1. Title of the project

Electrical transport properties at the domain walls of thin films of hexagonal rare-earth manganites

2. Abstract

Domain walls in (multi)ferroic materials are regarded to have a huge potential in realization of new functionalities for future nanodevices. Domain walls, in ferroelectric materials in particular, show intriguing properties and could address many challenges lying ahead in electronics such as the trend of continued shrinking of device dimensions and lower power consumption. Although there has been a number of reports on conduction properties at Domain walls of conventional ferroelectrics such as $BiFeO_3$, hexagonal rare-earth manganites, especially in thin film form, have so far remained mostly neglected with regards to transport properties. This proposal mentions why DWs of hexagonal rare-earth manganites are promising candidates for electrical transport, and suggests a research plan for investigating their behaviour in thin film form, which would be the form that could be useful also for applications in electronics industry.

3. Applicant(s)

Arash Tebyani

4. Key publications of the applicant(s)

Recent developments in organic semiconducting materials with high dielectric constant (research paper for Nanoscience topmaster programme, supervised by Prof. dr. J. C. (Kees) Hummelen)

5. FOM research group

N/A

6. Institute

Nanostructures of Functional Oxides group, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

7. Duration of the project

Four years (PhD position), to be started Autumn 2017

8. Personnel

8.1 Senior scientist

Prof. dr. Beatriz Noheda	Supervisor	7%

8.2 Junior scientists and technicians:

Arash Tebyani	PhD student	90%
Jacob Baas	Technical support	5%
Henk Bonder	Technical support	5%

9. Cost estimates

9.1 Personnel positions

One PhD student For a duration of four years
Budget k€ 216 in total

9.2 Running Budget

Standard expenses for one experimental position
Budget: 4 × k€ 15 in total

9.3 Equipment

N/A

9.4 Other Support

N/A

9.5 Budget summary

	2017	2018	2019	2020	2021	TOTAL
Personnel (positions): PhD students Postdocs Students Guests	 1/3 - - -	 1 - - -	 1 - - -	 1 - - -	 2/3 - - -	 4 - - -
Personnel (costs) (k€) Running budget (k€) Equipment (k€)	18 5 -	54 15 -	54 15 -	54 15 -	36 10 -	216 60 -
TOTAL (requested from FOM)	23	69	69	69	46	276 (≤ k€ 425/600)

10. Research programme

10.1 Introduction

Transition metal oxides have attracted much attention from condensed matter research community due to their exotic properties and rich physics. A lot of transition metal oxides exhibit one or more ferroic properties, such as ferroelectricity, ferromagnetism and ferroelasticity. (Multi)ferroic materials spontaneously form domains: regions in which the order parameter has different, energetically equivalent orientations, separated by domain walls (DWs). DWs are a special type of interface which occur naturally in these materials. In contrast to interfaces in heterostructures of two materials where the interface is spatially fixed, DWs can move, be created or erased, thus allowing for another degree of freedom. Most research has traditionally been focused on the domains as the main part of (multi)ferroic materials, the part which can find applications in (future) devices. However, in the recent years it has been proposed that the DWs (or domain interfaces), rather than being defects to be avoided, could in fact be the desirable part of the material, e.g., by being able to carry information or act as memory devices. [7] Hence, at the moment there is a growing amount of research dedicated to these nanoscale structures.

According to Kittel's law, the size of the domains is proportional to the square root of the film thickness. Hence, as the trend of shrinking device dimensions continues, the domains get smaller and the concentration of DWs in the material increases. With rough estimations, DWs take between 6 and 20 percent of the volume of a 100-nm thick film. [5] Indeed the fraction of the material's volume that is occupied by the DWs is inversely proportional to the film thickness. This implies the possibility that the observed macroscopic properties of the material could be dominated by those of the DWs, with the bulk properties even being of secondary importance. [6] As an example, $TbMnO_3$films were grown on $SrTiO_3$ substrate with domains so small (about 5 nm in width) that about half of the material volume consisted of DWs.[5] With decreasing thickness, macroscopic magnetization of the nominally antiferromagnetic material was observed to increase. [5]

Domain walls are regions for transition between two different orientations of the order parameter. Inside the DWs, the order parameter is suppressed and there are strong gradients, while the order parameter is homogenous inside the domains. [5] DWs have different structures and different symmetries to those of the domains. They also have different free energies to those of the domains and hence, as first proposed by Lajzerowicz and Niez in 1979, can undergo their own internal phase transitions. [5] They have different thermodynamic properties as well. Also, the suppression of a primary order parameter inside a DW can lead to emergence of a suppressed secondary ferroic order, as first explained in 1991 by Houchmandzadeh, Lajzerowicz and Salje. [5] Therefore it is no wonder that DWs can and do exhibit exotic properties which are absent in the domains themselves. In multiferroics, emergent behaviour at the DWs is even more complex, because several order parameters are involved.

