Phase engineering in oxides by interfaces

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Optical second harmonic generation and piezoresponse force microscopy are used to investigate manifestations of ordered states directly related to the presence of an oxide interface. Three examples, each with a very different scope, are reviewed in order to highlight the richness of interface-related phenomena in oxides. (i) The orbital states involved in the emergence of an interfacial conducting state in LaAlO$_3$/SrTiO$_3$ heterostructures are investigated, which reveal a surprising decoupling of orbital and transport properties; (ii) the distribution of ferroelectric and antiferromagnetic domains in epitaxial films of the multiferroic hexagonal manganites is investigated, which reveals striking differences to the corresponding bulk crystals; and (iii) the distribution of trimerization–polarization domains in the hexagonal manganites is investigated, which reveals the presence of topologically protected domain walls with properties different from the bulk.

Keywords: interfaces; oxides; multiferroics; nonlinear optics; piezoresponse force microscopy

1. Introduction: oxide interfaces and the spatial degree of freedom

Modern electronics devices greatly benefit from the rich and fascinating physics occurring at interfaces [1,2]. This is strikingly reflected by p- and n-type semiconductors: on their own, they show rather unspectacular bulk conductivity, yet, when brought together, their full potential unfolds because of the functionality at the interface, which allows us to design those diodes and transistors on which today’s information technology relies [3]. In oxide electronics, interfaces now play an equally important role because the technology for the growth of ultrathin oxide films or heterostructures has approached a level of atomic control similar to that achieved with semiconductors [4]. Yet, in excess of the single-electron approach applied to semiconductor systems, strong electronic correlations and an entanglement of spin, charge, orbital and lattice degrees of freedom generate striking interface phenomena in oxides such as insulator–metal transitions, magnetism and superconductivity [5–8].

Interfaces contribute to the emergence of these phenomena in multifarious ways. They provide dimensional confinement, strain, chemical interactions, topological singularities, and discontinuities of the electromagnetic field and

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the related potential. The presence of an interface involves two types of discontinuities. On the one hand, we have the obvious inhomogeneities occurring in the direction perpendicular to the interface. On the other hand, inhomogeneities may also occur in directions parallel to the interface. In a simplified approach, the latter may be neglected but, as shown explicitly in Nakagawa et al. [9], manifestations of disorder such as an inherent roughness along the interface can be the key to a deeper understanding of exotic interface phenomena. In order to access both types of inhomogeneities, spatially resolving detection techniques are required. For instance, atomic resolution can be conveniently obtained by force microscopy techniques. However, here we aim for experimental techniques providing spatial resolution on length scales around one micrometre so that, in particular, those phenomena involving the presence of domains are addressed.

In this contribution to the Royal Society meeting on ‘The new science of oxide interfaces’, I discuss three examples for interface phenomena in oxides, where spatial resolution on length scales of nanometres to micrometres is essential for their understanding. The examples are chosen from rather different backgrounds in order to emphasize the general influence interfaces have on the properties of oxides. (i) Polarization-dependent optical second harmonic generation (SHG) spectroscopy reveals that the emergence of a conducting state at the interface between LaAlO$_3$ and SrTiO$_3$ is related to two types of electronic reorganization processes on length scales of about one and about 10 monolayers, respectively [10]. (ii) In multiferroic hexagonal (h-)manganite films of 10–1000 nm, SHG measurements show that the formation of ferroelectric and antiferromagnetic domains is quite different from the bulk. The presence of the interface promotes a single-domain ferroelectric matrix holding ferroelectric nanodomains of a preferred orientation. In contrast, the magnetic domains are three to four orders of magnitude smaller than in the bulk [11]. (iii) In ferroelectric h-YMnO$_3$, the presence of a crystallographic anti-phase boundary is found to control the spontaneous polarization across a distance of about 100 unit cells. Piezoresponse force microscopy (PFM) reveals that this leads to an unusual topology of the ferroelectric domain structure, with a poling behaviour that is quite different from that of other ferroelectrics [12].

