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## 1. Title of the Project

"Investigation of Magneto-electric BiFeO<sub>3</sub> Thin Films"

## 2. Applicant

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## 4. Abstract

Recently it has been shown that optical probes are very powerful to explore the coupling and imaging the magnetoelectric material. These techniques can reveal valuable information from the physical and chemical properties of all kinds of materials. Here we like to employ these techniques to understand the spin interactions with phonons and their coupling with electrical polarization in magnetoelectric BiFeO<sub>3</sub> thin films. There are many publications and studies on BFO due to its magnetic and ferroelectric properties. But, the researches still are on the first steps to explore its magnetoelectric physical properties and their origin.

Here we propose to study the BFO thin film magnetoelectric material using optical probe techniques. These techniques have many advantages. They are non-disturbing, commercial probe methods and have easy technical operating system with fast and precise measurement.

BFO thin films show mostly the bulk behavior with large enhancement of polarization and related properties in heteroepitaxial constrained form [<sup>1</sup>]. Its structural and magnetic behaviors and phase transitions are studied extensively but still there are many questions that are needed to explore. It shows different kind of structural phase transitions that explored and revealed its physics. But the magnetic specially spin reorientation phase transitions is not studied enough and the origin of spin reorientations are not clear in BFO. If we can distinguish the nature of spin dynamics in this material and their behavior in different physical conditions like different temperatures, and under applied magnetic and electric field, then we will be able to understand the magnetoelectric coupling physics.

Here we propose to study the spin reorientation phase transitions using time resolved Raman scattering of electromagnons and understand how the magnons behave in the BFO thin film. What is the nature of their reorientation phase transitions? How they couple to electrical polarization and what is the order of coupling. We are going to explore how the electromagnons reveal the coupling and how electric field can affect the magnetic properties and vice versa. Femtosecond pump probe spectroscopy is the right tool to investigate the spin dynamics because they happen mostly in the short time scales and time resolved spectroscopic methods can detect the events at very short time scales [<sup>2</sup>]. It is shown that time resolved electrical pump-optical method can image the evolution of the magnetic domain under magnetic or electric field and we will study the BFO magnetic behavior with this technique in different temperatures and under both electric and magnetic fields [25].

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## 5. Duration of the Project

4 years, starting from September 2011

## 6. Personnel

### 6.1 Senior-scientists

Name	Task in Project	Time
Prof. P.H.M.van.Loosdrecht	Supervision and Management	10 %

### 6.2 Junior-scientists and technicians

Name	Task in Project	Time
PhD Student	Experiments and Analysis	90 %
Antonio Caretta	Experiments and Analysis	5 %
Foppe de Haan	Technical Support	2.5 %
Ben Hesp	Technical Support	2.5 %

## 7. Cost Estimates

### 7.1 Personnel Positions

One 'onderzoeker in opleiding' position for four years.

### 7.2 Running Budget

15 k€/year for conferences, summer schools and maintenance.

### 7.3 Equipment (k€)

Equipment	Costs k€
Pulsed Laser Deposition (Targets)	~10

### 7.4 Other Support

This Project will be done in Zernike Institute for Advanced Materials, Groningen University, that is a multidisciplinary scientific environment with expertise in different research fields specially physics and chemistry. It is very easy in our intitute to use the facilities of all research groups and their well equipped labs.

### 7.5 Budget Summary (in k€)

The expenses are summarized in the following table:

		2011	2012	2013	2014	2015	Total
Position	PhD Student	25	50	50	50	25	200
	Postdocs	-	-	-	-	-	-
	Technicians	-	-	-	-	-	-
	Guests	-	-	-	-	-	-
Costs	Personnel	25	50	50	50	25	200
	Running Budget	5	15	15	15	10	60

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	Equipment	5	35	-	-	-	10
Total		35	100	65	65	35	300

## 8. Research Programme

### 8.1 Introduction

ABO<sub>3</sub> perovskite oxides, are very well known class of materials which they show interesting physical properties like magnetic, ferroelectricity, and so on. Recently there is a growing interest in magnetoelectric multiferroic material, which shows the magnetic and ferroelectric ordering at the same time [3] and it seems they will have an important role in the modern technology due to their potentiality that offer a whole range of new applications, including the emerging field of spintronics, new data-storage media, sensors and multiple-state memories. Magnetoelectric material is the most interesting of multiferroics in which the electric polarization can be tuned by an applied magnetic field and vice versa and offers many applications as mentioned few of them [4,5,6].

As mentioned magnetism and ferroelectricity coupling can potentially be used in the construction of novel multifunctional spintronic devices. This needs the coupling of magnetism and ferroelectricity. But coupling procedure is currently among the most challenging topics in solid state physics. Scientists have employed different techniques to observe the coupling mechanism. Optical probe techniques are effective tools that seems have a great potential to study these kinds of materials. Because any changes in the crystal structure, magnetic and other physical properties can affect the frequency, bandwidth and intensity of the Raman peaks, absorbance, transmittance and reflectivity of sample that can be detected using proper spectroscopy methods like Raman and proper kind of pump probe spectroscopy methods.

