Analysis of Stress-Coupled Magneto-Electric Effect in BaTiO₃-CoFe₂O₄ Composites using Raman Spectroscopy

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Abstract— The Magneto-Electric Effect refers to the electric polarization induced due to an external magnetic field in certain substances known as Multiferroics. In recent years the ME effect has drawn a lot of attention, partly owing to its use in Memory Devices and partly due to extensive studies conducted on Multiferroic Composites.

Index Terms— Magneto-Electric Effect; Raman Spectroscopy; Multiferroics; Vibrating Sample Magnetometer; Piezoelectric; Magnetostriction

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Introduction

Though Maxwell's equations laid out the relation between Electricity and Magnetism, it was much later that similar relations were found for the two, in terms of relating ferro-electric and magneto-elastic tendencies, in polarisable media. This was largely because most ferro-electric substances are Transition Metal compounds (in most cases oxides) with empty d orbitals whereas magnetic substances require partially filled d-orbitals, often with long-range magnetic ordering due to uncompensated spin interaction.[1]

The school of thought that we were interested in and tried to work on in this project was the stress-induced coupling of phases leading to ME effect. The ME effect is attributed to the cross-interaction of the piezo-electric and magnetic phases in multi-ferroic composites. The ME effect can be broken down into two distinct effects: The magnetostrictive effect that leads to the mechanical strain produced due to application of external magnetic field, and the piezoelectric effect that causes the stress, so formed, to produce an electric polarization.[2] The idea of phase connectivity[3] is useful in assigning notations such as 2-2 and 1-3, in which each number signifies the connectivity of the respective phases in a composite.

Before we proceed any further, we would like to clarify the subtle difference between multi-ferroics and magneto-electric substances.

Substances that are ferro-electric *and* ferro-magnetic are multiferroic substances. *W. Eerentstein* et al.[4] point out "Magnetoelectric coupling is an independent phenomenon that can, but need not, arise in any of the materials that are both magnetically and electrically polarizable. In practice, it is likely to arise in all such materials, either directly or via strain."

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Landau Theory

The magnetoelectric effect in a crystal is traditionally described in Landau theory by writing the free energy of the system in terms of an applied magnetic field H and an applied electric field.

$$-F(E,H) = \frac{1}{2}\varepsilon_0\varepsilon_{ij}E_iE_j + \frac{1}{2}\mu_0\mu_{ij}H_iH_j + \alpha_{ij}E_iH_j + \frac{\beta_{ijk}}{2}E_iH_jH_k + \frac{\square_{ijk}}{2}H_iE_jE_k \ldots$$

The first term on the right hand side describes the contribution resulting from the electrical response to an electric field, where ε_{ij} (T) is relative permittivity.

The second term is the magnetic equivalent of the first term, where μ_{ij} (T) is relative permeability. The third term describes linear magnetoelectric coupling via α_{ij} (T).

Other terms represent higher-order magnetoelectric coupling coefficients.

The magnetoelectric effect can be established in the forms

$$P_i(H_j) = \alpha_{ij}H_j + \frac{\beta_{ijk}}{2}H_jH_k + \ldots$$

$$M_i(E_j) = \alpha_{ij}E + \frac{\square_{ijk}}{2}E_jE_k + \ldots$$

Symmetry Groups and Character Tables

Group theory is used to assign various symmetry and point groups to certain molecular lattice structures as per the modes of vibrations they produce.

At room temperature, perovskite BaTiO₃ has a tetragonal c4v point group, while CoFe₂O₄ has a spinel structure.

According to crystallography, there are eight Raman active modes for tetragonal BaTiO₃ ($4E_1+3A_1+1B_1$) and five

Raman active modes for cubic inverse spinel CoFe2O4 ($A_{1g}+1E_{g1}+3T_{2g}$).

