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Annealing-driven suppression of disorder and restoration of metallic ferromagnetism in high-entropy manganite thin films

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Abstract

We investigate how oxygen stoichiometry influences magnetism and magnetotransport in epitaxial high-entropy manganite thin films. The as-grown $\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Sr}_{0.2}\text{MnO}_3$ film exhibits a glassy, strongly localized insulating state with low T_C and large resistivity. Post-growth oxygen annealing dramatically reorganizes the energy landscape and nearly doubles the Curie temperature from $T_C \approx 125$ K to $T_C \approx 225$ K, achieves more than 200% enhancement in spontaneous magnetization, and about 50 % reduction in coercivity, evidencing reduced pinning and improved domain dynamics. Magnetotransport evolves from insulating variable-range hopping to a metallic regime, showing a diffusive $\sim T^{1/2}$ Altshuler–Aronov correction with a weak $\sim T^2$ dependence in the low temperature regime. The annealed film displays a magnetic field-tunable insulator–metal transition ($T_{\text{IM}}(H = 0) \approx 223$ K) that approaches room temperature at $H=80$ kOe, along with a large negative peak $MR \sim 85$ % at $H=80$ kOe near T_C and $MR \sim 45$ % at $H=10$ kOe at $T \approx 200$ K. Analysis of the insulating state resistivity in the VRH model indicates a field-enhanced localization length and hopping distance after oxygenation. Structural probes point to vacancy passivation and smoother, more homogeneous films. Annealing-driven oxygen concentration uniformization and cationic ordering straighten Mn–O–Mn bonds, enhance bandwidth, and mitigate dead-layer effects. Our results demonstrate that controlled high-temperature annealing is an effective tool to tune the bandwidth-disorder competition and to rejuvenate ferromagnetic metallicity in high-entropy manganite films.

Introduction

High-entropy materials (HEMs),^{1,2,3} particularly high-entropy oxides (HEOs),^{4,5,6,7} have garnered significant attention due to their ability to stabilize a single-phase structure despite the presence of multiple elements on a crystallographic sublattice. The HEO family encompasses a wide range of crystallographic classes, including (i) transition metal (TM)-based rock salt and spinel materials,^{8,9,10,11} (ii) rare-earth (RE)-based fluorites,^{12,13} (iii) RE-TM-based perovskites^{14,15,16} and Ruddlesden-Popper phases.^{17,18} RE-TM perovskites, especially those containing Mn,^{14,15,16,19} are of particular interest due to the strong electronic correlation-driven phase-separation, colossal magnetoresistance (CMR), and large low-field magnetoresistance (LFMR).^{20,21,22,23} Perovskites of type ABO_3 allow multiple cations to occupy either the A- or B-site of the ABO_3 type structure. For example, in alkaline earth (AE) doped RE compounds such as manganites, the A/RE site can host multiple atoms (e.g., La, Pr, Nd, Sm, Gd, Yb, Er, Ca, Sr, Ba),^{16,19,24} while the B/AE site can accommodate multiple transition metals (e.g., Mn, Ni, Cr, Fe, Co).²⁵ A typical RE-site multielement substitution is $(La_{0.2}Nd_{0.2}Gd_{0.2}Sr_{0.2}Ba_{0.2})MnO_3$.¹⁶ Similarly, an HE-manganite with Mn-site equimolar substitution is $La_{0.8}Sr_{0.2}(Mn_{0.2}Fe_{0.2}Ni_{0.2}Co_{0.2}Cr_{0.2})O_3$. These examples illustrate the structural stability despite the compositional complexity of HE-manganites.

Alkaline earth-doped manganites exhibit intrinsic tolerance to multiple element substitution at both cationic sites.²¹ Key parameters for understanding the physics of manganites include (i) the average A-site ionic radii ($\langle r_A \rangle$), (ii) the tolerance factor (t), (iii) the A-site size variance (σ^2), and (iv) the e_g -electron bandwidth (W). External factors like substrate-induced strain and film thickness also significantly influence magnetic and magnetotransport properties.²² The average A-site cationic radius is given by $\langle r_A \rangle = \sum_i y_i r_i$, where r_i is the Shannon ionic radius (typically in 9-fold coordination) of the i^{th} cation, and y_i is its fractional occupancy. The tolerance factor is defined as $t = \frac{\langle r_A \rangle + r_O}{\sqrt{2}(r_B + r_O)}$, where r_B is the B-site radius (radius of the mixed valence Mn) and r_O is the radius of the oxygen ion. Near $t=1$ (e.g., $La_{1-x}Sr_xMnO_3$), the structure is cubic ($Pm\bar{3}m$) or rhombohedral ($R\bar{3}c$) with straight Mn–O–Mn bonds ($\theta = 180^\circ$) with straight Mn–O–Mn bonds ($\theta = 180^\circ$). Smaller A-site cationic radii (e.g., $Sm_{1-x}Sr_xMnO_3$) result in $t < 1$ and an orthorhombic structure ($Pmna$, $Pbnm$) with cooperative tilts/rotations of MnO_6 octahedra and Mn–O–

Mn bond angles significantly lower than 180°. The phase-separated region expands as one moves from $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ to $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$. The e_g -electron bandwidth is given by $W \sim \frac{\cos(\pi - \angle \text{Mn-O-Mn})}{d^{3.5}}$, where d is the Mn-O bond length. Smaller $\langle r_A \rangle$, t , and W reduce the Mn-O-Mn bond angle, weakening the double exchange (DE) mechanism driving FM order^{26,27,28,29} and strengthening JT distortion and superexchange driving AFM order.^{29,30} The variance, $\sigma^2 = \sum_i y_i r_i^2 - \langle r_A \rangle^2$, decreases the tolerance factor, and the FM order starts transforming to AFM order.^{31,32} The variance quantifies quenched disorder deforming the Mn-O-Mn network by impacting bond angle and length. Reduced bond angle reduces the e_g BW impacting magnetic and magnetotransport properties.

The phase separation regime is considered central to the physics of manganites (e.g., $\text{La}_{1-x-y}\text{Pr}_x\text{Ca}_y\text{MnO}_3$).^{33,34,35} Recently, multielement substitution at the A-site has been used to improve the TCR in manganites.^{36,37} Recent studies of high-entropy manganites with multi-cation disorder reveal unconventional magneto-transport behavior. In $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Sr}_{0.2}\text{Ba}_{0.2})\text{MnO}_3$, T_C decreases as $\langle r_A \rangle$ increases from 1.2416 to 1.2516 Å¹⁶, contrary to the canonical bandwidth trend.^{31,32} This suggests that A-site size variance σ^2 dominates, and despite the disorder, the system remains purely ferromagnetic without AFM or frustrated phases. The proposed mechanism involves fragmentation of B-site exchange by multi-cation substitution, where local distortions of MnO_6 octahedra enhance carrier localization and shorten the double-exchange length scale, lowering T_C . In $(\text{Gd}_{0.25}\text{La}_{0.25}\text{Nd}_{0.25}\text{Sm}_{0.25})_{1-x}\text{Sr}_x\text{MnO}_3$,¹⁹ the orthorhombic perovskite structure is stabilized with homogenous cation distribution. At low hole concentrations ($x = 0-0.1$), asymmetric superexchange (SE) yields an insulating canted-AFM (CAF) state. At intermediate doping ($x = 0.15$ & 0.2), competing AFM-SE and FM-DE interactions drive multiple magnetic transitions. Epitaxial $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Sr}_{0.2})\text{MnO}_3$ (HEO-Mn) films on cubic-STO (100), orthorhombic-NGO (110), and cubic-LAO (100) exhibit distinct magnetism compared to bulk. Films exhibit a single ferromagnetic transition attributed to coherent epitaxial strain homogenizing Mn-O-Mn bond geometry. Regardless of strain, T_C is suppressed relative to bulk, most strongly on LAO ($\approx 38\%$ lower). Single-crystal $\text{La}(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})\text{O}_3$ films demonstrate entropy-assisted synthesis yielding compositionally disordered, positionally ordered lattices, and designable magnetism. Beyond a continuously tunable Curie temperature, these films exhibit a robust

exchange-bias response absent in parent oxides, indicating spin functionalities without heterostructuring.²⁵ The foregoing survey shows that, to date, no study on high-entropy manganites that are based on the physics of colossal magnetoresistance (CMR) has systematically targeted A- or B-site cation ordering through the mitigation of oxygen vacancies and evaluated the resulting magnetic and magnetotransport responses.

In the present study, the A-site disordered manganite $\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Sr}_{0.2}\text{MnO}_3$ thin films have been grown on (001)-oriented LaAlO_3 substrate, and the influence of the oxygen annealing on magnetism and magnetotransport mechanisms has been investigated. The average A-site cationic radius is estimated to be $\langle r_A \rangle = 1.200 \text{ \AA}$ and the corresponding variance is found to be 3.758×10^{-3} . In contrast, the average A-site cationic radius and the corresponding variance are estimated to be $\langle r_A \rangle = 1.2348 \text{ \AA}$ and 1.410×10^{-3} , respectively for the canonical 20% Sr-doped LaMnO_3 . As the size of the RE cation decreases, the $\langle r_A \rangle$ decreases and σ^2 increases rapidly. Thus, for $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and $\text{Sm}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, $\langle r_A \rangle = 1.1924 \text{ \AA}$ and $1.1676 \text{ \AA}$, while $\sigma^2 = 0.0588$ and 0.0712 , respectively. The σ^2 values are much higher than for the manganite $\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Sr}_{0.2}\text{MnO}_3$. Our study shows that the as-deposited films exhibit a glassy, strongly localized insulating state with low magnetic moment, low T_C and large resistivity. Oxygen annealing enhances the (i) Curie temperature from $T_C \approx 125 \text{ K}$ to $T_C \approx 225 \text{ K}$, (ii) magnetization by 200% enhancement, and (iii) reduces coercivity by about 50%. Magnetotransport evolves from insulating variable-range hopping to a metallic regime, showing a diffusive $\sim T^{1/2}$ Altshuler–Aronov correction with a weak $\sim T^2$ dependence in the low temperature regime. These results bring out that controlled high-temperature annealing is an effective tool to tune the bandwidth-disorder competition and strengthen ferromagnetic metallicity in high-entropy manganite films.