BiFeO<sub>3</sub> is a robust multiferroic since it presents a coexistence of ferroelectric and antiferromagnetic order up to unusually high temperatures, namely above room temperature. Since Raman Effect is very sensitive to any kind of changes in the crystal structure, it can reveal any changes in phonon and magnon behavior in the crystal.

Indeed, BFO has a very high ferroelectric polarization reaching 100  $\mu\text{C cm}^{-2}$  below  $T_C = 1,143$  K and becomes an antiferromagnet below  $T_N = 643$  K [21]. Magnetic property of BFO comes from exchange interaction of Fe<sup>3+</sup> cations. It has got lots of interests due to enhancement of ferroelectric and magnetic properties in BFO thin films [7]. BFO thin films advantages and simplicity of the structure has been caused to attract considerable research efforts. In spite of extensive research works on the BFO physical properties, there are just a few publication has studied the phonon behavior and explored the magnetoelectric BFO coupling using optical spectroscopy methods.

The dynamical properties can be realized by magnetic and phonon vibrations and their coupling that is known as electromagnons. Ultrafast optical spectroscopy can provide insight from the fundamental microscopic dynamics and especially about the coupling multiple degrees of freedom which governs the functional properties of the materials. Therefore, pump-probe studies can reveal the answer the questions like achievable switching speeds in multiferroics. The ability to probe phonon and magnon response in the time scale is the most well known feature of pump probe spectroscopy. This will make this technique suitable to explore the dynamical properties of multiferroics.

Phonons are very sensitive to any kind of physical changes in the crystal and it is well known that they can be influenced by spin correlation and couple to each other. Raman effect measures phonon behavior in the Brillouin zone center and have very well defined selection rules so it will be able to detect modifications in the crystal structure even subtle changes in the lattice, and spin wave (magnons) behavior that coupled to phonons [8]. We will discuss much more about the Raman applications in the next sections.

Ultra fast pump-probe spectroscopy methods have employed to study the multiferroics recently. This technique has different variants that each have their own advantages and can

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reveal dynamic processes of lattice vibration and spin and also their interaction with perturbing factors like light or electrical fields.

Femtosecond pump probe study of multiferroic LuMnO<sub>3</sub> is revealed that the coherent excitation of optical and acoustical phonons is the signature of the elasticity and magnetism coupling and the speed of sound exhibit an anomaly at the antiferromagnetic transition temperature [9]. Takashi et al have investigated BFO thin films (that we are interested also) femtosecond optical investigations and they found the charge injection and applied electric field can lead to the ultrafast modulation of electrical polarization [10].

Talbayev et al detected coherent magnons using ultrafast pump-probe reflectance spectroscopy in multiferroics Ba<sub>0.6</sub>Sr<sub>1.4</sub>Zn<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub>. Modulation of material dielectric tensor by magnons is demonstrated which enables the detection of coherent magnons by pump probe reflectance spectroscopy [11]. KJ Jang et al measured temperature dependency of coherent phonon mode in YMnO<sub>3</sub> by using femtosecond pump-probe differential reflectance spectroscopy. They found that for the wide range of temperature, coherent acoustic phonon was coupled to magnons above the T<sub>N</sub>. They have attributed the origin of acoustic phonons to magnetic ordering [12].

Nonlinear optical processes developed as a tool to probe the magnetic properties of materials. When an electromagnetic wave with frequency of  $\omega$  interacts with the matter, harmonic generation from electromagnetic field  $E(\omega)$  and  $H(\omega)$  can induce a polarization. Linear optical effects like Faraday and Kerr rotations are not suitable for antiferromagnets because these linear effects just measure the absolute magnetization. The simplest nonlinear optical effect is the electric-dipole type Second Harmonic Generation (SHG) described by the equation

$$P(2\omega) = \epsilon_0 \chi_{ijk} E_j(\omega) E_k(\omega)$$

This means that incident light induces a second harmonic polarization.  $\chi_{ijk}$  is the SHG susceptibility denotes the coupling between the light fields at  $\omega$  and  $2\omega$  to the magnetic property of matter [13]. So this technique will enable us to explore the ultrafast and magnetoelectrics phase transitions. Recently Fiebig et al. have imaged the magnetic domain evolution using this technique. They used Electrical-pump-optical-probe spectroscopy to monitor spin evolution and to image the domain changes under magnetic and electric external field [25].

In multiferroic materials, spin fluctuation can produce unusual dynamic effects due to strong spin lattice coupling. Time resolved optical spectroscopy directly studies coupled dynamics between spin and lattice. The experimental works that we mentioned above show the potential of pump probe techniques especially ultrafast reflectance spectroscopy and SHG method.

To say further, optical methods are non-perturbing probe, rapid detection and identification method to find the phase changes in different forms of material like in bulk, thin film and ultra thin film. These advantages imply that optical probe techniques are powerful method to investigate the material behavior in different physical conditions.

