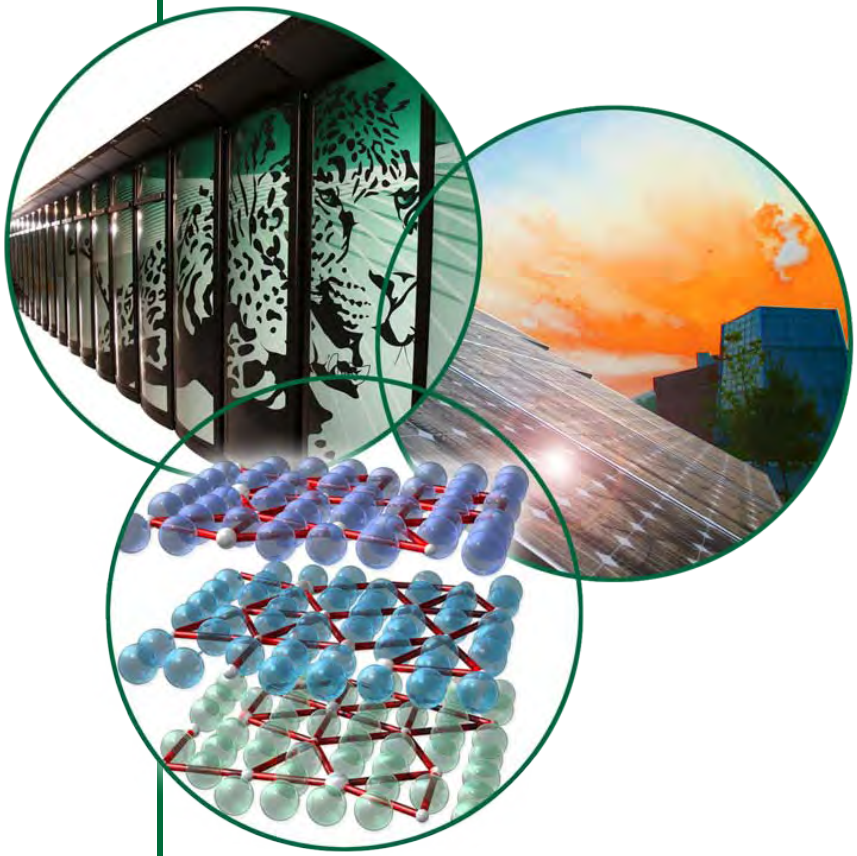
Materials Characterization Capabilities at the High Temperature Materials Laboratory

Project ID
lm028_laracurzio_2010_o

Edgar Lara-Curzio
HTML User Program
Materials Science and Technology Division
Oak Ridge National Laboratory



Sponsored by
U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies

U.S. DEPARTMENT OF ENERGY

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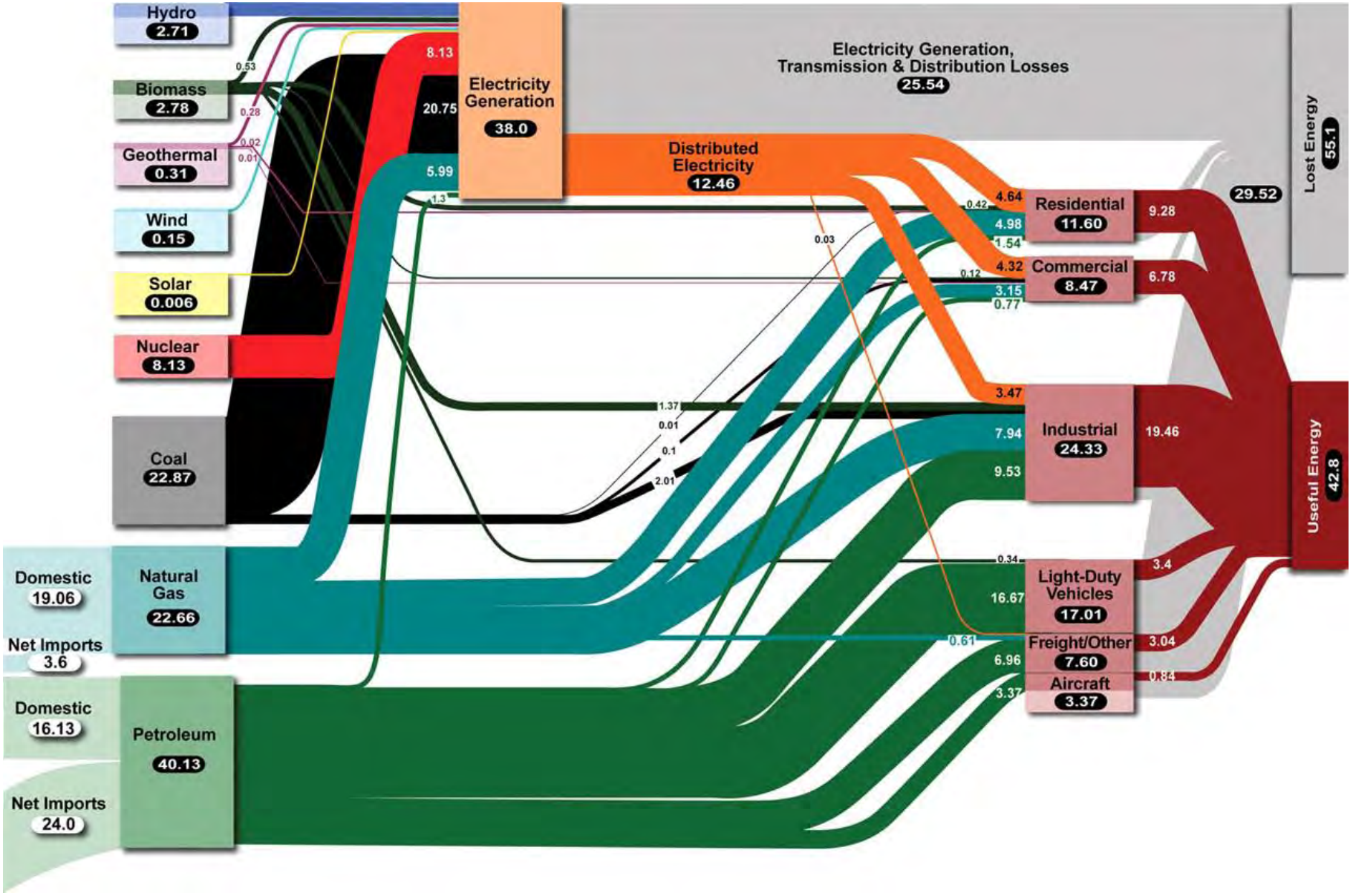

