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# Exploration of Multilayer Barium Titanate and Gadolinium Ferrate Ceramics for Multiferroic Application

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**Abstract—***Multi-ferroics are a novel class of next generation multifunctional materials, which display simultaneous magnetic spin, electric dipole, and ferroelastic ordering, and have drawn increasing interest due to their multi-functionality for a variety of device applications. In order to attain high value of magneto electric coupling, interfacial contact has been increased by fabricating alternating layers of ferroelectric Barium Titanate (BTO) and antiferromagnetic Gadolinium Orthoferrite (GOF). BTO and GOF have been synthesized by chemical method. Pure phase formation of tetragonal BTO and orthorhombic GOF has been confirmed by X-ray diffraction pattern. Diamagnetic behavior of BTO and weak ferromagnetic nature of GOF has been observed by magnetization measurement. Multilayer BTO and GOF composite showed anisotropy in magnetization that exhibit existence of interfacial interaction between two phases. Magnetoelectric coupling has been obtained 0.1 mV/cm-Oe for the multilayer ceramic by dynamic method.*

**Keywords***: Multilayer multiferroic ceramics, Barium titanate, Gadolinium Ferrate, Magnetoelectric coupling.*

## 1. INTRODUCTION

With the advancement of electronic innovation, composite materials have been generally utilized for electronic gadgets where higher densities, restricted space and multifunction are required [1]. Multiferroics, being materials where ferroelectric and ferromagnetic effects exist together, are at present drawing in significant consideration. Ferroelectric materials are used to make Capacitor, Non-volatile memory. Similarly, antiferromagnetic materials are used to make spin valve sensors, hard disk drive heads, magnetic RAM etc [2,3]. Ferrolectric random access memories (FeRAMs) have recently achieved faster access speeds (5ns), higher densities (256 Mb) and manifestation in several traditional materials [Pb (Zr, Ti) O3, (Ba, Sr) TiO3], but they are limited by the need for a destructive and reset operation and suffer from atmospheric contamination. By comparison, magnetic random access memories (MRAMs) have been lagging far behind. As ferroelectric polarization and magnetization are used to encode binary information in FeRAMs and MRAMs respectively, the coexistence of magnetization and polarization in a mutiferroic material allows the realization [4-6].

Growing interest for spintronics, nonvolatile ferromagnetic or ferroelectric memory gadgets, and information stockpiling media and so on the enthusiasm to examination of space designing in multiferroics is forever emerging [7-11]. Multiferroics represent a fascinating kind of multifunctional materials that coexist in several ferroic orders such as Ferroelectricity and Ferromagnetism, which brings about novel physical phenomena and exhibit many possibilities for new device functions. In multiferroics there is a coupling between magnetic and electric orders termed as magneto electric coupling. This coupling enables the control of ferroelectric polarization by a magnetic field and conversely, the manipulation of magnetization by an electric field [12-16]. The conceivable coupling amongst ferroelectric and antiferromagnetic areas has been talked about in a progression of trial and hypothetical works. As of late the magneto electric multiferroic composite materials were seriously explored for two uses: the magnetic–electric sensors in radio-hardware, optoelectronics, microwave gadgets and transducers and the minimized electrical channels for smothering electromagnetic obstruction (EMI). Magneto electric coupling depicts the impact of an attractive field (or an electric field) on the polarization (or charge) of a material. In the previous couple of years, broad exploration has been led on magneto electric impact in single stage and composite materials [17-19].

Most of the Multiferroics are composite based because of the scarcity of Single-phase multiferroics. In which most of the composite multiferroics are lead based which has adverse

effects and are not that successful as they claim to be. The lack of this understanding has limited the ability to achieve the theoretical response of the material by coordinating the local electro-magnetic couplings, via coherent elastic interactions between phases. In these materials the theory predicts the size of the ME α to be more than 5 mV/cm/Oe [20].

