ELECTRONIC SUPPLEMETARY INFORMATION:

Chemical synthesis of oriented ferromagnetic LaSr-2x4 manganese oxide molecular sieve nanowires

Details on the growth methodology, structural and magnetic characterization, and evolution with growth time of the LaSr-2×4 ferromagnetic nanowires.

GROWTH DETAILS:

(001)-oriented $Ce_{1-x}Gd_xO_{2-y}$ (CGO) buffer thin films (thickness ~ 20 nm) were grown on top of (001)-Yttria stabilized ZrO_2 (YSZ) substrates by chemical solution deposition (CSD).[1] Supported nanoporous polycarbonate (PC) films were produced following a track-etching method, which consists of an etching of heavy ion tracks to create the pores, as described in Ref. 2. Pore diameter was designed to be 100±10 nm, with a pore density optimized at 1×10^8 cm^{-2} and a PC porous layer between 1 and 2 μm thick. The supported nanoporous templates were filled by capillarity force using a sol-gel based polymer precursor solution of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and the specimens were heated in a furnace at temperatures 700 - 1000 °C for 30 min to 10 hours in a pure oxygen atmosphere.

The LSMO precursor solution was prepared using high purity (>99.99%) metal salts $La(NO_3)_3•6H_2O$, $Sr(NO_3)_2•4H_2O$ and $Mn(NO_3)_2•4H_2O$. Water used in the solution preparation was purified using the Milli-Q water treatment system. An aqueous solution of nitrates of lanthanum, manganese and strontium in their stoichiometric ratio was prepared, ethylene glycol was added with continuous stirring, and the whole solution was heated on a hot plate whose temperature was increased gradually to 150 °C. In this way, the polymerized ethylene glycol assists in forming a close network of cations and helps the reaction enabling the phase formation at low temperatures. The concentration

of the final solution was adjusted to 0.9 M in Mn and the viscosity values to η = 30 mPas. The chemical composition of the final solution has been investigated by inductively coupled plasma-atomic emission spectroscopy analysis on a Thermo Elemental Intrepid II XLS (Franklyn, MA, USA) spectrometer.

