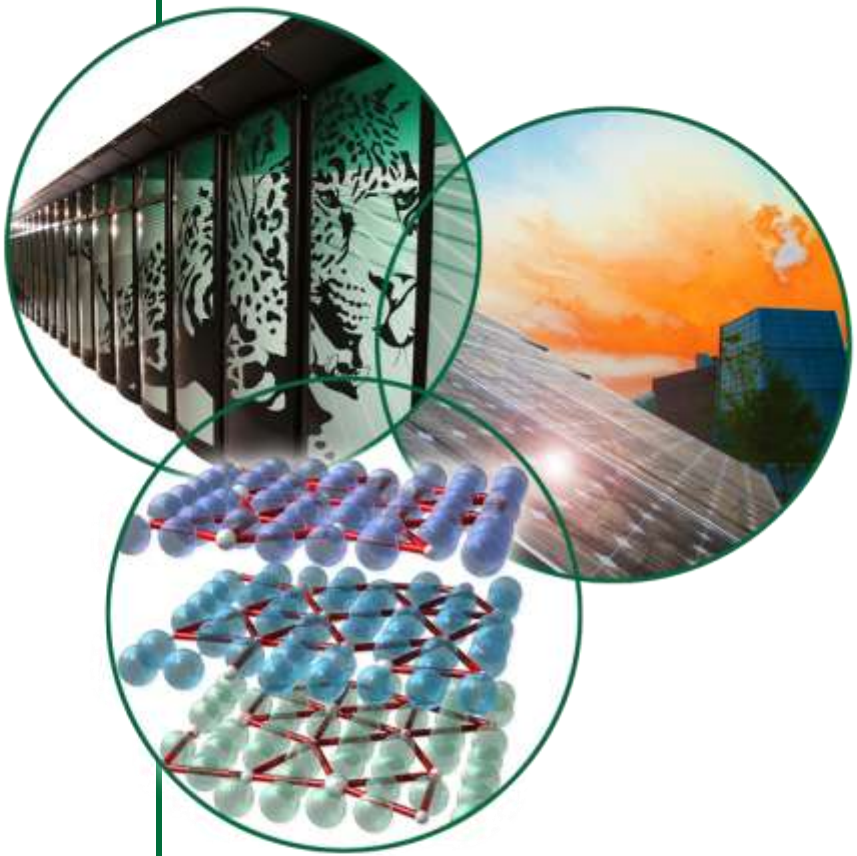
Structure Function Relationship of Energy Storage Materials



Ashfia Huq

NSSD SNS ORNL,

September 13, 2010

U.S. DEPARTMENT OF ENERGY

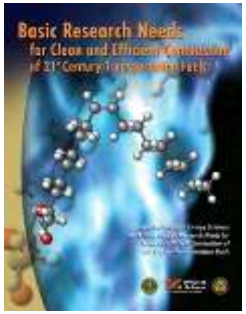
OAK RIDGE NATIONAL LABORATORY

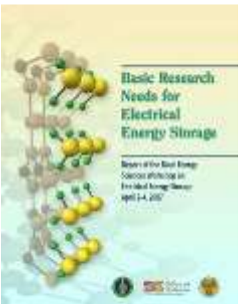
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

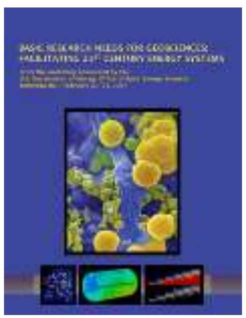
Outline:

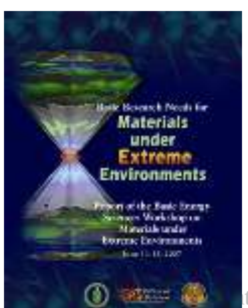
- Motivation
- Neutron Sample Environment Development
  - In-situ measurements to mimic operational condition.
- Intermediate Temperature SOFC (Structural and Physical Characterization)
  - New Cathode materials.
  - Proton Conductors (Electrolyte).
  - Anode materials for direct Hydrocarbon SOFC.

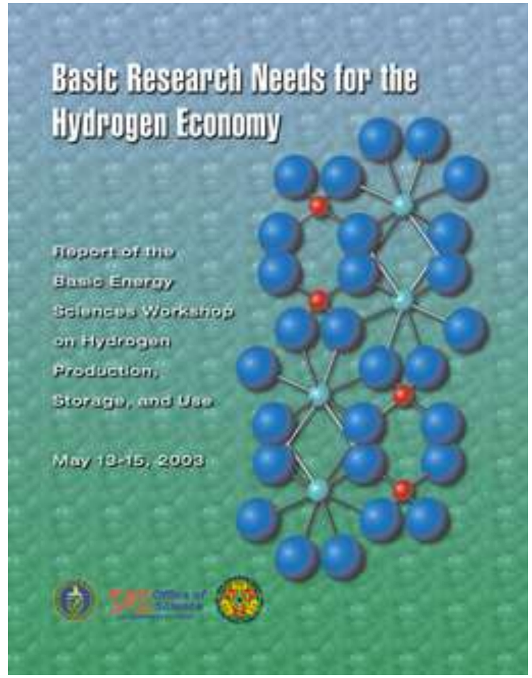
Grand Science Challenges:





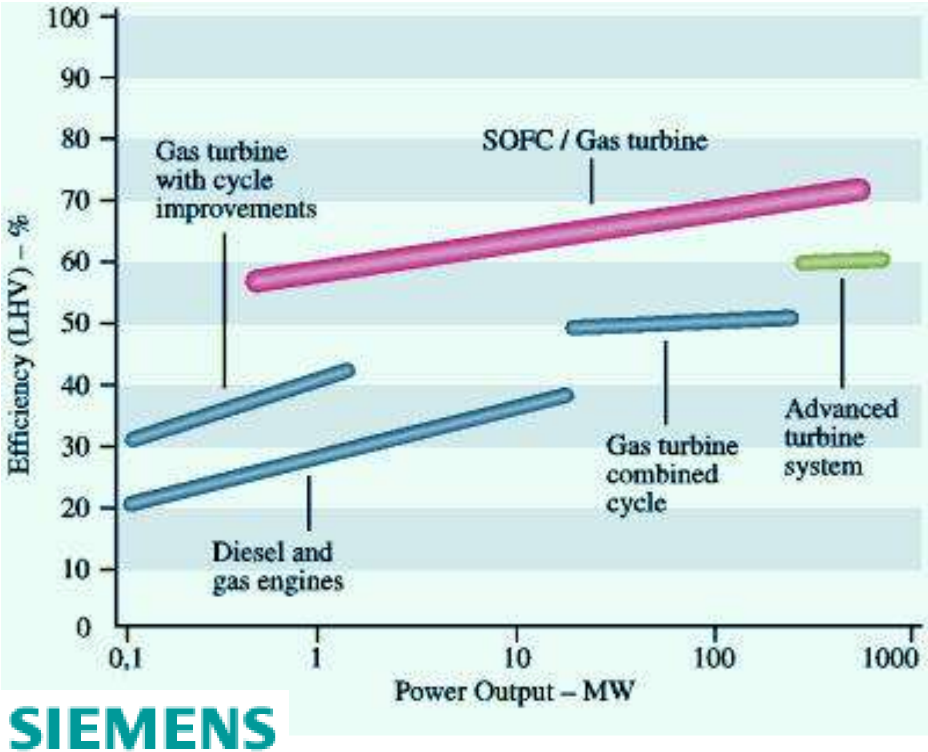






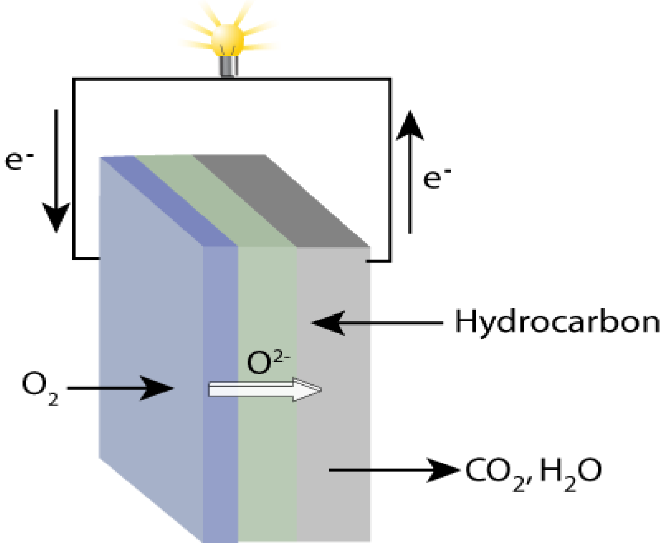
"Increasing the efficiency and affordability of fuel cells requires a better understanding of the molecular-level processes involved in oxidation and reduction at electrodes, catalytic processes, and ion and proton transport..... The performance of these components involves several size (nm to m) and time scales readily accessible with neutron scattering techniques."

Why use fuel cells?



- ✧ Fuel cells offer higher efficiency across a wide range of system size.
- ✧ Higher Energy density than batteries and recharged more quickly and easily.
- ✧ System is modular and potentially portable. Highly reliable & low maintenance. Scales with demand.
- ✧ Environmentally friendly.

Solid Oxide Fuel Cell (SOFC)



Electrolyte/Electrodes: Solid ceramic inorganic oxide

Fuel: Mixture of H_2 and CO (synthesis gas).

Operation Temp: 750-1000 °C

- **Cathode: Oxygen from air is reduced.**

$$O_2 + 4e^- \rightarrow 2O^{2-}$$

- **Anode: Oxidation of fuel. Current cells have a reformer to generate CO/H_2 fuels from hydrocarbons.**

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^-$$

Ideally we can utilize hydrocarbons directly:

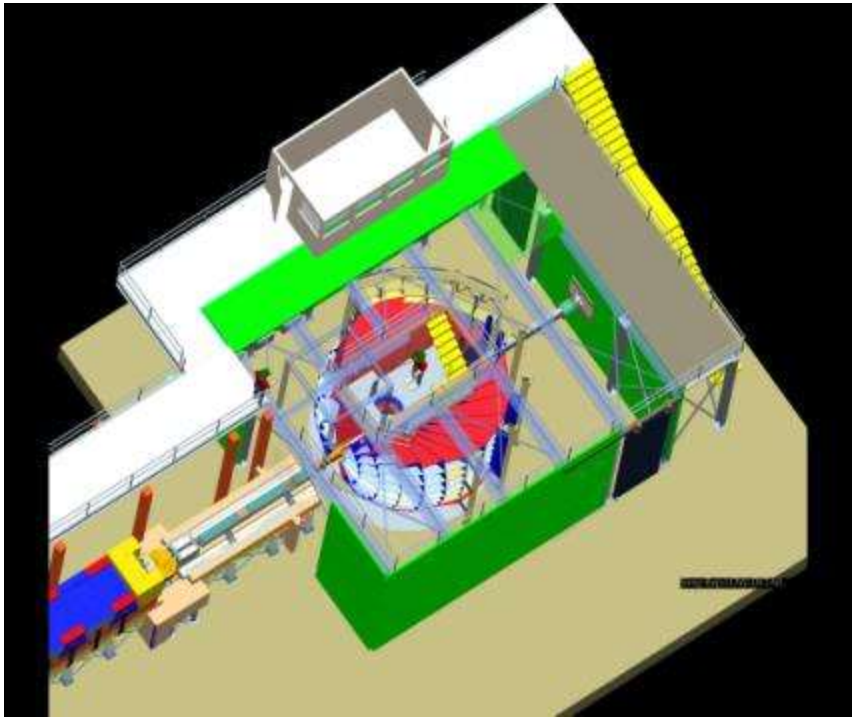
$$CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-$$