In this paper we report the activity of ferroelectric-antiferromagnetic laminar composite materials by an unexampled synthesis route for Barium Titanate Nanopowder i.e. Metal Oxide Decomposition Method and their potential applications in multiferroics . The synthesis of Nano powders of Barium Titanate and Gadolinium Orthoferrite induced magneto electric effect and which can be used for constructing an effectively in Multiferroic based device industry. The modified and simple technique to enhance interfacial effect on magneto electric coupling by stacking and bonding alternating ferroelectric BTO and antiferromagnetic GOF laminar composites has been investigated.

## 2. EXPERIMENTAL

### 2.1 Synthesis of Barium Titanate by Metal Oxide Decomposition

Analytical grade Barium Acetate [Ba [C2H3O2)2], Titanium Isopropoxide (C16H36O4Ti) and 2-ethyl Hexanoic acid were adopted as precursors for synthesis of phase pure Barium Titanate. 2-ethyl hexanoic acid (C7H15COOH) taken as a solvent and surfactant. Atomic ratio of 0.3 M Titanium Isopropoxide and 0.3 M 2-ethyl hexanoic acid was maintained as 1:1 and 0.3 M 2-ethyl hexanoic acid was maintained. The stoichiometric solution of Titanium Isopropoxide, Barium Acetate and 2-ethyl hexanoic acid kept for vigorous stirring with heating. After 1 hour, Barium Acetate started to dissolve in the solution at temperature 90-100$^o$ C and a dark brown-black tarry solution is formed. The solution was allowed for stirring and refluxing for 4 hours at 100$^0$ C. A gel starts to form with heating. With prolong heating a gummy gel is formed and not dried. To get xerogel, gummy gel was kept in the tube furnace for 10 hours at 750$^o$ C, which results in a powdered form of white color. And finally the resulting product is grinded to attain a sample free of impurities and highly dense by keeping it for sintering at 1000$^o$ C.

### 2.2 Synthesis of Gadolinium Orthoferrite by Co-Precipitation Method

Analytical grade Gadolinium Nitrate [Gd (NO3)3], Iron Nitrate [Fe (NO3)3] and Ammonium Hydroxide (NH4OH) were taken as precursors for synthesis of phase pure Gadolinium Orthoferrite. Atomic ratio of 0.2 M Gadolinium Nitrate in 50 mL and 0.2 M Iron (III) Nitrate in 50 mL was taken and stirred at 80$^o$ C and then 200 mL of hot NH4OH solution was added to it and a precipitate is formed. The precipitate is filtered out and the precipitate is washed with Distilled water and ethanol solution and kept for drying overnight. After drying the filtrate is dried and grinded and kept at 750$^o$ C for 10 hours for pre-sintering and final sintering at 1000$^o$ C for 2 hours for removal of impurities and obtaining pure phase product.

### 2.3 Preparation of Quad layered laminar Composites

Pellet fabrication involved 0.1 gms of Gadolinium Orthoferrite and Barium Titanate alternately stacked over each other by using 10 mm pellet dies using 10 ton Manual Hydraulic Press with thickness of 1.78 mm. The conductive silver paste was applied on top and bottom of the Quad layer pellet for its Magnetic and Magneto-Electric Measurements.

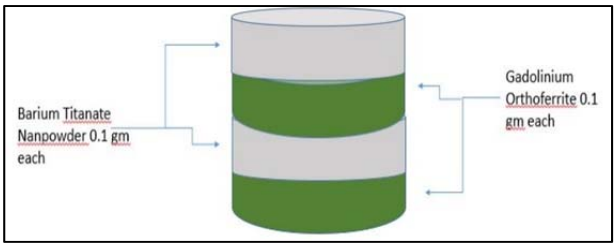
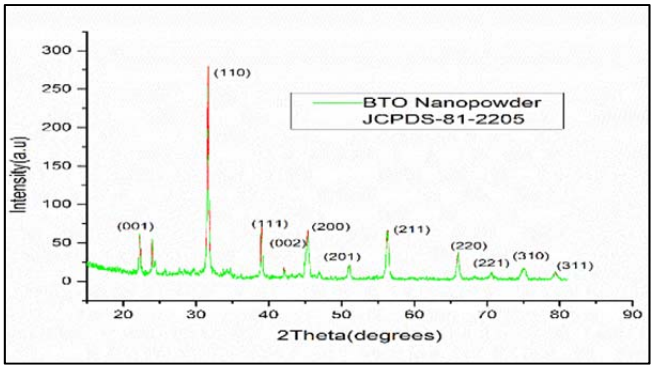



