Nanoscale Studies of Ferroic Materials for Energy Storage Applications

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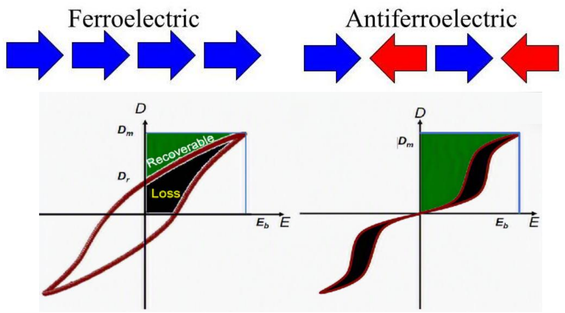
Introduction

This research project was focused on identifying conditions that optimize the ferroelectric and antiferroelectric properties of chosen materials that show promise for use in energy storage. To do so, a variety of ferroic materials were studied by comparing key variables like thickness, dopant concentration, capacitor type and size. Then techniques including scanning probe microscopy were used to analyze the ferroelectric and antiferroelectric response of these materials. With this information, the effectiveness of the chosen conditions can be gauged.

Ferroelectricity vs Antiferroelectricity

Ferroelectricity is a property that allows the material to have its polarization uniformly switched by an applied electrical field, and it will retain that polarization even in the absence of the field. Antiferroelectricity also polarizes when a field is applied, but, when the field is removed, will alternate polarized unit cells to create a net zero polarization.

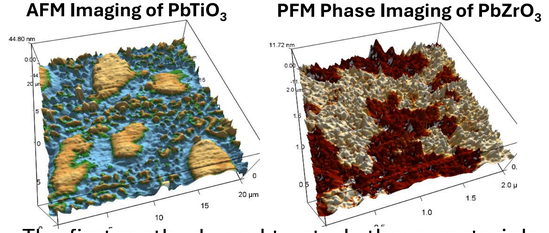


Ferroelectric Hysteresis Loop **Antiferroelectric Double - Hysteresis Loop**

Experimental Approach:

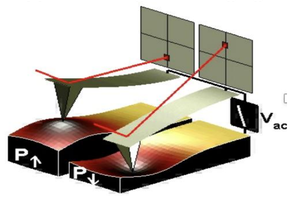
Scanning Probe Microscopy

AFM Imaging of $PbTiO_3$ **PFM Phase Imaging of $PbZrO_3$**



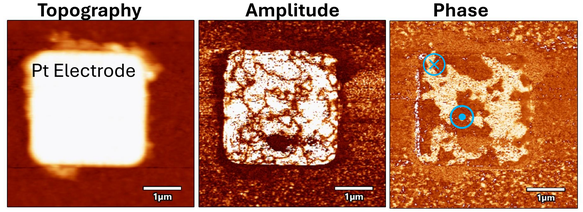
The first method used to study these materials is Atomic Force Microscopy (AFM). In this method, a small tip is touched to the surface. The tip moves while a laser shines onto the tip to measure its bending, which creates a map of the surface.

Sample response to bias applied during PFM imaging



The second method is Piezoresponse Force Microscopy, (PFM). In PFM, an electrical bias is applied through the tip, and the response in the sample is measured, which indicates the polarization of the material in that location.

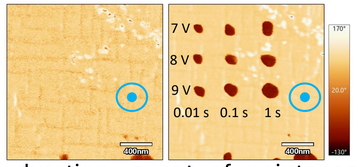
PFM images of ferroelectric $PbZrO_3$ capacitor



And lastly, PFM Spectroscopy applies alternating bias, rapidly switching the polarization. Ferroelectric materials will show a hysteresis loop, and antiferroelectric materials, the double hysteresis loop.

Local Polarization Switching

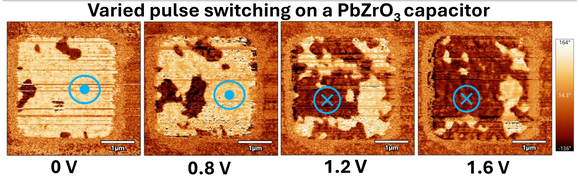
Pristine **Pulse Grid Applied**



Switching can be examined using a pulse grid. With pulses of varying intensity and duration, a set of points can be switched to analyze various factors, including domain growth and relaxation time. Here, increased duration or intensity result in slightly larger domains.

Capacitor Switching

Varied pulse switching on a $PbZrO_3$ capacitor

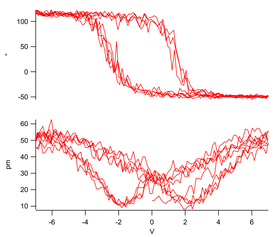


0 V **0.8 V** **1.2 V** **1.6 V**

Rather than applying pulses to points, capacitors can be used to carry bias across a larger surface. Here a series of pulses are applied to a negatively polarized sample, causing positive domains to nucleate and grow.

Investigation of Switching Behavior of Free-Standing Membranes

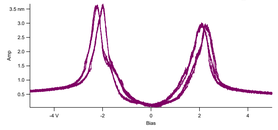
PFM Loops of Y-HfO_2 with free standing membrane



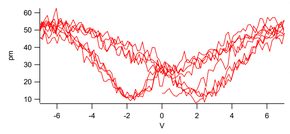
A free- standing membrane is a layer of material added atop a sample that isn't firmly fixed in place. Spectroscopy was performed to graph the switching behavior of the material under these conditions, and ferroelectric response was observed.

Antiferroelectric Switching Analysis

PFM Amplitude loop in antiferroelectric $PbZrO_3$



PFM Amplitude loop in ferroelectric Y-HfO_2



PFM amplitude loops allow ferroelectric and antiferroelectric to be easily differentiated. Ferroelectric materials have a single pair of peaks that correspond to the voltages at which the polarization is switched. Antiferroelectric materials, however, have two pairs of peaks because the applied electrical field induces not just polarization switching, but also reversible transitions between the ferroelectric and antiferroelectric phases. These phase transitions change the sample's response, creating another set of switching peaks on the loop.

Conclusion

The properties of various ferroic materials under chosen conditions were identified and analyzed, providing insight into conditions and variable trends that will help facilitate future research as well as support the development of future energy storage technologies.

The techniques utilized in this research will support future work, including research into antiferroelectricity in Hafnia, a material with great promise for technological innovation.

Acknowledgements

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