

# Enhancement of magnetic properties in compressively-strained PrVO<sub>3</sub> thin films

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## Abstract

Strain engineering is an important issue in oxides thin films to explore new functionalities. Here, a series of high quality epitaxial PrVO<sub>3</sub> (PVO) thin films were grown, by Pulsed Laser Deposition (PLD) technique, as a function of thickness on (La,Sr)(Al,Ta)O<sub>3</sub> (100) [LSAT (100)] and LaAlO<sub>3</sub> (100) [LAO (100)] substrates with nominal lattice mismatch of -0.8 % and -2.9 %, respectively. The X-ray diffraction revealed a constant *out-of-plane* lattice parameter of PVO/LSAT with increase in film thickness, while a rather continuous decrease for PVO/LAO films. Whereas thicker PVO films show a ferromagnetic-like behavior, at low thickness a surprising decrease of coercivity ( $H_c$ ) and increase of saturation magnetization ( $M_s$ ) is observed. This behavior is described using a classical model of “dead layer” which possesses a strong paramagnetic susceptibility. It is also shown how capping of PVO film can aid in recovering the pure magnetic properties of PVO, by diminishing the contribution from “dead layer”. Finally, the Néel temperature ( $T_N$ ) is examined as a function of film thickness, and found to vary in the range of 25 K and 30 K for LSAT and LAO, respectively. These results pave the way for the use of vanadate in thin film devices.

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## 13 I. INTRODUCTION

14 The perovskite oxides with generic formula  $ABO_3$  have attracted a great deal of scientific  
15 interest thanks to the strong correlation between orbital (electronic), spin (magnetic) and  
16 lattice degrees of freedom (structural). Consequently, owing to various functional proper-  
17 ties such as ferroelectricity, ferromagnetism, antiferromagnetism, colossal magnetoresistance,  
18 superconductivity, the oxides are exploited in the diverse technological applications for elec-  
19 tronics, data storage or sensing and so on [1–4]. While for bulk materials, these underlying  
20 properties can be expanded via lattice distortion by applying hydrostatic pressure [5, 6], a  
21 substrate-induced biaxial strain in  $ABO_3$  epitaxial thin films proved to be an effective tool  
22 to modify the spin-orbit-lattice coupling [7–10]. Among  $RVO_3$  ( $R$ : Rare earth element), the  
23 bulk  $PrVO_3$  (PVO), at room temperature, adopts an orthorhombic  $Pbnm$  crystal structure  
24 with the lattice parameters:  $a_o = 5.487 \text{ \AA}$ ,  $b_o = 5.564 \text{ \AA}$ , and  $c_o = 7.778 \text{ \AA}$  ( $o$  stands for  
25 orthorhombic) [11]. In the following, we will consider the pseudocubic unit cell of PVO  
26 that yields  $a_{pc} \approx a_o/\sqrt{2} \approx b_o/\sqrt{2} \approx c_o/2 \approx 3.901 \text{ \AA}$  ( $pc$  stands for pseudocubic). The bulk  
27 PVO is an antiferromagnet associated with C-type Spin Ordering (C-SO), where V spins are  
28 staggered in  $ab$ -plane and aligned ferromagnetically along the  $c$ -axis, with  $T_N \simeq 130 \text{ K}$  [12].  
29 However, for a PVO thin film, the DFT calculations reveal a G-type Spin Ordering (G-SO)  
30 in the ground state (where V spins are aligned antiferromagnetically along all three crystal  
31 directions), associated with a C-type Orbital Ordering (C-OO) through Kugel–Khomskii  
32 mechanism [13, 14]. In the course of our previous study, we revealed a new pathway to tune  
33 the magnetic properties of PVO thin films grown on  $SrTiO_3$  (STO) substrate by monitoring  
34 the concentration of oxygen vacancies in PVO films [13]. A careful crystal structural inves-  
35 tigation revealed that the tensile-strained PVO film on STO substrate adopts a monoclinic  
36  $P2_1/m$  crystal lattice [10, 13, 15]. In addition, we have scrutinized the effect of substrate-  
37 induced strain on the structural and magnetic properties, by growing PVO films on top of  
38 various lattice mismatched perovskite-oxide substrates [10]. The study revealed that a large  
39 compressive strain in PVO films not only promotes the superexchange interaction *i.e.* V–V  
40 interactions, but also changes the electronic structure of PVO. Recent investigations have  
41 unveiled that the layer-by-layer control of film through minute deposition tunes the strain  
42 states in a film, offering fascinating functional properties, namely, spin-glass behaviour in  
43 compressively strained  $BiFeO_3$  thin films [16], thickness dependent magnetic anisotropy in

44  $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  films [17] and the dimensional crossover of magnetization from 3D to 2D in  
45  $\text{SrRuO}_3$  thin films with decrease in film thickness [18]. Even if the  $\text{RVO}_3$  system is a good  
46 candidate to exhibit the spin-orbit-lattice coupling, only a few film thickness-dependence  
47 studies have been conducted in thin films [19, 20].

48 In this paper, we study the thickness-dependent **structural** and magnetic properties of the  
49  $\text{PrVO}_3$  (PVO) thin films grown on  $(\text{La,Sr})(\text{Al,Ta})\text{O}_3$  (LSAT) and  $\text{LaAlO}_3$  (LAO) substrates.  
50 While thick PVO films (100 nm) remain strained to the LSAT substrates, films of  $\sim 50$  nm  
51 show partial relaxation on the LAO substrates. We have evidenced a dead-layer at the film  
52 surface which possesses strong paramagnetic susceptibility, and is at the origin of observed  
53 magnetic properties. In addition, we have also explored the possibility to heal this layer by  
54 capping with few layers of LAO, in order to recover the magnetic properties of PVO.

