Growth of high-quality hexagonal ErMnO_3 single-crystals by the pressurized floating-zone method

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Abstract

Hexagonal manganites are among the most intensively studied multiferroics, exhibit unusual geometrically driven ferroelectricity and magnetoelectric couplings, and form domains and domain walls with intriguing functional properties. In order to study these electronic correlation phenomena and develop a comprehensive understanding about the underlying physics, the availability of high-quality single-crystals is crucial. In particular, different members of the RMnO_3 ($R = \text{Sc, Y, In, Dy to Lu}$) family require different growth condition in order to achieve stoichiometric single-phase crystals. Here, we report on the growth of high-quality ErMnO_3 single crystals with dimensions of 5 mm in diameter and up to 60 mm in length using the pressurized floating-zone technique. We present Laue diffraction, piezoresponse force microscopy, and conductive atomic force microscopy data, reflecting the quality of our single-crystals regarding the structure, as well as electronic properties on the level of domains and domain walls.

Keywords: floating-zone technique, multiferroic crystals, domain walls, hexagonal manganite, ErMnO_3

1. Introduction

Hexagonal manganites $RMnO_3$ ($R = Sc, Y, In, Dy$ to Lu) have been studied for more than 50 years and since then continuously challenge physicists and materials scientists alike due to their rich phase diagrams and complex correlations between charge, spin, and lattice degrees of freedom [1]. Their synthesis was first reported in 1963 [2] and, in the same year, their ferroelectric and magnetic properties were characterized [3,4,5]. Much later, in 2004, scientists recognized that the electric and magnetic subsystems in $RMnO_3$ do not just coexist, but strongly interact [6] - a seminal finding that significantly contributed to shaping the research on so-called multiferroics in the following years [7]. Back in the 1960s, Safrankova and co-workers made yet another important discovery by visualizing unusual ferroelectric domain patterns in $RMnO_3$ [8]. A microscopic explanation for the formation of these ferroelectric domains, however, was reported only half a century later and required the use of modern high-resolution characterization methods [9,10,11]. Currently, the scientific interest is shifting towards the magnetic and electric domain walls in $RMnO_3$ with a focus on their functional electronic properties [12]. Here, remarkable progress has been made in the last three years but the underlying domain wall physics are still largely unexplored. This is partly due to the challenging experimental access, but also to the difficulty to synthesize high-quality $RMnO_3$ compounds reproducibly. The latter is particularly crucial for domain wall studies, because the slightest deviations in e.g. the lattice constants or stoichiometry can cause substantial variations in the domain wall behavior [13].

Up to now, $RMnO_3$ single crystals were mainly synthesized either by the flux method [14] or traditional floating-zone techniques [15-20]. The flux method, however, only yields rather small single crystals that tend to grow in thin platelets. Thus, it is difficult or even impossible to prepare millimeter-sized specimens of a specific orientation. This problem can be

overcome using the float-zone technique as reported in refs. [21]. Here, the standard approach is to use stoichiometric feed rods, which has already been applied for growing stoichiometric single crystals of e.g. HoMnO_3 , YMnO_3 , and LuMnO_3 . The method, however, fails in the case of ErMnO_3 or TmMnO_3 [21] where it is reported to cause incongruent melting, which is most likely due to the volatilization of manganese during the crystal growth. Such issues might in principle be bypassed by preparing off-stoichiometric feed rods for the crystal growth. It remained unclear, however, if this alternative pathway can lead to homogenous growth results as manganese is escaping from the melt during the whole growth procedure.

Here, we first demonstrate the growth of high-quality hexagonal ErMnO_3 single crystals applying the pressurized float-zone method. This method effectively prevents the volatilization of manganese from the melt and hence makes it possible to grow stoichiometric single crystals. By optimizing the growth parameters we achieved ErMnO_3 crystals with dimensions of 5 mm in diameter and up to 60 mm in length that grew in (1 1 0)-orientation. Details of the growth and characterization are presented along with scanning probe microscopy data showing that the crystals develop the desired ferroelectric domain structure and domain wall functionalities.

2. Experimentation

As starting point for the growth, single-phase compounds of hexagonal ErMnO_3 were prepared by the solid-state reaction method [22]. Stoichiometric amounts of high-purity (99.999%) commercially available precursors of Er_2O_3 and Mn_2O_3 from *Sigma-Aldrich* were ground in an agate mortar. After sieving and loading in a Pt crucible, the mixture was heated up to 1450 °C in air in a cubic Muffle furnace for 48 hrs with intermediate grinding to ensure the pure target single phase was obtained. After verifying the pure hexagonal target phase ($\text{P6}_3\text{cm}$ space group symmetry) by powder X-ray diffraction (XRD), the synthesized powder

was packed into a silicon tube for compaction into a rod, typically 5.0 mm in diameter and 100 mm long, in a hydraulic isostatic press under 150 MPa for 20 minutes. After removal from the silicon tube, the rods were sintered at 1450 °C for 48 hrs in the same Muffle furnace as the one used to synthesize the compounds.