Experimental Details

$\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Sr}_{0.2}\text{MnO}_3$ thin films were grown by RF magnetron sputtering of a 2-inch diameter target. The target (2-inch in diameter and $\sim 3 \text{ mm}$ thick) was prepared by the standard solid-state route. The starting materials were 5N pure La_2O_3 , Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , and SrO , which were mixed in stoichiometric amounts and subjected to long-duration mixing. After thorough mixing, the material was calcined at $950 \text{ }^\circ\text{C}$ for 24 hrs. Calcined material was ground for several hrs and then heated at $1100 \text{ }^\circ\text{C}$ for 24 hrs. In the

third step, the material was reground and then pressed using a hydraulic press, and then sintered at 1350 °C for 24 hrs to obtain a 2-inch sputtering target. All the thermal treatments were carried out in a temperature programmable furnace (Nabertherm-Germany). The thin films were deposited by RF magnetron sputtering on (001)-oriented LaAlO₃ (LAO) substrates. During deposition, the substrate-target distance was fixed at $\approx$ 5 cm. The base pressure was $\sim 10^{-6}$ Torr, and the sputtering was done in Ar + O₂ (80 % + 20 %) ambience. The substrate temperature and deposition pressure were kept at $\approx$ 850 °C. The RF power used for the sputtering of both targets was 150 W. One set of films was annealed in flowing oxygen at 900 °C for 6 hrs. High-resolution X-ray diffraction (HR-XRD) measurements (X-ray reflectivity, 2 θ -omega (2 θ / ω) scans, and ω -scan (rocking scans) were done to evaluate the thickness and structural characteristics of the films. A Rigaku Smartlab X-ray Diffractometer equipped with a 2-bounce Ge monochromator was employed for the above measurements. The evolution of the surface topography was examined by atomic force microscopy (AFM, VEECO Nanoscope V), respectively. The electrical transport measurements of the samples were performed using a Quantum Design Physical Property Measurement System (PPMS, Dynacool Quantum Design) with contacts in a linear four-probe geometry. The contacts on the film surface were made through silver paste. Zero field cooled (ZFC), field cooled cooling (FCC), and field-cooled warming (FCW) magnetization and magnetic field-dependent magnetization were measured in a Quantum Design Superconducting Quantum Interference Device (SQUID MPMS3). The oxidation states and chemical compositions of all samples were examined by X-ray photoelectron spectroscopy (XPS PHI 5000 Versa Probe III). Energy dispersive X-ray spectroscopy (EDS, TESCAN MAGNA GMH, EDAX OCTANE ELECT SUPER) was used to examine the cationic homogeneity of the films.

Results and Discussion

Structure and morphology

EDS carried out from several places on the film showed that within the limits, the cationic concentration was close to the envisaged one. Fig. 1(a) presents the specular XRR of the as-grown film (10As) and oxygen annealed (10An) films) on a logarithmic intensity scale. A regime of total external reflection at small angles is followed by well-defined Kiessig oscillations, signifying a laterally uniform single film on a smooth substrate. To quantify

the thickness, we analyzed the oscillation period in momentum transfer, where the key relation comes from Kiessig-fringe periodicity in reciprocal space $q_z = \frac{4\pi\sin\theta}{\lambda}$. The film thickness is given by $t = \frac{2\pi}{\Delta q_z} = \frac{2\pi\lambda}{\Delta(4\pi\sin\theta)} = \frac{\lambda}{2\Delta(\sin\theta)} = \frac{\lambda}{2\Delta\theta\cos\theta} \approx \frac{\lambda}{2\Delta\theta}$. Using this formula and the positions of the second to fifth minima, the film thickness was found to be $t \approx 20$ nm. The oscillations persist to $2\theta \approx 3.8^\circ$ with gradual amplitude damping, consistent with modest interfacial and surface roughness. The low-angle “knee” occurs at a small 2θ , indicative of an oxide-like electron density. The solid lines are the Parratt fit to the experimental data, and the best fit has been obtained by incorporating a disordered interface layer of $\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Sr}_{0.2}\text{MnO}_3$ in contact with the substrate LAO. The as-grown has a much thicker (~ 3.3 nm) disordered HE-mangnaite layer, while the oxygen annealed film has a disordered layer thickness of ~ 1.5 nm. The XRR fit yields a surface roughness of ≈ 0.6 nm and ≈ 0.8 nm for the as-grown and annealed films, respectively. The roughness values from the XRR analysis should be treated as approximate because the high-angle region approaches the background/noise level. The marked reduction in the disordered interfacial layer after annealing indicates improved interfacial structural order and reduced defect density. This is expected to enhance the electrical conductivity by suppressing carrier scattering/localization at the interface and increasing the effective conducting volume of the film. Simultaneously, the reduction of the magnetically disordered interfacial region should strengthen exchange coupling, decrease spin frustration, and thereby improve the overall magnetic response, leading to a more robust long-range ferromagnetic state.

Thus, oxygen annealing of the as-grown film has a significant effect on the interface microstructure, and this in turn may have a great impact on the magnetic and transport properties. The total film thickness is found to be ~ 20 nm. HR-XRD data in Fig. 1(b) confirm the c-axis oriented and single crystalline growth. The average out-of-plane lattice constant of the as-grown and annealed films is $a_{\text{As}} = 3.8359$ Å and $a_{\text{An}} = 3.8543$ Å, respectively. The lattice constant increases by 0.48% on annealing in oxygen, indicating an increase in the in-plane compressive strain, which in turn stretches the MnO_6 octahedra in the out-of-plane direction. The observed expansion of the lattice is in contravention to the results reported for the canonical divalent doped manganites^{38,39,40}, wherein oxygenation leads to a decrease in the out-of-plane lattice constant and hence

relaxation of the strain. Oxygen annealing of manganite films on LAO, e.g., LSMO/LAO films, fills up the oxygen vacancies and enhances the $\text{Mn}^{4+}/\text{Mn}^{3+}$ and hence lowers the Mn-O-Mn bond lengths.^{38,39,40} The possible reason for the deviation from this canonicity could be size mismatch and the higher configurational entropy in the HE-manganite under study. The oxygen annealing-induced enlargement of the out-of-plane lattice constant could be understood in terms of the small value of $\langle r_A \rangle$, and a large A-site σ^2 which could yield stronger octahedral tilts and rotations under compressive strain. Passivation of the oxygen vacancies could enhance cooperative octahedral rotations and lead to octahedral elongation along the out-of-plane direction. Thus, it appears that at smaller $\langle r_A \rangle$, and larger σ^2 , the octahedral tilt/rotation dominates over the usual Mn-O bond shortening as seen in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ or other manganites with higher $\langle r_A \rangle$, and smaller σ^2 .^{41,42}

Another noticeable factor in the XRD is the asymmetry of the (00l) peaks of the as-grown film, which vanishes on oxygen annealing. There could be a possible oxygen concentration gradient, and this could, in turn, yield a lattice parameter gradient along the out-of-plane axis and hence asymmetry in the peaks.^{38,39,40} Furthermore, in HE-manganites, multiple octahedral tilts/rotations could also cause or add to the asymmetry. Additionally, the presence of point defects other than oxygen vacancies and dislocations could also contribute to the overall asymmetry. Oxygen annealing mitigates the lattice parameter gradient, uniformizes the octahedral tilt/rotations, and reduces the density of point defects and dislocations.

The $\omega - 2\theta$ scans of the two films (Fig. 1(c)) bring out that (i) well-defined Laue oscillations observed in the as-grown film get diffused in the oxygenated film, (ii) the separation between the substrate and film peaks increases from $\Delta\omega = 0.722^\circ$ in the as-grown film to $\Delta\omega = 0.968^\circ$ in the annealed film, and (iii) asymmetry is lowered on oxygen annealing. The Laue oscillations could become diffuse due to (i) lateral strain relaxation, (ii) reconfiguration of the twinning and enhance mosaic nature, and (iii) an increase in the surface roughness as well as the roughening of the buried surfaces.^{43,44} Fig. 1(d) shows the rocking curve of the two films. The full width at half maximum (FWHM) is calculated (from curve fitting) to be $\Delta\omega = 0.088^\circ$ and 0.081° for the as-grown and annealed films, respectively. The reduced FWHM in the oxygen annealed film could be due to improved

interface quality and oxygen stoichiometry. The as-grown rocking curve shows asymmetry, the reasons for which have already been discussed above.

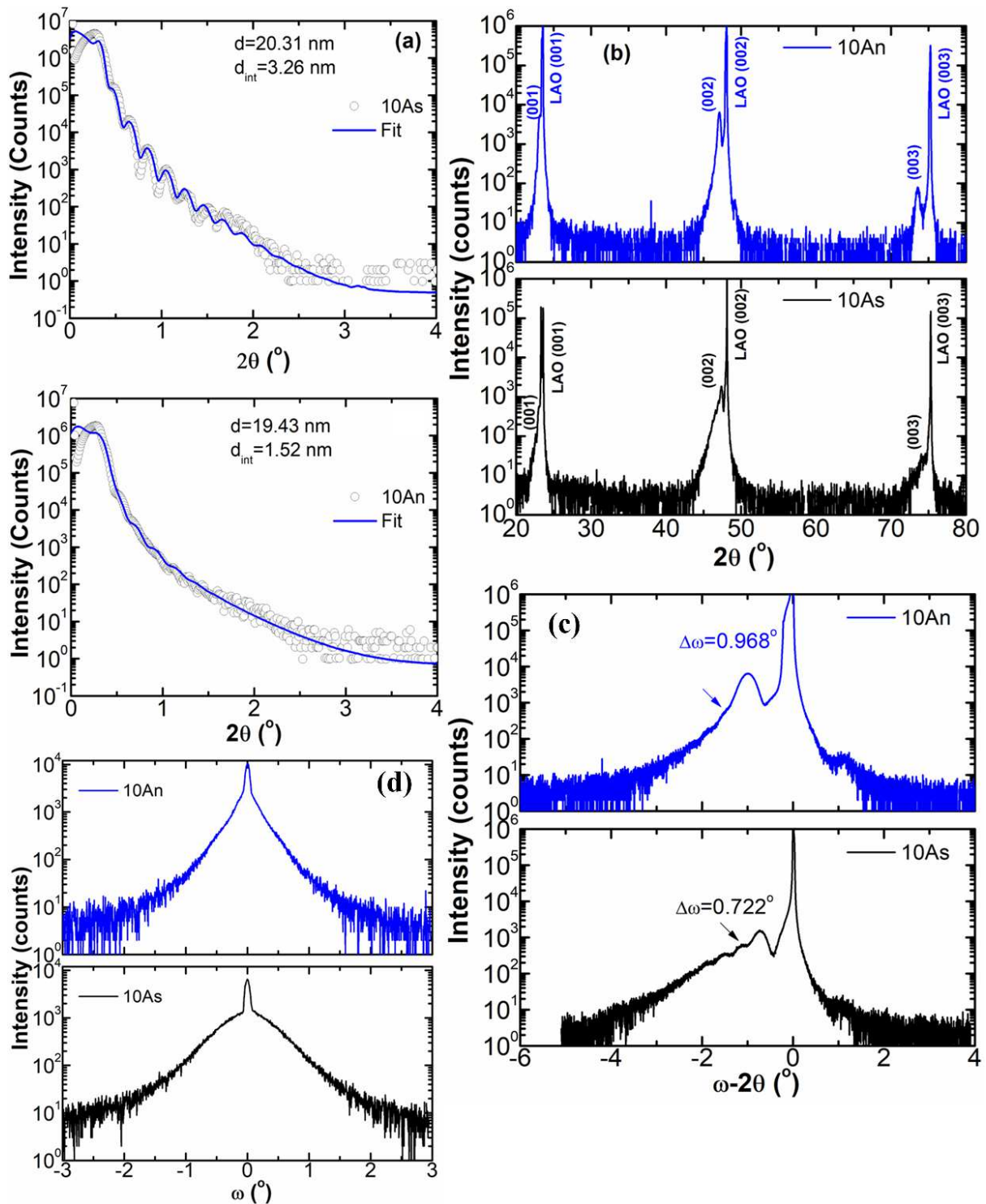


Figure 1: (a) The XRR data of the as-grown and annealed film, (b) 2θ - ω scans of the two films (c) ω - 2θ scan of the as-grown and annealed films, and (d) the rocking curve of the (002) cubic peak of the as-grown and annealed films.

