

# Electronic and structural properties of bismuth and rare-earth ferrites

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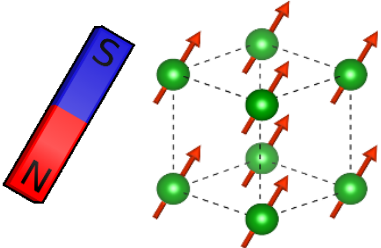
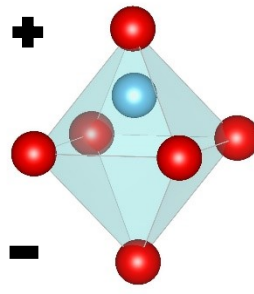
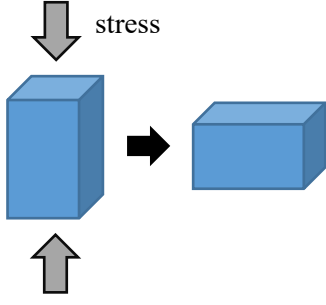
## Overall context

The work of this thesis stands in the larger framework of research on *multifunctional materials*. A functional material possesses a property that can be used in an application. If a material possesses several properties that can be simultaneously used in a device, it is referred to as multifunctional. Such materials are highly attractive for various applications in micro- and nanoelectronics and hence have stimulated intense international efforts towards both fundamental understanding and technological applications.

In this work, we focus on so-called *multiferroic materials*. Multiferroics, multifunctional materials par excellence, possess several ferroic orders such as magnetism, ferroelectricity and/or ferroelasticity<sup>1</sup> (see information box below). In a multiferroics such properties can interact, which we call coupling. In particular, the possibility to manipulate the magnetism with an electric field and vice versa is of technological appeal.

Whether a material is magnetic, depends on the number and distribution of electrons. Ferroelectricity, however, can be induced by different sources. Multiferroics are commonly classified by origin of the ferroelectricity.<sup>2</sup> *Type-I multiferroics* are materials where ferroelectricity and magnetism appear independently. Commonly these materials present strong ferroelectricity, but the coupling to magnetism is rather weak. In *type-II multiferroics*, ferroelectricity is induced by the magnetism of the material, leading to the desired strong coupling but weak ferroelectricity.

Furthermore, ferroelectric materials can interact with light, leading namely to photovoltaic phenomena.<sup>3</sup> These materials are termed *photoferroics* and attract currently a large international research attention.

Ferroic orders		
		
<b>Ferromagnetism:</b> The ferromagnetism is the oldest known ferroic order, already used in compasses for navigation B.C. A material is ferromagnetic if it exhibits spontaneous magnetization such as a bar magnet. The magnetization can be driven by an external magnetic field. In the microscopic picture, the red arrows indicate the magnetic moment of the atoms giving rise to a macroscopic magnetism.	<b>Ferroelectricity:</b> Ferroelectric properties have been studied since the 17 <sup>th</sup> century. The term ferroelectric was introduced much later in 1912 by Erwin Schrödinger. A ferroelectric material is characterized by an electric polarization reversible by an electric field. On a microscopic level the polarization is related to a displacement of positively charged cations with respect to the center of gravity of negatively charged anions, in the scheme in blue and red, respectively.	<b>Ferroelasticity:</b> For a long time, ferroelasticity was considered to be directly related to ferromagnetism and ferroelectricity. Only in the 70s of the last century, ferroelasticity was recognized as an independent property. Ferroelasticity is the property of spontaneous deformation, even without external stress. A mechanical stress can modify the macroscopic deformation state, which is also represented on an atomic level.

## Objective & Approach of this work

The overall objective of this work is to obtain a better fundamental understanding of coupling in multiferroic materials. Within this general aim we address two specific questions:

1. How does light couple to ferroelectricity in *type-I* multiferroics? What is the role of the electronic band structure in this interaction?
2. How does magnetism couple to atomic displacements (ferroelectricity) in *type-II* multiferroics? How does the coupling vary for different types of magnetism?

### Choice of materials

In order to answer the above questions, and aiming at generality, the right choice of materials to be investigated is essential. We have chosen to investigate materials of the so-called perovskite structure of  $ABO_3$  oxides, which is the most occurring oxide family in nature.