The growth apparatus was a CYBERSTAR[®] two-mirror floating-zone furnace. The furnace has two 1000 W halogen lamps, each placed at the focal point of one of the gold-coated ellipsoidal mirrors. This setup ensures that the radiation of infrared light from the two halogen lamps converges into a single spot. The growth chamber was isolated with an air-tight quartz tube, which ensures the strict control of the growth atmosphere and enables pressurization of up to 1 MPa.

3. Results and discussion

3.1 Floating-zone growth of erbium manganite single crystals

After preparing stoichiometric rods as discussed in the Experimentation section, the feed rod was suspended from the upper shaft while the seed rod was connected to the lower shaft. Both rods were aligned properly to make them centered. When growing the compound in standard growth atmosphere by the traditional floating-zone method, we recognized that it is extremely difficult to achieve congruent melting and stable growth states, which is caused by the volatilization of manganese. Thus, in order to prevent the manganese from evaporating from the melt, the growth chamber was pressurized to 0.8 MPa at a flow rate of 5 cc/min of Ar gas balanced with 5% O₂ during the whole growth process. A thermodynamic equilibrium between the liquid ErMnO₃ and the oxygen reservoir is established, thereby preventing the molten material from evolution of the volatile element of manganese. At the beginning, both rods were rotated at 25 rpm in the same direction and the two halogen lamps were powered up slowly until the lower end of the feed rod, which was located at the converged spot, melted as

shown in Fig.1 (a) and (b). The feed rod was then connected to the seed rod shown in Fig. 2 (c). After the melting zone stabilized,

Figure 1 – Series of photos recorded at the different growth stages discussed in the main text.

Figs. 1 (a) to (c) show the starting stage, Figs. 1 (d) and (e) display the necking and shouldering stage, while Figs (f) to (k) depict the stable stage.

the rotation rate of the seed rod was adjusted to 15 rpm – this time, however, with opposite direction with respect to the feed rod. After a clear growth interface appeared, both rods started traveling downwards simultaneously. Since the crystal was grown by spontaneous nucleation without using a single crystal seed, necking and shouldering processes were needed to ensure that a single-crystal was obtained as shown in Figs.1 (d) and 1 (e). During the growth processes, the travel rate of the feed rod was adjusted manually based on the growth situation, whereas the travel rate of the seed rod (growth rate) was kept at 1.5 mm/hr. After necking and shouldering, the travel rate of the feed rod was set to 1.65 mm/hr to keep the crystal growing with a diameter of 5.0 mm. Under this growth condition, we found that the crystallization orientation corresponds to the (110)-direction along the length of the crystal. Figures 1 (f) to (k) show a series of photos taken when the growth was stabilized after repeated necking and shouldering.

Two crystal ingots were grown by the pressurized floating-zone technique under the same conditions. The as-grown crystals show a very smooth appearance with nice consecutive

facets on the surface. Fig. 2 (a) shows one as-grown crystal sitting in the growth chamber – the repeated necking and shouldering we applied during the growth procedure is clearly visible.

Figure 2 – ErMnO_3 ingots and prepared samples. Fig. 2 (a) shows an as-grown crystal ingot in the pressurized quartz chamber. Fig. 2 (b) displays two crystal ingots with size of 5 mm in diameter and up to 60 mm in length. Fig. 2 (c) shows polished crystal platelets that were cut from the ingots in Fig. 2 (b).

Figure 2 (b) shows two as-grown crystal ingots with 5 mm diameter and a length of 50 to 60 mm. Powder X-ray diffraction (XRD) data was taken after grinding specimens from the two crystals to confirm the pure hexagonal target phase ($P6_3cm$ space group symmetry) as exemplified in Fig. 3, where we compare recorded XRD data with the PDF-4 2012 database under Entry # 04-016-1782.

Figure 3 – Powder XRD pattern revealing the pure hexagonal structure of the ErMnO_3 single crystals ($P6_3cm$ space group symmetry).

