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Sensing multiferroic states non-invasively using optical second harmonic generation

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Abstract

The current boost in the search for energy-efficient device paradigms motivates the integration of materials with coexisting and coupled electric and magnetic order parameters into application-relevant architectures. In the so-called multiferroic magnetoelectrics, the understanding of switching events, however, is most of the time obstructed by the complex physics involved and in the non-trivial domain and domain wall configurations. This perspective offers an insightful overview of the most recent progress in the non-invasive optical probe of technology-significant ferroelectricity and antiferromagnetic order: the optical second harmonic generation (SHG). Over the last decade, its use in materials science has evolved, and SHG now enables the monitoring of the emergence of polarization in thin films, even during the epitaxial deposition process. Its long working distance further expedites the probe of multiple order parameters in various environments and under multi-stimuli excitations. The potential for the probe of complex electric dipole textures, such as ferroelectric skyrmions and time-resolved measurements, using SHG-based approaches in the most recent materials systems will be discussed.

Keywords: Multiferroics, $BiFeO_3$, SHG, ferroelectrics, antiferromagnetic, thin films

INTRODUCTION

With this perspective article, we aim to give a brief overview of the recent developments in the characterization of functional materials exhibiting ferroic and multiferroic orders[1]. We start with a concise motivation describing the push for the integration of multiferroic materials in the next generation of logic and memory devices for energy-efficient operation. We also introduce the challenges remaining to be addressed for improving our understanding of multiferroic switching behavior. Next, we present the state-of-the-art techniques enabling non-invasive access to technology relevant to ferroelectric polarization and (anti-)ferromagnetic orders in materials and highlight, in particular, the potential of optical second harmonic generation (SHG). We dedicate a specific section to SHG investigations and place emphasis on the advantages of this symmetry-sensitive technique for advanced characterization of ferroelectric and antiferromagnetic order parameters non-invasively under various environments. We also discuss SHG investigations beyond the standard case of systems presenting a lack of space inversion-symmetry. In the last section, we reveal how SHG investigations may become instrumental for an improved understanding of the complex physics of ferroelectric materials at the nanoscale. In particular, we discuss *in-situ* polarization monitoring during ferroelectric thin film growth and the non-invasive characterization of polar textures at ferroelectric domain walls, motivated by recent studies dealing with ferroelectric skyrmions. Lastly, we highlight the future challenges for SHG-based investigations and the potential of time-resolved or near-field imaging approaches.

Multiferroics for energy-efficient devices

The imminent energy crisis routing from the increasing demand for more efficient electronic devices despite the already-reached fundamental size miniaturization of the transistor technology drives the push for alternative computing paradigm and the insertion of new materials allowing functionalities beyond the realm of the silicon-based microelectronic industry. For instance, materials exhibiting spontaneous magnetization, i.e., ferromagnets, play a significant role in data storage device architectures since a non-volatile magnetic bit can be written via electrical means in nanosecond timescales[2]. Hence, in contrast to existing volatile charged-based random access memories (RAM), the memory is kept, even in the absence of a power supply. In analogy, materials exhibiting a spontaneous electrical polarization, i.e., ferroelectrics, have been inserted in memory devices[1,3]. Here, the non-volatile positive or negative bound charge accumulation at the surface of the ferroelectric materials serves as the memory state. The integration of such functional materials in logic devices has recently boomed with the great promise of merging the computing and memory storage units[3,4]. Hence, the energy and time-consuming transfer of information between the two above-mentioned computing and storage entities, the so-called Von Neumann bottleneck, could be bypassed.

The magnetoelectric spin-orbit logic (MESO) device now emerges as a prototypical example of the integration of magnetoelectric material[1,5] into such an architecture[6]. The working principle of the MESO, see Figure 1A and B, relies on an electric-field-induced magnetoelectric switching controlling a ferromagnetic state[7]. It combines the best of the ferromagnetic and ferroelectric worlds and avoids current limitations of high-energy-consuming magnetic state writing using a high density of spin-polarized currents and would allow a non-destructive ferroelectric state readout. Here, integrating a multiferroic magnetoelectric material, exhibiting coexisting and coupled electrical and magnetic orders[1], enables the use of an electric field to control a non-volatile magnetic bit that is read out using the inverse spin Hall effect in the strong spin-orbit material, and the energy consumption per logic operation is expected to reach the attojoule level[6].

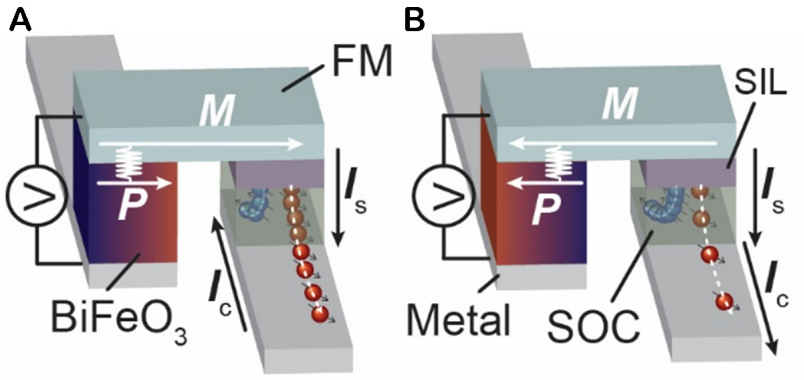

Figure 1. Integration of multiferroic magnetoelectric materials in energy-efficient logic devices. (A and B) In the magnetoelectric spin-orbit logic device, switching the electric polarization (P) of the magnetoelectric layer ($BiFeO_3$) sets the magnetization state (M) of the adjacent ferromagnetic layer (FM) (A). For the output readout (B), the spin-polarized current (Is) from the FM is injected into a layer with strong spin-orbit coupling (SOC) through a spin-injection layer (SIL). The spin-to-charge conversion results in a charge current Ic. Reprinted from[3], Copyright 2023 by the American Chemical Society.

The insertion of such logic devices in industry-relevant architectures requires an understanding of the charge-induced switching event in the functional multiferroic magnetoelectric layer and the dynamics involved. Measuring such properties, however, necessitates the ability to access magnetoelectric or ferroelectric polarization state operando once integrated into a device architecture in a non-invasive, non-destructive experimental approach.

We emphasize here that beyond the development of energy-efficient logic-device applications, the access to nanoscale multiferroic properties in films of only a few unit cells in thicknesses and the rich physics of materials systems exhibiting multiple order parameters motivates the research community to develop tools to non-invasively monitor multiferroic states. We can refer the reader to recent studies highlighting the concepts of magnetoelectric domain inversion[8] and electric and antiferromagnetic textures at multiferroic domain walls[9], which elegantly materialize the interest for multiferroic materials beyond the realm of electric-field control of magnetization[5].

Emerging non-invasive probes and current challenges in multiferroics investigation

The dominant experiment techniques for ferroelectric and ferromagnetic domain imaging at the nanoscale are based on scanning probe microscopy. We refer the reader to the following reviews[10-13] addressing the state-of-art dealing with piezoresponse force microscopy (PFM) and magnetic force microscopy (MFM). Similarly, X-ray diffraction experiments have appeared instrumental in the investigation of ferroelectric materials; however, the high brilliance needed to probe thin films requires large facility access[14]. With this perspective, while our focus is placed on non-invasive optical SHG investigations, we briefly highlight the most recent developments in scanning probe microscopy based on single-spin magnetometry and electrometry and in resonant X-ray diffraction (REXS). These experimental techniques may nicely complement SHG-based characterization of coexisting magnetic and electric order parameters.

Emerging non-invasive probes for multiferroic states

Here, we will discuss Nitrogen-Vacancy (NV)-based microscopy and REXS, both of which allow for the characterization of electrically and magnetically ordered domains and have been the subject of recent interest for the characterization of complex oxide thin films. We will highlight the most recent studies showcasing the exciting new experimental capabilities offered by these experimental approaches.