## 55 II. EXPERIMENTAL

56 The PVO thin films were epitaxially grown on top of (100)-oriented LAO and LSAT  
57 substrates, within thickness range of 10 to 100 nm, by using Pulsed Laser Deposition (PLD)  
58 technique. A KrF excimer laser ( $\lambda = 248$  nm) with repetition rate of 2 Hz and laser fluence  
59 of 2 J/cm<sup>2</sup> was focused on a  $\text{PrVO}_4$  ceramic target, with substrate-to-target distance of 5  
60 cm. The films were deposited at a growth temperature  $T_G = 650$  °C and oxygen partial  
61 pressure  $P_{\text{O}_2} = 10^{-6}$  mbar. To assure homogeneous oxygen vacancies throughout the growth,  
62 the samples were cooled down to room temperature in the same oxygen pressure. The  
63 crystallinity and the structure of the PVO films were characterized using x-ray diffraction  
64 technique (Bruker D8 Discover diffractometer, Cu  $K\alpha 1$  radiation,  $\lambda = 1.5406$  Å). The surface  
65 morphology of the films was investigated using Atomic Force Microscopy (AFM) PicoSPM.  
66 The magnetic measurements were performed using Superconducting Quantum Interference  
67 Device (SQUID) magnetometer, as a function of magnetic field  $H$  (parallel configuration)  
68 and temperature  $T$ . The magnetization-magnetic field ( $M$ - $H$ ) hysteresis curves were obtained  
69 at  $T = 20$  K and magnetization-temperature ( $M$ - $T$ ) data were carried out at  $H_{in-plane} =$   
70 50 Oe. The lattice constants of PVO, LSAT, and LAO in the *pseudo-cubic* structure are  
71 3.901 Å, 3.868 Å, and 3.791 Å respectively, establishing PVO to be grown under nominal  
72 compressive strain with lattice mismatch of -0.8 % (LSAT) and -2.9 % (LAO).

### 73 III. RESULTS AND DISCUSSION

74 Figure 1(a) and 1(b) display  $\theta - 2\theta$  x-ray diffraction measurements of a series of PVO  
 75 films grown on top of (100)-oriented LAO and LSAT substrates respectively, around  $(100)_{pc}$   
 76 (where *pc* refers to the *pseudo-cubic* notation) of each substrate. The clear thickness fringes  
 77 for PVO/LSAT films confirm uniform thickness, and well-defined film/substrate interface.  
 78 However, PVO films grown on LAO substrates display suppressed oscillations, presumably  
 79 due to presence of the twin domains in the LAO substrate [21]. The film thickness ( $t$ )  
 80 was calculated using these fringes, the details of which could be found elsewhere [10]. The  
 81 AFM analysis was performed on each sample, and a surface roughness less than 0.5 nm was  
 82 observed confirming the high-quality of the samples, without the presence of any islands  
 83 even in the thicker films (Fig. 1(d)). The *out-of-plane* and *in-plane* lattice parameters were  
 84 calculated using XRD  $\theta - 2\theta$  (Fig. 1(a), (b)) and reciprocal space map scans (Fig. 2),  
 85 respectively.

86 Figure 1(c) illustrates the evolution of PVO lattice parameters as a function of the film  
 87 thickness, for both LAO and LSAT substrates. First, we see that the *out-of-plane* lattice  
 88 parameter of all PVO films has increased for both substrates as compared to that of the  
 89 *pseudo-cubic* bulk PVO (solid red line in Figure 1(c)), which is in perfect agreement with the  
 90 *in-plane* compressive strain imposed by the LAO and LSAT substrate. Moreover, the *out-*  
 91 *of-plane* lattice parameter of PVO/LAO decreases continuously (in overall) with increase of  
 92 film thickness, although a slight increase between  $t = 19.63$  nm and  $t = 24.19$  nm, and also  
 93 between  $t = 55.93$  nm and  $t = 74.50$  nm is observed, and believed to be because of uncer-  
 94 tainty in the calculations of parameters. Second, PVO films grown on the LSAT substrates  
 95 show a nearly constant *out-of-plane* lattice parameter with increase of film thickness, and a  
 96 slight change is within the experimental accuracy. (The error bars were calculated by fitting  
 97 the film peak using the Voigt function, and then using the relation between the uncertainty  
 98 in lattice parameter ( $\Delta d$ ) and Bragg's angle ( $\Delta\theta$ ):  $\Delta d = \frac{\Delta\theta}{\tan\theta} \cdot d$ , directly derived from the  
 99 Bragg diffraction expression). This nearly constant behavior of *out-of-plane* lattice param-  
 100 eter of PVO film on LSAT substrate can be rather anticipated due to a smaller mismatch  
 101 between PVO and LSAT substrate ( $\sim -0.8$  %).

102 In order to further investigate the thickness-dependent structural evolutions, the asymmetri-  
 103 cal reciprocal space maps (RSMs) were recorded for PVO films, around  $(103)_{pc}$  Bragg's peak

