage co-efficient.

Chapter 5

RESULTS AND DISCUSSION

A. XRD ANALYSIS :

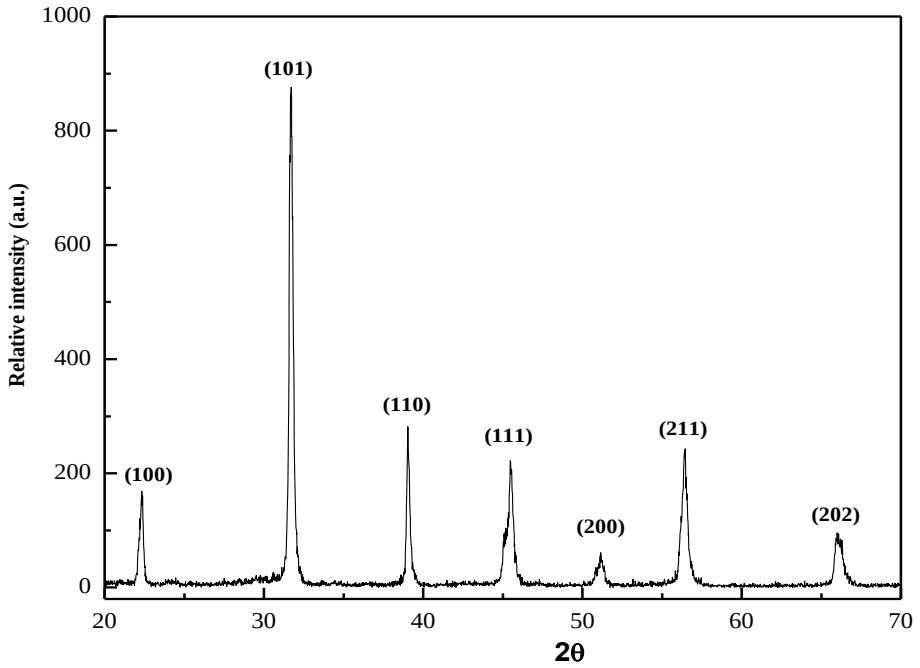


Figure3.: $BaTiO_3$ calcined at 1000 ^oC/4h

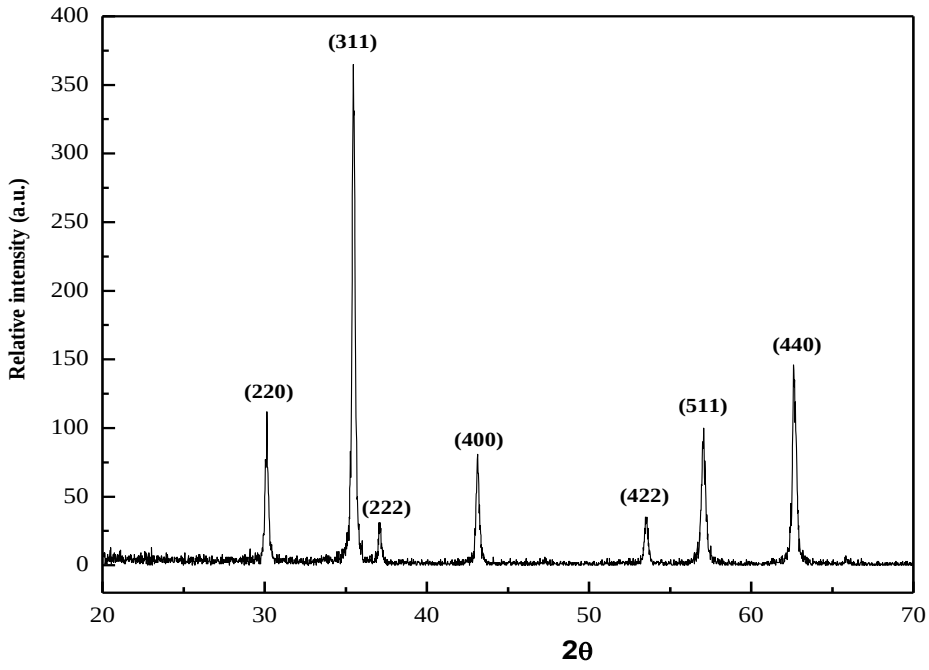


Figure 4.: $CoFe_2O_4$ calcined at 900 ^oC/2h