Imaging multiferroic domains with a single-spin scanning quantum sensor:

The single-spin magnetometer technique is based on point-like impurity nitrogen-vacancy defects in diamond[15]. The NV center can be visualized as a two-level system with an energy spacing in the microwave range. The energy splitting caused by an external magnetic field is read out optically by measuring the fluorescence activity of the NV center while sweeping a microwave frequency excitation. Once mounted at the apex of a scanning probe tip, the resulting ultra-sensitive magnetometry revealed, for the first time, the local magnetic order in multiferroic antiferromagnetic $BiFeO_3$ thin films in real space[16]. The striking periodic contrast, corresponding to the spin density wave accompanying the onset of the antiferromagnetic spin cycloid, can now be accessed within every single ferroelectric domain[17,18]. The latest development in NV-based scanning probe microscopy takes advantage of the Stark effect on the NV center[19]. When a gradiometric detection scheme is accomplished[20], taking advantage of the high-frequency tip oscillation, the local electric fields emerging at the surface of ferroelectric domains can be detected, see Figure 2A and B. The transition from magnetic field to electric field sensing is then enabled by the application of an external magnetic bias field of a few mT, transverse to the reference frame of the NV, as indicated in Figure 2A. In that configuration, the Stark effect is larger, and the NV response to a magnetic field is suppressed. Here, the spin transition frequencies are linearly sensitive to electric fields. Hence, the same probe allows, in principle, for non-invasive detection of magnetic and electrical orders depending on the external bias field application. We emphasize here that the NV detection is quantitative, and the net polarization of model systems, such as ferroelectric $Pb[Zr_{0.2}Ti_{0.8}]O_3$, see Figure 2C and D, and multiferroic $YMnO_3$ multiferroic materials was measured in a non-contact mode[19]. Hence, NV electrometry may revolutionize quantitative polarization measurement in thin films.

Reciprocal investigations of ferroic materials using resonant X-ray diffraction (REXS):

Starting from a standard diffraction configuration, the tuning of the energy of the X-ray photons to absorption edges of specific elements provides additional contributions to the scattering amplitude. They are usually referred to as resonant scattering amplitudes. The latter is now not only sensitive to the position of atoms but also to charge, orbital, and magnetic ordering[21-23]. The need for X-ray energy and polarization tunability makes this experimental technique only available in large facilities such as synchrotrons and free electron lasers. However, as a diffraction technique, in practice, a certain degree of periodicity is required. Lately, REXS has proven to be a great asset to tackle topology issues in ferroic systems. Pioneering studies revealed how circular dichroism (CD) at the diffraction peaks can be related to the sense of magnetic windings in magnetic flux closure domains[24]. More recently, REXS has been used to investigate the complex textures of chiral polar objects in ferroelectric superlattices[25,26], and it has allowed the study of entangled antiferromagnetic and ferroelectric chiral arrangements $BiFeO_3$ thin epitaxial layers showing ferroelectric stripe patterns[9,27], see Figure 2E-G. REXS remains, however, a fairly complex technique and requires thorough analysis.

Challenges in simultaneously probing multiple order parameters, device integration, and time resolution

The investigation of multiferroic materials relies on the capacity to probe electric and magnetic order in matter. The ability to collect such information with spatial resolution is key in the determination of the mechanism involved in the coexistence of the multiple order parameters. Unfortunately, only a few experimental techniques allow “simultaneous” investigations of polarization and magnetization states, and even fewer are compatible with operando analysis. We will discuss the superiority of optical SHG experiments for such a survey in the following section.

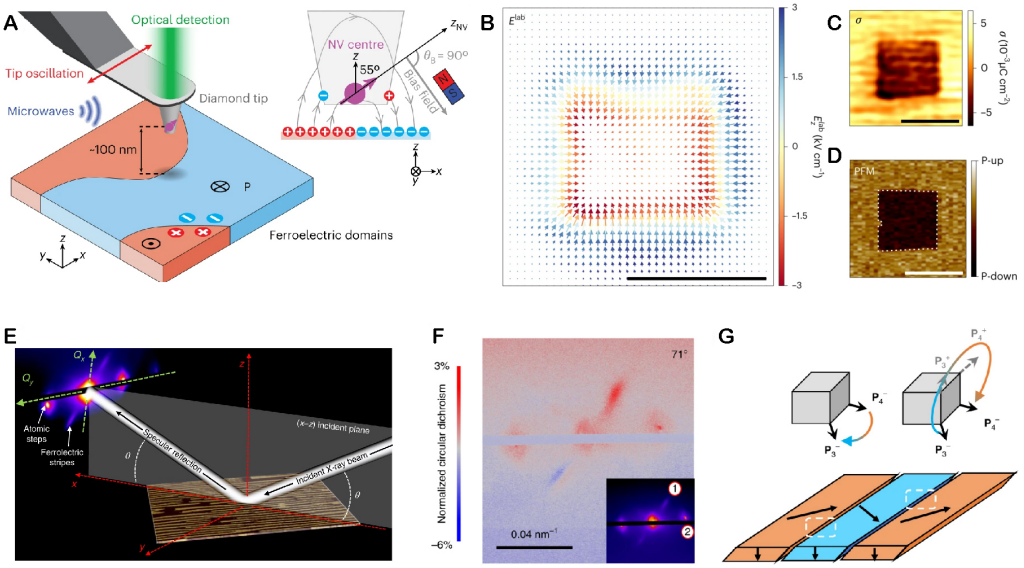

Figure 2. Probing ferroelectricity with a single-spin scanning sensor and resonant X-ray diffraction. (A) Schematization of the scanning NV electrometer, (B) Plot of the electric field reconstructed after scanning a poled region in a $Pb[Zr_{0.2}Ti_{0.8}]O_3$ thin films, (C) Reconstructed surface charge density revealed the poled domain, (D) corresponding PFM image. Reprinted with permission from Huxter *et al.* Copyright 2023 by the Authors under Creative Commons Attribution 4.0 International License, published by the Nature Publishing Group[19]. (E) Schematic representation of the REXS experiment in reflection geometry on a BFO thin epitaxial layer hosting a ferroelectric stripe pattern. (F) Circular dichroism of the diffraction pattern (inset) at the O K edge. (G) Sketch of the ferroelectric texture (domains and domain walls), which can lead to the observed circular dichroism of the diffraction pattern. (E-G) are reprinted with permission from Chauleau *et al.* Copyright 2020 by the Nature Publishing Group[9].

In addition, to better reflect the technology-relevant materials systems, the multiferroic state should be probed once the material is buried under an electrode or integrated into a device architecture. It is well established that finite screening lengths of conducting electrodes have an influence on electrostatic boundary conditions and thus affect the final polarization state in the films[28-30]. In materials where the electric and magnetic order parameters are coupled, a resulting change in the magnetic order may be expected as well when top or bottom electrodes are considered. While the spatially resolved experimental access to the ferromagnetic state may remain unaffected by the insertion of the top electrode using MFM, an efficient metallic capping may, however, screen the piezoresponse of the buried material and render most commonly used PFM-based or above-mentioned NV electrometry investigations of ferroelectric domains less efficient.

Finally, time-resolved measurements on magnetoelectric switching events are still lacking. Only a few studies have addressed this issue, mainly based on optical SHG[31,32]. Hence, most non-invasive experimental techniques, such as X-ray diffractions and REXS, requiring high acquisition times or intense synchrotron radiation sources, have remained incompatible with laboratory scale and daily ultrafast characterization. The combination of the above-mentioned difficulties renders accessing simultaneously an electrical polarization and a long-range magnetic order extremely challenging. Beyond static experiments, bringing the capacity to monitor switching events with time resolution would be greatly beneficial and would allow benchmarking the use of multiferroic materials for real, competitive technologies. We note that spin-orbit torque-based switching exhibits ultra-fast reversal dynamics with switching pulse width down to 180 ps[33]. The dynamics of magnetoelectric switching, however, required the combination of several areas of expertise to achieve a new type of pump-probe experiment, in which the non-invasive probe of the multiferroic state must be synchronized with ultrafast electrical pulsing.

The following section is dedicated to optical SHG, which enables non-invasive probing of materials, even in buried configuration, and is compatible with time-resolved measurements.

NON-INVASIVE PROBE OF MULTIFERROICS USING SHG

Let us now discuss the investigation of complex ferroic and antiferroic states using optical SHG. Starting with a description of the basic working principles, we will discuss relevant examples in both bulk and thin film forms.

Working principle of optical SHG

Probing ferroelectricity

Optical SHG is the lowest order of a large variety of non-linear optical processes. It can be described by considering an incident light at a frequency ω (wavelength λ) generating a reemitted light at twice the incident frequency, 2ω ($\lambda/2$) in a given system. In the leading order, i.e., in the electron dipole (ED) approximation, SHG is only allowed in systems exhibiting a lack of spatial inversion symmetry; however, it is not an absolute prerequisite as, beyond this ED approximation, other SHG contributions can be allowed in centro-symmetric media, as discussed in the following. The large majority of the SHG studies are focused on the ED approximation on non-centro-symmetric systems.