for the U.S. Department of Energy

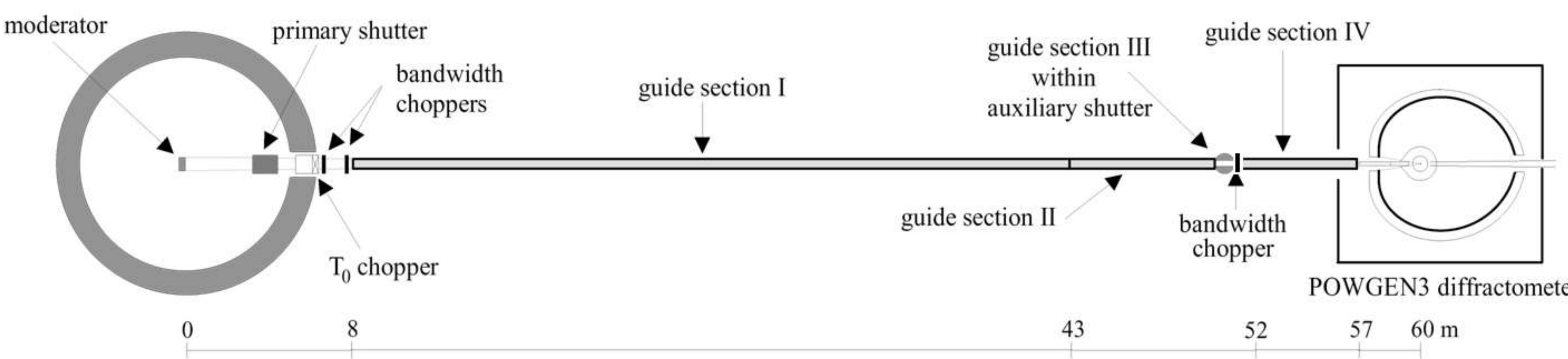
Current Materials Palette

- Cathode is a composite: Both electronic and ionic conductivity
  - $La_{0.8}Sr_{0.2}MnO_{3-\delta}$(LSM) and YSZ.
  - $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF)
- Electrolyte : Oxygen ion conductor but electronic insulator.
  - Yttria-stabilized Zirconia (YSZ)
  - 'Common' alternative is $Gd_{0.2}Ce_{0.8}O_{2.9}$ (shows some electronic conductivity)
- Anode : Electronic and ionic conductivity and catalytic activity
  - Ni-YSZ composite
  - Ni free anodes for direct hydrocarbon conversion such as $(La,Sr)_2M_{1-x}Cr_{1+x}O_{6-\delta}$