**Fig. 1: Schematic diagram of 10 mm Barium titanate-Gadolinium Ortho ferrite Quad layer.**

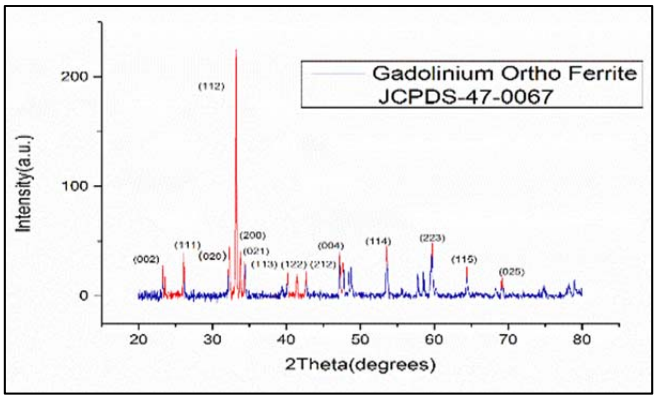
## 3. RESULTS AND DISCUSSION

The structural composition and phase purity of the products was characterized by Rikagu ULTIMA. FIG. 2 shows the X-ray diffraction pattern of the sintered Barium Titanate (BTO) and Gadolinium Orthoferrite powder samples. Barium Titanate Nanopowder having space group as P4mm(99) and lattice parameters a=3.995 and c=4.4035. Intense diffracted peaks for Barium titanateNano-powder was observed at 2θ= 22.21, 31.663, 38.969, 44.90, 45.362, 56.329 corresponding to (001), (110), (111), (002), (200), (211) planes respectively. It shows pure phase formation of Nano BaTiO3 synthesized using metal oxide decomposition The XRD patterns revealed the Nano BaTiO3 is well crystalline. Particle size was calculated, using Scherer's formula$D = 0.9\lambda \div \beta cos\theta$ where λ is the wavelength of the $CuK_\alpha$ and β is the FWHM (Full width Half Maxima) of the maximum intensity peak (here peak (110)) and the average particle size came out to be 33 nm for Barium titanate.

Gadolinium Otho-ferrite prominent peaks were confirmed at 23.12, 25.757, 32.839, 33.47, 33.995, 42.31, 43.36, 44.30, 47.37, 53.28, etc. corresponding to (002), (111), (020), (112), (200), (021), (113), (122), (212), (004) and (114) having space group Pbnm(62) and lattice parameters a=5.349 b= 5.610 and c= 7.667.Likewise the JCPDS card number for Gadolinium Orthoferrite was confirmed 47-0067 and it can be concluded that the GdFeO3 crystals were orthorhombic. The average particle size of Gadolinium Ortho ferrite was also calculated using Scherer's formula which was around 20 nm.




**(a)**




**(b)**

**Fig. 2: X-ray diffractions of (a) Barium Titanate Nanopowder and (b) Gadolinium Ortho-ferrite.**

**Table 1: Lattice constants and Crystallite size of Barium Titanate and Gadolinium Ortho-ferrite.**

| Compound | Lattice parameter (nm) a b c | | | Crystallite Size |
|---|---|---|---|---|
| Barium Titanate | 3.995 | - | 4.4035 | 33 nm |
| Gadolinum Orthoferrite | 5.349 | 5.610 | 7.667 | 28 nm |

The ferroelectric polarization of BTO-GOF Quad layer has been compared with the ferroelectric polarization of BTO nanopowder via Marine India P-E loop tracer. The ferroelectric behavior of the quad layer has shown a lossy loop like a lossy linear capacitor and receded a lot because of the presence of antiferromagnetic Gadolinium Orthoferrite sandwiched between the ferroelectric Barium Titanate.