Raman Spectroscopy

Figure 1: *Renishaw InVia Raman Spectroscopy System*

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Photons of the laser light are absorbed by the sample and then re-emitted. Frequency of the re-emitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman Effect. This shift provides information about vibrational, rotational and other low frequency transitions in molecules. In the present study, I have used the Raman spectrum of un-magnetized and magnetized Multiferroic composites to analyze the Stress-Coupling in the composites, which has been taken as a cause of Magneto-Electric Effect by various individuals.[5,6]

Light scattering from particles much smaller than the wavelength can be divided into two categories:

> *Rayleigh scattering*, in which the incident photon is scattered elastically and its frequency remains unchanged.

> *Raman scattering*, in which the incident photon inelasticity scatters and is noted by a shift in frequency.

Raman Spectroscopy has been used to determine stress/strain measurements by the analysis of the shifts in the Raman spectrum.

Vibrating Sample Magnetometer

A vibrating sample magnetometer is an instrument that measures magnetic properties of a given substance. In the process, a sample is placed inside a uniform magnetic field to magnetize the sample. The sample is then physically vibrated, typically through the use of a piezoelectric material. The induced voltage in the pick-up coil is proportional to the sample's magnetic moment. Usually, the induced voltage is measured through the use of a lock-in amplifier using the piezoelectric signal as a reference (signal). By measuring in the field of an external electromagnet, it is possible to obtain the hysteresis curve of a material.

Materials and Methods

Samples used in this project were prepared using the sintering process to produce pellets of Barium Titanate and Cobalt Ferric Oxide and the BT-CFO composites. Two kinds of composites were targeted for the primary work while the Raman spectrum of BT-CFO 82 (80% $BaTiO_3$, 20% $CoFe_2O_4$) was also recorded. The dimensions of the pellets were 5 mm. radius and 1 mm. thickness.

The samples used were prepared in the *Dept. of Physics and Astrophysics, University of Delhi*. For preparation, components such Co_3O_4, Fe_3O_4, BaO and TiO_2 are mixed in a certain distinct stoichiometric molar ratio, in an organic solvent like an ether. The mixture is ground and then sonicated. The mixture is then transferred to a crucible and loaded into a furnace at about 800°C. After taking the sample out of the furnace, it is cooled to room temperature. The powder is pressed into pellets (diameter of 10 mm. and thickness of 1 mm.) and sintered at a high temperature. After coating the ceramics with silver electrodes on the flat faces, they are electrically polarized in an external electric field. The effect of preparation conditions on the magneto-electric effect, especially on the coupling between the magnetostrictive and piezoelectric phases in the composites, has been studied and well documented. [7]

The microstructure and stress produced due to the external magnetic field was studied using Raman Spectroscopy. Raman Spectroscopy was performed in the convention right-angle scattering geometry at room temperature. The sample was excited by the 514 nm Argon-ion laser using the *InVia Renishaw Raman Microscope*. For applying external magnetic field four NdFeB button-magnets were used.

The hysteresis curve, obtained using a Sorensen Vibrating Sample Magnetometer (V.S.M.), was used to study the magnetization pattern of the composites for varying external magnetic field intensity. The frequency of vibration was kept at 75 Hz. and readings were taken. For graphing, the magnetic moment per unit weight was calculated for comparing equivalent values for V.S.M. data that represents response taken from the bulk of the sample.

Results and Discussion

Laser Raman Spectroscopy

By Laser Raman Spectroscopy, the spectrum obtained for the substances were found to comply with values referred from literature, though the discrepancies for the values could be explained by referring to conditions of preparation and processes taking place in the perovskite $BaTiO_3$, spinel $CoFe_2O_4$ or the composites. For BT, as per

literature and past experimental results[8, 9, 10], the Transverse Optical (TO) Mode Frequencies and Longitudinal Optical (LO) Mode Frequencies were analyzed.

