Phase transitions in a Pr$_{0.9}$Ca$_{0.1}$MnO$_3$ thin film studied by environmental in-situ heating nano-beam electron diffraction

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The rich phase diagram of bulk Pr$_{1-x}$Ca$_x$MnO$_3$ resulting in a high tunability of physical properties gave rise to various studies related to fundamental research as well as prospective applications of the material. Amongst others, the structural orthorhombic to pseudo-cubic transition that occurs at high temperatures is of major interest. In more detail, due to static Jahn-Teller distortions and tilting of the octahedra spanned by manganese and its surrounding oxygen atoms, a pronounced lattice constant anisotropy is present in the low temperature phase reacting very sensitively to small compositional changes. In this paper, we show that a structural transition exists for $x = 0.1$ in ion-beam sputtered thin films as well and point out differences to the bulk by employing in-situ heating nano-beam electron diffraction to follow the temperature dependence of lattice constants. In addition, we demonstrate that controlling the environment during heating, i.e. preventing oxygen loss, is crucial in order to avoid irreversible structural changes.

Transition metal oxide perovskites, and in particular Pr$_{1-x}$Ca$_x$MnO$_3$ (PCMO), have raised attention due to their strongly correlative nature and prospective application to e.g. resistance random access memory, catalysis, and photovoltaics.

Besides various studies of the magnetic ground states at low temperatures, neutron and X-ray diffraction experiments have been conducted on PCMO powders for low Ca concentrations showing a structural transition from an orthorhombic to pseudo-cubic phase at elevated temperatures where the difference in lattice constants is small. More specifically, the cooperative Jahn-Teller (JT) distortion as well as the alternating tilt of neighbouring MnO$_6$ octahedra are drastically reduced in the high-temperature phase leading to a higher isotropy. Still, there is yet no direct evidence that orbital ordering is the driving force of the structural orthorhombic to pseudo-cubic phase transition. For $x = 0.1$, where the corresponding critical temperature is experimentally well-accessible, the lattice parameters of the $Pbnm$ unit cell at room temperature, i.e. in the orthorhombic phase, amount to $a = 5.442$, $b = 5.617$, and $c = 7.635$. A major unsolved problem, however, is whether and how such data can be transferred to epitaxial thin films which are the typical basis for technological application. More generally, this is equivalent to the question whether bulk phase diagrams remain unchanged in thin film systems where neutron and X-ray characterizations, i.e. resolving the in-plane lattice parameters, are much more challenging. In fact, particularly in the context of transition metal oxides, various reports exist about tunable physical properties by epitaxial strain and oxygen vacancies possibly affecting phase transition temperatures as well.

In this study, we show that the high-temperature structural transition exists in a 400 nm thick PCMO ($x = 0.1$) epitaxial thin film grown on a SrTiO$_3$ (STO) substrate by extracting the lattice parameters locally by means of in-situ heating nano-beam electron diffraction (NBED) in a 4D-STEM mode. In contrast to macroscopic X-ray or neutron diffraction, this method allows the observation of individual in-plane directions in nanotwinned films yielding overlapping peaks in macroscopic diffraction techniques. The environmental capabilities of the electron microscope are used to control the type and reversibility of phase transitions.

A 400 nm thick PCMO film was grown on a commercial (100) oriented STO substrate by ion beam sputtering from a single target of composition ($x = 0.1$). Deposition parameters were: $p_{Ar} = 3 \times 10^{-4}$ mbar (beam neutraliser), $p_{Xe} = 1 \times 10^{-4}$ mbar (sputter gas), and $p_{O} = 1.6 \times 10^{-4}$ mbar (film oxidation). The deposition temperature was set to $820^\circ$C using a Tectra boron nitride heater which results in approx. $720^\circ$C at the substrate surface. Subsequently, the film was annealed in air for 20h at $900^\circ$C with a ramping speed of $100^\circ$C per hour.

TEM lamellas were extracted using an FEI Nova NanoLab Dual Beam focused ion beam and mounted on first generation four-contact DENSsolutions heating chips. The final thinning step was done using an acceleration voltage of 5 kV. TEM experiments were conducted in an FEI Titan ETOMIC G2 80-300 operated at 300 kV using a DENSolutions Lightning D7+ holder and a semi-convergence angle of 0.8 mrad. NBED patterns were recorded with a self-written DigitalMicrograph plugin controlling the beam position and reading out an UltraScan 1000XP camera binned to 256×256 pixels.

In order to extract the lattice parameters from resulting NBED patterns, their auto-correlation is calculated...
in a first step. Subsequently, a two-dimensional reciprocal lattice is fitted up to the second order to the positions of the local maxima at

$$k(i, j) = (k_x(i, j), k_y(i, j)), -2 \leq i, j \leq 2$$  \hspace{1cm} (1)

closest to the multiple orders of an initial guess \((i b_{10} + j b_{20})\) by solving the linear optimization problem:

$$\min_{b_1, b_2} \sum_{i,j} I(i,j)^2 (k(i, j) - i b_1 - j b_2)^2$$  \hspace{1cm} (2)

Here, \(I(i,j)\) corresponds to the intensity of the local maximum at \(k(i,j)\) and serves as a weighting factor. Please note that this strategy of lattice parameter extraction is inspired by and thus very similar to those of previous reports [17,18]. Throughout this paper, the manually estimated (110) and (001) reflections of the STO substrate at room temperature were used as initial guesses \(b_{10}\) and \(b_{20}\). In the orthorhombic Pbmn unit cell of PCMO, these reflections translate approximately to (100)/(010) and (002). The moduli of real space lattice parameters were calculated by taking the inverse of the moduli of the reciprocal lattice parameters.