The most trivial manifestation of inversion symmetry emerges at the surface of any material. Here, the abrupt material discontinuity triggers an SHG activity, as nicely illustrated by the early use of SHG as a powerful probe for surface reconstruction[34,35]. In ferroelectric materials, spatial inversion symmetry is inherently broken by definition, and hence, SHG appears as an ideal tool to probe ferroelectric materials. Such materials are, in fact, used as efficient frequency-doubling crystals in optical setups such as the well-known -$BaBO_3$. We note that a careful analysis of the properties of reemitted SHG is absolutely necessary to properly assess ferroelectric states and polar textures[36].

Formally, the source of emitted electromagnetic radiation can be expanded into multipoles whose first order is a time oscillating electric dipole[37]. Therefore, the dominant source of SHG is an oscillating electric dipole ($\vec{P}(2\omega)$) at twice the frequency of the incident light ($\vec{E}(\omega)$). These two quantities are related to each other by 2nd-order non-linear susceptibilities (χ) that reflect the symmetry of the system and, according to the Von Neumann principle, of the order parameter[38] in the following way.

$$\vec{P}(2\omega) = \epsilon_0 \chi : \vec{E}(\omega) \otimes \vec{E}(\omega)$$

Noteworthy, in most of the SHG experiments, the measured quantity is the light intensity that, in the ED approximation, can be written as $I(2\omega) \propto \left|\vec{P}(2\omega)\right|^2$. As a non-linear effect, SHG can be weak, and intense incident light intensities are usually required. For this reason, SHG measurements are often performed with pulsed (nanosecond to femtosecond) lasers for which the peak electric field is fairly high. Besides, as an optical technique, one can benefit from a large panel of experimental configurations already well mastered in the optical community, such as wide-field or scanning microscopies and spectroscopies, transmission or reflection geometries, far-field or near-field, static or time-resolved approaches[36]. This makes SHG measurements very versatile and able to tackle a large variety of condensed matter and materials science issues.

Probing magnetically ordered materials, magnetoelectrics and multiferroics

Time-inversion symmetry breaking is another important ingredient that can come into play in SHG processes. Magnetism and magnetic orders, which can, to some extent, be time-noninvariant, can be revealed by SHG investigations[39]. The SHG source terms can then be rewritten by including both the time-invariant (i) and the time-noninvariant (c) susceptibilities in the following way in which magnetic symmetry groups have to be taken into account[38]:

$$\vec{P}(2\omega) = \epsilon_0(\chi^{(i)} + \chi^{(c)}) : \vec{E}(\omega) \otimes \vec{E}(\omega)$$

Besides, these non-linear susceptibilities can be directly related to various order parameters such as the ferroelectric polarization, as discussed by Sa *et al.* where they derived a theory of SHG from energy considerations[40]. Regarding magnetism, the "intrinsic" interface sensitivity of SHG has been used to probe magnetic interfaces and, in particular, address the differences between bulk and surface magnetism[41-43]. However, MFM, optical Faraday rotation, or X-ray magnetic CD-based techniques, among others, are nowadays preferred to probe ferromagnetic textures. On the other hand, SHG stands as a perfectly suited probe to investigate complex and entangled multiferroic orders, in particular magnetoelectric systems, as illustrated by the pioneering work of Fiebig *et al.*[44]. In this work, the multiferroic state of a $YMnO_3$ crystal has been imaged by SHG, revealing both ferroelectric and antiferromagnetic domains, see Figure 3.

SHG measurements are usually performed in the visible and near-infrared ranges, for which, even in near-field configurations, the spatial resolutions are far from allowing atomic details to resolve. However, one striking advantage of SHG lies, in particular, in the fact that it is highly sensitive to the symmetry of the order parameters in the atomic cell, and even without atomic resolution, one can differentiate between complex spin texture arrangements. For instance, it has been evidenced that a thorough analysis of the dependence of the SHG intensity on the light polarization directions could reveal the different spin configurations in hexagonal manganites depending on the temperature and their composition[45]. Different magnetic populations could even be imaged. The case of ferroelectric-antiferromagnetic multiferroic materials is quite peculiar. In these materials, not only does the crystal lattice obviously break the space inversion symmetry, but the magnetic lattices can also be non-centrosymmetric. This makes it possible to straightforwardly observe antiferromagnetism in the ED approximation, where the ferroelectric polarization can be seen as an SHG "amplifier". However, in a more general framework and beyond the mere ED approximation, sources of SHG are fairly numerous. Indeed, the sources of electromagnetic radiation can be expanded to higher orders[37], and not only oscillating electric dipole ($\vec{P}(2\omega)$) but oscillating magnetic ($\vec{M}(2\omega)$) dipole and electric quadrupole ($\vec{Q}(2\omega)$) can contribute. Furthermore, it is not only the oscillating electric field ($\vec{E}(\omega)$) of the incident light that matters but also its magnetic field ($\vec{H}(\omega)$). Extended reviews of the formal development of SHG formalism and the various scenarios can be found in the review articles of Fiebig *et al.*, Denev *et al.*, and Kiriliuk *et al.*[36,39,41].

The SHG emission may be allowed in systems in which both crystal and magnetic lattices are fully centrosymmetric, as illustrated in Figure 4. This is the case of the Nickel oxide (NiO), which is not a multiferroic but is a prototypical insulating antiferromagnet whose interest lies in its high implication in THz and ultrafast spintronics research. In the case of NiO, while all the ED types of SHG are forbidden, a strong second harmonic intensity could be measured[46]. It has been demonstrated that the source term of this observed SHG in NiO involves the magnetic field ($\vec{H}(\omega)$) of the incident fundamental light as follows: $\vec{P}(2\omega) \propto \chi(l^2) : \vec{E}(\omega) \otimes \vec{H}(\omega)$ where the symmetry of the 2nd-order non-linear susceptibility depends on the

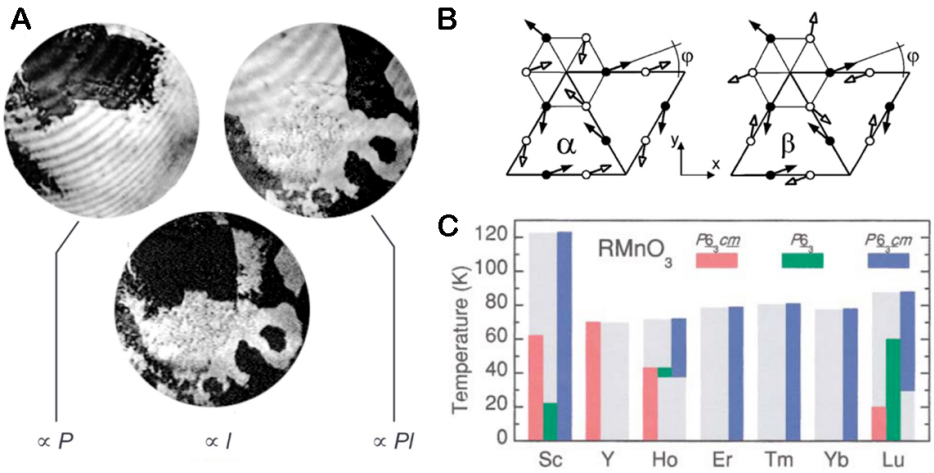

Figure 3. Pioneer work revealing entangled ferroic orders. (A)SHG images evidencing the ferroelectric, coupled ferroelectric/antiferromagnetic, and antiferromagnetic textures in $YMnO_3$ single crystal, reprinted with permission from Fiebig *et al.* Copyright 2002 by the Nature Publishing Group[44]. (B) Possible magnetic states of hexagonal manganites, reprinted from Fiebig *et al.* Copyright 2000 by the American Physical Society[45]. (C) Identification of the various magnetic in hexagonal manganites depending on the Rare-Earth and temperature, reprinted with permission from Fiebig *et al.* Copyright 2000 by the American Physical Society[45].