In the RSM of the as-grown film (Fig. 2a), the sharp, intense spot at $Q_x \approx 0$ and $Q_z \approx 0.528$ corresponds to the LaAlO_3 (002) substrate, whereas the film appears as a broader, weaker feature centered near $Q_x \approx 0$ but at a lower $Q_z \approx 0.523$, implying a larger $d_{(002)}$ (expanded c-axis). The vertical alignment of the film and substrate peaks at $Q_x \approx 0$ shows that the in-plane lattice parameter of the as-grown $\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Sr}_{0.2}\text{MnO}_3$ film matches that of LAO within instrumental resolution; thus, the as-grown film is coherently strained and pseudomorphic, with no obvious in-plane relaxation. A stronger broadening along Q_z (with a tail to lower Q_z) indicates a distribution of out-of-plane lattice spacings, consistent with A-site cation disorder and oxygen-concentration gradient typical of high-entropy manganites. The comparatively narrower spread in Q_x , together with the specular rod and off-specular streaks, confirms good epitaxial alignment; any diagonal elongation is minor and does not signal relaxation. Overall, the as-grown film is single-phase, epitaxial, and in-plane clamped to LAO, exhibiting $\sim 1\%$ out-of-plane expansion. For the oxygen-annealed film (Fig. 2b), the LAO (002) peak remains at $Q_x \approx 0$ and $Q_z \approx 0.528$; however, the film peak shifts closer to the substrate in Q_x , indicating improved in-plane coherence and stronger pseudomorphic locking. Its slightly lower Q_z reflects a further increase in $d_{(002)}$, i.e., enhanced c-axis expansion, likely associated with coherent clamping and defect passivation. Annealing also markedly reduces Q_z broadening, pointing to diminished microstrain and fewer vertical inhomogeneities (such as oxygen-concentration gradients), while the cleaner specular feature suggests improved interface/surface correlation. Hence, oxygen annealing enhances epitaxy and overall structural and compositional homogeneity.

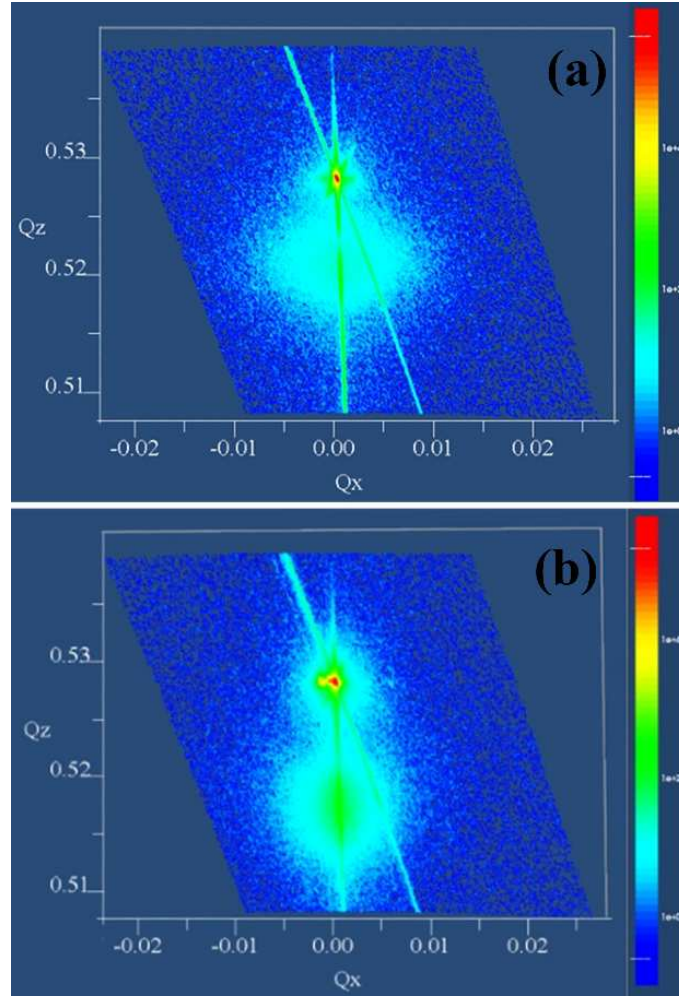


Figure 2: The reciprocal space mapping of the (002) peak of the substrate and as-grown film (a) and oxygen annealed (b) $\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Sr}_{0.2}\text{MnO}_3$ film.

The surface morphology of the as-grown film, as represented in Fig. 3(a), shows dense, fine nano-granular and nearly planar surface with no discernible large particulates. The average surface roughness is ≈ 0.52 nm, which is nearly the unit cell scale. Annealing in oxygen is expected to drive uniformization of the oxygen concentration gradient, island or outgrowth formation, and hence a surface reconstruction. The AFM image of the [Fig. 3(b)] agrees with the above statement. The surface of the oxygen annealed film consists of faceted crystalline platelets with a smoother background. The z-scale (30 nm) suggests outgrowths above the planar background surface rise tens of nm above the matrix and hence enhanced surface roughness. The average surface roughness is ≈ 2.2 nm, which is nearly four times that of the as-grown film. The XRR fitting yields surface roughness values of approximately 0.6 nm and 0.8 nm for the as-grown and annealed films, respectively. For the as-grown film, the roughness obtained from XRR agrees well

with that measured by AFM. However, for the annealed film, the XRR-derived roughness does not show similarly good agreement with the AFM value. This discrepancy may arise from an underestimation of the roughness in the XRR analysis, possibly due to the relatively weak and less well-defined Kiessig fringes in the annealed film.

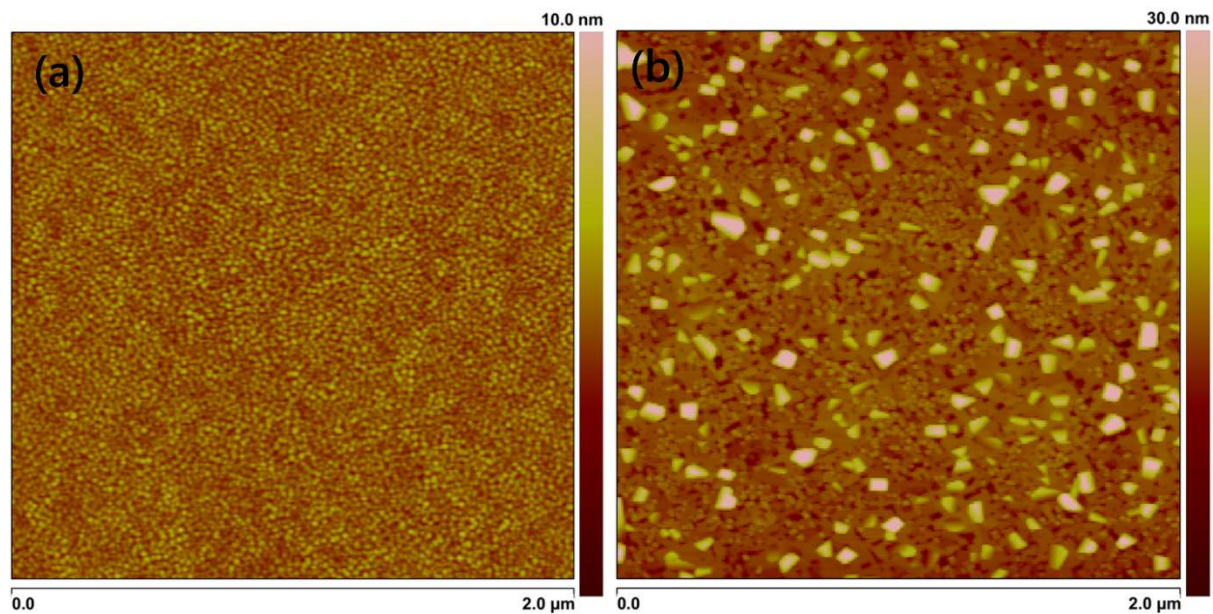


Figure 3: The AFM images of the as-grown and annealed films.

X-ray Photoelectron Spectroscopic investigation

The $Mn - 2p_{3/2}$ core-level X-ray photoelectron spectra (XPS) of the as-grown and oxygen-annealed $La_{0.2}Pr_{0.2}Nd_{0.2}Sm_{0.2}Sr_{0.2}MnO_3$ films were analyzed by Shirley-background-subtracted multiple-peak fitting using Mn^{3+} and Mn^{4+} main components together with their corresponding satellite features (Fig. 4). For the as-grown film (Fig. 4a), the unconstrained fit yields an $Mn^{3+}:Mn^{4+}$ main-peak area ratio of 75.9:24.1, with the Mn^{3+} and Mn^{4+} components centered at about 641.0 and 642.25 eV, respectively. For the oxygen-annealed film, the corresponding unconstrained fit gives 81.6:18.4, with the Mn^{3+} and Mn^{4+} peak positions located at about 641.14 and 642.42 eV. These values are all close to the nominal mixed-valence ratio of 80:20 expected for the composition. To assess whether the experimental spectra require any substantial deviation from the nominal Mn valence balance, both spectra were also fitted using a constrained $Mn^{3+}:Mn^{4+}$ ratio of 80:20. In the as-grown film, the constrained fit reproduces the spectral envelope almost as well as the unconstrained fit, with only a marginal change in fit quality (R^2 decreases from 0.99483 to 0.99470). Similarly, for the oxygen-annealed

film, the unconstrained and constrained fits are essentially indistinguishable in quality ($R^2 = 0.99462$ and 0.99461 , respectively). This shows that the measured $Mn - 2p_{3/2}$ spectra are fully consistent with the nominal mixed-valence state and do not require any significant redistribution of Mn^{3+} and Mn^{4+} .