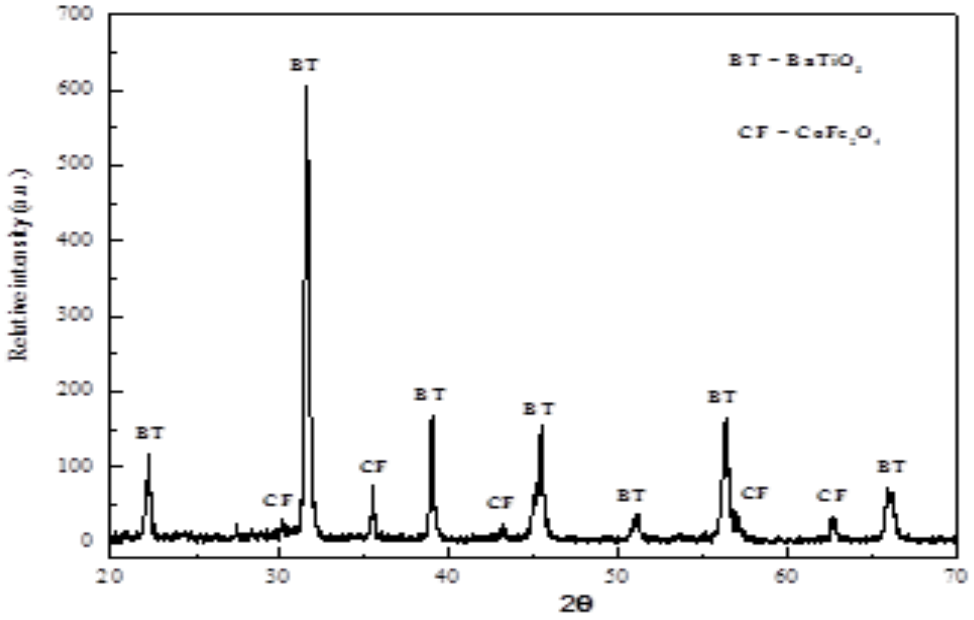


Figure 5.: XRD of mixed $BaTiO_3$ and $CoFe_2O_4$ powder

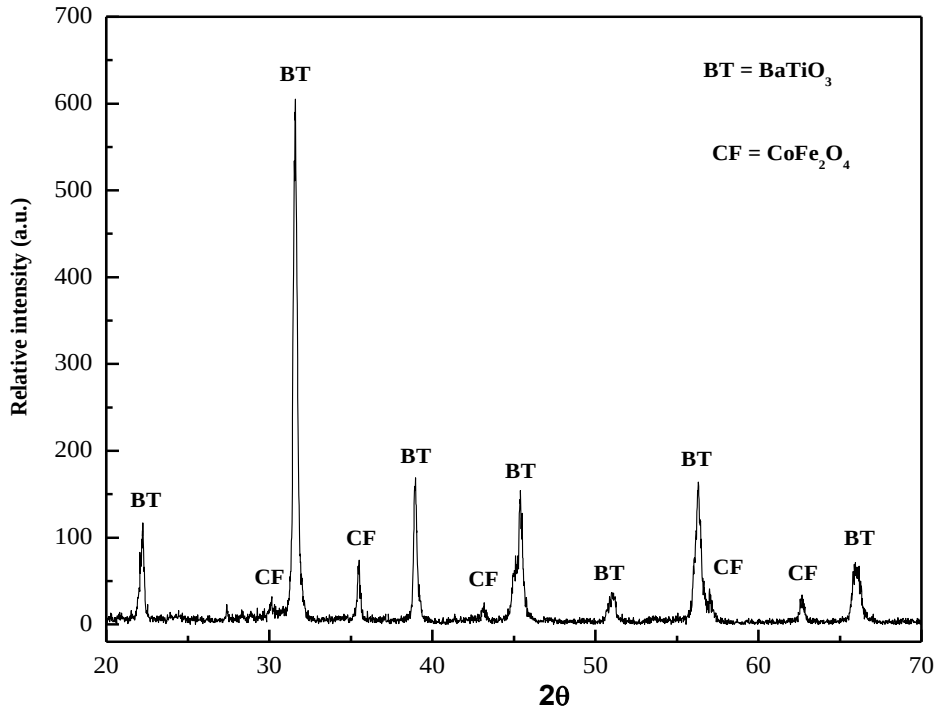


Figure 6.: XRD of $0.7BaTiO_3$-$0.3CoFe_2O_4$ composite
(Pellet sintered at 1230 ^oC/3h)

