

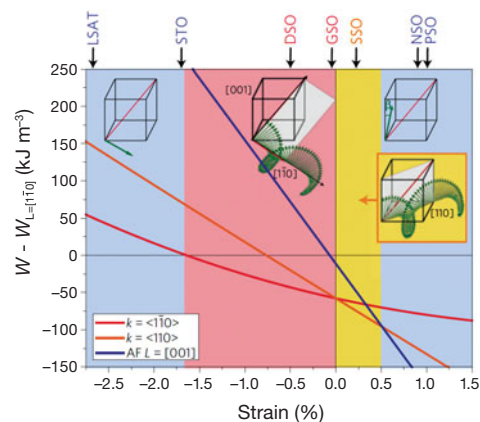
Epitaxial strain tunes spintronic behavior of multiferroic BiFeO₃

Researchers in pursuit of higher density memories have set their sights on a new generation of spintronic materials, in which both electron charge and spin are used to convey information. The magnetoelectric multiferroic BiFeO₃ (BFO), which exhibits direct coupling between ferroelectric and antiferromagnetic order, is particularly interesting for such an application. However, the complex interplay of strain and magnetic response in this system is only poorly understood. Now, Daniel Sando and colleagues at the Unité Mixte de Physique CNRS/Thales shed light on the fundamental mechanisms governing antiferromagnetism and demonstrate tunable control of this ordering for spintronics devices.

As described in the April 28 online edition of *Nature Materials* (DOI: 10.1038/nmat3629), the researchers first deposited 70-nm thick BFO films onto differ-

ent substrates using pulsed laser deposition, thereby imparting different in-plane strain states ranging from -2.6% compressive to 1.3% tensile strain. They next probed the hyperfine interactions of ⁵⁷Fe nuclei in BFO using Mössbauer spectroscopy, which allowed them to access the local magnetic environment around the Fe³⁺ ions. The results showed that at high strains, the typical helical antiferromagnetic spin cycloid vanishes.

To better understand this, the researchers conducted Landau-Ginzburg and effective Hamiltonian theory calculations. These demonstrate that at low strain states one of two spin cycloid orderings is stable, while at higher strains a collinear antiferromagnetic ordering is preferred. The researchers confirmed these results using Raman spectroscopy and tested the effect of these strains on magnetic hysteresis. It is therefore possible to greatly change exchange bias and giant magnetoresistance (GMR) using strain. This understanding suggests that coupling BFO to a piezoelectric material such as PbZr_xTi_{1-x}O₃



Proposed magnetic phase diagram for BiFeO₃ as a function of strain state. For strains ranging from -1.6% to 0.5%, a Type-I (red) spin cycloid with wave vector along $[1\bar{1}0]$ or a Type-II (orange) spin cycloid with average wave vector along $[110]$ is preferred. However, at higher strains a collinear antiferromagnetic ordering (blue) is preferred. Reproduced with permission from *Nature Mater.* (2013), DOI: 10.1038/nmat.3629. © 2013 Macmillan Publishers Ltd.

(PZT) could enable antiferromagnetic ordering to be dynamically tuned, for use in a range of exciting device applications.

Steven Spurgeon

Energy Focus

Tetrathiafulvalene mediates oxidation, reduces polarization in Li-O₂ energy batteries

Non-aqueous Li-air (O₂) batteries promise a significantly higher theoretical energy-storage density than conventional lithium-ion batteries. However, major increases in the lithium-oxygen round-trip charging/discharging efficiency and cycle life are needed before lithium-air batteries become viable.

When a Li-O₂ battery discharges, electrons, lithium ions, and oxygen gas react to form nanoparticles of Li₂O₂, and the opposite may be expected when the battery charges. However, transporting charge between the Li₂O₂ particles and the solid electrode surface is very difficult, and in practice, most of the Li₂O₂ polarizes, preventing the battery from completely recharging. Reporting online May 12 in *Nature Chemistry* (DOI: 10.1038/NCHEM.1646), Y. Chen, S.A. Freunberger, Z. Peng, O. Fontaine, and P.G. Bruce

from the University of St. Andrews, Graz University of Technology, Chinese Academy of Sciences, and Université Montpellier may have found a solution to the polarization puzzle in the form of a redox mediator, tetrathiafulvalene (TTF).

In a discharging Li-O₂ battery, oxygen accepts electrons (reduces) when it forms lithium peroxide in the porous electrode bathed in non-aqueous electrolyte. When the battery charges, only the surface of the nanoparticles in direct contact with the electrode readily gives up electrons (oxidizes). Realizing that they could prevent polarization and increase charging if they could find a way to oxidize all of the Li₂O₂ particles, the researchers identified TTF as a highly promising mediator.

They surmised that upon charging, TTF adjacent to the electrode and in the electrolyte would first be oxidized to TTF⁺. The TTF⁺ would then in turn oxidize Li₂O₂ across its entire surface, while simultaneously transforming the mediator back to TTF. The mediator would create more efficient electron transfer.

In identical Li-O₂ test cells with and without the mediator, the TTF cells maintained low, steady voltages on cycling across a range of charging rates. The porous TTF test cell electrode had the equivalent capacity of a carbon electrode with 3000 mAh/g carbon. Up to the highest charging rate, the cells with TTF allowed stable cycling for 100 cycles while the cells without TTF were impossible to charge. Using infrared spectroscopy, surface-enhanced Raman spectroscopy, and differential electrochemical mass spectrometry, the researchers showed that the electrochemical results came from the formation and oxidation of Li₂O₂ and not just TTF.

Explaining that TTF is just one of a whole range of potential mediators, the researchers state that “[this study] demonstrates the feasibility of using a redox mediator to oxidize Li₂O₂ in a Li-O₂ cell and thereby overcome the difficulty of an inherently insulating active material.”

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