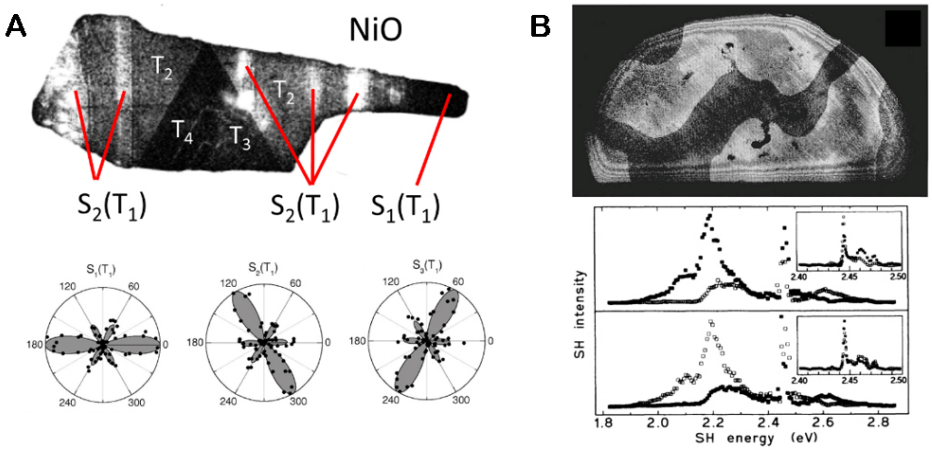

Figure 4. Direct visualization of the AF order in insulating antiferromagnets. (A) SHG imaging of the antiferromagnetic state of a NiO crystal and the SHG intensity angular dependences corresponding to the various antiferromagnetic S domains, top panel reprinted with permission from Fiebig *et al.* Copyright 2001 by the American Physical Society[46]. The lower panel reprinted with permission from Sänger *et al.* Copyright 2006 by the American Physical Society[47]. (B) SHG imaging of 180° antiferromagnetic domains in a Cr_2O_3 crystal and the dependence in energy of the SHG intensity presenting the large circular dichroism at resonance, which leads to the SHG antiferromagnetic contrast. Top panel reprinted with permission of AIP Publishing from Fiebig *et al.* and lower panel reprinted with permission from Fiebig et al. Copyright 1994 by the American Physical Society[48,49].

square of the antiferromagnetic $\vec{l}$[47]. Note that, generally speaking, this source of SHG is expected to be several orders of magnitude smaller than the terms allowed in non-centrosymmetric materials. However, in the case of NiO, SHG is experimentally detectable only at certain incident wavelengths, for which it is highly enhanced by a double absorption process driven by both by $\vec{E}(\omega)$ and $\vec{H}(\omega)$, addressing special electronic transitions of the Ni^{2+} ion. Nonetheless, it has been proven to be able to resolve the fairly complex and silent magnetic texture of NiO, directly measuring antiferromagnetic vectors, distinguishing it from other techniques.

On the other hand, while tuning the incident wavelength can be solely used to enhance the SHG intensity, it can also promote interferences between time-invariant (i-type) and time-noninvariant (c-type) SHG source terms that can be extremely valuable as magnetic orders can be a source of time symmetry breaking. For instance, in the magnetoelectric antiferromagnet Cr_2O_3, whose magnetic order is non-centrosymmetric, the interference below the Néel temperature between two source terms, namely $\vec{M}(2\omega) \propto \chi^{(i)}: \vec{E}(\omega) \otimes \vec{E}(\omega)$ and $\vec{P}(2\omega) \propto \chi^{(c)}: \vec{E}(\omega) \otimes \vec{E}(\omega)$, allows to directly image 180° antiferromagnetic domains[48,49]. Note that the interferences between i-type and c-type source terms are evidenced at given wavelengths when incident light absorption is present and where non-linear susceptibilities are complex.

Most importantly, all the discussed observations of ferroic textures by SHG are not possible using standard linear optical approaches. Indeed, SHG represents one of the few techniques enabling direct probe antiferromagnetism that is a very "silent" magnetic order, exhibiting no net magnetization, rendering it quite challenging to assess. Therefore, SHG emerges as a powerful tool to reveal hidden and entangled electric and antiferromagnetic orders in multiferroics. However, one noticeable downside of SHG lies in the fact that knowing the symmetry of the system of interest is an important prerequisite for an unambiguous analysis of SHG and its ferroic textures. While on bulk crystals, this knowledge could usually be fairly known, and the case of thin epitaxial layers can be more subtle. Therefore, performing an SHG experiment on a fully unknown system would most probably fail in providing a deep understanding of its ferroic texture. In addition, for an insightful SHG analysis, the incident light has to propagate in a single and controlled direction.

Probing ferroic orders in thin films

As discussed in this perspective article, multiferroic thin epitaxial layers could play a major role in the next generation of information technology devices, and their ferroic textures need to be fully understood and mastered. SHG is undoubtedly a useful and powerful experimental approach to tackle materials science issues and, in particular, in the science of ferroic materials [Figure 5], as highlighted in several recent studies. For instance, SHG has been able to successfully discriminate different kinds of complex ferroelectric domain arrangements in thin films [Figure 5A][50], and it could even provide important information on the nature of ferroelectric domain walls [Figure 5B][51], revealing the non-Ising type of these domain walls. In prototypical ferroelectric lead zirconate titanate thin films with a single domain, out-of-plane oriented configuration, a net in-plane polarization has been detected at 180° ferroelectric domain walls. For such a tetragonal system, SHG is sensitive to polar displacements confined in a plane perpendicular to the k vector of the incoming fundamental light[52]. Hence, in a normal incidence optical configuration, in-plane polarization components within an out-of-plane oriented matrix can be investigated, free of background signals[53]. Further analysis of the SHG signal using polarimetry measurements allowed for determining the orientation of this in-plane polarization component. In lead zirconate titanate films, the in-plane polarization appeared to point in a direction perpendicular to the plane of the domain walls, indicating a Neel character of the wall. Note that Bloch-type ferroelectric walls, exhibiting a domain-wall polarization lying within the plane of the domain wall, have been reported in $LiTaO_3$ crystals[51].

Besides, in the same vein as the pioneering work of Fiebig *et al.* on single crystals, SHG imaging allowed to directly image both ferroelectric and antiferromagnetic textures, this time in a thin epitaxial layer of $BiFeO_3$ with a sub-micron spatial resolution [Figure 5C][44,54].

Hence, complementary to scanning probe-based investigations[10-13], optical SHG characterizations are key for the understanding of complex magnetic and electric ordering in both bulk and thin materials. In the following section, we will discuss the evolution of SHG investigations and highlight some exciting trends in the field.

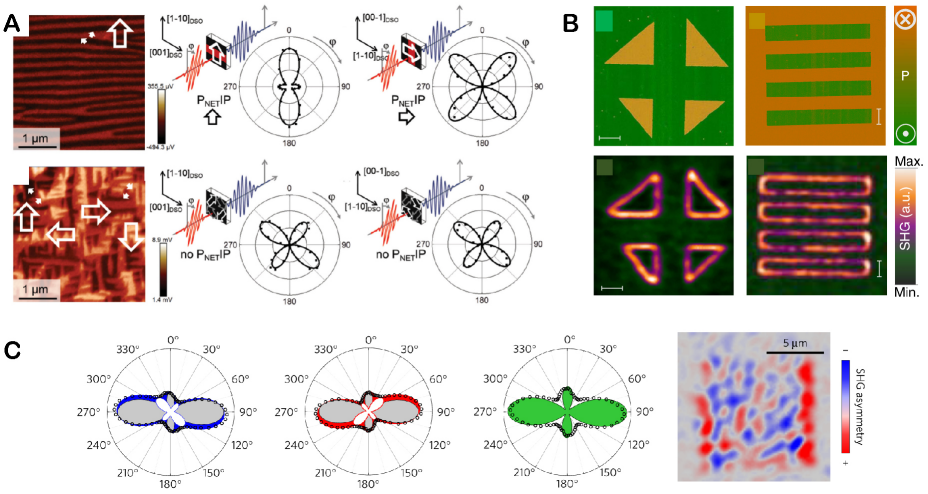

Figure 5. SHG Insights in ferroic thin film textures. (A) SHG measurements of two different types of ferroelectric textures in $BiFeO_3$ thin epitaxial layers, reprinted with permission from Trassin *et al.* Copyright 2015 by Wiley- VCH[50]. Panel (B) top images: piezoresponse force images of a crystal. Bottom images, related SHG images evidencing the non-Ising type of the ferroelectric domain walls, reprinted with permission from Chérifi-Hertel *et al.* Copyright 2017 by the Authors under Creative Commons Attribution 4.0 International License, published by the Nature Publishing Group[51]. Panel (C) SHG study of $BiFeO_3$ thin epitaxial layers imaging both the ferroelectric and antiferromagnetic domains, reprinted with permission from Chauleau *et al.* Copyright 2017 by the Nature Publishing Group[54].

EMERGING CONCEPTS AND MATERIAL STUDIES

The study of multiferroic materials, subject to a revival over the last two decades with the stabilization of high-quality thin films and technological developments, has triggered combined efforts of both the ferroelectric and magnetic research communities. Recently, the observation of ferroelectric skyrmions[25], hitherto believed to be restricted to magnetically ordered materials, further supports this synergy. In the following, we will show how SHG investigations keep on supporting the most recent achievements in the field of ferroelectric and multiferroic oxides thin film research.