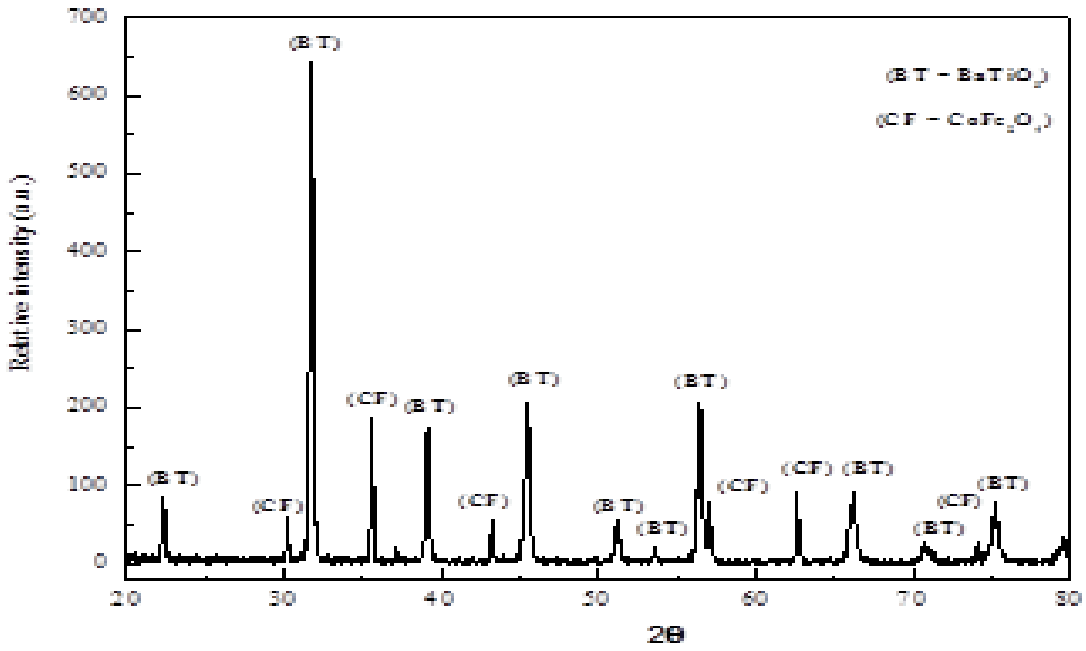


Figure 7.: XRD of $0.6BaTiO_3$-$0.4CoFe_2O_4$ composite
(Pellet sintered at 1230 ^oC/3h)

Figure 3 & 4 shows the XRD pattern of pure barium titanate and cobalt ferrite respectively.

For the identification of $BaTiO_3$ reference pattern of JCPDS taken as 75-2120

The crystal system in which it belongs to→ tetragonal

For the identification of $CoFe_2O_4$

Reference pattern of JCPDS: 22-1086

The crystal system in which it belongs to→ cubic

The XRD pattern of three ferroelectric-ferrite composite sample sintered at 1230^0C, for 3 hours has been shown in Figure 6 & 7. As there were no additional peaks except the $BaTiO_3$ and $CoFe_2O_4$ compound, it could be

concluded that composites were produced by the aforementioned technique is successful.

APPARENT POROSITY/BULK DENSITY CALCULATION

.7BT-.3CF	**B.D**	**A.P(%)**	**Average**
Pellet1	4.96	9.6	4.94
Pellet2	4.93	11	
Pellet3	4.92	13.6	
Pellet4	5.09	8.94	
Pellet5	4.84	7.9	

.6BT-.4CF	**B.D**	**A.P(%)**	**Average**
Pellet1	5.61	7.4	5.61
Pellet2	5.66	9.5	
Pellet3	5.49	11	
Pellet4	5.68	6.2	

.8BT-.2CF	**B.D**	**A.P(%)**	**Average**
Pellet1	5.74	9.90	5.67
Pellet2	5.52	12.44	
Pellet3	5.75	11.5	

Table 1 AP/BD calculation of pellets.

