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Second Harmonic Generation on 2D ferroelectrics

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Abstract

Recent years have seen growing interest in the study of two-dimensional (2D) ferroelectrics due to their potential applications in electronic devices. The stable layered structures and reduced surface energy of 2D materials offer a path to explore low-dimensional ferroelectricity and make ultra-high-density devices possible. In complementary metal-oxide-semiconductor (CMOS) technology, 2D ferroelectrics can be used as capacitors, transistors, and memory devices, among others.

In our work, Second harmonic generation (SHG), a non-linear optical process, was used to study the 2D ferroelectrics. SHG has been widely used as a tool to study the ferroelectric materials such as their polarization and domain structure. SHG can be used for the detection of ferroelectric domains and for characterizing ferroelectric devices, providing crucial information for the development and optimization of 2D ferroelectric-based electronics. The study of 2D ferroelectrics through SHG has two main objectives: first, to investigate their intrinsic nonlinear optical properties and second to utilize nonlinear optical techniques to examine the symmetry, structure, and electronic properties of 2D ferroelectrics, particularly near phase transitions. The use of SHG provides a powerful tool for exploring these properties. SHG is also used to study the phase transition of 2D chalcogenides such as pure and doped Germanium Telluride (GeTe).

In conclusion, 2D ferroelectrics and their use in CMOS technology, as well as the application of SHG, are significant research topics in the field of electronics and materials science. These materials and techniques have the potential to revolutionize electronics and lead to the development of novel, low-power, high-performance devices.

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Introduction

In this thesis we will review the experimental results of my doctoral research that have been obtained mainly by applying two advanced optical spectroscopic techniques: Second harmonic generation (SHG) and Terahertz (THz) spectroscopy. The thesis is divided in two parts, part 'A' deals with the SHG on 2D ferroelectrics and part 'B' is devoted towards study of diatoms using THz spectroscopy.

Second harmonic generation (SHG) is a nonlinear optical technique, possible only after the invention of the lasers. It is noninvasive, nondestructive, and non-contacting and can probe the whole volume of thin film structures, including buried heterostructures, provided that the medium is transparent at optical frequencies. In two-dimensional (2D) ferroelectrics, SHG can be used to probe the structural and electronic properties of these materials. This can be done by measuring the intensity of the second harmonic light as a function of the crystal orientation, temperature, and applied electric field. The temperature dependent measurement usually provide the information about parameter and type of phase transition. The SHG signal is sensitive to the orientation of the ferroelectric domains and the strength of the ferroelectric polarization, making it a useful tool for characterizing these materials. Additionally, SHG can be used to study the properties of 2D ferroelectric interfaces and heterostructures, as well as to probe the dynamics of ferroelectric switching.

On the other hand, Terahertz time-domain spectroscopy (THz-TDS) is a powerful technique for the study of the low frequency excitations in materials, including large-scale vibrations in biological matter. In this thesis we applied this technique to the investigation in-vivo of diatoms. Diatoms are a diverse group of microalgae that are widely distributed in aquatic environments, and are characterized by their unique siliceous cell walls. THz-TDS can be used to probe the absorption and transmission of terahertz radiation by diatoms. The technique is non-destructive, and can be used to study both living and fossil diatoms. THz-TDS measurements can be carried out on whole diatom cells or on isolated silica frustules, and the results can be used to identify different diatom species and to study the effects of environmental factors on diatom physiology and ecology. Moreover, THz-TDS can also be used to study the optical properties of diatom-based materials, such as biogenic silica, which has potential applications in a wide range of fields, including optics, electronics, and biomedical engineering.

In chapter 1, we generally introduce the concept of ferroic materials, ferroelectricity, and the types of ferroelectric materials. We also introduce the theory of ferroelectricity by introducing the Landau theory. We also emphasize on the Rashba effect and FerroElectric Rashba SemiConductors (FERSC). By introducing the structure of our materials such as Hafnium

Zirconium Oxide (HZO) and Germanium Telluride (GeTe). At the end, we introduced the literature on NLO used to study HZO and GeTe.

In chapter 2, First we focused on the theory of NLO and related concepts and then we introduced the concept of SHG. We present the deposition techniques such as Pulsed Laser Deposition (PLD) and Molecular Beam Epitaxy (MBE). A brief introduction of electrical characterization methods such as PUND and DLCC have been presented. At the end we introduced the basic idea of SHG symmetry analysis application on point group mm2 and 3m.

In chapter 3, we discuss about the fabrication of thin film by PLD and present a brief explanation on characterization by XRD and ferroelectric measurements. Then we introduce the SHG results on HZO thin film. We explain the effect of HZO thickness on different polarization combinations. Furthermore, we introduce the concept of operando electrical measurements on HZO thin film and provide some important results.

In Chapter 4, fabrication of pure and doped GeTe thin film by MBE is explained briefly and for characterizing the film we use XRD and linear spectroscopy. We also explain the basic SHG measurements such as SHG signal intensity vs pump power, SHG spectra, SHG vs fixed Incident wavelength and incident angle vs SHG intensity. Then we move onto the comparison part where we explain the basic difference among the SHG response of silicon, pure GeTe and doped GeTe during the temperature scans. Finally we measure the SHG images of both the samples and concluded that the ferroelectric domains have a nanometric size.

In chapter 5, generation, and detection of Terahertz (THz) by air plasma is explained briefly. We introduce some important detection methos such as Electro-Optic Sampling (EOS). Then we provide with a short introduction on Terahertz Time Domain Spectroscopy (THz-TDS) with experimental set-up. Teravision: a LabVIEW software is also explained in different functionalities. We also provide the brief overview of diatoms and we explain why they are important for aquatic environment. Finally, we introduced the sample preparation methodology and important results. We have demonstrated the ability of THz-TDS in sensing the diatoms in aqueous model systems.

PART A

Chapter 1 Theoretical Background

1.1 Ferroic materials

Ferromagnetic, ferroelectric or ferroelastic materials comes under the category of ferroic materials and are defined by an order parameter (η). Ferromagnetic materials show an ordering of magnetic moments (spins) below a certain temperature, while ferroelectricity and ferroelasticity are induced by a distortion of the atomic structure or ions, leading to a net electric dipole moment (ferroelectricity) or a spontaneous strain (ferroelasticity). To qualify as ferroic, the order must be switchable by the application of a conjugate field (i.e., magnetic field, electric field, or stress). In case of a ferromagnetic material, we can switch this ordering by applying an external magnetic field, similarly in ferroelectrics and ferroelastics the atomic displacement can be reoriented by either applying an external electric field or stress. Because of the switching property of ferroic orders, these materials have enormous application in today's technology, for example, ferromagnets are used for digital data storage and are used in hard drives and magnetic tape.

Materials that exhibit more than one primary ferroic order in the same phase have been defined as multiferroics in 1994 by Hans Schmidt [1]. Materials having more than one order can lead to new interactions like the magnetoelectric effect, i.e., changing the Magnetization M by an external electric field E or vice versa, altering the polarization P by an external magnetic field H(see arrows in Fig. 1.1b).



Figure 1.1. Primary types of ferroic orders and their coupling in multiferroics. a) Ferroic orders and their transformation properties under parity operations [2]. b) Ferroic orders and coupling, ordering include polarization (P), magnetization (M) and spontaneous strain.

The ferroic state of a material evolves during ferroic phase transition, when it goes from a highsymmetry to a low-symmetry phase upon cooling below a critical temperature T_c .

We can define multiferroics in two main types depending upon how simultaneous magnetic and ferroelectric orders emerged. These are type-I or type-II multiferroics [3].

- In type-I multiferroics, the electric polarization and the magnetic order emerge in two separate phase transitions.
- In type-II multiferroics, the ferroelectric polarization and magnetic order emerge jointly. These are those materials in which the magnetic ordering breaks the inversion symmetry and directly causes the ferroelectricity. Sometimes we also call it spin driven multiferroics.

An example of type-I multiferroics is BiFeO₃ (T_c =1100 K), with the ferroelectricity driven by the active lone pair of the Bi³⁺ ion and the magnetic ordering caused by the super-exchange mechanism [4]. TbMnO₃ (T_c = 28 K), is one of the famous examples of type-II multiferroic in which a non-centrosymmetric magnetic spiral breaks the inversion symmetry and causes the ferroelectric polarization [5].

1.2 Ferroelectricity

The word 'ferroelectric' (FE) in some sense is misleading as there is no presence of iron in ferroelectric materials. The historical reason for this name lies in the similar character between ferroelectricity and ferromagnetism, which was evident since the discovery of this kind of behavior (1920) in the so-called Rochelle salt [6], whose piezoelectric properties were known since the beginning of the Nineteenth century and so the "analogous" to the magnetic hysteresis in the case of iron [7], gave the name to ferroelectric polarization exists even in absence of an external applied electric field. In analogous with ferromagnets, this polarization is called "spontaneous." Electric Polarization in a finite system can be defined as the dipole moment per unit volume for a given charge distribution.



Figure 1.2. a) Hysteresis of a non-ideal ferroelectric. b) The lattice structure of ferroelectric and paraelectric PbTiO₃ [8]. c) Free energy as a function of polarization.

In addition to this, the spontaneous polarization must be switchable by an external electric field, as happens for the magnetization under external magnetic field in case of ferromagnets. Both ferroelectric and ferromagnetic materials show a hysteresis or hysteretic behavior. Fig.1.2a

shows a typical FE hysteresis loop of HZO thin films measured in bottom-top configuration (Bottom-Top approach is explained in Chpt. 2).

This FE polarization can be switched by an applied electric field (E). The relationship between the polarization (P) and the external electrical field of the material is often represented by a hysteresis curve (Fig. 1.2a), which shows the coercive field (E_c) and spontaneous polarization (P_s) . The spontaneous polarization in ferroelectrics has two or more orientational states and may be switched from one state to the other by an external electric field, or in some cases, by a mechanical stress. Ferroelectric materials are characterized by the presence of spontaneously ordered domains within the material, which can be switched between different configurations by the application of an external electric field. The coercive field (E_c) is a measure of the strength of an external electric field required to switch the polarization of a ferroelectric material between its two stable states. The coercive field is an important property of ferroelectric materials, as it determines the minimum electric field that must be applied in order to switch the material between its two stable states of polarization. When the coercive field is reached, the polarization is permanently reversed through a combination of domain nucleation and domain growth by domain-wall movement. Ferroelectricity arises from a ferroic phase transition, which can be either first- or second order. The first-order transitions are discontinuous and involve the formation of the stable phase through nucleation and growth while in second-order transitions, the stable phase evolves smoothly.

The Curie temperature (T_c) is the temperature at which certain materials undergo a phase transition from a ferroelectric to a paraelectric state. In ferroelectric materials, the electric polarization can be reversed by the application of an external electric field. Above the T_c , the material becomes paraelectric and loses its spontaneous electric polarization. In order to explain how the T_c depends on the crystal structure, let's take the example of lead titanate (PbTiO₃). The crystal structure of PbTiO₃ is shown in Fig.1.2b. PbTiO₃ is a tetragonal below its T_c , which is typically in the range of 490-493 °C [9]. Above T_c , it becomes cubic and paraelectric. The polarization of PbTiO₃ is shown by the displacement of the Ti atom in the O octahedron [10]. Above T_c , this displacement disappears and there is no spontaneous polarization.

In Fig.1.2c, Gibbs free energy (Φ) is plotted as a function of spontaneous polarization. One stable state exists in the prototype phase, (dark blue curve) when ($T > T_c$). and two energy and displacement equivalent states are present in the ferroic phase (orange curve). In external field below T_c favors one ferroic state over the other (dashed sky-blue curve) which means in the presence of an electrical field that is coupled to the order parameter, the two domain states of the system become energetically nonequivalent. The thermodynamic approach can be used to calculate the energies of these states and understand the behavior of the system under these conditions (explained in section 1.2.1) In order to do this, it is necessary to specify the thermodynamic potential that will be used for the calculations. This potential is a function that describes the energy of the system as a function of various variables, such as the temperature

and the order parameter. By using this potential, one can understand how the energy of the system depends on the state of the system and the external parameters that are being varied.

1.2.1 Proper and improper ferroelectricity

Ferroelectricity is a property of certain materials that exhibit a spontaneous electric dipole moment in the absence of an externally applied electric field. In general, we categorize FE in two types, proper and improper FE, depending on the driving force which causes the polarization.

In proper **ferroelectrics**, the spontaneous polarization that develops during the ferroic phase transition is represented by the primary order parameter. One example of a proper ferroelectric material is barium titanate (BaTiO₃) [11].

Ferroelectricity in barium titanate arises due to the asymmetrical arrangement of the titanium and oxygen ions in the crystal structure. When an external electric field is applied, the direction of the polarization can be reversed, leading to a change in the electrical properties of the material. Second such example is lead titanate, $PbTiO_3$ (PTO) [8] which is shown in Fig.1.2b. The loss of inversion operation during the phase transition results in the formation of two possible ferroic states with distinct orientations. In this case, the shift of the metallic cations directly determines the direction of polarization.

The ferroic phase transition of a proper ferroelectric can be described using Landau theory [11]. In this approach, a second-order phase transition is considered and the interaction between the polarization (*P*) and its conjugate electric field (*E*) is included. Here we use a thermodynamic potential Φ , called the Gibbs energy [12] which is a function of polarization P_i and stress tensor σ_{ij} as independent variables. Its differential can be written as:

$$d\Phi = E_i \, dP_i - \varepsilon_{ij} d \, \sigma_{ij} \tag{1.1}$$

where E_i stands for the electric field and ε_{ij} for the strain tensor. The differential of a potential, by definition, is a function of the differentials of its independent variables and can be written as:

$$\left(\frac{d\Phi}{dP_i}\right)_{\sigma} = E_i \tag{1.2}$$

$$\left(\frac{d\Phi}{d\sigma_{ij}}\right)_P = \varepsilon_{ij} \tag{1.3}$$

The expansion of Φ with respect to the order parameter *P*, in general, can take the form:

$$\Phi = \Phi_0 + \frac{1}{2}\alpha p^2 + \frac{1}{4}\beta p^4 - PE$$
(1.4)

Where Φ_0 is the *P* independent part of the potential. α and β are expansion coefficients and in principle depends on the temperature.

To determine the stable ground states of the homogeneous system, we omit the last term in eq. 1.4 and determine $\frac{\partial \Phi}{\partial P} = 0$ and $\frac{\partial^2 \Phi}{\partial^2 P} > 0$.

Above the phase transition temperature ($T > T_c$), only one stable state exists, corresponding to a minimum in the dark blue curve shown in Fig. 1.2c. This stable state has a polarization of zero (P = 0). In the ferroelectric phase ($T > T_c$), there are two degenerate solutions, as shown by the minima in the orange curve. These solutions correspond to different stable states of the system. Landau theory can be used to describe the phase transition and determine the stable states in the ferroelectric phase.

In the ferroelectric phase $(T < T_c)$, we find the two degenerate solutions.

$$\pm P_s = \pm \sqrt{\alpha_0 (T - T_c)} / \beta \tag{1.5}$$

which leads to the potential distribution in the ferroelectric phase, described by the blue curve in Fig. 1.2c. This curve has two minima, corresponding to the two degenerate stable states of the system. The spontaneous polarization (P_s) in these states shows a square root dependence on temperature, which is characteristic of proper ferroelectrics. An external electric field can be applied to the system, lifting the degeneracy of the two ground states. This is shown by the dashed sky-blue line in Fig. 1.2c, which shows the potential distribution with the applied field. The electric field favors one of the stable states, leading to a switch in the polarization of the ferroelectric. This is the basis for the switching behavior of ferroelectrics under external fields.

Improper ferroelectrics are a class of materials that exhibit ferroelectric behavior, but in a manner that is distinct from that of proper ferroelectrics. Unlike proper ferroelectrics, which have a spontaneous electric polarization that is reversible by the application of an external electric field, improper ferroelectrics exhibit ferroelectric behavior due to the coupling of two or more order parameters. Ferroelectric phase transitions for which the order parameter is not the polarization, but a quantity having another physical meaning and possessing other transformation properties are called improper ferroelectrics. Improper ferroelectrics differ significantly in many of their properties (dielectric anomalies, characteristics of the phonon spectrum near the transition point, the nature of the twinning, etc.) from the ordinary ferroelectrics [13].

The electric polarization in improper ferroelectrics can be described by the following equation:

$$P = \alpha E + \beta D \tag{1.6}$$

where *P* is the electric polarization, *E* is the electric field, *D* is the lattice distortion, and α and β are constants.

1.2.2 Microscopic origin of ferroelectricity

Ferroelectricity can be driven by various microscopic mechanisms. In the case of proper ferroelectrics, one of the sources of ferroelectricity is the distortion in the cubic perovskite structure ABO₃. Within this structure, two different displacive mechanisms can lead to the breaking of inversion symmetry and the formation of permanent dipoles. These mechanisms are responsible for the development of ferroelectricity in proper ferroelectrics.

The two mechanisms are:

- Covalent bonding between the d₀ orbitals of the B cation (such as Ti⁴⁺, Zr ⁴⁺, or Nb⁵⁺) and the 2p orbitals of the surrounding oxygen atoms can cause the B cation to be displaced from its central position, as in the case of BaTiO₃ or KNbO₃.
- Long-range ordering of the electron lone pairs of A cations with a 6s² configuration (such as Bi²⁺ or Pb²⁺) can create polarity, as in the case of BiFeO₃.

Thus, these two mechanisms can facilitate ferroelectricity in proper ferroelectrics with the cubic perovskite structure. Displacive mechanisms usually results in the large values of polarization. It should be noted that perovskite structure doesn't qualify a material to be FE, in fact HZO and GeTe both are ferroelectric but not perovskite.

Ferroelectricity in improper ferroelectrics can be driven by various microscopic mechanisms, including geometric, charge-order, and magnetic mechanisms. In the case of geometric ferroelectrics, ferroelectricity arises from buckling or rotation of atomic polyhedra, which causes non-polar distortions of the lattice that break inversion symmetry. These distortions are often accompanied by an increase in the volume of the unit cell. Below a certain transition temperature, a spontaneous polarization begins to develop due to a nonlinear coupling between the polarization and the lattice distortion. Examples of geometric ferroelectrics include hexagonal manganites $RMnO_3$ [14] and the Ruddlesden-Popper compound (Ca, Sr)₃ Ti₂O₇ [15] which belongs to a class of materials known as hybrid improper ferroelectrics, in which the combination of two non-polar lattice distortions leads to ferroelectricity.

Charge-order driven ferroelectricity can be realized by combining symmetry breaking of charge ordering with symmetry breaking of layered cation ordering to generate polar variants. There are a few examples of charge ordering and one of them is LaVO₃/SrVO₃, in which layered charge ordering of V³⁺ and V⁴⁺ combines with the layered ordering of La and Sr to break up–down symmetry normal to the layers, generating 2 polar variants [16]. Ferroelectricity driven by charge ordering is characterized by a switching polarization that results primarily from the transfer of electrons between ions when the charge ordering pattern is changed. This type of ferroelectricity is distinct from geometric ferroelectricity, in which the switching polarization arises from a displacement of the atoms within the crystal structure.

The magnetic mechanism of origin of ferroelectricity can be explained by Dzyaloshinski-Moriya interaction (DMI) [17]. The (DMI) is a type of spin-orbit coupling that arises in magnetic

systems with broken inversion symmetry, which is a prerequisite for the emergence of polarity in magnetically induced ferroelectricity. RMnO₃, RMn₂O₅ (R: rare earths), CuFeO₂, MnWO₄ etc. are some examples of magnetic ferroelectric.

1.3 Ferroelectricity in 2D

Ferroelectric films were previously thought to be stable and retain their polarization only when they were above a critical thickness of around tens of nanometers due to combined behavior of electric dipoles [18] and depolarization effects caused by uncompensated interfacial charges [19]. However, with advancements in perovskite oxide thin film fabrication, it is now believed that ferroelectricity can be retained at reduced dimensions, such as 1.2 nm for PbTiO₃ [20], 2.4 nm for BaTiO₃ [21], and 3 nm for BiFeO₃ [22]. In some cases, ferroelectricity can even be enhanced at low dimensions, as seen in strain-free SrTiO₃ films [23]. Recently, it is observed that the critical thickness for BFO and BTO to be larger than 4-unit cells using SHG [24]. However, maintaining the functional properties of ferroelectric oxides at reduced dimensions often requires careful selection of oxide substrates with a small lattice mismatch to the ferroelectrics, limiting their potential use in nanoelectronics. Additionally, defects such as oxygen vacancies, which are often introduced during high-temperature thin film growth and nanostructure fabrication, can degrade the intrinsic ferroelectric properties [25]. Recently, binary oxides such as HO₂ and ZrO₂ [26] doped with elements like Si, Al, Y, Ga, La, and Sr have also received attention for their robust ferroelectricity/antiferroelectricity [27].

Ferroelectricity has been observed in thin films of Hf_{0.5}Zr_{0.5}O₂ down to a thickness of approximately 2.5 nm [28]. This type of ferroelectricity is significant because it has the potential to be integrated into van der Waals heterostructures and because 2D materials, such as those made of graphene, do not have dangling bonds, which can lead to benefits such as high carrier mobility [29], tunable band gaps [30], and structural flexibility [31]. The discovery of 2D ferroelectricity in PVDF organic polymers [32] dating back to two decades ago. However, it was not until the discovery of graphene [33] in 2004 that the search for 2D ferroelectrics really took off.

1.4 Fluorite Hf_{0.5}Zr_{0.5}O₂

 $Hf_{0.5}Zr_{0.5}O_2$ based materials are binary oxides with a fluorite like structure shown in Fig.1.3 and have been used in semiconductor industry for many years as a high dielectric material. Hafnium oxide (HfO₂) can be found in three different crystal systems: monoclinic, tetragonal, and cubic as shown in Fig.1.4. Monoclinic is the only one, which is stable at room temperature. The transformation from monoclinic to tetragonal occurs at 1700 °C and from tetragonal to cubic at 2700 °C [34].



Figure 1.3. The basic cubic fluorite structure is depicted. The cations (yellow) occupy the positions of a face centered cube, while the anions (in grey) occupy the interstitial sites.

In bulk, the stable form of HfO_2 (and ZrO_2) based compounds crystalize in a monoclinic phase (P2₁/c, m-phase) at room temperature. Other common phases exist at high-pressure and high pressure namely, tetragonal (P4₂/nmc, t-phase) and cubic (Fm-3m, c-phase) phases.



Figure 1.4. Crystal structures observed in common HfO₂ films [35].

Ferroelectricity in $Hf_{0.5}Zr_{0.5}O_2$ based materials was found a decade ago by doping HfO_2 with Si [36]. This discovery was unexpected since bulk HfO_2 and ZrO_2 at room temperature and ambient pressure adopts a non-polar monoclinic phase and the predicted phases at different temperature and pressure were found to be non-polar. Ferroelectricity in these types of materials has been a milestone for the development of devices based on ferroelectric oxides.

(Hf, Zr) O_2 can be stabilized in different structural phases, both polar and non-polar as shown in Fig.1.5. Ferroelectricity has been ascribed to the orthorhombic polar phase $Pca2_1$.



Figure 1.5. Sketch showing the (a) paraelectric monoclinic (b) Ferroelectric orthorhombic (c) antiferroelectric tetragonal phases. Adapted from [37].

 HfO_2 is a material that can exhibit various structural phases, such as monoclinic, tetragonal, cubic paraelectric, and polar orthorhombic (*Pca2*₁) (Fig.1.5). The *Pca2*₁ phase is often assumed to be present due to the ferroelectric polarization of the films, although it can be difficult to identify by x-ray diffraction due to degenerated reflections from other polymorphs. The stabilization of the ferroelectric phase rather than the non-polar polymorphs can be influenced by various factors, including doping, deposition conditions, surface energy, and grain size. HfO_2 can be doped with elements such as Zr, Si, Y, Sr, or La to tune its properties, such as polarization and fatigue [38]. Epitaxial films of HfO_2 grown on perovskites have been less studied than polycrystalline samples.

The recent discovery of ferroelectricity in extremely thin layers of HfO₂-based materials represents a significant advancement in the field. It suggests the existence of a new type of ferroelectricity that only emerges at the nanoscale and becomes more robust at smaller sizes. Furthermore, their compatibility with silicon, straightforward chemistry, and low toxicity makes them highly desirable compared to other commonly used ferroelectric layers. Hafnia-based thin films are a popular choice for integrating ferroelectricity at the nanoscale into future memory and logic devices, as their ferroelectric polarization becomes more stable when reduced in size. However, the type of ferroelectricity HZO is not yet fully understood.

1.5 Introduction to Germanium Telluride (GeTe)

1.5.1 Rashba effect

Before explaining the GeTe, we must explain what is Rashba effect and why it is important in spintronics. The Rashba effect, also called Bychkov-Rashba effect, is a momentum-dependent splitting of spin bands in bulk crystals and low-dimensional condensed matter systems (such as heterostructures and surface states). The splitting is a combined effect of spin—orbit interaction and asymmetry of the crystal potential, in particular in the direction perpendicular to the two-dimensional plane (as applied to surfaces and heterostructures). Emmanuel Rashba discovered this effect [39], hence the Rashba effect.