As examples of such properties, it has been predicted that in magnetoelectric multiferroics, the ferroelectric walls can be ferromagnetic even though the domain are antiferromagnetic. Or non-polar insulating ferromagnets can have DWs possessing local polarization. Preferential doping along the DWs has led to enhanced resistivity in phosphates and superconductivity in WO_{3-x}. DWs of metallic ferromagnets are found to be more resistive than the domains, possibly due to spin canting. [5] DWs of the paraelectric non-polar $SrTiO_3$are suggested to possess ferroelectric polarization, [3] and it's expected for the DWs of antiferroelectrics to be ferroelectric, or at least pyroelectric. [5]

Conductivity at the DWs in thin films of $BiFeO_3$ has been the subject of a lot of reports. The findings of some of these reports are briefly mentioned below. They serve the purpose of highlighting various parameters that could alter the DW conductivity (in thin films) or mechanisms and causes responsible for the conductivity which could be insightful for investigating other materials as well.

Conductivity at the 109˚ and 180˚ DWs of the multiferroic $BiFeO_3$, while the domains are insulating, was first reported by Seidel et al. in 2009. [3]. Changes in electrostatic potential (caused by a small change in the normal component of the polarization) and the electronic structure leading to a decrease in the bandgap were proposed as the causes of the observed conductivity in $BiFeO_3$, as those would accumulate charge carriers at the DW in order to screen the polarization discontinuity.[3,8] Possibility of tuning the band structure change by epitaxial strain was also suggested.[3] In another study by Seidel et al. in 2011, oxygen vacancies were reported to have a key role in conductivity at DWs of La-doped $BiFeO_3$.[4] Conduction through 71˚ DWs of $BiFeO_3$ was also later reported in 2011, and was proposed to be due to n-type carriers, and defect density was mentioned as a key parameter in current density. [11] Substrate induced strain and elastic interactions were also suggested to be partially responsible for conduction of 71˚ DWs in $BiFeO_3$, by causing formation of bound charge at the DW. [2] Fe^{4+} cations (which contribute holes) were proposed in a very recent study as the major defects in $BiFeO_3$ DWs and the different concentration of Fe^{4+} cations in DWs and the domains was speculated as the main reason for their significantly different conductivities, with a possible reduction in the local bandgap at the DWs as a secondary effect. [1] This p-type conductivity at the DWs is different to some previously reported n-type conductivity at the DWs, which was attributed to different processing conditions for the bulk samples and the films leading to Fe^{2+}. [1]

Also, the geometric shape and curvature of the DWs has been the subject of some studies. 500% modulation in the conductivity of the DWs OF $BiFeO_3$ was found as a function of their curvature. The local carrier concentration was reported to vary by more than an order of magnitude depending on the charge on the DW (which attracts carriers or vacancies moving to neutralize it). [2] The conductivity of curved charged DWs in improper ferroelectrics $HoMnO_3$ and $ErMnO_3$ has been observed to vary by up to three orders of magnitude. [2]

Conduction through 180˚ DWs of insulating ferroelectric PZT thin films has also been reported. [10] The examples are not limited to thin films. Reports of conductivity in single crystals have also been published. One of the earliest and most interesting examples is the reported observation of superconductivity in twin DWs of the crystal WO_3 by Aird and Salje. [15] By reducing WO_3 with sodium vapor, which changed the twin wall composition from WO_3 to Na_xWO_3 or WO_{3-x} [7], transport measurements showed superconductivity, while magnetic measurements did not, suggesting that superconductivity existed only at the DWs. [5] There has been also reports of DW conductivity in other crystals such as in single crystals of lithium niobate ($LiNbO_3$). [9]