There is no saturation polarization observed in the case of BTO-GOF quad layer .The saturation polarization of Pure BTO is 19.747 μC/cm$^2$, coercivity= 3.323 kV/cm Remnance μC/cm2=07.368.

Magnetization measurement of Pure Gadolinium Ortho Ferrite and BTO-GOF Quad layer is carried out at Room temperature between the range -5000 oerested to 5000 oerested with the help of Lakeshore 7300 Vibrating Sample Magnetometer.

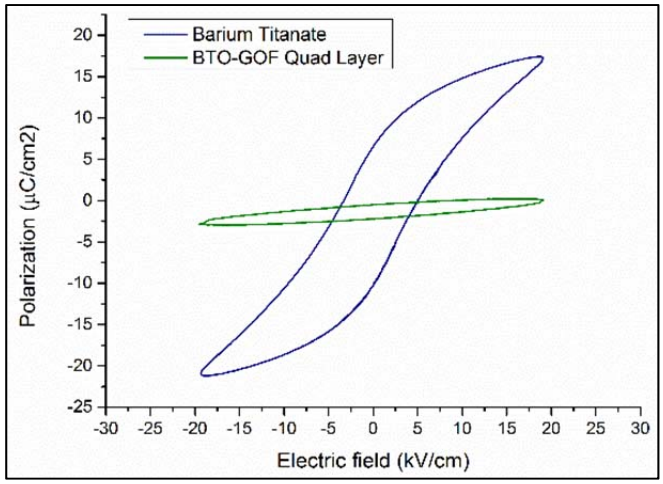
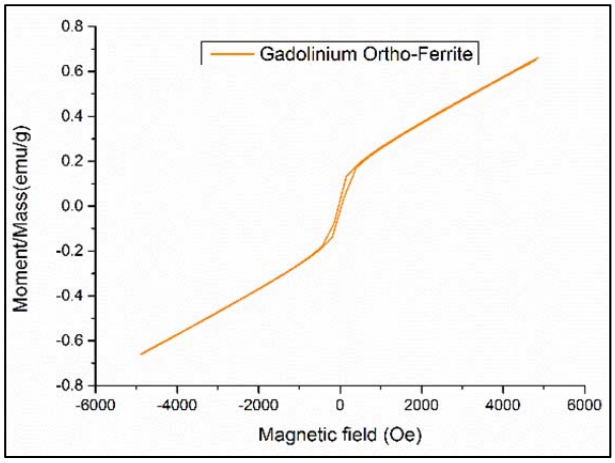
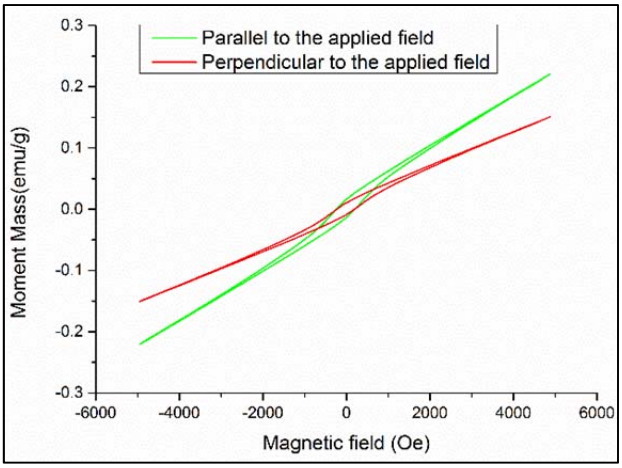



**Fig. 3: Polarization vs. electric field plot of (a)Barium Titanate and (B)BTO-GOF Quad Layer.**

A feeble ferromagnetism has been observed in pure antiferromagnetic GOF due to spin canting of antiferromagnetically aligned spins. The M-H loop for BTO-GOF multilayer composite has been taken in in-plane and perpendicular to magnetic field direction as shown in FIG. 4(a).It has been observed that there is a little anisotropic behavior although anisotropy is not a bulk phenomenon as it is only observed in thin films but because of the presence of multiple interfacial layers this phenomena occurred. It was observed from the MH loop that coercivity value of multilayer sample increased than pure GOF sample. It may be due to pinning of antiferromagnetic interfacial spins of GFO by BTO layer. Due to incorporation of BTO mass with Gadolinium Ortho-ferrite in multilayer composite it reduced the magnetic moment than the pure GOF.