The Rashba effect is most easily seen in the simple model Hamiltonian known as the Rashba Hamiltonian which can be expressed as:

$$\widehat{H} = \alpha_R \, n. \, (\widehat{\sigma} \times p) \tag{1.7}$$

where α_R is the Rashba coupling, p is momentum, $\hat{\sigma}$ is Pauli spin vector, where n is the unit vector along the z-axis.

In crystals lacking an inversion symmetry, electronic energy bands are split by spin-orbit (SO) coupling. The Rashba SO coupling, a SO coupling linear in momentum p, was originally proposed for non-centrosymmetric wurtzite semiconductors [40]. Bychkov and Rashba applied it to the SO coupling in a two-dimensional electron gas (2DEG) with structural inversion asymmetry such as semiconductor heterostructures [41].

The origin of Rashba effect can be described by the presence of spin-polarized surface or interface states [42]. Indeed, a structural inversion symmetry breaking (i.e., a structural inversion asymmetry (SIA)) causes the Rashba effect to occur: this effect breaks the spin degeneracy of the energy bands and it causes the spin polarization being locked to the momentum in each branch of the dispersion relation [43]. In the case of a bidimensional Rashba gas, where this band splitting occurs, [44] this effect is called Rashba–Edelstein effect [42].

If we now add the Rashba Hamiltonian and the dispersion relation, we will get a global Hamiltonian as:

$$H = \frac{\hbar^2 k^2}{2m^*} + \alpha_R \, n. \, (\hat{\sigma} \times p) \tag{1.8}$$

with eigenvalues:

$$E_{k,\downarrow\uparrow} = \frac{\hbar^2 k^2}{2m^*} \pm \alpha_R |k|$$
(1.9)



Figure 1.6. Spin-momentum locked surface states. (a)Energy dispersion and (b) Fermi contours resulting from Rashba effect [42].

Thus, the Rashba Hamiltonian produces an energy term linear in k which splits \uparrow and \downarrow bands, being \uparrow and \downarrow the spin polarizations perpendicular to k. A sketch for the interpretation of

splitting can be shown in the Fig. 1.6a. In Fig. 1.6b, the Fermi surface of the Rashba gas can be seen.

1.6 Ferroelectric Rashba SemiConductors (FERSC)

The study of modern materials science often involves the combination of multiple functionalities into a single compound in order to discover new properties, effects, and mechanisms. Semiconductor spintronics is no exception to this. Researchers have found that when a significant spin-orbit coupling is paired with ferroelectricity in a material like GeTe, new multifunctional materials called FerroElectric Rashba Semi-Conductors (FERSC) are created. These materials have unique spin textures that can be controlled and switched by an electric field due to a large Rashba spin-splitting. This specific spin-electric coupling is particularly effective in small-gap insulators such as chalcogenides and can bring new capabilities to the field of electrically controlled semiconductor spintronics.

FERSC, can be consider as an integration of different fields after the remarkable results on GeTe. Some of them are:

- *Ferroelectricity* (granting the switchability of ferroelectric polarization by an electric field, traditionally exploited in non-volatile memory elements),
- *Rashba effects* (bringing in spin-degrees of freedom and usually exploited in logic semiconducting-based architectures),
- Semiconductor Spintronics (granting the integration with existing semiconductor-based technology) [45].

GeTe has been predicted, [46] to show a giant Rashba spin-splitting. GeTe itself, however, has several pitfalls from the experimental point of view as it shows a high tendency to form Ge vacancies [47]. This in turn leads to a p-degenerate semiconducting behavior, thus it is highly unlikely to switch the ferroelectric state in such a "conducting" material, therefore hindering the control of spin-texture via an electric field.

However, ferroelectric switching of GeTe has only been demonstrated at the nanoscale using Piezoresponse Force Microscopy (PFM) of thin films [48], using transmission electron microscopy with nanometre-scale crystals [49] and nanowires [50], and using X-ray spectroscopy [51]. The screening of the external electric field by the large density of free carriers prevents the penetration of external electric fields, thus preventing the polarization reversal and resulting in high dielectric loss [52]. Although there are some reports showing evidence of ferroelectric inversion even in polar metals [53,54], it should be noted that there are only a few reports on SHG studies on polar metals. One of the first material which is considered to be polar metal was LiOsO₃ which is simultaneously non-centrosymmetric and metallic.

1.7 Structure of GeTe

GeTe, with its unique combination of ferroelectric, Rashba, and semiconductor properties, has the potential to be used in spin-FET devices for non-volatile memory storage and logic operations. In these devices, the Rashba-induced spin precession of the injected current is controlled by the ferroelectric state of the GeTe material. By utilizing normal magnets as spin injectors and detectors, the spins within the ferromagnetic elements can be coupled through the current, and the resistance of the device can be controlled by the ferroelectric polarization of GeTe.

GeTe is a phase change material (PCM) that exhibits a reversible transition between an amorphous and crystalline state when subjected to electrical or optical field. This property makes it well-suited for use in rewritable optical data storage due to its fast-switching speed and large contrast in properties between the amorphous and crystalline states. At room temperature, GeTe has a distorted rhombohedral NaCl-type crystal structure, with space group R3m. In its amorphous state, GeTe has a covalently bonded, fourfold coordinated sp³ tetrahedron configuration, which is common among amorphous semiconductors. As shown in Fig.1.7, GeTe can exist in two different crystal structures: a rhombohedral structure and a cubic or rock salt structure. In the cubic structure, the Ge atom is located at the center of an octahedron formed by six Te atoms. In the rhombohedral structure, the Ge atom is positioned off-center within the octahedron, which leads to an asymmetry in the Ge-Te bonds. Specifically, there are three longer bonds (shown in green dotted lines) and three shorter bonds (shown in red lines) in the distorted octahedral structure of the rhombohedral GeTe, as depicted in Fig.1.7a.



Figure 1.7. GeTe Structure: a) rhombohedral structure; b) cubic structure [55].

1.8 Nonlinear optics and ferroelectrics

In photonics, nano-photonics, and bio-photonics technologies, nonlinear optical materials are essential. Thin films provide the added design advantages of minimal volume and strong

compatibility with the manufacturing of waveguide and integrated nonlinear photonics devices. It's intriguing to note that the majority of ferroelectric thin films have physical traits including high dielectric constant, high optical transparency, large nonlinear response. Nonlinear optical properties of a ferroelectric not only depend on the material itself but also on laser pulse duration and excitation wavelength. There are some reports on SHG being used to study HZO thin films [56]. Composition dependency of SHG, refractive index, extinction coefficient, and optical bandgap is described. They are found that with increasing ZrO_2 content, the refractive index generally rises, with all values falling between 1.98 and 2.14 between wavelengths of 880 nm and 400 nm. The indirect optical bandgap shows composition dependence, falling from 5.81 eV for HfO₂ to 5.17 eV for Hf_{0.4}Zr_{0.6}O₂. For compositions with x > 0.6, the bandgap rises and reaches 5.31 eV for Hf_{0.1}Zr_{0.9}O₂. The measurement of second harmonic signals for incident light at 880 nm. It has been reported that ferroelectric Y:HfO2-based hybrid nonlinear optical metasurfaces exhibit high SHG production. SHG is increased by three times at the incident wavelength compared to the ferroelectric Y:HfO2 to non-ferroelectric HfO₂-based devices [57].

Metal chalcogenides are promising materials for nonlinear optical (NLO) applications working in the infrared (IR) region of the electromagnetic spectrum. The synthesis of new materials in the chalcogenide class during the past 20 years has produced a number of novel compounds with exceptionally high NLO responses [58]. In particular, GeTe has been recently studied by SHG where they found thick film contains large domains visible in SHG images, and a thin film in which the domains' size is below the SHG resolution limit. They also used machine learning-assisted methods and proved that that both samples exhibit four domain variants of the same type [59]. In my thesis our approach is to study HZO thin films by SHG polarimetry. Also, we are going to use the same technique to study the phase transition in GeTe thin films.

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Chapter 2 Experimental methods

2.1 Introduction

The development of lasers was one of the most important technological advancements in the 20th century. Lasers find their applications in everyday life ranging from medical, such as surgery, industrial, cutting and welding, barcode scanners, reading disk media and laser pointers. Being monochromatic, coherent, and highly intense, lasers offer a suitable tool to study high field physics such as Non-Linear Optics (NLO). Such properties of lasers are achievable through the exploitation of a controlled population inversion and stimulated emission processes, allowing lasers to be the ideal tool for spectroscopic studies. NLO is the branch of physics in which the electric polarization density of the medium is studied as a nonlinear function of the electromagnetic field of light. Nonlinear interaction between light and matter leads to a wide spectrum of phenomena, such as optical frequency conversion, optical solitons, phase conjugation, and Raman scattering [1]. Before the advent of lasers, NLO was not possible due to the weak intensity of incoherent light sources. Charles Townes was the first to develop a successful self-sustaining stimulated emission source in 1954 using excited ammonia molecules in a resonant cavity [2]. In fact, one year later, the first NLO phenomenon was discovered. In this experiment [3], the first frequency doubled light was detected using a ruby laser and quartz as a nonlinear crystal. The fundamental light at 694.3 nm wavelength was partially converted into light with a wavelength of approximately 347.2 nm: Second Harmonic Generation (SHG) was born (Fig.2.1). It was surprising that the data point showing the SHG, was removed by the publisher as they thought it was an error in the image. The advancement of NLO and the use of different nonlinear crystals make a significant development in many areas of science and technology, creation of new laser sources, and the understanding of light-matter interaction. The scope of this field includes all phenomena in which the optical parameters of materials are changed with irradiation by light. Generally, this requires highly intense optical sources, which is the main reason why NLO grows always in parallel with laser technology.



Figure 2.1 SHG signal at 3784 Å indicated by an arrow. The wavelength scale is in the units of 100 Å [4]

In Fig.2.2, blue, light blue, and salmon pink represent types of higher-order nonlinear susceptibility, nonlinear processes corresponding to different NLO susceptibility and their applications, respectively. In principle, light-matter interaction can be described by classical means. In the first order, these interactions refer to models formulated by Fresnel, Huygens,

and Maxwell in the 19th century. The basis of these elementary laws lies grounded in the superposition principle. However, when the incident light intensity becomes high enough, i.e., a material's dielectric response becomes strong enough for the higher order terms to be nonnegligible, superposition breaks down producing a variety of wave mixing and multiphotonic effects. In order to visualize the nonlinear effects for scientific measurements, strong electric fields are necessary. Lasers are the only source of light that can produce electric fields as high as 10^{12} V/m and this field is enough to produce nonlinear effects in the medium. Bloembergen et al [5] estimated the scaling ratio of n-th order multiphoton processes as $(E_{linear}/E_{multiphoton})^n$. From his estimation, if a medium's linear dielectric response is on the order of unity, then the second order correction will be roughly 10^{-12} , the third order 10^{-24} , and so on.

Nonlinear optics				
	X ⁽²⁾	χ ⁽³⁾	$oldsymbol{\chi}^{(n)}$	Q U A
	 Second Harmonic Generation (SHG) Difference Frequency Generation (DFG) Pockels Effect OPA/OPO 	 Third Harmonic Generation (THG) Four Wave Mixing (FWM) Optical Kerr effect 	 High Harmonic Generation(HHG) 	N T U M O P T
	 OPO/OPA Electric optic modulator UV source THz generation 	 Ultrafast laser Optical modulator 	 Strong Field Physics Attoscience 	l C S

Figure 2.2. Different applications of Nonlinear Optics (NLO).

2.1.1 Linear optics

Light is an electromagnetic wave, which means there is an electric and magnetic oscillating field perpendicular to each other and the direction of propagation of the wave is perpendicular to both. Generally, we only considered the electric part of the optical wave in optics. When an electric field is applied to the material medium, it responds to the field linearly. In conventional optics many basic mathematical equations are linear. To apply those equations in order to understand phenomena such as refraction, reflection, dispersion, scattering and so on, we should consider an important physical quantity: the electric polarization induced in the medium. In the regime of conventional optics, the electric polarization vector **P** of a medium is simply assumed to be linearly proportional to the electric field strength **E** of an applied optical field, i.e.:

$$P = \epsilon_0 \chi E \tag{(2.1)}$$

where ε_0 is the free-space permittivity and χ is the susceptibility of a given medium.



Figure 2.3. Response of dielectric medium to the electric field. (a) without applied electric field (b) with electric field.

Fig.2.3b shows that the presence of an electric field displays positive and negative charges within individual atoms and molecules and thus they try to separate from one another resulting in a shifting of electronic clouds relative to their nuclei. At this moment when the separation of charge happens, the dielectric medium is polarized. We should note that, this is particularly called as electric polarization. Although, there are other ways to polarize the materials such as ionic polarization (sometimes referred to as atomic polarization) and orientational polarization. All non-conductive materials can become electronically polarized, which is why they are all dielectrics to some extent. In contrast, materials with ions or permanent dipoles are the only ones that can exhibit ionic or orientational modes of polarization. Space charge, or the accumulation of mobile charges at structural surfaces and interfaces, is another factor that can contribute to polarization. However, this only occurs in surfaces and heterostructures and is not a property of a single material.

2.1.2 Non-linear optics

Fig.2.4 shows the potential energy of a charge in the material as a function of position r. The sharp increase of the potential shows the repulsive forces that acts on the charge. The bottom of the curve represents the equilibrium position r_0 of the charge. When the incident light energy is low, the oscillation of each dipole can be viewed as harmonic in the linear domain. At high incident intensities, (e.g., laser light) the oscillations in the dipoles may not accurately follow the frequency of the incoming wave and the radiated wave can contain different frequency components. This gives the higher order (nonlinear terms) in the induced polarization.

When the intensity of the light source is sufficiently high as in the case of a laser, we get the higher order terms in the total polarization and the basic equation can be written as:

$$P = P_L + P_{NL} \tag{2.2}$$

where P_L is a linear function and P_{NL} is a nonlinear function of the applied field, respectively. The nonlinear polarization is a source for the generation of new waves. It can be expressed as a power series expansion in the applied field as:

$$P = \epsilon_0(\chi^{(1)}E + \chi^{(2)}E \cdot E + \chi^{(3)}E \cdot E \cdot E) + \cdots$$
(2.3)

where $\chi^{(1)}$ corresponds to the linear susceptibility tensor of the medium and it is responsible for all the linear phenomena in optics such as reflection, refraction, etc. and $\chi^{(n)}$ is the susceptibility tensors of *n*-th order (n = 2,3,...). It should be noted that the magnitude of the elements of the susceptibility tensor decreases with the increasing power of χ as ($\chi^{(1)} > \chi^{(2)} > \chi^{(3)} > ... > \chi^{(n)}$). It should be emphasized that the $\chi^{(2)}$ and $\chi^{(3)}$ are responsible for the nonlinear optical phenomena such as SHG, Third Harmonic Generation, Kerr effect, selffocusing, etc. It is important to mention here that $\chi^{(3)}$ is an effective third-order nonlinear susceptibility which we are going to use when we explain the generation of THz in Chpt.5.



Figure 2.4. Electron potential (red curve). In linear domain (green area), the charge oscillation can be approximate by a harmonic potential (black dashed line). For higher electric fields, the response becomes anharmonic, entering in nonlinear domain (light blue)

2.2 Second Harmonic Generation (SHG)

The main technique used throughout my Ph.D. work was Second Harmonic Generation (SHG). SHG is well developed optical technique to investigate the emergence of polar phases, which probes the material symmetry. It is background-free, non-invasive, and highly sensitive; it can be employed in different experimental fashions such as pump probe for dynamical measurements or SHG Microscopy for lateral spatial resolution, although in standard cases the resolution is restricted by diffraction to about 1 μ m or slightly less, depending on the wavelength. It is also possible to apply near field techniques to improve the resolution. SHG is a

non-linear process, in which two photons of frequency ω simultaneously interact the material under investigation and reemitted as a single photon when the electrons go back to the ground state. Here, we should emphasize that SHG is possible even without absorbing the photon. In this case, the excited state can be virtual in the sense that it doesn't exist, but the absorption and emission of the photon happens at the same time, so that the time in which the system stays in the virtual state is approximately zero. Photons will be only absorbed when the excited is real and, in this case, SHG has a resonance. It is clear that the one photon which is emitted must have double energy compared to the incident photons in order to fulfill energy conservation and thus it must have a frequency which is exactly twice the fundamental frequency ω . This process is sketched in Fig.2.5. Using the time dependent perturbation theory, each transition probability can be derived in the framework of quantum mechanics and spectral dependences of the SHG can be calculated. Keeping in mind that we only used SHG spectroscopy to maximize the signal yield, a detailed discussion about spectral features will not be discussed here.



Figure 2.5. Sketch of the energy levels and the transitions at play in the SHG process.

Two photons from an incident light pulse (e.g., 800 nm) are simultaneously absorbed and excite an electronic state. The excited state then decays via the coherent emission of a single photon of the doubled frequency, which in total leads to second harmonic photon 2ω .

Let us use a classical wave-picture, in which light-matter interaction is described by the oscillating electric field of the light wave.

$$E(\omega) = Eo \ e^{-i\omega t} + c.c, \tag{2.4}$$

where $E(\omega)$ represents the incoming electric field that displaces the electrons and thus induces an oscillating dipole moment P in the material. For the case of high electromagnetic fields, the
spatial components of this induced polarization can be expanded in powers of $E(\omega)$ Let us rewrite here Eq. 2.3 with explicit dependence on the frequency variable ω as:

$$P_{i}(\omega, 2\omega, 3\omega, ...) = \varepsilon_{0}(\chi_{ij}^{(1)}E_{j}(\omega) + \chi_{ijk}^{(2)}E_{j}(\omega)E_{k}(\omega) + \chi_{ijkl}^{(3)}E_{j}(\omega)E_{k}(\omega)E_{l}(\omega) + ...)$$
(2.5)

Here, ε_0 denotes the vacuum permittivity, $\chi_{ijk}^{(2)}$ are the spatial components $i, j, k = \{x, y, z\}$ of the corresponding (n + 1)-ranked susceptibility tensor. The $P(2\omega)$ in the above equation is responsible for the SHG frequency oscillating at double the incoming light frequency and is also one of the most relevant for our experimental method.

We can write the second order polarization term as:

$$P_i(2\omega) = \varepsilon_0 \chi^{(2)}{}_{ijk}{}^{ED} E_j(\omega) E_k(\omega)$$
(2.6)

Eq.2.6 represents the SHG process which can be shown schematically as in Fig.2.5. Both the transitions at ω and 2ω can be virtual transitions, i.e., the excited state does not correspond to any of the available high-energy states for the electron system. In this case the electronic state is occupied for a time determined by the time-energy uncertainty relation [6], hence we call the state as "virtual". If, on the other hand, the excited state is real, the process yield is greatly enhanced and it is referred to as "resonant," for obvious reasons. Although generally the resonant processes are favorable because of a strong and easy-to-detect signal, they often display features which are related with that particular material resonance rather than with general features of the material, and therefore the choice of the excitation frequency being resonant or not (and what resonant transition to choose in the former case) is a delicate task which depends on the type of measurements as well as the experimental conditions.

Until now, we only considered electric dipole transitions that usually dominate the generation of an SH wave as shown in Eq. 2.7. However, if this process is forbidden by symmetry, we should take account of higher orders of the multipole expansion of the electromagnetic field.

Let us briefly discuss the higher order terms such as magnetic or quadrupole contributions.

We begin by considering an electric field $E_i(r,t)$ of polarization (i = x, y, z) at position r and time t radiated due to the interaction of an incident field with a medium. This radiated field $E_i(r,t)$ is given by the inhomogeneous wave equation as:

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)E_i(r,t) = S_i(r,t)$$
(2.7)

where c is the speed of light and $S_i(r, t)$ is the induced source in the sample generated by the incident field. In the plane wave approximation, $E_i(r, t) = E_0 e^{-i(k \cdot r - \omega t)}$ and the radiated field

strength is proportional to the induced sources. To the lowest order in the multipole expansion, $S_i(r, t)$ is given by:

$$S_{i}(r,t) = \mu_{0} \frac{\partial^{2} P_{i}(r,t)}{\partial t^{2}} + \mu_{0}(\varepsilon_{ijk \nabla_{j}}) \frac{\partial}{\partial t} M_{k}(r,t) - \mu_{0}(\nabla_{j} \frac{\partial^{2} Q_{ij}(r,t)}{\partial t^{2}})$$
(2.8)

where μ_0 is the vacuum permeability, $P_i(r, t)$ is the induced polarization (electric dipole moment/unit volume) of the medium, ε_{ijk} is the Levi-Civita symbol, $M_k(r, t)$ is the induced magnetization (magnetic dipole moment/unit volume), and $Q_{ij}(r, t)$ is the induced quadrupolar density. The electric field term ($\propto P$) is the leading term in Eq.2.8 and is typically $\sim \lambda/a$) times stronger than the second order magnetic dipole ($\propto M$) while the electric quadrupole term is proportional to ($\propto Q$), where λ is the wavelength of light and 'a' is the lattice constant.

It should be noted that, both the electric and magnetic components of incident radiation can interact with the sample. The induced dipolar/multipolar densities can be expressed as linear, second and higher order nonlinear expressions of electric $E(\omega)$ and $H(\omega)$ fields of the incident light and can be represented as:

$$P_{i} \propto \chi_{ij}^{ee} E_{j} + \chi_{ij}^{em} H_{j} + \chi_{ijk}^{eee} E_{j} E_{k} + \chi_{ijk}^{eem} E_{j} H_{k} + \chi_{ijk}^{emm} H_{j} H_{k} + \cdots$$

$$M_{i} \propto \chi_{ij}^{me} E_{j} + \chi_{ij}^{mm} H_{j} + \chi_{ijk}^{mee} E_{j} E_{k} + \chi_{ijk}^{mem} E_{j} H_{k} + \chi_{ijk}^{mmm} H_{j} H_{k} + \cdots$$

$$(2.9)$$

$$(2.9)$$

and

$$Q_{ij} \propto \chi_{ijk}^{qe} E_k + \chi_{ijk}^{qm} H_k + \chi_{ijkl}^{qee} E_k E_l + \chi_{ijkl}^{qem} E_k H_l + \chi_{ijkl}^{qmm} H_k H_l + \cdots$$

$$(2.11)$$

Let us now try to understand the meaning of above equations by taking Eq.2.9 as an example. This equation describes the polarization of a medium, denoted by P_i , which is proportional to a combination of electric and magnetic fields, denoted by E and H, respectively. The subscripts on the E and H, symbols indicate the direction of these fields applied to system. The proportionality is determined by the material's susceptibility, denoted by χ , which is a measure of how the material responds to an external field. The subscripts i, j, and k on the χ symbols indicate that these tensors have multiple components, and the superscripts of χ refer to the operator responsible for the electronic transition, both from absorption and emission, i.e., 'e' represents dipole transitions, 'm,' the magnetic dipole transitions.

The terms on the right side of the equation can be understood as follows:

• The term $\chi_{ij}^{ee} E_j$ represents the contribution to the polarization due to the particle or system being subjected to an electric field E_j .

- The term χ^{em}_{ij}H_j represents the contribution to the polarization due to the particle or system being subjected to a magnetic field H_j.
- The term $\chi_{ijk}^{eee} E_j E_k$ represents the contribution to the polarization due to the particle or system being subjected to the product of two electric fields, E_j and E_k .
- The term $\chi_{ijk}^{eem} E_j H_k$ represents the contribution to the polarization due to the particle or system being subjected to the product of an electric field E_j and a magnetic field H_k .
- The term $\chi_{ijk}^{emm}H_jH_k$ represents the contribution to the polarization due to the particle or system being subjected to the product of two magnetic fields, H_i and H_k .

In short, this equation describes how the quantity P is influenced by the electric and magnetic fields E and H, as well as the susceptibilities that describe the response of a material to these fields. Similarly, we can also explain the other two equations.

2.2.1 Second order nonlinear susceptibility tensor

Before going the susceptibility tensor, let us define electrical susceptibility. It is a dimensionless proportionality constant that indicates the degree of polarization of a dielectric material in response to an applied electric field, which means that the electric susceptibility will be large if the response of a material to the field is large. The susceptibility tensor connects the polarization vector to the electric field vector and is composed of 3(n + 1) components. $\chi^{(2)}_{ijk}$ is a second-order nonlinear susceptibility and is a third rank tensor (3x3x3) composed of 27 components. [i, j, k] corresponds to the crystallographic axes of the crystal [x, y, z]. $\chi^{(2)}_{ijk}$ can be written as:

$$\chi^{(2)}_{ijk} = \begin{bmatrix} \chi^{(2)}_{xxx} & \chi^{(2)}_{xxy} & \chi^{(2)}_{xxy} \\ \chi^{(2)}_{xyx} & \chi^{(2)}_{xyy} & \chi^{(2)}_{xyz} \\ \chi^{(2)}_{xxx} & \chi^{(2)}_{xyy} & \chi^{(2)}_{xzz} \end{bmatrix} \begin{bmatrix} \chi^{(2)}_{yxx} & \chi^{(2)}_{yyy} & \chi^{(2)}_{yyz} \\ \chi^{(2)}_{yyx} & \chi^{(2)}_{yyy} & \chi^{(2)}_{yyz} \\ \chi^{(2)}_{yzx} & \chi^{(2)}_{yzy} & \chi^{(2)}_{yzz} \end{bmatrix} \begin{bmatrix} \chi^{(2)}_{xxx} & \chi^{(2)}_{xxy} & \chi^{(2)}_{zyz} \\ \chi^{(2)}_{zyx} & \chi^{(2)}_{yzz} \\ \chi^{(2)}_{yzx} & \chi^{(2)}_{yzy} & \chi^{(2)}_{yzz} \end{bmatrix} \begin{bmatrix} \chi^{(2)}_{xxx} & \chi^{(2)}_{xxy} & \chi^{(2)}_{zyz} \\ \chi^{(2)}_{zyx} & \chi^{(2)}_{zyz} & \chi^{(2)}_{zyz} \\ \chi^{(2)}_{zzx} & \chi^{(2)}_{zzy} & \chi^{(2)}_{zzz} \end{bmatrix}$$
(2.12)

2.2.2 Reducing $\chi^{(2)}$ via symmetry

This symmetry property can be used in a frequency range in which the absorption is negligible. Let us note that this symmetry should not generally apply to resonant SHG, although sometimes the absorption is still sufficiently small to leave the approximation unaffected. The frequencies can be freely permuted without permuting the corresponding subscripts, and vice versa, and the susceptibility remains unchanged. This is known as Kleinman symmetry [7].