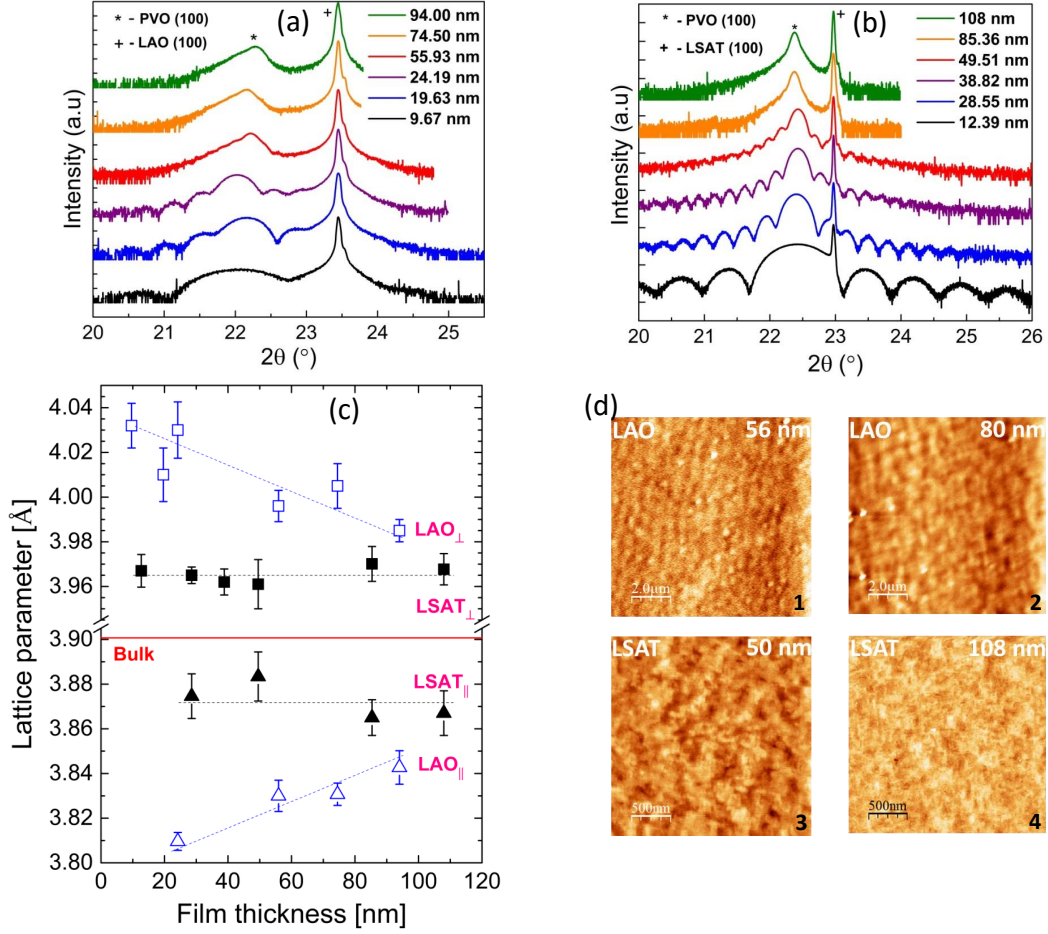


Figure 1:  $\theta - 2\theta$  x-ray diffraction measurements of a series of PVO films grown on (a) LAO and (b) LSAT substrates, around  $(100)_{pc}$  of each substrate. The asterisk (\*) and plus (+) represents PVO film and substrate, respectively. (c) *Out-of-plane* (square symbols in top panel) and *in-plane* (triangle symbols in bottom panel) lattice parameters of PVO films grown on LAO (blue open symbols) and LSAT (black close symbols) substrates, as a function of the film thickness, plotted along with the error bars.  $\perp$  and  $\parallel$  symbols represent the *out-of-plane* and *in-plane* lattice parameters of PVO, respectively. The dashed lines serve as guide to the eyes. Red line indicates PVO bulk *pseudo-cubic* lattice parameter. (d) Representative AFM images of PVO thin films grown on LAO ( $10 \times 10 \mu\text{m}^2$ ) and LSAT ( $2.5 \times 2.5 \mu\text{m}^2$ ) substrates. Different thicknesses are shown. The surface roughness ( $R_q$ ) from 1 to 4 is: 0.18 nm, 0.43 nm, 0.22 nm and 0.42 nm, respectively.

104 of LAO and LSAT (see Figure 2(a) and 2(b) for PVO/LAO and PVO/LSAT, respectively).  
 105 We note that the thinner PVO film ( $t \leq 24$  nm) is *in-plane* strained when grown onto LAO,  
 106 whereas thicker films start to relax (Figure 2(a)), as the position of films peak along the