2. Samples and interfaces

(a) The perovskitic LaAlO$_3$/SrTiO$_3$ system

A striking example for interface-driven effects in oxides is the formation of a two-dimensional electron liquid (2DEL) at the interface between two textbook-type band insulators, LaAlO$_3$ and SrTiO$_3$ [13]. The 2DEL is formed if four or more monolayers of LaAlO$_3$ are grown onto the SrTiO$_3$ and its formation is accompanied by the emergence of properties such as bistable conductivity, magnetic order and superconductivity [14–16]. Key aspects of the 2DEL, in particular (i) the microscopic mechanisms driving it and (ii) the distribution of charges around the interface, are a topic of controversial discussions. With respect to (i), the emergence of the 2DEL at the LaAlO$_3$/SrTiO$_3$ interface was originally ascribed to the electrostatic instability arising from the polar discontinuity at the interface. Charge carrier transfer to the interface would avoid
the limitless increase of the electrostatic potential [17] and may promote the formation of the 2DEL. The compelling intuition behind this model is diminished by a variety of inconsistencies. For example, the carrier density expected at the interface is an order of magnitude larger than the density observed in Hall measurements [14], an issue termed the ‘missing charge problem’ [18]. Regarding (ii), discussions about the width of the 2DEL are controversial. Propositions range from band-bending scenarios reminiscent of semiconductors [19] to confinement in a single monolayer [20] (with a prevalence towards the latter). In both cases, (i) and (ii), an experimental technique probing the LaAlO₃/SrTiO₃ interface with spatial sensitivity in the range of nanometres and a capability to distinguish between the electronic processes contributing to the emergence of the 2DEL is highly desirable.

(b) The multiferroic hexagonal manganites

Compounds uniting magnetic and ferroelectric order in the same phase are termed multiferroics. The multiferroic order can promote pronounced magneto-electric cross-correlations, an important ingredient for the design of novel multifunctional devices. The h-RMnO₃ compounds with $R = \text{Sc, Y, Dy–Lu}$ constitute a system of textbook multiferroics in which the magnetic and ferroelectric order occur independently. Ferroelectric ordering occurs in a two-stage transition [21,22], with a Curie temperature $T_C$ of around 1000 K and a spontaneous polarization of about 5.5 $\mu$C cm⁻². At a Néel temperature $T_N$ between 70 and 130 K, antiferromagnetic ordering of the magnetic Mn³⁺ spins occurs in the basal plane perpendicular to the sixfold $z$-axis [23,24]. The spins are oriented along the $x$- or $y$-axis in a triangular fashion [25,26]. Between 4 and 8 K, additional magnetic $R^{3+}$ ordering with reordering of the Mn³⁺ spins occurs in the compounds with partially filled 4f shell [27].

Our interest in the h-RMnO₃ compounds is twofold. On the one hand, they display pronounced magnetoelectric effects, including a ferromagnetic state induced by an electric field as well as a coupling of antiferromagnetic and ferroelectric domain walls. Here, the growth of thin h-RMnO₃ films would allow us to achieve high electric fields with battery voltages and employ interfacial strain as an additional degree of freedom for optimizing the magnetoelectric performance. On the other hand, the ferroelectric state in h-RMnO₃ is improper and driven by electrostatic effects in contrast to the primary, displacive mechanisms found in other ferroelectrics. This has fundamental consequences for the structure and properties of the ferroelectric domain walls, which can therefore be regarded as mobile oxide interfaces with interesting new functionalities. Spatially resolving detection techniques would allow us to study the distribution of the magnetic and the electric domains as well as their coupling.

3. Experimental techniques with spatial resolution on the meta-scale

(a) Optical second harmonic generation

Optical SHG is a powerful non-invasive technique that is specifically sensitive to interfaces. It is based on the induction of light waves of frequency $2\omega$ by incident waves of frequency $\omega$ and described by the equation $P_i(2\omega) = \varepsilon_0 \chi_{ijk} E_j(\omega) E_k(\omega)$.
Here $E(\omega)$ denotes the electric field of the incident light, whereas the induced nonlinear polarization $P(2\omega)$ acts as source term for the SHG light wave with the intensity $I_{\text{SHG}}(2\omega) \propto |P(2\omega)|^2$. The susceptibility $\chi_{ijk}$ connects the $j$- and $k$-polarized components of the fundamental light to the $i$-polarized component of the SHG light. The interface sensitivity of the SHG process results from its coupling to the broken inversion symmetry at the interface, while contributions from the centrosymmetric bulk material are suppressed [28,29]. Microscopically, the loss of inversion symmetry corresponds to a uniform displacement of ionic and electronic charges, and SHG probes the ensuing distribution of polarization. This also works when uniform polarization discontinuities evolve on the background of a non-centrosymmetric host material. In this case, the geometry of the SHG experiment is chosen such that SHG contributions from the polarity of the host material are suppressed by addressing SHG susceptibilities that are not sensitive to it. The SHG contributions from the polar discontinuities can then emerge free of background.