According to Neumann's principle the symmetry properties of a crystal must also apply to its physical properties [8]. Applying the symmetry operations to the susceptibility tensor reduces the number of independent elements. For the second order susceptibility tensor of rank three, this is achieved with the following transformation operation:

$$\chi^{(2)'}{}_{ijk} = R_{i\alpha} R_{j\beta} R_{k\gamma} \chi^{(2)}{}_{\alpha\beta\gamma}$$
(2.13)

where R is a transformation matrix, $\chi^{(2)}_{\ \alpha\beta\gamma}$ is the untransformed tensor and $\chi^{(2)'}_{ijk}$ is the tensor after transformation. Let us now demonstrate one of the key symmetry properties of SHG: the system must break inversion symmetry for SHG to occur.

The inversion operation is given by:

$$R_{ij} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$
(2.14)

which represents the transformations of coordinate as:

$$\begin{array}{l} x \rightarrow -x \\ y \rightarrow -y \\ z \rightarrow -z \end{array}$$

Let us define a Kronecker delta δ_{ij} as:

$$\delta_{ij} = \begin{cases} 0, & \text{if } i \neq j \\ 1, & \text{if } i = j \end{cases}$$

$$(2.15)$$

After applying inversion operation, Eq. 2.13 takes the form:

$$\chi^{(2)'}{}_{ijk} = (-\delta_{i\alpha})(-\delta_{j\beta})(-\delta_{k\gamma})\chi^{(2)}{}_{\alpha\beta\gamma} = -\chi^{(2)}{}_{ijk}$$
(2.16)

Here we draw a very important conclusion: if the system possesses a given symmetry it must be left unchanged after undergoing any transformation of that symmetry. Therefore in those system having inversion symmetry we find that $\chi^{(2)'}_{ijk} = -\chi^{(2)}_{ijk}$ which is true only if the all the tensor components are vanishing. $\chi^{(2)'}_{ijk} = 0$, thereby demonstrating that SHG cannot occur in centrosymmetric systems. It is worth noting that this result is true only under dipole approximation. A centrosymmetric material can still produce a significant SHG signal if the quadrupole or other higher order terms are sufficiently strong and/or if something is there to naturally break the inversion symmetry, as it is generally the case of surfaces or interfaces between different centrosymmetric materials.

Depending on the symmetry involved, the number of independent components can be calculated. Let us explain the procedure with a practical example. Consider the symmetry

operation of 4-fold rotations, (Point group, 4). A medium possesses this symmetry when it is unchanged by a rotation of multiples of 90° around its symmetry axis. In the case of rotation around the *z*-axis the transformation matrix is given by:

$$R_{ij}(\theta z = \pi/2) = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}$$
(2.17)

It would be extremely time consuming to solve the equations in order to find the number of components survived after the application of all transformations. But we can also apply a direct inspection method in which we operate on each tensor element individually.

For 4-fold rotational symmetry, the operations are:

$$\begin{array}{c} x \to -y \\ y \to x \\ z \to z \end{array}$$

These operations can be applied directly to the indices of a tensor element, such as $xxx \rightarrow -yyy$ or $-xxx \rightarrow -yyy$ which means $xxx \rightarrow -xxx$. This is possible only if $xxx \rightarrow 0$. After applying the same procedure for all the tensor elements, we get the susceptibility for the point group '4' as:

$$\chi_{ijk}^{(2)}(4) = \begin{bmatrix} 0 & 0 & 0 & xyz & xxz & 0 \\ 0 & 0 & 0 & xxz & yxz & 0 \\ zxx & zxx & zzz & 0 & 0 & zyx \end{bmatrix}$$
(2.18)

This tensor presents only 8 non-vanishing elements out of 27 initial ones. This clearly demonstrates the effectiveness of applying symmetry considerations when dealing with any SHG process.

2.2.3 Prerequisites for a material to be SHG active

SHG can occur, as we have seen above, only in non-centrosymmetric crystals, i.e., in crystals that do not have inversion symmetry. In centrosymmetric material, all elements of even-order susceptibility tensors are equal to zero and consequently such materials cannot produce SHG. CentroSymmetry is also the reason why the SHG is usually not active in liquid and gaseous phases as well as amorphous solids (such as glass). In these cases, something needs to happen which can break the random distribution of molecules, i.e., a symmetry breaking induced by an external field or by phase transitions. All the crystal structures in 3D belongs to one of the 32 crystal classes or point groups. Out of them, 11 possess inversion symmetry, so those materials are SHG inactive, at least in the dipole approximation, shown as green in Table 2.1.

Centrosymmetric groups	Non-centrosymmetric groups (ferroelectric)	Non-centrosymmetric groups (not ferroelectric)
Ī	1	222
2/m	2	32
mmm	3	23
4/mmm	4	422
$\overline{3}m$	6 m	432
6/ <i>mmm</i>	<i>mm</i> 2	622
m	3 <i>m</i>	$\overline{4}$
$\overline{3} m$	4 <i>mm</i>	ō
4/ m	6 <i>mm</i>	$\overline{4}2m$
3		$\overline{6}2m$
6/ m		$\overline{4}3m$
m3		

Table2.1. Centrosymmetric and non-centrosymmetric point groups

Out of the remaining 21-point groups, 10 groups do not possess inversion symmetry and can develop an electric polarization. These point groups shown in blue are non-centrosymmetric and eventually be defined as polar groups and consequently the materials belonging to those groups are SHG active. The point groups shown in red are non-centrosymmetric and SHG active, but they do not show ferroelectricity as they possess inversion symmetry. For any material to be truly ferroelectric, the key point is the ability to switch the ferroic order in presence of external electric field.

2.2.4 Direction of SHG polarized light

Using matrix form, the Eq. 2.6, can be expanded as:

$$\begin{bmatrix} P_{x}(2\omega) \\ P_{y}(2\omega) \\ P_{z}(2\omega) \end{bmatrix} = \begin{bmatrix} xxx & xyy & xzz & xyz & xxz & xxy \\ yxx & yyy & yyz & yyz & yxz & yxy \\ zxx & zyy & zzz & zyx & zxz & zxy \end{bmatrix} \begin{bmatrix} E_{x}(\omega)^{2} \\ E_{y}(\omega)^{2} \\ E_{z}(\omega)^{2} \\ 2E_{y}(\omega)E_{z}(\omega) \\ 2E_{x}(\omega)E_{z}(\omega) \\ 2E_{x}(\omega)E_{y}(\omega) \end{bmatrix}$$
(2.19)

Depending on the specific form of the nonlinear tensor, i.e., on the material symmetry, and according to the input polarization of the incident light, the emitted SHG light will be generally polarized, and not necessarily in the same direction of the fundamental beam. Let us now elucidate this important feature with a typical SHG transmission experimental layout shown in Fig.2.6.



Figure 2.6. Sketch for SHG experiment in transmission. Polarization angle = ϕ

Let us assume that a given material belongs to the 4mm point group at room temperature, which allows the following non-zero components of the SHG susceptibilities: χ_{zzz} , χ_{xxz} , χ_{zxx} , χ_{yyz} and χ_{zyy} .

The indices of the nonlinear susceptibilities are related to the polarization (Eq. 2.6)

Suppose our analyzer is fixed along the y- direction (0^0) and we adopt the geometry as shown in Fig.2.6, then the incoming light is propagating in x direction. In this case we can only see χ_{yyz} and χ_{yzy} ($\chi_{yyz} = \chi_{yzy}$).

Thus, equation 2.19 will take the form:

$$P_{y}(2\omega) = \chi_{yyz}E_{y}(\omega)E_{z}(\omega) + \chi_{yzy}E_{z}(\omega)E_{y}(\omega) = 2\chi_{yyz}E_{y}(\omega)E_{z}(\omega)$$
(2.20)

Let us consider the electric filed vector in this form

$$E = E_0 \begin{bmatrix} 0\\ \cos\varphi\\ \sin\varphi \end{bmatrix}$$

We will obtain:

$$P_{y}(2\omega) = 2\chi_{yyz}E_{0}^{2}\cos\varphi\sin\varphi = \chi_{yyz}E_{0}^{2}\sin2\varphi$$
(2.21)

The intensity $I_{2\omega}(\varphi)$ would depend upon the rotation angle $\varphi = [0^0, 360^0]$ of the polarizer rotation in the following manner:

$$I_{2\omega}(\varphi) = P_y^2(2\omega) = \chi_{yyz}^2 E_0^4 \sin^2(2\varphi)$$
 (2.22)

As defined earlier the analyzer is fixed along the y direction (0^0). Usually, these types of measurements where you fixed the analyzer (outgoing polarization) and rotate the incoming polarization is called polarizer measurements. In Chpt. 3, we have defined them as α scans,

where α is input optical polarization angle. Fig. 2.7 shows an example of the polar plot given by Eq. 2.22.



Figure 2.7. SHG response of 4mm point group in polar coordinates.

2.3 Thin film deposition

In my PhD work, two techniques has been used to grow thin films, the first one is Pulsed Laser Deposition (PLD) and second Molecular Beam Epitaxy (MBE). In the coming sections we will explain both techniques briefly.

2.3.1 Pulsed Laser Deposition (PLD)

We have used the Pulsed Laser Deposition (PLD) for the growth of HZO thin films. PLD was the technique of choice for the growth of HZO films since this is usually considered the best techniques for the deposition of complex stoichiometry as the one of ternary oxides. It is a physical vapor deposition technique where a high-power pulsed laser beam is focused to strike a target. It reproduces target stoichiometry in an oxidizing ambient of the desired composition. The PLD process can be divided into three stages:

- Laser ablation of target
- Dynamic of plasma
- Film nucleation and growth

The laser-target interaction (electromagnetic energy) is converted into electronic excitation and then into thermal/mechanical energy to cause ablation. Ablation is a process that involves the removal of material from a surface by means of a high-energy beam, such as a laser beam or an ion beam. In thin film deposition, ablation is used to vaporize a target material, which is then deposited onto a substrate to form a thin film. The interaction of the laser beam with ejected material leads to the formation of high temperature expanding plasma, called the plume. A plume (atoms, molecules, electrons, ions, clusters, particles, etc.) expands with hydrodynamic

flow characteristics and finally reached the substrate. The growth processes depend on the surface energies of the substrate, film, and the film-substrate interface. As soon as the atoms land on the substrate, depending on the substrate temperature, they arrange on the surface, but a too high temperature can lead to re-evaporation of some species from the substrate. Therefore, for the quality and stoichiometry of a thin film, the substrate temperature and gas pressure are the key parameters.

Ablation is a technique that allows for precise control of the thickness and composition of thin films, making it a widely used approach in a range of applications, including in the semiconductor industry and in materials science.

There are several different mechanisms by which ablation can occur, depending on the type of energy beam used and the properties of the target material. One common mechanism is photothermal ablation, in which the absorbed energy from the laser beam is converted into heat, causing the target material to vaporize.

Material is vaporized and deposited as a thin film on a substrate facing the target. This process can occur in ultra-high vacuum or in the presence of a background gas, such as oxygen when depositing films of oxides. This technique allows crystallizing very complex crystalline structure by ablating material from a polycrystalline target using a highly energetic pulsed laser. The vacuum chamber is filled with oxygen at a given pressure (normally in the $10^{-4} - 0.3$ mbar range), which can be used to control the energy of the atoms in the plume as well as to avoid oxygen deficiency in the film. The total number of pulses are set to obtain a specific film thickness if the setup is not equipped with RHEED.



Figure 2.8. PLD set up. Picture (a) and scheme (b).

Fig.2.8a shows the picture of Reflection High Energy Electron Diffraction (RHEED) assisted PLD which consists of deposition chamber, KrF excimer laser source, RHEED and sputtering system used for the deposition for the electrodes. The PLD process utilizes a high-power-pulsed excimer KrF UV laser (λ = 248 nm), the rotating target facilitated by a motor, and a heated substrate mounted at ~ 4 – 5 cm from the target (Fig. 2.8b). The distance between target and substrate can be varied by displacing the substrate holder.

2.3.1.1 Reflection High Energy Electron Diffraction

Reflection high-energy electron diffraction (RHEED) is a surface analysis technique that uses a beam of high-energy electrons to probe the surface structure of a material. RHEED is typically used to study the growth of thin films, such as in the deposition of materials by physical vapor deposition (PVD) or chemical vapor deposition (CVD), MBE etc.

In a RHEED experiment, a beam of high-energy electrons is directed at the surface of the sample. The electrons are diffracted by the crystal lattice of the material. By analyzing the diffraction patterns, it is possible to obtain information about the surface structure and quality.

RHEED is commonly used to study the growth of thin films in real-time, allowing for the optimization of process conditions and the characterization of the film properties. RHEED is also used to monitor the surface morphology and crystallinity of the film during growth, as well as to identify the presence of defects or impurities. The RHEED pattern is typically visualized using an oscilloscope or a camera and can be seen as in Fig.2.9.



Figure 2.9. RHEED oscillations for the LAO layer grown on a STO substrate. The inset shows the RHEED pattern after growth [9].

These intensity fluctuations can be used to monitor the progress of the growth process and to determine the thickness of the film as shown in Fig.2.9. Each peak in the intensity oscillation corresponds to the formation of a new monolayer of the film. At this point, the degree of order in the film is at a maximum, and the diffraction spots will have maximum intensity because the maximum number of diffraction centers in the new layer contribute to the diffracted beam. As the film grows, the overall intensity of the oscillations will decrease because the electron beam is focused on the original surface and becomes less focused as more layers are added.

2.3.1.2 Advantages and disadvantages of PLD

PLD has a number of advantages over other thin film deposition techniques, including:

- PLD can be used accurately to reproduce the films with the stoichiometry of the target, especially for complex compounds with three or four elements. This differentiate PLD from the other techniques.
- PLD can achieve high deposition rates due to the high energy of the laser beam and the ability to adjust the laser pulse width and repetition rate.
- PLD can produce high-purity films due to the high-vacuum growth conditions and the ability to vaporize the target material directly from a solid target.
- PLD can be used to deposit a wide range of materials, including metals, semiconductors, and oxides.
- PLD allows for precise control over the film properties, including thickness, composition, and microstructure, through the manipulation of process parameters such as laser energy, pulse width, and target-to-substrate distance.
- PLD can be used to deposit films on a variety of substrate materials, including metals, ceramics, and semiconductors.

While PLD has a number of advantages, there are also some limitations to consider:

- PLD requires specialized equipment, including a high-energy laser source and a UHV chamber, which can be expensive compared to the other deposition such as CVD or Magnetron sputtering.
- PLD is typically limited to depositing thin films with thicknesses ranging from a few nanometers to several hundred nanometers.
- The size of the substrate that can be used in PLD is limited by the size of the vacuum chamber.
- PLD can be a complex process, requiring the optimization of multiple process parameters and the maintenance of high-vacuum conditions.
- While PLD allows for good control over the film thickness and composition, the film morphology (the surface and internal structure of the film) may be less well-controlled.

2.3.2 Molecular Beam Epitaxy (MBE)

Molecular Beam Epitaxy (MBE) is an epitaxial deposition technique carried out in Ultra High Vacuum (UHV) conditions that allows the growth of high quality epitaxial heterostructures of metals, semiconductors, and insulators. The MBE shown in Fig.2.10 is a Physical Vapor Deposition technique (PVD), in which the deposited material goes from a vapor phase to the condensed one, while no chemical reaction occurs in the gaseous phase of materials to be deposited. MBE is a highly precise and controlled process that allows for the growth of high-

quality, single-crystalline films of materials such as silicon, germanium, and III-V compound semiconductors (such as gallium arsenide and indium phosphide).

MBE was used for the deposition of Tin Telluride (SnTe) and Germanium Telluride (GeTe) thin films discussed in chapter 4. It is possible to define three main physical processes taking place during deposition as:

- The target material (i.e., a high purity metallic rod or a metallic crucible containing the material) is heated up in UHV causing either its evaporation or sublimation. In Fig.2.10. the rectangular boxes shown in green, blue, and orange are act as target material called as effusion cells.
- Propagation of the molecular beam towards the sample of the surface.
- and in the last step, the depositant beam reaches the substrate surface which is relatively at high temperature and interacts with it and this process is called crystallization.

In MBE, UHV conditions allow us to reduce the contaminant agents inside the chamber, a very large mean free path for atoms emitted from the target and eventually guarantee almost zero scattering events to them. It turns out to be a highly directional process and allows for the growth of ordered epitaxial thin films and is also commonly used for the growth of single-crystalline metals and oxides. To achieve this crystal quality, deposition rates are of the order of few Å/min.



Figure 2.10. Schematic representation of a Molecular Beam Epitaxy setup.

MBE relies on the migration of individual atoms or molecules, rather than the bulk movement of materials, which can lead to defects and impurities in the film. MBE is also highly flexible, allowing for the growth of a wide range of materials and the ability to stack multiple layers of different materials on top of each other to create complex multilayer structures. Some of the main disadvantages of MBE include the high cost of the equipment (more expensive than PLD). MBE is also a relatively slow process, which can limit its practicality for some applications.

2.4 Characterization of thin films

2.4.1 X-Ray Diffraction (XRD)

For structural characterization, we used X-Ray Diffraction (XRD), discovered by Max von Laue, in 1912. He suggested that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths like the spacing of planes in a crystal lattice. XRD is now a common technique for the study of crystal structures and atomic spacing. The basic schematic of XRD can be shown as in Fig.2.11. It is based on the interaction of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when the conditions satisfy Bragg's law:

 $2dsin\theta = n\lambda$ (2.23) where 'n' is order of diffraction, λ is wavelength of X-rays, 'd' is the spacing between two planes and ' θ ' is the angle of incidence.



Figure 2.11. Schematic representation of x-ray diffraction [10].

XRD is a non-destructive technique which reveals information about the crystallographic structure and physical properties of materials which are in the form of powder, bulk, and thin films. X-rays have wavelengths of the order of an angstrom (Å =10⁻¹⁰m), in the range of typical inter atomic distances in crystalline solids. Therefore, X-rays can be diffracted from the repeating patterns of atoms that are characteristic of crystalline materials. X-ray diffraction is based on the elastic scattering i.e., the change of direction of the electromagnetic waves without any energy change. The diffracted intensities are plotted against the detector angle 2θ . Bragg's law states the condition for sharp diffraction peak from the crystal. Actual diffraction peaks have

finite width resulting from imperfections, in addition to the natural broadening. As crystallite dimension enter the nanoscale, the peaks broaden.

2.4.2 Electrical characterization of ferroelectric thin films

In principle, there are two measurement configurations for electrical characterization of thin films, the bottom-top and top-top. The bottom-top configuration, which can be visualized in Fig. 2.12.



Figure 2.12. Scheme of bottom-top configuration.

In the bottom-top approach, the bottom electrode, usually a conductor (in HZO thin films we used LSMO) is connected to the top electrode, Platinum (Pt) in our case. This is an asymmetric configuration as the top/film interface and the bottom/film interface are different. An asymmetric contact configuration could result in asymmetric PE loops.



Figure 2.13. Scheme of top-top configuration.

The top-top configuration can be shown in the Fig. 2.13. This approach was used for measuring the Hafnium Zirconium Oxide (HZO) hysteresis loops explained in Chpt.3. in which top electrodes were contacted. In the top-top configuration for measuring the capacitance of a thin film capacitor, the two identical capacitors are connected in series through the bottom electrode. This configuration is equivalent to measuring the capacitance of a single capacitor with double the thickness of the original thin film. The advantage of this configuration is that any

asymmetries caused by the different metal-insulator interfaces are cancelled out, resulting in a more accurate measurement of the capacitance.

A net up/down polarization will produce accumulation of screening negative/positive charges at the top surface, and opposite charges at the bottom. Upon switching, induced by the applied electric field, these screening charges are also reversed by flowing through the circuit. In an ideal ferroelectric film and considering an initial zero polarization, the polarization can be defined as:

$$P(t) = \int_{0}^{t} I(t) dt / A$$
 (2.24)

Where I(t) is the current and can take positive or negative values, and A is the area of contact. According to the equation above, the polarization of a ferroelectric material can be obtained by measuring the current associated to the switching of ferroelectric domains while switching is induced by an electric field. FE loops have been performed using a TFAnalyser2000 platform (Aix ACCT Systems GmbH. Co.). It can measure the current vs voltage up to 25 V at frequencies between 5 x 10⁻⁴ Hz and 2 x 10⁶ Hz. The most basic method used to measure hysteresis dynamically is known as Dynamic Hysteresis Measurement (DHM) [15] shown in Fig.2.14. It consists in applying four bipolar triangular voltage pulses with a time frequency v_0 and a delay time between the different pulses τ . The first pulse serves to polarize the film in the down state, while the second pulse measures the switching from up to down. The third and fourth pulses do the same for the inverse polarity of the applying filed, completing the polarization hysteresis loop.



Figure 2.14. Voltage train pulses are applied in DHM, shaded areas correspond the pulses where current measurement is performed.

There are, in general, two ways to extract the remanant polarization: (i) Positive Up Negative Down (PUND) [11] (ii) Dynamic Leakage Current Compensation (DLCC). These two approaches are described below.

(i) PUND is a well establish method to reliably measure the remanent polarization [11]. In PUND measurement, five voltage pulses are applied the sample as shown in Fig. 2.15. The first pulse is negative and pre-polarizes the sample to a negative polar state. The second and third pulses are

positive, the second (P) polarizes the sample and therefore the corresponding current contains the ferroelectric and non-ferroelectric contributions, while current in the third pulse (U) only contains the non-ferroelectric contributions.



Figure 2.15. Voltage train pulses during PUND (Positive Up Negative Down).

Therefore, their subtraction allows isolate the ferroelectric contribution to a certain extent. The same applies to the fourth (N) and fifth (D) for the negative state. PUND current only contains the switchable ferroelectric contribution and all the other contributions are excluded. This compensation technique is only used if accurate values of remanent polarization are needed or in the presence of large leakage currents.

(ii) DLCC is a well-known compensation method developed by Mayer *et.al.* [12]. This is used when only the leakage contribution is desired to be removed from the polarization. In DLCC, the I-V curves obtained by DHM are corrected for leakage effects using two assumptions: that the leakage current is independent of frequency and the dielectric current and the current due to the ferroelectric switching both depends linearly on frequency. Under these circumstances, the DHM cycles at two frequencies (v_0 and $v_0/2$) as shown in Fig. 2.16 allow the subtraction of leakage current and only displacement current remains. DLCC allows to measure the reliable parameters from the D-E loops.



Figure 2.16. Voltage train pulses during DLCC (Dynamic Leakage Current Leakage).



Figure 2.17. Ferroelectric polarization from different methods [16]

A comparative hysteresis loops obtained by the above discussed techniques can be visualized as in Fig.2.17. It can be seen that by using DHM, ferroelectric switching peak for positive voltage at around 3 V and an increasing current for higher voltages leading to the leakage current. A similar current peak is observed when we applied negative voltage. It should be also noted that the leakage contribution widens the ferroelectric loop. This widening could be solved by using DLCC as it reduces the leakage current contribution. It is still not free from extrinsic contribution. In PUND, the current is non-zero during the switching peaks. As mentioned above, it only contains switchable polarization. It is not perfect since it usually provide an overestimation.

2.5 Symmetry analysis

For HZO:

HZO and GeTe belong to the mm2 and 3m point group symmetry respectively. In order to find the SHG response from In an SHG experiment, the frequency of the incident light is doubled by the interaction with the material and can be written as:

$$P_i^{NL}(2\omega) = \epsilon_0 \chi^{(2)}{}_{ijk} E_j(\omega) E_k(\omega)$$
(2.25)

Here P_i^{NL} is the non-linear polarization induced by incoming field, ε_0 is the vacuum dielectric constant, $E_j(\omega)$ and $E_k(\omega)$ are the incoming electric fields oscillating at frequency ω , and is the second-order susceptibility tensor that couples the fundamental and the second harmonic fields. The indices ijk assume the values of the system coordinates xyz and a sum is assumed over repeated indices.

It should be noted that the Eq.2.25 is written in the lab coordinates. Therefore, we should know the $\chi^{(2)}_{ijk}$ tensor in that coordinate system. It is much more convenient to write it in the crystal principal axes *abc* coordinate system, where symmetry vanishes most of the elements.