Exotic polar phase stabilization in oxide superlattices

With the recent progress in material design and the ability to monitor epitaxial thin film growth with atomic accuracy, ferroic systems are becoming more and more elaborate. Mastering the synthesis of oxides heterostructures and so-called superlattices has led to the emergence of exotic ferroic phases, in particular if multiferroics are involved. Using the immense potential of oxide interface engineering and tuning electrostatic and elastic boundary conditions in ferroelectric/dielectric[55], ferroelectric/metal[56], and even more recently, ferroelectric/ferroelectric interfaces[57,58], the electric dipole configurations can be manipulated at will, and ferroelectric vortices, ordered ferroelectric domains formation, and electric exchange, such as interactions, have been reported, respectively.

The canonical material system is undoubtedly the periodic stacking of $PbTiO_3/SrTiO_3$ systems. Here, the right combination of depolarizing field-induced domain formation and strain states leads to the controlled formation of ferroelectric nanosized domains[59,60], including flux-closure type domains, ferroelectric vortices, or ferroelectric skyrmions. However, so far, most of the electric dipole ordering investigations have relied on destructive scanning transmission electron microscopy or large-scale facility X-ray diffraction experiments. None of these techniques are compatible with the convenient laboratory-scale investigation of the dynamics of such nanoscale polar objects.

A recent study revealed how optical SHG could bring relevant insights into the complex domain ordering in the $PbTiO_3/SrTiO_3$ superlattice[61]. Symmetry analysis based on SHG measurements enabled the identification of the vortex phase in a matrix of in-plane oriented ferroelectric domains. Because SHG probes the entire volume of the superlattice, a thickness-dependent interference pattern between successive $PbTiO_3$ layers provided information on the relative orientation of the axial component of the vortices' polarization, see Figure 6A.

In other ferroelectric/dielectric type superlattices such as in the case of the epitaxial layering of $BiFeO_3$ and $TbScO_3$, a centrosymmetric antipolar phase in $BiFeO_3$ has been reported to coexist with a ferroelectric $BiFeO_3$ matrix[62]. Here, the intense depolarizing field caused by the absence of charge screening in the dielectric layer enforces a phase transition from polar to antipolar in the $BiFeO_3$ layer. Many experimental approaches have been performed to investigate this complex system, and SHG stood out as a perfect tool, see Figure 6B. Indeed, as previously described in the earlier section, no SHG intensity is measured from the antipolar centrosymmetric regions, leading to a large SHG contrast between the two phases. As a non-invasive technique, in-operando SHG could be performed to evidence the electrical switching between the two phases. Hence, SHG appeared instrumental in the demonstration of electric field-induced reversible phase transition.

Emerging polar textures and chirality in ferroelectrics

The joint efforts in both theoretical methods and experiments to investigate and stabilize chiral electric dipole configuration have reached an important milestone with the observation of ferroelectric skyrmions[25,63]. Originally predicted by second-principle calculations[64], the stabilization of Bloch-type domain walls in ferroelectric leads to the formation of polar skyrmions, see Figure 7A. In the previous section, we revealed how the SHG-based detection of in-plane polarization components at 180° domain walls has been key in the demonstration of the Neel-type character of ferroelectric domain walls written using scanning probe microscopic tip-induced voltage[51,53], as shown in Figure 7B. Such Neel-type rotation of the electric dipole across the domain wall has been confirmed by local polarization mapping using transmission electron microscopy[53]. Hence, enriched by the observation of non-Ising type domain walls in tensile-strain lead zirconate titanate thin films, one may expect to demonstrate the stabilization of Neel-type skyrmions in strained thin film heterostructures in the near future.

The experimental characterization of chiral Bloch-type skyrmions is challenging and has so far been relying on advanced electron microscopy imaging[25]. Chirality, as such, is not an easy quantity to measure, and while most studies conclude on chirality based on its consequence on macroscopic dynamic behaviors, CD measurements stand out as an efficient determination of net chirality in material systems. As mentioned in the introduction, CD REXS measurements are one possible way. CD[65] in SHG intensity is another approach to assess chirality. Recently, Behera *et al.* have used CD-SHG to elegantly reveal complex ferroelectric winding in $PbTiO_3/SrTiO_3$ heterostructures [Figure 7C-E][66]. By performing the difference image between two SHG images acquired with circularly right and left polarizations, it is possible to distinguish domains of ferroelectric textures having opposite chiral arrangements [Figure 7F and G]. Chirality is an important ingredient of topology that is, nowadays, one of the major concepts of modern condensed matter, and therefore, SHG measurements could be a great asset to unveil the complex textures of topological ferroic systems.

Direct monitoring of polarization during the epitaxial design

Because of its long working distance, optical SHG has been used to probe surface reactions for many years[67]. Only recently, the first report dealing with its implementation for the diagnostic ferroelectric thin film growth appeared[28,68,69]. The substrate-induced strain involved in the epitaxial growth of most classical

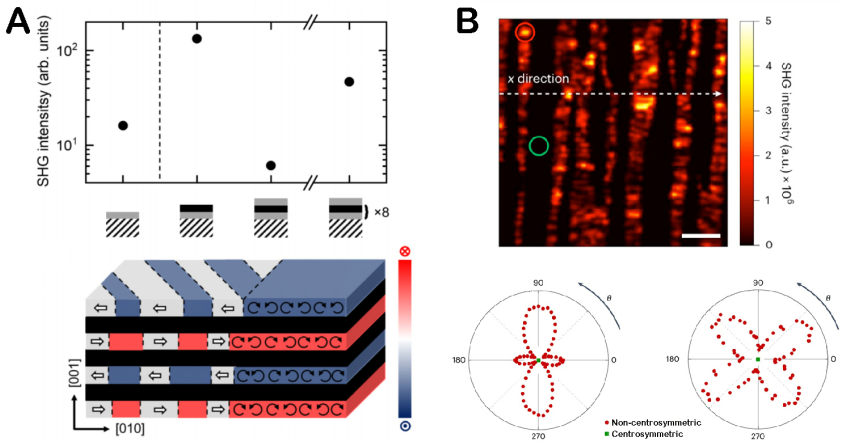

Figure 6. SHG measurements in ferroic superlattices. (A) Integrated SHG intensity as a function of the number of $PbTiO_3$/$SrTiO_3$ bilayers in the superlattice. The oscillation between odd and even numbered $PbTiO_3$ constituents is the signature of destructive interferences between the SHG waves emitted from the ferroelectric layers, hence, of locally reversed polarization in neighboring PTO layers, reprinted with permission from Strkalj *et al.* Copyright 2022 by the American Physical[61]. Panel (B) SHG image of a $BiFeO_3$/$TbScO_3$ heterostructures evidencing centrosymmetric (antipolar) and usual non-centrosymmetric (polar) domains and SHG intensity angular dependence showing a typical ferroelectric behavior in the non-centrosymmetric areas, reprinted with permission from Caretta *et al.* Copyright 2022 by the Nature Publishing Group[62].

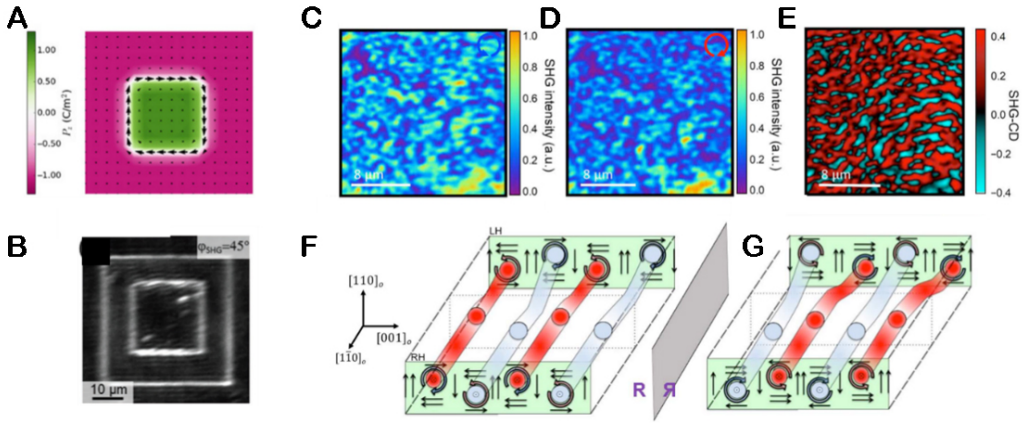

Figure 7. Polar skyrmions and chirality in ferroelectrics. (A) calculated stabilization of Bloch-type skyrmions in $PbTiO_3$. Reprinted from Gonçalves *et al.* Reprinted with permission of AAAS publications[64]. (B) SHG imaging revealing Neel-type domain walls in $PbZr_{0.2}Ti_{0.8}O_3$ thin films. Reprinted with permission from De Luca *et al.* Copyright 2017 by Wiley-VCH[53]. (C-E) SHG images of $PbTiO_3$/$SrTiO_3$ heterostructures. SHG images acquired for circular left (C) and right (D) incident light, respectively. (E) Resulting difference showing areas of opposite dichroism. This latter can be related, to some extent, to two possible ferroelectric winding in the heterostructure (F and G), reprinted from Behera *et al.* with permission of AAAS publications[66].

ferroelectric thin films boosts the Curie temperature of the films to temperatures largely exceeding the growth temperature[70]. Hence, optical SHG is allowed during the first few unit cells deposited. This *in-situ* SHG (ISHG) approach resulted in seminal studies revealing the interface contributions on the onset of ferroelectricity, the determination of the critical thickness, and the ferroelectric transition temperature in $BiFeO_3$[68], $BaTiO_3$[28], and $PbTiO_3$[71] model systems.

