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Robust templates for domain boundary engineering in $ErMnO_3$

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Abstract

Emerging properties of domain boundaries define the emerging field of domain boundary engineering. For many applications, the domain boundary acts as template onto which the desired properties, such as (super-) conductivity, polarity, ferroelectricity, magnetism, are imposed. This requires for most applications that the domain structures remain unchanged under appropriate chemical doping. Hassanpour *et al* (2016 *New J. Phys.* **18** 043015) have now shown, for the first time, that the magnetic and electric domain structures remain indeed robust against charge carrier doping (Ca^{2+} and Zr^{4+}) of the workbench multi-ferroic $ErMnO_3$. This opens the way into novel functionalities based on the nanostructure of $ErMnO_3$.

Nano-scale device materials can be designed as emerging properties of domain boundaries as active elements. Examples are twin boundaries, which are (super-)conducting [2, 3], polar [4], ferroelectric [5], or show magnetotransport [6] while the bulk of the same material has none of these properties. Including even finer scale structures, such as Bloch walls and walls inside walls [7], these developments lead to thin functional sheets or lines inside materials which have characteristic length scales of ca. 1nm. They represent some of the most advanced design technologies in nano-science currently available [8]. Two approaches are typically taken: firstly one uses the domain structure simply as a template to piggyback the desired properties onto the domain boundaries. In this case, the key question is how to tune the material properties towards a technologically feasible working range, without affecting the electric and magnetic order that give rise to the functional behavior.

The second approach is more demanding as it requires the domain structure itself to change under external fields while the wall properties change with them. This latter approach leads often to domain glass states, which allows for extremely high time sequences for computational devices but complicates the design of single active locations in device materials (see figure 1).

One of the most important multiferroic design materials is $ErMnO_3$. The parent compound of the doping series, $ErMnO_3$, exhibits geometrically driven improper ferroelectricity below T_C near 1470 K with the spontaneous polarization P oriented parallel to the hexagonal c-axis ($P||c$). Its characteristic domain structure includes lines and vortex structures and was tacitly assumed to belong to the second class of materials where even small changes of the bulk properties may drastically alter the domain pattern. Hassanpour *et al* [1] have shown that this is not the case, however. They demonstrated that electronic properties of this semiconducting multiferroic can be modified by introducing impurities, analogous to conventional semiconductors, while sustaining their intrinsic electric and magnetic domain structures. Their procedure for modifying electronic material properties is the introduction of n- or p-type properties to implanted defects. They showed that the electronic conductance of $ErMnO_3$ can be tuned within a range of about two orders of magnitude by introducing either divalent (Ca^{2+}) or tetravalent (Zr^{4+}) ions into the system. Using piezoresponse force microscopy (PFM) and optical second harmonic generation (SHG) they imaged the ferroelectric and antiferromagnetic domain structures of doped $ErMnO_3$ and found that the key parameters of the multiferroic domain state, such as the formation of ferroelectric vortices and the pattern of antiferromagnetic domains, are robust against the ionic alteration. This proves the usability of chemical doping for enhancing the functionality of the geometric multiferroic domain state in $ErMnO_3$. The result gives great encouragement to other systematic studies in the field of domain boundary engineering and may well lead to the design of defect adjusted multiferroics where the design functionalities lay in the domain walls rather than in the bulk of the material.

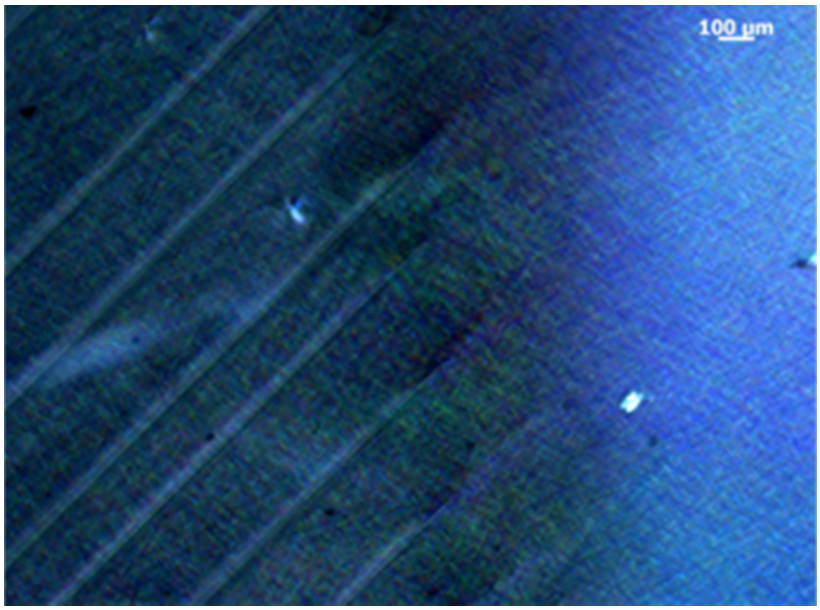

Figure 1. Domain glass state in $LaAlO_3$. Local tweed structures are intermingled with twin boundaries [9]. These structures are generated at high temperatures when the domain structures are highly mobile and then quenched to room temperatures where they remain frozen. The tweed structure is weakly polar.

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