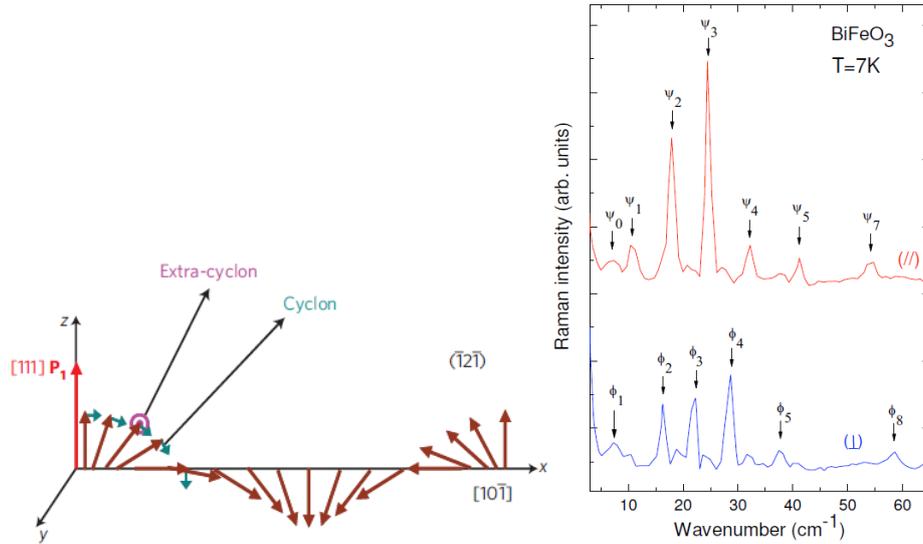
## 8.2 Electromagnons

It is well known that magnetoelectric coupling in single crystals couples spin waves (magnon) and polarization waves (optical phonons). This causes low frequency magneto-optical resonances in the dielectric susceptibility which is known as electromagnon excitation [14].

BFO is a model multiferroic material and have both ferroelectric and antiferromagnetic orders at room temperature with a large electric polarization and cycloidal spiral magnetic ordering at the same time. The incommensurate magnets have magnon zone folding and an investigation by optical probes of unusual spin waves which couples to optical phonons (electromagnons) is possible. BFO shows electromagnetic coupling at room temperature. de Sousa *et al* have given a theory on spin wave dynamics in incommensurate multiferroic BFO that predicts the observation of two species of low-energy electromagnon resonances by an optical probe [15]. Cazayous et al have reported the observation of these two species that has well defined energy level structure and good agreement with theory [16]. This level structure is related to magnon zone folding that is induced by the cycloid and coupling with electrical polarization.

They have assigned the two observed sets of energy level to the electromagnon mode excitation in and out of the cycloid plane in BFO with a wavelength of 62nm and associated wavevector,  $q=2\pi/\lambda$ . The spiral propagation is along  $[10\bar{1}]$  direction with a spin rotation within  $(-12\bar{1})$  plane. These two electromagnons are shown in Figure 1 (left) schematically [16].

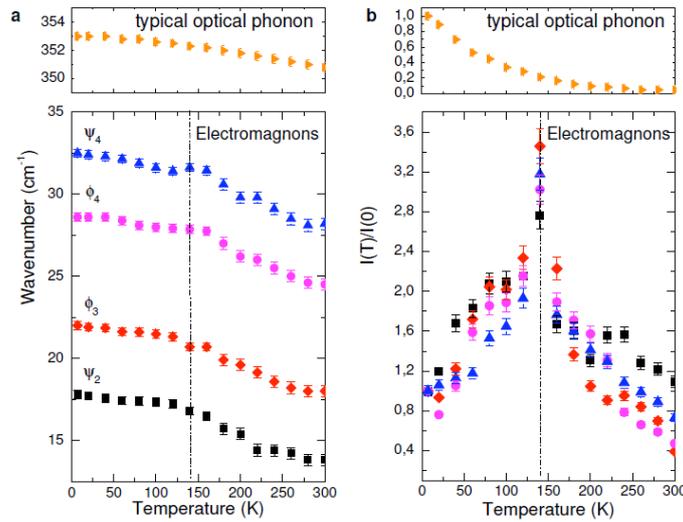
Figure 1 (right) shows the low energy of Raman spectra from BFO single crystal. The light is radiated to the crystal so that incoming and outgoing light polarizations are in the plane of cycloidal magnon wave propagation,  $(010)$ . In parallel ( $//$ ) polarizations and crossed polarizations in the  $(010)$  plane, Raman scattering gives two distinct sets of peaks that denoted  $\Psi$  and  $\Phi$  respectively in Figure 1. This figure shows that  $\Phi$  modes are equally spaced from zero frequency with sequence of  $\sim 7.4 \text{ cm}^{-1}$ . But  $\Psi$  modes are not regularly spaced at low frequency as it can be seen from the figure.