Firstly, the Raman spectra for $BaTiO_3$ and $CoFe_2O_4$ were studied. The data obtained shows peaks for $BaTiO_3$ at 166 cm^{-1}, 174 cm^{-1}, 258 cm^{-1}, 306 cm^{-1}, 518 cm^{-1} and 717 cm^{-1} for six of the eight modes as per the referred resource[11]. The modes that were not obtained were for 2 E_1 Raman modes. For $CoFe_2O_4$, we obtained distinct peaks nearly at all the mentioned frequencies[12] for the Raman Modes at 210 cm^{-1}, 310 cm^{-1}, 474 cm^{-1}, 575 cm^{-1}, 616 cm^{-1} and 694 cm^{-1}.

Raman Peaks Observed

Peaks mentioned here include the ones that do not fall under a Raman Active Mode Denotation as per Symmetry Group Character Tables.

BT	CFO	BC 55	BC 37	BC 82
73# cm^{-1}	76 cm^{-1}	76# cm^{-1}	76# cm^{-1}	73# cm^{-1}
258# cm^{-1}				244# cm^{-1}
306# cm^{-1}	310# cm^{-1}	307# cm^{-1}	307# cm^{-1}	305# cm^{-1}
	474# cm^{-1}	476 cm^{-1}	473# cm^{-1}	
518# cm^{-1}		513# cm^{-1}		515# cm^{-1}
	575 cm^{-1}		575 cm^{-1}	
	616 cm^{-1}	625 cm^{-1}	628 cm^{-1}	
717# cm^{-1}	694# cm^{-1}	682# cm^{-1}	694# cm^{-1}	718# cm^{-1}
# – Major Peaks				

Raman Mode Frequency Tables in CoFe$_2$O$_4$

Modes	Reference Raman Mode	Observed Raman Mode
A_{1g} - 1	695 cm^{-1}	694 cm^{-1}
A_{1g} - 2	625 cm^{-1}	616 cm^{-1}
T_{1g} – 1	575 cm^{-1}	575 cm^{-1}
T_{1g} – 2	470 cm^{-1}	474 cm^{-1}
E_g	312 cm^{-1}	310 cm^{-1}
T_{1g} – 3	210 cm^{-1}	210 cm^{-1} (Local Maxima)

After this, the Raman spectra for $BaTiO_3$-$CoFe_2O_4$ composite in 50%-50%, 30%-70% and 80%-20% proportion were analyzed. One can see that for BC-55, the peaks obtained were: at 307 cm^{-1}, analyzed as the cumulative effect of one E_1 (TO) mode of BT and the E_g mode of CFO; at 476 cm^{-1}, due to a T_{1g} mode of CFO; at 513 cm^{-1}, due to an A_1 (TO) mode of BT; at 682 cm^{-1}, due to an A_{1g} mode of CFO and the T_{1g} mode of BT.

Raman Mode Frequency Tables in BaTiO$_3$

Modes	Reference Raman Mode (cm^{-1})	Observed Raman Mode (cm^{-1})
A_1 (TO)	165	166 Local Maxima Negligible Height
E	172	174 Local Maxima Negligible Height
A_1 (TO)	246-270	258
E (TO)	303-307	306
E Mixed Character	370-400	-
E (TO)	470	-
A (TO)	512	518
Mixed Longitudinal (with both A and E character)	710	717

One can analyze the spectrum obtained for the BC-37 and BC-82 cases, and can see that, as per the dominating constituent of the composite, the spectrum displays peaks that are due to the Raman modes of the constituent having a greater constituent proportion. One can see that in BC-37 we obtain a peak at 575 cm^{-1} due to a T_{1g} mode of CFO, which is not obtained either for BC-55 or BC-82, and also at 628 cm^{-1}, largely attributed to an A_{1g} mode of CFO at 616 cm^{-1}.

Similarly, for BC-82, one can see that we obtain a peak at 244 cm^{-1}, which can be attributed to an A_1 (TO) mode of BT, and the peak at 515 cm^{-1}, due to another A_1 (TO) mode.