The electric fields in Eq.2.25 are written inside the material. We will write it as a function of the external fields, by introducing to the Snell law. To introduce the Snell law in vector form, we make use of the Fresnel tensor L. This tensor couples the transmitted \vec{E}_t and incident \vec{E}_i electric fields through the relation, $\vec{E}_t = L$. \vec{E}_i . Let us now refer to Fig.3.3a (Chapter 3) for the notation. In that system, it is possible to write the diagonal terms of L as a function of the input-output angles and the two indices of refraction across the interface:

$$L_{xx} = \frac{2n_1 \cos \beta_2}{n_2 \cos \beta_1 + n_1 \cos \beta_2}$$

$$(26)$$

$$L_{yy} = \frac{2n_1 \cos \beta_2}{n_1 \cos \beta_1 + n_2 \cos \beta_2}$$

$$(27)$$

$$L_{zz} = \frac{2n_1^2 \cos \beta_1}{n_2(n_2 \cos \beta_1 + n_1 \cos \beta_2)}$$
.28)

Using the Fresnel tensor, we can now define an effective $\chi^{(2)}$ tensor (in the following we will remove the superscript (2) for simplicity.) which contains all the information about the geometry of the incident and emitted fields. Only the amplitude of those fields will be left outside. The effective tensor χ^{eff} tensor will be than a function of the frequency and the polarization of the incident and emitted light:

$$\chi_{\alpha_{in},\alpha_{out}}^{eff} = e_{\alpha_{out}}^{(2\omega)} i \ L_{ii}^{(2\omega)} \chi_{ijk}(\omega, 2\omega) \ L_{jj}^{(\omega)} \ L_{kk}^{(\omega)} \ e_{\alpha_{in}}^{(\omega)} j e_{\alpha_{in}}^{(\omega)} k$$
(2.29)

Fig 2.18 represents the interface between two media with index of refraction n_1 and n_2 . The incident plane corresponding to the (*xz*) plane, in a (*xyz*) reference system of the laboratory.



Figure 2.18. Experimental Layout. Note, here incident angle is $\beta_1 = \theta$ (as in Fig.3.3a). Taken from [13].

The fundamental light in our case was 800 nm wavelength (red line) and the SHG light emitted from the sample is represented by blue line and has a 400 nm wavelength. The incidence angle is β_1 and the refracted angle into the n_1 medium is β_2 . The angle φ between the laboratory xdirection and we can change the crystal principal axis a by rotating the sample around the normal to its surface, while different input and output configurations can be set by using a Polarizer and an Analyzer. Here 'p' is the direction parallel to the incident plane, 's' is parallel to the sample surface and d is at 45 between the two. The general polarization unit-vector \hat{e} forms an angle α with respect to the 'p' direction in the ps plane.

In Eqs. 2.26, 2.27, 2.27 and 2.28 the incident angle β_1 , the indices of refraction are depending only on the frequency ω once we made the choice of the specific material, and the transmitted angle β_2 is given as a function of β_1 and $n_{1,2}$ by the Snell law. Therefore, the value of a specific tensor element L_{ii} will depend only on the frequency, which is in our case either ω or 2ω . Thus, in the following we make use of a simplified notation: $L_i(\omega) = L_{1i}$ and $L_{ii}(2\omega) = L_{2i}$. Finally, \hat{e} are the unit vectors representing the direction of the incoming and outcoming fields and the angles α_{in} and α_{out} represent the input and output polarizations respectively, as depicted in Fig. 3.11, p, s and d directions corresponds to the $\alpha = 0^0$, 90^0 , 45^0 respectively. The emitted SHG light intensity will be then proportional to the square modulus of the emitted SHG electric field, and thus it will be in turn proportional to the square modulus of χ^{eff} . So, for a given choice of the input and output polarization angles, we basically measure $|\chi^{eff}|^2$ and therefore we can go back to the χ^2 . We have an arbitrary scaling factor, A, for our measurements, due to the response of the experimental setup. In general, we can write that our SHG signal I_{SHG} is given by:

$$I_{SHG} = A. \left| \chi^{eff} \right|^2 \tag{2.30}$$

From here, we can start our calculations and the experimental layout is sketched is shown in Fig.2.18. In this figure, we have $\hat{e} = \cos\alpha$. $\hat{p} + \sin\alpha$. \hat{s} for both input and output. Also, for the input we have $\hat{p} = \cos\beta_1$. $\hat{x} + \sin\beta_1$. \hat{z} and $\hat{s} = \hat{y}$ and for the output we have same notation but with changed sign in the p_x component. Therefore, we have:

$$\hat{e}^{in} = \begin{bmatrix} \cos\alpha_{in}\cos\beta_{1} \\ \sin\alpha_{in} \\ \cos\alpha_{in}\sin\beta_{1} \end{bmatrix} ; \quad \hat{e}^{out} = \begin{bmatrix} -\cos\alpha_{out}\cos\beta_{1} \\ \sin\alpha_{out} \\ \cos\alpha_{out}\sin\beta_{1} \end{bmatrix}$$
(2.31)

Thus, the scalar product for the input waves is written like this:

$$L_{1} \cdot \hat{e}^{in} = \begin{bmatrix} L_{1x} & 0 & 0 \\ 0 & L_{1y} & 0 \\ 0 & 0 & L_{1z} \end{bmatrix} \begin{bmatrix} \hat{e}^{in}_{x} \\ \hat{e}^{in}_{y} \\ \hat{e}^{in}_{z} \end{bmatrix} = \begin{bmatrix} L_{1x} \cos \alpha_{in} \cos \beta_{1} \\ L_{1y} \sin \alpha_{in} \\ L_{1z} \cos \alpha_{in} \cos \beta_{1} \end{bmatrix}$$
(2.32)

Similarly:

$$L_{2} \cdot \hat{e}^{out} = \begin{bmatrix} -L_{2x} \cos \alpha_{out} \cos \beta_{1} \\ L_{2y} \sin \alpha_{out} \\ L_{2z} \cos \alpha_{out} \cos \beta_{1} \end{bmatrix}$$
(2.33)

Finally, we have to apply a rotation by an angle φ around the z axis in order to bring the vector in the crystal coordinate system. Let us call \vec{R} the rotated vector:

$$\vec{R}^{in} = \begin{bmatrix} \cos\varphi & -\sin\varphi & 0\\ \sin\varphi & \cos\varphi & 0\\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} L_{1x}\cos\alpha_{in}\cos\beta_1\\ L_{1y}\sin\alpha_{in}\\ L_{1z}\cos\alpha_{in}\cos\beta_1 \end{bmatrix}$$
(2.34)

Again, \vec{R}^{out} is obtained by the above-mentioned substitutions and changing the sign of only the first term of the x and the y components of \vec{R}^{in} .

Now it is possible to rewrite Eq.2.29 in terms of \vec{R}^{in} and \vec{R}^{out} as:

$$\chi_{\alpha_{in},\alpha_{out}}^{eff} = R_{\alpha_{out}}^{out} i \chi_{ijk}(\omega, 2\omega) R_{\alpha_{in}}^{in} j R_{\alpha_{in}}^{in} k$$
(2.35)

The Eq. 2.35 is written in the crystal system, so we should use the coordinates (abc) instead of (xyz).

We know o-HZO belongs to the space group $Pca2_1$ which corresponds to the orthorhombic point group mm2 and the allowed tensor components are shown in Table 2.2. It should be noted that the above analysis is true for all materials having mm2 point group symmetry.

Symmetry	Non-vanishing elements	
o-HZO, mm2	xzx = xxz	
	yyz = yzy	
	ZXX	
	zyy	
	ZZZ	
m-HZO, 2/m	Each element vanishes.	
t-HZO, 4/mmm	Each element vanishes.	

Table 2.2 Allowed tensor components for orthorhombic, monoclinic, and tetragonal HZO.

We use the method explained above to get the final formulas in order to fit the experimental data. The same method was used to write a MATLAB code (Appendix A1) and the output $\chi^{eff}_{\alpha_{in},\alpha_{out}}$ for different point groups shown in Table 2.2 can summarize as:

For *m22*,

 $\chi_{ss}=0$

 $\chi_{ds} = A \sin 2\varphi + B \cos \varphi + C \sin \varphi$

 $\chi_{ps} = A \sin 2\varphi$

 $\chi_{pp} = \chi_{sp} = A + B \cos 2\varphi$

where α_{in} represents s, p, and d and α_{out} can take s and p only. The simulated results can be seen in the Fig.2.19.

For 4/mmm and 2/m, the $\chi_{\alpha_{in},\alpha_{out}}^{eff}$ is zero as all the tensor components in the corresponding point groups are zero.



Figure 2.19. Simulation for mm2 point group.

For 3m point group symmetry:

In centrosymmetric systems , electric diploe contribution to SHG is zero because $\chi^{(2)}$ in those material is zero. Germanium telluride (GeTe) belongs to the 3m point group which is non centrosymmetric (polar) in nature. In this polar 3m phase, if the mirror plane is perpendicular to Y, the tensors which are allowed are:

$$xzx = yzy = xxz = xxz$$
$$zyy = zxx$$
$$xxx = -xxy = -yyx = -yxy$$
$$zzz$$

Suppose we are incident the laser beam in near normal incidence onto the zy plane (Fig.4.4), we can only access the zzz and yyz(=xxz) components.

The measurement where we measure SHG signal as a function of rotation of input and output light polarization gives rise to what we call anisotropy measurements (Fig.4.6). The number of tensor components detected depends on the experimental geometry. Most of the tensors can be probed in reflection (45⁰) geometry. An anisotropy measurement also allows to identify the crystallographic directions if the orientation of the crystal axes is unknown.

The intensity of the generated SHG signal can be obtained by taking the square of the second harmonic polarization. i.e.,

$$I(2\omega) \propto \left|P_i^2(2\omega)\right|^2$$

where

 $P_i^2(2\omega) = \chi_{ijk}^2 E_j(\omega)E_k(\omega)$; (indices i, j and k denote the polarization of the optical field).

Now , if we use the allowed tensor components of 3m point group symmetry , the susceptibility tensor takes the form as:

$$\chi^{(2)} = \begin{pmatrix} \begin{pmatrix} xxx \\ 0 \\ xxz \end{pmatrix} & \begin{pmatrix} 0 \\ -xxx \\ 0 \end{pmatrix} & \begin{pmatrix} xxz \\ 0 \\ 0 \end{pmatrix} \\ \begin{pmatrix} 0 \\ -xxx \\ 0 \end{pmatrix} & \begin{pmatrix} -xxx \\ 0 \\ xxz \end{pmatrix} & \begin{pmatrix} 0 \\ xxz \\ 0 \end{pmatrix} \\ \begin{pmatrix} zxx \\ 0 \\ 0 \end{pmatrix} & \begin{pmatrix} 0 \\ 2xx \\ 0 \end{pmatrix} & \begin{pmatrix} 0 \\ 0 \\ zzz \end{pmatrix} \end{pmatrix}$$

$$I(2\omega) \propto |A(xxx)\cos 3\phi|^2$$

It should be noted that, for polarizer = Analyzer = 0^{0} and Polarizer = Analyzer = 90^{0} , we got the same formula as given in the above equation.

For doped GeTe, we used the fit function from reference [14], which can be written as:

$$I(2\omega) \propto \frac{1}{4}A(\cos 3\phi) + B\cos(2\beta + \phi))^2$$

where ϕ is the polarization angle and β is principal of strain orientation.

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Chapter 3 Second Harmonic Generation on Hf_{0.5}Zr_{0.5}O₂/La_{0.67}Sr_{0.33} MnO₃ Interfaces

3.1 Introduction

The part of the chapter 3 [section 3.4) was done at ETH Zurich with Marvin Muller and Morgon Trassin

Doped Hafnium oxide thin films have received significant attention in recent years due to their unique electrical and dielectric properties. These films have a great technological importance, as they exhibit ferroelectricity (FE) at room temperature in films thinner than 5 nm [1,2]. Being fully compatible with CMOS technology, it is expected to have large impact on microelectronics [3]. When hafnia is doped with zirconium, the FE varies with composition, but around a 50% doping level, Hf_{0.5}Zr_{0.5}O₂ (HZO) shows the highest polarization [3]. HfO₂ (ZrO₂)- based compounds adopt a monoclinic paraelectric (P2₁/c) phase but at high-temperature and highpressure tetragonal or cubic phases can be stabilized by doping [4]. It is rather surprising to have a FE in hafnia-based films, first because the above phases are non-polar, second because it is well-known that the FE is often suppressed upon decrease of the film thickness. HZO has been shown to have good ferroelectric properties, including a high T_c and a large remnant polarization. It has also been found to have good stability and can maintain its ferroelectric properties even after being subjected to high temperatures or mechanical stress [5]. In addition to its potential use in electronic devices, HZO has also been investigated for its potential use as a protective coating for a variety of materials. The high dielectric constant and good electrical conductivity of HZO make it an attractive material for use in energy storage applications, such as supercapacitors [6]. Overall, HZO has shown promise as a ferroelectric thin film with a range of potential applications in electronics and other fields.

SHG is noninvasive, nondestructive, and noncontacting and can probe the entire volume of thin film structures, including buried heterostructures. The use of second harmonic generation on thin films and interfaces has become a very popular research direction in recent years. Interface SHG (iSHG) can be extremely important to study the interfaces which are hidden and are not possible to detect in other optical techniques. At interfaces, there is always as breaking a symmetry breaking giving rise to iSHG signal. In our case it is HZO/LSMO interface which is going to explain in upcoming sections.

In the next sections we will explain the fabrication of films using Pulsed Laser Deposition (PLD), their electrical characterization (hysteresis measurements) and optical second harmonic polarimetry on HZO thin films in particular HZO/LSMO interfaces.

3.2 Experimental section

3.2.1 Growth of HZO thin films

The HZO thin films, buffered with a La_{0.67}Sr_{0.33}MnO₃ (LSMO) bottom electrode, were grown by reflection high energy electron diffraction (RHEED)-assisted pulsed laser deposition (PLD), using a KrF excimer laser (wavelength 248 nm) on SrTiO₃ (STO) (001) substrates. Two sets of films were fabricated. Set 1 consists of different HZO film thicknesses and a fixed LSMO thickness, while Set 2 consists of different LSMO thicknesses and a fixed HZO thickness. Set 1 is composed of a reference sample (LSMO/STO, indicated in the following as "0 nm HZO thickness") and three HZO/ LSMO/STO samples with HZO thicknesses of 4.6, 9.2, and 18.4 nm. In sample Set 1, we keep the LSMO thickness constant (25 nm). Sample Set 2 is composed of two HZO/LSMO/STO samples, with LSMO thicknesses of 8 and 20 nm and a fixed HZO thickness of 9 nm. The growth details are as follows: LSMO films were grown at a laser repetition rate of 5 Hz, substrate temperature T_s = 700 °C, and oxygen pressure P₀₂= 0.1 mbar, HZO layers were grown with T_s = 800 °C and P₀₂ = 0.1 mbar, and samples were finally cooled with P₀₂ = 0.2 mbar and the heater off.

For the set 2 of films, LSMO layers were grown at a repetition rate of 1 Hz, T_s of 770 °C, P_{O2} of 0.1 mbar and HZO was grown at repetition rate of 2 Hz, T_s of 800 °C and P_{O2} of 0.1 mbar. At the end of the deposition, the samples were cooled down at 10 °C/min in the oxygen background of P_{O2} 0.1-0.2 mbar. The structural characterization was performed by Rigaku X-ray diffractometer, Cu K α radiation (1.5406 Å).

3.2.2 Structural characterization

Fig.3.1. shows the X-ray diffraction (XRD) θ -2 θ -scans obtained in the Bragg-Brentano configuration for sample Set 1. The highest peaks mark the (001) Bragg reflections of the STO substrate and the LSMO bottom electrode in all the three samples (Fig.3.1 a, c, and e).

The main feature in the Fig.3.4.a, c, e, is the orthorhombic HZO(111) peak at $2\theta \approx 30^{\circ}$. For the thinnest film (4.6nm), this peak appears at a slightly smaller angle, an indication of the elongation of the out-of-plane spacing d₁₁₁ axis. This is consistent with the fact that the thinner film undergoes compressive in-plane strain, leading to an elongation along the out-of-plane d₁₁₁ direction. Previous reports suggested that this could be assigned to the orthorhombic phase [7] and also to the rhombohedral phase [8]. The presence of Laue fringes clearly indicates the high crystal quality of the grown films and a well-defined interface. With the increase of film thickness, the film gets relaxed, and the d₁₁₁ peak shift decreases. Moreover, for 9.2 nm thick films, a new weak peak appears at ~35° which is ascribed to the non-FE (002) monoclinic phase of HZO [9]. For HZO films thicker than 9.2 nm, this peak becomes stronger. We can see from the Fig 3.1 epitaxial o-HZO(111) crystals grow across the entire film thickness as the peak is getting sharper. The m-HZO(002) peak seen in 18.4 nm film is an evidence of an increasing fraction of

the monoclinic phase with respect to the orthorhombic phase with thickness. Whereas the monoclinic phase is not detected in the t = 4.6 nm film the thickest film.



Figure 3.1. (a),(c) and (e) shows X-ray diffraction θ -2 θ scans for HZO thin films, with varying thickness t in broad range of 2 θ values. Fig.3.1. (b), (d) and (f) are resolved peaks orthorhombic phase (ferroelectric) indicated as o-HZO(111).

3.2.3 Electrical measurements

Ferroelectric polarization loops for different thin films are shown in Fig. 3.2. There is hysteresis in all of the samples, and there are not wake-up effects as observed in polycrystalline films in previous reports [3,10]. The measurement was conducted at 1 KHz using TFAnalyzer2000 as described in the chapter 2 (top-bottom configuration, with Pt and LSMO as top and bottom electrodes respectively). The top electrodes were deposited using the magnetron sputtering. The 9.2 nm HZO thin film has the highest remnant polarization $P_r \approx 20 \,\mu\text{C/cm}^2$ significantly high with comparison with thinner films.



Figure 3.2. Polarization loops of different HZO films.

3.3 SHG on HZO thin films

3.3.1 Experimental methodology

We measured the SHG signal as a function of the input polarization angle α (for $\phi = 0$ a given Por S-output polarization angle) and as a function of the sample azimuthal angle ϕ (for given input-output polarization angles), by keeping the incidence angle fixed ($\theta = 45^{\circ}$). A sketch of the experimental geometry is shown in Fig. 3.3a. Red arrows represent the incoming photon (λ = 800 nm) and blue arrows the SHG at λ = 400 nm. The incidence angle θ is fixed at 45°. For output polarization angles, the label P represents incidence plane polarization, while the label S represents a polarization parallel to the sample surface. The iSHG signal is measured as a function of the input optical polarization angle α ($\alpha = 0$ means parallel to P, $\alpha = 90^{\circ}$ means parallel to S) and the sample azimuthal angle ϕ . The nonzero incident angle geometry is required in order to observe a linear combination of all the components of the nonlinear tensor, so to include those involved with the direction normal to the sample surface, as the surface has a weaker contribution to the iSHG (the "i" is not explained) signal in a normal-incidence geometry. The light polarization angle α is taken to be zero in the direction parallel to the incident plane (P) and 90° in the direction parallel to the sample surface plane (S), whereas the intermediate 45° angle has been labeled with letter D. The experimental setup is shown in Fig. 3.3b. A laser source , a series of waveplates (WP) and polarizers (P) is used to set the incident and reflected light polarization, filters (F), and a monochromator (MC) are used to remove the fundamental frequency before signal detection. The fundamental light has an 800 nm central wavelength (red line in Fig. 3.3b), and the iSHG light emitted from the sample has a 400 nm central wavelength (green line in Fig. 3.3b). and a photon multiplier tube (PMT) (not shown) is used to detect the signal. The angle φ between the laboratory x direction and the crystal principal axis a can be changed by rotating the sample around the axis normal to its surface, while different input and output configurations can be set by using a polarizer and analyzer half waveplates.



Figure 3.3. (a) Optical geometry with levels diagram. (b) Experimental setup. [WP : Waveplate, P : Polarizer, L : Lens, F : Filter, MC : MonoChromator].



Figure 3.4. SHG verification tests. (a) Scanning of the monochromator grating for a fixed incident wavelength $\lambda\omega$ (in our it was 800 nm) results in a peak at $\lambda\omega/2$ (400 nm) that has a typical full width at half maximum of about 20 nm. (b) SHG power dependence (black curve) and the expected quadratic curve (red line).

The first step in every SHG experiment is to verify whether our signal can be really ascribed to SHG. High light intensities of fs laser pulses have the potential to excite many nonlinear optical processes that are capable to generate light at a frequency 2ω . White-light generation and two-photon luminescence are some examples. Thus make sure that our signal has SHG origin, we follow:

- (a) Spectral dependence: the SHG intensity has a spectral peak at 2ω with a spectral width that is given by the bandwidth of the incident light pulses. In contrast to fluorescence or white light that feature a broad emission spectrum, the spectral shape of the emitted light is analyzed by scanning the monochromator for a fixed wavelength of the fundamental light, with a result similar to the one shown in Fig. 3.4a.
- (b) Intensity dependence: the SHG intensity scales quadratically with the incident pulse energy. For both the tests we used 9.2 nm HZO as a reference. We used fundamental wavelength 800 nm and monochromator was fixed at 400 nm and the potential applied across PMT was 1.5KV which was measuring the SHG. Moreover, the polarizer and analyzer were fixed at 0^o and measurement was done in reflection geometry shown in Fig. 3.3b. The output SHG intensity was quadratically dependent on input laser power as $I(2\omega) \propto I^2(\omega)$.

In this experimental setup as shown in Fig. 3.3b, a titanium-sapphire laser is used as the light source. It generates pulses with a repetition rate of 1 kHz, an average power of 4 W, a duration of 35 fs, and a central wavelength of 800 nm. The beam spot size is approximately 150 micrometers in diameter, and the energy per pulse is around 10 microjoules. This results in an estimated average laser intensity of $5.7 \times 10^5 \text{ W/m}^2$ and a peak intensity of $17 \times 10^{15} \text{ W/m}^2$. These values are considered weak enough to not significantly affect the fundamental properties of the material being studied. These numbers, provided that the absorption length at 800 nm is much larger than the film thickness [11], ensure that the optical excitation is weak enough to

assume a negligible effect on the fundamental properties of the material. The iSHG signal is generated when the beam is reflected by the sample surface.

Two motorized half-wave plates are used to adjust the input and output polarizations angles. Filters and a monochromator are used to remove any unwanted fundamental wavelength light, and a photon multiplier is used to detect the iSHG signal.

The monochromator is used to scan the iSHG line and ensure that no unwanted optical noise is present, and the iSHG signal is measured as a function of the incident laser power to confirm that it behaves quadratically as expected (Fig. 3.4b). The iSHG patterns are also measured at different laser powers to ensure that there are no unwanted laser-induced effects. In order to minimize systematic errors, the samples are measured in a random order and several times, and the setup is completely realigned between different sets of measurements. The resulting standard errors are used as error bars in the data.



3.3.2 Results

Figure 3.5. iSHG measurements on sample set 1 as a function of the input angle α for two different output polarizations, namely P (a) and S (b). Circles represent data points, while solid lines represent empiric best-fit curves. Colored straight lines represent the main input-output polarization combinations: dark blue for PP, red for SP, green for DS, pink for PS, and orange for SS. Different colors refer to the HZO thickness according to the legend, the black curve represents the LSMO (0 nm HZO).

iSHG measurements as a function of input polarization angle, α shown in Fig. 3.5, the main directions are labeled with lines of different colors: P_{in}/P_{out} is dark blue and S_{in}/P_{out} is wine-red Fig. 3.5a), D_{in}/S_{out} is green, P_{in}/S_{out} is pink, and S_{in}/S_{out} is orange (Fig. 3.5b). The same color code applies in Fig. 3.6. According to Fig. 3.5, we get a significant iSHG signal for P_{in}/P_{out} (from now on, PP for simplicity), S_{in}/P_{out} (SP), and D_{in}/S_{out} (DS) combinations, while the P_{in}/S_{out} (PS) and

 S_{in}/S_{out} (SS) iSHG yields are more than 1 order of magnitude smaller. In order to correctly visualize the behavior of the signal in each component, Fig. 3.6 shows a cut of the α -P and α -S measurements as a function of the HZO thickness (i.e., for each measured sample, including the reference sample).



Figure 3.6. iSHG yield as a function of HZO thickness for given input– output polarizations. The error bars represent the standard error on repeated measurements and are smaller than the point diameter, if not visible.