10.2 Hexagonal rare-earth manganites

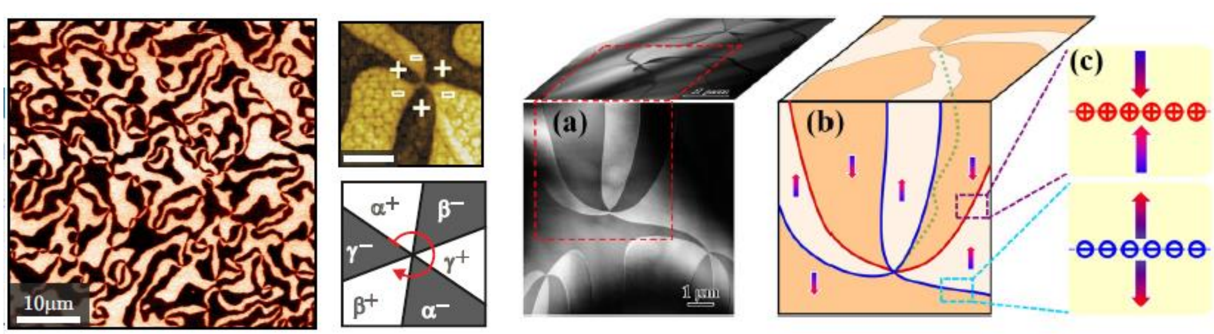
The target materials for this proposal are hexagonal rare-earth manganites, also noted as h-$RMnO_3$, with R standing for the rare-earth element which could be Y, Sc, In, or any of the lanthanoides.

Rare-earth manganites form both orthorhombic (R = La – Dy) and hexagonal (R = Ho – Lu) structures. [22] The orthorhombic case crystallizes in a distorted perovskite structure with Jahn-Teller distortion elongating one axis of the MnO_6 octahedron. In rare-earth elements with smaller R^{3+} ions the hexagonal crystal structure is more stable. [16] Also, rare-earth manganites with R ions (such as Dy, Tb and Gd) at the verge of stability of orthorhombic/hexagonal form have been stabilized in thin film with hexagonal structure. [18]

The h-$RMnO_3$ structure consists of alternating layers of R^{3+} ions and layers of corner-shared trigonal MnO_5 bipyramids. In the paraelectric phase, all bipyramids align along the z-axis and the R^{3+} ions form a flat layer in the xy-plane. [16] All "hexagonal" rare-earth manganites show multiferroic behaviour. The origin of ferroelectric ordering is considered to be the tilting of the rigid MnO_5 trigonal bipyramids. The ferroelectric transition temperature is very high (typically above 590K). [22] At cryogenic temperatures, typically around 70K-120K, [22] a magnetic ordering, mostly antiferromagnetism, develops. [16] In "orthorhombic" rare-earth manganites, however, only three compounds with R= Dy, Tb and Gd show multiferroic behaviour. The ferroelectricity has a different origin and has very low ferroelectric ordering temperatures (ca. 27 K). [22]

Ferroelectricity is hexagonal rare-earth manganites is said to be "improper", which means that the ferroelectric order emerges because the primary order parameter, which could be magnetic ordering or a non-polar lattice distortion, breaks the inversion symmetry of the crystal. Improper geometric ferroelectricity, as in h-$RMnO_3$, is caused by breaking of the inversion symmetry of the crystal due to structural distortion, usually by rotations or tilts of the polyhedral in order to reach closer packing, leading to differences in R-O bond length which cause local dipole moments. [16] Also, the uniaxial nature of the ferroelectricity allows only 180˚ DWs. [21]

In 2010, by Choi et al. [17] the unique structure of ferroelectric domains in h-$RMnO_3$ was illustrated. When cooling down, at relatively high transition temperatures topological defects known as vortices form, which resemble a cloverleaf pattern made of six domains. These topologically protected domain intersections wind through the crystal. Combining the two possible polarization states and three trimerization domain states, in total six ferroelectric domain states are possible. The structural configuration at the vortex includes all six allowed trimerization domain states which can be named $\alpha+$, $\beta-$, $\gamma+$, $\alpha-$, $\beta+$, $\gamma-$ in a vortex or $\alpha+$, $\gamma-$, $\beta+$, $\alpha-$, $\gamma+$ in an anti-vortex which has an opposite rotation. Around the vortex core the polarization changes sign six times. The vortices are stable. The alternation in trimerization and polarization state establishes a topological protection upon applications of electric fields. [16] Even strong electric fields only lead to modification of domain sizes, unable to eliminate unfavourable domains and create a monodomain state. [20] The pictures below picture illustrates the six states and the topologically formed vortices [left: PFM image, from ref.16; right: TEM image from ref.21]:



Due to the topological origin of the domain structure in h-$RMnO_3$, and despite the uniaxial ferroelectricity, the domain structure evolves isotropically and an excessive number of nominally charged head-to-head and tail-to-tail DWs occur which are typically avoided in uniaxial ferroelectrics.[16] These topologically occurring charged DWs are one of the most attractive features of hexagonal rare-earth manganites. In conventional ferroelectrics, charged DWs, because of electrostatic or strain energy cost, would be thermodynamically unstable. [21]

DW conductivity in conventional ferroelectrics such as $BiFeO_3$ has been the subject of much research as briefly mentioned in the introduction, but $BiFeO_3$ has significant differences to hexagonal rare-earth manganites, since it is a multiaxial ferroelectric, as well as being a ferroelastic material. On the other hand, most of the research on hexagonal rare-earth manganites has focused on multiferroic properties, and reports of investigations of its electrical conduction are rare. Furthermore, most of the reported results have been on crystals and not thin films. Although there exist a number of reports on growth and properties of epitaxial thin films of hexagonal rare-earth manganites, the investigation of (DW) conductivity in hexagonal rare-earth manganites has been mostly neglected in "thin films." There have, however, been a few publications on DW conductivity of hexagonal rare-earth manganites which serve to show the rich physics behind the observed behaviour:

In an interesting very recent paper, the previously observed conducting behaviour of tail-to-tail DWs and insulating behaviour of head-to-head DWs in single crystals of $ErMnO_3$ [8] was further investigated. Given that the h-$RMnO_3$ materials are p-type semiconductors and holes are the majority carriers, the conductivity at the tail-to-tail DWs has been attributed to accumulation of holes at these negatively charged interfaces to screen the local electrostatic potentials, and depletion of them from head-to-head DWs has been assumed to be the reason for low-conductivity. [19, 16] However, in this recent study it was found out that by increasing the applied voltage, the head-to-head DWs show a switching behaviour to conducting mode. This transition was attributed to the formation—and eventual activation—of an inversion layer (i.e. accumulation of electrons) that acts as a channel for charge transport. At low voltages, the electrons being in a localized polaronic state cannot contribute to conductivity, while for voltages higher than a threshold of 4.8 V, the electrons dominate the conductivity. This explanation introduces a mechanism for conductivity of head-to-head DWs which is fundamentally different to majority-carrier transport at tail-to-tail DWs, since the latter does not involve significant lattice coupling. [14] As suggested by the authors, a new functionality can be envisioned. The head-to-head DWs, having positive charge can act like a transistor's gate, forming a channel of electrons around it. The strength of the channel depends on the polarization charge at the DWs and upon application of voltages higher than a certain threshold, the channel becomes conducting. This reminds us of a field-effect transistor, realized with a single DW!

DWs of the multiferroic $YMnO_3$ were found to be more insulating than the domains, with a potential cause being the increase of the Y-O bond distance at DWs [17], while significantly enhanced conductivity was observed in neutral DWs of $YMnO_3$ after poling. The reason was reported to be oxygen vacancy ordering at the DWs, leading to change of the local band structure. [12] Recently enhanced conductivity in electrically-neutral DWs of semiconducting hexagonal ferroelectric $TbMnO_3$ thin films was observed. [13] Observation of enhanced conductance at high forward bias at tail-to-tail DWs of $HoMnO_3$ crystals has also been reported. [21].

DWs in hexagonal rare-earth manganites are especially attractive as building blocks of future nanodevices. Due to their topological origin, they provide a unique structure for devising new functionalities and exploiting the existence of charged domain walls with tunable anisotropic conductance, which are absent in conventional ferroelectrics. [16] In thin film form, there exist also possibilities for modifying the properties of the material, such as polarization, to be different to those of the bulk via substrate-induced strain, or other factors. Furthermore, the fact that ferroelectric DWs in this class of materials exist at room temperature is another practical advantage of them.

10.3 Goal

Optimization of a growth recipe for deposition of epitaxial thin films of hexagonal rare-earth manganites with pulsed laser deposition

Investigation of electrical transport properties at the domain walls in films grown under different conditions, to understand the fundamental physical mechanisms at work, as well as modifying and tailoring the transport properties

Investigation of the possibilities of introducing new functionalities at the domain walls (such as switch, transistor, memory, etc.)

10.4 Plan

To be able to investigate any of the properties of the hexagonal rare-earth manganites, the first step is obtaining high-quality thin films. Due to the expertise and experience of the host lab in growing multiferroic oxide thin films using pulsed laser deposition (PLD), that will be the method used in this project.