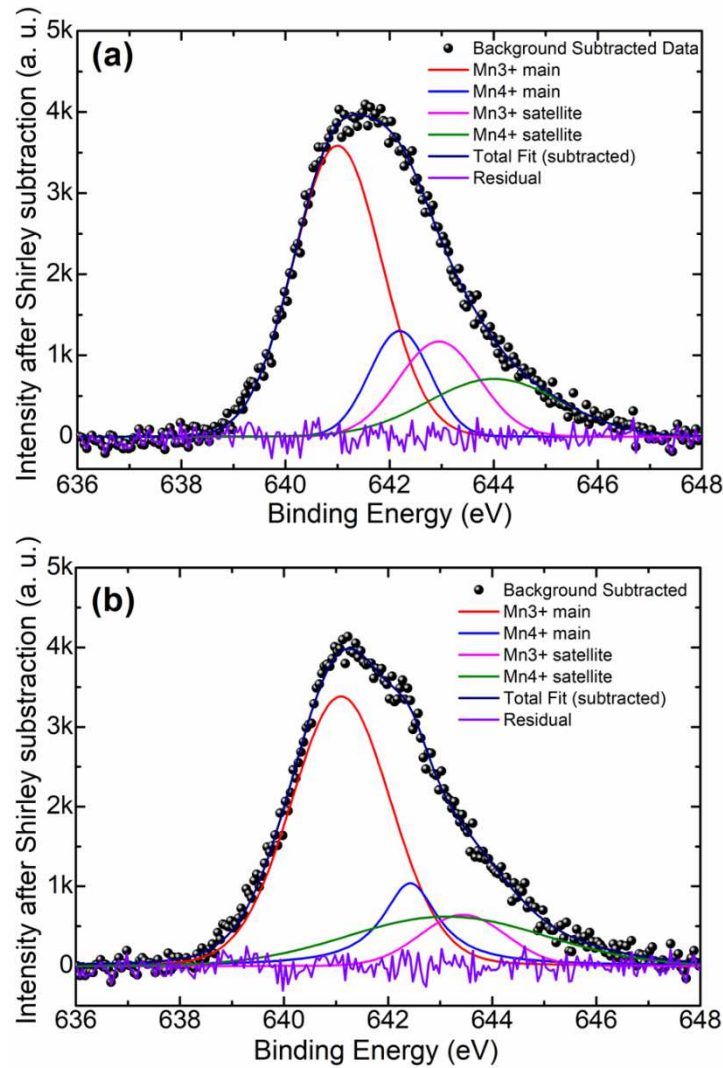


Figure 4: (a) Deconvolution of the $Mn - 2p_{3/2}$ spectrum using Mn^{3+}/Mn^{4+} main peaks and satellite features gives a free-fit ratio of 75.9:24.1, while a constrained 80:20 fit yields nearly identical fit quality, confirming that the Mn mixed valence is close to the nominal composition. (b) $Mn - 2p_{3/2}$ spectrum of the oxygen-annealed film fitted using Mn^{3+} and Mn^{4+} main peaks along with their satellite contributions after Shirley background subtraction. The unconstrained fit yields a $Mn^{3+}:Mn^{4+}$ ratio of 81.6:18.4, which is close to the nominal 80:20 composition.

Taken together, the XPS results indicate that both the as-grown and oxygen-annealed films retain an Mn valence distribution very close to the nominal 80:20 ratio. Although the best unconstrained fits give slightly different Mn^{4+} fractions for the two samples, these

differences are small and remain within the fitting uncertainty associated with the broad satellite structure and its correlation with the background-subtracted main-peak areas. Therefore, the most robust conclusion is that oxygen annealing does not induce any substantial change in the Mn mixed-valence state, and both films preserve the intended Mn^{3+} and Mn^{4+} balance.^{45,46}

Magnetic behaviour

Fig. 5(a) displays the temperature dependence of the magnetization measured under a small dc field of $H=100$ Oe (applied parallel to the film plane along the longer direction) in the ZFC, FCC, and FCW protocols. The as-grown film is paramagnetic (PM) in the higher temperature range and develops a ferromagnetic (FM) state on cooling. The ZFC curve starts from a small moment [$M_{ZFC}(2\text{ K}) \approx 6.09$ emu/cm³], increases with temperature, and exhibits a broad maximum at $T_P \approx 62$ K with $M_{ZFC}(T_P) \approx 87$ emu/cm³. On cooling (FCC), the magnetization rises rapidly below the Curie transition and attains a peak value of $M_{ZFC}(T_P) \approx 164$ emu/cm³ at $T_P \approx 23$ K and $M_{ZFC}(2\text{ K}) \approx 156$ emu/cm³. Surprisingly, the FCW branch remains below the FCC curve at low temperature, and consequently, the magnetization irreversibility temperature T_{irr} of ZFC-FCC is higher than that of the ZFC-FCW. The observed ZFC peak together with the large ZFC-FCC/FCW divergence is indicative of strong domain-wall pinning and a distribution of energy barriers, i.e., a glassy dynamics rather than a simple reversible ferromagnet. The PM-FM transition is not sharp, and the FCC and FCW Curie temperatures are found to be $T_C^{FCC} \approx 127$ K and $T_C^{FCW} \approx 140$ K. The midpoint of the T_C , as indicated by the inverted peak in the temperature derivative of the magnetization (insets of Fig. 5a), appears at ~ 100 K. These observations indicate an FM ground state with substantial defect-mediated pinning. The small cooling-warming hysteresis near T_C suggests that the transition is predominantly second-order, and the history effects arise from irreversible domain processes. The oxygen annealed film shows a dramatic improvement (Fig. 5(b)) in the magnetic properties, which is reflected by a huge jump in the Curie temperature to $T_C \approx 225$ K (in ZFC, FCC, as well as FCW), a colossal increment in the spontaneous magnetization ($M_{FCW/FCC}(T_P \approx 12\text{ K}) \approx 447$ emu/cm³), overlapping of the FCC-FCW magnetization curves and mega irreversibility between the ZFC and FCC/FCW magnetization. In the annealed film, the midpoint of the T_C (insets of Fig. 5b), appears at ~ 200 K. The irreversibility

temperature is found to be $T_{irr} \approx 205$ K. The peak in the ZFC magnetization occurs at $T_p \approx 183$ K. The magnetization values at 2 K are $M_{ZFC}(2\text{ K}) \approx 38$ emu/cm³, $M_{FCC}(2\text{ K}) \approx 435.3$ emu/cm³, and $M_{ZFC}(2\text{ K}) \approx 435.6$ emu/cm³. The peak in the FCC/FCW M-T appears at $T_p \approx 12$ K, below which the magnetization shows a slight decrease, and a similar decrease is noticed in the ZFC M-T curve also. The pronounced ZFC–FCW bifurcation at $T < T_{irr}$, together with the ZFC maximum (existence of T_p), is a manifestation of the cluster-glass-like dynamics in the FM state. The above results show that oxygen annealing enhances the FM order (as evidenced by large low-temperature magnetization) and sharpens the PM–FM transition, consistent with improved stoichiometry and reduced disorder.

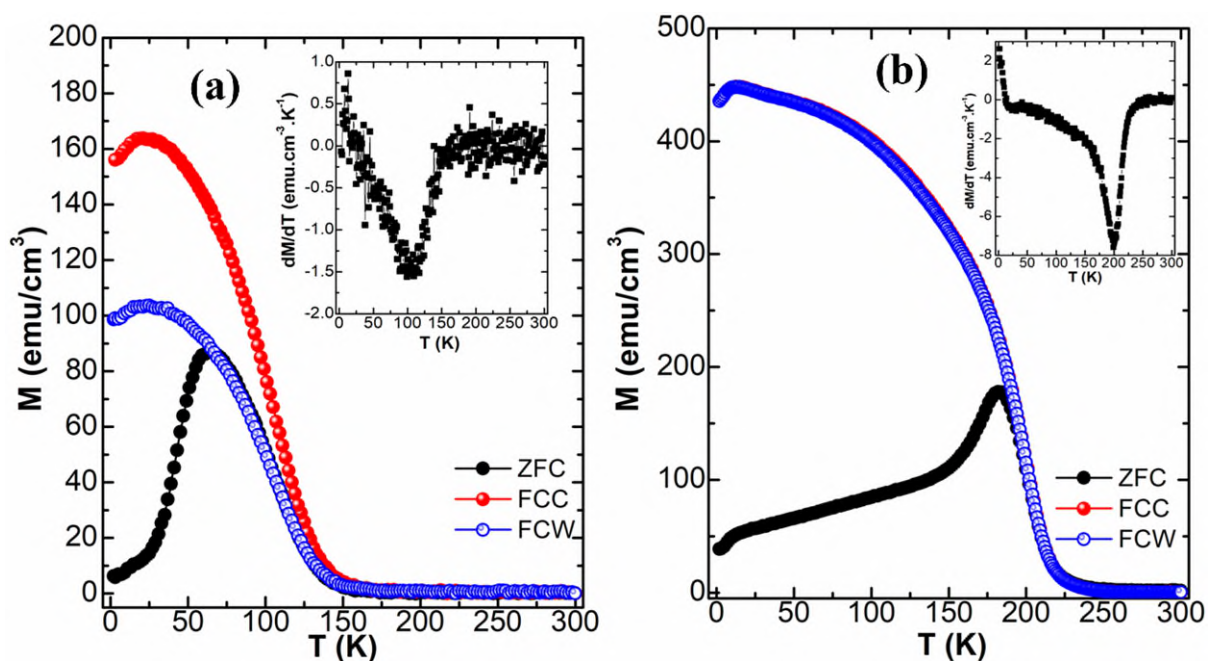


Figure 5: The temperature dependence of the magnetization measured under a small dc field of $H=100$ Oe in the ZFC, FCC, and FCW protocols. The insets show the temperature derivative of the respective FCW magnetizations.

