Supporting information for

Persistent type-II multiferroicity in nanostructured MnWO₄ ceramics

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Characterization methods

Laboratory powder X-ray diffraction. X-ray diffraction (XRD) patterns were collected at room temperature on a Bruker D8 Advance instrument using monochromatic Cu_{K-L3} (λ = 1.540598 Å) X-rays and a LynxEye detector. Le Bail and Rietveld analyses of the XRD data were performed using JANA 2006 [Petricek, V.; Dusek, M.; Palatinus, L. Crystallographic Computing System JANA2006: General Features. Z. Für Krist. 2014, 229 (5), 345–352.] and the Cheary-Coelho fundamental approach for XRD profile parameters [Cheary, R. W.; Coelho, J. Appl. Crystallogr. 1998, 31 (6), 851–861 ; J. Appl. Crystallogr. 1998, 31 (6), 862–868.].

<u>Magnetic susceptibility.</u> A Quantum Design MPMS-XL7 equipped with an Evercool dewar was used to collect temperature-dependent DC and AC magnetization data. Zero field cooled (ZFC) and field cooled (FC) DC magnetization measurements were taken from 2 to 300 K in an applied field of $\mu_0 H = 0.1$ T. Data were corrected for the diamagnetism of the sample holder as well as for core diamagnetism using Pascal's constants [Bain, G. A.; Berry, J. Chem. Educ. 2008, 85 (4), 532.]. Dielectric permittivity. Dielectric measurements were performed on dense pellets (≈ 6 mm diameter, ≈ 1 mm thick) using an HP4194a impedance bridge. Samples were loaded into a Quantum Design Physical Properties Measurement System (PPMS). Measurements were taken in the frequency (f) range of 1 kHz–400 kHz and in the temperature range of 5 - 20 K.

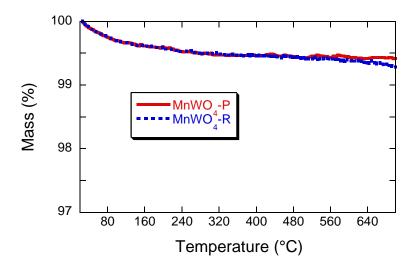


Figure S1. Thermogravimetric curves for MnWO₄ nanopowders in flowing air. The small weight loss (≈ 0.5 %) at around 100° C is due to evaporation of adsorbed water.

Table S1. Cell parameters of nanopowders and of nanostructured ceramics of MnWO₄ as determined from Rietveld or Le Bail refinements of X-ray diffraction patterns recorded at room temperature. Refinements to the XRD data were made using the published *P2/c* structural model of MnWO₄ [Lautenschläger, G.; Weitzel, H.; Vogt, T.; Hock, R.; Böhm, A.; Bonnet, M.; Fuess, H. Phys. Rev. B: Condens. Matter Mater. Phys. 1993, 48, 6087–6098.].

	a (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)
MnWO ₄ -P	4.827(1)	5.761(1)	5.001(1)	91.16(2)
nanopellets	1.027(1)	5.701(1)	0.001(1)	91.10(2)
MnWO ₄ -R	4.826(2)	5.758(4)	4.996(1)	91.19(1)
nanorods	1.020(2)	5.756(1)	1.550(1)	<i>y</i> 1.1 <i>y</i> (1)
Nanostructured	4.830(1)	5.760(1)	5.000(1)	91.18(1)
ceramic-P	1.050(1)	5.700(1)	5.000(1)	J1.10(1)
Nanostructured	4.829(1)	5.758(2)	5.000(1)	91.21(3)
ceramic-R	7.029(1)	5.756(2)	5.000(1)	<i>y</i> 1.21(3)

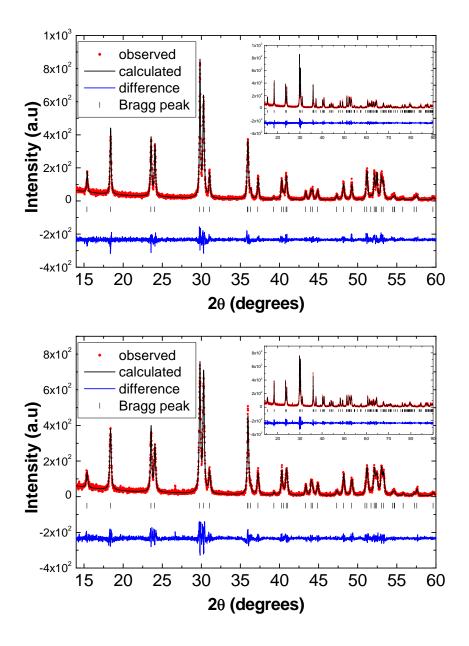


Figure S2. Final Rietveld refinement plots of the XRD data ($\lambda = 1.540598$ Å) for nanopellets MnWO₄-P (upper graph) and nanorods MnWO₄-R (lower graph) powders. The Rietveld refinements were obtained using the published *P2/c* structural model of MnWO₄ [Lautenschläger, G.; Weitzel, H.; Vogt, T.; Hock, R.; Böhm, A.; Bonnet, M.; Fuess, H. Phys. Rev. B: Condens. Matter Mater. Phys. 1993, 48, 6087–6098].

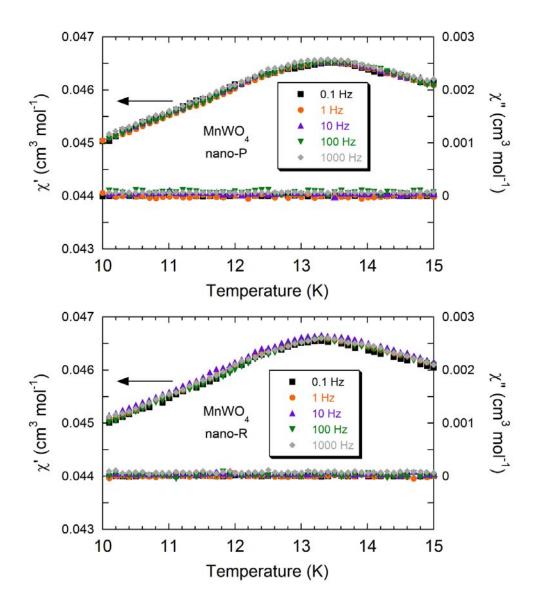


Figure S3. Temperature dependence of the in-phase, χ' (left scale), and out-of-phase, χ'' (right scale), components of the AC susceptibility for nanostructured MnWO₄ ceramics prepared by SPS at 520 °C and 450 MPa using nanopellets MnWO₄-P (upper graph) or nanorods MnWO₄-R (lower graph). Data were taken at zero DC magnetic field for driving frequencies in the range of 0.1 Hz – 1000 Hz. Amplitude of the driving field was $H_{AC} = 3$ Oe.

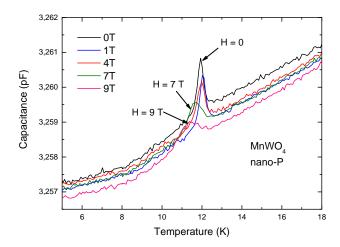


Figure S4. Temperature profiles of the dielectric capacitance at selected applied magnetic fields for nanostructured MnWO₄ ceramics prepared by SPS at 520 °C and 450 MPa using nanopellets MnWO₄-P. Data were collected at 385 Hz.