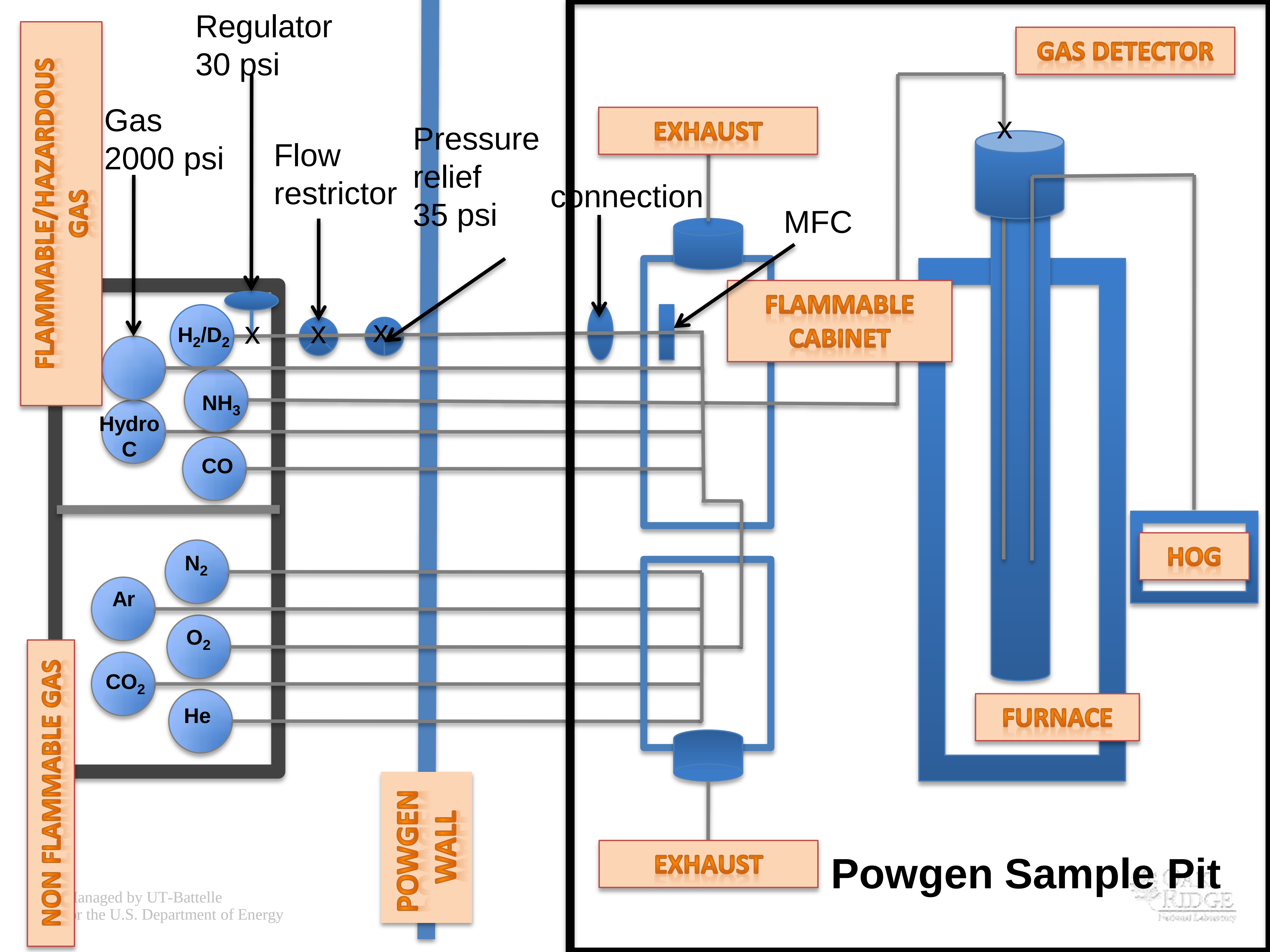
Powgen : Powder Diffractometer at SNS



Moderator	decoupled poison super critical H_2
Source to sample	60m
Sample to detector	1-6m
Detector angular coverage	6<2Θ<170 (current 20-130)
Total detector coverage area	44 m^2 (current 4m^2, 7.2 m^2 end of 2010)
Bandwidth	~1 Å
Frame 1	0.3Å - 10Å (0.3-4Å)
Frame 6	3 Å- 66 Å
Resolution	0.001<Δd/d<0.016

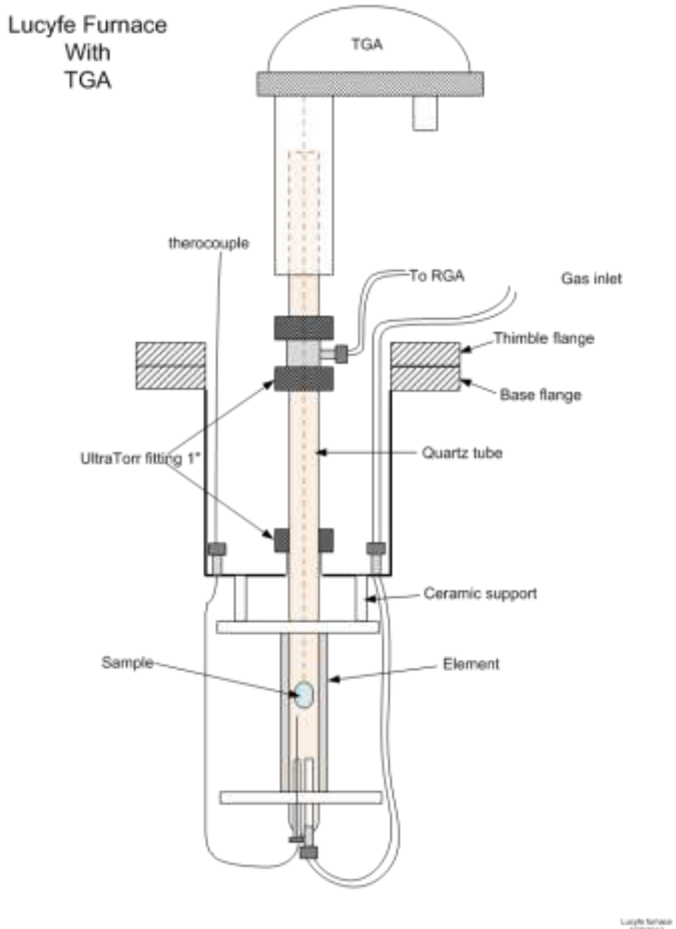


Sample environment for *in-situ* measurement at POWGEN



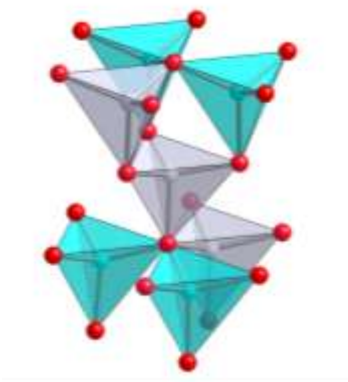
FLAMMABLE/HAZARDOUS GAS
Regulator 30 psi
Gas 2000 psi
Flow restrictor
Pressure relief 35 psi
connection
MFC
GAS DETECTOR
EXHAUST
FLAMMABLE CABINET
H2/D2
NH3
Hydro C
CO
N2
Ar
O2
CO2
He
HOG
FURNACE
NON FLAMMABLE GAS
POWGEN WALL
EXHAUST
Powgen Sample Pit

Dedicated Gas Handling system

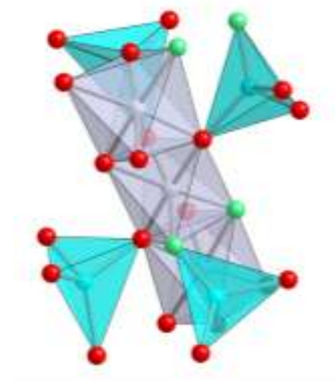


Intermediate Temperature SOFC

Work of Jung-Hyun Kim



$YBaCo_4O_7$



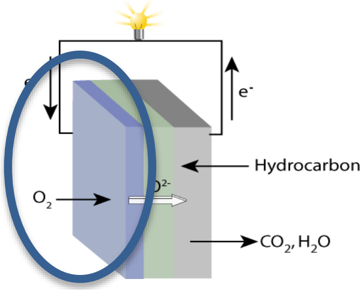
$YBaCo_4O_8$

Science Goals:

- Develop new cathode material for intermediate temperature SOFC.
- Characterize phase stability and it's dependence on ionic size.

O. Chmaissem, H. Zhen, A. Huq, P. W. Stephens, J. F. Mitchell, "Formation of Co^{3+} octahedra and tetrahedra in $YBaCo_4O_{8.1}$", ***J. of Solid State Chemistry* 181**, 664 (2008)

Ashfia Huq, John F. Mitchell, Hong Zheng, Laurent C. Chapon, Paolo G. Radaelli, Kevin S. Knight and P.W. Stephens, "Structural and magnetic properties of the Kagome antiferromagnet $YbBaCo_4O_7$", ***J. Solid State Chem.* 179**(4)**,** 1136 (2006)



New Low Thermal Expansion Mixed Ionic-Electronic Conductors

Objective: Need to reduce operational temperature (< 800C) to reduce materials cost.