Fig. 6(a) shows the field-dependent magnetization $M(H)$ of the as-grown film measured at 5 K, 50 K, and 100 K. At 5 K, the M-H loop shows a coercivity of $H_c \approx \pm 816$ Oe, which decreases sharply to $H_c \pm 37$ Oe and $H_c \pm 34$ Oe at 50 K and 100 K, respectively. At further higher temperatures, the loop disappears as the PM phase takes over. The remanence is found to $M_r \approx \pm 136$ emu/cm³ at $T=5$ K, which decreases to $M_r \approx \pm 42$ emu/cm³ and $M_r \approx \pm 38$ emu/cm³ at 50 K and 100 K, respectively. The M-H loop at $T=5$ K is nearly square, as seen by a high value of the squareness ratio $\frac{M_r}{M_s}(\text{As grown}) \approx 0.96$. At higher temperatures, the squareness is lost. The scaling of the coercivity with

temperature is shown in Fig. 6(d). In the oxygen annealed film, the magnetization behaviour undergoes dramatic changes (Fig. 6(b)). In the oxygenated film (i) magnetization is enhanced multifold at corresponding temperatures, (ii) the coercivity is squeezed to a much lower value, and (iii) well-defined M-H loops are seen up to ~200 K. The squareness of the M-H loop (Fig. 6c) at T=5 K is slightly lower, $\frac{M_r}{M_s}(\text{Annealed}) \approx 0.91$, than the corresponding value for as-grown film, but the loop exists up to T~200K, the temperature where the reverse peak of the dM/dT curve of the oxygenated film occurs. The squareness of the M-H loop decreases gradually to $\frac{M_r}{M_s}(\text{Annealed}) \approx 0.79$ at T~150 K and then suddenly drops to $\frac{M_r}{M_s}(\text{Annealed}) \approx 0.20$ at T=200 K. This could be attributed to the enhanced thermal fluctuations as the Curie transition is approached, with some contribution from the high intrinsic entropy could also be there. At 5 K, $H_c=409$ Oe and gradually decreases to 11 Oe at 200 K. The scaling of H_c with temperature is shown in Fig. 6(d). The rapid rise of M at low fields, followed by a short approach-to-saturation interval, indicates enhanced double-exchange connectivity and a reduction of non-FM background after oxygenation. The coercive field is smaller and the remanent magnetization larger than in the as-grown film. This points to fewer pinning centers (vacancies/defect clusters) and improved domain mobility. The nearly symmetric loop about H=0 shows no measurable exchange bias in the ZFC state, consistent with a dominant FM phase and reduced FM/AFM interfacial coupling.

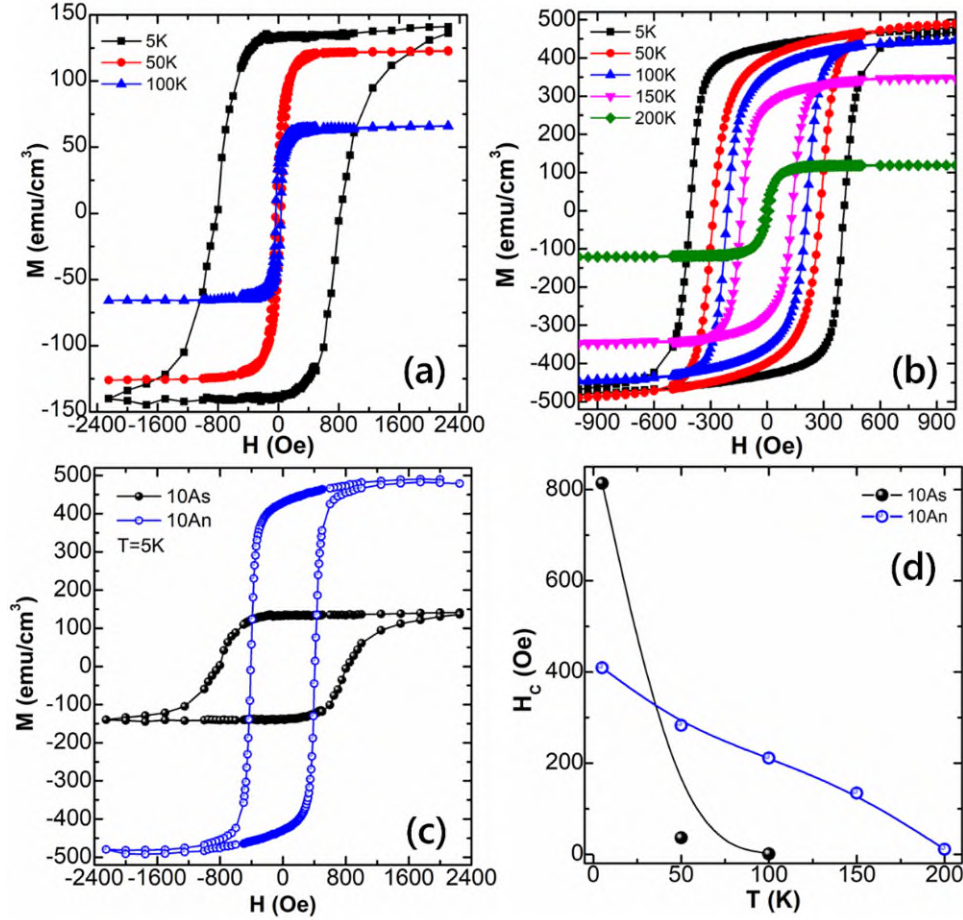


Figure 6: (a) M-H loop of the as-grown film measured at several temperatures $T < T_c$, (b) M-H loop of the annealed film measured at several temperatures $T < T_c$, (c) comparison of the M-H loops of the as-grown and annealed films measured at $T=4K$, and (d) temperature dependence of the coercivity of the two films.

The scaling of the coercivity in rare-earth manganites over a broad low-temperature to mid-temperature range is described by an equation of the type $H_c(T) = H_0 \left(1 - \frac{T}{T_0}\right)$, which represents weak domain wall pinning^{47,48,49,50,51}, where, $H_c(0)$ is the zero-temperature coercivity and an effective barrier temperature, $k_B T_0 \sim U_0$ where U_0 is the characteristic energy landscape resisting domain wall motion. A larger value of T_0 corresponds to a higher temperature regime up to which the domain wall pinning extends. The experimental data (symbols) and the best fit (solid line) to it using the strong pinning model are shown in Fig. SI-1a. The weak pinning model seems to describe the scaling of H_c with temperature and therefore underlines that the magnetization reversal is controlled by a motion of the domain walls through an assembly of shallow pinning centres, which are overcome due to thermal activation. The best fit yields

$H_0=404.086\pm16.083$ Oe and $T_0 = 209.128\pm8.764$ K. We further analyzed the H_C - T behavior of the annealed film within the framework of the strong domain wall pinning model given by $\sqrt{H_C}(T) = H_0 \left[1 - \left(\frac{T}{T_0} \right)^{2/3} \right]$.^{48,49} This mechanism is expected to dominate when the pinning centers are sparsely distributed. The corresponding fit is presented in Fig. SI-1(b). It is evident that the model provides a satisfactory description of the experimental data only up to $T \leq 150$ K, while substantial deviations emerge as the temperature approaches T_C . The fitting yields $H_0 = 436.845 \pm 7.432$ Oe and $T_0 = 260.128 \pm 6.025$ K. Notably, the extracted T_0 is anomalously large and even exceeds the T_C of the film, indicating that strong domain wall pinning is not the appropriate mechanism for describing the coercivity behavior of the oxygen-annealed HE manganite film. A H_C - T behaviour of the as-grown film could not be carried out because of the limited temperature range of the data. Even so, the comparatively larger H_C and the shape of the low-temperature hysteresis loop points to stronger pinning in the as-grown film.

The presence of oxygen vacancies is one factor responsible for lower magnetization and T_C as observed in the as-grown film. Another factor that could further ruin magnetic properties in the as-grown film is the high A-site disorder as quantified by a large variance $\sigma^2= 3.758 \times 10^{-3}$. Since the bond angle $\angle \text{Mn} - \text{O} - \text{Mn}$ and the Mn-O bond length will be different for the different cations in the high entropy compound, and therefore spatial fluctuations of bandwidth and double exchange are intrinsic to it. The presence of oxygen vacancies would further escalate the bandwidth and double exchange fluctuations. Such a scenario could also depress the T_C and lower the magnetization. The coexistence of FM regions with AFM/PM clusters can produce (i) irreversibility akin to a cluster-glass state, (ii) stronger domain-wall pinning at phase boundaries, and (iii) a broad ZFC maximum. An additional disorder that could reduce magnetization and the Curie temperature comes from the higher configurational entropy (ΔS_{defect}) in the as-prepared film with non-uniform oxygen concentration, and random cationic distribution. The oxygen annealing could reduce the configurational entropy associated with these disorders.

The oxygen annealing-induced enhancement in total magnetization and the Curie temperature can be understood in terms of the impact of oxygen stoichiometry on the Mn valence, bandwidth control, suppression of the Jahn-Teller effect, and mitigation of the

dead layer. For $\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$, charge neutrality gives the average Mn valence $V_{\text{Mn}} = 3.2 - 2\delta$. Oxygen deficiency $\delta > 0$ depresses the Mn^{4+} fraction and weakens DE; oxygen annealing, which makes $\delta \approx 0$, restores Mn^{4+} stoichiometry and therefore strengthens DE. The scaling of the DE strength with the e_g , the electron (itinerant) bandwidth is given by

$$W \sim \frac{\cos\phi}{d^{3.5}}$$

Here $\phi = \frac{\pi - \angle \text{Mn-O-Mn}}{2}$ and d is the Mn – O bond length. Filling up of the oxygen vacancies pushes the Mn–O–Mn angle closer to 180° and also shortens the Mn – O bond length. Oxygen vacancies favour the localization of the Mn^{3+} and yield strong JT distortions. Annealing in oxygen delocalizes the Mn^{3+} ions, which favours the DE mechanism and, consequently, the FM metallic phase. Oxygen annealing heals disorders and reduces the magnetically “dead” layer at the film/substrate interface, which is very common in manganite films. Damping of the dead layer effect can also contribute to the increase in magnetization, T_c enhancement, and enhanced metallicity. The squareness, defined by $S = \frac{M_r}{M_s} < 1$ suggests multi-domain reversal with pinning at structural and chemical inhomogeneities, e.g., the A-site disorder, oxygen-vacancy clusters, etc. Oxygen deficiency ($\delta > 0$) reduces the Mn^{4+} fraction, weakening DE and promoting localized Jahn–Jahn-Teller-distorted regions. The resulting phase coexistence scenario accounts for (i) incomplete saturation and (ii) enhanced H_c from pinning. Strain and defect landscapes in the as-grown film further stabilize this mixed state; oxygen annealing (discussed earlier) typically straightens Mn–O–Mn bonds and restores Mn^{4+} , increasing bandwidth and collapsing the high-field tail.

The M-H loop of the oxygen-annealed film displays a well-developed ferromagnetic response with a square inner core and a much weaker high-field tail than in the as-grown film. The rapid rise of M at low fields followed by a short approach-to-saturation interval indicates enhanced double-exchange connectivity and reduction of non-FM background after oxygenation. The coercive field is smaller and the remanent magnetization larger than in the as-grown state, yielding a higher squareness $S = \frac{M_r}{M_s}$. This points to fewer pinning centres (vacancies/defect clusters) and improved domain mobility. The features of the M-H loops of the as-grown film and the annealed film are consistent with

oxygenation-driven restoration of the Mn^{4+} valence to the optimal value, A-site cationic ordering, straightening of the Mn–O–Mn bonds (larger bandwidth), and healing of magnetic ‘dead’ regions.