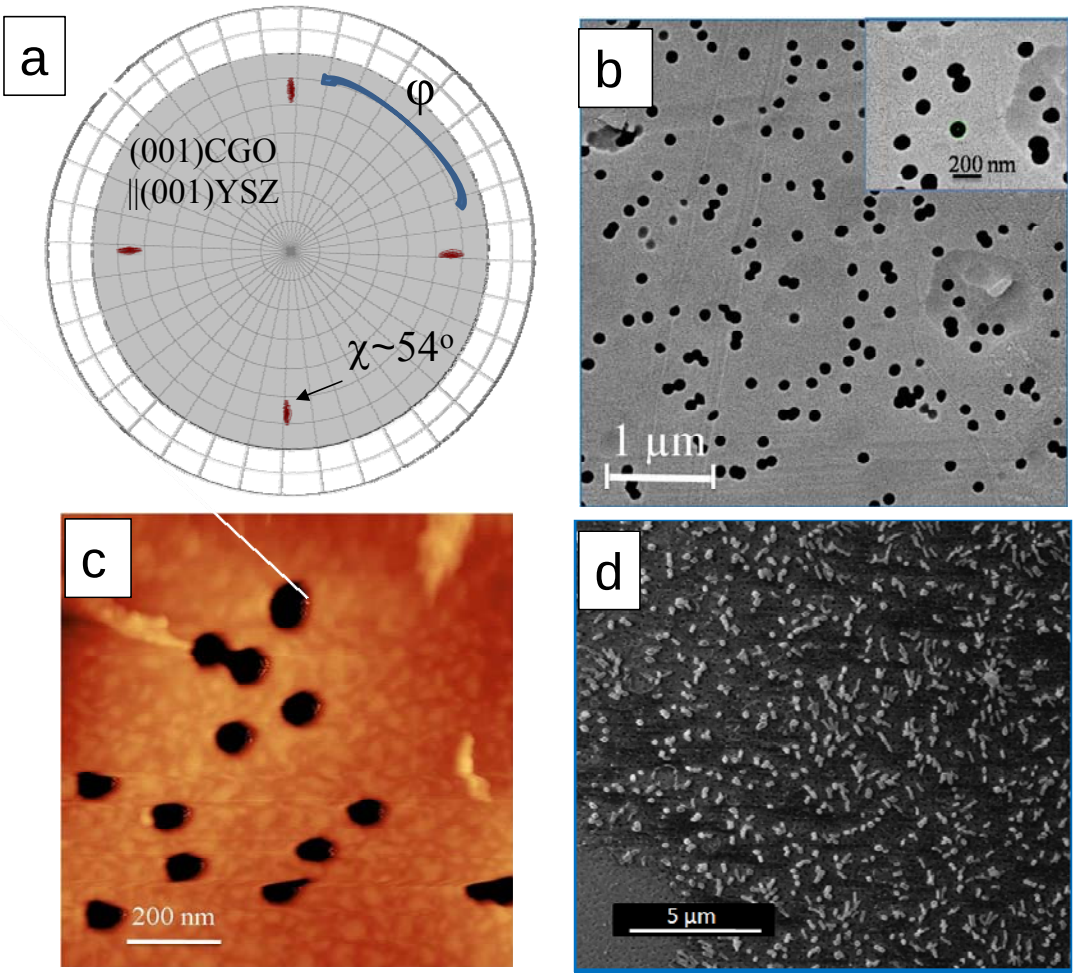

Figure S1. (a) Pole figure of a CGO thin film grown on a (001)-YSZ substrate, the poles observed at χ=54º correspond to CGO cube on cube orientation (001)CGO[100]//(001)YSZ[100]. (b) FESEM image of a polycarbonate nanoporous membrane deposited on (001)-oriented CGO/(001)-YSZ single crystal substrate (c) AFM image of the polycarbonate nanoporous membrane. (d) Top view of vertical nanorods grown at 500ºC standing on the CGO substrate with diameters of ~100 nm and lengths of ~1.0 µm. The size and density of the nanorods coincide with the original pore size and density in the polymer template

STRUCTURAL CHARACTERIZATION

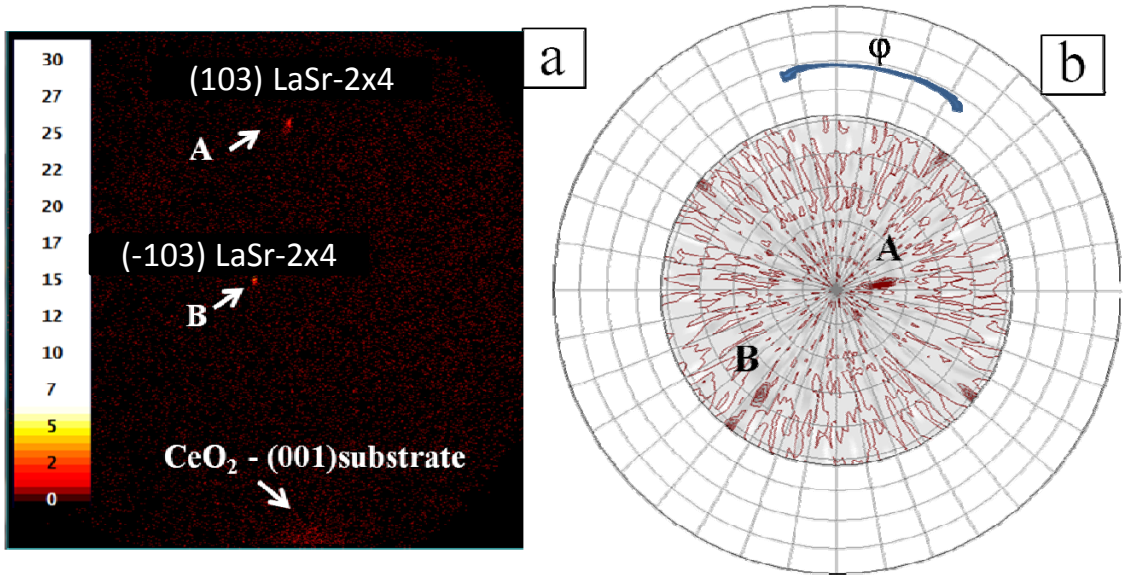

Figure S2. (a) XRD2 pattern showing the reflections (-103) LaSr-2x4 and (001)-CGO of a LaSr-2x4/CGO nanowires sample grown at 1000º C. (b) Pole figure of the same nanostructured system, where peaks observed at χ=12.6º (A) and χ=40º (B) correspond to LaSr-2x4 nanowires oriented (001) LSMO [010]// (001) CGO [1-10]. The four peaks at χ=54º correspond to the (001)-CGO substrate.