Most strikingly, the direct access to the polarization during the growth revealed dynamical processes and transient polarization states only present during the deposition of the film. The ability to monitor the polarization of films during the growth and right at the growth interruption allows disentangling the contribution of top and bottom interfaces, see Figure 8A, and, hence, expedites the understanding of competing and cooperative effects towards the stabilization of ultrathin ferroelectricity[72,73]. These

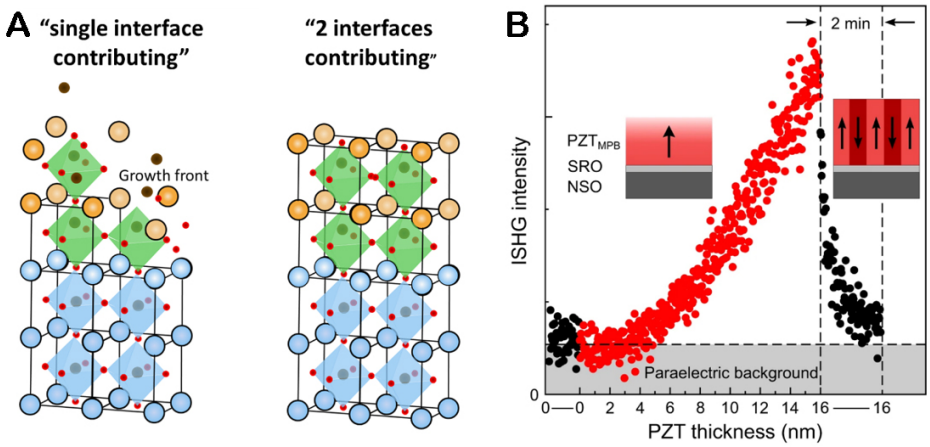

Figure 8. *In-situ* monitoring of ferroelectric polarization. (A) During epitaxial thin film growth, the top surface is melted into the growth front; so, transiently, the polarization state is driven solely by the bottom interface contribution, leading to a so-called single-interface contributing system. At the growth completion, the top interface is settled, and a two-interface contribution system is recovered. (B) Depolarizing field effect and surface off-stoichiometry stabilize nanometric domain formation in lead zirconate titanate thin films near the morphotropic phase transition composition (PZT_{MPB}), leading to an abrupt suppression of the ISHG signal at the growth completion. Reprinted with permission from Sarott *et al.* Copyright 2022 by the Authors under Creative Commons Attribution 4.0 International License published by the Nature Publishing Group[75].

investigations highlighted the role of the growth atmosphere[74], epitaxial strain in the domain formation during growth[71], and the impact of buffer termination and surface off-stoichiometry[72] on the final polarization state.

Here, in contrast with synchrotron-based measurements where periodic domain formation leads to additional satellite peaks in the diffraction pattern, the formation of 180° domains leads to destructive interferences of the SHG waves and, thus, to a suppression of the total SHG yield[50]. Tracking the ISHG intensity variation during the growth results in an efficient probe of oppositely oriented domain formation in thin films[71]. The most recent outcome of such ISHG investigations rendered possible the interface-controlled stabilization of nanometric domains in lead zirconate titanate thin films at a composition near the morphotropic phase transition, see Figure 8B, for reliable multilevel polarization switching[75], key for memristive and neuromorphic type computing schemes[76,77].

Here, direct access to the targeted functionality supports our understanding of the role of the depolarizing field in the ultrathin regime and can become an indispensable tool to assess the growth mechanisms of complex oxides in general[78]. This *in-situ* diagnostic tool has been instrumental in the recent demonstration of the suppression of the depolarizing field effects in thin films using an artificial flux closing architecture. Here, the epitaxial combination of out-of-plane and in-plane polarized ferroelectric layers enables polarization continuity at the interfaces and annihilates the detrimental effect of the depolarizing field[79]. The SHG performed during the growth of $BaTiO_3$ and $BiFeO_3$ thin films on an ultrathin in-plane polarized buffer[80] revealed the onset of polarization from the very first unit cell deposited.

SHG as a probe of ultrafast ferroic phenomena

With the increasing need to process information at a faster rate and lower energy cost, the investigation of ferroic systems presenting picosecond and sub-picosecond characteristic dynamics has become of great importance. This is, nowadays, a vast full-fledged field of research[81,82], and various ultrafast time-resolved techniques are available. SHG stands out thanks to its compatibility with ultrafast time-resolved studies for

both electrically and magnetically ordered materials. Nowadays, SHG experiments are mostly performed with femtosecond lasers, and therefore, there are no intrinsic restrictions for ultrafast pump-probe experiments. One limitation might only lie in the reduced intensity of the SHG signals to assess small time-dependent variations. Time-resolved SHG studies have brought important insights into the dynamics of the various systems and, in particular, of ferroic orders. The ultrafast manipulation of the ferroelectric polarization under mid-infrared excitation[83] or the magnetic dynamics in pure antiferromagnetic insulators[84,85] and in multiferroic materials[86] are excellent examples. A substantial effort is still required to reach a full master of the sub-picosecond dynamics of ferroic orders at the nanoscale in order to integrate them into future ultrafast and THz technologies, and therefore, time-resolved SHG experiments will have a main role to play.

SHG, beyond the optical diffraction limit

Given the adage *"Seeing is believing"*[87], intense efforts are being devoted to the visualization of ferroic and antiferroic domains. Here, scanning probe microscopy-based techniques dominate the current experimental capacity with nanometer spatial resolution[10-13]. Mostly performed at visible wavelengths, spatial resolutions accessible with SHG experiments are usually in the range of several hundreds of nanometers to a micron. However, most ferroic objects in epitaxial thin layers, i.e., domains and domain walls, have characteristic sizes of a few tens of nanometers, preventing far-field optical techniques from imaging them properly.

However, one can go beyond the optical diffraction limit by considering near-field approaches and performing scanning near-field optical microscopy (SNOM). Indeed, in the particular case of ferroelectric textures, Neacsu *et al.* have demonstrated the possibility of imaging 200 nm wide ferroelectric domains in $YMnO_3$ with an ultra-high spatial resolution[88]. More recently, near-field SHG has brought some insights into the study of the complex oxide heterostructures hosting polar vortices[89]. The phase coexistence between ferroelectric (strong SHG emission) and vortex phase (weak SHG emission) was imaged with tens of nanometer resolution. However, performing near-field SHG microscopy is, up to now, far from being a routine technique and requires particularly careful analysis. For example, in the case of $YMnO_3$, the observed SHG yield corresponds to an interference signal between near-field and far-field contributions. Yet, with the need for a better understanding of ferroic objects, in particular in antiferromagnetic or multiferroic textures, mastering near-field SHG would be a clear asset. In particular, apertureless SNOM can also be compatible with ultrafast measurements and, therefore, could uniquely image the dynamics of these ferroic entities with a rather uncharted territory.

CONCLUSION

In this short perspective article, we presented the evolution of the field dealing with the investigation of functional materials using optical SHG. Together with emerging non-invasive probes such as NV-electrometry and REXS, SHG became instrumental in the ongoing investigations of ferroic and multiferroic thin films. We highlight the unmatched capabilities of SHG to probe complex polar systems and discuss some of the most recent materials studies involving exotic polar phases and polar skyrmions. We discussed the power of *in-situ* motoring to facilitate the design of the next generation of ferroelectric material-based heterostructures. Finally, we give our point of view on the future challenges and development of time-resolved and near-field imaging approaches that could revolutionize the experimental investigation of technologically relevant systems.

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Author's contributions
Chauleau JY and Trassin M wrote the manuscript jointly.