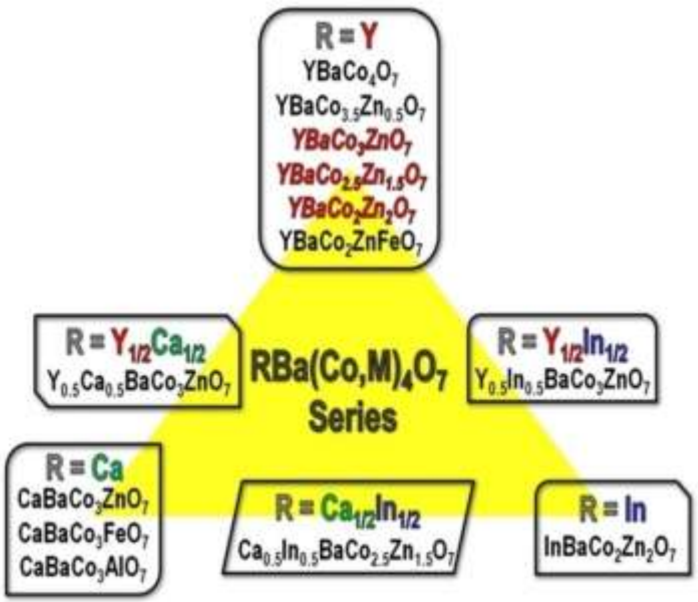
1. Mixed Ionic-electron conductivity (MIEC)
2. Oxygen Reduction Reaction (ORR)
3. Good Catalytic Activity
4. Thermal Expansion Coefficient (TEC) matched to Electrolyte.
5. OT < 800C

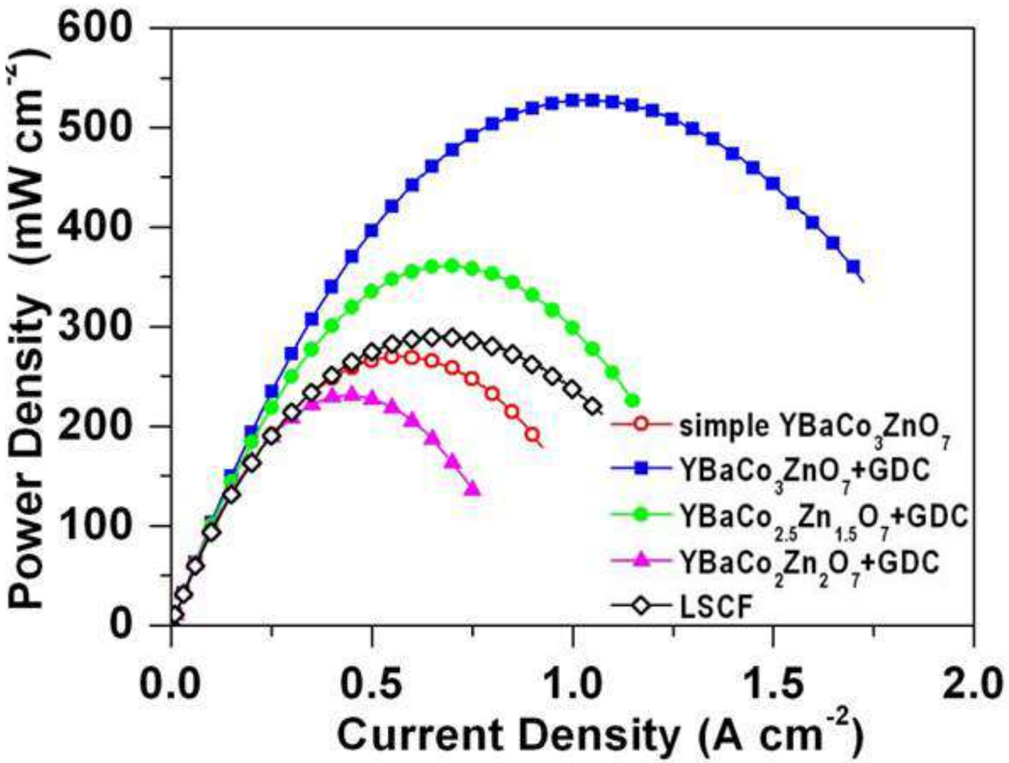
- ✧ LSM : Not 5, if 5 not 1 & 3
- ✧ LSCO ($La_{1-x}Sr_x(Co,Ni,Fe,Mn)O_{3-d}$) : Not 4, if 4 not 3
- ✧ **Doped $RBaCo_4O_7$: VERY PROMISING**