In the present SHG spectroscopy experiment, frequency-tunable laser pulses of 130 fs are generated at 1 kHz by an optical parametric amplifier pumped by a Ti:sapphire amplifier system. The LaAlO$_3$/SrTiO$_3$ interface was investigated with a standard 90° reflection setup [30] with light incident at 45° to the surface of the sample. Three independent non-zero contributions to the SHG susceptibility are allowed: $\chi_{zzz} = \chi_{yzy}$, $\chi_{xxz} = \chi_{yxz} = \chi_{yyz} = \chi_{yzy}$ and $\chi_{zzz}$. The $h$-RMnO$_3$ films were investigated with a standard reflection setup [30]. Their magnetic properties were probed with light incident along the hexagonal $z$-axis with which the ferroelectric order is not addressed. In turn, the ferroelectric order is addressed with light incident non-normally to the film, whereas the magnetic order is suppressed by measuring above $T_N$.

The lateral resolution of the SHG experiments ranges between 1 and 20 µm for far-field experiments. Near-field SHG experiments can enhance the resolution [31] but were not applied here. The vertical resolution of the SHG experiments is determined by absorption, evanescence and phase-matching effects, and may reach limits of the order of a single monolayer.

(b) Pizoresponse force microscopy

In the PFM experiments, scanning force microscopy is used for probing the piezoelectric deformation of a ferroelectric sample subjected to an electric field applied via the force microscope tip. We simultaneously recorded the topography of the sample and the distribution of the ferroelectric domains [32–34]. The amplitude of the alternating voltage applied to the tip for the PFM measurements is typically 15 V$_{pp}$ at a frequency of $\approx 40$ kHz. The PFM images presented here show the in-phase output channel from the lock-in amplifier. Typical settings are a sensitivity of 100 µV and a time constant of 10 ms. Scanning was performed with a typical velocity of $\approx 1$ µm s$^{-1}$, always recording both the out-of-plane and the in-plane piezoresponse of the sample with two separate lock-in amplifiers.

(c) Sample preparation

In the experiments on the LaAlO$_3$/SrTiO$_3$ system, two sets of samples were used (for details, see [10]). In both sets, interfacial conduction (sheet conductance $\sigma_S = 10^{-5}–10^{-4}$ Ω$^{-1}$ at 300 K) emerges at $n = 4$, while all the $n < 4$ samples show a
Figure 1. SHG intensity at 3.6 eV measured on a LaAlO$_3$/SrTiO$_3$ interface as a function of the number \(n\) of LaAlO$_3$ monolayers deposited on the SrTiO$_3$ substrate. The data are shown for the 90$^\circ$ reflection setup with p-polarized incident fundamental and reflected SHG light. The orbital reconstruction occurring at \(n = 3\) is indicated by the dashed line. Error bars have the size of the data points.

sheet conductance below the detection limit of $10^{-9}$ \(\Omega^{-1}\). A standard linear-optical characterization was performed by spectroscopic ellipsometry.

In the experiments on the h-RMnO$_3$ films, a variety of \(R\) ions, growth types and values of film thickness were compared (for details, see [11]). The films possessed a thickness of 20–1000 nm and were grown on YSZ(111) by pulsed laser deposition (PLD) or by liquid-injection metal organic chemical vapour deposition (MOCVD). The substrates had been polished on both sides for optical transmission experiments. The quality of all films was analysed by X-ray diffraction. The $\theta$–$2\theta$ diffractograms, rocking curves and pole figures indicated epitaxial hexagonal and \(z\)-oriented growth of the films. The ferroelectric properties of the h-RMnO$_3$ films were investigated under ambient conditions. For probing the magnetic order, the samples were mounted in a liquid-helium-operated optical cryostat.

In the experiments on ferroelectric domains in the h-RMnO$_3$ bulk crystals, flux-grown \(z\)-oriented platelets of YMnO$_3$ were investigated. The lateral extension of the samples is a few millimetres in the basal plane and about 50 $\mu$m along the \(z\)-axis. The samples were cut and polished, and investigated under ambient conditions.

