Powder Diffraction Group

Description:

The Powder Diffraction Group uses high-resolution synchrotron x-ray and neutron powder diffraction to investigate the structure of multifunctional complex materials with exciting magnetic, electronic, dielectric and catalytic properties. Our main activity is basic research to understand the structural response of crystalline matter to variations of pressure, temperature, composition and electric fields using beam line X7A at the National Synchrotron Light Source as our main facility. Powder diffraction is *the* prime tool for structural investigations in Materials Science. Since suitable single crystals of complex and new materials are seldom available in the early stages of research all structural information must be obtained using polycrystalline materials. At the same time, information about nanoscale properties of materials (texture, particle size, stacking faults) can also be acquired by powder diffraction. A new program to explore the unique pressure-induced chemistry, taking place in nanopores has been initiated. A small in-house chemical synthesis effort is also maintained, and provided the first MgB_2 samples at BNL. We intend to expand this effort and are currently in the process of hiring a synthetic chemist. A strong collaborative program is maintained with groups at BNL as well as with national and international academic and industrial groups specialized in synthesis and crystallography of novel materials.

Scientific Highlights:

- Discovery of a monoclinic phase at the morphotropic phase boundary in PZT and related piezoelectrics. Noheda et al. Appl. Phys. Lett. 74(14), 2059 (1999)
- First combined theoretical and experimental study on MgB_2 revealing nearly isotropic mechanical and BCS-like behavior under pressure. Vogt et al Phys. Rev B63, 220505(R) (2001)
- First structural confirmation of pressure-induced hydration in nanoporous materials. Y.Lee et al JACS in print and J.A. Hriljac et al submitted to Science
- Structural characterization of dumbbell substitution in novel, environmentally benign and economically competitive non-stoichiometric battery electrodes $La(Ni,Sn)_{5+x}$ Vogt et al Electrochem. Sol. State Lett. 2, 111 (1999), Reilly et al U.S. patent 6,238,823
- Demonstrated intrinsic and extrinsic phase separation in $Ca_{1-x}Bi_xMnO_3$ and $Nd_{1/2}Sr_{1/2}MnO_3$ Santosh et al Phys. Rev B62, 14928 (2000) and Woodward et al Chem. Mat. 11, 3528 (1999)
- Unraveled complex interplay of charge-order induced spin-state transitions in $YBaCo_2O_5$ and $TbBaFe_2O_5$ .Vogt et al Phys. Rev. Lett. 84, 2969 (2000),Karen et al Phys. Rev. B64,214405 (2001)
- A novel type of wafer-based composite neutron monochromator first implemented at the high-resolution neutron powder diffraction beam line (H1A) at the HFBR is nowadays used at major steady state neutron sources such as Institute Laue-Langevin, the SINQ facility at the Paul Scherrer Institut in Switzerland and will be utilized in instruments at the Replacement Research Reactor in Sydney, Australia and the FRM-2 reactor in Munich, Germany.

Impact:

In the last three years the group made significant contributions to our understanding of piezoelectric materials, charge and spin ordering in doped metal oxides and non-stoichiometric alloys used in nickel-metal hydride batteries. The Powder Diffraction group remains one of the leading groups worldwide in high-resolution powder diffraction.

Interactions:

- U.S.: Ohio State University, Delaware University, Michigan State University, SUNY Stony Brook, Oregon State University, University of Illinois, Chevron Corp.
- International : Universities of Oslo, Sydney, Sendai, Munich, Madrid, ANSTO & PSI

Personnel:

Tom Vogt (Physicist), Beatriz Noheda (Assistant Physicist), Yongjae Lee (since 10-1-01, Research Associate)

Recognition:

85 peer-reviewed articles, 15 invited talks, 2 invited book chapters, 1 US patent granted, 1 pending, 1 invention disclosure, 2001 Barrrett Award (D.E. Cox, emeritus), Brookhaven Lecture (T. Vogt), Popular Mechanics 2002 Design and Engineering Award (collaboration with J. Reilly, MSD), member of the International Advisory Team at the Replacement Research Reactor project in Sydney (T. Vogt)