Single Cell Performance of $YBaCo_{4-x}Zn_xO_7$ Cathodes

Cell Configuration: Cathode | GDC | LSGM(0.5mm) | LDC | Ni+GDC

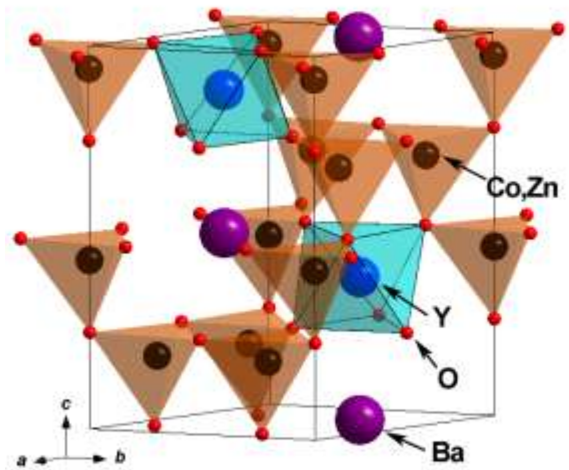
Diagram of the $RBa(Co,M)_4O_7$ Series



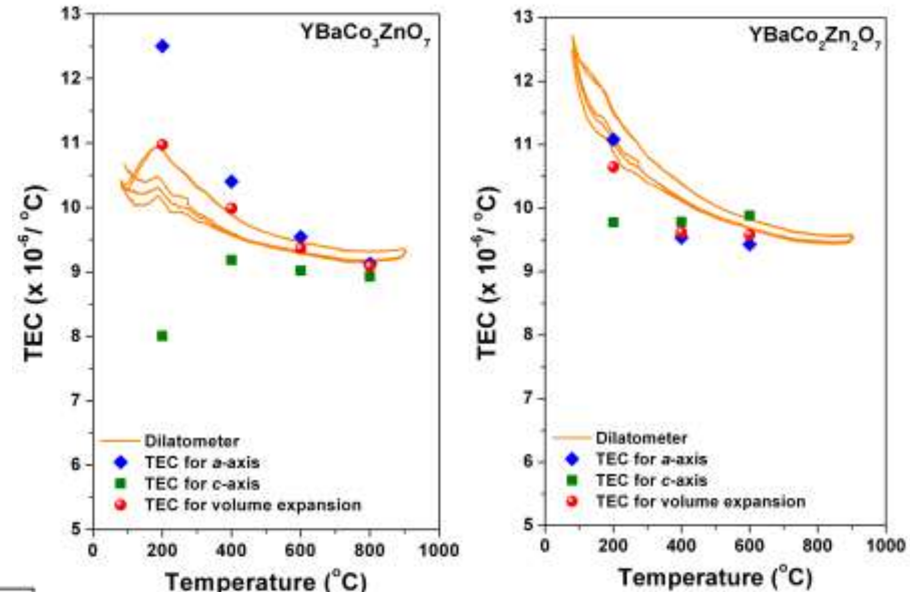


In situ Neutron Diffraction $YBa(Co,Zn)_4O_7$

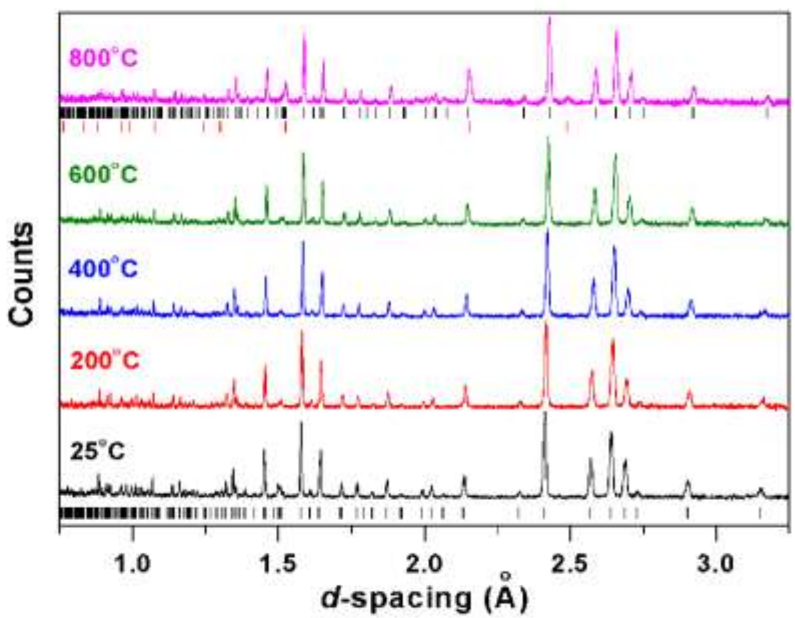
Crystal Structure



Thermal Expansion Coefficient (TEC)



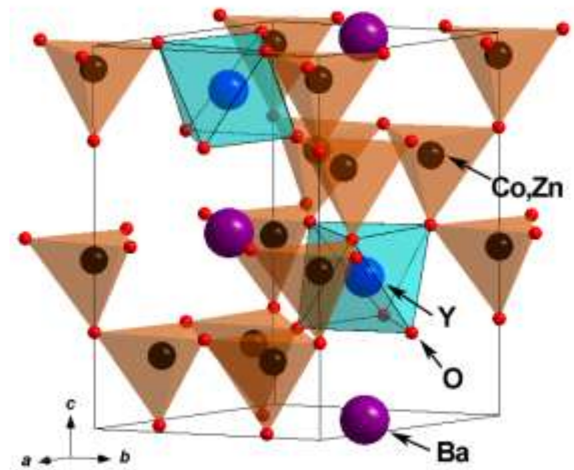
In-situ Neutron Diffractions



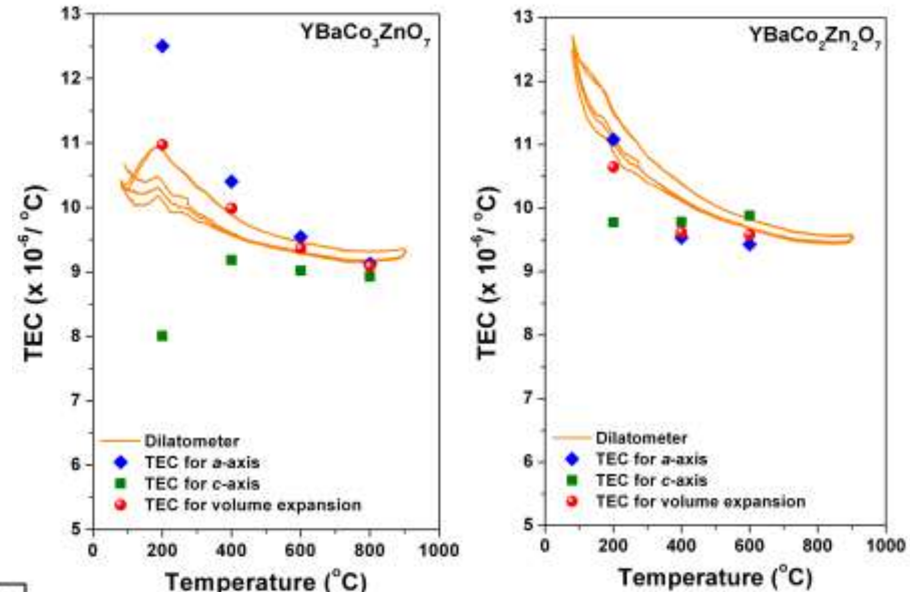
- *In-situ* neutron diffraction of the $YBa(Co,Zn)_4O_7$ was successfully measured in POWGEN at 25 – 800°C.
- TEC values obtained from *in-situ* neutron diffraction show a good agreement with dilatometer data.

