# Measurements and Predictions of Local Structure

Objective

Our goal is to provide analytical tools that allow measurement and prediction of local structure to enable the development of ceramic materials for electronic applications. Under this project, we develop data analysis methods for quantitative determination of local structure from multiple experimental techniques, and theoretical methods for prediction of local atomic configurations from first principles.
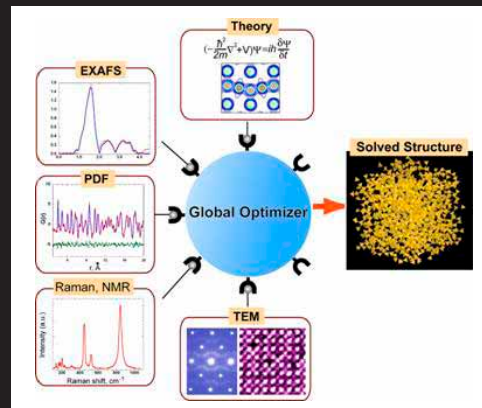

Impact and Customers

- The availability of methods and analytical tools for measuring local structure will accelerate the formulation of structure-property relations for advanced electronic ceramics and allow more rapid selection and optimization of these materials, thereby decreasing the development time for new electronics devices.
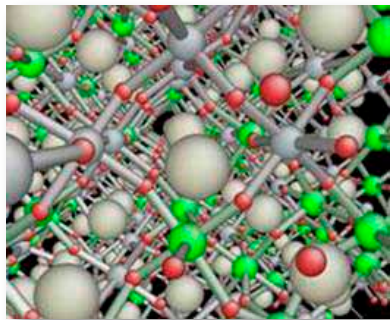
- Computer software for simultaneous refinements of atomic arrangements using diffraction and x-ray absorption fine structure data was developed and transferred to our partners at the ISIS pulsed neutron and muon source in the United Kingdom, for web posting.

- An invited review article in Science, which described the problem of solving structure at the nanoscale, followed by input from scientists from industry (e.g., GE, Exxon/Mobil, Ford, IBM, Sematech), government agencies, and universities, inspired a NIST workshop, "Measurement Needs for Local Structure Determination", that took place in February, 2008.

Approach

Electronic ceramics enable applications in the computer, data storage, and wireless communication sectors. The properties of many of these ceramics are critically dependent on deviations of local atomic arrangements from the global average of the crystal. No single measurement technique can provide an accurate description of the local structure. Therefore, our efforts focus on developing analytical tools (methods and software) that allow integration of measurements from multiple experimental methods, and theory to enable accurate and comprehensive determination and prediction of local atomic configurations. Specifically, we develop methods and software for structural refinements using simultaneous fitting of diffraction and x-ray absorption data, and modeling tools for *ab initio* simulations of diffuse scattering in systems with nanoscale order, Raman spectra in systems with local disorder, and point defects and their complexes in oxide dielectrics. All of this input is needed for the determination of local structure in electronic ceramics.

CERAMICS

NIST

Materials Science and Engineering Laboratory
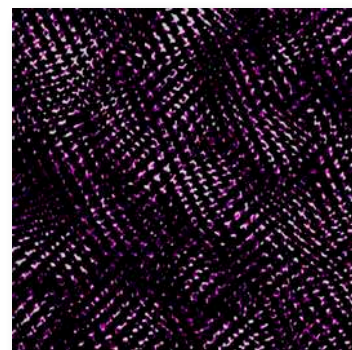
Accomplishments

Electronic ceramics with the perovskite structure are widely used in functional device applications. Most of the technologically relevant perovskites are solid solutions and therefore their local atomic arrangements necessarily deviate from those described by the average crystallographic positions. These local deviations control the functional properties of such perovskites; therefore, accurate knowledge of the local structure is needed to determine structure-property relationships.

Relaxor ferroelectrics represent a prominent example of technologically useful materials that crystallize with perovskite-like structures. The origin of the relaxor behavior has been a topic of intense research for over a decade. These materials exhibit both chemical and polar inhomogeneity that give rise to diffuse X-ray and neutron scattering, which therefore provide useful probes of local structure. We have greatly improved existing models of the classical relaxor ferroelectric $Pb(Sc_{0.5}Nb_{0.5})O_3$ by developing simulations of diffuse scattering based on first-principles calculations. Our simulations reproduced major features of experimental diffuse scattering. The
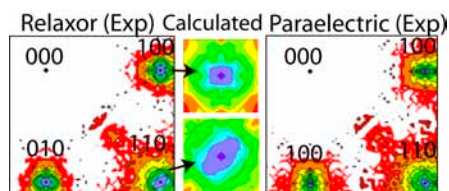

Experimental and calculated diffuse scattering

relaxor phase exhibits "butterfly" and rod-like shapes of diffuse scattering around the [100] and [110] reflections, respectively, whereas the high-temperature paraelectric phase exhibits radial diffuse streaks around all the Bragg peaks. We have determined that the rod and butterfly features arise from polar nanoregions, whereas the radial streaks originate from atomic displacements associated with chemical disorder. This work illustrates the power of a combined experimental and theoretical first-principles based approach to the local-structure problem.

We have significantly extended the capabilities of the software for combined quantitative refinements of local structures using simultaneous Reverse Monte Carlo fitting of the neutron and X-ray total scattering and X-ray absorption fine structure (EXAFS) data. The latest version of this software incorporates a new algorithm that allows for the explicit treatment of multiple-scattering effects in EXAFS thereby enabling accurate modeling of the EXAFS data over distances encompassing several coordination shells around the absorber atoms. The software was tested using several model systems, including Ni and the complex perovskite $Sr(Al_{0.5}Nb_{0.5})O_3$, and, as a next step, will be applied to the technologically relevant $Ag(Nb,Ta)O_3$ dielectrics whose exploitable properties are dominated by local-structure effects.

In February 2008, we organized a NIST workshop on "Measurement Needs for
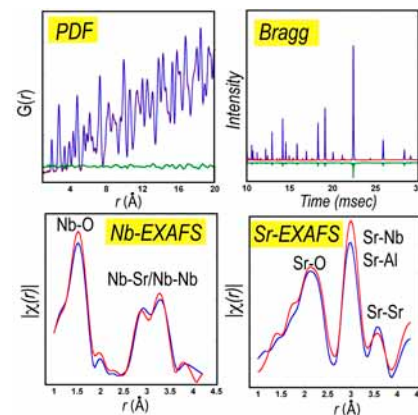
Simultaneous fits of multiple types of data for $Sr(Al_{0.5}Nb_{0.5})O_3$

Local Structure Determination in Inorganic Materials." This 2-day meeting brought together experts in the key experimental and theoretical areas relevant to local-structure measurements. The group included representatives of several major industrial sectors, academia, government labs, DOE, and NSF. The participants unanimously agreed that solving the local-structure problem – an important frontier in materials characterization – necessitates a coordinated interdisciplinary effort that transcends the existing capabilities of any single institution, including national laboratories, centers, and user facilities. Development of methodology and software for: (1) combining inputs from multiple techniques and theory in a global modeling framework, and (2) theoretical modeling of nanoscale structures and their measurement responses, were identified as the highest priority issues.

Learn More

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Publications

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Burton BP, Cockayne E, Tinte S and Waghmare UV The Effect of Nearest Neighbor [Pb-O] Divacancy Pairs on the Ferroelectric-Relaxor Transition in $Pb(Sc_{0.5}N_{0.5})O_3$ Phys. Rev. B, 77: 144114 (2008)