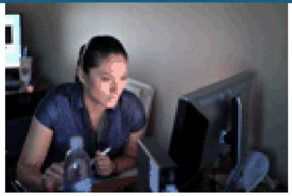
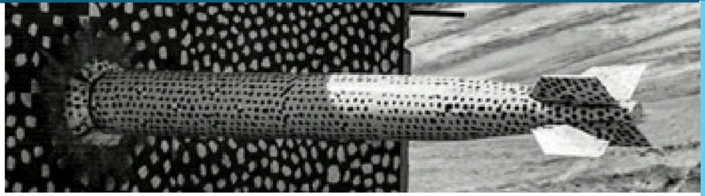
SAND2018-12165C

Stabilization of ferroelectric phase of $Hf_{0.5}Zr_{0.5}O_2$ on NbN at 4 K





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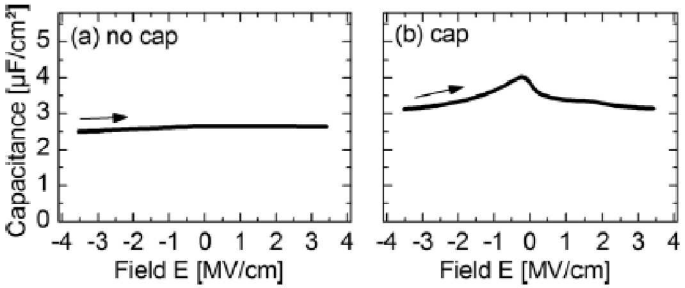
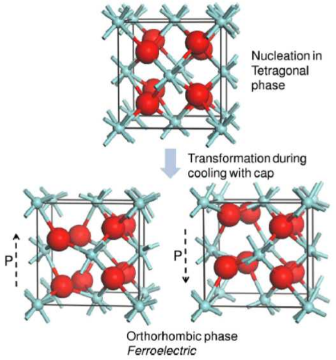
Outline of Ferroelectricity on Superconducting NbN

- Introduction into HfO_2 Ferroelectricity
- Behavior of $Hf_{0.5}Zr_{0.5}O_2$ on NbN
  - Cryogenic Behavior
  - Wake-up Effects
  - Electrical Properties
  - Freeze Out of Oxygen Vacancies
- Conclusion

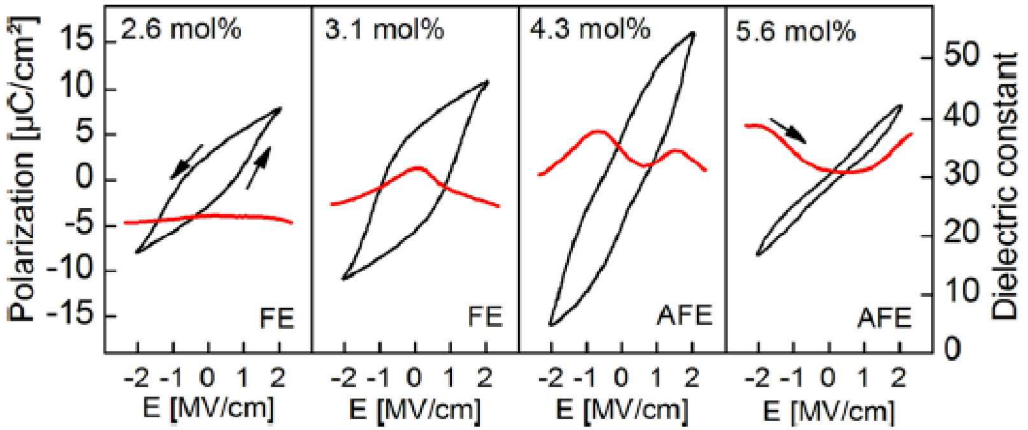
Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. The authors acknowledge and thank the staff of Sandia's MESA fabrication facility. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Introduction to Ferroelectric Hf & Zr Oxides

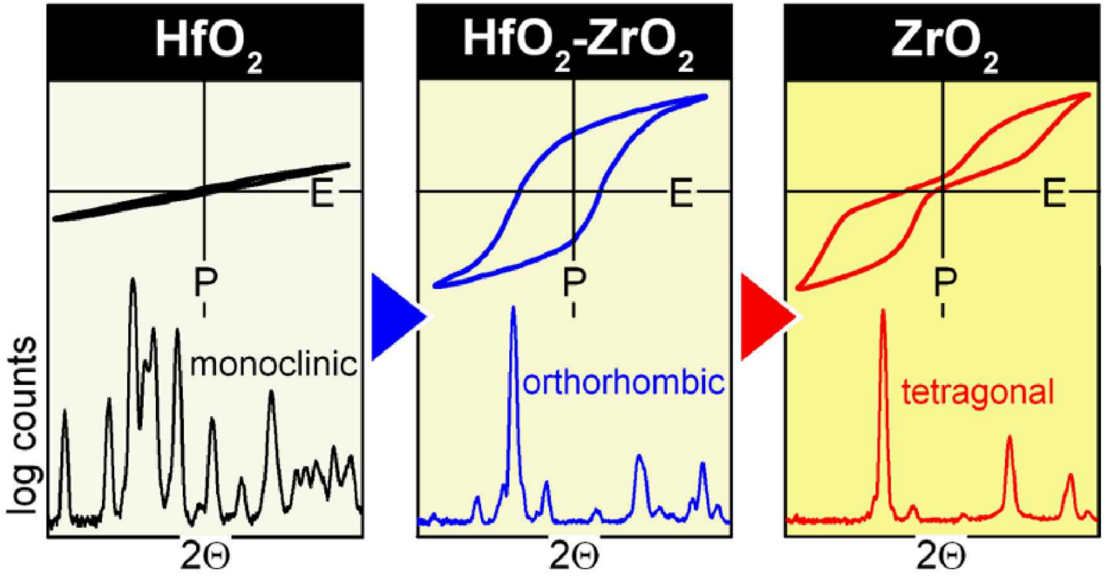




Observation of a polarization of MIM Cap (TiN/HfO2/TiN) occurring under ideal conditions, can induce a orthorhombic phase to emerge from a tetragonal or monoclinic phase. This amazing discovery lead to the idea of mixtures (SiO2, ZrO2) and dopants (Si, Gd, La, Y) to improve the ferroelectric response. However, only very specific sets of electrodes were observed to enable this transformation suggesting a close link to the nucleation of the needed phase to the electrodes.

