Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information:

Enhanced ferroelectricity in $NaNbO_3$-$LaCoO_3$:Mn epitaxial thin film

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Contents

Experimental section:

Target preparation and thin film growth:

Na_2CO_3, Nb_2O_5, and MnO_2 powders were mixed to prepare $NaNb_{0.95}Mn_{0.05}O_3$ ceramic. Na_2CO_3 and Nb_2O_5 powders were mixed to prepare $NaNbO_3$ ceramic. Then calcined these powders at 850℃ for 3h. Next, the powders were pressed into 60 mm diameter disk at 30MPa using polyvinyl alcohol (PVA) as the binder and sintered at 750°C for 2 h. For the $LaCoO_3$ target, La_2O_3 and Co_3O_4 were mixed and calcined at 1200℃ for 10h. Then these powders were also pressed into 60 mm diameter disk at 30MPa using PVA and sintered at 1000°C for 3 h.

The epitaxial thin film was deposited by RF sputtering on (001) $LaAlO_3$ substrates at 600℃. The pressure is 1.5 Pa with Ar and O_2. By controlling the sputtering power, we can get thin films with different La and Co contents. And the optimal power is 12W of $LaCoO_3$ target and 112W of $NaNbO_3$:Mn target. Before the deposition of the NNO thin film, a buffer layer of $SrRuO_3$ (SRO) was first sputtered at 680℃ as the bottom electrode. And the pressure is also 1.5 Pa with Ar and O_2. Mask with 100μm holes was used to deposited Pt top electrode.

Characterization:

The *θ-2θ* X-ray diffraction (XRD) at room temperature, phi scan, and reciprocal space mapping (RSM) were collected at the diffuse X-ray scattering station of the Beijing Synchrotron Radiation Facility (1W1A beamline). The high temperature XRD was measured by a powder diffractometer (X'Pert(III), PANalytical, λ = 1.5406 Å). The rocking curve was collected by a single crystal diffractometer (Bruker AXS GmbH).

The ferroelectric *P-E* hysteresis loops, *I-V* loops, *J-V* curves, and fatigue tests were measured using a ferroelectric tester (TF-Analyzer 1000, aixACCT, Germany). The dielectric constant as a function of temperature was collected by an impedance analyzer (4294, Hewlett Packard) connected with a high temperature probe system (HFS600E-PB2, Linkam, UK).

The X-ray absorption spectra were measured at the photoelectron spectroscopy

station of the Beijing Synchrotron Radiation Facility (4B9B beamline). The X-ray photoelectron spectroscopy (XPS) were collected using a spectroscopy spectrometer (Thermo ESCALAB 250XI).

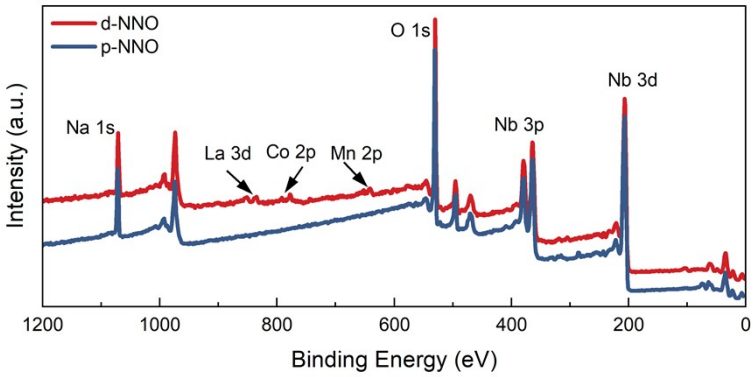

Fig.S1 XPS of the p-NNO and d-NNO thin films with all the major peaks indicated.

Compared with the p-NNO, the peaks appeared at 641 and 652, 780 and 792, 836 and 850 eV in the d-NNO thin film are ascribed to the Mn 2p, Co 2p and La 3d[1,2,3], proving the presence of these elements in d-NNO thin film.

