Supplementary data for manuscript

**Revealing the solid-state processing mechanisms of Antiferroelectric AgNbO3 for energy storage**

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Figure S1. X-ray diffraction pattern of stoichiometric AgO/Nb2O5 mixture before milling. The set of tick marks represents the reflections associated with the structures of Nb2O5 and AgO (for labels, please refer to the PDF-ICDD database, 2011). All reflections are identified as either AgO or Nb2O5



Figure S2. Photo of stoichiometric AgO/Nb2O5 powder mixture before (left) and after (right) ball milling. The mixture on the left was hand-mixed using a spatula.



Figure S3. Particle size distribution of the stoichiometric powder mixture after homogenization milling in ethanol (16 h at 250 rpm), prior to calcination. The measurement was carried out using a laser granulometer (Saturn DigiSizer 5200, Micromeritics, USA ). The powder mixture consisted of AgO and Nb2O5 before milling and transformed into a mixture of metallic Ag and Nb2O5 after high-energy milling.



Figure S4. Evolved gas analysis (EGA) of the ball milled nominal AgO/Nb2O5 powder mixture (actual composition Ag/Nb2O5) as a function of temperature. The analysis was performed using Fourier Transform Infrared Spectrometer (Bruker Tensor 27, Mid-infrared range with gas cell, Bruker Optics, Gemany). Gases evolved during the mass loss around 200  °C were acetic acid (C2H­4O2), carbon dioxide (CO2), and carbon monoxide (CO), which point towards a reaction of ethanol with oxygen, which was catalyzed by the presence of metallic Ag.



Figure S5. *In situ* XRD of the unmilled stoichiometric mixture as a function of temperature from room temperature (RT) to 600 °C. The set of tick marks represents the reflections associated with the structures of AgO, Nb2O5, AgNbO3, and Ag (for labels, please refer to the PDF-ICDD database, 2011). Unlike for the milled powder, large amounts of unreacted Ag and Nb2O5 were observed even at 600 °C.



Figure S6. Scanning electron microscopy (SEM) imaging of the thermally etched AgNbO3 samples.



Figure S7. Optical microscopy imaging of the polished AgNbO3 samples, examined in the reflected polarized light microscopy mode using the Axio Imager 2 microscope (Zeiss, Germany). Black arrows indicate the presence of inclusions, which are present in all four samples.



Figure S8. Back-scattered electron (BSE) imaging of the polished AgNbO3 samples. Black arrows indicate inclusions, the composition of which was examined using energy dispersive X ray (EDX) spectroscopy in the scanning electron microscope (XL 30 FEG, Philips, Eindhoven, Netherlands). The EDX results show that these inclusions are Ag-rich, as shown in Figure S9.

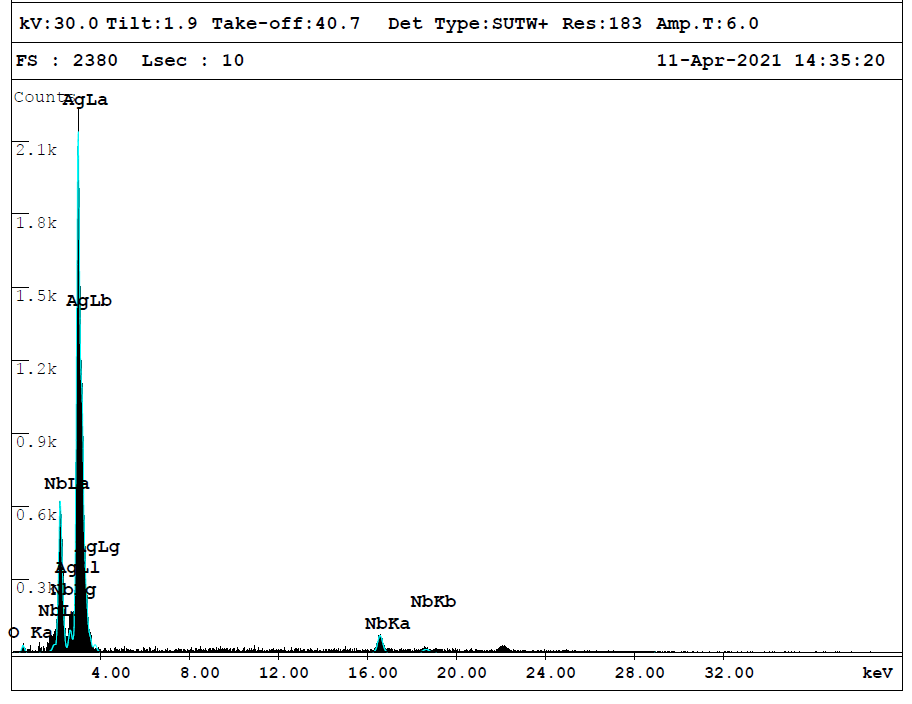


Figure S9. Energy dispersive X-ray (EDX) point analysis of the inclusions of AgNbO3 samples, showing the inclusions are Ag-rich.



Figure S10. AgNbO3 pellets processed in N2 atmosphere (3 h at 1080 °C). The pellet diameter is about 9 mm. The silver oxide is reduced, while the formation of AgNbO3 is prevented, which results in the formation of droplets of metallic silver at sample´s surface.



Figure 11. X-ray diffraction pattern of ball milled AgO/Nb2O5 powder mixture after calcination in N2 at 850 °C and 6 h. The measurement was performed on an X-ray diffractometer with Bragg-Brentano geometry (XRD, Bruker AXS D8 Advance, Germany) with Cu K*α* radiation. The set of tick marks represents the reflections associated with the structures of Ag, Nb2O5, and AgO. All reflections are identified as either Ag or Nb2O5, i.e., no formation of perovskite AgNbO3 was observed in N2 atmosphere.



Figure S12. (a) Polarization and (b) strain hysteresis loops of AgNbO3 samples under an electric field of 14 kV/mm (1st cycle, measured at 1 Hz).