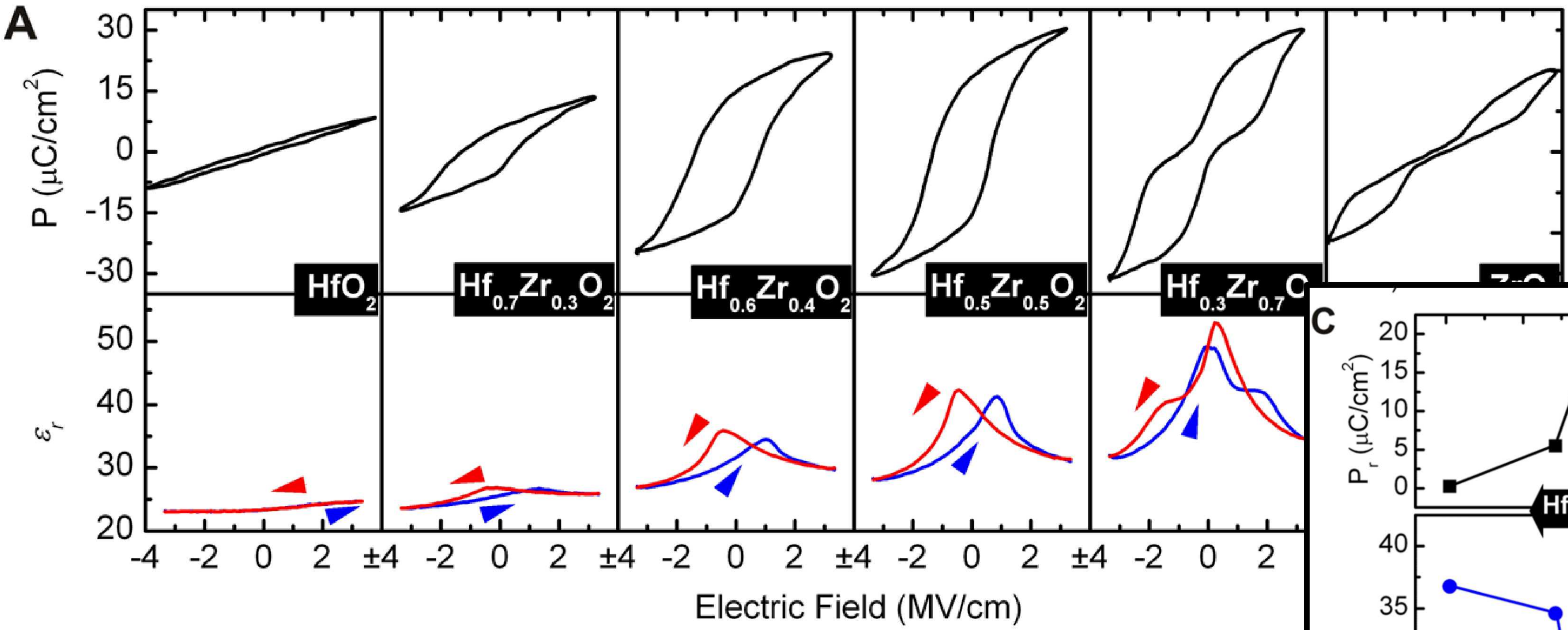


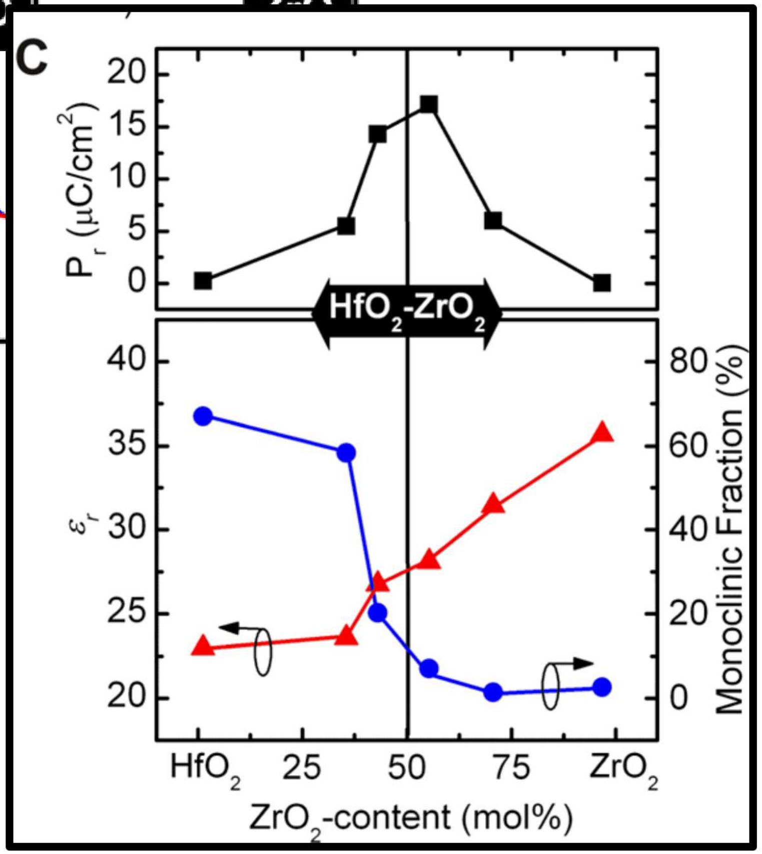
T.S. Boscke et al., APL, 99, 102903, (2011).



J. Muller et al., Nano Lett., 12, 4318-4223, (2017).

Addition of ZrO_2 to HfO_2 – TiN electrodes

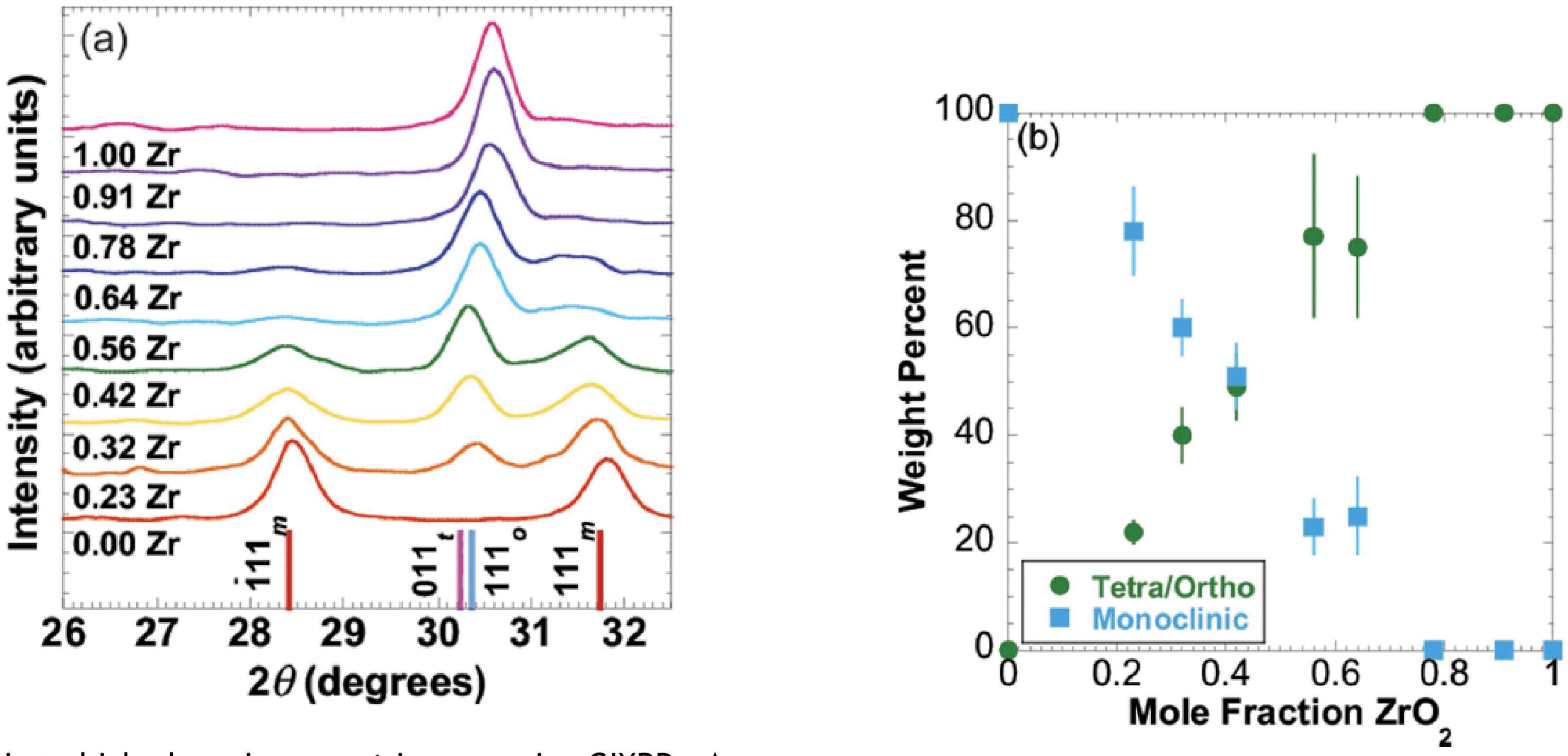




As ZrO_2 is mixed into the ALD process, an improvement in P_r is observed as a stronger ferroelectric phase emerges (ortho). Note ZrO_2 goes antiferroelectric.