**Figure 1- (Left)** The spin cycloid ground state. The spin excitations correspond to in-plane modes  $\Phi$  with an ellipsoidal shape elongated along  $y$  (cyclons) and out-of-plane modes  $\psi$  (extra-cyclons) with an ellipsoidal shape elongated along the tangent vector that belongs to the  $xz$  plane, **(Right)** Raman spectra of electromagnons in  $\text{BiFeO}_3$ .  $\Psi$  and  $\Phi$  electromagnon modes selected using parallel ( $//$ ) and crossed (perpendicular) polarization respect to spiral vector, [16].

Cazayous *et al* have tried to interpret the mentioned Raman spectra using the theoretical prediction of possible observation of electromagnons in BFO spiral magnet by optical methods [15]. In this method effective Ginzburg-Landau free energy defines the energy system and comprises the coupling between magnons and electrical polarization. Based on this theory there is two kinds of electromagnon excitations which located in and out of cycloidal plane, that is named as cyclon and extra cyclon modes. They have distinct energies depending on the coupling to electrical polarization that for cyclone it is given by  $E_c(n) = \epsilon_c(q)n$  and extra-cyclon by  $E_{exc}(n) = \epsilon_c(q)(n^2 + 1)^{1/2}$ . These electromagnons experimental results are in good agreement with theory that is  $5.3 \text{ cm}^{-1}$  for cyclon energy mode that experimental value is  $7.5 \pm 0.2 \text{ cm}^{-1}$  [16].

The evolution of electromagnon energy is shown in Figure 2. To compare, typical phonon evolution by temperature is shown on top of the Figure a and b. As shown, electromagnon energies have an anomaly around 140K in which is different than optical phonon behavior. Also Figure 2b shows that the integrated intensity of electromagnons has a maximum at 140K and then decrease slowly as temperature increases.



**Figure 2 (Middle)** Temperature dependence of the four electromagnon energies ( $\Psi_2$ ,  $\Phi_3$ ,  $\Phi_4$  and  $\Psi_4$ ) and of one typical optical phonon mode, **(Right)** integrated intensity (area under the Raman peaks) of the electromagnon and phonon excitation [16].

Singh et al also have tried to see the electromagnon behavior using Raman scattering of electromagnons [17]. Their results are nearly similar to what we discussed above. In this work Raman spectra from magnon scattering is similar to  $\Psi$  modes BFO single crystal of Figure 1. Their observed phenomena also indicates that diverging cross section and the frequency shift occurs not only at  $\sim 140$  but also at  $\sim 200$  K in which both of them implies a spin-reorientation phase transition as it happens in orthoferrites. The origin of the spin reorientation phase transition is unknown, similarly other RFeO<sub>3</sub> materials are known to show such spin reorientation (e.g. 84–94 K in TmFeO<sub>3</sub>) [18]. We think this needs further researches to elucidate what is the origin of such a behavior. What is the physics behind? Time resolved Raman Scattering can help to answer these questions. Because it will enable us to study the electromagnons at very short time scale and at the same time Raman technique can give valuable information about subtle changes of the structure. Ultrafast spectroscopy methods can monitor the spin-phonon coupling, and this coupling is the signature of spin reorientation phase transitions. Thus, if we understand how the phonons couple to the spin and how it affects the magnetoelectric state of the matter, then we will be able to answer the questions. Ultrafast pump probe reflectance spectroscopy will reveal the role of optical and acoustical phonons in these phase transitions. This method can reveal the modulation of dielectric constant around phase transition temperatures as the people have done on Ba<sub>0.6</sub>Sr<sub>1.4</sub>Zn<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub> multiferroics in ref [11] to determine the dielectric susceptibility modulations when magnetoelectric states changes.

### 8.3 Electric Field Control of Spin Waves

In analogy with photonics that relies on electromagnetic waves, Magnonics proposes to use spin waves to carry and process information. It includes several advantageous features such as potential operation in the terahertz range and excellent coupling to spintronics [19]. Having control on spin waves in materials like BFO makes it a promising material for new applications in information processing.