$2\theta_{exp}$	$2\theta_{theo}$	hkl	χ_{exp}	χ_{theo}
26.8º	26.8º	(-103)	40º	40.12º
26.8º	26.8º	(103)	12.68º	12.22º
33.9º	33.8º	(-12-1)	84º	83.14º
28.5º	28.4º	(21-3)	55.25º	53.5º
35.5º	35.8º	(12-3)	65.75º	67.26º
34.7º	34.2º	(1-10)	85.76º	87.52º
33º	33º	(-22-1)	85º	85.12º
40.6º	40º	(3-2-1)	80º	80.40º

Table S1. Experimental and simulated 2θ and χ values of poles figures (using the Carine software, Ref. 3) with the corresponding reflections of the monoclinic LaSr-2x4 phase.

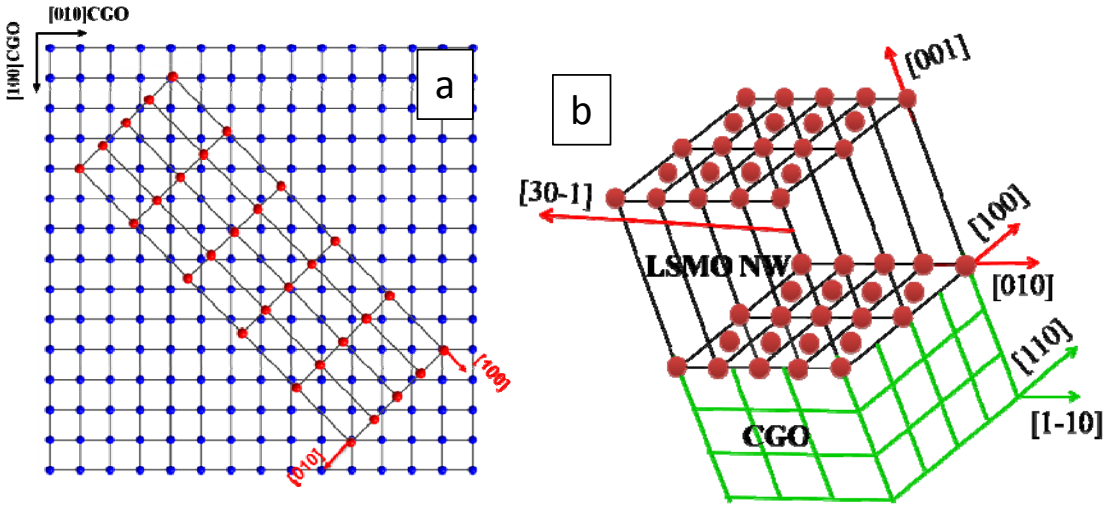

Figure S3. (a) Solid sphere model displaying a planar-view of the compatibility of the epitaxial growth of LaSr-2x4 on (001)-CGO, considering the domain match epitaxy (DME) scheme. Blue spheres correspond to the (001)-fluorite substrate and red spheres correspond to the LaSr-2x4 structure. Good residual misfit εr = 0.74% is achieved along both directions LSMO[010]//CGO[110] and LSMO[100]//CGO[1-10]. (b) 3D solid spheres model that shows the relative orientation of the LSMO nanowire and CGO substrate according to the epitaxial arrangement LSMO[010]||CGO[1-10] along de [30-1] zone axis.