J. Muller et al., Nano Lett., 12, 4318-4223, (2017).

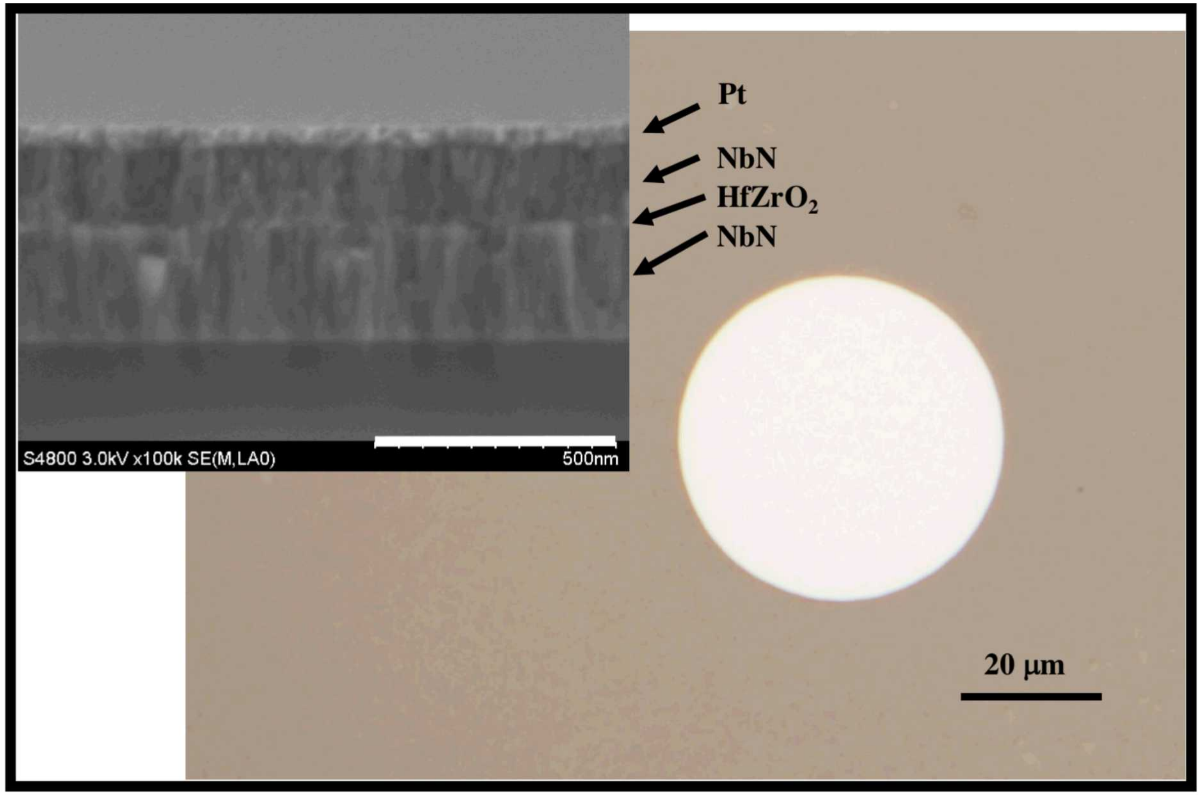
Phase Control and Identification of $Hf_xZr_{1-x}O_2$ with TaN Electrodes



Knowing which phase is present is seen using GIXRD. As films are pressed from HfO_2, a transition occurs from monoclinic to tetragonal and orthorhombic.

S.W. Smith et al., APL, 110, 072901 (2017).

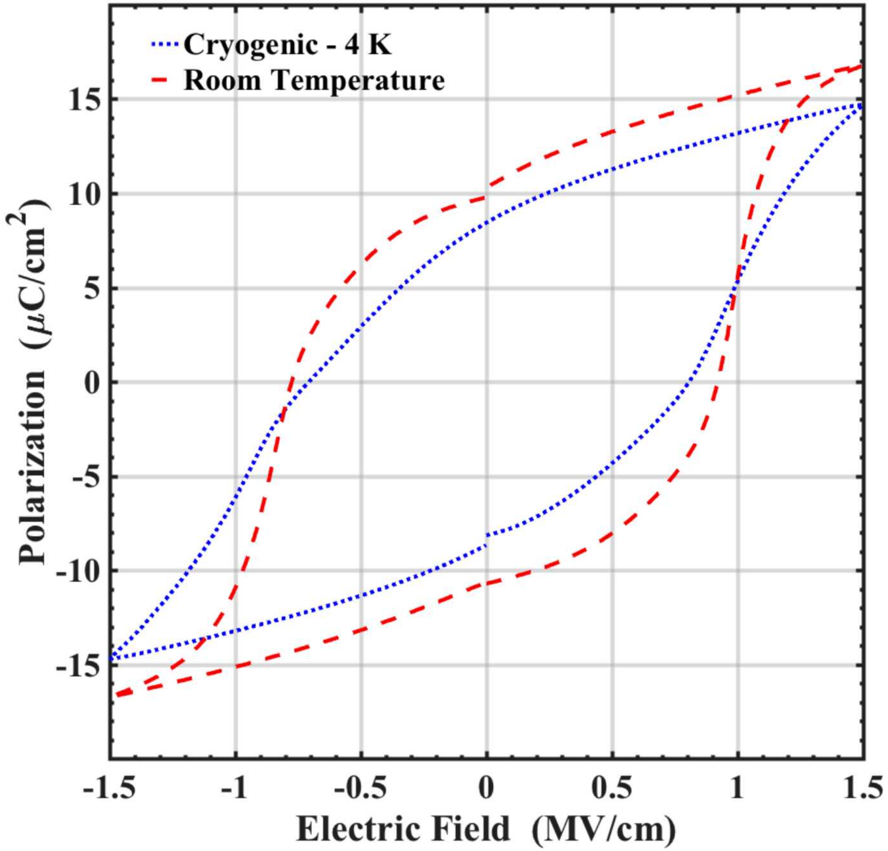
Utilizing NbN Electrodes for $Hf_{0.5}Zr_{0.5}O_2$ (NbN/HZO/NbN)



Using a 20 nm HZO film, a clear ferroelectric phase is observed at room temperature and under cryogenic conditions.