It is evident that the iSHG components are affected by the HZO coverage but not all in the same way. In particular, for the thinnest HZO sample (4.6 nm), the PP component shows a maximum where the SP component has a minimum. Both components are relaxing back to values similar to the reference for thicker HZO films, i.e., where the paraelectric monoclinic phase starts to appear (see Figure 3.1). Besides this, it is worth noting that the FE polarization in HZO is well known to have a maximum value for very thin films, around 4-6 nm [9] and that the SHG signal from HZO grown by atomic layer deposition (ALD) on TaN/Si substrates is known to correlate with FE as a function of chemical Zr doping [11]. This makes us to think that we are observing a signal correlated with the FE order parameter in HZO. The DS, PS and SS component seems to be very much unaffected and in particular PS and SS are hardly visible on the scale. This observation demonstrates that the variation of iSHG in the other two components cannot be ascribed to experimental artifacts or to some overall enhancement of the iSHG signal due to a structural change in the HZO/LSMO interface compared to the air/LSMO interface. On the other hand, the shape of the α -scan looks quite similar overall between the reference (LSMO only) sample and the HZO films. This suggests that the main features we observe are coming from the LSMO side of the interface. In order to understand the origin of iSHG, we performed the ϕ -scan measurements shown in Figs. 3.7 and 3.8. Considering the geometry of the experiment, it is evident that the rotation of the sample will also slightly change the direction of the outcoming iSHG beam, since the surface plane of the sample and the rotation plane of the holder can never be perfectly parallel to each other. Therefore, the iSHG signal has been manually maximized on every single point to recover a correct alignment. This explains why the point-by-point noise of these measurements is larger than the one of a typical α -scan.



Figure 3.7. iSHG measurements on sample Set 1 as a function of the azimuthal angle ϕ for different samples: (a) P-input/P-output polarizations (PP); (b) S-input/P-output polarizations (SP); (c) D-input/S-output polarizations (DS). Note that the 4.6 nm sample PP curve shows a stronger isotropic contribution with respect to all other curves. Circles represent data points, while solid lines represent empiric best-fit curves. Different colors refer to the HZO thickness according to the legend.

In Fig.3.7, it is seen that not only the amplitude but also the ratio between the isotropic contribution and the anisotropic contribution does change for the thinnest HZO sample (4.6 nm) with respect to others. In other words, there is a constant term (appearing as a circle in the polar plot) that is larger compared to the lobes in the 4.6 nm sample with respect to the other samples, including the reference. The SP component, on the contrary, does not show a particular change in shape, as the curve is reasonably well-described by a circle (isotropic constant term) for all samples. Finally, the DS component shows a clear fourfold structure, and it does not show any particular trend by changing the HZO coverage. These results clearly show that there are not definite changes in the symmetry of the samples, as it would result if a direct iSHG signal was detected from HZO with a nonvanishing in-plane polarization component.



Figure 3.8. iSHG signals as a function of azimuthal angle ϕ for PS (a) and SS (b) components. Different colors refer to the HZO thickness according to the legend. Circles represent data points, while solid lines represent empiric best fit curves.

Overall, these results indicate that the changes in the iSHG signal observed for the thinnest HZO sample are primarily due to the influence of HZO on the LSMO layer, rather than a direct iSHG contribution from the HZO itself.

Let us now turn our attention to the PS and SS components of Fig. 3.8, we see that those components do not change in shape or amplitude, but the shape in this case is quite different with respect to the other three components, and the amplitude is more than 1 order of magnitude smaller. In particular, both terms show an eight-lobe structure, separated in four large and four small lobes by a 45° rotation. Finally, we note that none of the above shown results are consistent with the threefold and sixfold symmetries that are expected to dominate the signal of the (111)-oriented HZO thin-film [9,12]. From Figs. 3.7 and 3.8, it is quite apparent that the iSHG signal mainly comes from the LSMO film. The LSMO/STO interface has been previously studied by means of iSHG polarimetry by Zhao et al. [13] which showed that the output signal is a combination of isotropic and anisotropic terms, originating from the LSMO surface and LSMO/STO interface, respectively.

The impact of the HZO film on the iSHG from LSMO is clear from the results shown in Figure 3.6. In order to understand the separate contributions of LSMO and HZO to the signal, additional samples were grown using pulse laser deposition (PLD). These samples had the same HZO coverage of 9 nm, but different LSMO thicknesses of 8 and 20 nm (detail in section 3.2.1). The α -P and α -S curves were measured for these samples, as shown in Fig. 3.9, and the ratio between the curve measured on the thicker LSMO sample and that measured on the thinner LSMO sample was calculated.



Figure 3.9. (a) alpha-in P-out and (b) alpha-in S-out for the set 2 samples.

If the iSHG signal was perfectly proportional to the LSMO coverage, the resulting curve would be a perfect circle with a radius equal to the scaling factor between the two curves. In Figure 3.10, the S-output curve (blue) and P-output curve (black) are shown, along with a reference circle of radius 1 for comparison. While there are some minor variations, the S-output curve appears to be similar to a circle with a radius of 3, while the P-output curve is significantly elongated along the PP direction. The SP component, on the other hand, is located almost exactly around a radius of 1. These results suggest that the observed iSHG signal cannot be generated solely within the bulk LSMO film, but rather has a significant contribution from the interface, at least in the case of the PP component.



Figure 3.10. Ratio between LSMO-thick and LSMO-thin samples in sample Set 2, in the case of S-output (blue circles) and P-output (black circles) polarizations. The red circle represents the unity, as a reference for the eye.

Now if we compare our simulated results (Fig.2.18) with the Fig.3.7, we can see that PP and DS components are well fitted with the theoretical model but in the case of SP (Fig.3.7b) we have a circle which contradicts the theoretical results in which it is shown that PP and SP components are similar in shape. Moreover, our results also contradict the PS and SS components (not shown). In our experimental results we have eight-fold lobes in case of PS and SS as shown in Fig.3.8. But after applying the symmetry analysis we found that SS component should be zero and PS should have four lobes as shown in Fig.2.18 (Chpt 2). So, the presence of eight lobes in these cases might have another origin. It is clear now from the above analysis that if we apply electric dipole SHG approximation, it is not possible to fit the experimental data.

We tried the second way by considering the electric quadruple SHG contribution to our signal. In particular we used the results from de la Torre *et al.* [15]. Keeping in mind that the point group they have chosen was tetragonal 4/m. The fitting results can be seen in Fig.3.8.

For 4/m, we found the following fit functions:

$$\chi_{pp} = Asin 4\varphi + B \cos 4\varphi + C$$

$$\chi_{sp} = Asin 3\varphi + B \cos 2\varphi + C$$

$$\chi_{ds} = Asin 4\varphi + B \cos 4\varphi + C$$

$$\chi_{ps} = Asin 4\varphi + B \cos 4\varphi + C$$

$$\chi_{ps} = Asin 4\varphi + B \cos 4\varphi + C$$

Where *A*, *B* and *C* are fitting parameters and are defined in such that the final formulas should fit the curve. It should be noted that, in case of χ_{sp} we have changed the formula as it was in [15] in order to fit the experimental data.



3.4 SHG studies on the wake-up effect of HZO

Figure 3.11. (a) Hysteresis loops obtained by integrating the current in PUND measurements on 9.2 nm HZO thin films (b) Pt electrodes deposition using photolithography (c) AFM image of single (d) Height of electrode during AFM scanning.

From the above symmetry analysis, it is clear that we did not get the origin of SHG even after applying the o-HZO point group symmetry (mm2) and quadruple 4/m tetragonal point group.
In order to solve this issue, we tried a different approach [16]. In this method, Marvin *et al.* used the non-invasive optical SHG on La-substituted BiFeO₃ films. It is shown that a weak net in-plane polarization remains imprinted in the pristine films despite the apparent domain disorder. They test the functionality and the performance of capacitors by applying the electric-field training and performing ferroelectric fatigue tests and then they perform an operando study of the dynamics of the in-plane polarization component. We will use the same procedure to see if there is any polarization emergence during cycling. For these measurements, we deposited platinum electrodes of different thickness (measured using AFM shown in Fig.3.11d). The polarization loops were measured in top-top measured explained in Chpt.2.

For the SHG measurements, an amplified Ti:sapphire laser /optical parametric amplifier emitting 130 fs pulses with a repetition rate of 1KHz was used. For the experiments, a fundamental wavelength of 1300 nm (0.95 eV) is chosen. The polarization of the incoming fundamental light beam was rotated using a half -wave plate (polarizer). The polarization of the detected SHG light was selected with a Glan Taylor prism (analyzer). The SHG light was detected with a liquid - nitrogen-cooled CCD camera. For the SHG microscopy experiments, a long working distance microscope objective was used. All the measurements were performed in normal incidence geometry. Anisotropy scans were obtained by rotating the polarization of the fundamental light and of the projected polarization of the SHG light simultaneously in 10⁰ steps. The scans were repeated several time for each SHG measurement in order to get the more statistics. The experimental setup can be shown in the Fig.3.12 [Adapted from]



Figure 3.12. Schematic for SHG wake up effect measurements on HZO thin films. Adapted from [17]

For in situ electrical characterization of HZO thin film, the optical set up was connected to a ferroelectric tester via a function generator and voltage source as shown in Fig.3.13. So, we used the optical SHG setup to measure the response of a thin film during the cycling. The response of film depends on many factors such as direction of ferroelectric polarization, the setup geometry, the incoming laser wavelength, etc. We will discuss these factors in upcoming section.

After measuring the hysteresis loops (Fig.3.11a), we also measured the fatigue in an optical SHG setup keeping pulse width and pulse duration constant and try to find the best values of applied electric fields (Fig 3.13). We found that there was not much influence on fatigue with voltages, but we saw that higher voltage induce earlier breakthrough. So, we decided to keep a fixed voltage (16 V) for further measurements. Remember that the dP = Switching P (black curves) – Non-switching P (blue curves). Keeping the voltage fixed at 16 V, we changed the pulse width and duration and we found there was a remarkable effect of pulse width on fatigue. The shorter the pulse, the later the fatigue onset (Fig.3.13). At larger pulse width, we did not see any big change in the polarization but it affects the leakage current contribution and hence the breakthrough.



Figure 3.13. Fatigue measurements at different voltages.

The best results we found with pulse width of 1 μ s and 5 μ s PUND (pulse duration) and the remanent polarization always after cycling stays at 3-4 μ C/cm². During the measurements electrodes seems to be fairly stable against light pulses up to 3 μ J. Repeated electrical pulsing , especially with high pulses, seems to burn the electrode away.



Figure 3.14. Fatigue measurements at different pulse width and pulse duration keeping voltage constant.

Our final goal was to make an SHG anisotropy scan of the electrode before pulsing and then repeat the SHG anisotropy at every point of the fatigue measurement. By subtracting the SHG anisotropies of the fatigue test from the pristine (measured before), we expect the emergence of polarization. For these measurements, what we call operando SHG, we lapped the substrate and roughly removed 2 mm of STO in order to enhance transmission.

In the optical setup (Fig.3.11), we mount the sample and reproduced the electrical characterization and then we try to measure in transmission but we saw almost no SHG signal, then we rotated the sample and around 45[°] incidences angle we saw a very small signal. Therefore, every data point of a SHG anisotropy was averaged over 9500 laser pulses. Still, the Signal to Noise Ratio (SNR) was very bad. Thus, 10 SHG anisotropies were averaged and eventually we found double lobe peak maximum along 90° and 270°. i.e., along the normal direction, pointing to a predominant role of the surface contribution (Fig3.15). In Fig.3.15b, the black curve represents the SHG signal which can be extracted from the Fig.3.16a as:

$$\Delta = SHG \ signal \ at \ 0 \ pulses - SHG \ signal \ at \ 15 \ pulses \tag{3.1}$$

and same for the red circles (190 cycles) and green triangles (8440 cycles). This was done in order to see the cycling effect on polarization but we didn't see any response from the material (emergence of ferroelectric polarization).



Figure 3.15. Anisotropy of HZO thin film in optical set up at different cycles.

3.5 Discussions

These results suggest that the LSMO thickness has a dramatic effect on S-out curves (such as DS, PS, and SS in the ϕ -scan), which are on the other hand not affected by the HZO coverage. As for the P-out curves (PP and SP), the effect is negligible for SP, while it is quite strong for PP. We should not forget here that the LSMO coverage has a significant impact on the HZO ferroelectricity, [18] so that a layer of about 20 nm of LSMO is required to build an optimized FE HZO layer, whereas the 8 nm LSMO layer is not sufficient. Therefore, we conclude that the negligible increase in SP is due to the competition between two opposite tendencies: the onset of FE behavior in HZO is lowering the SP component according to Fig. 3.6, while the larger LSMO thickness tends to increase the signal. Regarding the PP component, its increase by roughly a factor 3 is the result of the larger LSMO thickness and the onset of FE in HZO together. The PP and SP components appear thus to be those more influenced by FE in HZO, but the mechanism through which it happens still remains to be clarified. Operando optical SHG measurements suggests either the polarization is out of plane or the wavelength we are using is not suitable for these experiments and we need to properly scan the sample in broad wavelength region (SHG spectroscopy). Possible explanations for the above doubtful behavior of HZO are ranging from a relatively simple electrostatic effect to the possible presence of oxygen migration [19] Particularly intriguing would be the possible interaction between the FE phase of HZO and the ferromagnetic phase of LSMO, similar to what was already reported in the case of lead zirconate titanate LSMO/PZT heterostructures, [20,21] where substantial changes in the transport and magnetic property of LSMO ultrathin films under the influence of ferroelectric polarization have been reported. Similar experiments on HZO/LSMO interfaces would be beneficial in order to explore this possibility. Recently, a theoretical approach has been carried out in which they showed ferroelectric phase of hafnia-related materials, potentially including field- and temperature-driven transitions. They also suggested that the introduction of an orthorhombic Pbcm centrosymmetric high-temperature phase would solve some inconsistencies of the Hafnia system and HZO should be considered a proper ferroelectric [22]. It is also important to mention that they couldn't solve the long-standing problems such as kinetic origin and ferroelectric switching in HZO. The switching of the FE polarization in HZO by applying an electric field while monitoring the iSHG response could, in principle, help to disentangle different possibilities. Although this idea presents some important experimental difficulties, it will be pursued certainly in the future. A more detailed analysis of the iSHG spectrum, phase, field effects, and temperature will help to shed light on the microscopic origin of the observed coupling.

3.6 References

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Chapter 4 Second Harmonic Generation on Germanium Telluride thin films (GeTe)

4.1 Introduction

Germanium telluride (GeTe) is a functional material with a range of unique properties. It is one of the most known material for its ability to change between crystalline and amorphous phases, which have different physical characteristics [1,2]. Both crystalline and amorphous phases of GeTe have been extensively studied through experiments and computational techniques [3,4]. GeTe is a polar material, which means that it has a net electrical polarization along a particular direction in the crystal. It is also a p-type semiconductor, meaning that it has a high concentration of holes (positive charge carriers) that give it a significant conductivity [5]. Ferroelectrics properties are unusual in highly doped semiconductors and in metals, since the screening is usually responsible for a non-polar nature of materials [6]. The co-existence of polar and metallic properties in GeTe gives rise to exotic phenomena such as the Rashba effect [7] and multiferroicity in magnetically doped GeTe systems [8].

4.2 Experimental section

4.2.1 Growth of GeTe and SnGeTe thin film

The main focus was to create and study ultra-thin film of the ternary alloy $Ge_xSn_{1-x}Te$ with varying levels of tin (Sn). In our case we grow GeTe and SnGeTe films for the studies of SHG. The growth and X-ray Photoelectron Spectroscopy (XPS) was done at Politecnico di Milano (Polimi) under the supervision of Prof. Christian Rinaldi. We will briefly describe the growth conditions and characterization here. It was found that the interdiffusion of Ge atoms into the SnTe matrix is significant when two layers of GeTe and SnTe are grown one in contact with the other, if the sample is annealed at temperatures above 520 K. Thus, the deposition of a bilayer and its subsequent interdiffusion of Ge and Sn. It was discovered that the doping of the surface layers can be controlled by adjusting the thickness of the deposited SnTe layer, for example, a thicker SnTe layer results in a lower concentration of Ge. One of the major benefits of growing similar crystal heterostructures is that it results in minimal lattice constant differences, which reduces crystal defects during the process. In the case of SnTe deposited onto GeTe, the mismatch is only about 4%, with lattice constants of $a_{GeTe} = 4.373$ Å and $a_{SnTe} = 4.537$ Å.

GeTe (24 nm) thin films were epitaxially grown by MBE on 5 cm × 5 cm sized Si(111) substrates (p-type B-doped, resistivity 1–10 Ω cm, miscut < 0.1°, 100 nm thermal oxide capping layer). The substrates were cleaned before loading them into the MBE system.

SnTe was grown on top of a 24nm thick GeTe film using molecular beam epitaxy (MBE) from a single crucible containing SnTe pellets. To achieve high crystal quality during growth, the deposition rate was kept low (about 2.4 Å/min) and the temperature of the sample should be

around 473 K. A higher substrate temperature improves the surface mobility of the deposited material, leading to higher crystal quality, but also increases the rate of desorption. Therefore, the optimal temperature for SnTe growth was 473 K. Additionally, the high concentration of Sn vacancies in the SnTe growth process also results in a p-doped character, allowing the dopants to fill the vacancies during the diffusion process. This process is pictorially shown in the Fig.4.1a.



Figure 4.1. (a) Epitaxial growth of SnGeTe thin film. (b) : XPS spectra of the $Sn_{1-x}Ge_xTe$ alloy.

XPS measurements were used to determine the concentrations of Te, Sn, and Ge in the alloy $Sn_{1-x}Ge_xTe$ as shown in Fig.4.1b. The spectra were collected at various photon energies and the peaks analyzed were the low binding energy peaks of Te4d, Sn4d, and Ge3d. The presence of the Sb4d peak in Fig.4.1b is a result of the mixing of a layer of antimony with the GeTe substrate on Si(111) during the process of Van der Waals epitaxy. This occurs during thermal annealing of the sample.

4.2.2 Linear spectra and XRD of GeTe and Silicon (111).

Fig.4.2a shows the X-ray diffraction (XRD) θ -2 θ -scans obtained by Panalytical X'Pert diffractometer. The XRD pattern collected with Cu K α radiation corresponds to the well-known rhombohedral structure. The highest peak at around 28.4^o corresponds to the (111) Bragg reflections of the silicon substrate [9] and the other two peaks at around 25.55^o and 52.04^o corresponds to the GeTe peaks [10]. For a basic optical sample characterization we use a microspectrophotometer (Jasco MSV-370) in which linear spectroscopy can be performed over a large spectral range starting in the ultraviolet regime at a wavelength of 190 nm up to the near-infrared with a wavelength of 2500 nm. The micro-spectrometer can perform both in transmission as well as in reflection geometry. For GeTe thin film, we used transmission geometry and the results are shown in Fig.4.2b. The curve in blue drops abruptly at around 1100 nm corresponds to the band gap of Si (111) [11]. The drop in case of GeTe (pink curve) is earlier than Si and its around 1750 nm (~0.70 eV), corresponds to the band gap of GeTe.



Figure 4.2. (a) XRD of GeTe thin film (b) Linear spectroscopy of Silicon and GeTe.

4.3 Experimental setup

The layout of SHG setup is shown in Fig.4.3. We used light pulses from Optical Parametric Amplifier (OPA) pumped by a Ti:Saphire laser amplifier system (central wavelength 800 nm, pulse width \approx 120 fs, repetition rate 1 kHz and average power 8W). The beam spot size is approximately 100 micrometers in diameter, and the energy per pulse is around 2-3 microjoules. These values are considered weak enough to not significantly affect the fundamental properties of the thin films. The measurements were performed with a fundamental wavelength of 1000 nm. The laser light passed through a variable neutral density filter, a linear polarizer, and a halfwave plate, reflected by a metallic mirror, and focused by a lens onto the sample. Anisotropy measurements were obtained by simultaneously rotating both polarizer and analyzer over 360°. The angle between polarizer and analyzer was fixed at 0° or 90°.

Fig.4.4 shows the sketch of the SHG normal reflection geometry used in all our measurements. Although, we vary the incident angle (θ) depending upon the experiment we were doing, e.g. In case of temperature scans, the incident angle was around 3^o and in SHG imaging measurements it was around 15^o. For heating measurements, a heating/cooling stage (Linkiam THMS 600) was used in reflection geometry. We changed the temperature with different rates (1K/min, 3K/min, 5K/min) and measured the corresponding SHG signal with different polarizer/analyzer angles in order to rule out possible artifacts and/or systematic errors. It should be also noted that some of the heating experimemts were done under different gas atmosphere such as helium and nitrogen. This was done to avoid the oxidation of film in air atmospherse.







Figure 4.4. Sketch of normal reflection SHG geometry.

4.4 Experimental results

4.4.1 Prerequisites to be SHG active

To verify that a signal is truly from SHG, several protocols are followed. The first step is to check the spectral dependence, which should have a peak at 2ω with a width determined by the incident light's bandwidth. This is done by scanning a monochromator at a fixed wavelength of the fundamental light. Next, the intensity dependence is checked, which should scale quadratically with the incident pulse energy. This is done by measuring the SHG intensity using a GeTe thin film as a reference, with a fundamental wavelength of 1000 nm and a monochromator fixed at 500 nm. The measurement is done in normal reflection geometry using a polarizer and analyzer set to 0^0 and a potential applied across a PMT was 2kV. The output SHG intensity should be proportional to the square of the input laser power, $I(2\omega) \propto I^2(\omega)$. This was done several times in order to get more statistics.



Figure 4.5. SHG verification tests. (a) SHG power dependence (black squares) and the expected quadratic curve (blue line). (b) Scanning of the monochromator grating for a fixed incident wavelength $\lambda\omega$ (in our it was 1000 nm) results in a peak at $\lambda\omega/2$ (500 nm) that has a typical full width at half maximum of about 20 nm.

4.4.2 SHG vs Wavelength

We also perform some anisotropy scans at different incoming wavelengths in order to find the maximum signal. We used the normal reflection geometry as shown in Fig.4.4. GeTe was chosen as a reference. We choose four different incoming wavelengths to measure SHG. The polarizer and analyzer was fixed at 0^o (Parallel). By rotating both, we measure the SHG response from the film and we found the signal at 1000 nm was maximum (Fig.4.6, red curve) so we choose this wavelength for further measurements. The signal at 1100 nm was small and we have to multiply it by some factor in order to see it on the graph.



Figure 4.6. SHG Anisotropy at different wavelengths.

4.4.3 SHG dependence on incidence angle



Figure 4.7. (a) SHG dependence on angle of incidence. (b) SHG spectra at corresponding incident angles.

We also measured the SHG response as a function of incidence angle to find the direction of ferroelectric polarization in thin film. Fig.4.7a represents the SHG signal as a function of incident angle and it can be seen that as we increase the angle SHG signal also increased. It is a common fact that more we increase the incident angle more tensor components will be seen by incoming light hence more SHG. Moreover, it also gives us an idea about the direction of ferroelectric polarization. If this direction is out of plane with respect to the crystal surface, the SHG signal should be zero in case of perfect normal reflection and once we increase the angle, SHG should also increase. Fig.4.7b represents the SHG spectra at corresponding incident angles and the shift in SHG peak is due to the artifact in the apparatus and it could be, the beam hitting the monochromator opening was not perfectly aligned when we changed the incident angle.



4.4.4 Comparative SHG results of GeTe and Si (111)

Figure 4.8. SHG signal from GeTe and Silicon.

The SHG anisotropy from both the GeTe and Si (111) was measured in order to find the strength of the signal. As we know GeTe has rhombohedral structure and possess 3m point symmetry and the response of GeTe is shown in Fig.4.8a in which black squares are data points and red curve only represent the points but not the fitting formula. (Symmetry analysis is explained in section 4.6). Fig.4.8b presents the SHG anisotropy of Si (111) and the six lobes corresponds to the surface contribution to SHG [12]. We should emphasize here that the signal from the GeTe film was around 30 times stronger that of the substrate as shown by black arrow in Fig4.8b which is direct proof that the SHG signal in Fig4.8a was coming only from the GeTe film.



4.4.5 Temperature dependent SHG

Figure 4.9. Temperature scans of (a) GeTe and (b) Silicon.

We compare the temperature dependent SHG signal both from the sample and substrate as shown in Fig. 4.9. It can be seen that the Si (111) SHG signal is extremely small as compared to the signal from GeTe.

GeTe undergoes a ferroelectric phase transition from the low temperature rhombohedral structure α -GeTe (space group R3m) to cubic structure β -GeTe (space group Fm3m) at the critical temperature (Tc) around 700 K [13]. In our measurements in case of pure GeTe, the phase transition is quite sharp (Fig.4.9), possibly indicating a first order phase transition [14]. For comparison, we have measured the SHG signal of the Silicon Si(111) substrate (blue triangles), pure and doped GeTe as shown in the Fig.4.10a. There is a striking qualitative



Figure 4.10.(a) SHG vs Temperature for doped GeTe (red dots), Pure GeTe (black squares) and substrate (blue triangles). (b) Polarization anisotropy of Pure GeTe and doped GeTe are shown by black and red circles respectively. (Circles represent data points, solid lines represent best fit curves according to the 3m point group).

difference, as the signal slightly increases over the investigated temperature range in case of Si (111).

We started from measuring the anisotropy curve of GeTe thin films to confirm the rhombohedral phase at room temperature (Fig.4.10b) and we found six lobes at about 60°, confirming the polar 3m point group. It is very interesting to observe that the presence of Sn-doping seems to significantly introduce stress/strain in the system, as shown by the peculiar shape of the anisotropy curve of the doped samples (red circles). Once sure that the SHG signal displays the correct symmetry, we accessed the phase transition by measuring the temperature dependence of SHG as shown in Fig.4.10a. We found a sharp decrease in the SHG signal, corresponding the phase transition of GeTe at 711K (black squares). Doped GeTe (red dots) display a 6 times lower signal and a transition at lower critical temperature 505 K. In addition, the SHG yield is more than 30 times lower in Silicon, the reason being that it is centro-symmetric and therefore it shows no SHG from the bulk, only from the surface where the centrosymmetry is naturally broken.