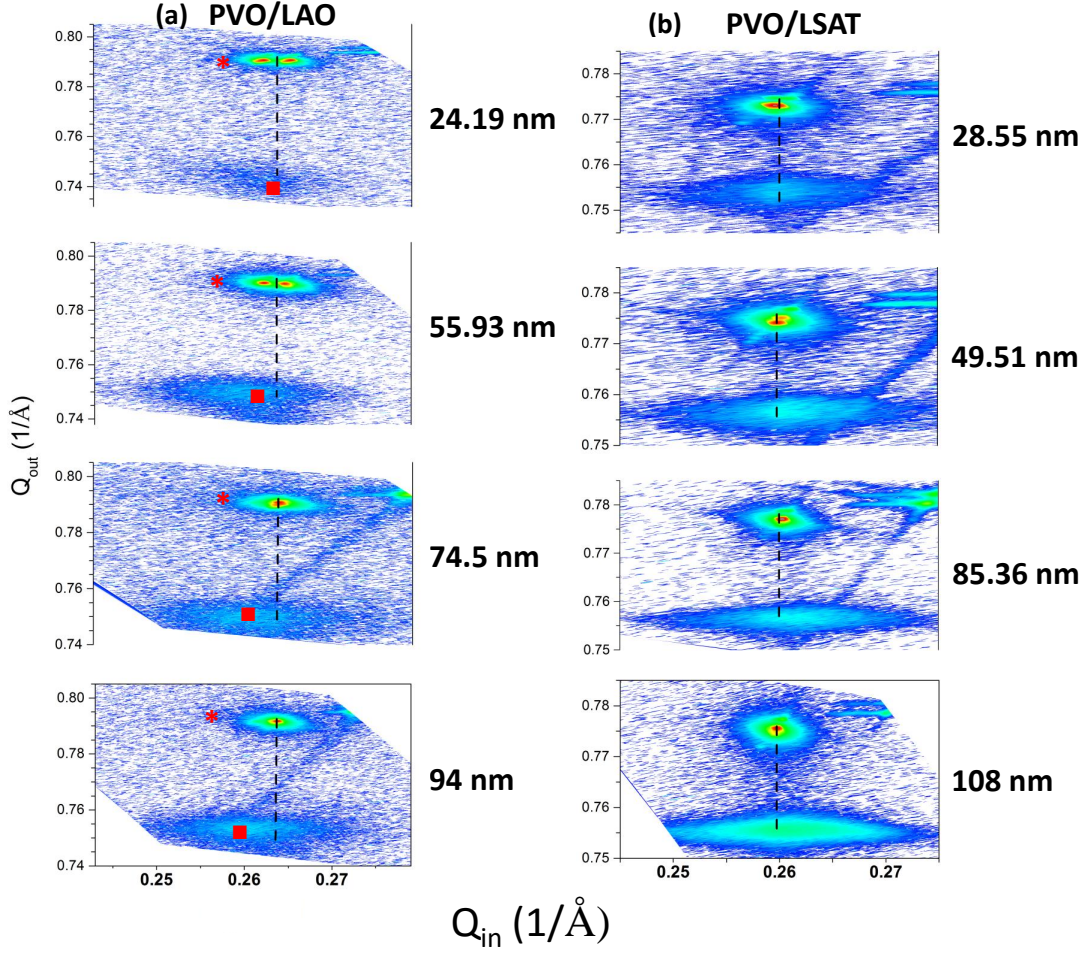


Figure 2: Asymmetrical Reciprocal Space Maps (RSMs) performed for a series of PVO thin films grown on (a) LAO and (b) LSAT substrate, around *pseudo-cubic* (103) of the substrate. The horizontal axis is  $Q_{in}$  and vertical axis is  $Q_{out}$  for all RSMs. The substrate and film peaks are located in the upper and lower region of RSMs, and marked by the asterisks and solid square symbols respectively, for both substrates. The double peaks for the LAO substrate are due to twin domains in the substrate. The vertical dashed lines are only guide to the eyes.

107 horizontal  $Q_{in}$  axis shifts toward lower value. This is in perfect agreement with the highly  
 108 mismatched PVO films grown on the LAO substrate which tend to relax easily over small  
 109 thickness, due to a decrease in the strain states as the thickness increases. The *in-plane*  
 110 lattice parameters of PVO were calculated using these maps (within the instrumental error)  
 111 (Fig. 2), and the results are plotted as a function of film thickness in Figure 1(c). On  
 112 the LAO substrate, the *in-plane* lattice parameter of film increases linearly with the film

113 thickness. This behavior is typical of a partially relaxed films, and is in accordance with the  
 114 decrease of *out-of-plane* lattice parameter with increase in film thickness, for a film with an  
 115 ideal Poisson's ratio [27]. On the LSAT substrates, the situation is different as the PVO  
 116 films are strained with the substrate, even at  $t \sim 100$  nm. This is clearly seen in Figure  
 117 2(b) where the horizontal position of film peak coincides with the one of LSAT substrate.  
 118 Thus, the film and substrate have same *in-plane* lattice parameter. Also, the film peak  
 119 width along  $q_{in}$ -axis increases slightly with increase of film thickness, and could be possibly  
 120 due to the presence of different domains in the PVO film, as shown in the earlier reports  
 121 [10, 13, 15]. Moreover, a range of film thickness analyzed by using electron microscopy [10]  
 122 in combination with pole figures yield PVO  $[001]_o$ -axis along in-plane of film, and thus in-  
 123 ducing  $[110]_o$ -axis growth. A detailed microstructure of the films will be published later. To  
 124 summarize, the PVO films are strained when grown on the LSAT substrates, even at  $t \sim 100$   
 125 nm, whereas films of  $t \geq 50$  nm display partial relaxation when grown on LAO substrates.

126 Figure 3 details the magnetization-magnetic field ( $M$ - $H$ ) measurements recorded at  $T = 20$   
 127 K. In order to clearly observe the PVO magnetic contribution, the diamagnetic signals of the  
 128 substrates were subtracted from the total measured signal. The magnetic hysteresis cycles for  
 129 the selected PVO samples are shown in Figure 3(a), (b) for LAO substrate and Figure 3(e),  
 130 (f) for LSAT substrate. A clear opening of the hysteresis loop is observed with increase in the  
 131 film thickness, evidencing a low temperature ferromagnetic-like behavior of the PVO films.  
 132 The magnetic moments are however canted, leading to a canted-antiferromagnetic state  
 133 via antisymmetric spin-spin interaction ( $D_{ij} \cdot (S_i \times S_j)$ , with  $D_{ij}$  the Dzyaloshinskii–Moriya  
 134 term) [15]. Additionally, the magnetization of PVO films could be described as combination  
 135 of a soft and a hard magnetic phase, similar to what was observed in orthoferrite  $\text{YFeO}_3$   
 136 [22, 23], and is consistent with our previous observations [10]. In fact, we have shown  
 137 earlier that the weightage of each magnetic phase can be tuned by the epitaxial strain  
 138 imposed by different substrates [10]. In the present case, where strain is induced via different  
 139 thicknesses, we observed a decreasing trend of soft magnetic phase with increase of film's  
 140 thickness. From Figure 3(a), (b) for PVO/LAO and 3(e), (f) for PVO/LSAT, we extract  
 141 that, the thinner films indeed possess a larger soft magnetic phase (paramagnetic) with large  
 142 saturation magnetization ( $M_s$ ), and with the increase of film thickness, the fraction of film  
 143 that is made up of paramagnetic phase reduces, and / or the relative contribution of PVO  
 144 layer, associated with hard magnetic phase, increases. Moreover, we have shown previously