Prior to considering the temperature dependence of the given lattice parameters, a brief overview of the thin film epitaxy and heterogeneity shall be given. Generally, epitaxial growth throughout all investigated areas can be confirmed. As shown in Fig. 1, the two relations \([100]_{PCMO}||[110]_{STO}\) and \([010]_{PCMO}||[110]_{STO}\) are predominantly found, i.e. \([001]_{PCMO}\) is oriented out-of-plane in both cases. In fact, the in-plane orientation flips quite regularly on a few hundred nanometer scale and the resulting domains extend through the entire film as clearly visualized by the 4D-STEM analysis shown in Fig. 1(b)-(d). This reflects a nanotwinned state of the film as it is often observed in orthorhombic systems [19,20]. Interestingly, there is no unique relation between orientation and bright and dark appearance in the ADF-STEM image in Fig. 1(a), i.e. the two most left positioned [100] oriented (cyan) domains in Fig. 1(b) appear bright resp. dark. This matches the observation of slightly varying zones axis alignments in the domains, i.e. a twisting, which does not solely correlate with the orientation but rather seems to be caused by the local strain state. Additionally, contrast heterogeneities in the STO are visible in Fig. 1(a) as well indicating a strained lattice in the substrate. This is important since it prevents finding a (sufficiently thin) unstrained reference inside the TEM lamella and thus only relative lattice parameters can be extracted.

The temperature dependent lattice parameters averaged over the upper half of the scanning field in Fig. 1 and normalized to their values at \(T = 350\) K are shown in Fig. 2. The error bars represent the standard deviation in the averaged range. The in-plane parameter, averaged over \(a\) and \(b\), decreases with higher temperature and shows a slight hysteresis. In contrast, the out-of-plane parameter, i.e. \(c\), increases and is strongly hysteretic. The latter indicates an irreversible change of the TEM lamella during heating which is confirmed by a change in the crystal symmetry: Figure 2(a) resp. (b) show series of NBED patterns of \(a\)- resp. \(b\)-oriented domains. While in the former case a 2\(b\) superstructure emerges at
800 K, the (101) reflections vanish in the latter. Both effects persist at lower temperatures after heating and in addition, the initially extinct (100) reflections show up in b-oriented domains. The appearance of superstructures, although not exclusively occurring in b direction, has been reported before in the context of catalytical studies of PCMO (x = 0.36) and was attributed to oxygen vacancy ordering [6]. The circumstance that the effect is only observed in b direction might be related to the results in Ref. [21] for x = 1 showing that in the presence of strain certain lattice sites are preferred for oxygen vacancy formation. Furthermore, the extinction rules are strongly coupled to the tilt pattern of neighbouring MnO$_6$ octahedra [22] and thus the observed changes in b-oriented domains suggest severe modifications in the collaborative tilt resp. distortion pattern.

In order to suppress oxygen vacancy formation, an analogous experiment was conducted facilitating the ETEM gas-inlet capabilities and using an oxygen partial pressure of 0.1 mbar. The resulting lattice parameters obtained in the gaseous environment are shown in Fig. 4. As a matter of fact, c still increases strongly with temperature but in contrast to the experiment in high-vacuum no hysteresis is visible. Furthermore, neither a 2b superstructure nor a change in the extinction rules was observed in the gaseous environment confirming oxygen vacancy formation to be directly linked to the previous irreversible changes. Nevertheless, the averaged in-plane parameter exhibits a sudden jump during heating at 600 K which is not reverted during cooling and consequently the experiment is not entirely hysteresis-free. This finding might be explained by thin sample effects, e.g. a lower energy strain state of the above mentioned twisting of neighbouring domains being possible due to the enhanced surface volume fraction in the TEM lamella. Alternatively, the extended annealing during the heating experiment could have lead to further strain relaxation which is possible in macroscopic samples as well. Following the curve after the jump reveals a reversible decrease of the averaged in-plane parameter at high temperatures. To disentangle the behaviour of the so far averaged in-plane lattice parameters a and b, the temperature dependent histograms of detected in-plane lattice constants during heating and cooling are shown in Fig. 5(a) and (b), respectively. Please note that the histograms above T = 650 K in Fig. 5(b) are replotted from (a) as no additional data exists. Generally, before and after heating, a bimodal distribution is observed at low temperatures and the separable peaks with lower resp. higher lattice parameter correspond to domains with [010] resp. [100] zone axis orientation. As the temperature is raised, the two peaks start to merge leading to a pseudo-tetragonal structure. Please note that no claims on whether the structure is pseudo-tetragonal or pseudo-cubic can be made due to the missing unstrained reference and the more general former term will be used in the following. Interestingly, the sudden jump during heating at 600 K mentioned above occurs right at the pseudo-tetragonal transition in Fig. 5(b) suggesting that isotropic lattice constants are beneficial for this type of rearrangement.