A. BET surface area of calcined powder

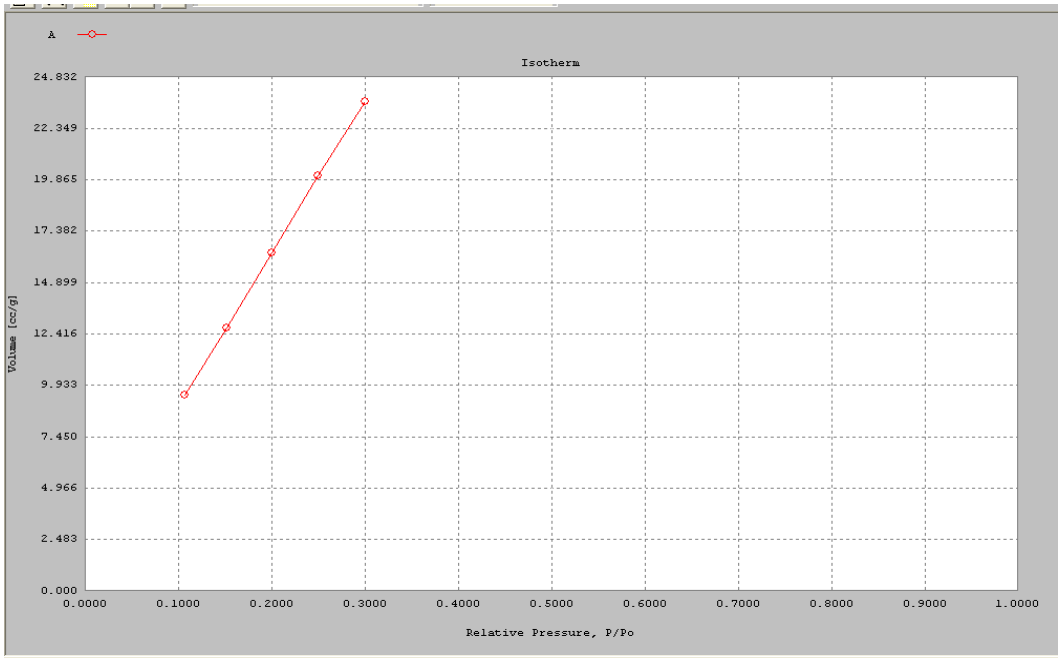


Figure -8 BET surface area of calcined $CoFe_2O_4$ powder

Area = 1.156E+02 m^2/g

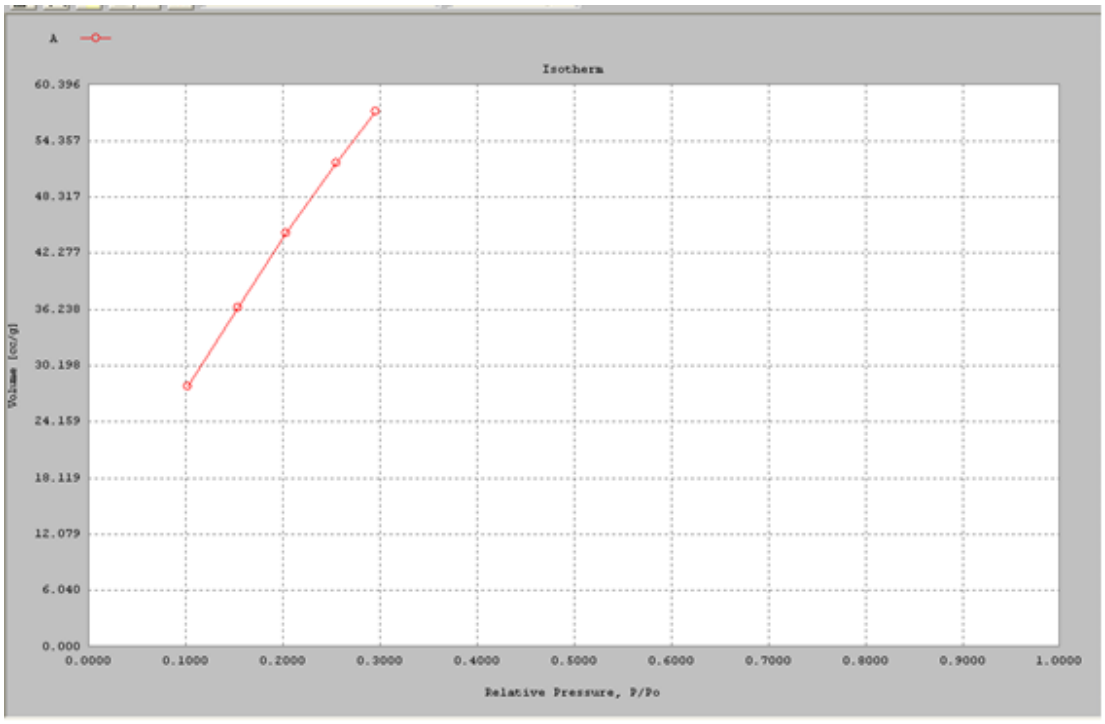


Figure 9. BET surface area of calcined $BaTiO_3$ powder

Area = 2.301E+02 m^2/g

B. Microstructural characterization: Scanning Electron Microscopy

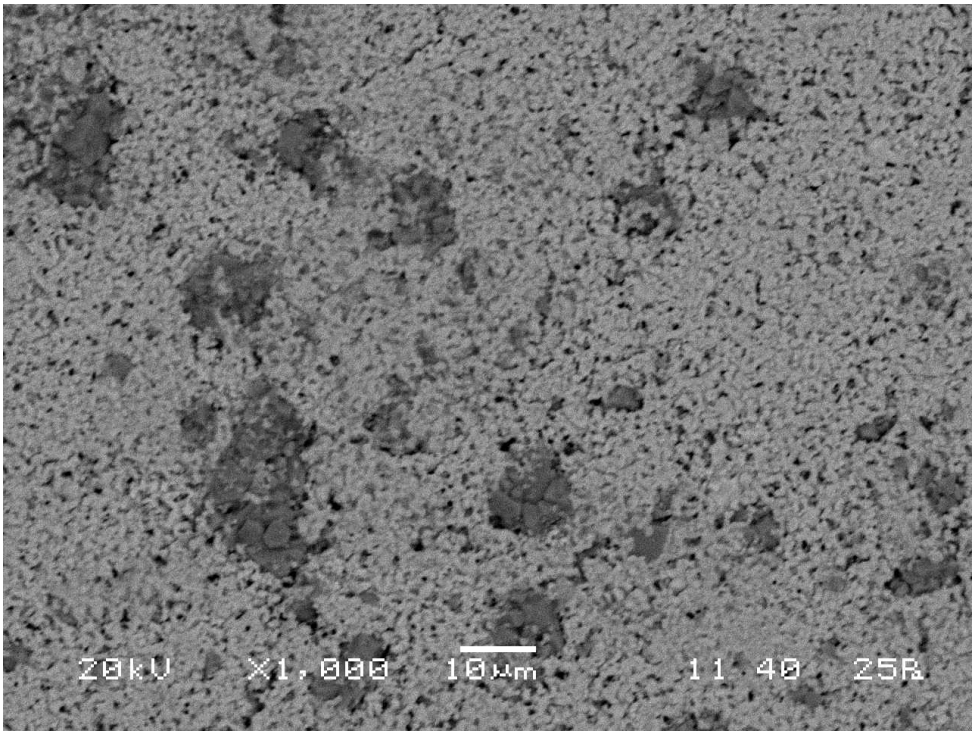