For the epitaxial growth along the [100]LSMO||[110]CGO and [010]LSMO||[1-10]CGO directions, the nominal crystalline mismatch determined from the comparison of lattice parameters ($\sqrt{2}a_{CGO}$=7.65 Å and the monoclinic LaSr-2×4 *ab* lattice plane with a_{LaSr}-2×4 = 13.87 Å, and $b_{LaSr\text{-}2\times4}$ =5.78 Å [2]) would be huge, ε ~ 81% and ε ~ -24% respectively. No coherent growth would be possible under such large strain. This fact suggests that the LSMO nanowires may grow on top of the LSMO substrate following the domain matching epitaxy (DME) scheme,[4] which assumes that the nanowires are accommodated through the formation of domains with integral multiples of lattice planes separated by one regularly separated misfit dislocation. The compatibility of the crystal structure of monoclinic LSMO with (001) plane of CGO can easily be shown by the drawing of Fig. S3(a), were we plotted the solid sphere model of the (001) plane of the CGO fluorite lattice and the monoclinic LaSr-2×4 *ab*-lattice plane. According to the

DME scheme, for the longitudinal nanowire axis [010]LSMO||[1-10]CGO, 4 LSMO cells fit well with 3 fluorite cells of the substrate, whereas for [100]LSMO||[110]CGO direction 5 LSMO cells match well with 9 CGO cells. With this configuration, the calculated residual mismatch between the nanowire and substrate along the [100] and [010] wire planes will be $(5a_{LSMO}-9\sqrt{2}\ a_{CGO})/9\sqrt{2}a_{CGO}$ = 0.74% and $(4b_{LSMO}-3\sqrt{2}\ a_{CGO})/3\sqrt{2}\ a_{CGO}$ = 0.74%, respectively. Therefore, the DME model predicts the same residual misfit in both directions.

We infer that the large intrinsic anisotropy of the monoclinic LaSr-2x4 structure, is what promotes the 1D growth along the Nws [010] direction (the direction of smallest interplanar distance). This fact combined with the low isotropic residual misfit along the <110> CGO directions permitted the self-assembly of LSMO nanowires along these directions.

Figure S3(b) shows 3D solid spheres model of a LaSr-2×4 NW with the epitaxial relation LSMO[010]//CGO[1-10] viewed along the [30-1]-zone axis. Notice that the LSMO nanowire in the ADF images was tilted 36° with respect to the [100] zone axis, i.e. [30-1] ∧ [100]+(βLSMO-90°). Due to this particular sample orientation, the CGO substrate was not oriented in the ADF image.

EVOLUTION WITH GROWTH TIME

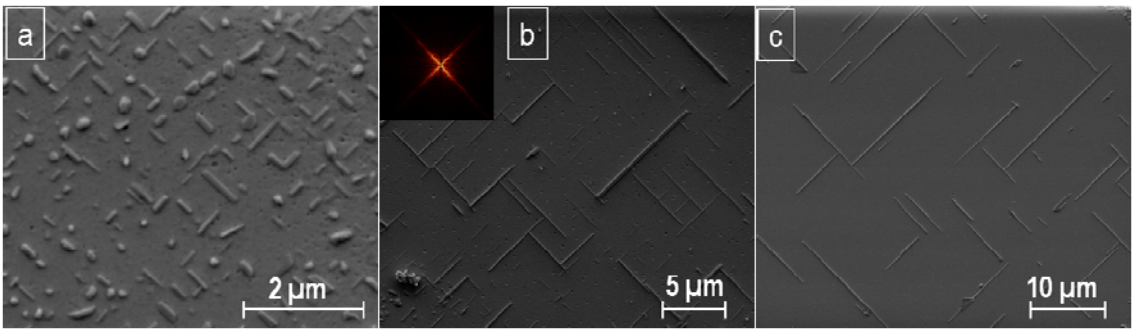

Figure S4. FESEM images showing the temporal evolution of the formed LaSr-2x4 nanowires after a thermal treatment at 1000 °C during (a) 1 hour (b) 5 hours (c) 10 hours, in oxygen atmosphere and its preferential growth directions with longitudinal axis parallel to the [110] and [-110] directions of the (001)-CGO substrate. Inset in figure 3(b) shows the 2D fast Fourier transform (FFT), where the two lines indicate the preferential orientation of the nanowires along two specific perpendicular directions.