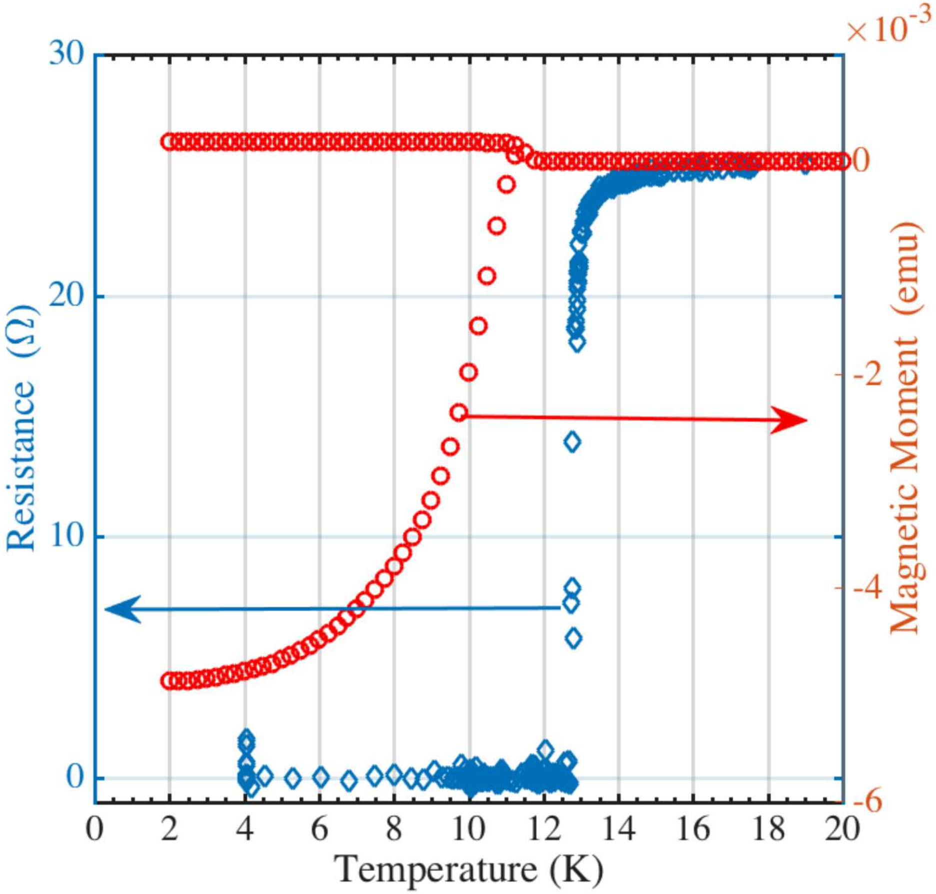
ALD growth was done in an Ultratech Savannah flow-through style ALD reactor. Tetrakis(dimethylamino)hafnium and tetrakis(dimethylamino)zirconium, each at 75 °C, were used as the precursors with water used as the oxidant and N2 as the carrier gas.

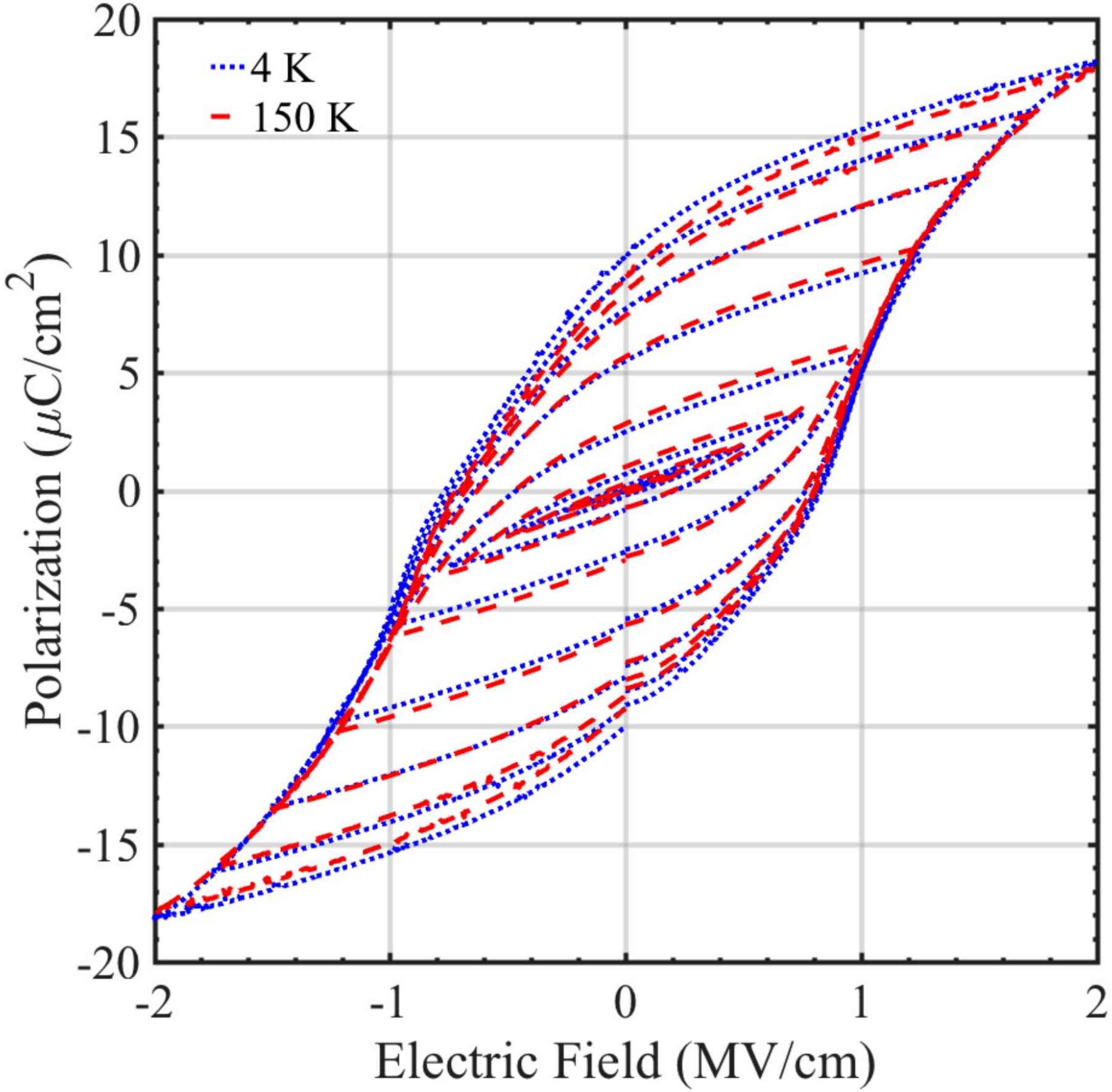
Cryo measurements performed in a LakeShore open flow probe station utilizing a LakeShore 331 stage temperature controller and Precision Multiferroic II.



M.D. Henry et al., APL, in submission (2018).