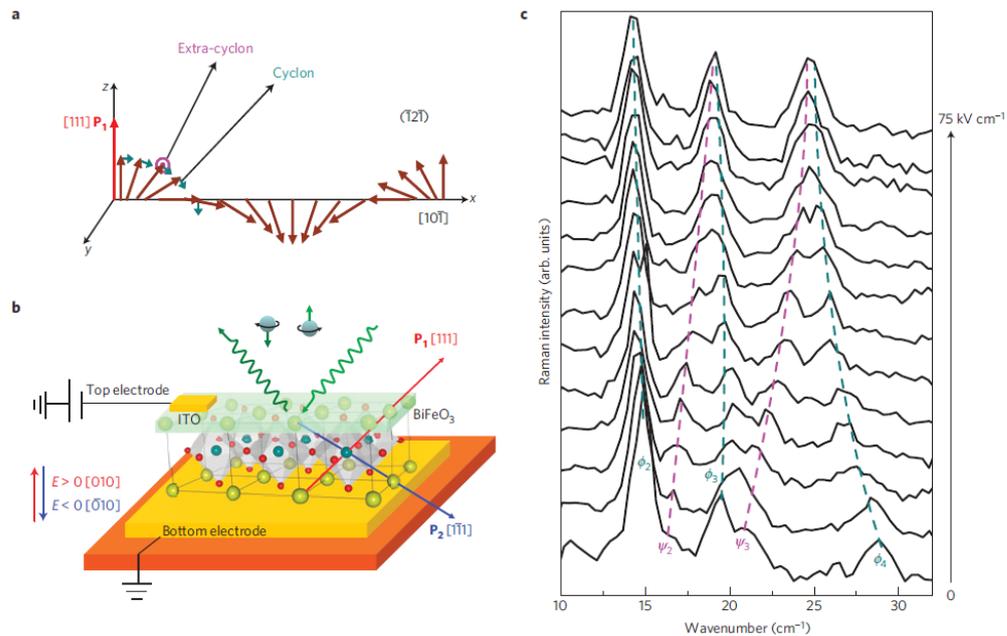
Rovillain et al have shown the spin wave frequency ( $>600$  GHz) in BFO can be tuned at room temperature by over 30% in a non volatile way using electrical field [20]. In previous section we discussed prediction of electromagnons and then experimental proof of them by Raman scattering [15, 16]. Here we are going to discuss the electromagnons Raman signature that moves when the electric field is applied through the sample and proves the linear magnetoelectric coupling exists in BFO thin film (Linear relationship of frequency change with applied electric field). Different researchers have shown that electric field can induce the flop of the polarization and the cycloidal plane, also it can switch the antiferromagnetic-

ferroelectric domains in BFO [21, 22, 23]. Here we will deal with the study of spin wave flop using Raman scattering of electromagnons in BFO.

Figure 3a shows the cycloid structure of the spins with a wavelength 62nm and wave vector  $q$ . As mentioned before, it lies in the (-12-1) plane with polarization  $P_1 // [111]$  and the cycloid wave vector  $q // [10-1]$ . Figure 3c shows the Raman scattering of the cyclon ( $\Phi_n$ ) and extra-cyclon ( $\Psi_n$ ) modes - the spin oscillations in and out of the cycloidal plane.

These two kinds of magnons come from symmetry breaking of the cycloidal ground state. The total momentum can be increased or decreased by a multiple of cycloid wave vector  $q$  that causes the magnon zone folding at the Brillouin zone centre in which  $\Phi_n$  and  $\Psi_n$  are related to the magnon wavevector equal  $k=nq$  [20].

Figure 3b schematically shows the experimental set up that is used to detect optical excitation of magnons while applying electric field. To have the capability to apply electric field and measure the Raman signature of magnons along the [010] and [0-10] directions, transparent electrodes are used on both sides of the sample. Figure 3c shows the effect of applied electric field along the [010] direction on magnons. Raman signature shows the blue shift for  $\Phi_2$  and  $\Psi_3$  and red shift for  $\Psi_2$ ,  $\Psi_3$  and  $\Psi_4$ .