Figure 10 shows the microstructure of .7BT-.3CF composition

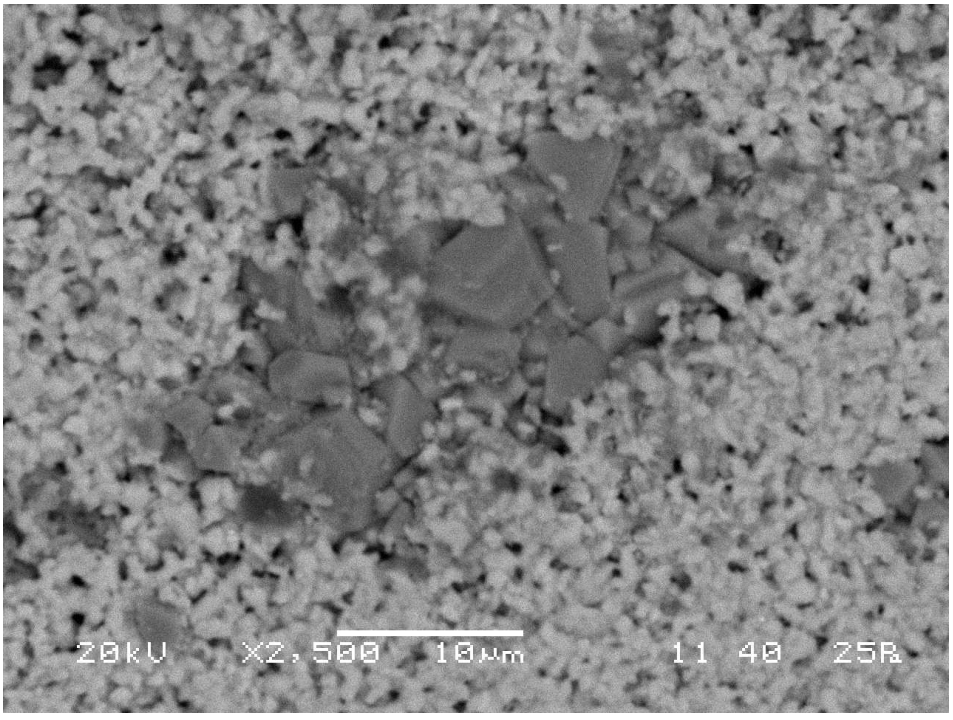


Figure 10 shows the microstructure of .7BT-.3CF composition

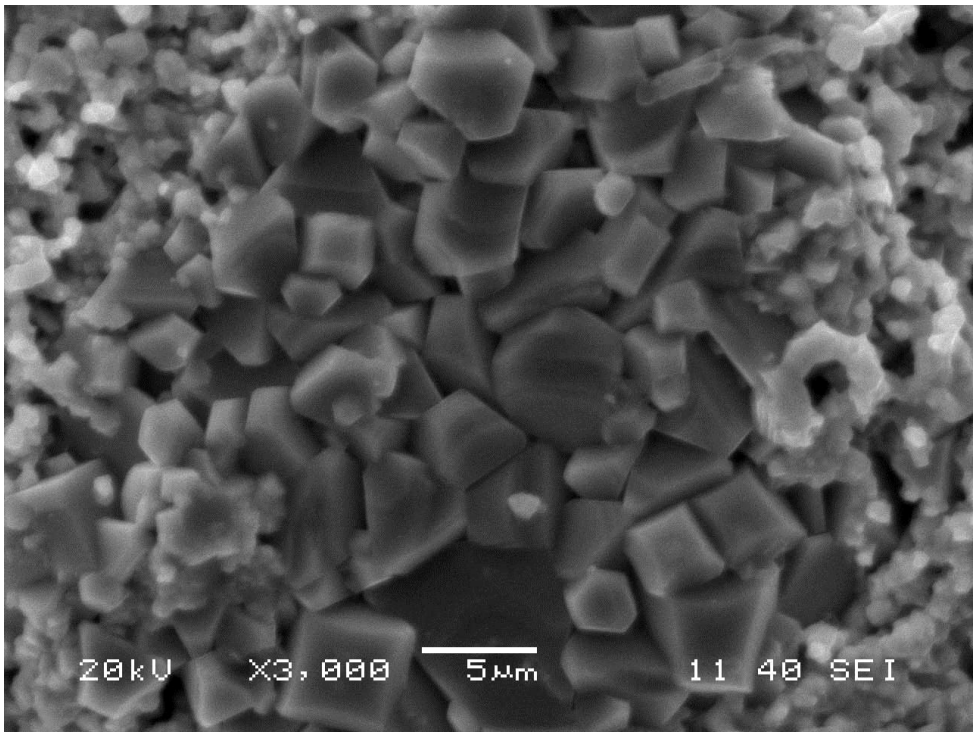


Figure 10 (c). shows the microstructure of .6BT-.4CF composition

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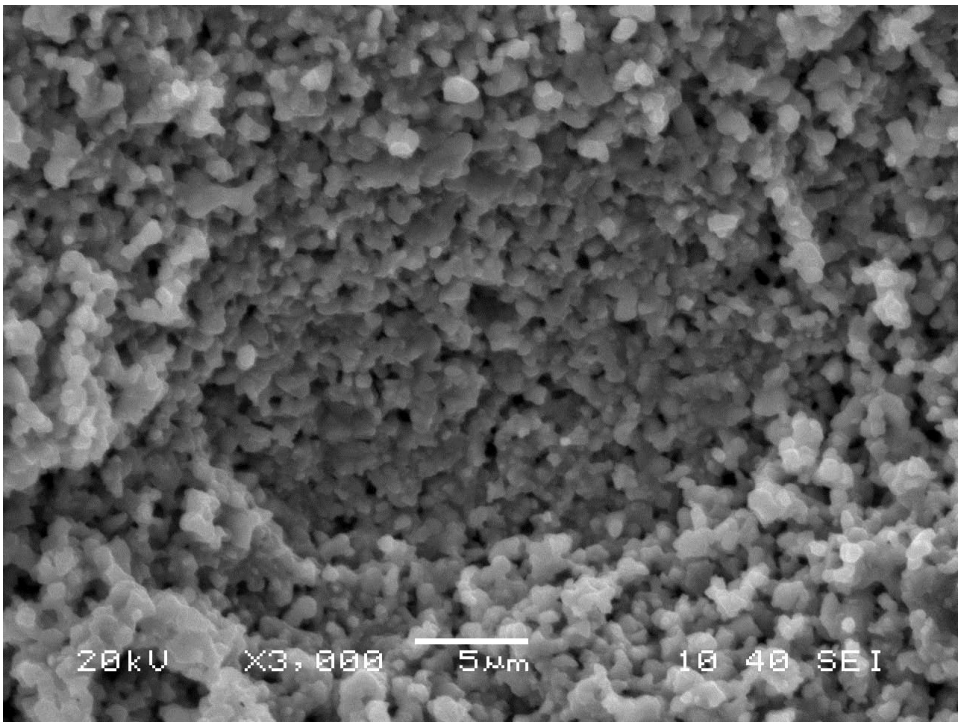

Figure 10 (d)Shows the microstructure of .8BT-.2CF composition

In fig.10 micrograph shows that there is significant agglomeration of Cobalt Ferrite ($CoFe_2O_4$) in the matrix of Barium Titanate. One of the reasons behind

this type of agglomeration is attribute to the rapid drying of the precipitate from which $CoFe_2O_4$ was obtained by calcination. The use of Humidity dryer could have been better with the agglomeration free ferrite particles

.

