Supplementary Information

$KNbO_3$-based multiferroic heterostructures: a lead-free alternative for strain driven magnetic modulations

Hemanita Sharma[a,b], Deepak Dagur[b,†], Federico Motti[b], Aleksandr Yu. Petrov[b], Prajna Bhatt[b], Luca Sbuelz[b], Gian Marco Pierantozzi[b], Riccardo Cucini[b], Giorgio Rossi[b,d], Piero Torelli[b] and Giovanni Vinai[*b]

a. Department of Physics, University of Trieste, Piazzale Europa, 1, Trieste 34127, Italy.

b. CNR - Istituto Officina dei Materiali (IOM), Unità di Trieste, Strada Statale 14, km 163.5, 34149 Basovizza (TS), Italy

c. Department of Physics, University of Milan, Via Celoria 16, Milan I-20133, Italy.

†Current address: ALBA Synchrotron, Carrer de la Llum, 2-26, 08290 Cerdanyola del Vallès, Barcelona, Spain.

*vinai@iom.cnr.it

Experimental details for XAS measurement:

X-ray absorption spectroscopy (XAS) measurements were performed at APE-HE beamline of the NFFA facility at Elettra Sincrotrone Trieste[1]. The spectra were acquired at room temperature using the total electron yield (TEY) mode, where the sample current was normalized to the incident photon flux at each photon energy. During the measurements, the sample surface was oriented at an angle of 45° relative to the incoming X-ray beam, resulting in an illuminated beam footprint of approximately 200 µm on the sample surface.

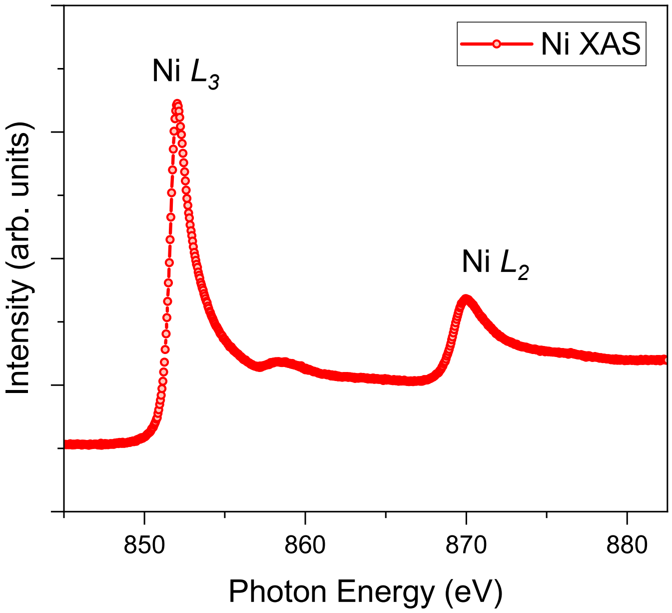

Figure S1: X-ray absorption spectroscopy (XAS) scan at Ni $L_{2,3}$ edges of KNO/Ni heterostructure.