The oxygen annealing-induced changes in the magnetization behaviour can be understood as follows. The enhancement of magnetization and the reduction in coercivity after oxygen annealing can be understood in terms of improved oxygen stoichiometry and the consequent strengthening of the $\text{Mn}^{3+}\text{--O--Mn}^{4+}$ double-exchange interaction. In the as-grown film, oxygen vacancies reduce the Mn^{4+} fraction, promote Jahn–Teller distorted Mn^{3+} -rich regions, and generate spatial fluctuations in bandwidth and magnetic exchange. These effects favour the coexistence of ferromagnetic regions with antiferromagnetic or paramagnetic clusters, thereby lowering the net magnetization and increasing domain-wall pinning. Oxygen annealing restores the Mn valence balance, improves Mn–O–Mn connectivity, increases the electronic bandwidth, and suppresses the non-ferromagnetic background. Consequently, the ferromagnetic volume fraction and spontaneous magnetization increase markedly. At the same time, the reduction of oxygen-vacancy-related defects, defect clusters, and magnetic phase boundaries decreases the number of effective pinning centres, allowing easier domain-wall motion and thereby reducing the coercive field.

Magnetotransport behaviour

As-grown film shows strong insulator characteristics (Fig. 7(a)), as shown by high room temperature resistivity ($0.235\ \Omega\text{-cm}$), a rapid rise in resistivity with decreasing temperature ($71.863\ \Omega\text{-cm}$ at 115 K), immeasurable resistivity at $T < 115\text{ K}$, and absence of any signature of metallic transition. Furthermore, a magnetic field as large as 80 kOe fails to induce an insulator-metal transition (IMT), and its only effect is to soften the insulating state, as confirmed by the reduction in the resistivity. The insulating state is robust, so much so that at 80 kOe magnetic field, despite a decrease by a factor of six (about 6 times decrease at 115 K), the resistivity remains immeasurable at $T < 79\text{ K}$ ($\sim 68\ \Omega\text{-cm}$). Oxygen annealing has a dramatic effect on the overall electrical transport behavior. The room temperature resistivity decreases by nearly two orders of magnitude ($\sim 0.0058\ \Omega\text{-cm}$) as compared to that of the as-grown film, and an IMT appears at $T_{\text{IM}} \approx 223\text{ K}$, below which the resistivity drops by nearly two orders of magnitude as the temperature lowers to 2 K. In

this case, the magnetic field causes (i) an overall drop in resistivity, (ii) a shift in the T_{IM} to higher values, being ≈ 291 K at 80 kOe, and (iii) a sharp drop in the peak resistivity ρ_{IMT} . The scaling of T_{IM} and the peak resistivity ρ_{IMT} with the magnetic field is plotted in the inset of Fig. 7(b). An interesting feature of the ρ - T behavior is the occurrence of a minimum and upturn around $T(\rho_{min}) \approx 13$ K. The applied magnetic field lowers the resistivity, but the nature of the upturn remains unchanged. In the present case, the strong A-site cationic disorder coupled with chemical inhomogeneity due to the random distribution of A-site cations can make the carrier transport diffusive in nature. The resistivity minimum and following upturn could be a consequence such as transport in the annealed film, and the possible mechanism has been discussed in the coming sections.

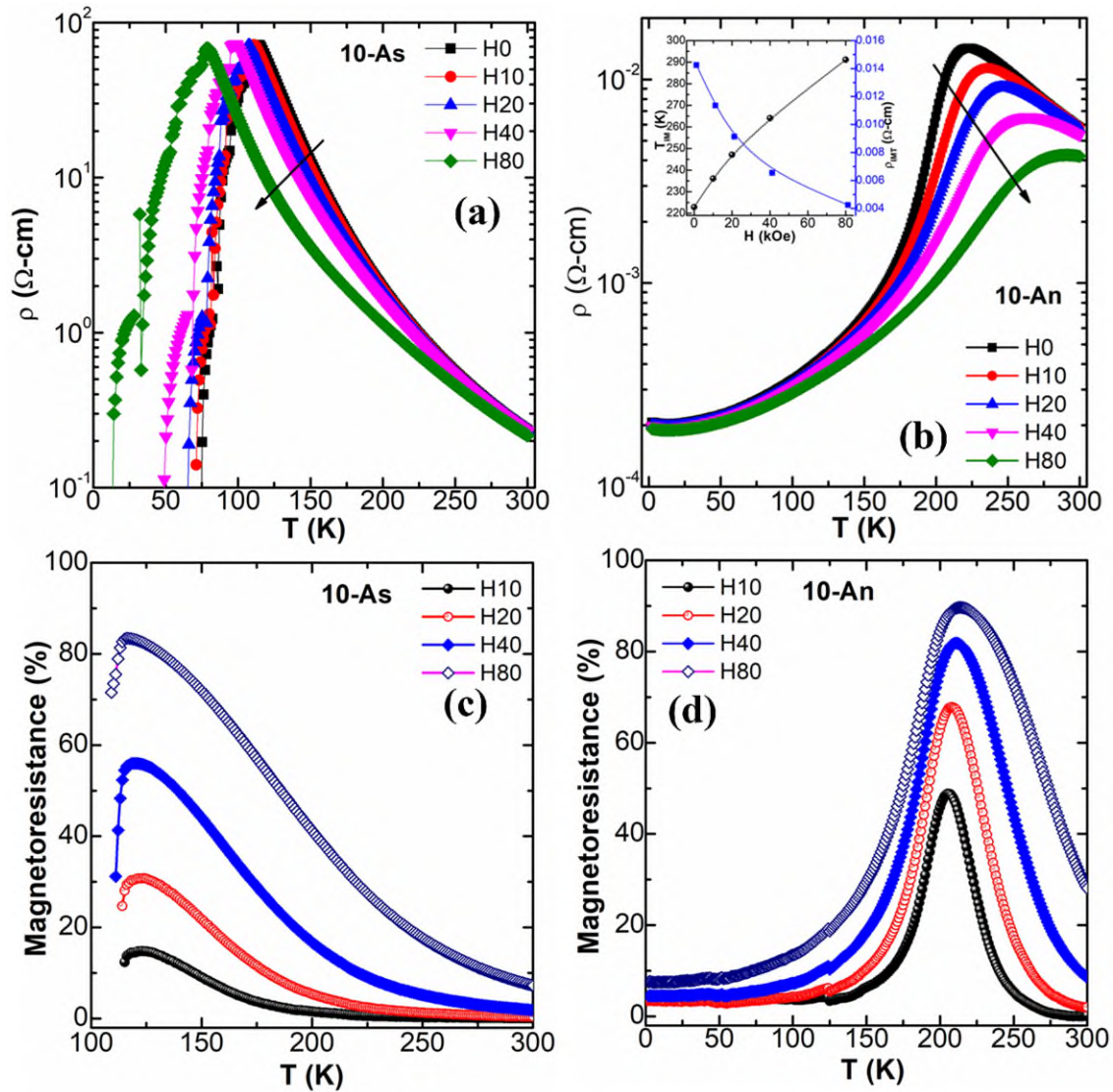


Figure 7: The temperature dependence of resistivity of the (a) as-grown films, (b) annealed film. The magnetoresistance versus temperature curves of the as-grown film (c) and the annealed film (d).

The temperature dependence of magnetoresistance (MR–T) for the as-grown (10As) and oxygen-annealed (10An) films, measured at several magnetic fields, is shown in Figs. 6(c) and 6(d). In the 10As film, MR is small at 300 K ($\approx 0.08\%$ at 10 kOe) and increases upon cooling and with field, reaching $\approx 15\%$ at 10 kOe near 123 K and peaking at $\approx 83\%$ at 80 kOe around 116 K, close to the PM–FM transition ($T_c \approx 120$ K), consistent with field-driven suppression of spin disorder in the paramagnetic state. By contrast, the 10An film exhibits markedly enhanced MR: at 300 K, MR $\approx 0.2\%$ at 10 kOe and $\approx 28\%$ at 80 kOe, and it grows on cooling to just below T_c , attaining $\approx 49\%$ at 10 kOe (206 K) and $\approx 90\%$ at 80 kOe (214 K). Below the peak, MR drops rapidly and becomes small at low temperatures ($\approx 8\%$ at 80 kOe). The MR–H data (Fig. SI-2) further underscore the superior performance of the annealed film: both its room-temperature MR and its peak MR exceed those of the as-grown film. MR is most pronounced near T_c , for example, at 200 K, MR $\approx 45\%$ at 10 kOe, and $\approx 84\%$ at 80 kOe (see Fig. SI-2).

Electrical transport mechanisms

The contrasting magnetotransport behaviors of the as-grown and annealed films motivate a detailed analysis of temperature-dependent resistivity under applied magnetic fields. In the low-temperature regime ($T \lesssim 80\text{--}116$ K), the resistivity of the as-grown film becomes immeasurably large, whereas the annealed film remains metallic and exhibits a low-T upturn below ≈ 13 K. We therefore analyze the ρ – T data of the oxygen annealed film first. In the low temperature region, the resistivity minimum followed by an upturn, which is only weakly affected by moderate to high magnetic fields, points to quantum corrections to the conductivity. In this situation, the applied field primarily suppresses spin disorder, lowering the overall resistivity without altering the characteristic shape of the low-T upturn. Other mechanisms that get manifested in the form of an upturn in the ρ – T curve, such as weak localization or the Kondo effect, are typically quenched by a magnetic field, which is not observed here. For a three-dimensional diffusive metal, the Altshuler–Aronov (AA)^{52,53} interaction correction reduces $\sigma(T)$ as T decreases, leading to an empirical resistivity form:

$$\rho(T) = \frac{1}{\sigma_0 + \sigma_1 T^{0.5}} + a_p T^p \quad (1)$$

where σ_0 is the temperature-independent (impurity) contribution to the conductivity, $\sigma_1 T^{0.5}$ encodes the AA interaction correction, with weak field sensitivity set by diffusive screening and dimensionality. The third term, $a_p T^p$ captures Fermi-liquid/quasiparticle (and low-T single-magnon) scattering. Zero-field data are best fit by this expression for $T < 63\text{K}$, while at finite fields, good fits extend up to $T < 70\text{K}$. The measured ρ - T curves and corresponding fits are shown in Fig. 8(a), and the field evolution of the three coefficients σ_0 , σ_1 and $a_p T^p$ are summarized in Fig. 8. The magnetic field scaling of the three coefficients yields a clear physical picture. Both σ_0 , and σ_1 exhibit a sharp increase at $H = 10\text{ kOe}$; beyond this, the former grows slowly and approximately linearly with H , while the latter tends toward a plateau. The initial jump in the residual conductivity σ_0 reflects the rapid suppression of spin disorder and domain-wall scattering at low to moderate fields, a hallmark of the transport in phase-separated manganites, where small H aligns FM clusters and collapses spin-flip channels. The slower increase of σ_0 for $H \gtrsim 20\text{kOe}$ indicates that most spin-disorder pathways are already quenched; higher fields can only weakly reduce long-wavelength magnons or residual barriers, yielding a modest conductivity gain.