Superconductivity with NbN/HZO/NbN

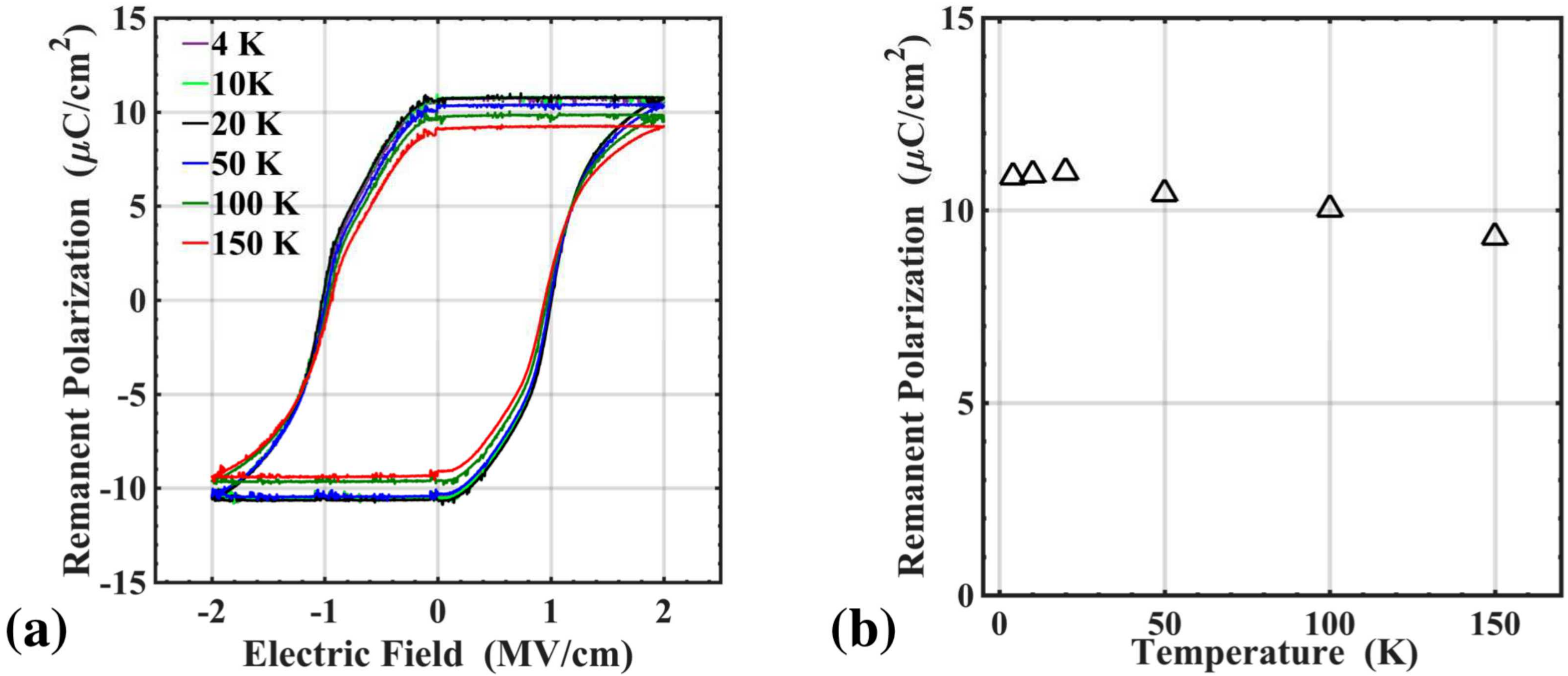




The 150 nm thick, NbN top electrode was reactively sputtered in a Denton Discovery deposition tool using a 99.5% pure Nb target, Ar and N_2 at room temperature.

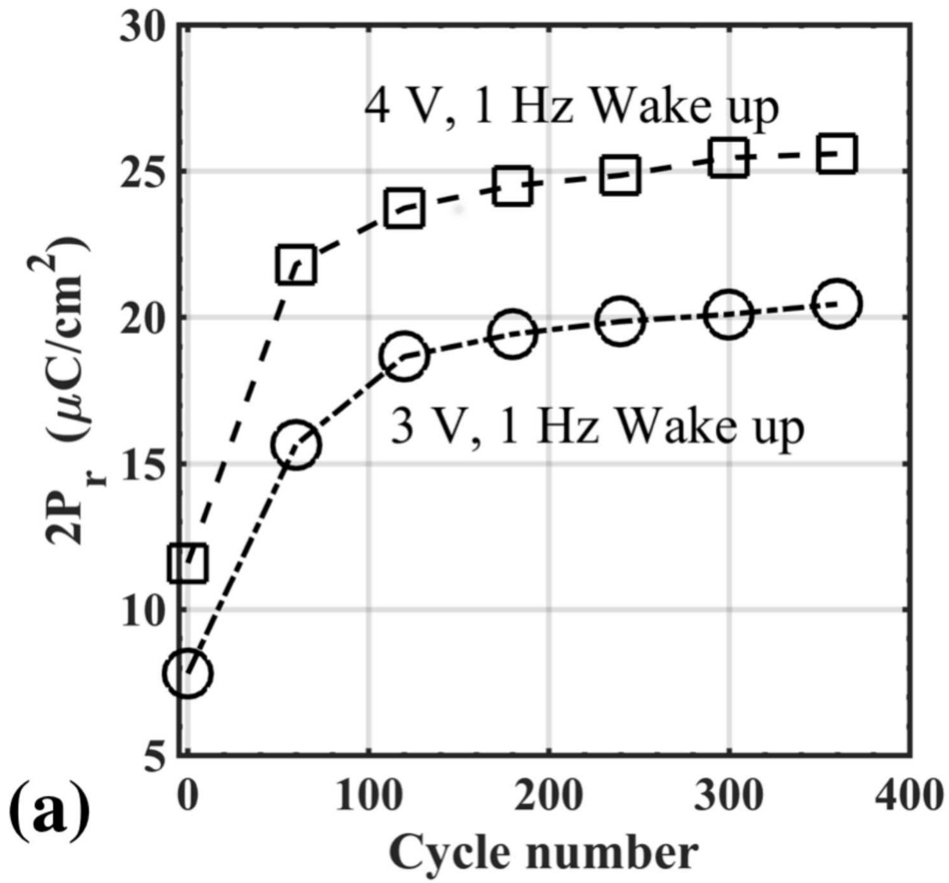
M. D. Henry et al., IEEE Trans. Appl. Supercond., 27, (4), (2017).

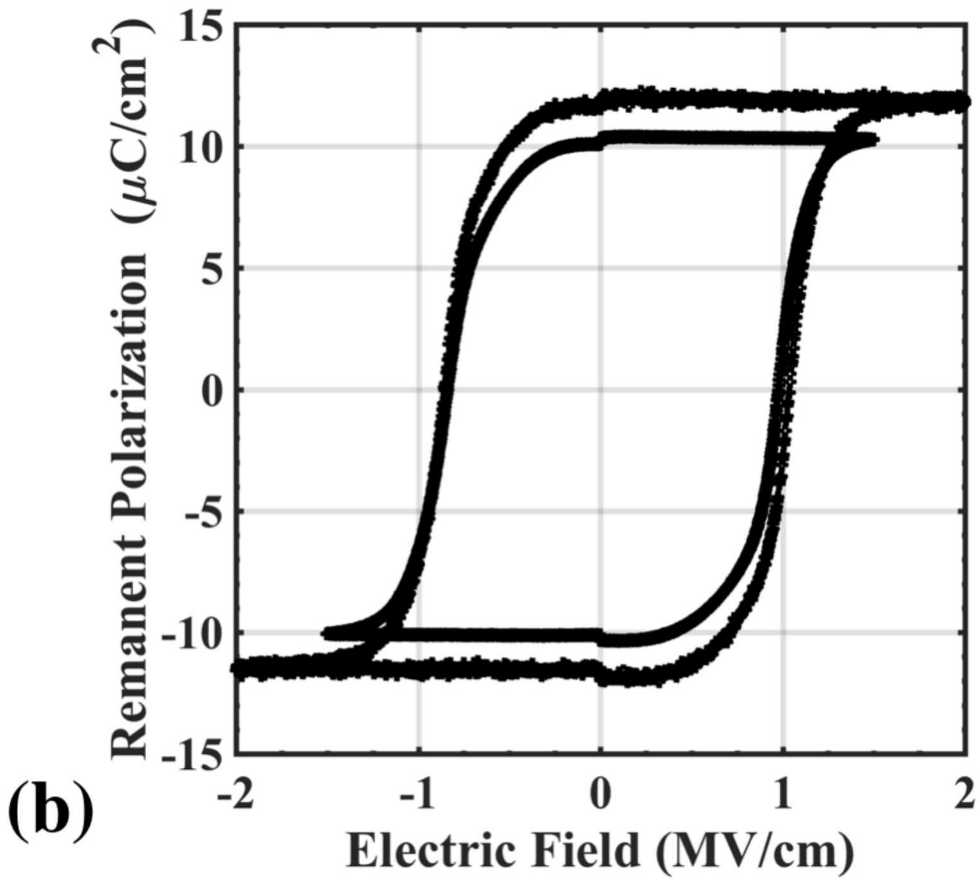
Variation of NbN/HZO/NbN Ferroelectric Response over Temperature