$CoFe_2O_4$	Average grain size
70:30 composite	4.60mm
60:40 composite	2.26mm
80:20 composite	3.26mm

Table 2 Average grain size of cobalt ferrite from microstructure analysis

C. ME CO-EFFICIENT MEASUREMENT

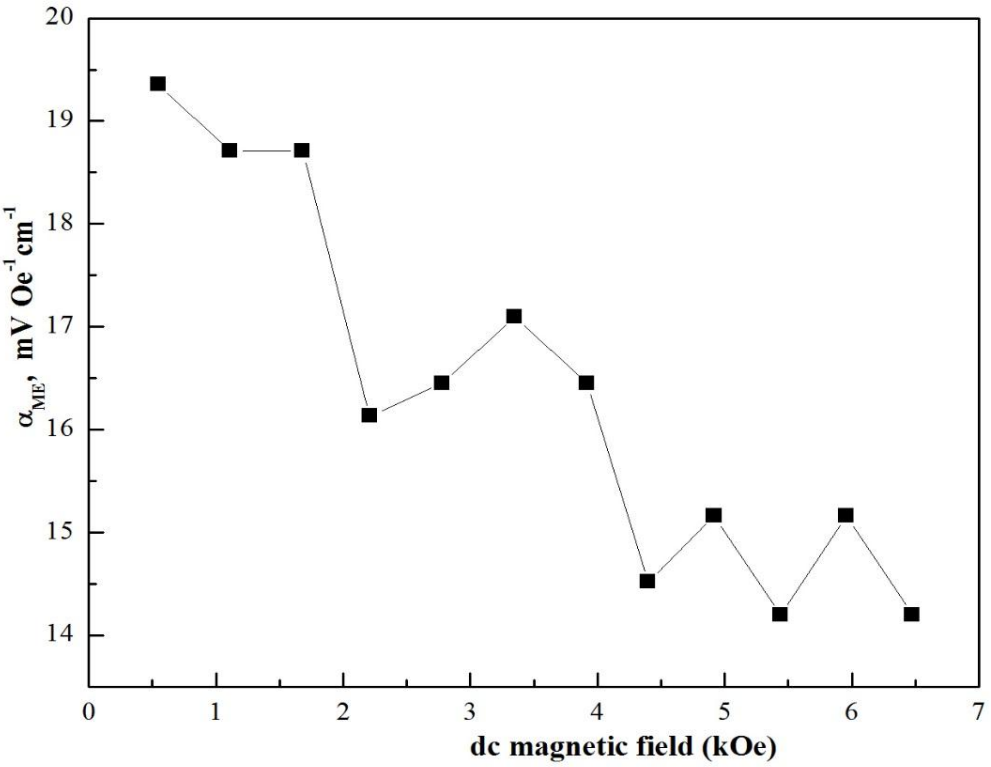

Figure 11 (a). Magnetoelectric voltage co-efficient of BTCF composite (BT60% + CF40%)

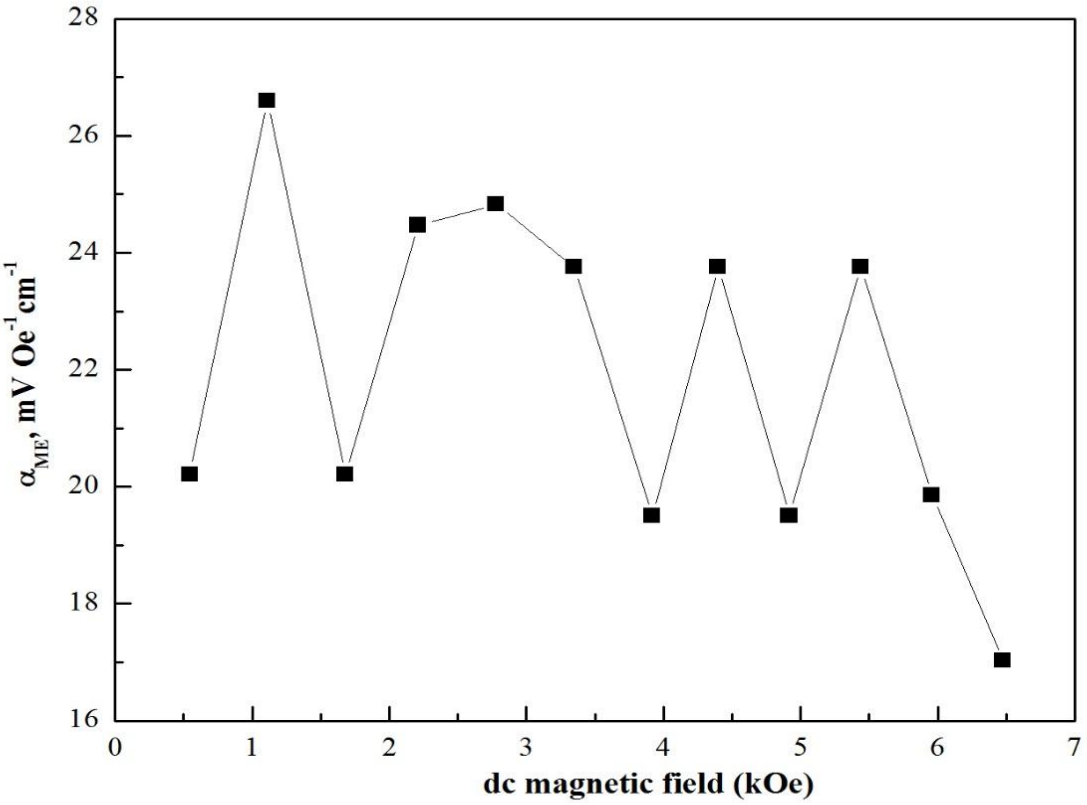

Figure 11 (b). Magnetoelectric voltage co-efficient of BTCF composite (BT70% + CF30%)