Before proceeding with the results for Raman spectroscopy for magnetized-samples, I would like to highlight a result that has not been observed or mentioned in any definitive work on Multiferroics or poled-samples' Raman spectra. We observed that after magnetically poling the sample, the Raman spectrum-curve shifted downwards uniformly in terms of the intensity of scattered light. This was observed both for BC-37 and BC-55. Having kept this as a follow-up task for verification, I have not reached any conclusive reason for the phenomenon.

Coming to the magnetized sample readings, let us firstly analyze the BC-37 readings.

The reading at 307 cm^{-1}, considered as a result of E_1 (TO) mode of BT and E_{1g} mode of CFO, shifted by 1 cm^{-1} towards the individual E_{1g} CFO Raman mode. Similar is the case for the peak at 694 cm^{-1}.

Table 1: Raman Peaks Observed		
BC 37		
Unpoled	**Poled, Unmagnetized**	**Poled, Magnetized**
76 cm^{-1}	75 cm^{-1}	71 cm^{-1}
307 cm^{-1}	307 cm^{-1}	308 cm^{-1}
694 cm^{-1}	694 cm^{-1}	692 cm^{-1}
628 cm^{-1}	628 cm^{-1}	630 cm^{-1}
575 cm^{-1}	575 cm^{-1}	582 cm^{-1}
473 cm^{-1}	473 cm^{-1}	472 cm^{-1}

The peak at 628 cm^{-1} is shifted by 2 cm^{-1}. Tthis peak is largely due to an A_{1g} mode of CFO, as mentioned earlier.

There is a significant shift of 7 cm^{-1} for the BC-37 peak due to a T_{1g} mode of CFO, previously at 575 cm^{-1}.

There is a shift of 1 cm^{-1} for the BC-37 peak occurring at 473 cm^{-1}, largely due to a T_{1g} mode of CFO.

The observations for BC-55 are noted for poled and unpoled samples:

There is a cm^{-1} shift in the peak at 307 cm^{-1} towards the frequency of the E (TO) mode of BT at 306 cm^{-1}.

There is a 3 cm^{-1} shift of the peak at 476 cm^{-1}, attributed to a T_{1g} mode of CFO.

There is a 1 cm^{-1} shift in the peak at 513 cm^{-1}, which is a result of the A_1 (TO) mode of $BaTiO_3$.

There is a significant 5 cm^{-1} shift in the peak-location at 625 cm^{-1}, attributed to an A_{1g} mode of CFO.

There is a 14 cm^{-1} shift in the peak at 582 cm^{-1}, attributed to be a partial super-position of the individual T_{1g} mode of BT and an A_{1g} mode of CFO.

One can analyze the spectral signature by studying various sections of the curve. We can divide the Raman spectra into 4 regions.

Table: Raman Peaks Observed		
BC 55		
Unpoled	**Poled, Unmagnetized**	**Poled, Magnetized**
76 cm^{-1}	76 cm^{-1}	72 cm^{-1}
307 cm^{-1}	304 cm^{-1}	306 cm^{-1}
476 cm^{-1}	474 cm^{-1}	473 cm^{-1}
513 cm^{-1}	519 cm^{-1}	514 cm^{-1}
625 cm^{-1}	623 cm^{-1}	620 cm^{-1}
682 cm^{-1}	699 cm^{-1}	696 cm^{-1}

- In Region I, one can see the significant spectral signature of Barium Titanate. One can see that BC-55, which has more BT content, has a peak that coincides with that of Barium Titanate. In general, BC-55 gives more intensity for all the Raman shifts in this region.
- In Region II, one can see that BC-55 has an evened out curve profile given that BT and CFO have a peak each at distinct, different values of Raman shift and a nearly flat curve profile elsewhere in the entire region. BC 37, which has more CFO content than BC-55, in a 70-30 ratio with the BT content, has a strong peak nearly coinciding with the peak of CFO.
- In Region III, only Cobalt Ferrite has a sharp spectral peak. BC-37, having a greater CFO content has a stronger peak than that of BC-55, and that coincides with the peak of CFO.
- In Region IV, there are no significant peaks.