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Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
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Consent for publication
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REFERENCES
1. Fiebig M, Lottermoser T, Meier D, Trassin M. The evolution of multiferroics. *Nat Rev Mater* 2016;1:16046. DOI
2. Wolf SA, Awschalom DD, Buhrman RA, et al. Spintronics: a spin-based electronics vision for the future. *Science* 2001;294:1488-95. DOI
3. Müller M, Efe I, Sarott MF, Gradauskaite E, Trassin M. Ferroelectric thin films for oxide electronics. *ACS Appl Electron Mater* 2023;5:1314-34. DOI
4. Varotto S, Nessi L, Cecchi S, et al. Room-temperature ferroelectric switching of spin-to-charge conversion in germanium telluride. *Nat Electron* 2021;4:740-7. DOI
5. Trassin M. Low energy consumption spintronics using multiferroic heterostructures. *J Phys Condens Matter* 2016;28:033001. DOI PubMed
6. Manipatruni S, Nikonov DE, Lin CC, et al. Scalable energy-efficient magnetoelectric spin-orbit logic. *Nature* 2019;565:35-42. DOI
7. Heron JT, Bosse JL, He Q, et al. Deterministic switching of ferromagnetism at room temperature using an electric field. *Nature* 2014;516:370-3. DOI
8. Leo N, Carolus V, White JS, et al. Magnetoelectric inversion of domain patterns. *Nature* 2018;560:466-70. DOI
9. Chauleau JY, Chirac T, Fusil S, et al. Electric and antiferromagnetic chiral textures at multiferroic domain walls. *Nat Mater* 2020;19:386-90. DOI
10. Gruverman A, Alexe M, Meier D. Piezoresponse force microscopy and nanoferroic phenomena. *Nat Commun* 2019;10:1661. DOI PubMed PMC
11. Kalinin SV, Morozovska AN, Chen LQ, Rodriguez BJ. Local polarization dynamics in ferroelectric materials. *Rep Prog Phys* 2010;73:056502. DOI
12. Seidel J. Scanning probe microscopy investigation of topological defects. *Symmetry* 2022;14:1098. DOI
13. Balke N, Maksymovych P, Jesse S, et al. Differentiating ferroelectric and nonferroelectric electromechanical effects with scanning probe microscopy. *ACS Nano* 2015;9:6484-92. DOI
14. Fong DD, Thompson C. In situ synchrotron X-ray studies of ferroelectric thin films. *Annu Rev Mater Res* 2006;36:431-65. DOI
15. Rondin L, Tetienne JP, Hingant T, Roch JF, Maletinsky P, Jacques V. Magnetometry with nitrogen-vacancy defects in diamond. *Rep Prog Phys* 2014;77:056503. DOI PubMed
16. Gross I, Akhtar W, Garcia V, et al. Real-space imaging of non-collinear antiferromagnetic order with a single-spin magnetometer. *Nature* 2017;549:252-6. DOI

17. Dufour P, Abdelsamie A, Fischer J, et al. Onset of multiferroicity in prototypical single-spin cycloid $BiFeO_3$ thin films. *Nano Lett* 2023;23:9073-9. DOI
18. Haykal A, Fischer J, Akhtar W, et al. Antiferromagnetic textures in $BiFeO_3$ controlled by strain and electric field. *Nat Commun* 2020;11:1704. DOI PubMed PMC
19. Huxter WS, Sarott MF, Trassin M, Degen CL. Imaging ferroelectric domains with a single-spin scanning quantum sensor. *Nat Phys* 2023;19:644-8. DOI PubMed PMC
20. Huxter WS, Palm ML, Davis ML, et al. Scanning gradiometry with a single spin quantum magnetometer. *Nat Commun* 2022;13:3761. DOI PubMed PMC
21. Fink J, Schierle E, Weschke E, Geck J. Resonant elastic soft x-ray scattering. *Rep Prog Phys* 2013;76:056502. DOI
22. van der Laan G. Soft X-ray resonant magnetic scattering of magnetic nanostructures. *CR Phys* 2008;9:570-84. DOI
23. Lovesey SW, Scagnoli V. Chirality, magnetic charge and other strange entities in resonant x-ray Bragg diffraction. *J Phys Condens Matter* 2009;21:474214. DOI PubMed
24. Durr HA, Dudzik E, Dhesi SS, et al. Chiral magnetic domain structures in ultrathin FePd films. *Science* 1999;284:2166-8. DOI
25. Das S, Tang YL, Hong Z, et al. Observation of room-temperature polar skyrmions. *Nature* 2019;568:368-72. DOI
26. McCarter MR, Kim KT, Stoica VA, et al. Structural chirality of polar skyrmions probed by resonant elastic x-ray scattering. *Phys Rev Lett* 2022;129:247601. DOI
27. Fusil S, Chauleau J, Li X, et al. Polar chirality in $BiFeO_3$ emerging from a peculiar domain wall sequence. *Adv Elect Mater* 2022;8:2101155. DOI
28. Strkalj N, De Luca G, Campanini M, et al. Depolarizing-field effects in epitaxial capacitor heterostructures. *Phys Rev Lett* 2019;123:147601. DOI
29. Shin YJ, Kim Y, Kang SJ, et al. Interface control of ferroelectricity in an $SrRuO_3/BaTiO_3/SrRuO_3$ capacitor and its critical thickness. *Adv Mater* 2017;29:1602795. DOI
30. Tagantsev AK, Gerra G. Interface-induced phenomena in polarization response of ferroelectric thin films. *J Appl Phys* 2006;100:051607. DOI
31. Roy K, Bandyopadhyay S, Atulasimha J. Switching dynamics of a magnetostrictive single-domain nanomagnet subjected to stress. *Phys Rev B* 2011;83:224412. DOI
32. Hoffmann T, Thielen P, Becker P, Bohatý L, Fiebig M. Time-resolved imaging of magnetoelectric switching in multiferroic $MnWO_4$. *Phys Rev B* 2011;84:184404. DOI
33. Garello K, Avci CO, Miron IM, et al. Ultrafast magnetization switching by spin-orbit torques. *Appl Phys Lett* 2014;105:212402. DOI
34. Heinz TF, Loy MM, Thompson WA. Study of Si_{111} surfaces by optical second-harmonic generation: reconstruction and surface phase transformation. *Phys Rev Lett* 1985;54:63-6. DOI PubMed
35. Mcgilp JF. Optical second-harmonic generation for studying surfaces and interfaces. *J Phys Condens Matter* 1989;1:SB85-92. DOI
36. Denev SA, Lummen TTA, Barnes E, Kumar A, Gopalan V. Probing ferroelectrics using optical second harmonic generation. *J Am Ceram Soc* 2011;94:2699-727. DOI
37. Pershan PS. Nonlinear optical properties of solids: energy considerations. *Phys Rev* 1963;130:919-29. DOI
38. Birss RR. Symmetry and magnetism. Amsterdam: North-Holland Publishing Company; 1964.
39. Fiebig M, Pavlov VV, Pisarev RV. Second-harmonic generation as a tool for studying electronic and magnetic structures of crystals: review. *J Opt Soc Am B* 2005;22:96-118. DOI
40. Sa D, Valentí R, Gros C. A generalized Ginzburg-Landau approach to second harmonic generation. *Eur Phys J B* 2000;14:301-5. DOI
41. Kirilyuk A, Rasing T. Magnetization-induced-second-harmonic generation from surfaces and interfaces. *J Opt Soc Am B* 2005;22:148-67. DOI
42. Maydykovskiy A, Temiryazeva M, Temiryazev A, Murzina T. Nonlinear optical microscopy of interface layers of epitaxial garnet films. *Appl Sci* 2023;13:8828. DOI
43. Mamonov EA, Novikov VB, Maydykovskiy AI, et al. Magnetic force and nonlinear optical microscopy of the surface domain structure in an epitaxial iron garnet film. *J Exp Theor Phys* 2023;136:31-8. DOI
44. Fiebig M, Lottermoser T, Fröhlich D, Goltsev AV, Pisarev RV. Observation of coupled magnetic and electric domains. *Nature* 2002;419:818-20. DOI PubMed
45. Fiebig M, Frohlich D, Kohn K, et al. Determination of the magnetic symmetry of hexagonal manganites by second harmonic generation. *Phys Rev Lett* 2000;84:5620-3. DOI
46. Fiebig M, Fröhlich D, Lottermoser T, Pavlov VV, Pisarev RV, Weber HJ. Second harmonic generation in the centrosymmetric antiferromagnet NiO. *Phys Rev Lett* 2001;87:137202. DOI PubMed
47. Sänger I, Pavlov VV, Bayer M, Fiebig M. Distribution of antiferromagnetic spin and twin domains in NiO. *Phys Rev B* 2006;74:144401. DOI
48. Fiebig M, Fröhlich D, Krichevtsov BB, Pisarev RV. Second harmonic generation and magnetic-dipole-electric-dipole interference in antiferromagnetic Cr_2O_3. *Phys Rev Lett* 1994;73:2127-30. DOI PubMed
49. Fiebig M, Fröhlich D, Sluyterman V L G, Pisarev RV. Domain topography of antiferromagnetic Cr_2O_3 by second-harmonic generation. *Appl Phys Lett* 1995;66:2906-8. DOI
50. Trassin M, De Luca G, Manz S, Fiebig M. Probing ferroelectric domain engineering in $BiFeO_3$ thin films by second harmonic generation. *Adv Mater* 2015;27:4871-76. DOI PubMed