After confirming the anticipated target phase, the ingots were oriented by Laue diffraction and cut into specimens of different orientation, i.e., with surfaces normal to the (110)- or (001)-direction, in order to facilitate microscopy experiments on crystal surfaces with the ferroelectric polarization ($\mathbf{P} \parallel (001)$) being in-plane or out-of-plane, respectively. Disc-shaped platelets with in-plane polarization are shown in Fig. 2 (c). The corresponding Laue back diffraction data is presented in Fig. 4 (a) confirming the (110)-orientation and corroborating the single-crystallinity of the samples (the same Laue photograph, indexed with the Cologne Laue Indexation Program (CLIP), is presented in Fig. 4 (b) [23]). After preparing oriented samples, flat surfaces with a roughness in the order of a few nanometers were achieved by chemo-mechanical polishing using silica slurry. Such samples have e.g. been used for realizing high-resolution X-ray photoemission electron microscopy (X-PEEM) studies reported in ref. [24]. In the following, however, we will restrict ourselves to the discussion of scanning probe microscopy data, demonstrating that the pressurized floating-zone method yields the desired electric crystal properties on the macro- and nano-scale, i.e., on the level of domains and domain walls.

Figure 4 – Laue back diffraction data. Fig. 4 (a) shows a Laue photograph performed on the ErMnO_3 ingot in the lower panel of Fig. 2(b). Fig. 4 (b) displays the corresponding indexing, which was performed using the CLIP software [23].

3.2 Domain and domain wall characterization in ErMnO_3 crystals by scanning probe microscopy

The polished ErMnO_3 specimens (Fig. 2(c)) were characterized by piezoresponse force microscopy (PFM) and conductive atomic force microscopy (cAFM) in order to probe the as-grown distribution of ferroelectric domains and the electronic domain wall properties. Figure 5(a) displays a PFM scan taken at room-temperature on a (110)-oriented sample, i.e., with the spontaneous polarization $\mathbf{P}$ of ErMnO_3 ($\mathbf{P} \parallel (001)$) lying in the plane. The PFM image shows the in-plane contrast with dark and bright areas corresponding to ferroelectric domains of opposite orientation with $\mathbf{P}$ pointing to the right and left, respectively. The assignment of polarization directions and contrast levels was achieved by calibration of the PFM system using a LiNbO_3 reference sample. The probed ferroelectric domain structure reflects the six-fold meeting points characteristic of the hexagonal RMnO_3 family [9,10], as well as isolated bubble domains [25]. Most important, we find an equal population of $+\mathbf{P}$ and $-\mathbf{P}$ domain states (bright and dark areas), which is indicative of a stoichiometric sample growth. In clear contrast to what is seen in Fig. 5(a), off-stoichiometric specimens develop a pronounced asymmetry in the domain population caused by chemical self-poling [26].

Figure 5 – Scanning probe microscopy data taken on ErMnO_3 . Fig. 5(a) shows a PFM scan (in-plane contrast) taken on a (110)-oriented sample. Domains of opposite ferroelectric

polarization are clearly distinguishable due to their bright and dark contrast levels. Fig. 5(b) displays cAFM data detected on a (110)-oriented specimen with ferroelectric domain walls appearing as bright and dark lines.

After confirming that the ErMnO_3 crystals show the desired ferroelectric domain structure, we performed complementary cAFM scans to measure the electronic transport properties of the associated domain walls. Figure 5(b) presents cAFM data taken on (110)-oriented ErMnO_3 with a bias voltage of -2.3 V applied to the AFM tip. The cAFM image reveals that $+\mathbf{P}$ and $-\mathbf{P}$ domains exhibit identical conductance properties as expected for samples with in-plane polarization [12]. The domain walls, however, have significantly different electronic conductance properties and hence are clearly visible as dark and bright lines in the scan. Domain walls in so-called head-to-head ($\rightarrow\leftarrow$) configuration are darker than the surrounding domains reflecting suppressed conductance, whereas tail-to-tail ($\leftarrow\rightarrow$) domain walls are brighter indicating enhance electronic conductance. This behavior and the measured current values are in tune with previous domain wall studies on flux-grown ErMnO_3 [12] and the excellence of the scan reflects the high-quality of the surfaces we were able to gain by chemical polishing.

4. Conclusion

High-quality single crystals of hexagonal ErMnO_3 were grown by the pressurized floating-zone technique. Without a single crystal seed, the crystallization of ErMnO_3 under 0.8 MPa pressure was grown along the (1 1 0)-orientation along its length. The hexagonal crystal structure ($P6_3cm$) was confirmed independently by XRD and Laue diffraction. Piezoresponse force microscopy was applied to show that the ErMnO_3 crystals develop a balanced pattern of ferroelectric $+\mathbf{P}$ and $-\mathbf{P}$ domains, which is indicative of stoichiometric

sample growth [26]. The electronic properties of associated domain walls were investigated by local conductance measurements (cAFM). Our results demonstrate that high-quality ErMnO_3 single-crystals can be grown by the pressurized float-zone method. This enables the reproducible growth of stoichiometric ErMnO_3 samples and provides the basis for reliable and systematic studies of the inherent electronic domain and domain wall functionalities.

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Figure 1

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