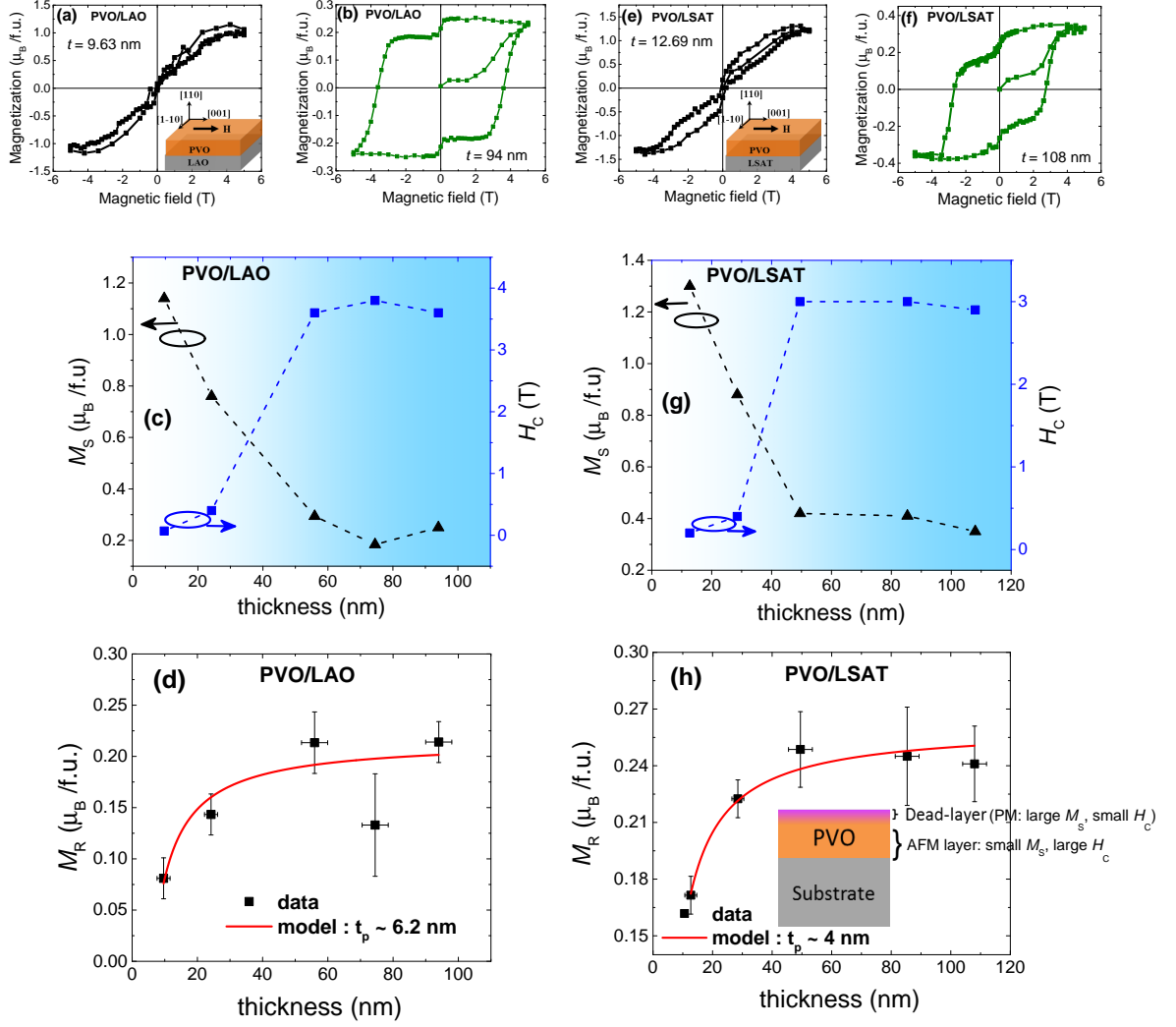


Figure 3: Magnetization ( $M$ ) vs *in-plane* magnetic field ( $H$ ) measurements obtained at 20 K for: PVO films grown on (001)-oriented LAO substrate, for film thickness (a)  $t = 9.63$  nm and (b)  $t = 94$  nm, and for PVO/LSAT films (e)  $t = 12.69$  nm, (f)  $t = 108$  nm. Plot of the saturation magnetization ( $M_S$ ) (left scale) and magnetic coercivity ( $H_C$ ) (right scale) as a function of the film thickness for (c) PVO/LAO, and (g) PVO/LSAT films. The shaded area represents thickness range where  $M_S$  and  $H_C$  almost freeze and does not change with film thickness. Thickness-dependence of the remanent magnetization ( $M_R$ ) for (d) PVO/LAO, and (h) PVO/LSAT films. The red line is a fit to  $M_R$  vs.  $t$  plot, using equation (2). The right down-inset in (a),(e) represents schematic of magnetization measurements, where the directions refer to the orthorhombic symmetry of PVO. The inset of (h) is a scheme of dead-layer on the surface of film. The dashed lines are only guide for the eyes.



145 that the soft magnetic component also depends upon the temperature, namely, it disappears  
 146 at temperature  $T > 20$  K for PVO/LSAT, and  $T > 80$  K for PVO/LAO films of  $t \sim 50$  nm[10].  
 147 We will come back to this later in the  $MT$  section. The magnetic coercivity ( $H_c$ ), extracted  
 148 from the hysteresis loops (hard magnetic phase) and the  $M_s$  are plotted as a function of  
 149 film thickness (See Figure 3(c) for LAO and Figure 3(g) for LSAT). A continuous decrease  
 150 in  $M_s$  and increase in  $H_c$  are observed for both the substrates with increase in the film's  
 151 thickness, until a nominal value is reached, which remain nearly constant for thick films.  
 152 Additionally, the shape of hysteresis loop changes from a square like  $MH$  to a paramagnetic  
 153 like S-shaped as thickness is reduced. Here, we suggest that a large value of  $M_s$  for thinner  
 154 films is reminiscent of the presence of a non-magnetic/paramagnetic layer at the surface of  
 155 film, namely a "dead layer", similar to the previous observation in DyTiO<sub>3</sub> thin films [25].  
 156 When the film surface is exposed to air, the surface can get over-oxidized, and the magnetic  
 157 V<sup>3+</sup> ions can indeed be replaced by V<sup>4+</sup>/V<sup>5+</sup> (non-magnetic) ions, decoupling Pr<sup>3+</sup> ions  
 158 and thus unleashing their strong paramagnetic response. Therefore, the soft magnetic phase  
 159 is due to presence of the dead layer at the film surface. It is indeed true that a dead  
 160 layer may also be present at the film/substrate interface [24]. We hypothesize that the  
 161 layer presents at the surface of film dominates, due to excess oxidation, resulting from air  
 162 exposure. To estimate the thickness of this layer, we use a model described by equation (1)  
 163 [25], which assumes that this layer is paramagnetic, has null magnetization at remanence,  
 164 and a huge magnetization at high fields. We then fit the thickness-dependence of remanent  
 165 magnetization ( $M_R$ ) and saturation magnetization ( $M_s$ ) with the proposed dead layer model,  
 166 using the following equation:

$$M_{tot.} = m_{tot.}t = m_P t_P + m_{AF} t_{AF} \quad (1)$$

$$m_{tot.} = (m_P - m_{AF})t_P/t + m_{AF} \quad (2)$$

168 where,  $t = t_P + t_{AF}$  is the total thickness of film,  $t_P$  is the thickness of paramagnetic layer,  
 169  $t_{AF}$  is the thickness of antiferromagnetic layer,  $m_P$  is the moment per unit volume of the  
 170 paramagnetic layer,  $m_{AF}$  is the moment per unit volume of the antiferromagnetic layer. Set-  
 171 ting  $m_{AF} \sim 0.7 \mu_B/\text{f.u.}$  (f.u.: formula unit)[26] (for bulk PVO) and  $m_P = 0$  (for  $M_R$ ), a dead  
 172 layer thickness  $t_P$  of  $\sim 6$  nm for LAO (Figure 3(d)) and  $\sim 4$  nm for LSAT (Figure 3(h)) was  
 173 obtained by fitting the remanent magnetization. Furthermore, setting  $m_P$  to the maximum  
 174 magnetization of the thinnest sample and using  $t_P$  as fitting parameter, we evaluated  $t_P \sim$

175 10–12 nm from fitting of  $M_s$  (not shown). The inconsistency in the computation of  $t_P$  from  
 176 fit of  $M_R-t$  and  $M_s-t$  can have two possible explanations. First, when the diamagnetic sub-  
 177 strate contribution is subtracted, there is always some uncertainties concerning  $M_s$ . **Second,**  
 178 **the magnetic moments associated with the paramagnetic layer, which typically consists of**  
 179 **isolated  $\text{Pr}^{3+}$  ions, may not necessarily be saturated at 5T (especially for thinner films),**  
 180 **and thus a large error in the calculation of  $t_P$  from  $M_s-t$  fit may be induced. Nevertheless,**  
 181 **this error could be minimized at higher magnetic fields, as the moments would be close**  
 182 **to saturation. Therefore, the proposed model can be improved at higher magnetic fields.**  
 183 It is worth noting that, for low thickness films (Figure 3a,e), the saturation magnetization  
 184 remains low compared to  $3.58 \mu_B/\text{f.u.}$  expected for isolated  $\text{Pr}^{3+}$  ions, suggesting that there  
 185 is still a small fraction of antiferromagnetic (AFM) interaction in the thinner films.  
 186 Remarkably, a similar trend in  $H_c$  and  $M_s$  was also observed for ferrite thin films, which  
 187 likely indicated a change in the magnetization spin axis, in addition to a reorientation of the  
 188 domains above critical thickness [28, 29]. In PVO thin films, however, a strong paramagnetic  
 189 response for thinner films is indicative of dead layer at the surface of films, which consists  
 190 isolated  $\text{Pr}^{3+}$  atoms. **In addition, a decrease of  $M_s$  with increase in film thickness is also**  
 191 **evidenced by a decrease in the proportion of the paramagnetic phase. Likewise, the increase**  
 192 **of  $H_c$  with increase of film thickness could be related to the increase in the density of pinning**  
 193 **sites due to increase in the number of domains, and/or domain boundaries. Indeed, due to**  
 194 **a partial strain-relaxation, the film could energetically favor multiple domains, as shown**  
 195 **earlier [10]. For thick PVO films, the magnetization and coercive field approach a nominal**  
 196 **value, meaning that the magnetic contribution from each layer is static, and independent of**  
 197 **film thickness. Nevertheless, the magnetization remains lower than the bulk value ( $\sim 0.6 -$   
 198  $0.7 \mu_B/\text{f.u.}$ ) for thick films, and may be related to the presence of  $\text{V}^{4+} / \text{V}^{5+}$ , which can  
 199 affect the electron hopping, and thus suppress the magnetization considerably.**

200 Further magnetic analyses were carried out by performing magnetic measurements as a  
 201 function of temperature  $T$ . For clarity, only Field Cooled (FC) measurements are shown in  
 202 Fig. 4(a) and 4(c) for LSAT and LAO substrate, respectively. On the LSAT substrate, PVO  
 203 films show three distinct anomalies at temperatures  $T_N$ ,  $T_{SO2}$  and  $T_{SO3}$  (Fig. 4(a)) while  
 204 sweeping the temperature from 300 K to 10 K (further confirmed by plotting  $dM/dT$  and  
 205  $\chi^{-1}(T)$ ). The rising signal at temperature  $T_N$  shows the onset of G-type spin ordered state  
 206 of the vanadium moments, where these moments align antiferromagnetically ( $\parallel$  to  $[001]_o$ -