ELECTRON MAGNETIC CIRCULAR DICHROISM (EMCD) OBSERVATIONS:

The detection of circular dichroism in the TEM is well described in the literature,[5] and consist basically of detecting the EEL spectra in the diffraction plane, and selecting the scattering angles such that $\boldsymbol{q} \perp \boldsymbol{q}'$. Two spectra are acquired by effectively placing the aperture in two different conjugate positions in the nanodiffraction pattern, position (+) and position (-), as depicted in Fig. S5(b).The difference in manganese $L_{2,3}$ edges coming from conjugated spots in the nanodiffraction diagram, which are equivalent to the two beam polarizations used in XMCD measurements, is proportional to the local magnetization magnetic moment and is shown in the manuscript's figure 3(d).

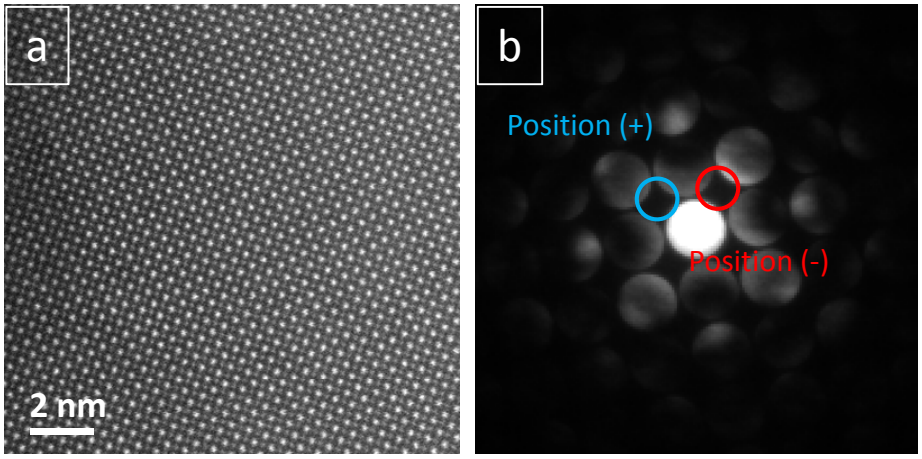

Figure S5, EMCD experiments. (a) region where the two spectra were acquired. (b) Shows the nanodiffraction pattern of this region and the positions (+) and (-) from where the spectra were extracted.

We have to say that, due to experimental constrictions, the configuration used in this paper and in Ref. 5 are not identical: we considered a manganite nanowire epitaxially grown onto a substrate oriented in the [010] zone axis, whereas a two-beam configuration was used in ref. 5. Yet, Calmels and Rusz have shown in recent papers (see Ref. 6), for the case of magnetite layers oriented in the [001] zone axis, that one can also detect dichroic signals in different orientations. $L_{2,3}$ ratios were obtained using the so called 2nd derivative method,[7] and generated with the Digital Micrograph software. It consists in first calculating the 2nd derivative of the raw spectra, and then using the maximum of the corresponding 2nd derivatives of the L_3 and L_2 peaks to obtain the $L_{2,3}$ ratio.

REFERENCES

1 M. Coll, J. Gázquez, F. Sandiumenge, T. Puig, X. Obradors, J. P. Espinós, R. Hühne, *Nanotechnology* 2008, **19**, 395601.

2 A. Carretero-Genevrier, J. Gázquez, J. C. Idrobo, J. Oró, J. Arbiol, M. Varela, E. Ferain, J. Rodríguez-Carvajal, T. Puig, N. Mestres, X. Obradors, *J. Am. Chem. Soc.* 2011, **133**, 4053.

3 http://carine.crystallography.pagespro-orange.fr/

4 J. Narayan, B. C. Larson, J. of Appl. Phys. 2003, **93**, 278.

5 P. Schattschneider, S. Rubino, C. Hebert, J. Rusz, J. Kunes, P. Novák, E. Carlino, M. Fabrizioli, G. Panaccione, G. Rossi, *Nature* 2006, **441**, 486.

6 L. Calmels, J. Rusz, *J. Appl. Phys.* 2011, **109**, 07D328.

7 G. A. Botton, C. C. Appel, A. Horsewell, W.H. Stobbs, *Journal of Microscopy* 1995, **180**, 211.