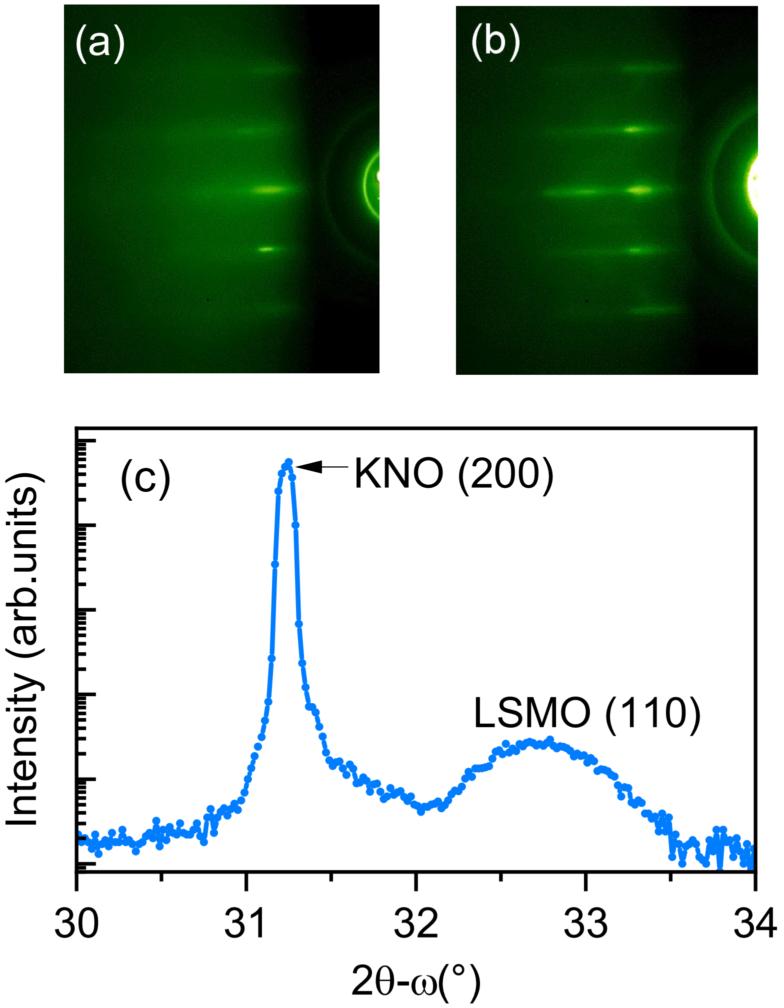

Figure S2: RHEED images acquired *in situ:* (a) before deposition (b) after deposition of 40-unit cells of LSMO at RT; (c) 2θ-ω scan of the KNO/LSMO heterostructure, acquired at room temperature

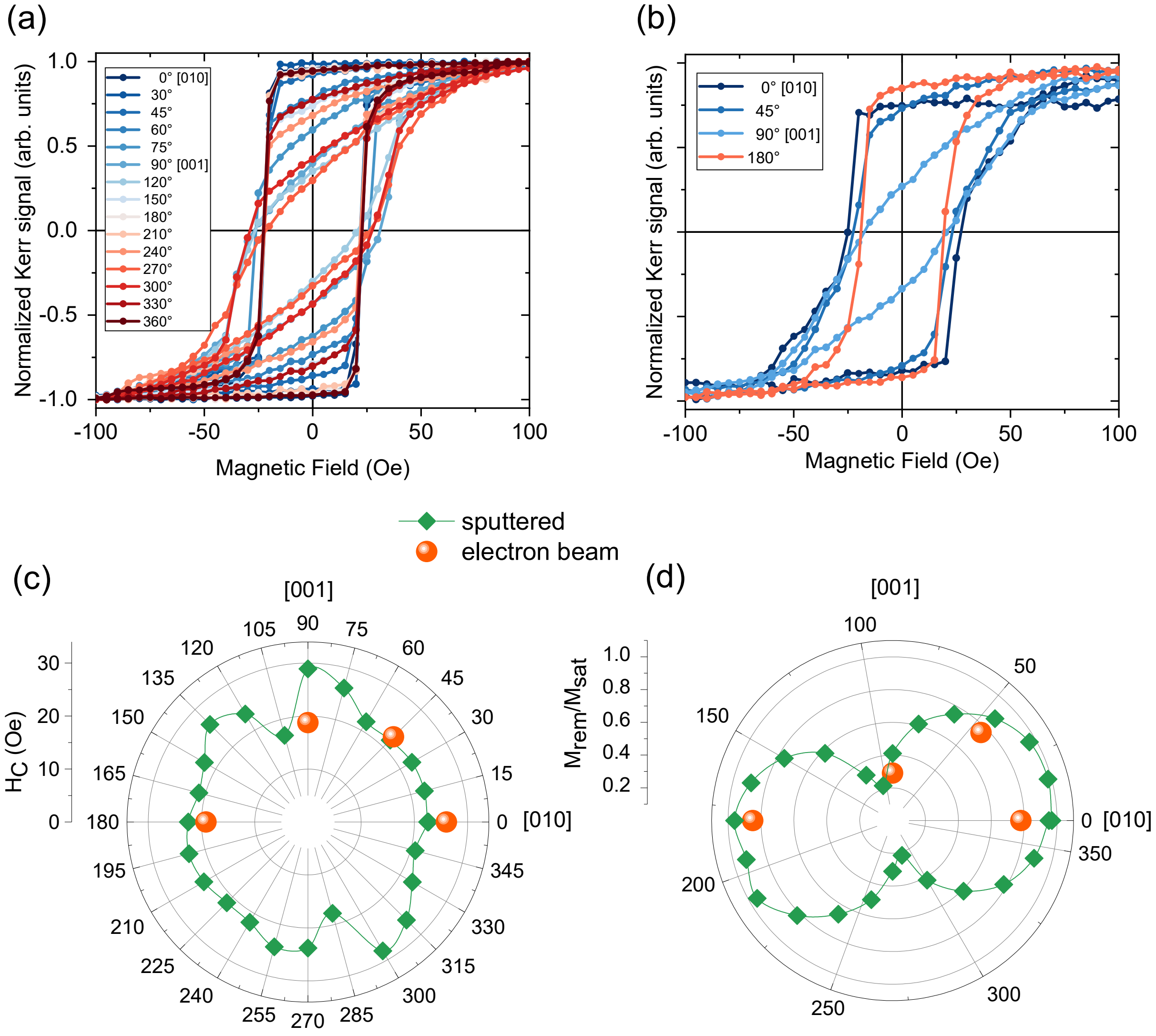

Figure S3: Angular dependent room temperature MOKE measurements of KNO/Ni heterostructure (a) by using sputtering, capped by Al, (b) by electron beam evaporation at MBE Cluster, capped by MgO. Polar plots showing angular dependence of (c) coercive field (H_C) and (d) remanence (M_{rem}/M_{sat}) in the above cases.

