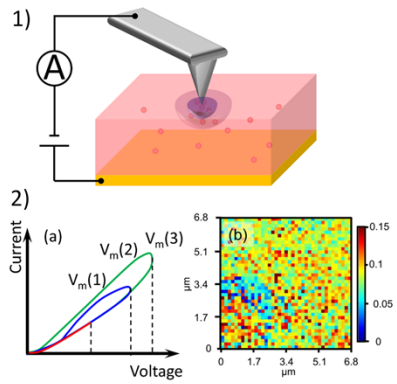
CNMS Staff Science Highlight

# Probing Nanoscale Ionic Dynamics in Functional Oxides




1) Schematic of FORC-IV method: current-voltage response is measured at individual locations on the sample's surface.
2) a) current-voltage curves displaying hysteretic behavior b) FORC-IV loop area map showing different distribution of electrochemical activity across the surface.

Work was performed at the Center for Nanophase Materials Sciences, ORNL

## Scientific Achievement

**A novel scanning probe microscopy technique for measuring electrochemical activity at the nanoscale was developed and employed to probe the ionic activity in Ca-doped $BiFeO_3$.**

## Significance and Impact

**FORC-IV (first-order reversal curve current-voltage) is a simple method for probing ionic dynamics at the nanoscale and will find application in studying batteries, memristors, and fuel cells, whose operation relies on nanoscale-size elements that control ion flow.**

## Research Details

- FORC-IV utilizes hysteresis in current-voltage curves measured locally to determine local ionic activity.
- Application of FORC-IV to Ca-doped $BiFeO_3$ distinguished electronic and ionic contributions to conductivity and demonstrated the link between oxygen vacancy dynamics and the metal-insulator transition.
- Variable-temperature FORC-IV allowed local measurement of ion activation energies.

E. Strelcov, Y. Kim, S. Jesse, Y. Cao, I. N. Ivanov, I. I. Kravchenko, C.-H. Wang, Y.-C. Teng, L.-Q. Chen, Y. H. Chu, S. V. Kalinin, Nano Lett. (2013) DOI:10.1021/nl400780d

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The cross-coupled phenomena are not only of great fundamental scientific interest, but also underlie the work of such applications as batteries, fuel cells, memristors, smart glasses, etc., where of particular importance is the control over the opto-electronic properties of materials achieved via ionic motion. As the length scales of devices or the underlying interactions are usually below 100 nm, these should be studied at the nanoscale. Our first-order reversal curve current-voltage (FORC-IV) SPM method allows addressing ionic motion locally, at the nanoscale. Different from the Electrochemical Strain Microscopy or similar techniques, it also is able to distinguish between the electrochemical and other bias-driven responses, such as piezoresponse. FORC-IV is not only a powerful, but also a flexible technique, allowing for different operation modes that can provide thermodynamic and kinetic characterization of materials' local properties, revealing phenomena at several different characteristic time scales.

FORC-IV imaging mode is applied to a Ca-substituted bismuth ferrite (Ca-BFO) system to separate the electronic and ionic phenomena in this material and visualize the spatial variability of these behaviors. The variable-temperature measurements further demonstrate the interplay between the thermally and electric-field-driven resistance changes in Ca-BFO. The FORC-IV is shown to be a simple, powerful and flexible method for studying electrochemical activity of materials at the nanoscale and, in conjunction with the Electrochemical Strain Microscopy, for differentiating ferroelectric and ionic behaviors.

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