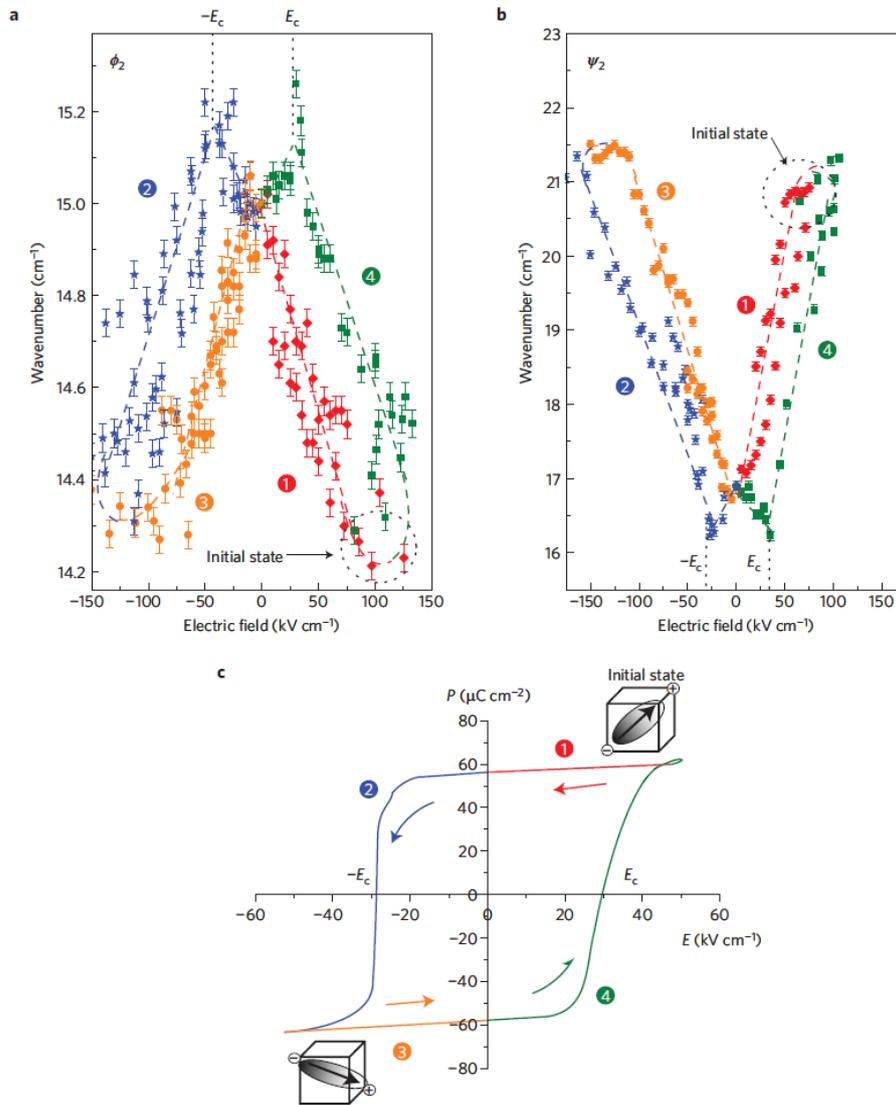


**Figure 3** - Electrical control of spin waves. (a), the spin cycloid ground state. in-plane modes  $\Phi$  (cyclons) and out-of-plane modes  $\psi$  (extra-cyclons) (b), experimental set-up scheme used to apply an external electric field  $E$  single crystal and to probe its spin excitations using Raman spectroscopy. Raman scattering is carried out through the ITO top electrode with light polarizations in the (010) plane. (c), Raman spectra showing the magnon modes  $\Phi_2$ ,  $\psi_2$ ,  $\Phi_3$ ,  $\psi_3$  and  $\Phi_4$  when the applied field ranges from 0 to 75  $\text{kV cm}^{-1}$  [20].

Figure 4a, b shows evolution of the  $\Phi_2$  (cyclon) and  $\Psi_2$  (extra-cyclon) modes by variation of electric field. It clearly shows the spin wave modes has direct relation with polarization hysteresis loop shown in Figure 4c. Path 1 (red diamond, Figure. 4a) shows by decreasing the applied electric field ( $E//[010]$ ),  $\Phi_2$  mode frequency increase (initial polarization state  $P_1 // [111]$ ). And along the path 2 by increasing the negative electric field ( $E//[0-10]$ )  $\Phi_2$  mode frequency increases up to  $E_c \sim -35 \text{ kV cm}^{-1}$  that flip of  $P$  along the [1-11] direction ( $P_2$ ) occurs. By increasing negative applied voltage the frequency of  $\Phi_2$  decreases. The hysteresis cycle is completed by travelling path 3 and 4 as shown in the figure.  $\Psi_2$  mode is shown in the Figure 4b that also shows connection to the polarization loop. Its behavior in comparison with  $\Phi_2$  shows opposite trend and shows much stronger frequency shift under the applied electric field

(e. g at  $50 \text{ kV cm}^{-1}$ ,  $\Delta\omega=(+2.1 \pm 0.1)\text{cm}^{-1}$ ).  $\Psi_2$  frequency has over  $5 \text{ cm}^{-1}$  at maximum applied field. This amount is 30% shift of its natural frequency.

These results clearly show the coupling of spin waves and the electrical polarization of the material that can be controlled by applying an electric field. The capability of spin wave control in BFO opens an important port to develop the spin wave based devices.



**Figure 4** - Spin-wave hysteresis loop. Voltage dependence of  $\Phi_2$  (a) and  $\Psi_2$  (b) magnon modes. (c), (P-E) hysteresis loop at room temperature. The shift of the spin-wave frequencies follows the polarization loop along path 1 (red diamond), 2 (blue star), 3 (orange circle) and 4 (green square) [20].

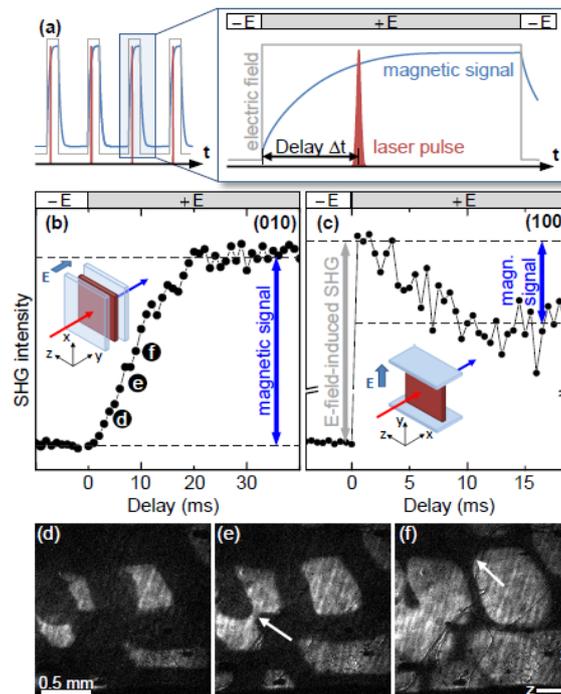
Till now we just discussed about the bulk BFO single crystal. As Ramesh and Spaldin have explained in ref [6], "The availability of high-quality thin-film multiferroics makes it easier to tailor their properties through epitaxial strain, atomic-level engineering of chemistry and interfacial coupling, and is a prerequisite for their incorporation into practical devices" then BFO thin film can show some interesting properties that is different than bulk. Some optical studies is done on it but based on our knowledge till now there are not available and trustful studies on it. BFO thin film bears strain due to growth mismatch with substrate and its thin