Experimental detail for photocurrent measurements:

Wavelength dependent photocurrent measurements were performed by using an ORPHEUS collinear Optical Parametric Amplifier (OPA) tool manufactured by Light Conversion company. The setup configuration is equivalent to the one reported elsewhere.[2] Photocurrent values were recorded using a Keithley 6485 picoammeter/voltage source, both in absence and presence of laser illumination. Finally, a 405 nm wavelength continuous laser source with variable power (0–800 mW cm^{-2}) from RGB Laser systems was used for photocurrent measurements.

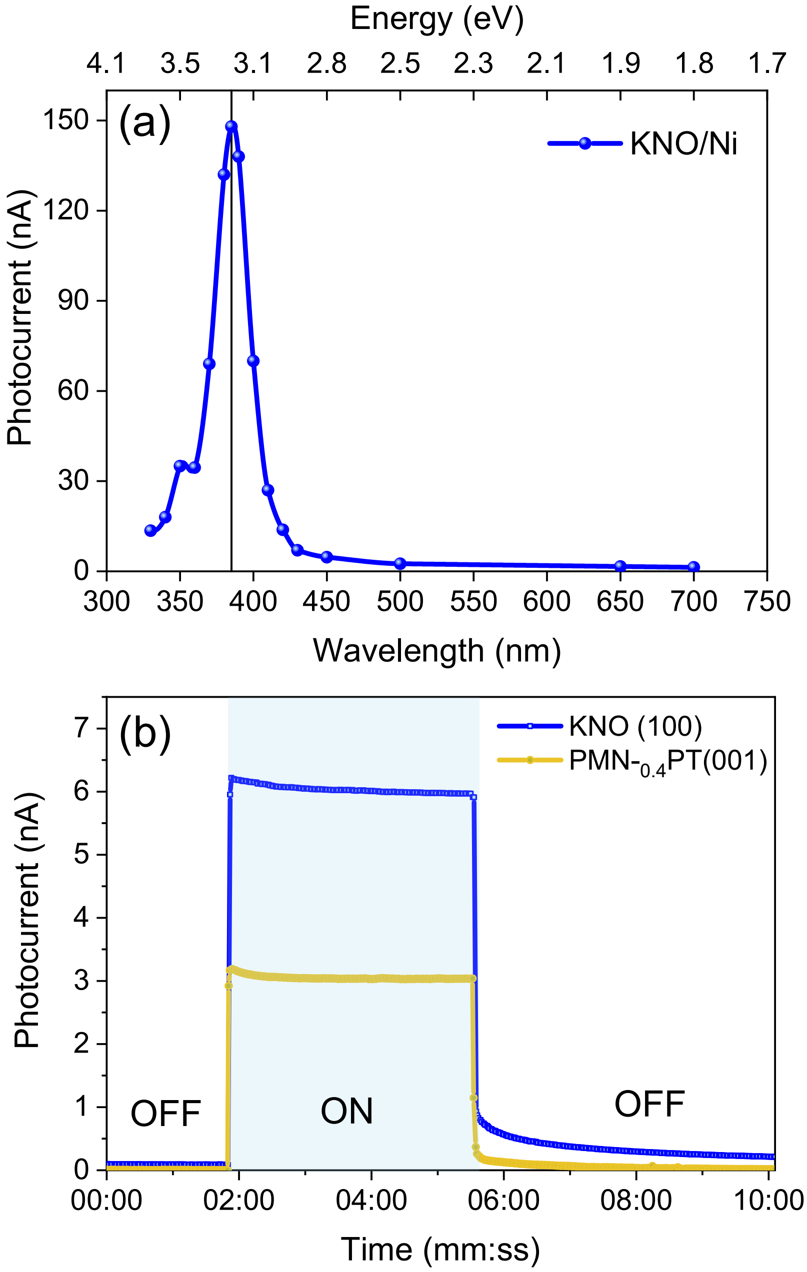

Figure S4: (a) Wavelength dependent photocurrent measurements and corresponding photon energies; (b) Photocurrent measured as a function of time comparing KNO (100) and PMN-$_{0.4}$PT (001) responses under 405 nm continuous laser illumination at 800 mW cm^{-2} power.