In situ Neutron Diffraction $YBa(Co,Zn)_4O_7$

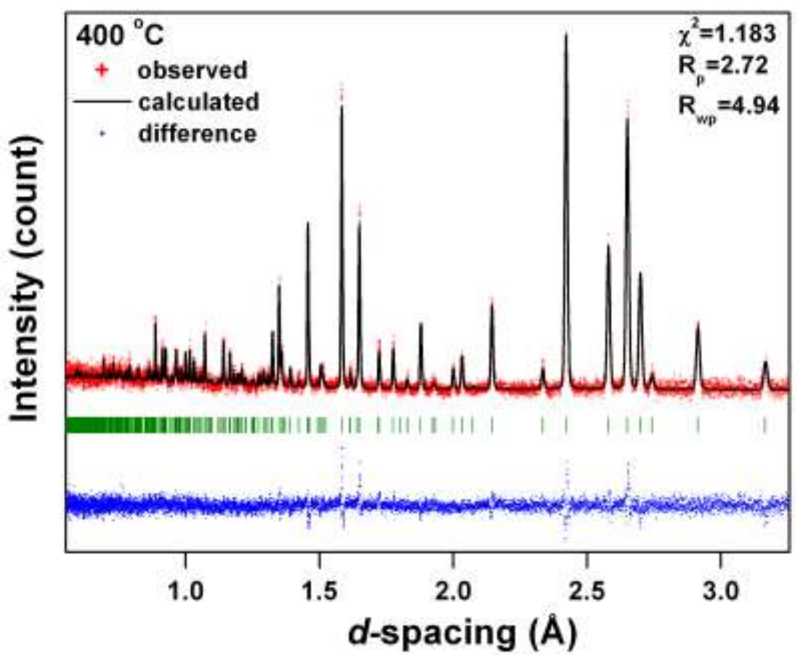
Crystal Structure



Thermal Expansion Coefficient (TEC)



In-situ Neutron Diffractions



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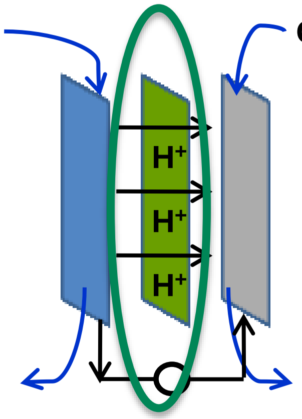


Oxygen reduction:

$\frac{1}{2} O_2 + 2e^-_M + 2OH_O^\bullet \rightarrow H_2O + 2O^X_O$

Hydrogen oxidation on a metallic site:

$2s_M - H + 2O^X_O \rightarrow 2OH_O^\bullet + 2e^-_M$

Proton Conduction SOFC

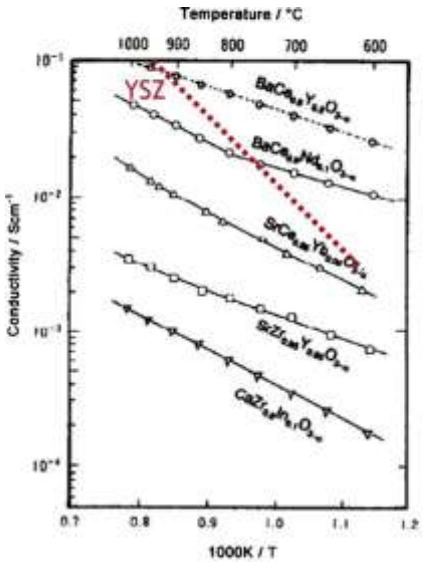
Work of Zhonghe Bi

Science Goals:

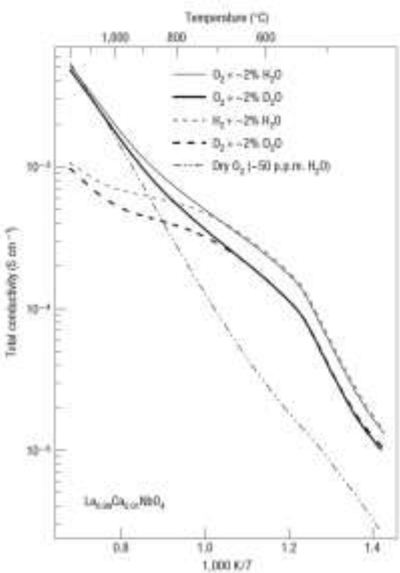
- Understanding the Structure, function properties of Ca-doped rare-earth ortho-niobates and ortho-tantalates that are more stable in CO_2 containing atmospheres.

- By changing doping concentration of different elements
  - Solve the thermal expansion problem caused by changes due to structural phase transitions.
  - Increase conductivity.

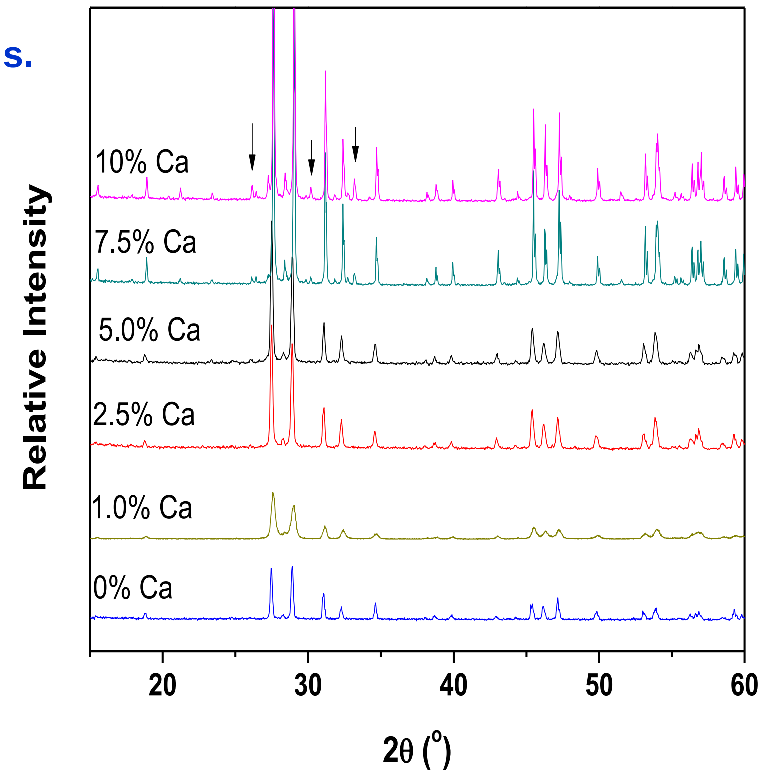
Characterization of the Ca-doped $La_{1-x}Ca_xNbO_{4-\sigma}$