One can thus observe that there is significant Raman shift in peaks that have a contribution from the modes of magnetostrictive $CoFe_2O_4$ or of BT that have a strain resulting from the magnetostrictive behaviour of CFO.

Also, one can analyze the significant difference in the value of poled and un-poled composite samples in the observations. One can attribute this appreciable difference to the fact that due to magnetostriction, the configuration changes that are brought about have a direct effect on the scattering of the Laser light for Raman Spectroscopy.

I intend to follow-up this work of mine with a study on these characteristic changes in the observations for Raman Spectroscopy for poling of the sample.
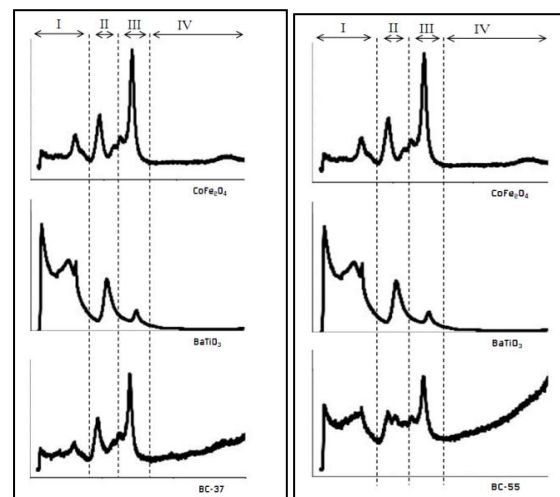
Vibrating Sample Magnetometer (V.S.M.)

The VSM data shows decreasing retentivity but greater coercivity for greater amount of $CoFe_2O_4$ showing lesser magnetic property in the composite, as expected.

The magnetic moment per unit weight for zero magnetic field, which is a measure of our retentivity, for different composites has been tabulated.

Sample	Residual Magnetic Moment	
CFO	-1.55 emu/gm.	1.55 emu/gm.
BC 37	-2.38 emu/gm.	2.37 emu/gm.
BC 55	-1.56 emu/gm.	1.55 emu/gm.

Sample	Magnetic Field	
CFO	180 Oe.	-180 Oe.
BC 37	450 Oe.	-440 Oe.
BC 55	390 Oe.	-380 Oe.

Interestingly, it has been observed that the residual magnetic moment is almost the same for CFO and BC 55 for the magnetization and demagnetization process.

However, one can see that the magnetic field to nullify residual magnetic moment in the substance has distinct values for the composites and CFO, as tabulated.

Conclusion

The structural changes due to Magneto-electric effect have been studied using Raman Spectroscopy. One can see that distinct relative shift in the Raman spectrum for poled and unpoled samples are observed. This gives us a physical picture of how the magnetic dipoles are affected by the poling process.

One can also observe strong peaks in certain sections of spectrum, coinciding with the piezoelectric $BaTiO_3$ in the composite's spectral signature. For certain lattice elements and conditions, magneto-electric effect can be explained in terms of the stress/strain developed in the lattice interfaces, as is apparent in the Raman shifts.