There are many parameters involved in thin film deposition with PLD, each of which could be hugely influential. These parameters include the substrate temperature, the energy and deposition frequency of the laser, the oxygen pressure in the chamber, the distance between the target hit by the laser and the substrate, as well as the choice of the right substrate and many other factors. Hence the **first year and a half** of the project will have to be dedicated to optimization of growth of epitaxial thin films and making an optimal recipe. The project will not focus on only one hexagonal rare-earth material; hence, growth of at least 3 or 4 materials with different rare-earth elements is required.

The **next two years** would be devoted to investigation of the properties of the films. The work in this period would have a cyclical nature of growing a sample, investigation of its properties, coming up with ideas to change growth parameters for the next sample to test theories and ideas, and thinking of various ways of modification and investigation of the grown films. The parameters that could be changed for the deposition of next samples could be using new substrates, introduction of dopants to the material, related PLD parameters, and other things. The main tools to be used would be thin film X-ray diffraction for analyzing the thin film quality and structure, scanning probe techniques such as cAFM and PFM for local probing of individual domain walls, modifying the domain structure and creating new DW geometries, physical properties measurement system for analysis of the polarization, as well as techniques such as Transmission Electron Microscopy for better understanding of the DW structure.

It's hard to divide this two-year period into subsets, but as the understanding and insights into the physics of the DWs increases, experimentation with realizing DWs with tailored properties for specific functionalities, and making basic devices using clean-room facilities available at Zernike institute, or investigating the ways to functionalize a network of DWs is expected. This could happen near the beginning of the fourth year.

The **last six months** would be dedicated to writing a thesis and additional experiments to provide supporting data.

11. Infrastructure

Most of the infrastructure required for the project in available in the host group. The main equipment include:

1. Pulsed-laser deposition for deposition of the thin films
2. Scanning probe techniques (AFM, PFM, c-AFM)
3. X-ray Diffraction and reflectometry of thin films
4. Physical properties measurement system

Other measurement set-ups and equipment required for the project are available from collaborators from within the institute or in other institutes, including:

1. Transmission Electrom Microscopy (Prof. dr. Bart Kooi group)
2. Cleanroom facilities (Physics of Nanodevices group)

12. Application perspective in industry, other disciplines or society

In the electronics industry, the dimensions of the devices have been steadily shrinking and it's often mentioned that they have followed Moore's law, which predicted that the number of transistors on an electronic chip would double almost every year. Considering the current state of the art in semiconductor industry, the devices have become so small that they are almost reaching the limit of that law, since the current devices cannot become much smaller and still maintain the same architecture. Furthermore, quantum mechanical effects would start to alter the performance of the devices, and the interconnecting wirings will become problematic. Also, there is the issue of power consumption that needs to be addressed. All of these issues suggest looking for new approaches and for materials possessing new functionalities for new device architectures. (Multi)ferroic oxides and in particular DWs in these materials have recently caught the attention of many researchers in the community as viable alternatives. DWs, and in particular ferroelectric DWs, are attractive because they are very narrow, with a width of a few and even down to one unit cell. [16] They can exhibit properties which do not occur in the bulk, especially because of the reduced symmetry in them, and their position and even existence can be controlled by via application of external electric fields, and given that we are concerned with thin films, modest voltages can produce fields of enough strength. So, they have the potential to address the energy consumption issue as well. Also, they are naturally occurring features in the material. Their properties and the networks they form can be designed by the growth conditions.

The type of DWs proposed in this project are those occurring in in hexagonal rare-earth manganites. Thanks to their topological structure, they are a promising candidate for new functionalities, be it as switches, transistors, or perhaps even memristors. The fact that they are stable and cannot be erased by electric fields (but can be moved) as well as their existence at room (and much higher) temperature also makes them suitable for practical applications.

However, it's not just in the electronics industry that they are important. DWs in the proposed material are a type of topological defects, and such topological features occur in a variety of physical systems and are subjects of enquiry also in other fields. In fact, topological defects were first introduced in the context of early universe evolution, and its first transitions leading to formation of topological defects known as cosmic strings. A scaling law on their abundance and formation has already been investigated on their condensed matter analogues, which are these topological DW structures. Topological defects also occur as vortices in superfluid He, in superconductors and Bose-Einstein condensates. [16] Hence, a better understanding of the physics of these exotic DW structures could also be a step forward in those other fields.

13. Data Management

All the results of the research and generated data will be presented to the host group and will be available in the computers and labjournals of the group.

The data will be organized in such a way as to be useful by other members of the group.

14. FOM subfield classification

NANO

15. References

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