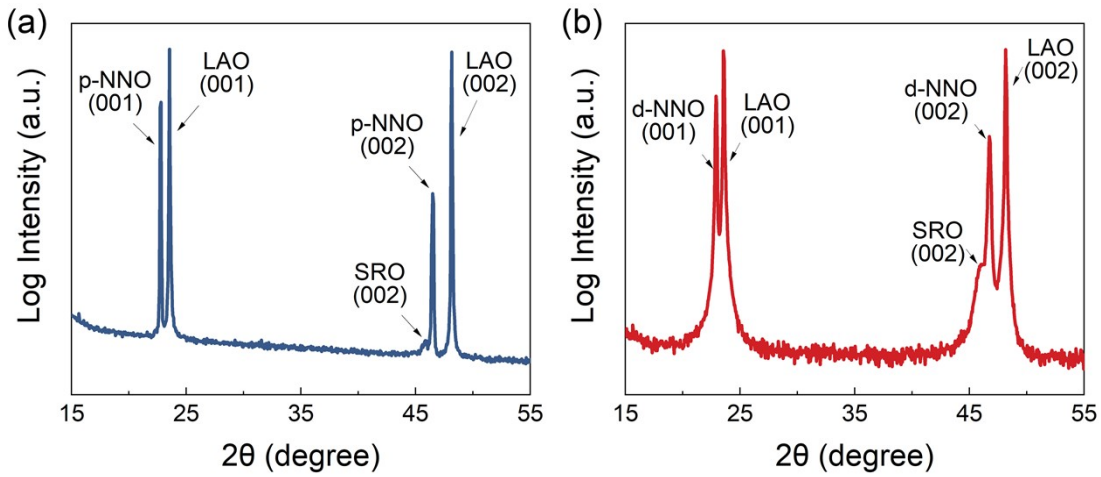

Fig.S2 Out-of-plane XRD patterns of the p-NNO (a) and d-NNO (b) thin films.

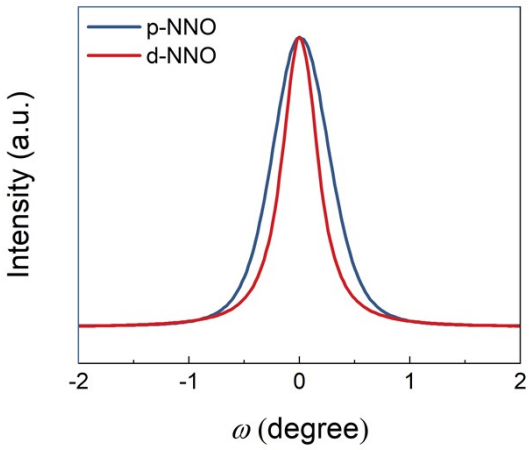

Fig.S3 Rocking curves of p-NNO and d-NNO thin films.

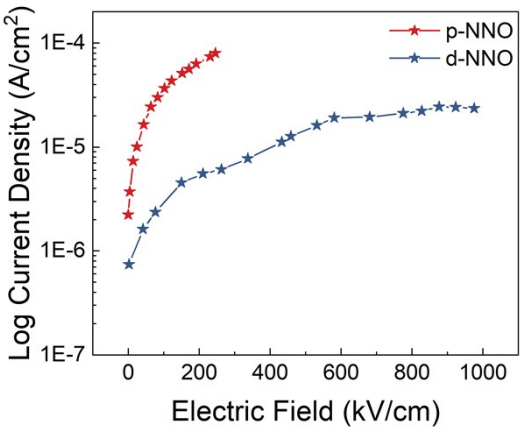

Fig.S4 Leakage current density as a function of electric field for p-NNO and d-NNO thin films.

References:

1 M. S. J. Marshall, D. T. Newell, D. J. Payne, R. G. Egdell and M. R. Castell, Atomic and electronic surface structures of dopants in oxides: STM and XPS of Nb- and La-doped $SrTiO_3$(001), *Phys. Rev. B*, 2011, **83**, 035410.

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