Budget: 278K+150K

Current Staff

Tom Vogt (Physicist, Group Leader)	X-ray synchrotron and neutron powder diffraction, crystallography, structural and synthetic solid-state chemistry, high-pressure x-ray and neutron diffraction
Beatrz Noheda (Assistant Physicist)	Piezoelectrics, ferroelectric materials, diffraction under electric fields, heterostructures and thin films
Yongjae Lee (Research Associate)	Synthesis and crystallography of micro- and mesoporous materials, X-ray and neutron powder diffraction, high-pressure x-ray and neutron powder diffraction
Dave E. Cox(Emeritus)	continues to collaborate on piezoelectrics and ferroelectric materials
Al Langhorn (Sr. technical specialist)	
Sharon Smith (1/3 Secretary)	

Funding from other sources:

Industry (40K, part of A. Langhorn's salary),
LDRD "Pressure in nanopores" (80K, Y. Lee)

Research facilities:

High-resolution 6-circle diffractometer X7A at the NSLS operated in four principle modes:

1. The high-resolution mode where a water-cooled Si(111) monochromator and a Ge(220) analyzer provides a resolution of ?d/d = 2 x 10^{-4}. This configuration is used for ab-initio solution of complex structures, investigations of phase transitions (subtle lattice distortions, weak superlattice reflections) and studies involving diffraction in the vicinity of absorption edges.
2. The high-throughput mode using a linear position-sensitive detector gating on the Kr-escape peak built by Graham Smith (Instrumentation, BNL) without an analyzer crystal. The lower resolution (?d/d~10^{-3}) allows for much higher counting rates from smaller samples or much faster data collection as a function of temperature. Typically samples are investigated as a function of temperature between 20 and 700K.
3. The PDF-mode, where a semiconductor detector is employed. Compromising resolution even further but providing good counting statistics combined with reasonable energy discrimination provides data for pair-distribution function (PDF) studies.
4. The high-pressure mode using a triangular asymmetrically cut Si(220) monochromator, which is bent cylindrically by applying a force to the crystal tip. This configuration is used to provide a horizontally focused beam of about 0.7 Angstrom to measured samples in diamond-anvil cells at room temperature and as a function of temperature.

Future Plans:

Powder Diffraction involving substantial beam line upgrade and innovation of sample environment:

- Beyond 'classical crystallography" – combined pair distribution analysis of x-ray and neutron powder diffraction data. (new detectors, higher energies, 'smarter analysis')
- Time-dependant powder diffraction (detector electronics, optics, sample environment)
- High Temperature Powder Diffraction (image furnace, thermometry)
- Systematic Studies of high pressure phase transitions in oxides, alloys and soft matter

Nanoscience & Synthesis:

- Hybrid organic-inorganic materials, Quantum-confined nanostructures under pressure
- Ferroelectric oxide heterostructures
- Search currently being conducted for a synthetic chemist

Principal Collaborators outside BNL:

D. Buttrey	Dept. of Chemical Engineering, U. Delaware
A.K Cheetham	Materials Science Dept., U. California, Santa Barbara
M. Crawford	DuPont Corp.
T. Egami	Physics Dept. Penn State Univ.
P. Fischer	SINQ, Paul Scherrer Institut, Switzerland
B. Hunter	Australian Nuclear Science & Technology Orgganization, Sydney, Australia
J.A. Hriljac	Chemistry Dept. University of Birmingham, United Kingdom
P Karen	Chemistry Dept. Oslo University, Norway
B. Kennedy	Chemistry Dept. Sydney University, Australia
T. Kriven	Dept. of Materials Science and Engineering, University of Illinois
Ron Medrud	Chevron Corp.
S. Moss	Physics dept. Universit of Houston
J. Parise	SUNY, Stony Brook
V. Petkov	Dept. of Physics and Astronomy Michigan State University, East Lansing
A.W. Sleight	Chemistry Dept. Oregon State University
P. Woodward	Chemistry Dept. Ohio State University Columbus

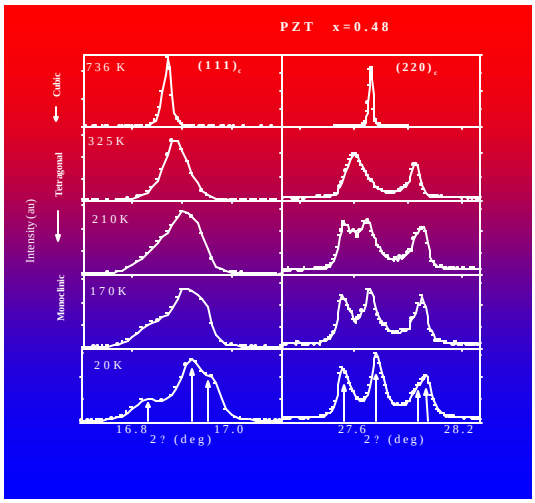
Internal BNL collaborations:

J. McBreen (MSD, metal hydrides),
G. Schneider & R. Werner (MgB_2, AB_{5+x}, nanopores, complex oxides, Theory),
A. Moodenbaugh (MSD, superconductors),
M. Huecker & G. Shirane (Neutron Scattering, nickelates, piezoelectrics),
C Homes & P. Johnson (PES, $CaCu_3Ti_4O_{12}$, MgB_2)
J. Hill & B. Ocko (X-ray Scattering, ferroelectrics)

The monoclinic phase in $PbZr_{1-x}Ti_xO_3$

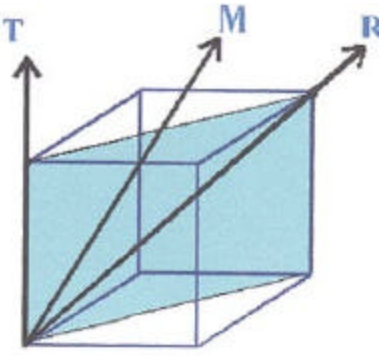
B. Noheda, G. Shirane, D.E. Cox (BNL) & S-E. Park, R. Gua, L.E. Cross (Penn. State U.)

Piezoelectric materials deform in the presence of an electric field and generate an electric field when deformed. This forms the basis of operations for electromechanical actuators. Work at X7A at the NSLS has radically changed the way we think about piezoelectricity. Noheda et al (Appl. Phys. Lett. 74, 2059) demonstrated the existence of a novel monoclinic phase in $PbZr_{1-x}Ti_xO_3$ (PZT) near the morphotropic phase boundary at x~0.5. For more than four decades, this boundary has been regarded as the dividing line in the phase diagram between regions having rhombohedral and tetragonal symmetry, and the discovery of this new phase of lower symmetry was unexpected.

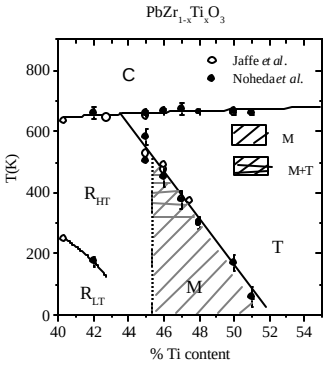


Subsequent studies have provided a microscopic picture in which the monoclinic phase serves as a "bridge" between the rhombohedral and tetragonal structures. Studies done with an electric field applied in situ have demonstrated that, around the monoclinic phase, the direction of the polarization can change under field. The outstanding performance of the oxides is due to the fact that the direction of polarization is not constrained to a unique crystallographic symmetry axis, but is free to rotate within the monoclinic symmetry plane.

Polarization rotation in the monoclinic plane



Phase diagram of $PbZr_{1-x}Ti_xO_3$

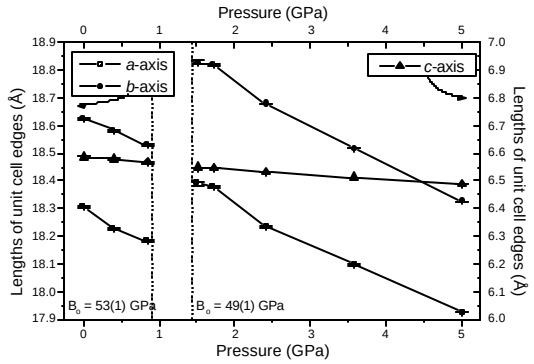


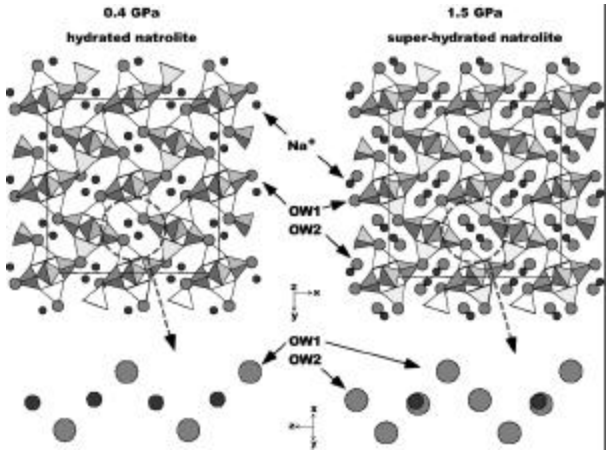
Noheda et al. PRL 86, 3891(2001), PR B61, 8687(2000), PR B63, 014103(2000), Appl Phys Lett. 74, 2059 (1999), Ferroelectrics 237, 237 (2000,) & Guo et al PRL 84, 5423 (2000)