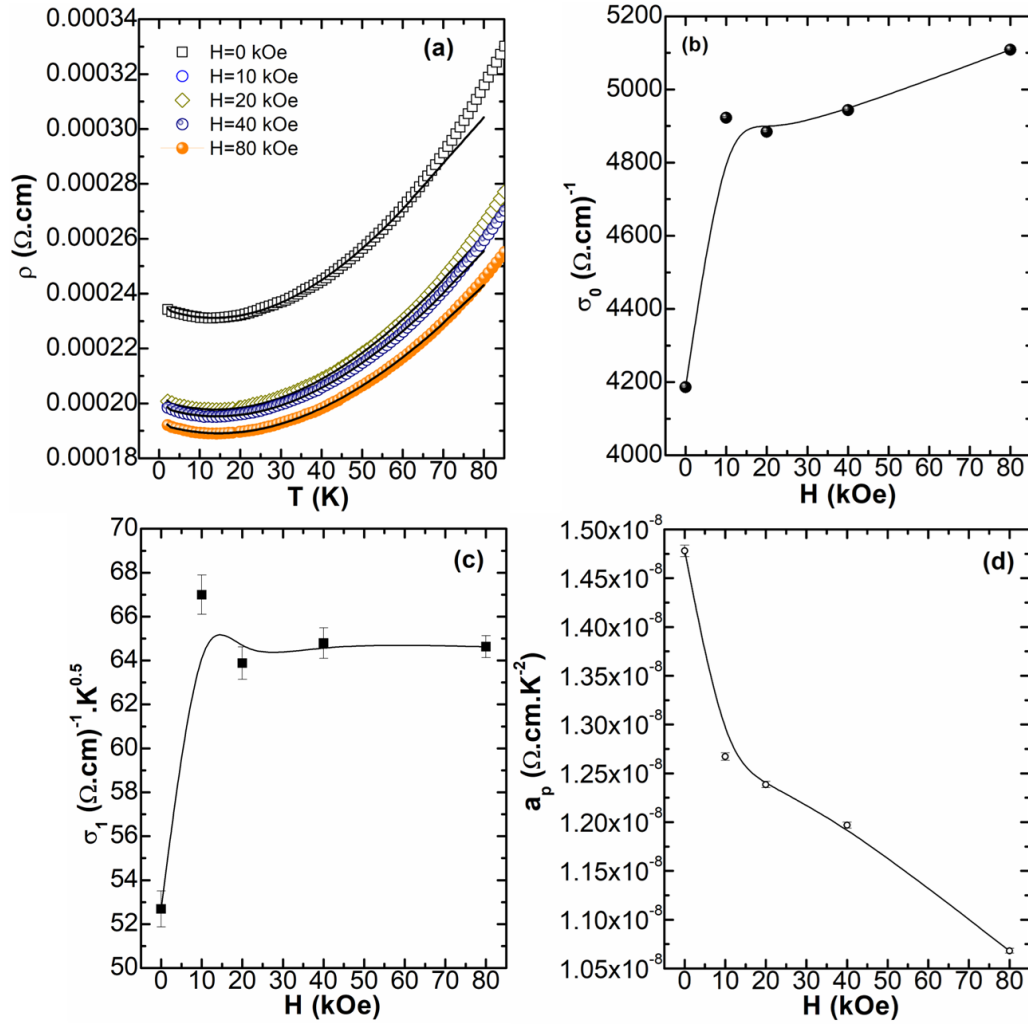


Figure 8: (a) The resistivity of the annealed film in the lower temperature region (symbols) and best fit to it (solid lines) using eq. (1). (b) variation of the residual conductivity with applied magnetic field. The magnetic field dependence of the coefficient σ_1 (c) and coefficient a_p (d).

The saturation-like behavior of σ_0 at high fields is also consistent with AA physics in the diffusive regime. As the magnetic length ℓ_B becomes comparable to (or shorter than) the phase-coherence length L_ϕ , the field efficiently cuts off the triplet interaction channel, producing a steep initial change in b. Once ℓ_B is sufficiently small (i.e., at $H \gtrsim 20$ kOe here), further increases in field no longer appreciably modify the interaction correction, resulting in the observed plateau of $\sigma_1(H)$ curve. Finally, the decrease of a_p with H [Fig.8(d)] is expected when the T^p channel contains a single-magnon component in a ferromagnetic metal. An applied field opens a Zeeman gap in the magnon spectrum, reducing the magnon population and thus the magnon-scattering contribution to resistivity; a purely Fermi-liquid T^2 term would be nearly field-insensitive. The reduction

of a_p with H , therefore, signals a small but tangible magnon (or spin-disorder) component in the low- T scattering of the annealed film.

We also analysed the $\rho - T$ data of the insulating regimes in both films in terms of the Mott variable range hopping transport^{54,55,56,57,58,59,60} given by

$$\rho(T) = \rho_0 \exp\left(\frac{T}{T_0}\right)^{\frac{1}{4}} \quad (2)$$

In Eq. (2), T_0 is the Mott parameter. Figure 9 shows the experimental resistivity data (symbols) and the corresponding fits to Eq. (2) (solid lines). For the as-grown film, T_0 is markedly larger than for the annealed film, and it decreases with increasing magnetic field. The fitted T_0 values were then used to calculate the localization length ξ and the average hopping distance R_h .

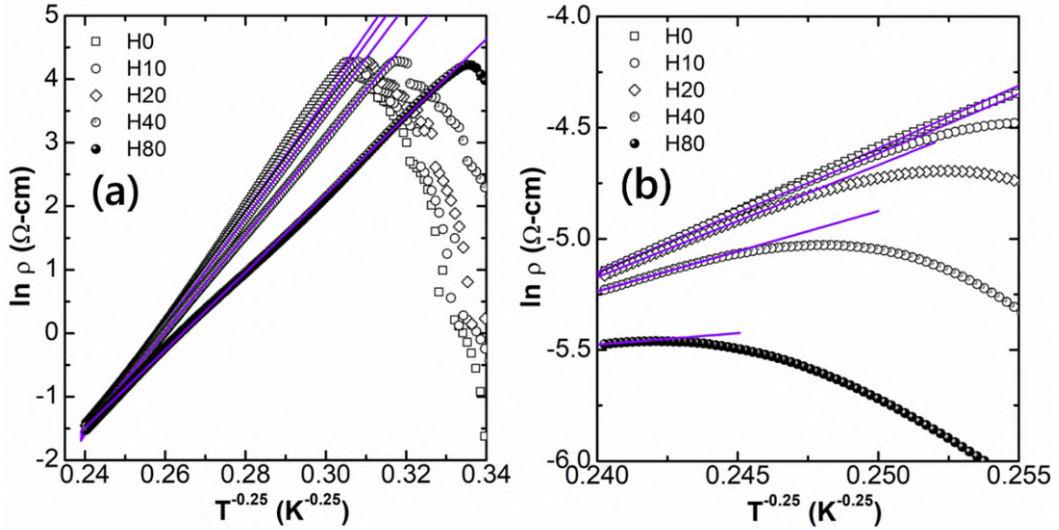


Figure 9: The $\ln \rho - T^{0.25}$ plots of the experimentally measured resistivity (symbols) and the best linear fit to it for the as-grown film (a) and annealed film (b).

Since the value of the parameter T_0 is a measure of the strength of the Jahn–Teller distortion and is inversely related to the extent of the localized states, the increasing value of T_0 suggests that increased lattice relaxation decreases the localization length, which in turn reduces the average hopping distance. We have evaluated the localization length (ξ) using the modified expression proposed by Viret et al.⁵⁷, who argued that in manganites with $\sim 30\%$ divalent substitution on the rare-earth site, carrier localization above T_C arises from a random magnetic potential generated by Hund’s-rule coupling $-J_H \mathbf{S}_i \cdot \mathbf{S}_j$ between localized Mn t_{2g} ion cores ($S = 3/2$) and spins of e_g electrons in the conduction band. The modified formula for localization length ξ in this model is given by

$$\xi = \left(\frac{171 U_m V}{k_B T_0} \right)^{1/3} \quad (3)$$

Here, $U_m = 3J_H/2$ is the splitting between the spin-up and spin-down e_g bands, and its value has been found from optical spectra to be 2 eV.^{57,58} V is the unit cell volume per Mn ion. Substituting the values of U_m and k_B , the above expression becomes

$$\xi = 158.294 \left(\frac{V}{T_0} \right)^{1/3} \quad (4)$$

At zero field, the fitted fourth-root values are $T_0^{1/4} = 90.356$ K (as-grown) and $T_0^{1/4} = 56.566$ K (annealed), corresponding to $T_0 = (90.356 \text{ K})^4$ and $T_0 = (56.566 \text{ K})^4$, respectively. Assuming a pseudocubic cell, the per-Mn unit-cell volume is estimated from the out-of-plane lattice parameter, which for the as-grown film is $a_{As} = 3.8359 \text{ \AA}$ and $a_{An} = 3.8543 \text{ \AA}$, yielding the respective lattice volumes to be $V_{As} = 56.442 \text{ \AA}^3$ and $V_{An} = 57.258 \text{ \AA}^3$, respectively. The mean nearest-neighbour hopping distance is

$$R_h = \frac{3}{8} \xi \left(\frac{T_0}{T} \right)^{1/4} \quad (5)$$

Physically, ξ is the spatial extent of the (polaronic) localized wavefunction; R_h is the average hopping length between localized sites. In manganites, polarons are frequently associated with the Mn ions, which have mixed valence states (Mn^{3+} and Mn^{4+}) and exhibit magnetic moments due to their partially filled d-orbitals. The magnetic nature of polarons stems from the coupling between the spin and the local magnetic moments of the Mn ions, often mediated by the double-exchange mechanism. This interaction aligns the spin of the carriers with the surrounding magnetic moments, making the polaron magnetically active. In the absence of a magnetic field, strong electron-phonon coupling in manganites creates small polarons with short localization lengths. Strong electron-phonon coupling and Jahn-Teller distortions favor small polarons at zero field. An applied field aligns Mn core spins, reducing the lattice distortion energy (Jahn-Teller effect) and weakening polaron binding. At high magnetic fields or in strongly ferromagnetic states, polarons may transition from small to large polarons, significantly extending the localization length. Magnetic field enhances the double-exchange interaction between Mn^{3+} and Mn^{4+} ions, and hence the transfer amplitude $t \sim \cos\left(\frac{\theta}{2}\right)$ and suppresses the random spin-dependent potential, thereby delocalizing carriers (larger ξ) and producing

negative MR. Oxygen vacancies act as traps and strengthen localization; oxygen annealing reduces such defects and strain-related disorder, broadens the effective e_g bandwidth, and facilitates polaron hopping, complementary to the spin-alignment route provided by the magnetic field. Like a magnetic field, oxygen annealing promotes polaron delocalization by reducing scattering and lattice distortions. However, while a magnetic field primarily acts through spin alignment, oxygen annealing modifies the lattice and electronic structure.