Conductivity of major proton conducting family of compounds.



$La_{1-x}Ca_xNbO_{4-\sigma}$

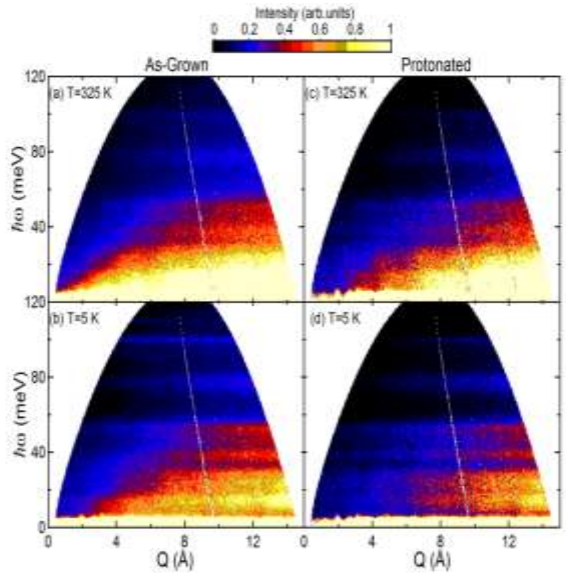


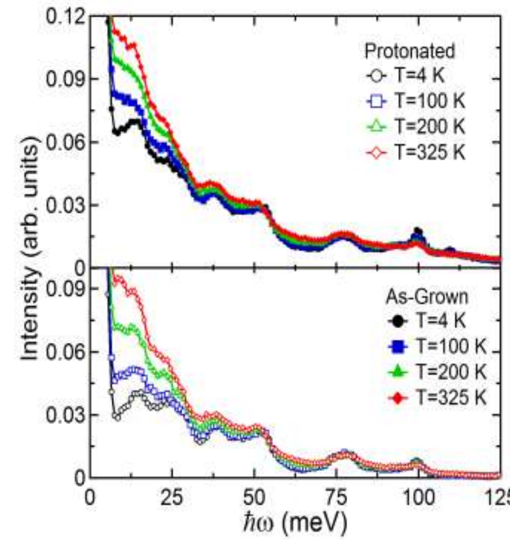
Very little impurities was observed while Ca content increased to 5.0%, which is higher than the results reported in literature.

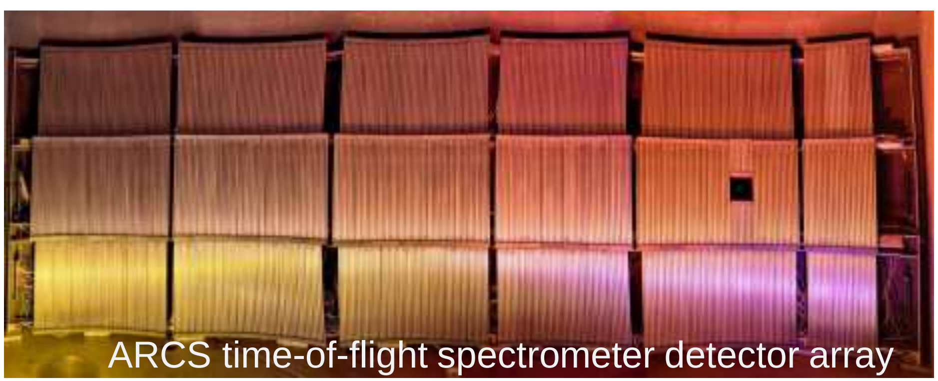
"R. Haugsrud and T. Norby, Nature Materials, 5 (2006) 193."

Proton Conduction in RE Ortho-niobates

The precise nature of interaction between the framework and mobile ions is an unresolved issue; the "softness" of some local phonon modes may be the key to understanding this phenomenon.






ARCS time-of-flight spectrometer detector array

Preliminary inelastic neutron scattering measurements observe phonon softening directly, and indicate possibility of measuring protonation in future measurements.

Research areas enabled by In-situ characterization platform

- Studying catalysis, separation membranes, gas storage such as clathrates, C capture mechanisms etc. under reaction conditions.
- Ion exchange mechanism in zeolites (often used for nuclear waste systems) and gas absorption in zeolites and other metal organic frame works.
- Mapping relationships between oxygen nonstoichiometry and electronic and magnetic properties of correlated electron oxides such as high-T_c superconductors and GMR materials.
- Novel solid state materials synthesis: During solid state materials synthesis it is very often desirable to know the intermediate phases that are being formed. However, only the final product is generally characterized using either X-ray or neutron diffraction.

Acknowlegement

- P. Paranthaman & Craig Bridges (CSD, ORNL), J. Hodges, M. Stone, A. Kolesnikov, Lou Santodonato (NSSD,ORNL), J-H Kim and Zhonghe Bi.
- A. Manthiram (UT Austin), J. Nino (U. of Florida), S. McIntosh (U of Virginia).
- Sample Environment team Luke Heroux (POWGEN SA) .

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