4. Experimental results and discussion

(a) Electronic reconstruction at the LaAlO$_3$/SrTiO$_3$ interface

Figure 1 shows the dependence of the total SHG yield on the number of LaAlO$_3$ monolayers deposited on the SrTiO$_3$. This is supplemented in figure 2 by the explicit spectral and polarization dependence of the three independent SHG susceptibilities $\chi_{xxx}$, $\chi_{xxz}$ and $\chi_{zzz}$ (see §3a). The SHG susceptibilities were derived

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Figure 2. Spectral dependence of the three independent susceptibilities ($\chi_{xzx}$, $\chi_{zxz}$, $\chi_{zzz}$) contributing to SHG from the LaAlO$_3$/SrTiO$_3$ interface. For the $\chi_{zzz}$ component samples with $n \geq 3$ (a) and $n \leq 3$ (b) are distinguished. (Online version in colour.)

from the SHG signal obtained with light polarized parallel, perpendicular, and diagonal to the plane of the reflected light beam as detailed in Rubano et al. [10]. All spectra show a resonance at 3.6 eV with a width of $\approx 0.1$ eV. In addition, the $\chi_{xzx}$ and $\chi_{zxz}$ spectra display a pronounced positive slope extending beyond 3.7 eV. As explained in Rubano et al. [10], the slope can be associated to the band edge of the $O_2^− \rightarrow Ti^{4+}$ charge-transfer excitation, whereas the resonance indicates an SrTiO$_3$ state bound to the interface but not existing in the bulk. The relation of the spectral features in figure 2 to the SrTiO$_3$ is confirmed by their presence even in the bare SrTiO$_3$ substrate ($n = 0$), whereas contributions from a LaAlO$_3$ reference sample were not observed in the spectral range investigated here.

Striking changes of the SHG signal occur, once the third monolayer of LaAlO$_3$ is deposited. The total SHG intensity in figure 1 increases jump-like. The enhancement at $n = 3$ affects the entire spectrum of the $\chi_{xzx}$ and $\chi_{zxz}$ components in figure 2 (with precursors in the $\chi_{xzx}$ component at $n = 1$ and in the $\chi_{zxz}$ component at $n = 2$). Note, however, that the spectral shape of these components does not change. In contrast, the $\chi_{zzz}$ component displays a constant amplitude but a spectral red shift by about 0.1 eV is observed at $n = 3$. The origin of these modifications is associated with changes in the Ti$^{4+}(3d(t_{2g}))$ rather than with those in the O$^2−(2p)$ orbitals because the former are known to be easily displaceable [35,36].

The uniform enhancement of the $\chi_{xzx}$ and $\chi_{zxz}$ spectra at $n = 3$ shows that the polarizations of two rather different spectral transitions are enhanced by the interface reconstruction: that of the bulk-like state represented by the 3.7 eV slope and that of the surface state represented by the 3.6 eV peak. Apparently, both
are affected by the interface reconstruction in the same way. In addition, none of the electronic orbitals probed via the $\chi_{xx}$ and $\chi_{zz}$ susceptibilities are shifted in energy in the course of the transition. We conclude that the surface state and the bulk-like state merely respond to polarizing effects generated elsewhere. Here ‘elsewhere’ refers to the site of the primary orbital reconstruction that, apparently, is not revealed by the $\chi_{xx}$ and $\chi_{zz}$ components.

This issue is elucidated by the response of the $\chi_{zzz}$ component. With three $z$ polarized light-waves involved, it is expected to display a particularly enhanced interface sensitivity because of the structural and, thus, polarization discontinuity along $z$ [37]. The insensitivity of the $\chi_{zzz}$ amplitude to $n$ is most likely caused by the symmetry breaking at the surface, which dominates the $\chi_{zzz}$ amplitude irrespective of the explicit value of $n$. The spectral redistribution of $\chi_{zzz}$ suggests a band splitting owing to an orbital reconstruction within the Ti$^{4+}$ surface state, which induces the aforementioned polarizing effects picked up by the $\chi_{xx}$ and $\chi_{zz}$ components. Theoretical calculations are in excellent agreement with this scenario: according to Lee & Demkov [38], the spectral redistribution may be associated with crystal-field splitting of the order of 0.1 eV due to population of the $d_{xy}$ orbital. Most importantly, the splitting is calculated to occur only at the very first SrTiO$_3$ interface monolayer [38]. This agrees very well with an order-of-magnitude estimate for the SHG intensities obtained from the $\chi_{xx}/\chi_{zz}$ and the $\chi_{zzz}$ susceptibilities [10]. We find that the signal from $\chi_{xx}$ and $\chi_{zz}$ is emitted from a region which has to be by an order of magnitude thicker than the region from which the signal from $\chi_{zzz}$ is emitted. From Ogawa et al. [39], we know that the SHG signal associated with the ionic displacements stems from about eight monolayers of SrTiO$_3$ next to the LaAlO$_3$/SrTiO$_3$ interface. Consequently, the SHG signal related to the orbital reconstruction is found to be associated mostly with a single layer.