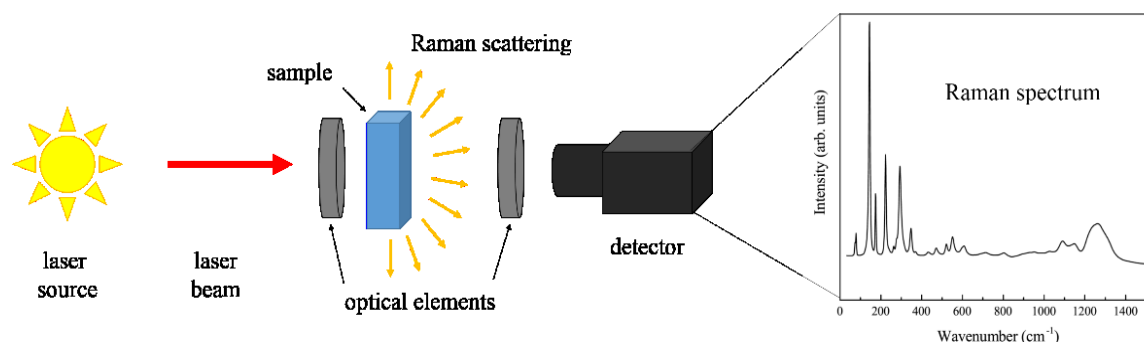
For the first question, we have chosen to investigate bismuth ferrite with the chemical formula  **$BiFeO_3$  (BFO)** where Bi stands for bismuth, Fe for iron and O for oxygen. BFO is the model *type-I* multiferroic and photoferroic material. In spite of nearly 6000 publications within the last 20 years on BFO (source: Web-of-Science), the electronic transitions and interaction with light of this model material remain unclear.

For the second question, we investigate the **rare-earth ferrites  $RFeO_3$**  (orthoferrites; *R* stands for a rare-earth element) which have in the past attracted interest for their various intriguing magnetic transitions as a function of temperature. Recently, some orthoferrites were identified as *type-II* multiferroics with magnetically induced ferroelectricity. The combination of multiple magnetic transitions with ferroelectricity makes it a model material system for the understanding of coupling mechanisms between magnetism and atomic displacements.

### Experimental approach

Ferroelectricity is linked to small displacements of atoms. Such displacements, and their coupling to other properties of the material are difficult to be detected. Based on this, we have chosen **Raman spectroscopy (RS)** as our technique of investigation. RS is indeed one of the best probes for detecting even subtle structural changes, including those introduced by magnetism. Raman spectroscopy is a laser-based technique and thus allows investigating the interaction of light with materials, adding further interest for our work.

A sketch of the RS setup is illustrated in Fig. 1. The sample is illuminated by a laser. The light scattered from the sample is measured and analysed. A typical recorded spectrum is given on the right in Fig. 1. The spectrum is characterized by a number of peaks. The peaks correspond to specific vibrations in-between atoms, for example. The position of the peak gives the frequency of the specific vibration. The Raman spectrum acts like a fingerprint of a material at given external conditions and allows the identification of a material. If the material is altered by changing the temperature, pressure, external fields etc., this is reflected in the Raman spectrum.



**Figure 1:**

Sketch of a Raman spectroscopy setup. The sample is illuminated by a laser. The scattered light is detected and analyzed. The result of a representative Raman spectrum is given at the right. Every peak represents the frequency of a specific vibration.

## Results

### 1. BiFeO<sub>3</sub> - Development of a “Raman methodology” & experimental investigation

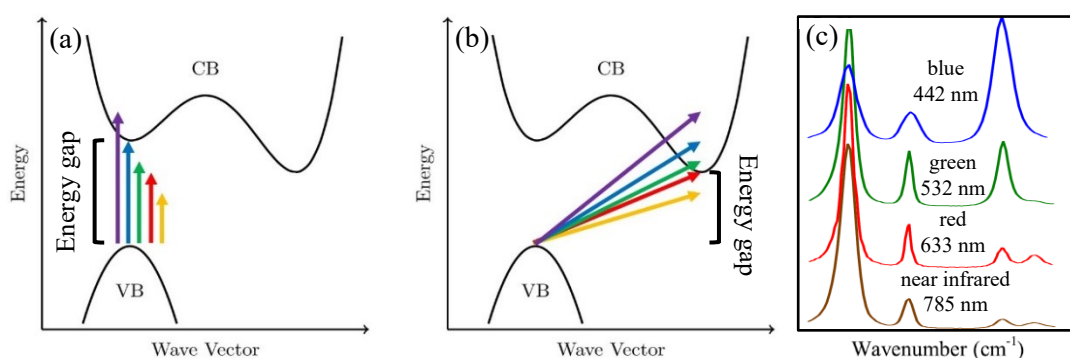
Despite the extensive study of BiFeO<sub>3</sub> as model multiferroic and photoferroic material, the understanding of the electronic transitions, i.e. how light of different colours interacts with the material, remains very limited from experimental and theoretical perspective.