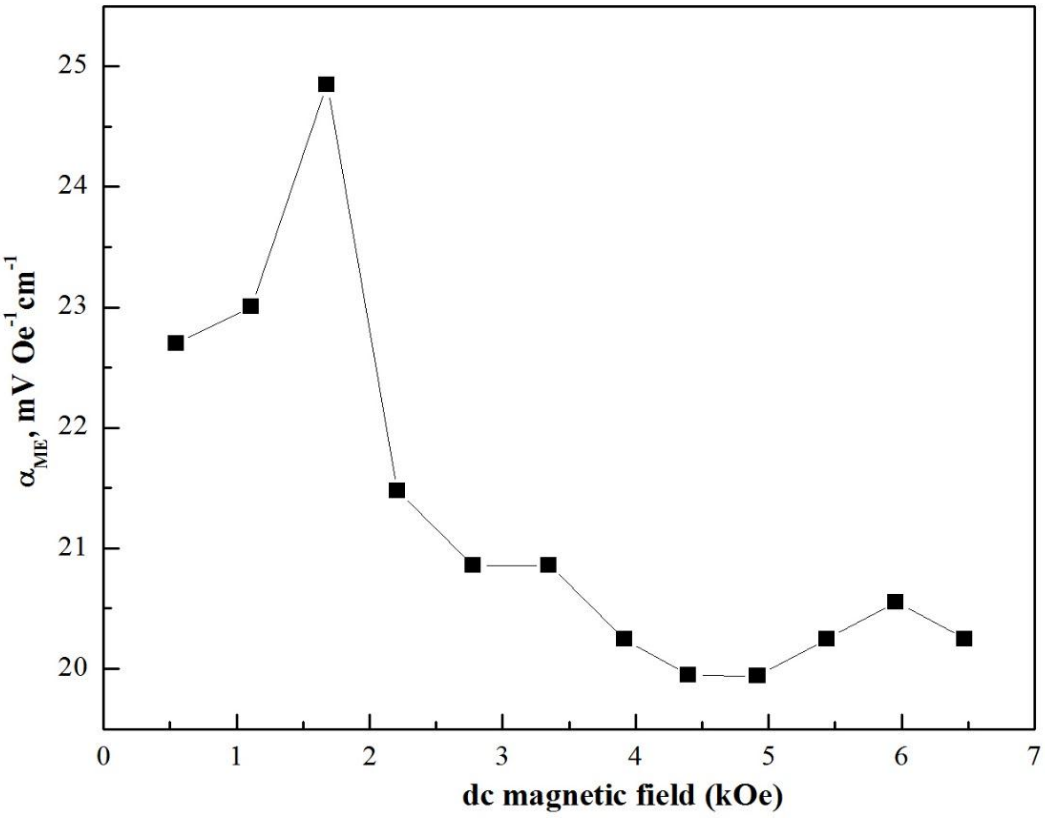

Figure 11 (c). Magnetoelectric voltage co-efficient of BTCF composite (BT80% + CF20%)

Composite	Highest ME voltage co-efficient (mV cm^{-1}. Oe^{-1})	Remark
(BT60% + CF40%)	19.35	The value is comparable to the literature working with $CoFe_2O_4$ in particulate composite
(BT70% + CF30%)	26.6	Though the values are zigzag in nature, a decreasing tendency of that value with the dc magnetic bias is evident from the graph. This value was expected to be a little higher. Possible reason: agglomeration of $CoFe_2O_4$ powder
(BT80% + CF20%)	24.84	The voltage co-efficient value was decreased from the previous composition as there were less ferrite grains (below the saturation value) in the microstructure that makes strain due to magnetostriction upon the ferroelectric phase (here $BaTiO_3$)

Table 3 . ME co-efficient of different compositions of composite

Conclusion

Barium titanate and Cobalt ferrite were prepared successfully.

Three composites were made out of phase pure Barium titanate ($BaTiO_3$)and Cobalt ferrite ($CoFe_2O_4$).

The average grain size of the $BaTiO_3$ (ferroelectric phase) was found to be in sub-micron range whereas the average grain size of the $CoFe_2O_4$ (ferrite phase) lies in between 2.0 to 5.0 μm.

The agglomeration of the ferrite phase in the matrix of $BaTiO_3$ could be minimized by subjecting the precipitate in controlled humidity drier.

The highest ME voltage co-efficient values for each composite was in the d.c. bias of 0.5 to 1.5 kOe.

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