Pressure-Induced Chemistry in Nanopores

Y. Lee, T. Vogt (BNL), J. Hriljac (Univeristy of Birmingham,UK), J. Parise (SUNY Stony Brook)

Our knowledge of pressure-induced phase transitions in meso- and microporous materials is very limited compared to the vast number of temperature-dependent studies performed over the past several decades. This is partly due to the required experimental complexities as well as the analytical ambiguities arising from the porous nature of the materials, which can lead to compositional changes upon interaction with pressure-transmitting media. Applying external pressure can alter the chemical environment within the pores. Powder diffraction data of natrolite, $Na_{16}Al_{16}Si_{24}O_{80}\cdot 16H_2O$, were measured as a function of pressure up to 5.0 GPa using a diamond-anvil cell and a 200 µm-focused monochromatic synchrotron X-ray beam. Upon pressure increase, there is an abrupt *volume expansion* (ca. 2.5 %) between 0.8 - 1.5 GPa, but no accompanying change in space group (***F****dd*2). Rietveld refinements using framework geometrical constraints reveal that this anomalous swelling is due to the *selective sorption* of water from the alcohol-based pressure-transmitting media into the expanded channels. This gives rise to a "superhydrated" phase of natrolite with an approximated formula of $Na_{16}Al_{16}Si_{24}O_{80}\cdot 32H_2O$, which contains infinite chains of hydrogen-bonded water molecules along the channels. This is the first structural investigation of a super-hydrated zeolite.





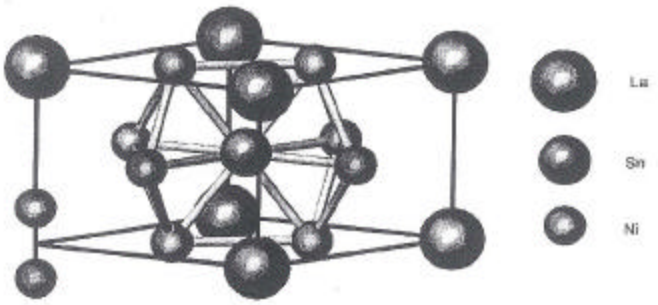
The applications for materials that show this type of behavior under moderate pressures are tremendous:

- Immobilization of radioactive and/or toxic ions under pressure. Pores are larger under pressure and allow large cations to diffuse in. After pressure release pores will shrink and the exchanged cations which will be trapped inside the nanopores ("pressure-induced trap-door mechanism")
- "High Pressure Drying" due to selective absorption of H_2O allows separation from organics without heating.
- Selective absorption of tritiated water (THO) in liquid radioactive waste management
- In other systems we identified systems where pressure up to 15 kbar do not lead to an expansion of the volume of the unit cell. These zeolites can be used on glass or silicone substrates as membranes for the selective separation of water.

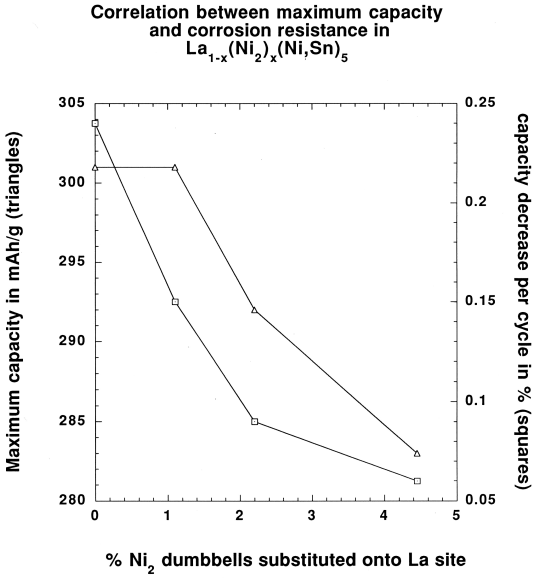
Lee et al. JACS 123, 8418 (2001), JACS in print, Science submitted

Dumbbells in Non-Stoichiometric AB_{5+x} alloys used as battery electrodes.