The above-described Raman scattering is known as “conventional Raman scattering”. While this is the basis for our work, we had to develop a new methodology to go beyond the state of the art for understanding mechanisms at play. This has required to acquire a deep theoretical understanding of the Raman processes.

In a first step, our detailed analysis of the quantum-mechanic description has revealed that Raman spectroscopy is sensitive to the colour of the laser. Illuminating the material with lasers of different colour reveals important information about the interaction mechanisms of light with the material, precisely the information how the light of different colour is absorbed in the material.

Experimentally, our study has required intense measurement campaigns, as it required subsequent investigations of BiFeO<sub>3</sub> with in total twelve (!) different laser energies ranging from the blue to the near infrared. This approach and process is illustrated in Fig. 2 (a), where two energy levels are depicted with an energy gap in-between. To enable the interaction between light and the material, it is important to bridge this energy gap with the additional energy of the light, which corresponds to its colour. When the light energy was close to, or coinciding with the gap energy, the intensity of the Raman signal is strongly increased as illustrated in Fig. 2 (c). This effect is called resonant Raman scattering (RRS). Thus multi-wavelength RS enables to probe for electronic transitions. Careful investigation of all quantum mechanic terms that described the Raman scattering process reveals that the Raman spectrum can be divided in one part that only allows for vertical transitions, so-called direct transitions, and a second part that enables to probe indirect transitions depicted in Fig. 2 (b). From an application point of view, it is crucial to distinguish between direct and indirect transitions since the indirect transitions are far less efficient compared to direct transitions.

Using multi-wavelength RS, it was thus possible to identify the direct and indirect transitions and furthermore to follow the evolution of the transitions to high temperatures. These results are of great value for the understanding of the light-matter interaction of the model multiferroic BiFeO<sub>3</sub>, namely why and how the material undergoes a transition from an insulating to metallic state at high temperature. It provides a basis for further experimental and theoretical work.



**Figure 2:**

Scanning electronic transition with light of different color/energy. Only light that can bridge the energy gap can be absorbed and interact with the material.

(a) Scanning of vertical/direct electronic transitions and (b) indirect electronic transitions. The energy gap for direct and indirect transitions can be very different. In the illustration the indirect gap is smaller and can be bridged using red light. The larger direct (vertical) transition requires blue light.

(c) Raman spectra of BiFeO<sub>3</sub> under the illumination of lasers of different colours. The spectra show clear differences in intensity as a result of the change in interaction of different laser colours.

The approach in this thesis to use Raman spectroscopy to probe the colour-dependent interaction of light and matter is, to the best of my knowledge, unique in the research field of complex and functional oxides. It is expected to be useful for the investigation of other materials and scientific questions in this vast family of materials.

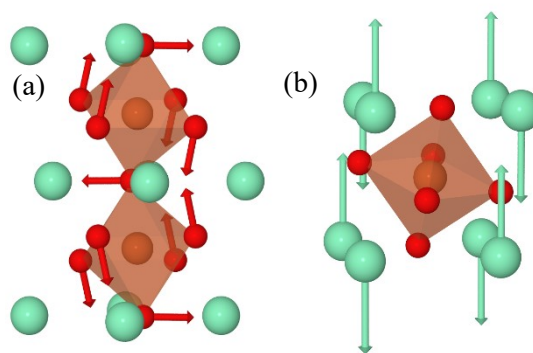
## 2. Raman spectroscopy on rare-earth ferrites $R\text{FeO}_3$

To lay the groundwork for investigation of magnetism-lattice interactions, structural properties of six rare-earth ferrites  $R\text{FeO}_3$  ( $R = \text{La}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}$ ) were analysed by Raman spectroscopy. Raman scattering gives access to interatomic vibrations which are a direct measure of the structure. The comparison with first-principle calculations enables the assignment of the measured peaks of the spectra to the distinct atomic vibrations (two of these vibrations are illustrated in Fig. 3). The knowledge of about the atomic vibrations gives a detailed picture of the structure of  $R\text{FeO}_3$ . To back-up the experimental results, a theoretical model based on Landau theory is developed, which confirms the experimental findings. Since all the atomic vibrations for the measured peaks in the Raman spectra are known, it is possible to directly relate any change in the Raman spectrum due to external influence or for instance due to changes of the magnetism to the structure.