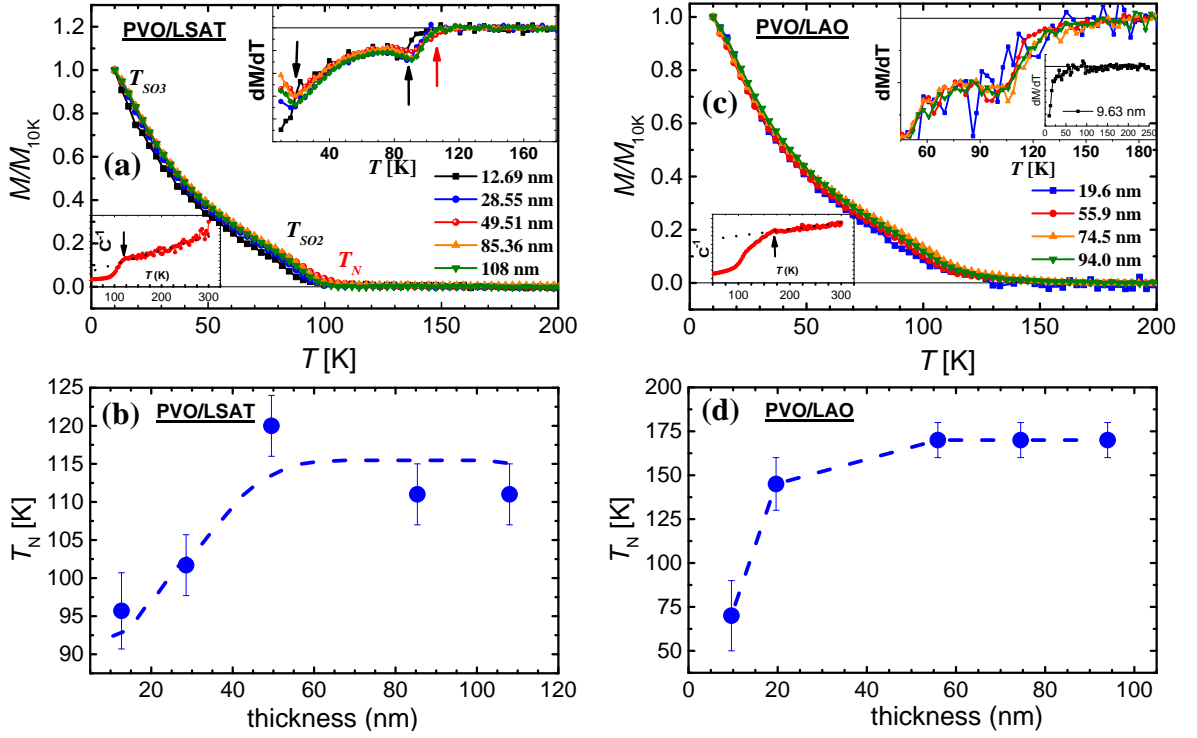


Figure 4: Normalized magnetization measurements for a series of  $\text{PrVO}_3$  films grown on top of (a) LSAT, and (c) LAO substrate, obtained at  $H_{\parallel} = 50$  Oe, displaying different transitions at  $T_{SO1}$ ,  $T_{SO2}$  and  $T_{SO3}$ . The inset is  $dM/dT$  for respective substrates. (b)  $T_N$  ( $T_{SO1}$ ) as a function of film thickness for (b) PVO/LSAT, (d) PVO/LAO films. The dashed lines are only guide to the eyes.

207 axis) along the three crystal axis directions *i.e.* *in-plane* and *out-of-plane*. While for bulk  
 208  $\text{PrVO}_3$ , the transition at  $T_N$  was previously ascribed to the onset of a C-type SO of the  
 209 canted vanadium moments [26, 30], for epitaxial  $\text{PrVO}_3$  thin films, the substrate-induced  
 210 strain results in a G-type SO, as evidenced by the DFT calculations [13]. The  $T_N$  displayed  
 211 by PVO films on LSAT substrates is clearly shown in the inset of Fig. 4(a), and plotted as  
 212 a function of film thickness in Fig. 4(b). This depicts the tunability of  $T_N$  in the range of  
 213 25 K for PVO films grown on LSAT substrates by varying film thickness. Moreover, PVO  
 214 films exhibit additional magnetic features at temperature  $T_{SO2}$  and  $T_{SO3}$ , established by  
 215 two kinks in  $MT$  (in  $dM/dT$  as well) at  $\sim 90$  K and 20 K respectively (Fig. 4(a)). These  
 216 orderings are however absent in the bulk PVO, but have been manifested by  $R\text{VO}_3$  with  
 217 smaller  $R$  size, *eg.*  $\text{DyVO}_3$ ,  $\text{TbVO}_3$  and so on [31–33]. The origin of the magnetic feature at  
 218  $T_{SO2}$  have two alternative explanations. First, it might be due to magnetic polarization of

219 the praseodymium sublattice in the presence of exchange field produced by the vanadium  
 220 moments, via Pr-V exchange, resulting in a ferrimagnetic structure [33]. Second, it could  
 221 be due to the reorientation of the vanadium spin configuration from G-type to C-type,  
 222 where  $V^{3+}$  spins are staggered in the *ab*-plane and aligned ferromagnetically along *c* axis.  
 223 Finally, the transition at  $T_{SO3}$  might represent the onset of ferromagnetic (FM) ordering of  
 224 Pr sublattice, and/or an AFM coupling between  $Pr^{3+}$  4f and  $V^{3+}$  3d moments. Although  
 225 the  $Pr^{3+}$  moments are canted, giving then rise to a finite magnetic moment ( $\sim 1.1 \mu_B$ ),  
 226 as explained by *Reehuis et. al.* for  $Pr_{1-x}Ca_xVO_3$  and bulk  $RVO_3$  ( $R = Ce, Dy, Ho, Er$ )  
 227 [31–34]. Remarkably, by comparing the soft magnetic component that was observed in *MH*  
 228 measurements at temperature  $T \leq 20$  K, and the magnetic feature at  $T_{SO3} \sim 20$  K, we  
 229 proposed earlier [10] that, the soft magnetic component could arise from the Pr-V AFM  
 230 interaction.