An issue that remains to be clarified is the striking separation of the orbital reconstruction at $n = 3$ from the emergence of the 2DEL at $n = 4$. Apparently, the charge carriers are still localized at the LaAlO$_3$/SrTiO$_3$ interface when the major carrier-induced orbital reconstruction has occurred. It is known that the $d_{xy}$ orbitals are prone to disorder-induced localization [36] so that one may speculate that local disorder may trap the carriers. Alternatively, the LaAlO$_3$ may stabilize a self-trapped polaron in SrTiO$_3$ [40]. It is remarkable that in terms of the SHG data, the emergence of conduction is so clearly separated from the orbital reconstruction. A variety of mechanisms may contribute to this. (i) SHG may be less sensitive to mobile than to localized carriers; (ii) application of the fourth LaAlO$_3$ monolayer may free some of the carriers trapped at $n = 3$, so that the total number of carriers at the interface (and the associated SHG yield) may not change; and (iii) the number of carriers contributing to conduction may be much smaller than the number of trapped carriers contributing to the orbital reconstruction. This latter point would also give a simple solution to the aforementioned ‘missing charge problem’ [14].

Thus, we have seen that polarization-dependent SHG spectroscopy probes the emergence of the 2DEL at the LaAlO$_3$/SrTiO$_3$ interface ‘at its root’ by probing the orbital states of the electrons participating in the reconstruction of the interface. This allows us to reveal a decoupling of the orbital reconstruction from the transport behaviour. Here, major changes occur when the third and fourth monolayer, respectively, of the LaAlO$_3$ is deposited. However, as figure 1
shows subtle changes in the electronic transition cover the entire range from $n = 1$ to $n = 6$. Because we are able to probe the vicinity of the interface with a spatial resolution in the nanometre range, we are able to distinguish regions contributing to the processes at the interface in a very different way, i.e. by orbital reconstruction and screening, respectively.

(b) *Interfacially induced nanodomains in hexagonal RMnO$_3$ films*

(i) *Ferroelectric domains*

Figure 3 shows the polarization and the temperature dependence of the SHG intensity from h-HoMnO$_3$ excited with light incident along the $z$-axis. Figure 3$a,b$ were obtained from a flux-grown HoMnO$_3$ bulk crystal, whereas figure 3$c,d$ were obtained from epitaxial HoMnO$_3$ films of 600 nm grown by PLD and mounted in the cryostat along with the bulk single crystal. Films grown by MOCVD reveal a similar result (not shown). The anisotropy measurements in figure 3$b,d$ were gained by detecting the component of the SHG light polarized parallel to the linear polarization of the incident fundamental light while rotating this polarization from 0° to 360°. Figure 3$b$ reveals a polarization dependence with a sixfold symmetry that is characteristic for the antiferromagnetic order. The rotation of the polarization dependence by 90° at $T_R = 40$ K indicates a uniform reorientation of the magnetic moments by 90° that is likewise characteristic for h-HoMnO$_3$. Spatially resolved SHG images reveal the presence of antiferromagnetic domains [25]. At $T_N$ the SHG signal drops to zero because as mentioned in §3a no SHG signal is expected in the paramagnetic state for light incident along the $z$-axis.

The HoMnO$_3$ films reveal a polarization dependence that is similar to the polarization dependence of the bulk crystal, yet with a SHG intensity that is 1–2 orders of magnitude weaker than for the bulk sample. At 300 K, the signal is 70 per cent lower than at 10 K but neither the spin reorientation at $T_R$ nor the transition to the paramagnetic state at $T_N$ are visible. Spatially resolved SHG images (not shown) do not reveal any domains. In spite of the similarity of figure 3$b,d$ this points against antiferromagnetic order as origin of the SHG signal in figure 3$d$ because, according to neutron diffraction, $T_N$ in the h-RMnO$_3$ films deviates by only approximately 10 per cent from $T_N$ in the h-RMnO$_3$ bulk samples [41].

Higher multipole or surface contributions would not lead to the SHG yield in figure 3 so that the most likely explanation for the signal are ferroelectric contributions. As mentioned before, ferroelectric contributions to SHG cannot be excited by light incident along the $z$-axis. However, they are possible for regions (crystallites) with secondary orientations, whose crystallographic $z$-axis is tilted with respect to the $z$-axis of the epitaxial matrix.