Extraction of remanent polarization separates the dielectric effect from the ferroelectric effect. When performed over temperature a slight decrease in polarization is observed. Approximately a 30 $\mu C/m^2K$ decrease should occur and we measure about 100 $\mu C/m^2K$; however this method does not isolate the pure pyroelectric phase.

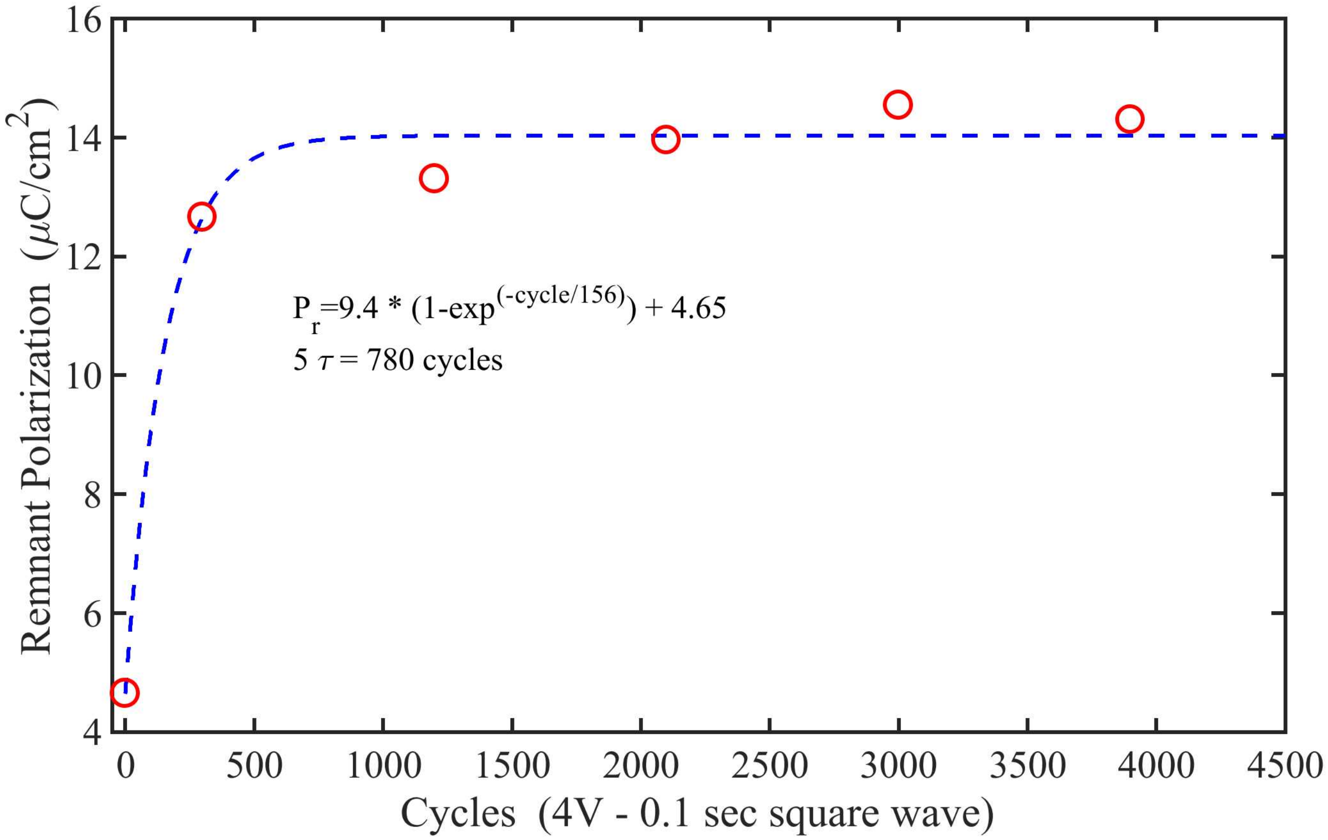
Wake-up Effects of NbN/HZO/NbN at Room Temperature



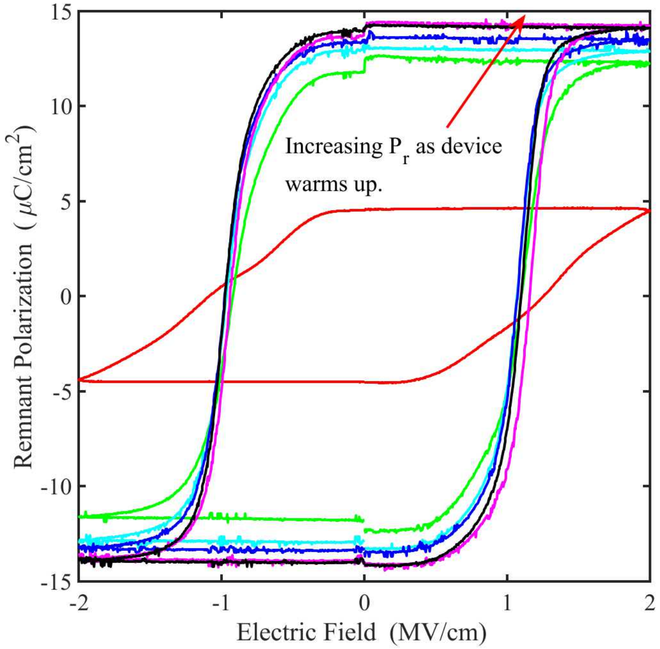


The wake-up effect is observed when the device is cycled from positive (3 or 4 V) to negative at relatively low frequencies. The regime is governed by a phase transformation from monoclinic to orthorhombic (Grimley et al-2016). A secondary effect is a reduction of a non-uniform defect rich tetragonal phase near the metal interface.