51. Cherifi-Hertel S, Bulou H, Hertel R, et al. Non-Ising and chiral ferroelectric domain walls revealed by nonlinear optical microscopy. *Nat Commun* 2017;8:15768. DOI PubMed PMC
52. Nordlander J, De Luca G, Strkalj N, Fiebig M, Trassin M. Probing ferroic states in oxide thin films using optical second harmonic generation. *Appl Sci* 2018;8:570. DOI
53. De Luca G, Rossell MD, Schaab J, Viart N, Fiebig M, Trassin M. Domain wall architecture in tetragonal ferroelectric thin films. *Adv Mater* 2017;29:1605145. DOI PubMed
54. Chauleau JY, Haltz E, Carrétéro C, Fusil S, Viret M. Multi-stimuli manipulation of antiferromagnetic domains assessed by second-harmonic imaging. *Nat Mater* 2017;16:803-7. DOI PubMed
55. Yadav AK, Nelson CT, Hsu SL, et al. Observation of polar vortices in oxide superlattices. *Nature* 2016;530:198-201. DOI
56. Hadjimichael M, Li Y, Zatterin E, et al. Metal-ferroelectric supercrystals with periodically curved metallic layers. *Nat Mater* 2021;20:495-502. DOI
57. Kavle P, Ross AM, Zorn JA, et al. Exchange-interaction-like behavior in ferroelectric bilayers. *Adv Mater* 2023;35:e2301934. DOI
58. Gradauskaite E, Meier QN, Gray N, et al. Defeating depolarizing fields with artificial flux closure in ultrathin ferroelectrics. 2022. Avaliable from: http://arxiv.org/abs/2212.11073 [Last accessed on 17 Nov 2023].
59. Strkalj N, Gradauskaite E, Nordlander J, Trassin M. Design and manipulation of ferroic domains in complex oxide heterostructures. *Materials* 2019;12:3108. DOI PubMed PMC
60. Ramesh R, Schlom DG. Creating emergent phenomena in oxide superlattices. *Nat Rev Mater* 2019;4:257-68. DOI
61. Strkalj N, Bortis A, Campanini M, Rossell MD, Fiebig M, Trassin M. Optical second harmonic signature of phase coexistence in ferroelectric|dielectric heterostructures. *Phys Rev B* 2022;105:174101. DOI
62. Caretta L, Shao YT, Yu J, et al. Non-volatile electric-field control of inversion symmetry. *Nat Mater* 2023;22:207-15. DOI
63. Shafer P, García-Fernández P, Aguado-Puente P, et al. Emergent chirality in the electric polarization texture of titanate superlattices. *Proc Natl Acad Sci USA* 2018;115:915-20. DOI PubMed PMC
64. Gonçalves MA, Escorihuela-Sayalero C, Garca-Fernández P, Junquera J, Íñiguez J. Theoretical guidelines to create and tune electric skyrmion bubbles. *Sci Adv* 2019;5:eaau7023. DOI PubMed PMC
65. Lovesey SW, van der Laan G. Circular dichroism of second harmonic generation response. *Phys Rev B* 2019;100:245112. DOI
66. Behera P, May MA, Gómez-Ortiz F, et al. Electric field control of chirality. *Sci Adv* 2022;8:eabj8030. DOI PubMed PMC
67. Hu XF, Xu Z, Lim D, et al. *In situ* optical second-harmonic-generation monitoring of disilane adsorption and hydrogen desorption during epitaxial growth on Si_{001}. *Appl Phys Lett* 1997;71:1376-8. DOI
68. De Luca G, Strkalj N, Manz S, Bouillet C, Fiebig M, Trassin M. Nanoscale design of polarization in ultrathin ferroelectric heterostructures. *Nat Commun* 2017;8:1419. DOI PubMed PMC
69. Nordlander J, Campanini M, Rossell MD, et al. The ultrathin limit of improper ferroelectricity. *Nat Commun* 2019;10:5591. DOI PubMed PMC
70. Choi KJ, Biegalski M, Li YL, et al. Enhancement of ferroelectricity in strained $BaTiO_3$ thin films. *Science* 2004;306:1005-9. DOI
71. Sarott MF, Fiebig M, Trassin M. Tracking ferroelectric domain formation during epitaxial growth of $PbTiO_3$ films. *Appl Phys Lett* 2020;117:132901. DOI
72. Strkalj N, Gattinoni C, Vogel A, et al. *In-situ* monitoring of interface proximity effects in ultrathin ferroelectrics. *Nat Commun* 2020;11:5815. DOI PubMed PMC
73. Gattinoni C, Strkalj N, Härdi R, Fiebig M, Trassin M, Spaldin NA. Interface and surface stabilization of the polarization in ferroelectric thin films. *Proc Natl Acad Sci USA* 2020;117:28589-95. DOI PubMed PMC
74. Sarott MF, Bucheli U, Lochmann A, Fiebig M, Trassin M. Controlling the polarization in ferroelectric PZT films via the epitaxial growth conditions. *Adv Funct Mater* 2023;33:2214849. DOI
75. Sarott MF, Rossell MD, Fiebig M, Trassin M. Multilevel polarization switching in ferroelectric thin films. *Nat Commun* 2022;13:3159. DOI PubMed PMC
76. Marković D, Mizrahi A, Querlioz D, Grollier J. Physics for neuromorphic computing. *Nat Rev Phys* 2020;2:499-510. DOI
77. Chanthbouala A, Garcia V, Cherifi RO, et al. A ferroelectric memristor. *Nat Mater* 2012;11:860-4. DOI
78. Sarott MF, Gradauskaite E, Nordlander J, Strkalj N, Trassin M. In situmonitoring of epitaxial ferroelectric thin-film growth. *J Phys Condens Matter* 2021;33:293001. DOI PubMed
79. Gradauskaite E, Meier QN, Gray N, et al. Defeating depolarizing fields with artificial flux closure in ultrathin ferroelectrics. *Nat Mater* 2023;22:1492-8. DOI
80. Gradauskaite E, Campanini M, Biswas B, et al. Robust in-plane ferroelectricity in ultrathin epitaxial aurivillius films. *Adv Materials Inter* 2020;7:2000202. DOI
81. Zhang Y, Dai J, Zhong X, Zhang D, Zhong G, Li J. Probing ultrafast dynamics of ferroelectrics by time-resolved pump-probe spectroscopy. *Adv Sci* 2021;8:e2102488. DOI PubMed PMC
82. Kirilyuk A, Kimel AV, Rasing T. Ultrafast optical manipulation of magnetic order. *Rev Mod Phys* 2010;82:2731-84. DOI
83. Mankowsky R, von Hoegen A, Först M, Cavalleri A. Ultrafast reversal of the ferroelectric polarization. *Phys Rev Lett* 2017;118:197601. DOI PubMed
84. Duong NP, Satoh T, Fiebig M. Ultrafast manipulation of antiferromagnetism of NiO. *Phys Rev Lett* 2004;93:117402. DOI PubMed
85. Satoh T, Van Aken BB, Duong NP, Lottermoser T, Fiebig M. Ultrafast spin and lattice dynamics in antiferromagnetic Cr_2O_3. *Phys Rev B* 2007;75:155406. DOI

86. Tzschaschel C, Satoh T, Fiebig M. Tracking the ultrafast motion of an antiferromagnetic order parameter. *Nat Commun* 2019;10:3995. DOI PubMed PMC
87. Cheong S, Fiebig M, Wu W, Chapon L, Kiryukhin V. Seeing is believing: visualization of antiferromagnetic domains. *npj Quantum Mater* 2020;5:3. DOI
88. Neacsu CC, van Aken BB, Fiebig M, Raschke MB. Second-harmonic near-field imaging of ferroelectric domain structure of $YMnO_3$. *Phys Rev B* 2009;79:100107. DOI
89. Damodaran AR, Clarkson JD, Hong Z, et al. Phase coexistence and electric-field control of toroidal order in oxide superlattices. *Nat Mater* 2017;16:1003-9. DOI