It is known that such inclusions can occur, but the circumstances of their presence and their distribution in the h-HoMnO$_3$ films have not been investigated. Therefore, we first of all confirmed the ferroelectric origin of the SHG signal in figure 3 by comparing its spectral dependence to that of the ferroelectric SHG signal gained from a h-RMnO$_3$ bulk sample. The resulting spectra (not shown) look very similar and differ distinctly from the spectral dependence of the antiferromagnetic SHG signal.
Further experiments revealed that the occurrence of the proposed inclusions is a very general phenomenon. They are present in all the h-RMnO$_3$ films investigated here, and even with a film thickness of 1000 nm, the density of the inclusions both at the surface oriented towards the substrate and at the surface oriented towards air is the same. Thus, the formation of the inclusions cannot be due to growth-induced strain imposed by the substrate. It is possible that local strain generated by the misoriented nano-inclusions leads to the formation of further inclusions upon continued growth even up to 1 μm. In any case, even at a macroscopic thickness, the crystallographic properties of the h-RMnO$_3$ films do not approach the properties of the bulk crystal [42]. Comparing the SHG yields of the h-RMnO$_3$ films with that of a bulk single crystal reveals $10^{-3}$ as volume density of the inclusions (with unsystematic variations among samples within one order of magnitude). This is beyond the sensitivity of X-ray diffraction experiments and explains why their presence has not been observed before.

Figure 4 shows the origin of the sixfold anisotropy of the SHG signal in figure 3. In the h-RMnO$_3$ system with its $P6_3cm$ space symmetry, there are six equivalent directions (110). In the $xy$ plane, this corresponds to the three possible directions $n = 1, 2, 3$ of the misoriented crystallites. Each direction is associated with a ferroelectric SHG signal with a polarization anisotropy in the shape of a double lobe [43], so that we get a sixfold polarization anisotropy after adding up the
Figure 4. Sketch of the distribution of differently oriented ferroelectric nano-inclusions in the epitaxial $z$-oriented h-RMnO$_3$ matrix along with the resulting intensity and anisotropy of the SHG signal. The direction of the local polarization of the nano-inclusions may be along $+z'_i$ (white arrows) or $-z'_i$ (black arrows) with $i = 1, 2, 3$. (a) The $z$ component of the polarization of the nano-inclusions in (b) and (d). (b) Sketch for equal distribution of nano-inclusions with polarization along $+z'_i$ and $-z'_i$. (c) The calculated net SHG intensity for a distribution of nano-inclusions as in (b) cancels, which is indicated by the dot at zero intensity. (d) Sketch for preferentially oriented polarization of the nano-inclusions, here along $+z'_i$. (e) Fit (solid line) of the SHG intensity for a distribution of nano-inclusions as in (d). SHG data (filled circles) obtained from a HoMnO$_3$ film of 100 nm grown by MOCVD confirm the scenario in (d) while disagreeing with (b) and (c).

SHG contributions for the three different orientations. The SHG data in figure 4 show that the distribution of nano-domains is not homogeneous. For each of the directions $i = 1, 2, 3$, a pair of crystallites with a polarization along $+z'_i$ and $-z'_i$ is possible. Their opposite polarization corresponds to the two ferroelectric $180^\circ$ domain states. Because of the opposite phase of the SHG light from opposite $180^\circ$ domain states, the overall SHG yield would cancel owing to destructive interference if domains polarized along $+z'_i$ and $-z'_i$ were equally distributed. The presence of the SHG signal shows that one set of nano-domains, here represented by white arrows, prevails and leads to a non-zero SHG yield. A preferred direction of polarization of the nano-inclusions indicates that the isotropy of the h-RMnO$_3$ film with respect to ‘up’ ($+z$) and ‘down’ ($-z$) is broken. This is the case if the direction of polarization in the epitaxial $z$ oriented h-RMnO$_3$ ‘matrix’ is also

Phil. Trans. R. Soc. A (2012)
uniform, i.e. if the matrix forms a ferroelectric single-domain state. This is indeed confirmed by spatially resolved SHG measurements, which revealed an absence of domain walls.