The magnetic properties are studied for the composites with varying amount of $CoFe_2O_4$ using the VSM data.
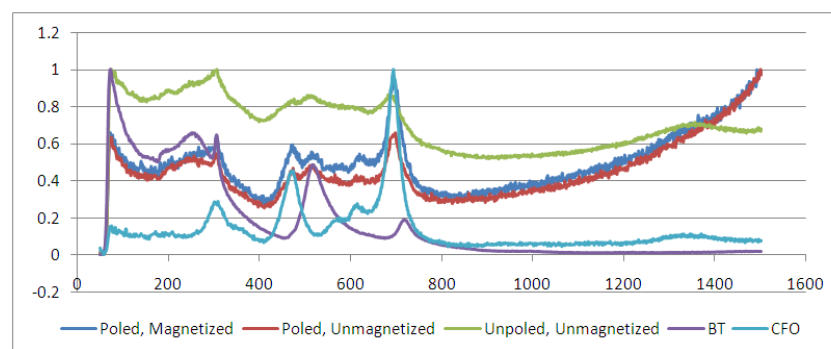
Figure 1: *Normalized Raman Spectrum for (i) BT, (ii) CFO, (iii) Unpoled, Unmagnetized BT-CFO 55 Composite, (iv) Poled, Unmagnetized BT-CFO 55 Composite, (v) Poled, Magnetized BT-CFO 55 Composite*
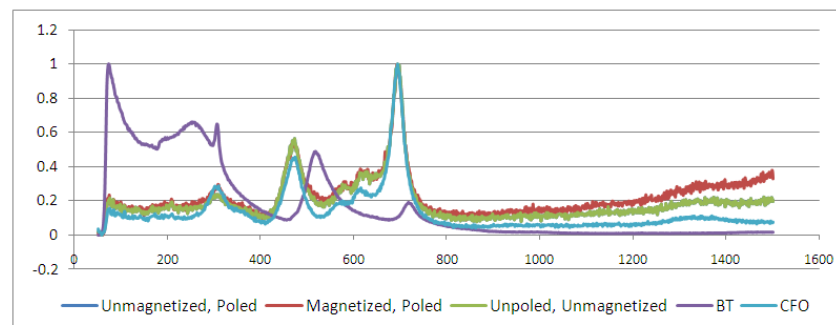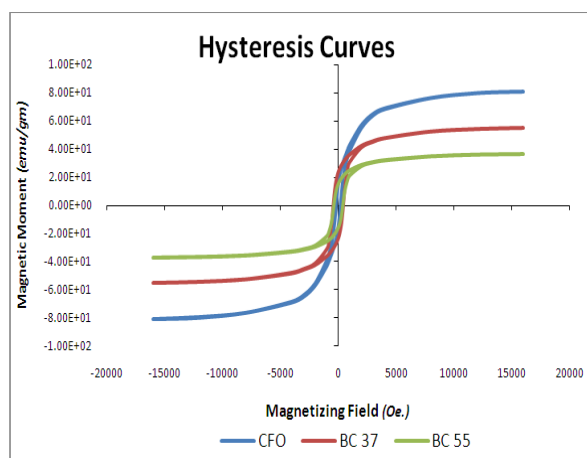

Figure 2: *Normalized Raman Spectrum for (i) BT, (ii) CFO, (iii) Unpoled, Unmagnetized BT-CFO 37 Composite, (iv) Poled, Unmagnetized BT-CFO 37 Composite, (v) Poled, Magnetized BT-CFO 37 Composite*
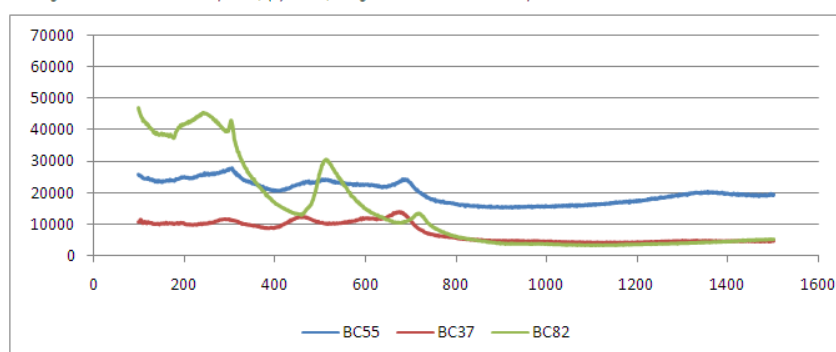
Figure 3: *Raman Spectrum of BT-CFO 55 composite, BT-CFO 37 composite and BT-CFO 82 composite*

Vibrating Sample Magnetometer Graph

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