4.5 SHG Imaging

Finally, to visualize possible ferroelectric domains we did SHG imaging at room temperature. All the measurements were done at quasi normal incidence (reflection) with an incidence angle of 15^{0} . The SHG signal was imaged by means of a liquid nitrogen cooled CCD. The fundamental wavelength was chosen 1000 nm and the average laser power was around 3 mW. A long working distance (2 cm) microscope objective was used having spatial resolution of around 1-2 μ m. Fig.4.11 (a) and (b) shows the SHG image of GeTe and SnGeTe, respectively. It can be seen that the ferroelectric domains are in nanometer size and are difficult to resolve with the optical microscopy. The corresponding anisotropy was measured with CCD keeping polarizer and analyzer parallel to each other and by rotating both with interval of 10^{0} we measured the

anisotropy. It clearly shows the six-fold pattern confirming the 3m point group symmetry of the material.



Figure 4.11. (a) and (b) SHG image of GeTe and SnGeTe respectively and (c) and (d) the corresponding anisotropy measured with CCD.

4.6 Discussion

GeTe is polar metal, which means that it has a non-zero dipole moment and metallic conductivity. The are a few reports where they used PFM and electric pulsing through metallic gate to switch the polarization in GeTe [17]. We used SHG to study the pure and doped GeTe. We also compare the SHG signal from silicon with the sample. It was found that the signal from silicon substrate was very weak as compared to GeTe because in the earlier case it was mainly coming from the surface. SHG imaging suggests ferroelectric domains are nanosized. This was well expected as the size of domains in ferroelectrics is usually comparable to their thickness [15]. We also measured the temperature dependent SHG and it can be seen in the Fig.4.10 that with **increasing concentration of Ge, Curie temperature can be altered**. In case of pure GeTe, T_c is approximately 711 K and it fits well with plot shown in Fig.4.12. Although, in case of doped GeTe, we saw a little shift from the predicted value.



Figure 4.12. Variation of Curie temperature with respect to the Ge concentration in SnGeTe alloy [16].

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PART B

Chapter 5 Terahertz Time Domain spectroscopy (THz-TDS) studies on diatoms

5.1 Introduction

The term "terahertz" (THz) refers to a unit of frequency used for the electromagnetic radiation, with 1 THz equaling 10¹² Hz. The THz range, which spans from 0.1 to 30 THz, lies between the microwave and infrared portions of the electromagnetic spectrum. In the past, this spectral range was known as the "THz gap" because of the lack of effective emitters and detectors [1,2]. However, with the development of advanced technologies, it is now possible to generate and detect continuous and pulsed coherent THz radiation, enabling the use of THz spectroscopy with sub picosecond THz pulses. This form of spectroscopy began to emerge in the 1980s thanks to the availability of intense femtosecond laser sources [3,4], and has since been further developed using techniques such as optical rectification [4] in nonlinear crystals and transient photocurrents in photoconductive antennas [5].

THz radiation, with its photon energy ranging from approximately 1 to 100 meV, has a strong interaction with physical processes that have lifetimes in the picosecond range and energy in the meV range. Examples of such processes and systems include phonons in crystalline solids [6], relaxation dynamics in aqueous liquids [7], weakly bonded molecular crystals [8,9], transient molecular dipoles [10], excitons [11], bound electrical charges [12], free charge plasmas [13], and more. These interactions can provide valuable insights into the properties and behavior of these systems, making THz spectroscopy a useful tool for studying a wide range of phenomena.

5.2 Diatoms

Diatoms are small, eukaryotic phytoplankton that carry out about one-fifth of the photosynthesis on Earth [14]. They can be found in waters worldwide where there is enough light and nutrients. Diatoms get their name from the Greek word "diatomos," meaning "cut in half," referring to their cell walls, which are made of silica and consist of two parts that fit together like a box. These cell walls are called frustules. Diatoms are important for the aquatic food chain and are used to monitor environmental conditions in various settings. Diatoms are a type of algae that are found in a wide range of aquatic environments, including oceans, rivers, and lakes. Diatoms are important members of the aquatic food chain, serving as a major source of food for many small aquatic animals. They are also important indicators of water quality and are used to monitor environmental conditions in a variety of settings. For example, changes in the types and abundance of diatoms present in a body of water can indicate changes in water quality, such as the presence of pollution or the effects of climate change. In addition to their ecological importance, diatoms have also been used for a variety of practical purposes.

Diatoms, which are a type of photosynthesizing microorganism found in the sea, play a vital role in the global carbon cycle. Each year, diatom photosynthesis generates a significant amount of

organic carbon, which is equivalent to the amount produced by all terrestrial rainforests combined [15]. This organic carbon is rapidly consumed and serves as a base for marine food webs, particularly in coastal waters where diatoms support some of the most productive fisheries. In the open ocean, a portion of the organic matter produced by diatoms sinks rapidly to deeper waters and becomes food for deep-water organisms [16]. A small fraction of this sinking organic matter is not consumed and instead settles on the sea floor, where it is eventually sequestered in sediments and rocks and contributes to the formation of petroleum reserves over geological timescales. Due to the importance of diatoms in the carbon cycle, there have been plans to intentionally fertilize certain areas of the ocean with iron in order to stimulate the growth of diatoms, with the goal of reducing atmospheric levels of carbon dioxide, a greenhouse gas that contributes to climate change [17]. However, this approach has been controversial.

Human activities such as climate change, eutrophication, and pollution are having an increasingly negative impact on the global marine environment [18]. Pollution, in particular, can have serious consequences for aquatic environments and the organisms that live there. Heavy metals are a type of pollutant that pose a significant threat because they are nondegradable elements that accumulate in water and soil, and they are present in many industrial, civil, and agricultural discharges [19,20]. Some heavy metals are essential for biological processes [21,22], but they can become toxic at high concentrations and cause damage to cells and their metabolism [23]. Exposure to heavy metals can affect the physiological state of microalgae, leading to changes in silicon metabolism [24], damage to the photosynthetic apparatus [25-27], alterations in cell and organelle morphology [28], and the production of oxidative stress [29].

5.3 Generation of THz

The THz frequency range was one of the least studied areas of the electromagnetic spectrum due to the challenges in generating and detecting THz radiation. In the 1980s, photoconductive antennas were commonly used for both generation and detection of THz radiation [30]. However, in recent years, various techniques have been developed for generating and detecting THz radiation. These methods, include photoconductive antennas [31], electro-optic materials such as ZnTe [32] and LiNbO₃ [33] and through the generation of plasma in air [34]. THz emission from gas plasma using femtosecond lasers has become an active area of research due to the high peak THz electric field strength and broad bandwidth that can be achieved. There are three primary methods for generating THz radiation from laser-induced plasma in gases:

- 1. Single-wavelength optical excitation: This method involves using a single-wavelength beam to create gas plasma and generate THz waves through the ponderomotive force.
- 2. Two-color mixing: This method involves focusing a fundamental beam (ω) through a thin beta barium borate (BBO) crystal to generate a second harmonic beam (2ω), which is then mixed with the residual fundamental beam in the gas plasma to generate THz radiation.

3. Dichroic mirror: This method involves using a dichroic mirror to combine the fundamental and second harmonic beams to generate THz radiation. All the three methods can be shown below in Fig.5.1.



Figure 5.1. Schematic illustration of three schemes for THz wave generation in gases [35]

Hamster *et al.* [34] was the first to demonstrate the generation of THz radiation from a onecolor photoinduced plasma in gaseous media. Using a femtosecond pulse with an energy of a few tens of microjoules, it is possible to reach the threshold intensity for ionizing gas molecules, resulting in the formation of plasma. This plasma can emit frequencies in the THz range through the mechanism of ponderomotive forces. In this thesis, in particular, we used the method defined in Fig.5.1b. THz radiation from air involves the nonlinear interaction of the fundamental and second harmonic beams in a laser-generated plasma in air. This process involves strong field ionization, plasma dynamics, and nonlinear optics propagation. This is a two-color femtosecond laser mixing effect which can be explained as a Four Wave Mixing (FWM) process:

$$E_{THZ} \propto \chi^{(3)} E_{\omega} E_{\omega} E_{2\omega} \tag{5.1}$$

where E_{THz} , E_{ω} and $E_{2\omega}$ are the THz, the fundamental and the second harmonic electric field respectively and $\chi^{(3)}$ is an effective third-order nonlinear susceptibility of the plasma filament.

There are two main models that have been proposed to explain the generation of THz radiation from plasma: the four-wave mixing (FWM) model and the asymmetric transient current (ATC) model. However, neither of these models can fully explain experimental observations, such as the origin of the third-order nonlinearity, the threshold behavior, and the phase dependencies of the THz emission efficiency. For example, the FWM model cannot explain the phase dependencies of the THz emission efficiency, and the ATC model cannot explain the threshold behavior. Additionally, the phase matching conditions for maximum THz intensity are different in the two models: in the FWM model, the maximum THz intensity is achieved when the phase

matching between the fundamental beam and its second harmonic is zero, while in the ATC model, the relative phase for maximum THz emission is $\pi/2$ [36].

While the phenomenological model described above can explain many of the key features of THz emission from gas plasma, the physical origins and effective magnitude of the third-order nonlinearity ($\chi^{(3)}$) are still the subject of intense debate. There is also debate about the role of higher-order nonlinear contributions in THz generation [37]. In 2007, Kim *et al.* [38] proposed the asymmetric photocurrent model as a theoretical framework for more accurately describing the broadband THz emission from two-color femtosecond laser-induced air plasma. According to this model, gas molecules experience tunnel ionization in the presence of strong two-color laser fields, resulting in the formation of a plasma filament and the emission of THz radiation through the successive acceleration of free electrons under the influence of temporally asymmetric laser field oscillations.



5.4 Detection of THz (Electro-optic sampling)

Figure 5.2. THz detection using balanced detection method.

Electro-optic sampling (EOS) is a technique that uses the electro-optic effect to measure the electric field strength of electromagnetic waves, such as terahertz (THz) radiation. The electro-optic effect refers to the change in the refractive index of a material when an electric field is applied to it. In EOS, a sample of the electromagnetic wave is passed through a crystal that exhibits the electro-optic effect, and the resulting change in the refractive index of the crystal is measured.

In Fig.5.2, a THz pulse is generated and passed through a crystal that exhibits the electro-optic effect. Electric field of the THz pulse causes a change in the refractive index of the crystal. This change in the refractive index can be measured using a detector.

The detector is typically a photodetector, which measures the intensity of a probe beam that is passed through the crystal. The probe beam is typically a pulsed laser beam with a wavelength that is different from the THz pulse. The intensity of the probe beam is modulated by the change in the refractive index of the crystal, which is proportional to the electric field strength of the THz pulse.

To quantify the electric field strength of the THz pulse, the change in the refractive index of the crystal is measured using a lock-in amplifier or signal integrator, which is synchronized to the THz pulse. The lock-in amplifier measures the amplitude of the modulated signal at the frequency of the THz pulse, and the electric field strength can be calculated using the equation:

$$E = (n - n_0) P$$
 (5.2)

where E is the electric field strength of the THz pulse, n is the refractive index of the crystal after the THz pulse has passed through it, n_0 is the refractive index of the crystal without the THz pulse, and P is the Pockels coefficient of the crystal. The Pockels coefficient is a material-specific constant that describes the sensitivity of the crystal to the applied electric field.

5.5 Terahertz Time Domain Spectroscopy

Terahertz time-domain spectroscopy (THz-TDS) is a spectroscopic technique used to measure the absorption and transmission of electromagnetic radiation in the THz frequency range, which is between microwaves and infrared radiation in the electromagnetic spectrum. THz-TDS uses ultrafast lasers to generate short pulses of THz radiation, which are then sent through a sample and detected on the other side. By analyzing the time delay and intensity of the THz pulse as it passes through the sample, it is possible to determine the absorption and transmission characteristics of the material at different THz frequencies. THz-TDS has a number of applications, including characterizing the dielectric properties of materials [39], detecting trace chemicals and explosives [40], and imaging biological tissues [41]. It is also used in the development and testing of THz communications [42] and imaging technologies [43].

There are several ways to conduct THz-TDS, including through transmission, reflection, and attenuated total reflection (ATR). In a reflection configuration, the reference signal can be obtained by using a reflector such as a dielectric or metallic surface, or by attaching a window to the sample. The THz beam reflected by the front surface of the window can be used as the reference signal, while the THz reflected from the interface between the sample and the window can be used as the sample signal. Researchers have used these techniques to measure the complex conductivity of materials such as n-type GaAs and n-type Si wafers, and to investigate the temperature-dependent far-infrared spectrum of water [44,45]. In crystalline materials, the THz properties are determined by the long-range order of the atoms, while in polar liquids, the THz spectrum is dominated by the relaxation of permanent dipoles. In nonpolar liquids, THz-TDS can be used to investigate the collision-induced dipole moments [46]. THz-TDS has seen significant developments in the last 20 years, but there is still room for improvement in terms of spectral resolution and spectral range. In the near future, THz-TDS technology is expected to

be a powerful tool for studying ultrafast phenomena in a wide range of scientific fields, including physics, chemistry, and biology. At the same time, the decreasing cost of lasers, the development of more efficient THz emitters and detectors, and the advancement of compact and advanced optical design are expected to increase the commercial potential of THz-TDS technology [47].

5.6 Experimental setup

The experimental set up used for the generation and detection of THz is shown in Fig.5.3. The femtosecond laser is a Ti:Sa mode-locked seed laser, amplified by a regenerative cavity. The fs-laser pulse, after passing through the beam splitter, is divided into a Pump (transmitted) pulse and a Probe pulse (about 10% of total power). The Pump is chopped by a mechanical chopper



Figure 5.3. Experimental setup of THz-TDS.

locked to half of the laser trigger frequency in order to block every second pulse. The pulse train chopping is very important because it allows measuring the difference between THz-ON and THz-OFF signals, as it will be further explained in the following. The pulse is then sent on a nonlinear optical crystal (Beta Barium Borate, β -BBO) where about 20% of the optical power is converted in SHG and then both fundamental and doubled pulses are focused on air by an achromatic doublet. In the plasma filament, usually about 1 cm long, the generated plasma is producing THz pulses via four-waves mixing processes in which the maximum THz amplitude depends on relative phase between the fundamental and second harmonic light [20]. The Probe is sent to a delay stage in order to introduce a controllable delay between Pump and Probe pulses and then it is incident on the detection crystal (usually ZnTe, GaSe or GaP, or just air for ABCD technique) together with the THz pulse in a collinear geometry, through a hole in the last

parabolic mirror. In the detection crystal the polarization state of the optical pulse is altered by the presence of a transient birefringence created by the THz electric field, and this change can be detected by separating two orthogonal polarizations of the pulse with a Wollaston Prism and measuring their signal difference in a balanced photodiode. As the delay between the two pulses is adjusted, the amplitude of the THz pulse can be sampled in time, and the full THz waveform can be reconstructed. In a standard THz-TDS experiment, the sample will be placed in the first focus (f1) of the parabolic mirror and the detection crystal is placed in the second focus (f2), to measure the THz waveform transmitted through the sample. The complex transmission coefficient is then obtained by measuring the signal without the sample in place, as an estimate of the incoming electromagnetic wave, and finally the complex ratio between the Fourier Transforms of those two measurements will deliver the complex transmission coefficient spectrum.

5.7 TeraVision: a LabVIEW software for THz Hyper-Raman Spectroscopy

In order to retrieve the data from the experimental setup, we wrote a code "TeraVision" in LabVIEW environment. The TeraVision software is designed to perform four types of measurements: 1) time-dependent THz-TDS, 2) time and wavelength-dependent THYR, 3) wavelength-only spectrum, and 4) input/output polarization-dependent signal anisotropy. These measurements can be performed with or without a THz pulse applied to the sample. In addition, the software includes features for optimizing the signal, monitoring the performance of the delay stage, and observing real-time scans of the signal on the screen with a large noise. The software also includes a signal-channel monitor that displays the actual values of each channel of the DAQ before averaging. Finally, the software can be used to manually measure the signal as a function of any variable that is not controlled by the software, such as temperature, external electric, or magnetic fields, etc. This reading can only be done by comparing the THz-ON and THz-OFF pulses, as the signal is revealed as the difference between these two pulse trains.

The TeraVision software is designed to manage the creation of folders and data files for saving experimental results, and it includes an initialization procedure that collects data from all devices to set safety limits and ensure that all parameters are within a safe range. It also rounds every value to the minimum time/angle/wavelength resolution to avoid overlap between subsequent points. The software automatically numbers measurement files incrementally to ensure that two runs with the same parameters and names are stored in different files, which can be saved or deleted at the end of each run according to the user's command. The software also includes a feature that rings a bell to alert the user when the measurement is finished but stops ringing as soon as the mouse is moved or a key is pressed. This allows the user to focus on other tasks while the measurement is running, without losing any time at the end of each run. The overall goal of the TeraVision software is to make measurements more efficient and convenient by eliminating unnecessary tasks and allowing the user to focus on the measurement itself.

The TeraVision software produces three separate files for each measurement: a large data file with every single point of every scan saved before averaging, a short data file with only the average of all points and scans saved, and an image file with a summary of the measurement including graphs and relevant parameters and comments by the user. This allows the user to quickly find the information they are looking for, easily analyze the averaged data, and also



Figure 5.4. TeraVision front panel

perform a detailed analysis of individual points if necessary while maintaining the full information content of the measurement. The data files are saved point-by-point during the run to prevent data loss due to system crashes, electrical outages, or other unforeseen problems. Fig.5.4 shows the front panel of the TeraVision software. The upper line of the panel includes the software name and version, as well as a Quit button that initiates the correct quitting procedure for the software. If the user quits the software in any other way, they will need to manually close all ports used by the program and all set parameters from the current session will be lost, with the software loading the previously saved parameters at the next startup. The front panel has two main sections: a central Tab panel, which is the core of the software, and a lateral column that is always displayed for any selected Tab. The explanation of each tab in explained in annexture A5.

5.8 Materials and methods

5.8.1 Sample preparation

The marine diatoms Skeletonema pseudocostatum were collected from the Sarno River mouth in Naples, Italy using the capillary pipette method [48] and identified using 18s and 28s rDNA genes which has been previously reported [49,50]. The microalgae (initial concentration: 900,000 cells/mL) were maintained in an f/2 medium [51] prepared with sterile, filtered (0.22 μ m), natural seawater collected from the oligotrophic areas of the Gulf of Naples. The diatoms were exposed to 0 ('control' sample), 10, or 100 μ M of copper. In the latter two cases, the copper concentration was obtained by dissolving appropriate amounts of copper sulfate pentahydrate in the culture medium. The concentration of living diatoms in the samples was determined using a Bürker chamber [52] and each experiment was repeated three times. After adding metals to the culture medium, 10 mL samples of each sample were taken for THz absorption spectra analysis. A 10 mL aliquot of the culture medium was also used as a reference for THz measurements.

5.8.2 THz-TDS experiment

A femtosecond laser (Coherent Legend) was used to generate THz pulses through a process called four-wave mixing. The laser had a central wavelength of approximately 800 nm and a bandwidth (full width at half maximum) of approximately 80 nm. A portion of the laser beam was focused through a lens and then passed through a nonlinear crystal (beta-barium borate) where it was converted into its second harmonic. At the focal point, these intense beams created a plasma through the ionization of air, which generated broadband and ultrashort THz pulses. The THz pulse's bandwidth was limited by the laser's bandwidth, with the highest generated frequency being 40 THz. The remaining, less intense portion of the laser beam was sent to an adjustable delay line and used to probe the generated THz pulse in time using the electro-optic effect in a crystal (LAPC) [53] for coherent detection of the THz electric field (amplitude and phase) up to 10 THz.

The spectrometer is closed in a chamber filled with high-purity (99.999%) nitrogen when collecting the time domain signal. A diagram of our THz spectrometer is reported in Fig. 5.5, while in Fig. 5.6 an example of power spectrum of a THz pulse propagating in nitrogen and detected by EO sampling in LAPC is reported in logarithm scale. Note that the signal is rather good well beyond 6 THz. However, both the silicon-windows of the sample holder and the water absorption strongly reduce the transmitted signal, so that the signal-to-noise ratio is good only up to 6 THz. Liquid samples are placed in a homemade variable-path cell with silicon access windows. Silicon is used because it has a good and flat transmission up to 20 THz. The cell path can be continuously varied from 1 mm down to few microns with an average step of about 14 µm. For technical reasons, the ruler ticks are not equally spaced. However, each step is finely calibrated by measuring the temporal delay from the main pulse of the THz pulse replica transmitted after reflections from the two air-silicon interfaces internal to the empty cell. Then,

we measure the THz pulses transmitted through the liquid samples for different thicknesses (Appendix A3).



Figure 5.5. Experimental setup used in the generation and detection of the THz.



Figure 5.6. THz EO-detection with LAPC. The FFT spectrum is shown in the main panel and the pulse temporal profile is shown in the inset.

5.9 Results

In the main panel of Figure 5.7, the THz absorption spectra of SBCM (blue curve) and SBCM with diatoms (red curve) are reported. We indicated these samples as 'baseline' and 'control' samples, respectively. In the inset of the figure, the corresponding refractive indices are shown too. The faded areas represent the measurement of statistical errors at a confidence level of 66% (one σ). It is worth noting that the curves became more oscillating and the shaded areas larger at the highest frequencies due to an overall decrease in the signal-to-noise ratio. These oscillations introduced peaked structures in the absorption spectra that were unphysical for liquid samples. Therefore, in the highest frequency portion of the spectra, we applied a spatially variant moving average filter, analogous to the one proposed by Pupeza et al. [54]. The absorption coefficient in the "control" sample was higher than the "baseline" sample across the entire frequency range, with the exception of around 4.2 THz where the two samples showed overlapping results. In the frequency range of 0.5 to 5 THz, the absorption increase was particularly strong, with an absorption "excess" of about 30% at 2 THz. The corresponding refractive index spectra showed only small deviations within the error bars, indicating that THz absorption spectra are sensitive to the presence of diatoms in SBCM, but refractive index spectra are not. These results demonstrate that THz absorption spectroscopy can be used to detect diatoms in aqueous environments.



Figure 5.7. The THz absorption spectra of SBCM (blue curve) and diatoms in SBCM (red curve). In the inset, the corresponding refractive indexes are shown. The shaded areas indicate the measurement statistical error with a confidence level of 66% (one σ). The shade areas overlap with the marker size up to 3.5 THz. On the upper x-axis we report the light wavenumber in cm⁻¹.

Therefore, in the following, we will focus our attention mainly on the absorption spectra. We note that the initial cell concentration (900,000 cells/mL) used in this work is much higher than those found in nature, but the main goal of this work is to validate a new methodology to detect diatoms and the copper-induced effects on them in real-time, rather than mimicking what happens in their natural environments. However, the large absorption enhancement we have measured showed that detecting lower densities of diatoms is highly feasible. This will be assessed in future experiments. Moreover, the 'matrix' effect mentioned before appears at sufficiently high concentrations. Therefore, the use of high concentrations allows us to find possible signatures of this effect in the THz spectra. Now, let us turn our attention to the variation of the absorption spectra when the samples are doped with pentahydrate copper sulfate (CuSO₄). In this study, we used two different concentrations of copper: 10 and 100 μ M. To compare the different samples, we introduced a new parameter that measures the absorption variation compared to the 'baseline' spectrum, i.e., $\Delta \alpha = \alpha$ sample – α baseline, where sample stands for 'control,' '10 μ M', or '100 μ M'. A sample displays an absorption 'excess' or 'defect' when $\Delta \alpha$ is positive or negative, respectively.



Figure 5.8. THz absorption variation as compared to the 'baseline' spectrum for diatom in SBCM, undoped (red line) and doped (green and purple lines). The dot-dashed blue line represents the zero level.

The absorption variation $\Delta \alpha$ for the three samples is shown in Fig.5.8. In accordance with the previous observation, the 'control' sample demonstrated an absorption 'excess' over almost the whole frequency range. Although in a range where fluctuations became stronger, we observed a significant peak of $\Delta \alpha$ around 5 THz. In both samples doped with copper there was an evident

reduction of $\Delta \alpha$ compared to the 'control' sample over the full frequency range, except for the region around 4.2 THz where the three curves almost overlapped with the zero level (blue dashed line). The graphs of $\Delta \alpha$ for the two concentrations strongly overlapped, indicating that starting from a concentration of 10 μ M the effect of the metal doping on the reduction of the absorption 'excess' had already saturated. In future research, it would be interesting to use lower concentrations to verify the existence of a trend in the reduction of $\Delta \alpha$ as a function of the concentration.

5.10 Discussion

One of the main findings of this work is the ability of THz-TDS to detect the presence of diatoms in aqueous solutions. To the best of our knowledge, this is the first time THz-TDS has been used to study living diatoms in a complex aqueous medium that mimics their natural environment. This was not a given, as it is often difficult to extract information on solutes dissolved in aqueous solutions due to the strong absorption of water in the THz range. For example, the absorption coefficient of most dried biomolecules is around 10 cm⁻¹ at 1 THz, while the absorption coefficient of liquid water at the same frequency is around 200 cm⁻¹. This leads to the question: what is the source of the observed "absorption excess" in Fig.5.7?