Wake-up Effects of NbN/HZO/NbN at Room Temperature



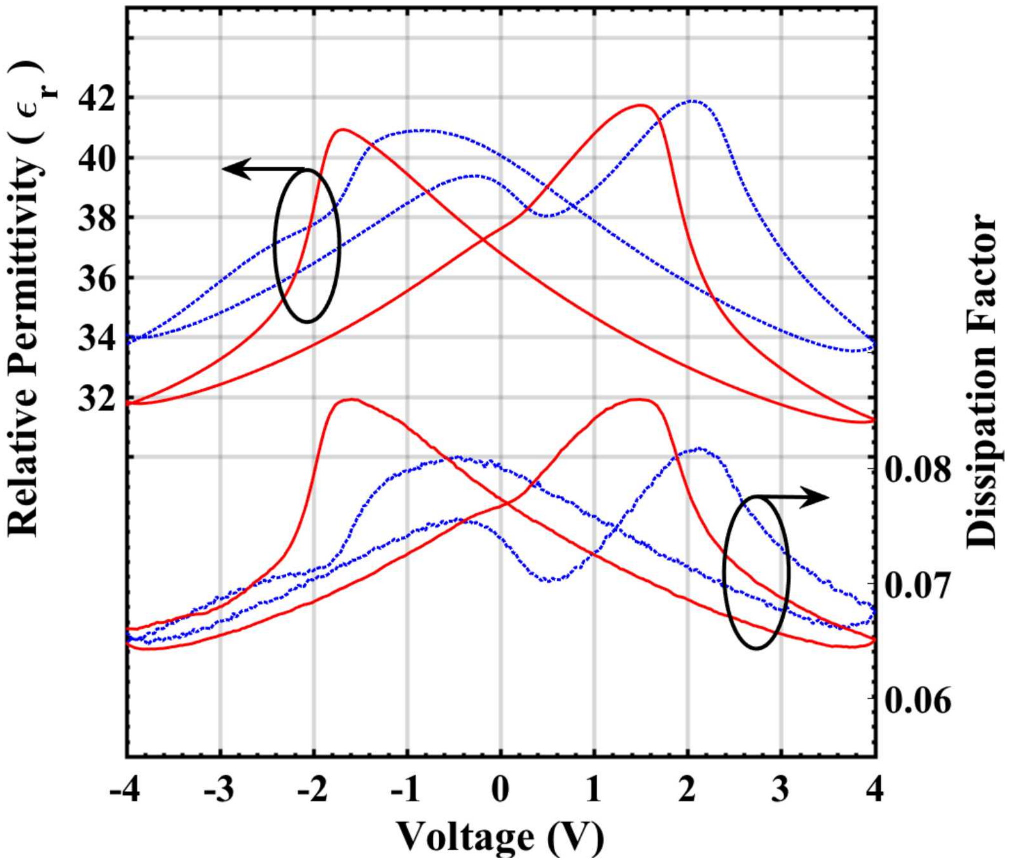
Wake up in a 77 um radius NbN/HfZrO2/NbN ferroelectric capacitor with a 20 nm film thickness using a 4 volt, 10 Hz cycle.



This wake-up is quickly observed by extracting the remanent polarization (at 0 volts) as polarization sweeps and square wave cycling of the film are intermixed.

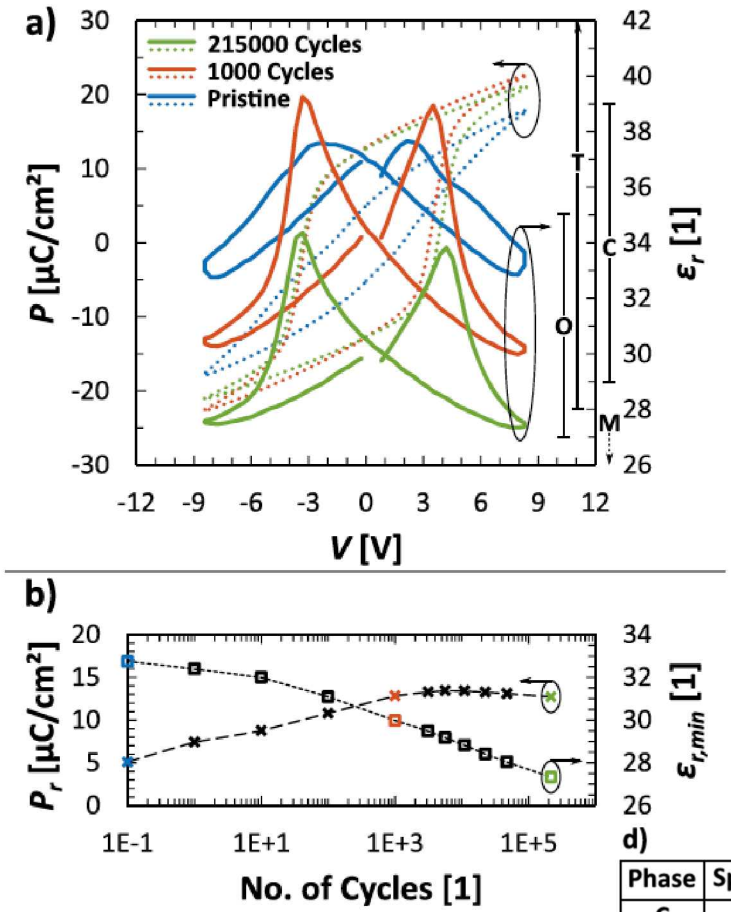
Wake-up Effects of NbN/HZO/NbN from Capacitance / Permittivity RT

NbN/$Hf_{0.5}Zr_{0.5}O_2$/NbN



Relative permittivity and dissipation factor at 100 kHz as voltage is swept from -4 V to 4 V and then from 4 V to -4 V at room temperature before (blue dot) and after a 360 second, +/- 4 V and 1 Hz wakeup at room temperature (red line).