### Interactions between magnetism and crystal lattice in samarium ferrite $\text{SmFeO}_3$

The precise knowledge about the lattice vibrations is used to investigate the impact of magnetic transitions on crystal lattice of samarium ferrite  $\text{SmFeO}_3$  as a potential *type-II* multiferroic. Out of several interesting magnetic changes in  $\text{SmFeO}_3$ , here, I would like to address the contribution of samarium to the magnetism below room temperature (at higher temperatures only iron contributes to the magnetism). In terms of magnetically induced ferroelectricity, this transition is very promising, since it was found in other  $R\text{FeO}_3$  that in particular this contribution can lead to multiferroicity.<sup>5,6</sup> In comparison to other rare-earth ferrites, it is unclear how the samarium magnetism contributes. Commonly, the contribution is measured by neutron scattering. However, samarium absorbs neutrons so strongly that neutron scattering measurements are not possible in  $\text{SmFeO}_3$ . Thus, the impact on the crystal lattice due the samarium magnetism remained unknown.

To investigate the impact of the magnetism on the lattice in this study, the temperature is tuned through magnetic transitions while the structural properties are probed by RS. With the contribution of samarium to the magnetism, clear changes of the Raman spectra are detected. This can be understood by a simple picture. The ions in the system feel the “new” magnetic contribution of the samarium. The magnetism can act attractive or repellent on other ions and, therefore, some vibrations become faster, some become slower and others are not affected at all. The exact knowledge about the response of all vibrations to the magnetism of samarium allows an investigation of the nature of the samarium contribution to the magnetism. This information was so far unknown, but is crucial to answer the question whether  $\text{SmFeO}_3$  becomes ferroelectric or not.



**Figure 3:** Different types of lattice vibrations of the rare-earth ferrite family. The rare-earth ions are indicated in pale green, the iron ions in center of the octahedra and the oxygens in red. The arrows point in the direction of movement of the respective ion. (a) illustrates an octahedra tilt vibration and (b) is a pure rare-earth displacements.

## Conclusion and Outlook

### 1- Electronic transitions in BiFeO<sub>3</sub>

The results on the light interaction with BiFeO<sub>3</sub> offer help to clarify the open question how light of different colours couples to BiFeO<sub>3</sub>. More generally, we expected that the developed approach of multi-wavelength Raman spectroscopy is applicable for a wide range of materials to measure optical properties when conventional techniques reach their limits. The general trend to more complex materials for solar cells such as kesterites or metal-organic Perovskites requires indeed such innovative characterisation techniques.

### 2- Rare-earth ferrites

The work on rare-earth ferrites provides the solid basis that is necessary to understand coupling properties in this family. Beyond rare-earth ferrites, the developed Landau theory model is applicable for all series of perovskite compounds in which only the different sizes of the A-cation trigger the degree of octahedra tilting.

Our work reveals that SmFeO<sub>3</sub> offers a large “playground” with a wide range of magnetism-lattice coupling possibilities. The results have already stimulated further research to investigate the open question about multiferroicity in SmFeO<sub>3</sub> in collaboration for thin film growth of SmFeO<sub>3</sub> with researchers from the ETH Zürich and for theoretical calculations with researches from the University of Liège and Luxembourg Institute of Science and Technology.

### General impact of the work

The above-presented work has been to date valorised by 3 papers as a first author in the international journal Phys. Rev. B. In addition to this, I have contributed to 3 additional co-authored papers. Finally, 2 additional first author publications are in preparation. Currently, I am invited for a talk at an international conference.

Since this work targeted new pathways to solve open questions in multiferroics-research, the interaction with other researchers was a cornerstone for the success of the thesis. We consider that this thesis has helped to tighten existing and to establish new collaborations with internationally renowned researchers e.g. from the Universities of Cambridge (UK) (Prof. Carpenter), Louvain-la-Neuve (BE) (Prof. Gonze), Paris Diderot (F) (Prof. Cazayous), Paris Centrale (F) (Dr. Dkhil), Massachusetts Institute of Technology/ETH Zürich (Prof. Rupp). By this, the present work has a positive impact on the international visibility of the University of Luxembourg, and Luxembourg as a rising research location.

Being based at LIST and registered at the University of Luxembourg under the guidance of Prof. Kreisel, professor at the University of Luxembourg and head of the MRT Department at LIST, I have naturally interacted with researchers from both institutions. This lead to fruitful exchange with other research groups of the University to Luxembourg, in particular with the groups of Prof. Wirtz and Prof. Siebentritt. This constant exchange contributed to interconnect the research within Luxembourg.

## References

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