Finally, the results obtained in oxygen environment after the rearrangement shall be compared to bulk measurements. As described in the introduction, a pseudo-cubic transition is expected in the bulk for x = 0.1. In Ref. [10], the critical temperature is drawn in the phase diagram at approximately 675 K (even though without presentation of experimental data in the paper or cited references). Our findings show that the transition oc-
FIG. 4: Temperature dependent averaged in- and out-of-plane lattice parameters obtained in a 0.1 mbar oxygen environment normalized to their values at 350 K. The error bars correspond to the standard deviations in the averaged range. While the averaged in-plane parameter decreases in temperature and exhibits a sudden jump during heating at 600 K, \(c\) shows a strong increase and no hysteresis.

curs at a slightly lower temperature in the thin film, i.e. at approximately 600 K. Unfortunately, since no temperature dependent lattice constants are published at this calcium concentration, we can compare the trends only qualitatively to the existing data obtained in the bulk for \(x = 0\) \([9, 12]\). Here, due to the pseudo-cubic transition at 1050 K, \(c\) increases by 3.9\%, \(b\) decreases by 3.9\%, and \(a\) increases by 1.9\%. Since the initial anisotropy at room temperature is weaker for \(x = 0.1\), it is to be expected that these changes are smaller due to the increased calcium content matching very well the observed increase of \(c\) by 3.0\% in Fig. 4 and the decrease of \(b\) by 3.0\% in Fig. 5(b). On the contrary, \(a\) behaves qualitatively differently as it decreases with temperature. Even though no direct comparison to the bulk can be drawn for \(x = 0.1\), it seems very likely that this effect is rather caused by strain than by the finite value of \(x\). We justify this claim with the fact that the increase of \(a\) is a fingerprint of the reduced MnO\(_6\) tilting angle having a stronger effect on \(a\) than the reduction of its JT distortion (which would in turn lead to an expansion in this direction). As the JT distortion is almost 50\% weaker for \(x = 0.1\) at room temperature \([10]\) and the tolerance factor, i.e. the main driving force for octahedral tilts changes only by a few percent \([9]\), we do not expect a reverted behaviour due to the increased calcium content and attribute the reverted trend of \(a\) to anisotropic strain.

Nano-beam electron diffraction in combination with in-situ heating was used to map the lattice parameters in a PCMO thin film proving the existence of a high-temperature structural transition with a slightly decreased critical temperature of approximately 600 K when compared to the bulk counterpart \([10]\) and a reverted behaviour of the in-plane lattice parameter \(a\) which was attributed to anisotropic strain due to the substrate. Furthermore, it was demonstrated that the heating environment can be used to control the reversibility of phase transitions. In fact, this appears particularly interesting given that in Ref. \([9]\) strong hysteric behaviour after heating is mentioned in the text and in Ref. \([12]\) no data during cooling is presented.

In detail, in a first experiment performed in high-vacuum, a strong hysteresis in \(c\) was observed accompanied with the emergence of a \(2b\) superstructure and a change in the extinction rules as shown in Fig. 2 and 3. We explained these effects with oxygen vacancy formation and ordering during heating as well as a possibly induced change in the tilt pattern of the MnO\(_6\) octahedra. Performing the experiment in an oxygen partial pressure

FIG. 5: Contour plot of the temperature dependent histograms of normalized in-plane lattice parameters obtained in the oxygen environment. The colors represent the relative frequency and the dashed resp. dotted grey lines are a guide to the eye to follow the \(a\) resp. \(b\) peak. (a) includes the data recorded during heating and shows a sudden jump at 600 K right after the \(a\)- (small) and \(b\)-peaks (large) merge. (b) shows the data recorded during cooling (except for \(T > 650\) K as only heating points exist) in which no jump is present. The splitting of \(a\) and \(b\) recurs after heating.
of 0.1 mbar confirmed the interpretation as it suppressed the hysteretic behaviour of $c$, the change in extinction rules, as well as the superstructure formation. Comparing only the heating ramps of the two experiments in [2] and [3], the drastic increase of $c$ happens at significantly lower temperatures in high-vacuum and consequently experiments performed under oxygen loss conditions might generally lead to underestimated critical temperatures of the underlying phase transition.

Considering the in-plane lattice parameters in oxygen environment, a sudden irreversible increase happened during heating at 600 K which we attributed to a relaxation of the strain state of the nanotwinned domain structure. It is possible that this relaxation is facilitated by the reduced thickness of the TEM lamella and does not happen in macroscopic samples. Still, it is very interesting that the relaxation happens right after the pseudo-tetragonal transition shown in Fig. [3](a), i.e. when $a$ and $b$ are approaching lifting the strain relaxation due to the alternating twinned domains.

In summary, we have shown that by employing an environmental TEM and NBED undesired irreversible compositional and accompanying structural changes of PCMO thin films during heating can be avoided allowing to investigate the high-temperature structural transitions successfully.

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