The localization length (ξ) and the hopping distance (R_h) increases with magnetic field in both films (Fig. 10(a), (b)), but the response is markedly stronger in the oxygen-annealed (An) film. In the as-grown sample, ξ grows only weakly, from 1.504 Å at zero field to 2.525 Å at 80 kOe, whereas the annealed film starts from a larger zero-field value (2.821 Å) and reaches 5.117 Å at $H=40$ kOe and then rises sharply to ≈ 27.24 Å at $H=80$ kOe. Given the 3D Mott-VRH relation $T_0 \propto [N(E_F) \xi^3]^{-1}$, the observed $\xi(H)$ indicates a strong field-induced reduction of T_0 in the annealed film, but only a modest change in the as-grown film. This trend is consistent with spin-disorder-controlled hopping in mixed-valence manganites; the applied field aligns Mn t_{2g} core spins, increases the double-exchange transfer amplitude $t \sim \cos\left(\frac{\theta}{2}\right)$, and suppresses the random spin-dependent potential, thereby delocalizing carriers (larger ξ) and producing negative magnetoresistance. Oxygen annealing further (i) reduces vacancies, (ii) lowers strain-driven static disorder, and (iii) enhances the effective e_g bandwidth, which together make the field-induced suppression of polaronic trapping more efficient and promote percolation of FM clusters. These effects yield the much larger and rapidly increasing $\xi(H)$ in the annealed film. The contrast between the two $\xi(H)$ curves thus quantifies better oxygen concentration due to annealing and points to spin-alignment-driven delocalization as the dominant mechanism governing the field dependence of the VRH parameters in these high-entropy manganite films.

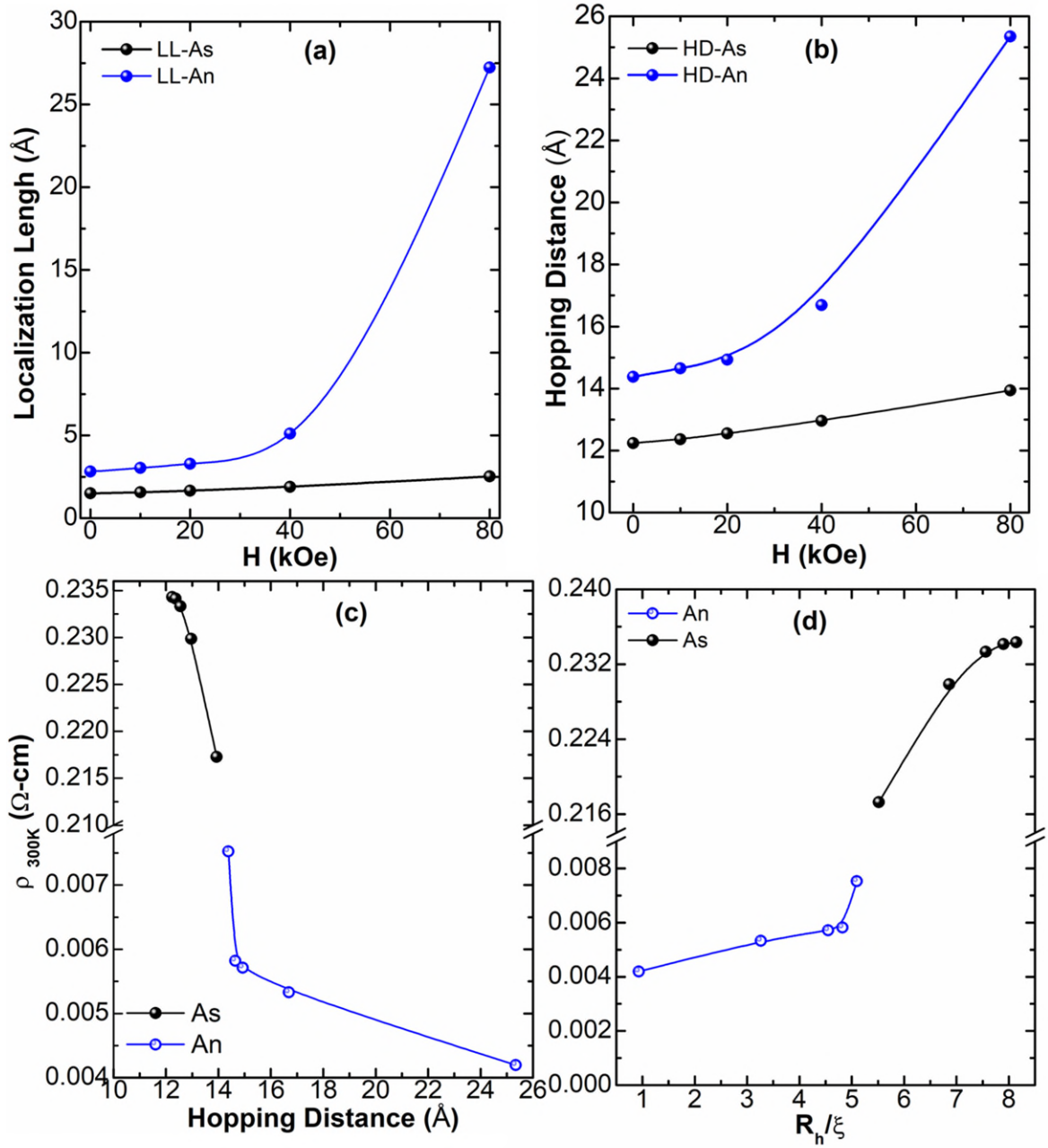


Figure 10: The magnetic field dependence of the (a) localization length and (b) hopping distance of the as-grown and annealed films. Fig. (c) shows the dependence of the room temperature resistivity on the hopping distance, while (d) shows the room temperature resistivity in terms of the ratio of the hopping distance and localization length R_h/ξ .

The hopping distance R_h evolves weakly in the as-grown film, increasing from $\approx 12.24 \text{ \AA}$ at $H=0$ to $\approx 13.96 \text{ \AA}$ at $H=80 \text{ kOe}$. By contrast, hopping distance in the annealed film shows a monotonic rise from $\approx 14.38 \text{ \AA}$ at $H=0$ to $\approx 14.93 \text{ \AA}$ at $H=40 \text{ kOe}$, followed by a sharp increase to $\approx 25.35 \text{ \AA}$ at $H=80 \text{ kOe}$. Using $R_h = \frac{3}{8}\xi\left(\frac{T_0}{T}\right)^{\frac{1}{4}}$ together with $T_0 \propto [N(E_F)\xi^3]^{-1}$ the pronounced field response in the annealed film indicates that the growth of ξ

dominates over the concomitant reduction of T_0 , enabling longer hops along better-aligned ferromagnetic pathways. At high fields, R_h in the annealed film approaches ξ ($R_h \gtrsim \xi$), signaling proximity to the VRH self-consistency boundary and an incipient crossover toward more extended/nearest-neighbor-like transport as spin disorder is quenched. In contrast, the as-grown film remains deep in the localized VRH regime over the entire field window. These trends are fully consistent with spin-alignment-assisted delocalization in mixed-valence manganites.

The variation of the room temperature resistivity with the hopping distance is shown in Fig. 10(c). In the as-grown film, ρ_{300K} decreases only weakly (from $\approx 2.34 \times 10^{-1} \Omega \cdot \text{cm}$ to $\approx 2.17 \times 10^{-1} \Omega \cdot \text{cm}$) as R_h grows from $\approx 12.24 \text{ \AA}$ to $\approx 13.94 \text{ \AA}$. By contrast, the annealed film shows a pronounced drop (from $\approx 6.8 \times 10^{-3} \Omega \cdot \text{cm}$ to $\approx 4.4 \times 10^{-3} \Omega \cdot \text{cm}$) when R_h jumps from $\approx 14.38 \text{ \AA}$ to $\approx 25.35 \text{ \AA}$. The observed decrease of ρ with increasing R_h , therefore, implies that the localization length ξ grows even faster than R_h under field (i.e., the ξ increase dominates over the accompanying reduction of T_0). This is borne out in Fig. 10(d), where plotting ρ versus R_h/ξ shows a clear downward shift. This lowering of the ratio R_h/ξ is consistent with spin-alignment-assisted delocalization in mixed-valence manganites. The as-grown film, dominated by stronger static disorder, shows only a modest decrease in R_h/ξ and accordingly, a small resistivity increase. The as-grown film, limited by stronger static disorder, shows only a modest decrease in R_h/ξ and, correspondingly, a small resistivity gain. The annealed film displays a much larger reduction in R_h/ξ , consistent with improved oxygen and cationic order, lattice strain mitigation, and a strengthened Mn–O–Mn network that amplifies field-induced delocalization. Notably, the ρ_{300K} – R_h curves for the two films approach one another, with an apparent crossover near $R_h \approx 13.94 \text{ \AA}$ marking the boundary between high- and low-resistivity transport regimes.

Conclusions

Oxygen annealing of epitaxial high-entropy $\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Sr}_{0.2}\text{MnO}_3$ thin film transforms the highly resistive and disordered magnetic state into a robust ferromagnetic metal: the Curie temperature increases from $T_C \approx 140 \text{ K}$ to $T_C \approx 225 \text{ K}$, spontaneous magnetization rises sharply, coercivity is reduced, and well-developed $M - H$ loops persist up to $T \sim 200 \text{ K}$. Magnetotransport evolves from a strong insulator in the as-grown

film into one that exhibits a canonical zero-field insulator-metal transition (IMT) at $T_{\text{IMT}} \approx 223$ K that shifts up to $T_{\text{IMT}} \approx 291$ K at an external magnetic field of $H = 80$ kOe. The room temperature and the peak MR are both much larger in the annealed film, with a significantly lower field MR $\sim 45\%$ at $H = 10$ kOe. The low temperature magnetotransport of the annealed film is metallic with an Altshuler–Aronov $\sigma \sim T^{1/2}$ correction plus a weak T^2 contribution, while the PM-insulating regimes of both films follow the 3D Mott-VRH mechanism. Oxygen annealing produces a pronounced field-driven increase in both the localization length and the hopping distance. Structural and AFM analyses suggest that oxygen annealing mitigates cationic and oxygen disorder while promoting defect homogenization, which likely straightens the Mn–O–Mn bonds and thereby enhances the electronic bandwidth. Oxygenation also appears to suppress dead-layer and pinning effects, consistent with the weak domain-wall pinning observed in the annealed state. These results demonstrate that cationic and oxygen disorder are crucial parameters for reducing disorder, engineering bandwidth, enabling the percolation of ferromagnetic pathways, and rejuvenating magnetotransport in high-entropy manganite thin films.

Authors Contribution

Km. Alka: Conceptualization, Methodology, Data Acquisition, Investigation, Formal Analysis, Writing Original Draft

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