film on SrTiO<sub>3</sub> substrate shows very high values of polarization ( $\sim 100\mu\text{C}/\text{cm}^2$ ) that is reached for very high quality single crystal of BFO [24]. Being under strain can induce magnetostriction effect that could couple with its ferroelectric property as well.

Raman spectroscopy have done by Palai *et al* on thin film BFO and they confirmed the existence of phonon anomaly at 140 and 200K that is due to diverging magnon cross section in these temperatures [24]. It will be instructing to see the electromagnons in thin film BFO in spite of many similarities with the bulk. But it was proven that sometimes thin films have very different properties from the bulk or much enhanced particular physical properties than its bulk form. As we mention the enhancement of polarization in thin BFO film. BFO thin film unlike the bulk is under strain and this strain causes many different properties like magnetostriction effect of strain mediated multiferroic property. About the possible experiments we discussed before all will be done on BFO thin films.

The next step can be the study of BFO thin film under applied electric field and probe the electromagnon as is discussed above.

The other instructing technique to study magnetoelectricicity of BFO thin film is time resolved imaging of magnetoelectric switching by electrical-pump-optical-probe technique. Fiebig *et al* using this technique have shown electrical induced reversal of magnetic order in MnWO<sub>4</sub>. They have imaged the evolution of its magnetic domains under static and dynamic electrical poling by mentioned technique [25]. Figure 5 shows the SHG intensity and image of domain evolution. Clearly can be seen the magnetic domain structure switches after applying electric field. This shows that this technique is very powerful technique in which can distinguish very easily magnetoelectric coupling. This technique looks quite promising technique in comparison with conventional systems like magnetic and piezoforce microscopies [26].



**Figure 5**-Evolution of the domain structure during dynamic electric-field poling with a voltage pulse ( $E = \pm 750 \text{ kV/m}$ , slope 50 ns). (a) Sketch of the repetitive electric-field poling with subsequent SHG probing. (b, c) SHG intensity as a function of the delay  $\Delta t$  to the voltage pulse at  $t = 0$  for (b) MnWO<sub>4</sub> (010) and (c) MnWO<sub>4</sub> (100). Insets show the position of the electrodes with respect to the laser beam. The dashed lines show the SHG intensity for the two single domain states. (d-f) Magnetic domain structure at various delays.

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We will study the BFO thin film under magnetic field using mentioned both pump-probe techniques to see the magnetically induced possible switch of the polarization in BFO magnetoelectric thin film. Since people mostly have been focused on electrical manipulating of magnetism, this proposed experiment may give better understanding of polarization switch under magnetic field.

#### **8.4 Measurement techniques**

Raman Spectroscopy is one of the powerful techniques to study the different physical and chemical properties of materials in different fields such as pharmacy, polymer, semiconductors, thin films and nano-materials. It gives precious information about chemical and physical structure of the matter. Raman technique is very sensitive to the subtle changes in the crystals [27]. Raman can be used to probe the optical phonon that couples to the spins in the crystals. Also this technique can be used using different light sources in our lab and doing Raman on BFO thin film under applied electric field is feasible from quite low (less than 4K) to above room temperature.

In the Pump- Probe Spectroscopy the light coming out from the laser is split into two separate pulses. One is used as the pump beam in which excites the sample and the other one is used to probe the sample to see what have been happened in the sample. There is a time delay between these two pulses. By changing the delay between them, one can get the spectrum of reflectivity, absorption, luminescence, or Raman scattering of the probe after the sample and the changes due to pump pulse is considered [28]. Femtosecond laser pulses can reveal precise information about the events can happen in very short time scale like spin flips in dynamic processes.

Except to these main facilities, we have different optical methods like MOKE (Magneto Optical Kerr Effect) and different spectroscopy methods in our research group that enable us to investigate the BFO magnetoelectric properties.

#### **8.5 Goal of the Proposal**

The general goal of this proposal is the study of spin wave behavior, and magnetoelectric coupling investigation in thin film BFO. As mentioned bulk BFO single crystal shows magnon cross section divergence in Raman scattering at 140 and 200K. Also it is shown that Raman spectroscopy from BFO thin films represent anomaly at the same temperatures. This behavior is related to the spin reorientation phase transition that it can be explored by time resolved optical probes. The second idea that we are interested about this matter is its spin wave behavior that it could be employed to make new spin wave logic devices. Based on our knowledge, there is no any study on BFO magnetoelectric thin film using optical techniques as we discussed for bulk BFO. Therefore it will be exciting to explore BFO thin film magnetic and electric coupling and also spin wave behavior using optical probe techniques as an open field.