231 Alike PVO films on LSAT substrates, the PVO films on LAO substrates show an abrupt  
 232 increase in  $T_N$  with increase in film thickness and approach a nominal value for the thicker  
 233 films (Fig. 4(d)). Moreover, it is observed that the transition at  $T_{SO2}$  is present only for  
 234 thicker films, and appear imperceptible for thinner films ( $t < 55$  nm) (see inset of Fig.  
 235 4(c)). This suggests a possible vanadium spin reorientation solely in the thicker PVO films.  
 236 Similarly, we observed a clear magnetic feature at  $T_{SO3}$  only for the thicker PVO/LAO films,  
 237 and perhaps related to a different strain states between thinner and thicker films. **Notably,**  
 238 **the  $T_N$  of PVO films decreases with the decrease of film thickness, which is in contrast to**  
 239 **the fact that “*the compressive strain enhances the magnetic exchange interactions in PVO***  
 240 ***films, leading to an increase of  $T_N$ ”.*** This discrepancy could be account for the absence  
 241 of  $T_{SO2}$  and  $T_{SO3}$  for the thinner PVO films, producing different magnetic ground states,  
 242 and may be a change in the spin configuration, which, further, are arranged in a way as to  
 243 decrease the exchange interaction between V-V neighbouring sites, and thus lowering  $T_N$  of  
 244 thinner PVO films. Interestingly, for thinner PVO/LAO films, the soft magnetic component  
 245 in the *MH* hysteresis loop was seen to persists up to  $T \sim 80$  K, meaning that the Pr - V  
 246 interaction is significantly enhanced for the LAO substrate, in agreement with our previous  
 247 observations [10]. This enhancement is possibly related to the presence of higher strain  
 248 states in PVO/LAO films, which raises the degree of Pr-V interaction in the same way as  
 249 V-V interaction ( $T_N$ ).

250 Finally, we have explored the possibility to reduce the film surface by capping it with few

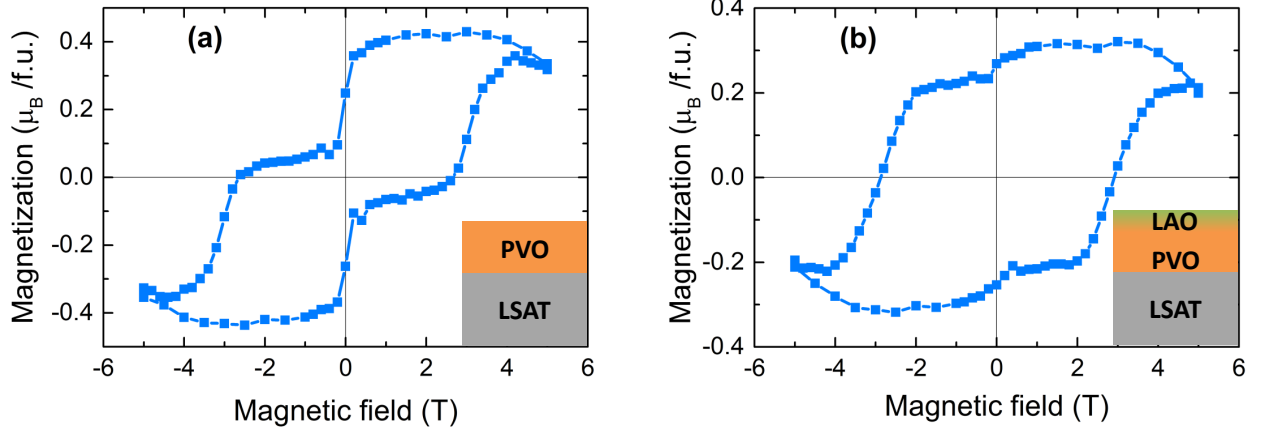


Figure 5: Magnetic hysteresis cycles at 20 K of a  $\sim 50$  nm PVO/LSAT film uncapped (a), and capped with  $\sim 8$  nm thick LAO (b).

251 layers of LAO. The capping of PVO film surface with a reducing material LAO essentially  
 252 decreases the formation of  $V^{4+} / V^{5+}$  at surface, and thus minimizes the contribution of  
 253 dead-layer. Following this, we capped PVO film with  $\sim 8$  nm of LAO grown in the same  
 254 deposition condition in PLD. Fig. 5 illustrates magnetic hysteresis loops of an approximately  
 255 50 nm PVO thin film at  $T = 20$  K, with and without capping layer. Fig. 5(b) shows a  
 256 clear improvement of the canted AFM properties of PVO capped with LAO, with a higher  
 257 remanent magnetization, lower saturation magnetization, and larger  $H_c$ . More importantly,  
 258 the soft magnetic component concomitant with the dead layer is strongly reduced.

259 In conclusion, we have investigated the effect of film thickness on the structural param-  
 260 eters (*in-plane* and *out-of-plane*) and magnetic properties of compressively-strained  $\text{PrVO}_3$   
 261 (PVO) thin films grown on  $(\text{La,Sr})(\text{Al,Ta})\text{O}_3$  (LSAT) (100) (lattice misfit  $\sim 0.8$  %) and  
 262  $\text{LaAlO}_3$  (LAO) (100) (lattice misfit  $\sim 2.9$  %) substrates, and evidenced a *dead layer* of  $t \sim$   
 263 4–6 nm for both sample series. The less strained PVO/LSAT films ( $\epsilon_{110} \sim 1.4$  % for  $t \sim$   
 264 50 nm) show highest  $T_N \sim 120$  K, lower than bulk value *i.e.* 130 K. On the other hand,  
 265 the  $T_N$  of highly strained PVO/LAO films ( $\epsilon_{110} \sim 2.5$  % for  $t \sim 50$  nm) raises up to  $\sim 170$   
 266 K, way above its counterpart bulk value. In addition, we have observed an increase in  $H_c$   
 267 and decrease in  $M_s$  with increase in film thickness for both substrates, and explained by the  
 268 reduction in the proportion of paramagnetic phase. A model based on *dead layer* is used to  
 269 quantify the salient origin of the large paramagnetic  $M_s$  for thinner PVO films. Finally, we

270 have attempted to cap the PVO film with  $\sim 8$  nm LAO film, in order to partially diminish  
271 the excess oxygen at the interface with PVO, and recover the magnetic properties related to  
272 the pure PVO. These observations suggest that the film thickness can be used to tune the  
273 strain/lattice deformation and thus functional properties in PVO thin films, and should be  
274 considered for other epitaxial perovskite thin films.

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