KNO single crystals are known to exhibit a pronounced photovoltaic response associated with bulk photovoltaic mechanisms arising from broken inversion symmetry,[3] wavelength-dependent photocurrent measurements were performed on KNO/Ni using an optical parametric amplifier (OPA) setup. A clear photocurrent was detected in the near-UV–visible range, with a maximum at ~385 nm (Fig. S4 (a)), in good correspondence with the bandgap of KNO (~3.2 – 3.4 eV).[3-5] Based on this result, the KNO/Ni heterostructure was subsequently illuminated with a constant wavelength of 405 nm, *i.e.* close to the spectral maximum, at an intensity of 800 mW cm^{-2} (Fig. S4 (b)). Upon illumination, a stable photocurrent of ~6 nA emerged immediately and disappeared almost completely when the laser was switched off, indicating a robust and reversible photo-response. Compared with an equivalent PMN-$_{0.4}$PT-based heterostructure in pristine (non-polarized) state, the photocurrent in KNO/Ni is significantly larger, demonstrating efficient photocarrier generation.[5-6] This is consistent with the high photovoltaic currents reported in literature for both bulk and thin film KNO.[7] The origin of this enhanced photovoltaic response can be understood in terms of polarization-driven internal electric fields in ferroelectric KNO. Previous studies have shown that polarization gradients in KNO can generate strong built-in electric fields, leading to enhanced photovoltaic currents by promoting charge separation.[6] A related mechanism has also been proposed for PMN-PT-based systems, where polarization instability, high dielectric susceptibility, and intrinsic nanoscale polarization heterogeneity, particularly near the morphotropic phase boundary, give rise to internal fields that amplify photovoltaic effects. Such result is potentially interesting once implemented on KNO-based magnetoelectric heterostructures, since interfacial photostriction, often reported in correlation with photocurrents in FE crystals, in an additional lever for tuning interfacial magnetic behaviour[8,9].

References

1 G. Panaccione, I. Vobornik, J. Fujii, D. Krizmancic, E. Annese, L. Giovanelli, F. Maccherozzi, F. Salvador, A. De Luisa, D. Benedetti, A. Gruden, P. Bertoch, F. Polack, D. Cocco, G. Sostero, B. Diviacco, M. Hochstrasser, U. Maier, D. Pescia, C. H. Back, T. Greber, J. Osterwalder, M. Galaktionov, M. Sancrotti, G. Rossi, “Advanced photoelectric effect experiment beamline at Elettra: A surface science laboratory coupled with Synchrotron Radiation”, Rev. Sci. Instrum. **80**, 043105 (2009)

2 D. Dagur, V. Polewczyk, A.Y. Petrov, P. Carrara, M. Brioschi, S. Fiori, R. Cucini, G. Rossi, G. Panaccione, P. Torelli, G. Vinai, “Visible Light Effects on Photostrictive/Magnetostrictive PMN-PT/Ni Heterostructure”, Adv. Mater. Interfaces **9**, 2201337 (2022).

3 D. Wang, G. Wang, Z. Lu, Z. Al-Jlaihawi, A. Feteira, “Crystal Structure, Phase Transitions and Photoferroelectric Properties of $KNbO_3$-Based Lead-Free Ferroelectric Ceramics: A Brief Review”, Front. Mater. **7**, 91 (2020).

4 G. Shirane, H. Danner, A. Pavlovic, R. Pepinsky, “Phase transitions in ferroelectric $KNbO_3$”, Phys. Rev. **93**, 672–673 (1954).

5 C.L. Diao, H.W. Zheng, “The preparation and surface photovoltage characterization of $KNbO_3$ powder”, J. Mater. Sci. Mater. Electron. **26**, 3108–3111 (2015).

6 S.H. Wemple, M. Di Domenico, “Behavior of the electronic dielectric constant in covalent and ionic materials”, Phys. Rev. B **3**, 1338–1351 (1971).

7 Y. Sun, Z. Zhang, X. Fang, Z. Huang, D. Zhou, H. Tian, G. Han, Z. Ren, “Polarization-gradient KNbO3 film with a large photovoltaic current”, APL Mater. **11**, 091116 (2023).

8 F. Motti, G. Vinai, A. Petrov, B.A. Davidson, B. Gobaut, A. Filippetti, G. Rossi, G. Panaccione, P. Torelli, “Strain-induced magnetization control in an oxide multiferroic heterostructure”, Phys. Rev. B **97**, 094423 (2018).

9 A. Ahlawat, S. Chowdhury, R. Roy, R. Raj, S. Ghosh, P. Sharma, S. Choudhary, R. Mishra, H. Zhang, J. Edwards, J. Seidel, P. Sharma, A. Keshri, D. Dagur, S. Verma, V.R. Reddy, M. Gupta, D. Shukla, R.J. Choudhary, V.G. Sathe, S. Das, “Photostriction-Driven, Light-Modulated Magnetization in Fe/PMN-PT Heterostructures”, Adv. Funct. Mater. **36**, e22373 (2026).