TiN/Gd:HfO_2/TiN

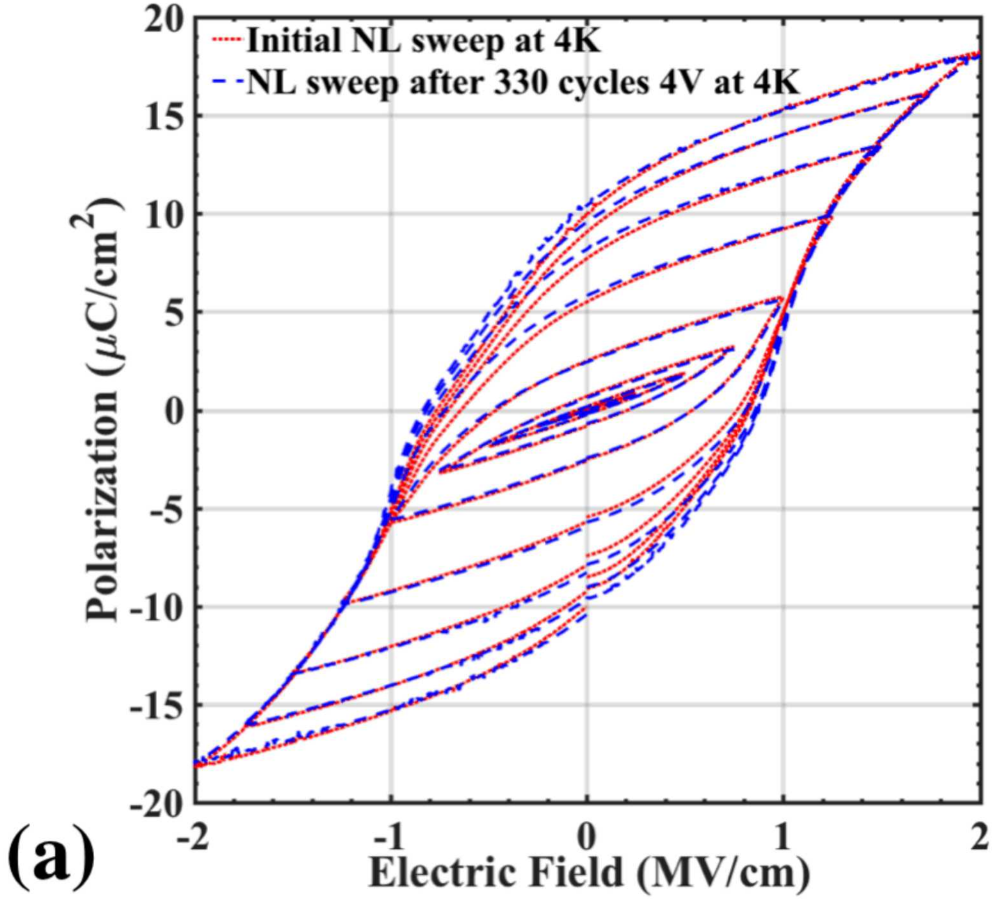


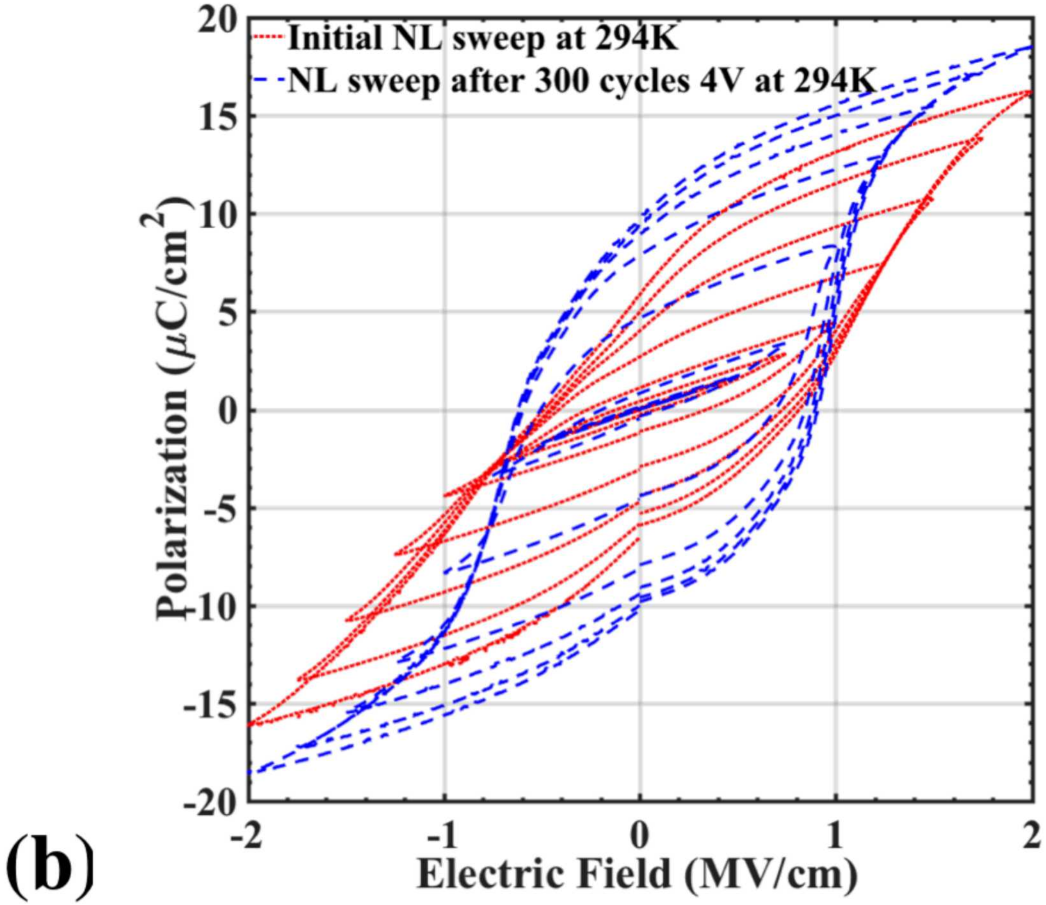
d)

Phase	Space Group	ϵ_r [1]	References
C	*Fm3m*	ϵ_r = 29...39	[2,48-51]
T	*$P4_2/nmc$*	ϵ_r = 28...70	[2,49,51]
O (FE)	*$Pca2_1$*	ϵ_r = 27...35	[2,48]
M	*$P2_1/c$*	ϵ_r = 16...20	[2,48-51]

E. D. Grimley et al., Adv. Elect. Mater., 2, 1600173, (2016).

Wake-up Effects of NbN/HZO/NbN – Cryo WU vs RT WU



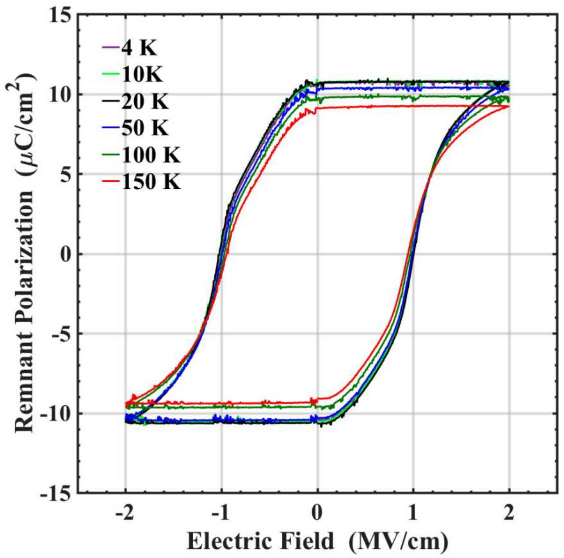


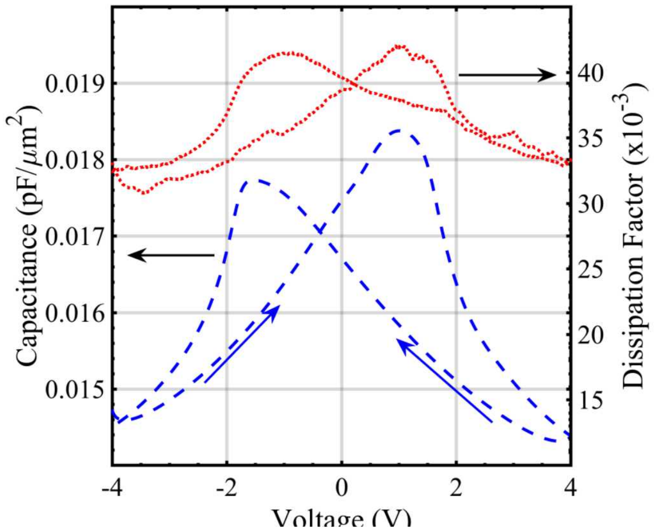
Oxygen vacancies at the top and bottom electrodes are speculated to be the source of the wake-up effect. At cryogenic temperatures, their mobility seems to freeze out at 4K.

This offers the intriguing potential for further studies of vacancy migration and possibilities for extending device life.

Conclusions

- This work has demonstrated ferroelectricity of HZO on superconducting NbN.
- Ferroelectricity of the films remain (no surprise) at 4 K however vacancy migration freezes out suppressing wake-up effects.
- Oxygen vacancy freeze out occurs suggesting a mechanism to study the wakeup effect.
- Potential applications in cryogenic or superconducting memory.





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Steve Wolfley, Nick Martinez, Darren Hoke, Erica A. Douglas.