**(a)**




**(b)**

**Fig. 4 Magnetization curve for (a) Gadolinium Ortho-ferrite and (b) BTO-GOF Quad Layer parallel and perpendicular to the field.**

In order to investigate interaction of magnetic and electric dipoles of BTO-GOF Quad layer, magneto-electric coupling was determined by dynamic method. In dynamic method, voltage developed across the sample has been measured by applying DC magnetic field with ac bias to nullify the effect of voltage generated by surface charges. The dynamic measurement was carried out at 5 Oe ac magnetic field with 992 Hz frequency applied collinearly with variable DC magnetic field from 0 to 8000 G.The linear term of magneto electric coefficient (α) was evaluated using equation $V_{out}/h_o$din the presence of DC magnetic field and the known values of α, $H_0$, $h_0$ and V. The signal outputs in Voltage represent the true value. The lock in amplifier is used to measure the output voltage. It was found that with the increase in DC magnetic field induced voltage was increasing, which shows the coupling between the antiferromagnetic Gadolinium Ortho Ferrite and Ferroelectric Barium Titanate which can be related to the elasticity as it causes strain to the grain boundaries of different material creating a charge separation increase, henceforth, the obvious change in Voltage. The magneto electric coupling of Barium Titanate- Gadolinium Ortho Ferrite Quad layer was found to be 0.1mV/cm/Oe. The local interaction between the ordered antiferromagnetic and ferroelectric sub lattice results in the polarization when it is placed in the external magnetic field. At room temperature the maximum value of '$\alpha$' obtained4.395 mV $cm^{-1}$ $Oe^{-1}$ at8000Oe compared to other reported polycrystalline single phase multiferroic in bulk. It shows magnetic spins induce a maximum voltage at 8000 Oe applied DC magnetic field. The origin of the magneto electric coupling in multiferroic systems is an ongoing discussion. Magneto electric coupling inantiferromagnetic compounds having complex spin arrangements have been explained based on the exchange interactions in canted spins. Some models considered magnetic symmetry to explain ME coupling. However, among all the proposed models, spin–orbit coupling is considered as the root cause for magneto electric effects. Based on existing ME theory it is expected that the interfacial interactions between spins of GOF layer with surface atom spins of ferroelectric electric dipoles result in the ME coupling.

## 4. CONCLUSIONS

In summary, multilayered BTO and GOF bulk composite stack of ferroelectric Barium Titanate and antiferromagnetic Gadolinium Ortho-Ferrite has been synthesized and investigated for its multiferroic properties. Phase pure nanoparticles of BTO and GOF have been synthesized by Metal oxide Decomposition and Co-precipitation methods. High temperature synthesized pellets of nanoparticles BTO and also GOF synthesized by co-precipitation exhibited a single phase Ortho-ferrite without any impurity phase. High temperature synthesized GOF nanoparticle shows an antiferromagnetic character with slight spin canting observed by M-H loop. Multilayered BTO-GOF mutiferroic composite showed magneto electric coupling0.1 mV/cm.Oe at 8000 Oe applied DC field.

Our investigation has demonstrated that multilayer multiferroics Barium Titanate and antiferromagnetic of Gadolinium Orthoferrite is coupled by magneto electric coupling. The real system deciding the antiferromagnetic example and the coupling of the antiferromagnetic and ferroelectric area structures is the inhomogeneous magnetoelectric cooperation of the Lifshitz sort cooperation. The character of spin arrangement plan is dictated by the grain boundaries conditions and unequivocally depends on the width of ferroelectric areas. Antiferromagnetic spin arrangement is being pinned by the ferroelectric domain walls.

As multiferroics possess properties of magnets and ferroelectrics their applicational value is vast. The magetoelectriceffecy offers a whole new dimension in application possibilities. Already, ideas of four-state memory, spintronics and magnetic field sensors are being under intense development.

## 5. ACKNOWLEDGEMENTS.

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