If water and its solute do not interact, the THz spectrum of the solution will be similar to that of pure water, with a decrease in the overall absorption coefficient due to the replacement of water volume by the less absorptive solute (known as the "volume-displacement" effect). This decrease in absorption becomes more significant as the solute concentration increases. However, research on proteins in water has often observed a different result, an 'excess' of the absorption in the THz range [55]. This effect has been ascribed to the formation of a 'hydration shell' around the solute that may extend for several molecular layers. The water molecules in this 'hydration shell' behave differently from those in the bulk, displaying a dynamic that may be both faster or slower than that in the bulk. This dynamic strongly depends on the nature of the solute–water interaction and hence, under some circumstances, the 'hydration shell' can become an indirect probe of the solute behavior [56].

The observed absorption enhancement in our samples, which contained unicellular microorganisms known as diatoms, was much larger than in previous research on proteins in water. This is likely due to the complexity of the diatoms, which are significantly larger than single proteins and have intracellular organelles and compartments where water molecules can be strongly confined. These water molecules behave differently from bulk water, similar to molecules in the hydration shell [57,58]. In addition to the complexity of the diatoms, we must also consider the "matrix" effect, in which diatom-diatom interactions mediated by water molecules can lead to a structural reorganization of the hydrogen bond network and an enhancement of specific collective vibrational modes in the THz range. In literature, all these forms of water that in biosystems behave differently from the bulk water are named 'biological water' [58]. At this stage, we are not able to weigh the specific contribution of all these effects, i.e., hydration shell, confined water, or 'matrix' water. However, it is clear that only the presence

in our system of 'biological water' could explain the observed absorption 'excess.' The latter is strongly influenced by the water- diatom and diatom-diatom interactions. Therefore, our THz absorption spectra carried information on these interactions and hence on the diatom viability.

When copper was added to our solutions, we observed a significant reduction in the absorption excess across the entire frequency range, with a residual enhancement of absorption around 4 THz. The addition of copper sulfate at the low concentrations used in this experiment is unlikely to have affected the spectra of SBCM through volume displacement, due to the small ion volume and low copper molar attenuation [59]. Therefore, the observed reduction of the absorption excess in the doped samples is likely due to the effect of metal doping on the diatoms, causing a disturbance of the "biological water" in the doped samples. Our results also showed that THz-TDS can detect structural changes in diatoms that are still alive but whose functionality has been affected by the toxic effects of metals. While the first spectrum was recorded a few hours after sample preparation due to logistical reasons, it is possible to monitor diatom viability almost in real-time with a single measurement taking less than one minute. We plan to explore this possibility in future experiments. Despite the large statistical fluctuations at higher frequencies, we observed that in the portion of the spectrum above 4.5 THz, $\Delta \alpha$ was almost zero, thus here the spectra of doped samples perfectly overlapped with that of SBCM. This must be compared with the peak of $\Delta \alpha$ observed in the 'control' sample. We highlighted that in pure water this part of the spectrum was largely influenced by the HB stretching modes [60]. Therefore, our results suggest that the diatoms poisoned by the metal were no more able to maintain the HB structure with a consequent loss of the spectral weight associated with these vibrational modes. This point deserves to be explored more in the future from both an experimental point of view, by increasing the signal-to-noise ratio at the highest frequencies, and from a theoretical point of view to single out the contributions to the THz spectrum of specific collective vibrational modes. The theoretical model for absorption coefficient is explained in Appendix A4.

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Conclusion and future perspective Part A:

HZO being a well-studied ferroelectric materials still needs a better understanding of origin of ferroelectricity. The mechanism behind the unusual ferroelectricity in HZO, ranging from an electrostatic effect to possible oxygen migration and interaction between the FE phase of HZO and ferromagnetic phase of LSMO. Further experiments, such as switching the FE polarization of HZO with an electric field and analyzing the iSHG response, could help clarify the origin. A detailed analysis of the iSHG spectrum, phase, field effects, and temperature would also provide insight. It should be important to mention that for field effects measurements, we have already started measuring thin films with different HZO coverage (5.6, 8.6,11, 22, 44 nm) but keeping the LSMO constant (5.5 nm). The preliminary measurements suggested some correlation between the Curie temperature (T_c), magnetic coercive field (H_c) and film thickness but for better understanding we need to further analyze the data.

Operando optical SHG measurements suggests either the polarization is out of plane or the wavelength we are using is not suitable for these experiments and we need to properly scan the sample in broad wavelength region (SHG spectroscopy).

In case of GeTe, we observed that the SHG signal from films were extremely strong as compared to the substrate signal. Our focused was temperature scans on thin films and substrate and we found that pure GeTe thin films have higher Curie temperature than that of the doped ones and it agrees with the previous values found in the literature.

In future, we are planning to investigate the GeTe thin films with different concentration of Ge. In this way, it would be possible to investigate the effect of doping as explained in the Fig.4.12.

Part B:

We have demonstrated the ability of THz-TDS in sensing the diatoms in aqueous model systems. Due to the strong absorption of water in the THz range, the spectral signatures of diatoms could not be detected directly, but we found their footprints in the water absorption variation due to the water–diatom interactions. We observed an 'excess' of absorption over the entire interval of the THz frequencies. This result allowed us to widen the set of spectroscopic tools for investigating marine organisms with instruments that provide complementary key information. In this respect, compared to the Raman and IAS spectroscopies, the THz-TDS may probe the large-scale vibrations of diatoms and the hydrogen-bond network of water and hence provide information on their global structural reorganization. When metal dopants were added, the 'absorption' excess was strongly reduced over the entire THz frequency range. This points to a strong structural change of the 'biological water' acting in the doped samples. These absorption variations could be used for probing the biocide effect of metals on diatoms. We note that these changes were already significant a few hours after the doping when the presence of dead diatoms was very low or completely absent. This demonstrates that THz-TDS is suitable to

monitor the poisoning effect at the earliest stage when the diatoms are still alive but have started to become unhealthy. Finally, we note that because of logistical reasons we were unable to monitor these effects just a few minutes after the doping, while, in principle, the technique has a time resolution of only a few minutes.

For the future perspectives, we already started measuring the different samples with varying concentrations of diatoms and in the preliminary measurements and we found that the results are similar what we discussed in Chpt. 5. At this moment of time, we are interested in studying the marine pollution and diatoms are good monitor for study water pollution. We are also interested in carrying out the experiments with different concentration of diatoms as a function of time and temperature to check the diatoms growth rate.

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ॐ असतो मा सद्गमय । तमसो मा ज्योतिर्गमय । मृत्योर्मा अमृतं गमय । ॐ शान्तिः शान्तिः शान्तिः ॥

> Om asato mā sadgamaya, tamaso mā jyotirgamaya, mṛtyormā'mṛtaṃ gamaya.

From the unreal lead me to the real!

From the darkness lead me to the light!

From death lead me to immortality!

[Brhadāraņyaka Upanişad (1.3.28.), 7th century BC.]

Appendix

```
A1 MATLAB code for chi_eff SHG (Electric dipole)
clear all
close all
clc
% This program computes the formulas for chi eff SHG
%% IN THIS SECTION THE USER CAN DEFINE THE GROUP TO WORK WITH:
% the flag "group" is a string which contains the name of the
symmetry
% group we want to calculate
% Triclinic:
%group='1';
%group='1bar'; % all elements are vanishing
% Monoclinic:
%group='2';
% group='m';
% group='2/m'; % all elements are vanishing
% Orthorombic:
% group='222';
%group='mm2';
% group='mmm'; % all elements are vanishing
% Tetragonal:
% group='4';
% group='4bar';
% group='422';
%group='4mm';
% group='4bar2m';
 %group='4/m'; % all elements are vanishing
% group='4/mmm'; % all elements are vanishing
% Cubic:
 %group='432'; % The 432 group has all vanishing elements once
one assumes the symmetry over last two indices
% group='4bar3m';
% group='23'; % This group is identical to 4bar3m once one has
the symmetry over last two indices
% group='m3'; % all elements are vanishing
% group='m3m'; % all elements are vanishing
% Trigonal (Rhombohedral):
```

```
%group='3';
% group='32';
% group='3m';
% group='3bar'; % all elements are vanishing
% group='3barm'; % all elements are vanishing
% Hexagonal:
% group='6';
% group='6bar';
% group='622';
% group='6mm';
% group='6barm2';
% group='6/m'; % all elements are vanishing
% group='6/mmm'; % all elements are vanishing
%% IN THIS SECTION THE ROTATION MATRICES ARE DEFINED
% This program is for calculating the Dipole SHG yield in
various symmetries by symbolic calculation.
% in the definition of variable the last-two-indices symmetry is
already considered. Example: variable xyx is not defined because
variable xxy is already defined. We choose to always use the
variable with the
% right order of labels (i.e. x(yx) not present and x(xy) used
instead,
\frac{1}{2} z(zx) becomes z(xz) and so on).
% M is the 3x3x3 matrix of chi2 elements
syms xxx xxy xxz xyy xyz xzz yxx yxy yxz yyy yyz yzz
zxy zxz zyy zyz zzz
% here Rin is the input rotation matrix and Rout as output
rotation matrix as
% a function of the Frenel factors L1x,y,z and L2x,y,z (labels 1)
and 2 are for
% fundamental and SHG frequencies). The angles are phi
(azimuthal) beta
% (incident) and al in out(polarization in - out)
syms L1x L1y L1z L2x L2y L2z phi beta alin alout
```

```
Rin(1)=L1x*cos(phi)*cos(alin)*cos(beta)-L1y*sin(phi)*sin(alin);
Rin(2)=L1x*sin(phi)*cos(alin)*cos(beta)+L1y*cos(phi)*sin(alin) ;
```

ZXX

```
Rin(3)=L1z*cos(alin)*sin(beta);
Rout (1) =-L2x*cos (phi) *cos (alout) *cos (beta) -
L2v*sin(phi)*sin(alout);
Rout (2) = -
L2x*sin(phi)*cos(alout)*cos(beta)+L2y*cos(phi)*sin(alout);
Rout(3) =L2z*cos(alout)*sin(beta);
%% IN THIS SECTION THE CHI2 TENSOR M IS DEFINED FOR A GIVEN
GROUP
% Triclinic:
if strcmp(group, '1')
    % in the following lines the full M matrix is defined with
accounting for
    % the jk=kj basic symmetry (18 terms instead of 27):
    M(1,1,1)=xxx; M(1,1,2)=xxy; M(1,1,3)=xxz; M(1,2,1)=xxy;
M(1,2,2)=xyy; M(1,2,3)=xyz; M(1,3,1)=xxz; M(1,3,2)=xyz;
M(1, 3, 3) = xzz;
    M(2,1,1)=yxx; M(2,1,2)=yxy; M(2,1,3)=yxz; M(2,2,1)=yxy;
M(2,2,2)=yyy; M(2,2,3)=yyz; M(2,3,1)=yxz; M(2,3,2)=yyz;
M(2, 3, 3) = yzz;
    M(3,1,1) = zxx; M(3,1,2) = zxy; M(3,1,3) = zxz; M(3,2,1) = zxy;
M(3,2,2)=zyy; M(3,2,3)=zyz; M(3,3,1)=zxz; M(3,3,2)=zyz;
M(3, 3, 3) = zzz;
elseif strcmp(group, '1bar')
    disp('All elements are vanishing')
    M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
% Monoclinic:
%elseif strcmp(group, '2') ==1
    %M(1,2,3)=xyz; M(1,3,2)=xyz; % (xyz=xzy)
    %M(1,1,2)=xxy; M(1,2,1)=xxy; % (xxy=xyx)
    %M(2,3,1)=yzx; M(2,1,3)=yzx; % (yzx=yxz)
    %M(3,2,3)=zyz; M(3,3,2)=zyz; % (zyz=zzy)
    %M(3,1,2)=zxy; M(3,2,1)=zxy; % (zxy=zyx)
    %M(2,1,1)=yxx; M(2,2,2)=yyy; M(2,3,3)=yzz; % (yxx) (yyy)
(yzz)
elseif strcmp(group,'2 ns')==1%ns means 'nonstandard'
orientation 2||x 3; simply exchange z and y
     M(1,2,3) = xyz; M(1,3,2) = xyz; % (xyz = xzy)
     M(1, 1, 3) = xxz; M(1, 3, 1) = xxz; % (xxz = xzx)
     M(2,2,3) = yyz; M(2,3,2) = yyz; % (yyz = yzy)
    M(2,1,3)=yxz; M(2,3,1)=yxz; % (yxz=yzx)
     M(3,1,2) = zxy; M(3,2,1) = zxy; % (zxy = zyx)
     M(3,1,1) = zxx; M(3,2,2) = zyy; M(3,3,3) = zzz; % (zxx) (zyy)
(zzz)
```

```
elseif strcmp(group, 'm') ==1
    M(1,1,1)=xxx; M(1,2,2)=xyy; M(1,3,3)=xzz; % ((xxx) (xyy)
(XZZ)
    M(1,3,1) = xxz; M(1,1,3) = xxz; % (xzx = xxz)
    M(2,2,3)=yyz; M(2,3,2)=yyz; % (yyz=yzy)
    M(2,1,2) = yxy; M(2,2,1) = yxy; % ((yxy=yyx))
    M(3,1,1) = zxx; M(3,2,2) = zyy; M(3,3,3) = zzz; % ((zxx) (zyy))
(zzz)
    M(3,3,1) = zxz; M(3,1,3) = zxz; % ((zzx = zxz))
 elseif strcmp(group, 'm ns') == 1% m perpendicular to x 3; simply
exchange z and y
     M(1,1,1) = xxx; M(1,2,2) = xyy; M(1,3,3) = xzz; % ((xxx) (xyy))
(XZZ)
     M(1,1,2)=xxy; M(1,2,1)=xxy; % (xxy=xyx)
     M(3,3,2) = zzy; M(3,2,3) = zyz; % (zyy = zyz)
     M(2,1,2) = yxy; M(2,2,1) = yxy; % ((yxy=yyx))
     M(2,1,1)=yxx; M(2,2,2)=yyy; M(2,3,3)=yzz; % ((yxx) (yyy)
(yzz)
     M(3,1,3) = zxz; M(3,3,1) = zxz; % ((zxz = zxz))
elseif strcmp(group, '2/m')
    disp('All elements are vanishing')
    M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
% Orthorombic:
elseif strcmp(group, '222') ==1
    M(1,2,3) = xyz; M(1,3,2) = xyz; % (xyz = xzy)
    M(2,3,1) = yxz; M(2,1,3) = yxz; % (yzx = yxz)
    M(3,1,2)=zxy; M(3,2,1)=zxy; % (zxy=zyx)
elseif strcmp(group, 'mm2') ==1
    M(1,3,1) = xxz; M(1,1,3) = xxz; % (xzx = xxz)
    M(2,2,3) = yyz; M(2,3,2) = yyz; % (yyz = yzy)
    M(3, 1, 1) = zxx; % (zxx)
    M(3,2,2)=zyy; % (zyy)
    M(3,3,3) = zzz; % (zzz)
elseif strcmp(group, 'mmm') ==1
    disp('All elements are vanishing')
    M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
% Tetragonal:
elseif strcmp(group, '4') ==1
    M(1,2,3)=xyz; M(1,3,2)=xyz; M(2,1,3)=-xyz; M(2,3,1)=-xyz; %
(xyz=xzy=-yxz=-yzx)
    M(1,1,3)=xxz; M(1,3,1)=xxz; M(2,3,2)=xxz; M(2,2,3)=xxz; %
(xxz=xzx=yzy=yyz)
    M(3,1,1) = zxx; M(3,2,2) = zxx; % (zxx = zyy)
    M(3,1,2)=0; M(3,2,1)=0; \& (zxy=-zyx)
    M(3,3,3) = zzz; % (zzz)
```

```
elseif strcmp(group, '4bar') ==1
    M(1,2,3)=xyz; M(1,3,2)=xyz; M(2,1,3)=xyz; M(2,3,1)=xyz; %
(xyz=xzy=yxz=yzx)
    M(1,1,3) = xxz; M(1,3,1) = xxz; M(2,3,2) = -xxz; M(2,2,3) = -xxz; %
(xxz=xzx=-yzy=-yyz)
    M(3,1,1) = zxx; M(3,2,2) = -zxx; % (zxx = -zyy)
    M(3,1,2) = zxy; M(3,2,1) = zxy; % (zxy = zyx)
elseif strcmp(group, '422') ==1
    M(1,2,3)=xyz; M(2,1,3)=-xyz; M(1,3,2)=xyz; M(2,3,1)=-xyz; %
(xyz=-yxz=xzy=-yzx)
    M(3,1,2)=0; M(3,2,1)=0; % (zxy=-zyx) %
elseif strcmp(group, '4mm') ==1
    M(1,3,1) = xxz; M(1,1,3) = xxz; M(2,2,3) = xxz; M(2,3,2) = xxz; %
(xzx = xxz = yyz = yzy)
    M(3,1,1) = zxx; M(3,2,2) = zxx; % (zxx = zyy)
    M(3,3,3) = zzz; % (zzz)
elseif strcmp(group, '4bar2m') ==1
    M(1,2,3)=xyz; M(2,1,3)=xyz; M(1,3,2)=xyz; M(2,3,1)=xyz; %
(xyz=yxz=xzy=yzx)
    M(3,1,2)=zxy; M(3,2,1)=zxy; % (zxy=zyx)
elseif strcmp(group, '4/m') ==1
    disp('All elements are vanishing')
    M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
elseif strcmp(group, '4/mmm') ==1
    disp('All elements are vanishing')
    M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
% Cubic:
elseif strcmp(group, '432') ==1
    disp('The 432 group has all vanishing elements once one
assumes the symmetry over last two indices.')
    M(1,2,3)=xyz; M(1,3,2)=xyz; M(2,3,1)=yxz; M(2,1,3)=yxz;
M(3,1,2)=zxy; M(3,2,1)=zxy; %(xyz=-xzy=yzx=-yxz=zxy=-zyx=0) !!!
Attention, here maybe there is a wrong minus sign in the Boyd!
elseif strcmp(group, '4bar3m') ==1
    M(1,2,3)=xyz; M(1,3,2)=xyz; M(2,3,1)=xyz; M(2,1,3)=xyz;
M(3,1,2)=xyz; M(3,2,1)=xyz; % (xyz=xzy=yzx=yxz=zxy=zyx)
elseif strcmp(group, '23') ==1
     disp('The group 23 is identical to 4bar3m once one assumes
the symmetry over last two indices.')
     M(1,2,3) = xyz; M(1,3,2) = xyz; M(2,3,1) = xyz; M(2,1,3) = xyz;
M(3,1,2)=xyz; M(3,2,1)=xyz; % (xyz=xzy=yzx=yxz=zxy=zyx)
elseif strcmp(group, 'm3') ==1
    disp('All elements are vanishing')
    M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
```

```
elseif strcmp(group, 'm3m') ==1
    disp('All elements are vanishing')
    M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
% Trigonal (Rhombohedral):
elseif strcmp(group, '3') ==1 %
    M(1,1,1) = xxx; M(1,2,2) = -xxx; M(2,1,2) = -xxx; M(2,2,1) = -xxx; %
(xxx = -xyy = -yxy = -yyx)
    M(1,2,3)=xyz; M(1,3,2)=xyz; M(2,1,3)=-xyz; M(2,3,1)=-xyz; %
(xyz=xzy=-yxz=-yzx)
    M(1,1,3)=xxz; M(1,3,1)=xxz; M(2,2,3)=xxz; M(2,3,2)=xxz; %
(xxz=xzx=yyz=yzy)
    M(2,2,2)=yyy; M(2,1,1)=-yyy; M(1,1,2)=-yyy; M(1,2,1)=-yyy; %
(yyy=-yxx=-xxy=-xyx)
    M(3,1,1) = zxx; M(3,2,2) = zxx; % (zxx = zyy)
    M(3,3,3) = zzz; % (zzz)
elseif strcmp(group, '32') ==1
    M(1,1,1)=xxx; M(1,2,2)=-xxx; M(2,2,1)=-xxx; M(2,1,2)=-xxx; %
XXX = -XVV = -VVX = -VXV
    M(1,2,3)=xyz; M(2,1,3)=-xyz; M(1,3,2)=xyz; M(2,3,1)=-xyz; %
(XYZ = -YXZ = XZY = -YZX)
    M(3,1,2)=0; M(3,2,1)=0; \& (zxy=-zyx)
elseif strcmp(group, '3m') ==1
    M(1,3,1)=xxz; M(1,1,3)=xxz; M(2,2,3)=xxz; M(2,3,2)=xxz;
% (xzx = xxz = yyz = yzy)
    M(3,1,1) = zxx; M(3,2,2) = zxx; % (zxx = zyy)
    M(2,2,2) = yyy; M(2,1,1) = -yyy; M(1,1,2) = -yyy; M(1,2,1) = -yyy;
%(yyy = ?yxx = ?xxy = ?xyx)
    M(3,3,3) = zzz; % (zzz)
% elseif strcmp(group,'3m ns')==1%m perpendicular to x 2 simply
exchange x with y
      M(1,3,1)=xxz; M(1,1,3)=xxz; M(2,2,3)=xxz; M(2,3,2)=xxz;
8
% (xzx = xxz = yyz = yzy)
00
      M(3,1,1) = zxx; M(3,2,2) = zxx; % (zxx = zyy)
      M(1,1,1) = xxx; M(1,2,2) = -xxx; M(2,2,1) = -xxx; M(2,1,2) = -xxx;
% (xxx = ?xyy = ?yyx = ?yxy)
      M(3, 3, 3) = zzz; % (zzz)
elseif strcmp(group,'3bar')==1
    disp('All elements are vanishing')
    M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
elseif strcmp(group, '3barm') ==1
    disp('All elements are vanishing')
    M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
% Hexagonal:
elseif strcmp(group, '6') ==1
```

```
M(3,1,1) = zxx; M(3,2,2) = zxx; % (zxx = zyy)
    M(2,2,3)=xxz; M(2,3,2)=xxz; M(1,1,3)=xxz; M(1,3,1)=xxz; %
(yyz=yzy=xxz=xzx)
    M(1,2,3)=xyz; M(1,3,2)=xyz; M(2,1,3)=-xyz; M(2,3,1)=-xyz; %
(xyz=xzy=-yxz=-yzx)
    M(3,3,3) = zzz; % (zzz)
elseif strcmp(group, '6bar') ==1
    M(1,1,1) = xxx; M(1,2,2) = -xxx; M(2,1,2) = -xxx; M(2,2,1) = -xxx; %
(XXX = -XVV = -VXV = -VVX)
    M(2,2,2)=yyy; M(2,1,1)=-yyy; M(1,2,1)=-yyy; M(1,1,2)=-yyy; %
(yyy=-yxx=-xyx=-xxy)
    M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
elseif strcmp(group, '622') ==1
    M(1,2,3)=xyz; M(2,1,3)=-xyz; M(1,3,2)=xyz; % (xyz=-yxz=xzy=-
yxz)
    M(3,1,2)=0; M(3,2,1)=0; \& (zxy=-zyx=0)
    M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
elseif strcmp(group, '6mm') ==1
    M(1,3,1)=xxz; M(2,3,2)=xxz; M(1,1,3)=xxz; M(2,2,3)=xxz; %
(xzx=yzy=xxz=yyz)
    M(3,1,1) = zxx; M(3,2,2) = zxx; % (zxx = zyy)
    M(3,3,3) = zzz; % (zzz)
elseif strcmp(group, '6barm2') ==1
    M(2,2,2)=yyy; M(2,1,1)=-yyy; M(1,1,2)=-yyy; M(1,2,1)=-yyy; %
(yyy=-yxx=-xxy=-xyx)
    M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
% elseif strcmp(group,'6barm2 ns')==1% m perpendicular to x 2
simply exchange x with y
     M(1,1,1) = xxx; M(1,2,2) = -xxx; M(2,2,1) = -xxx; M(2,1,2) = -xxx;
8
% (xxx=-xyy=-yyx=-yxy)
00
      M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
elseif strcmp(group, '6/m') ==1
    disp('All elements are vanishing')
    M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
elseif strcmp(group, '6/mmm') ==1
    disp('All elements are vanishing')
    M(3,3,3)=0; % the M matrix has to be defined as 3x3x3, so
this term is needed only to introduce the 3rd dimension.
end
%% FINAL CALCULATION
```

```
% the chi eff is the final result of the calculation:
chi eff=0;
for i=1:3
    for j=1:3
        for k=1:3
            chi term=Rout(i) M(i, j, k) Rin(j) Rin(k);
            chi eff=chi eff+chi term;
        end
    end
end
% Here we specify the angles to compute:
disp(strcat('Symmetry group: "',' ',group,'"',' incidence
angle: 45°'))
disp('Azimuthal effective Chi2')
% PP component
beta=pi/4; alin=0; alout=0;
chi eff pp=simplify(subs(chi eff));
chi eff pp=combine(chi eff pp, 'sincos')
% SP component
beta=pi/4; alin=pi/2; alout=0;
chi eff sp=simplify(subs(chi eff));
chi eff sp=combine(chi eff sp, 'sincos')
% DS component
beta=pi/4; alin=pi/4; alout=pi/2;
chi eff ds=simplify(subs(chi eff));
chi eff ds=combine(chi eff ds, 'sincos')
% PS component
beta=pi/4; alin=0; alout=pi/2;
chi eff ps=simplify(subs(chi eff)) %
chi eff ps=combine(chi eff ps, 'sincos')
% SS component
beta=pi/4; alin=pi/2; alout=pi/2;
chi eff ss=simplify(subs(chi eff));
chi eff ss=combine(chi eff ss, 'sincos')
disp('P-output effective Chi2 @ phi=0')
% alpha-P component
beta=pi/4; phi=0; alout=0;
chi eff alP=simplify(subs(chi eff));
chi eff alP=combine(chi eff alP, 'sincos')
disp('S-output effective Chi2 @ phi=0')
% alpha-S component
beta=pi/4; phi=0; alout=pi/2;
chi eff alS=simplify(subs(chi eff));
chi eff alS=combine(chi eff alS, 'sincos')
```