Here we propose a list of works (after the preparation of the samples) that is directly or indirectly connected to this research work:

- Raman spectra measurement of BFO thin film to see the electromagnons, because electromagnons are our finger print to see how they behave in thin film structure and how strain of thin film can affect their frequency.
- Time resolved Raman spectra close to spin reorientation phase transition at temperatures 140 and 200K, to study the spin wave dynamics,
- Measuring Raman spectra of BFO thin film under electric field, we expect to see nonlinearity of magnetoelectric coupling, because it is under strain and magnetoelectricity can be affected strain as well.
- Ultrafast Pump probe reflectance spectroscopy under magnetic field to explore the magnetic and electric field effect on spectrum to find optical and acoustical phonons coupling effect to spin waves in multiferroics,
- Imaging the domain revolution of thin film BFO under static and dynamic applied electric field and magnetic field using electrical- pump and optical probe technique.

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## 8.6 Collaborations

In this research work we can benefit from collaboration with different research groups inside and outside of the Zernike Institute. Interdisciplinary nature of this institute makes easy to have access to all the facilities in its inside. We will have cooperation with group of Prof. Noheda to make our samples and characterize their quality using the available techniques in their lab: Scanning probe techniques (AFM, PFM, EFM, CAFM ...). We already have collaboration with research group of Prof. Palstra and we are able to use their facilities like SQUID, and Electrical probe station if we needed. Also Prof. Petra has a very well equipped thin film lab that we can get the advantages of these facilities to characterize our thin films quantitatively.

We have collaboration with the group of Prof. M Fiebig of the Bonn University who has done very precious works using optical probes on multiferroics. Their recent work was "Time resolved imaging of magneto electric switching in multiferroic  $MnWO_4$ " that magnetic domain evolution of multiferroic  $MnWO_4$  has been monitored using electrical-pump-optical-probe measurement under electrical poling [25]. It will be very useful to have exchange of resources and ideas.

## 8.7 Plan of Work

The plan of work is summarized in the following table:

Time (months)	Activity
1 <sup>st</sup> year	<ul style="list-style-type: none"><li>✓ Preparation of BFO thin film using PLD system and optimizing its thickness with related characterizing methods like AFM, PFM and MFM</li><li>✓ Raman and Time resolved Raman measurements of electromagnons behavior from 100 to 300K, and determining spin dynamic with temperature in BFO thin film and determining the strain effect or strain mediated magnetoelectric coupling</li></ul>
2 <sup>nd</sup> year	<ul style="list-style-type: none"><li>✓ Raman measurement of electromagnons under applied electric field to measure the hysteresis loop of BFO thin film</li><li>✓ Ultrafast pump probe reflectance spectra measurements under both electric and magnetic fields</li></ul>
3 <sup>rd</sup> year	<ul style="list-style-type: none"><li>✓ Time resolved imaging of magneto electric switching using electrical-pump-optical probe technique (SHG) to monitor the domain evolution under static and dynamic applied magnetic field.</li><li>✓ Time resolved imaging of magneto electric switching using electrical-pump-optical probe technique (SHG) to monitor the domain evolution under static dynamic electrical poling.</li></ul>
4 <sup>th</sup> year	<ul style="list-style-type: none"><li>✓ In this year the complementary experiments can be done or if new experiments if were needed)</li><li>✓ Thesis writing</li></ul>

Of course, deviations from this scheme might occur depending on the problems or interesting new physics encountered.

## 9. Infrastructure

Optical Condensed Matter Physics group is equipped with variety of measuring and analyzing facilities. For this proposed research we have the most important facilities:

- Horiba Jobin Yvon T64000 UV with different light sources (green, red .... Lasers)
- Ultrafast Pump-probe reflectance Spectroscopy
- Time resolved electrical-pump-optical-probe spectroscopy (using SHG to image)

The group of Prof. Dr. Beatriz Noheda has the Pulsed Laser Deposition technique plus AFM, PFM and MFM machines. Other measurement set-ups like SQUID and MOKE which are not mentioned above do exist in our research group if we do need or if we find that they could be helpful for us, they can be employed depending on need.

## 10. Application perspective in industry, other disciplines or society

From technological view, in the first step the first application that one can propose for magnetoelectrics is the developing of magnetically written memories that is readable electrically and vice versa. This field can make a revolution in the memory storage field. The progress of magnetoelectrics has got applications to make new microwave devices transducers and magnetic field sensors as well [4].

Another approach of magnetism and ferroelectricity coupling can potentially be used in the construction of novel multifunctional spintronic devices [20].

This project will help to understand thin film magnetoelectrics and is a try to make a progress in spin wave based devices. These devices have the potential to make a breakthrough in information tools.

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