(ii) **Antiferromagnetic domains**

The absence of antiferromagnetic contributions to the SHG signal in figure 3d in spite of the presence of antiferromagnetic order [41,44,45] can be explained by a similar interference argument as in the previous section. Like in the case of the ferroelectric domains, the SHG contributions from opposite antiferromagnetic 180° domain states are phase-shifted by 180° with respect to each other so that the overall SHG yield cancels owing to destructive interference if domains with the antiferromagnetic order parameters +ℓ and −ℓ are equally distributed. The cancellation will be the more effective, the smaller the lateral size of the domains is. Here we estimate that their extension has to be below 150 nm and hence at least three orders of magnitude smaller than in bulk single crystals, in order to lead to a SHG signal that is not detectable by our experiment. The small size may be due to the strain [46] or due to a dense distribution of crystallographic discontinuities due to translation domains that might form because of the ambiguity of covering the substrate with the trimerized ferroelectric lattice (see following section).

We thus see that the interface between the substrate and the h-RMnO₃ film modifies markedly the size and distribution of ferroelectric as well as antiferromagnetic domains in the multiferroic h-RMnO₃ compounds. The modification is not limited to the vicinity of the interface, but it is maintained across macroscopic length scales so that the functionality of the epitaxial films in comparison to bulk single crystals is substantially modified.

(c) **Protected ferroelectric domain walls in hexagonal RMnO₃**

Figure 5 illustrates the unusual origin of the ferroelectric state in the h-RMnO₃ system. The primary order parameter is a deformation according to the $K_3$ mode of the symmetry group $P6_3/mmc$. The deformation corresponds to the uniform tilt of three MnO₅ bipyramids in relation to a central $R^{3+}$ ion. This triples the size of the unit cell and introduces three translation domain states denoted as $α$, $β$ and $γ$. They correspond to the three possible choices for the $R^{3+}$ ion around which the MnO₅ tilt can centre. The threefold tilt is rigidly coupled to the emergence of a spontaneous polarization described by a $Γ_{2}^−$ mode so that the ferroelectricity is improper. A tilt of the triplet of MnO₅ bipyramids towards, or away from, the $R^{3+}$ ion corresponds to the spontaneous polarization $+P_z$ or $−P_z$, respectively. In total, this leads to six trimerization–polarization domains (denoted as $α^±$, $β^±$, and $γ^±$).

Figure 6 shows the domain pattern on the $z$- and the $x$-face of a YMnO₃ crystal recorded by PFM under ambient conditions. On both faces (and also on the $y$ face, not shown here), similar domain patterns with a typical domain size of a few micrometres are resolved. Two grey levels correspond to the spontaneous polarization $+P_z$ and $−P_z$. The distribution of the ferroelectric domains is striking. It reveals a kaleidoscopic domain structure with intersections of always six domains.

*Phil. Trans. R. Soc. A* (2012)
Figure 5. Emergence of ferroelectric trimerization–polarization domains in h-YMnO$_3$. (a) Crystal at more than 1270 K with the unit cell (small diamond) and three possibilities for the trimerization at 1270 K (large diamonds). (b) Ferroelectric crystal with tripled unit cell. Sets of three MnO$_5^{3+}$ bipyramids (shaded triangles) tilt uniformly with respect to a central Y$^{3+}$ ion, thus generating a spontaneous polarization $+P_z$ or $-P_z$. The choice of the central Y$^{3+}$ ion determines the trimerization domain state as $\alpha$, $\beta$, or $\gamma$ (large diamonds). Mn$^{3+}$ ions, $z$ position in the unit cell; Y$^{3+}$ ions, local symmetry; O$^{2-}$ ions at different sites. (Online version in colour.)

Figure 6c shows how these intersections can be exemplarily assigned to an $\alpha^+$, $\beta^-$, $\gamma^+$, $\alpha^-$, $\beta^+$, $\gamma^-$ vortex of domains.\footnote{Scenarios such as (i) $\alpha^-$, $\alpha^+$, $\beta^-$, $\beta^+$, $\gamma^-$, $\gamma^+$ or (ii) $\alpha^+$, $\gamma^-$, $\beta^+$, $\alpha^-$, $\gamma^+$, $\beta^-$ are equivalent.} In the earlier studies [12,47], it was explained that trimerization and polarization domain walls are rigidly clamped. The crystallographic discontinuity characterizing a change of trimerization domain enforces a reversal of the spontaneous polarization, and vice versa, so that neither $\alpha^+$/ $\alpha^-$ nor $\alpha^+$/$\beta^+$ walls (and correspondingly) do occur. This is related to the distortion characterizing the $K_3$ mode. The smoothest transition from an $\alpha^+$ to a $\beta^+$ state occurs via a $\gamma^-$ state that explains the occurrence of a sequence of all six alternatingly polarized translation-polarization domains around an intersection. (A microscopic model describing this in a quantitative way is in development.) There is an apparent resemblance of the domain structure in figure 6 to domain structures in discommensurate systems undergoing a transition from an incommensurate to a commensurate charge-density wave [48,49]. Yet, a different mechanism must be at work in the $RMnO_3$ system that has no incommensurate phase and lacks many of the characteristic features of the discommensurate domain state. This includes an unexpected nearly homogeneous distribution of intersections in all three spatial directions. It was resolved by the PFM measurements in Jungk et al. [12] and points to a mechanism that is not influenced by the uniaxial structure of the crystal lattice.