Nickel-metal hydride batteries are environmentally benign alternatives to nickel-cadmium and lead-based batteries and are currently used in consumer electronics, lab tops and hybrid vehicles (e.g. Toyota Prius). The anode in commercially available anodes contains cobalt in order to reduce corrosion; however cobalt is expensive (10 weigh% of Co leads to 50% of the cost of an electrode). The recent discovery at BNL of long lasting cobalt-free alloys (Vogt et al, Elelctrochem. Sol. State letters 2,111(1999),Reilly et al U.S. Patent No. 6,238,823) prompted structural investigations to explore the details of these non-stoichiometric compounds. The substitution of La atoms by Ni_2 dumbbells and the accompanying relaxation of the lattice were identified as the key to the remarkable corrosion resistance of these materials.



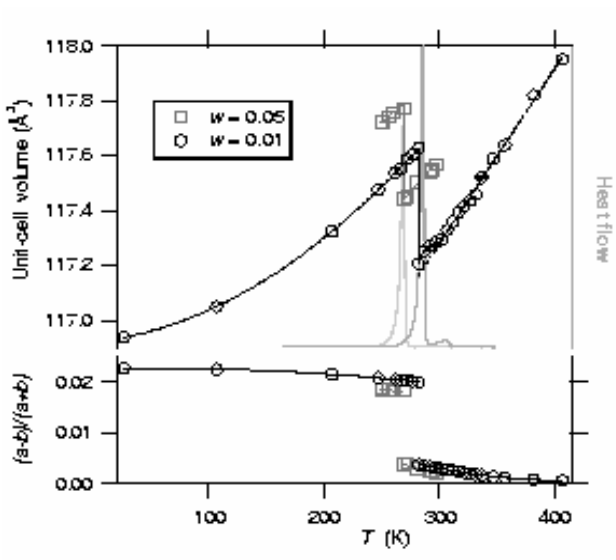
In collaboration with G. Schneider (Theory/BNL) LDA calculations are being performed to correlate the dynamics of the dumbbells to the motion of dislocations and the superior resistance of these materials towards electrochemical corrosion.

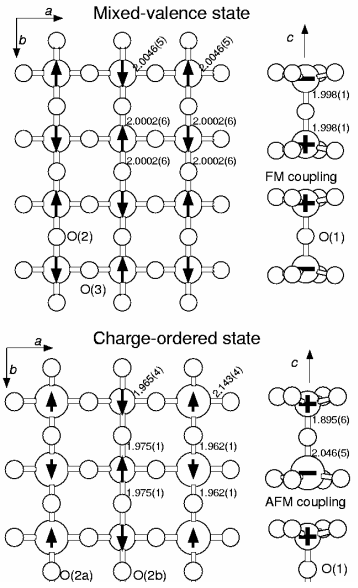


Vogt et al Electrochem. Solid State Lett. 2, 111 (1999), Reilly et al J. Alloys Comp. 293-295, 569 (1999)

$TbBaFe_2O_5$ – Two attempts to order charges.

Interest in charge-ordering occurring in mixed-valence oxides has been revived recently due to the interplay between electron localization and spin interaction in manganites where a ferromagnetic metallic state transforms into an insulating antiferromagnetic state. We extend these studies to systems containing cobalt ($YBaCo_2O_5$, Vogt et al PRL 84(13), 2969) and iron ($TbBaFe_2O_5$, Karen et al PRB in press)). Two distinct phase transitions in close proximity were identified in $TbBaF_2O_{5+w}$ ($0<w<0.05$) and their thermodynamic and transport properties were characterized including both the local and long range magnetic and nuclear structures. Upon cooling below 320K, spontaneous orbital ordering takes places in an antiferromagnetically ordered structure in which two mixed valence iron states ($Fe^{<+2.5}$ and $Fe^{>+2.5}$) with distinct magnetic and electric field tensors coexist. The lattice in this transient phase does not change symmetry but a minute and continuous volume change due to magnetostriction is observed. The antiferromagnetic Fe_2O_5 slabs are involved in a ferromagnetic coupling across the rare earth layer. Below 285K, a 'classical' Verwey transition is found where a large change in the unit cell volume, entropy and electrical conductivity occurs. The charge-ordered spins between the Fe_2O_5 slabs now show an antiferromagnetic interaction (G-type).





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