A2. Electric Quadrupole SHG for 4/m

```
clear all
close all
clc
i = sqrt(-1);
a=what;
parent=a.path;
phi theo=[0:0.01:2*pi];
plottafig=1; % =1 means you want to see all fit curves, 0= see
the final fit parameters
simm=1; % =1 means you want to symmetrize the experimental data
by 180° shift
inter=0; % =n means you want to linearly interpolate exp points
to n times, 0= no interp
shq pp yield=[0.9; 1.6; 1.5; 1.2]; % this is the HZOR, 1, 2, 3 SHG
yield in PP as measured with independent 6 set scan
% shq pp yield=[1; 1; 1; 1];
%% This program is for fitting the data on HZO samples
(Florencio) with quadrupole 4/m shq
for z=1:4
    %if z==1;
cd('C:\Users\ROHITKUMAR\Desktop\Esperimenti\THz\Data\SET1\HZOR')
; phi glob=2;
    %elseif z==2;
cd('C:\Users\ROHITKUMAR\Desktop\Esperimenti\THz\Data\SET1\HZO1')
; phi glob=45;
    %elseif z==3;
cd('C:\Users\ROHITKUMAR\Desktop\Esperimenti\THz\Data\SET1\HZO2')
; phi glob=-17;
    elseif z==4;
cd('C:\Users\ROHITKUMAR\Desktop\Esperimenti\THz\Data\SET1\HZO3')
; phi glob=20;
    %end
     if z == 1;
cd('C:\Users\ROHITKUMAR\Desktop\Esperimenti\THz\Data\SET2\HZOR')
; phi glob=13;
     elseif z==2;
cd('C:\Users\ROHITKUMAR\Desktop\Esperimenti\THz\Data\SET2\HZO1')
; phi glob=50;
     elseif z==3;
cd('C:\Users\ROHITKUMAR\Desktop\Esperimenti\THz\Data\SET2\HZO2')
; phi glob=33;
```

```
elseif z==4;
cd('C:\Users\ROHITKUMAR\Desktop\Esperimenti\THz\Data\SET2\HZO3')
; phi glob=22;
     end
      if z==1; cd('SET3\HZOR'); phi glob=0;
00
00
      elseif z==2; cd('SET3\HZO1'); phi glob=0;
00
      elseif z==3; cd('SET3\HZO2'); phi glob=0;
      elseif z==4; cd('SET3\HZO3'); phi glob=0;
00
8
      end
    load PP.mat; [phi,S pp]=symm(phi1,s1,simm,inter,phi glob);
    load SP.mat; [phi,S sp]=symm(phi1,s1,simm,inter,phi glob);
    load DS.mat; [phi,S ds]=symm(phi1,s1,simm,inter,phi glob);
    load PS.mat; [phi,S ps]=symm(phi1,s1,simm,inter,phi glob);
    load SS.mat; [phi,S ss]=symm(phi1,s1,simm,inter,phi glob);
   cd(parent)
    % par0 pp=[1 2.5 0 2.5 2 0 0]; %1st set A,B complex, C real
    % par0 pp=[pi/4 2.5 0 2.5 2 0]; % 2nd set, A,B complex, C
real
     par0 pp=[0 1 1 1]; %1st set A,B,C real, Sipe formula
8
    par0 pp=[.1 .1 2]; %1st set A,B,C real, Sipe formula, no
phi0
     par0 pp=[0 1 1]; %1st set, de la Torre formula
8
    % par pp=par0 pp;
    par pp=fminsearch(@chi sq pp,par0 pp,'',phi,S pp);
    s pp=chi2 EQ pp(par pp,phi theo);
   phi0 pp=par pp(1);
    % par0 sp=[pi/4 1 1 1 1 1]; %1st set A,B complex, C real
    % par0 sp=[pi/4 2.5 0 2.5 2 0]; % 2nd set, A,B complex, C
real
     par0 sp=[0 0 0 2]; %1st set A,B, C real, Sipe formula
8
    par0 sp=[.1 .1 1]; %1st set A,B, C real, Sipe formula, no
phi0
8
     par0 sp=[0 1 1]; %1st set, de la Torre formula
    % par sp=par0 sp;
    par sp=fminsearch(@chi sq sp,par0 sp,'',phi,S sp);
    s sp=chi2 EQ sp(par sp,phi theo);
    phi0 sp=par sp(1);
```

```
% par0 ds=[pi/4 2.5 0 2.5 2 0]; %1st set A,B complex, C real
    % par0 ds=[pi/4 2.5 0 2.5 2 0]; % 2nd set, A,B complex, C
real
8
      par0 ds=[0 0 0 2]; %1st set A,B, C real, Sipe formula
    par0 ds=[0 0 3]; %1st set A,B, C real, Sipe formula, no phi0
      par0 ds=[0 1 1]; %1st set A,B, C real, pseudo-de-la-Torre
8
formula
    % par ds=par0 ds;
    par ds=fminsearch(@chi sq ds,par0 ds,'',phi,S ds);
    s ds=chi2 EQ ds(par ds,phi theo);
    phi0 ds=par ds(1);
    % par0 ps=[0 1 1 1 1 1]; %1st set A,B complex, C real
    % par0 ps=[pi/4 2.5 0 2.5 2 0]; % 2nd set, A,B complex, C
real
2
      par0 ps=[0 2 .1 0]; %1st set A,B, C real, Sipe formula
    par0 ps=[2 .1 0]; %1st set A,B, C real, Sipe formula, no
phi0
8
      par0 ps=[pi/2 2]; %1st set A real, de la Torre formula
    % par ps=par0 ps;
    par ps=fminsearch(@chi sq ps,par0 ps,'',phi,S ps);
    s ps=chi2 EQ ps(par ps,phi theo);
    phi0 ps=par ps(1);
    % par0 ss=[0 1 1 1 1 1]; %1st set A,B complex, C real
    % par0 ss=[pi/4 2.5 0 2.5 2 0]; % 2nd set, A,B complex, C
real
     par0 ss=[0 2 .1 0]; %1st set A,B, C real, Sipe formula
2
    par0 ss=[2 .1 0]; %1st set A,B, C real, Sipe formula, no
phi0
8
     par0 ss=[pi/2 2]; %1st set A real, de la Torre formula
    par ss=fminsearch(@chi sq ss,par0 ss,'',phi,S ss);
    s ss=chi2 EQ ss(par ss,phi theo);
    phi0 ss=par ss(1);
    % here the data and fit are normalized to PP values, then
multiplied by the PP SHG yield factor
    f=shg pp yield(z)/max(s pp);
    S pp=S pp*f; s pp=s pp*f;
    S sp=S sp*f; s sp=s sp*f;
    S ds=S ds*f; s ds=s ds*f;
    S ps=S ps*f; s ps=s ps*f;
    S ss=S ss*f; s ss=s ss*f;
```

```
M pp(z,:)=[par pp];
    M \operatorname{sp}(z, :) = [\operatorname{par sp}];
    M ds(z,:) = [par ds];
    M ps(z,:)=[par ps];
    M ss(z,:) = [par ss];
    colori=['k','r','m','b']; c=colori(z); co=strcat('o',c);
    campioni=['HZOR';'HZO1';'HZO2';'HZO3'];
    fase=[0 0 0 0];
    if plottafig==1
        figure(1)
00
          polarplot(phi-phi0 pp,S pp,co, phi theo-
phi0 pp,s pp,c)
        polarplot(phi,S pp,co, phi theo,s pp,c)
        title('Quadrupole SHG; P-in P-out scan')
        legend('HZOR','','HZO1','','HZO2','','HZO3','')
        hold on
8
          pause
        figure(2)
          polarplot(phi-phi0 sp,S sp,co, phi_theo-
8
phi0 sp,s sp,c)
        polarplot(phi,S sp,co, phi theo,s sp,c)
        title('Quadrupole SHG; S-in P-out scan')
        legend('HZOR','','HZO1','','HZO2','','HZO3','')
        hold on
8
          pause
        figure(3)
          polarplot(phi-phi0 ds,S ds,co, phi theo-
phi0 ds,s ds,c)
        polarplot(phi,S ds,co, phi theo,s ds,c)
        title('Quadrupole SHG; D-in S-out scan')
        legend('HZOR','','HZO1','','HZO2','','HZO3','')
        hold on
8
          pause
        figure(4)
          polarplot (phi-phi0 ps, S ps, co, phi theo-
2
phi0 ps,s ps,c)
        polarplot(phi,S ps,co, phi theo,s ps,c)
        title('Quadrupole SHG; P-in S-out scan')
        legend('HZOR','','HZO1','','HZO2','','HZO3','')
        hold on
8
          pause
        figure(5)
          polarplot(phi-phi0 ss, S ss, co, phi theo-
8
phi0 ss,s ss,c)
```

```
polarplot(phi,S_ss,co, phi_theo,s_ss,c)
title('Quadrupole SHG; S-in S-out scan')
legend('HZOR','','HZO1','','HZO2','','HZO3','')
hold on
```

end

end

```
if plottafig==0
samp=[0 1 2 3];
figure(1)
plot(samp, M pp(:,1)*180/pi, samp, M sp(:,1)*180/pi, samp, M ds(:,1)*
180/pi,samp,M ps(:,1)*180/pi,samp,M ss(:,1)*180/pi)
legend('PP','SP','DS','PS','SS')
title ('\phi 0 (deg)')
figure(2)
plot(samp,M pp(:,2), samp,M sp(:,2), samp,M ds(:,2), samp,M ps(:,2)
, samp, M ss(:,2))
legend('PP','SP','DS','PS','SS')
title ('A')
figure(3)
plot(samp,M pp(:,3),samp,M sp(:,3),samp,M ds(:,3),samp,M ps(:,3)
,samp,M ss(:,3))
legend('PP','SP','DS','PS','SS')
title ('B')
figure(4)
plot(samp, M pp(:,4), samp, M sp(:,4), samp, M ds(:,4), samp, M ps(:,4)
, samp, M ss(:, 4))
legend('PP','SP','DS','PS','SS')
title ('C')
end
```

%% FUNCTIONS
% This function makes the point symmetrical for 180 rotation
function [X,S]=symm(x,a,simm,inter, phi_glob)
if simm==1 % this is the flag which tells to symmetrize or not
% if the vector a has an odd number of elements, the first
element is
% removed and the last one is the average with the first
(0°=360°)
 if rem(length(a),2)==1
 X=x(2:end);

```
a=a(2:end);
        a(end) = (a(1) + a(end)) / 2;
    else
        X = X;
    end
    m = length(a)/2;
    ss=zeros(m, 1);
    for k=1:m
        ss(k) = (a(k) + a(k+m))/2;
    end
    S=[ss ; (ss)];
else
    X = X;
    S=a;
end
if inter==0 % this flag is to interpolate data or not
else
    X=interp(X, inter);
    S=interp(S,inter);
end
% here the data are shifted by a given angle so they all match
the same phi0
X=X-phi glob*pi/180;
end
% chi squared functions
% This function calculate the chi squared value for PP:
function s=chi sq pp(par,phi,data)
f=chi2 EQ pp(par,phi);
s=norm(f-data);
end
% This function calculate the chi squared value for SP:
function s=chi sq sp(par,phi,data)
f=chi2 EQ sp(par,phi);
s=norm(f-data);
end
% This function calculate the chi squared value for DS:
function s=chi sq ds(par,phi,data)
f=chi2 EQ ds(par,phi);
s=norm(f-data);
end
```

```
% This function calculate the chi squared value for PS:
function s=chi sq ps(par,phi,data)
f=chi2 EQ ps(par,phi);
s=norm(f-data);
end
% This function calculate the chi squared value for SS:
function s=chi sq ss(par,phi,data)
f=chi2 EQ ss(par, phi);
s=norm(f-data);
end
                chi eff functions
8
% This function is the expected signal for quadrupole symmetry
as a function of phi
% for PP combination and 45° incident angle
function s=chi2 EQ pp(par,phi)
% A,B complex, C real
% phi0=par(1); A=par(2)+1i*par(3); B=par(4)+1i*par(5);
C=par(6);%+1i*par(7);
% % A,B, C real, both sin and cos of 4phi (Sipe87)
% phi0=par(1); A=par(2); B=par(3); C=par(4);
% chi eff=A*sin(4*(phi-phi0))+B*cos(4*(phi-phi0))+C;
% A,B, C real, both sin and cos of 4phi (EQ 4/m), no phil
A=par(1); B=par(2); C=par(3);
%chi eff=A*sin(3*(phi))+B*cos(2*(phi))+C*sin(phi);
chi eff=A*sin(4*(phi))+B*cos(4*(phi))+C;
% % B, C real, only cos of 4phi (de la Torre 2020)
% phi0=par(1); B=par(2); C=par(3);
% chi eff=B*cos(4*(phi-phi0))+C;
s=abs((chi eff)).^2;
end
% This function is the expected signal for quadrupole symmetry
as a function of phi
% for SP combination and 45° incident angle
function s=chi2 EQ sp(par,phi)
% phi0=par(1); A=par(2)+1i*par(3); B=par(4)+1i*par(5);
C=par(6);%+1i*par(7);
% % A,B, C real, both sin and cos of 4phi (Sipe87)
% phi0=par(1); A=par(2); B=par(3); C=par(4);
```

```
% chi eff=A*sin(4*(phi-phi0))+B*cos(4*(phi-phi0))+C;
% A,B, C real, both sin and cos of 4phi (EQ 4/m), no phi0
A=par(1); B=par(2); C=par(3);
chi eff=A*sin(3*(phi))+B*cos(2*(phi))+C;
% % B, C real, only cos of 4phi (de la Torre 2020)
% phi0=par(1); B=par(2); C=par(3);
% chi eff=B*cos(4*(phi-phi0))+C;
s=abs((chi eff)).^2;
end
% This function is the expected signal for quadrupole symmetry
as a function of phi
% for DS combination and 45° incident angle
function s=chi2 EQ ds(par,phi)
% phi0=par(1); A=par(2)+1i*par(3); B=par(4)+1i*par(5);
C=par(6);%+1i*par(7);
% % A,B, C real, Sipe formula, there is no del la Torre formula
for ds
% phi0=par(1); A=par(2); B=par(3); C=par(4);
% chi eff=A*sin(4*(phi-phi0))+B*cos(4*(phi-phi0))+C;
% A,B, C real, both sin and cos of 4phi (EQ 4/m), no phi0
A=par(1); B=par(2); C=par(3);
chi eff=A*sin(4*(phi))+B*cos(4*(phi))+C;
% % A,B, C real, pseudo-de-la-Torre formula (there is no del la
Torre formula for ds, used that of pp and sp)
% phi0=par(1); B=par(2); C=par(3);
% chi eff=B*cos(4*(phi-phi0))+C;
s=abs((chi eff)).^2;
end
% This function is the expected signal for quadrupole symmetry
as a function of phi
% for PS combination and 45° incident angle
function s=chi2 EQ ps(par,phi)
% phi0=par(1); A=par(2)+1i*par(3); B=par(4)+1i*par(5);
C=par(6);%+1i*par(7);
% % A,B, C real, Sipe formula
% phi0=par(1); A=par(2); B=par(3); C=par(4);
% chi eff=A*sin(4*(phi-phi0))+B*cos(4*(phi-phi0))+C;
```

```
% A,B, C real, both sin and cos of 4phi (EQ 4/m), no phi0
A=par(1); B=par(2); C=par(3);
chi eff=A*sin(4*(phi))+B*cos(4*(phi))+C;
% % A real, de la Torre formula
% phi0=par(1); A=par(2);
% chi eff=A*sin(4*(phi-phi0));
s=abs((chi eff)).^2;
end
% This function is the expected signal for quadrupole symmetry
as a function of phi
% for SS combination and 45° incident angle
function s=chi2 EQ ss(par,phi)
% phi0=par(1); A=par(2)+1i*par(3); B=par(4)+1i*par(5);
C=par(6);%+1i*par(7);
% % A,B, C real, Sipe formula
% phi0=par(1); A=par(2); B=par(3); C=par(4);
% chi eff=A*sin(4*(phi-phi0))+B*cos(4*(phi-phi0))+C;
% A,B, C real, both sin and cos of 4phi (EQ 4/m), no phi0
A=par(1); B=par(2); C=par(3);
chi eff=A*sin(4*(phi))+B*cos(4*(phi))+C;
% % A real, de la Torre formula
% phi0=par(1); A=par(2);
% chi eff=A*sin(4*(phi-phi0));
s=abs((chi eff)).^2;
end
```

A3. THz pulses as a function of sample thickness



Fig. A1. An example of THz pulses transmitted through a control sample on day 0 as a function of sample thickness.

A4. Absorption coefficient extraction

In the THz time-domain spectroscopy experiments, the presence of the sample leads to a reduction of the THz pulse amplitude (absorption) and to a temporal shift of the THz pulse (refraction). These two quantities can be determined for all the spectral components contained in the THz pulse and can be directly related to the frequency-dependent complex refractive index, $\tilde{n}(v) = n(v) + ik(v)$, of the sample. Here, v represents the frequency, n is the refractive index and k is the extinction coefficient. The latter is related to the absorption coefficient by $\alpha = 4\pi v k/c$. In principle, a comparison of the Fourier transforms of the THz temporal traces with and without the sample, with the second trace used as reference, provides the frequency-dependent refractive $\tilde{n}(v)$. However, the extraction of the complex dielectric function of liquid samples is complicated by the fact that they are contained in cells whose windows affect the THz signal as well. In this case, the complex refractive index is more reliably extracted by isolating the sample response from the window response through measurements at varying sample thickness d.

With this approach, the reference is the sample itself and the contribution of the cell is directly considered. In Fig. A1, we show typical examples of the time-dependent THz field E(t) transmitted through a control sample as a function of sample thickness. The time-domain data is converted to the frequency domain by means of a Fast Fourier Transform to obtain the complex field $\tilde{E}(v) = E(v)e^{i\phi(v)}$, where E(v) and $\phi(v)$ represent the module and the phase of

the complex field, respectively. From the latter data, the frequency-dependent complex refractive index may be obtained by using the following Beer-Lambert generalized relationships:

$$n(v) = c \ \frac{\phi(v, d + \delta d) - \phi(v, d)}{2\pi v \delta d} = \frac{c\Delta\phi(v)}{2\pi v \delta d},$$
(1)
$$k(v) = c \ \frac{\ln E(v, d) - \ln E(v, d + \delta d)}{2\pi v \delta d} = \frac{c\Delta \ln E(v)}{2\pi v \delta d},$$
(2)

where δd is the change in thickness between two subsequent measurements and c is the speed of light in vacuum. As it is apparent from Eqs. 1 and 2, the phase change $\Delta \phi(\nu)$ and the change in the natural logarithm of the electric field $\Delta \ln E(\nu)$ depend linearly on δd for a given frequency.

Therefore, at each frequency, a linear model can be used for describing the experimental results to extract n(v) and k(v), which become the slopes of these linear models. An example of the extracted data and the corresponding linear fits for the equation 2 is shown in Fig. A2 for some select frequencies. In the latter example, the thinnest sample is taken as reference and the variation of $\ln E(v)$ for the other thicknesses are calculated respect to this. We note that at higher frequencies the data become more scattered respect to the fitting line.



Fig. A2. The change in the logarithm of the electric field $\Delta \ln E(\nu)$ as a function of change in sample thickness δd .

A5. Teravision Software

The Tab panels

The "Acquisition" Tab in the TeraVision software is used for time-scan measurements, including regular THz-TDS using electro-optic detection, THz Hyper Raman (THYR) experiments with scanning in time at a single wavelength, and THz-TDS using alternative techniques such as the ABCD technique. This Tab includes two graphs: one for the measured signal in the time domain and the other for the Fast Fourier Transform (FFT) of the signal.

In the "Loop Scan" tab, the time scan is displayed without averaging and the delay stage is continuously moved between the start and stop points at a specified velocity and acceleration. This allows for faster acquisition of the waveform and allows the user to monitor the signal in real-time as they adjust the setup, similar to viewing the signal on an oscilloscope. This feature is useful for quickly adjusting the alignment of the setup.



Figure A3. The report jpeg file generated at the end of each experiment.

The third Tab is the "Move Stage" Tab. Here the user can set the Delay Stage parameters, and it displays a real-time chart which shows the stage position in time. This utility is used to manually move the stage step-by-step when searching for the signal after a major realignment, or to quickly move the stage in between two fixed positions.

The fourth "Single Channels" tab displays a real-time graph of the output of the DAQ for a specified number of points. The DAQ receives two signals: one from the photodetector and one from a photodiode that monitors the THz generation optical pulse after the chopper. This monitor is used to track the laser intensity and to identify which pulses have been chopped and which ones have not.

The fifth tab is the "PCM Spectrum" tab and it shows the signal as a function of wavelength for a fixed delay line position (time position). In this tab, the user can set the monochromator parameters and record a curve of the signal when the THz is on, off, or the difference between the two. It is also quite useful for quickly checking the presence of spurious effects, as for instance 2-photons luminescence.

The sixth tab is "2D Scan" tab, is used for THYR measurement, where the signal is measured in two dimensions as a function of both wavelength (x-axis) and time (y-axis). The graphs in this tab can be displayed as a 2D color mesh or a 3D graph. A typical THz measurement on this tab will show the first and second order Stokes and anti-Stokes bands, as well as their different time relaxation.

The last Tab is the "Rotors" Tab, in which the signal can be measured as a function of the incoming or outcoming optical polarization. This is of particular importance when studying the symmetry properties of the SHG signal generated by the sample.

Saving files and Experimental reports Fig.A3 shows an example of a report file with the measurement number and sample name at the top. The graphs of the measurement are in the center of the page, with a textbox below them containing all relevant parameters, units of each column in the data files, and a free comment textbox. The report file is saved in the JPEG format rather than PDF because it allows the user to easily browse through multiple measurements in a single window using a picture viewer, such as previewing the contents of a file without actually opening it.

This report function can serve as a digital logbook, partially replacing the need for a physical handwritten lab book. It is recommended to use this report function carefully and effectively to keep track of measurements.

Important definitions

- Wakeup effect: The "wake-up effect" in ferroelectrics refers to the phenomenon of restoring a portion of the ferroelectric polarization that was lost due to aging or exposure to high electric fields. This effect can occur after a brief period of electrical stimulation or thermal treatment, resulting in a partial recovery of the original polarization and electro-mechanical properties. It is associated with the re-orientation of domain walls and the reduction of defect density within the ferroelectric material.
- **Polarization (Ferroelectric):** Ferroelectric polarization is a characteristic of certain materials that exhibit spontaneous electric polarization, meaning they have a permanent electric dipole moment even in the absence of an external electric field. This polarization can be reversed or switched by applying an external electric field, leading to the development of ferroelectric memory devices and sensors.
- **Polarization (of light):** Polarization of light refers to the orientation of the electric field of a light wave in a particular direction. Light is a transverse electromagnetic wave, and the electric field in light can vibrate in any plane perpendicular to the direction of propagation. The polarization of light refers to the specific direction of the electric field in the plane perpendicular to the direction of propagation. Light can be linearly polarized, meaning the electric field is restricted to a single plane, or it can be circularly or elliptically polarized, meaning the electric field manner, respectively.
- **Curie Temperature (T_c):** The Curie temperature (T_c) in ferroelectrics is the temperature above which the spontaneous polarization of the material disappears and the material loses its ferroelectric properties. At T_c, the material undergoes a phase transition from the ferroelectric phase to a non-ferroelectric or paraelectric phase. This transition is accompanied by a change in the symmetry of the crystal structure and a change in the distribution of electric charges within the material.
- **Coercive field (E**_c): A coercive field (Ec) is defined as the strength of the electric field at which the macroscopic polarization of the ferroelectric capacitor disappears.
- **Fatigue:** Fatigue in ferroelectrics refers to a reduction in polarization and dielectric constant over time due to repeated electrical switching. It is a phenomenon that reduces the material's ability to retain its ferroelectric properties after undergoing repeated electrical stress, leading to a decrease in its performance over time.

Publications:

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- Qiucheng Yu, Rohit Kumar, Deepak Kumar, Alessia Sambri, Fabio Miletto Granozio, Ignasi Fina, Florencio Sánchez, Domenico Paparo, and Andrea Rubano. Optical second harmonic polarimetry on Hf_{0.5}Zr_{0.5}O₂/La_{0.67}Sr_{0.33}MnO₃ interfaces. ACS Appl. Electron. Mater. 2022, 4, 4, 2040–2046. 10.1021/acsaelm.2c00197.
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Poster presentation

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