Figure 7 reveals the most striking aspect of the trimerization–polarization domains. The image shows the domain structure of the h-YMnO$_3$ sample after scanning it with a constant voltage applied to the PFM tip. In contrast to displacive ferroelectrics, it is not possible to convert the entire YMnO$_3$ sample into a single-domain state. Interstitial domains with a width of $60 \pm 10$ nm (about 100 unit cells) remain between the domains polarized parallel to the applied electric
Figure 6. PFM images recorded (a) on the z face and (b) on the x face of a h-YMnO$_3$ crystal. In (c), the intersection of the trimerization–polarization domains is depicted schematically.

Field. Apparently, these interstitial domains are enforced by the electrostatic discontinuity occurring at the wall between two trimerization domain states. Unlike conventional ferroelectric domain walls, the trimerization–polarization walls cannot be removed by the poling procedure so that the walls and their intersections are topologically protected. As such, they represent mobile but persistent interfaces. It was already shown that the conductance of the domain walls varies by one order of magnitude around the conductance of the bulk [47,50]. Many other properties classifying ferroelectric domain walls in the h-RMnO$_3$ system as oxide interfaces with specific functionalities are conceivable.

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5. Summary

In summary, optical SHG spectroscopy and PFM allowed us to investigate different manifestations of phase engineering at oxide interfaces with spatial sensitivity. Three examples were reviewed.

(i) The generation of the 2DEL at the LaAlO₃/SrTiO₃ interface was found to originate in a reconstruction of the Ti⁴⁺(3d) orbitals centred around \( n = 3 \) monolayers coverage. The reconstruction manifests as a spectral redistribution of a previously unseen Ti⁴⁺-related surface state. According to an order-of-magnitude estimate, it predominantly affects a single SrTiO₃ monolayer next to the interface. It is accompanied by a buildup of polarization in about ten monolayers around the interface that is presumably caused by small displacements of the Ti⁴⁺ ions. The carriers involved in the orbital reconstruction are trapped. The onset of conduction occurs as a separate process at \( n = 4 \). It involves a minority of carriers and leads to the emergence of a 2DEL with only minor changes of the electronic states involved.

(ii) The ferroelectric and the antiferromagnetic structure of epitaxial h-RMnO₃ films were characterized on nanoscopic length scales by optical SHG. The interfacially triggered formation of ferroelectric nano-inclusions with secondary orientations with respect to the \( z \)-axis of the epitaxial film matrix was observed in all samples, irrespective of growth technique and film thickness. The density of the inclusions is of the order of \( 10^{-3} \). The inclusions behave as nano-domains with a preferred direction of the spontaneous polarization, whereas the epitaxial \( z \) oriented matrix forms a ferroelectric single-domain state. Antiferromagnetic domains possess a mean lateral size of less than 150 nm, which is attributed to strain and antiphase boundaries.

(iii) The discontinuity at the trimerization–polarization domain walls in the improper ferroelectric h-RMnO₃ compounds was shown to induce locally polarizing fields that determine the spontaneous polarization within a range of 100 unit cells in all three spatial dimensions. Unlike conventional ferroelectric domain walls, the trimerization–polarization walls cannot be removed by the poling procedure so that the walls and their intersections are topologically protected. As such, they represent mobile but persistent interfaces with transport properties and potential functionalities different from the bulk.

The examples reviewed here show that the aspects of both oxide interfaces as well spatial resolution can be employed in a wider sense than is commonly done. Interfaces may include domain walls as natural and mobile boundaries between different states. Spatial resolution is not restricted to imaging experiments but may refer to the different length scales that are probed by a technique once the coupling parameter connecting microscopy and macroscopy (e.g. a susceptibility component) is varied.

who contributed to the work reviewed in this contribution to the Royal Society meeting on ‘The new science of oxide interfaces’.

References