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The HTML User Program – Objectives & Relevance

- The HTML is a DOE Designated National User Facility. The Vehicle Technologies Program funds the operation of the HTML User Program to maintain **world-class expertise and instrumentation capabilities for materials characterization** to work with industry, universities and national laboratories to address critical technical barriers to achieving the goals of DOE's Vehicle Technologies Program.
- User projects address technical barriers in most of the Vehicle Technologies Program technology areas.
- The HTML User Program capabilities are also being utilized to support Vehicle Technologies Program projects at ORNL in the program's technology areas of Lightweight Materials, Propulsion Materials, Energy Storage and Thermoelectric Conversion.

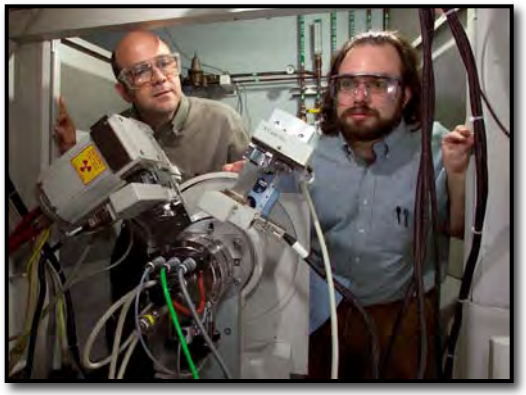
HTML User Program – FY2009 Participating Organizations

Industry	Universities	National Laboratories
• BorgWarner Morse TEC • Capstone Turbines • Caterpillar • Deere and Company • General Motors • Innegrity • Materials Innovation Technologies • Motorola Energy Systems • Plasan Carbon Composites • Pratt & Whitney • USCAR	• Columbia University • MIT • Michigan State University • Mississippi State University • Ohio State University • University of Florida • University of Massachusetts-Amherst • University of Michigan • University of Missouri-St Louis • University of New Mexico • University of Tennessee-Knoxville • University of Tennessee-Martin • University of Texas-Austin • Worcester Polytechnic Institute	• ORNL • BNL • PNNL

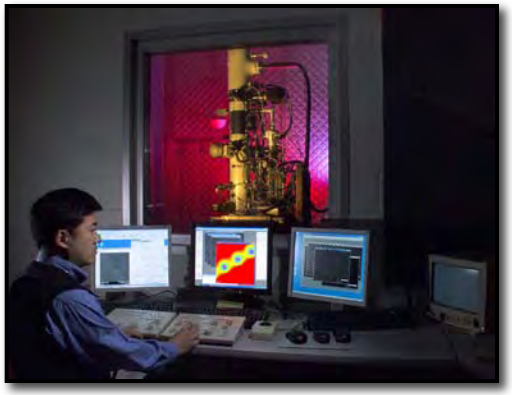
Approach

The HTML is organized into 6 User Centers,

which are clusters of highly skilled staff and sophisticated, often one-of-a-kind instruments for materials characterization

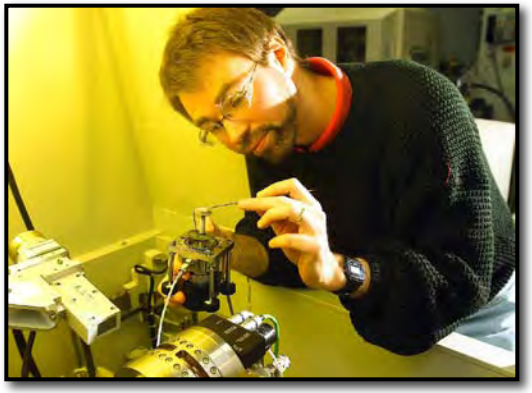


Diffraction



Materials Analysis

Mechanical Characterization

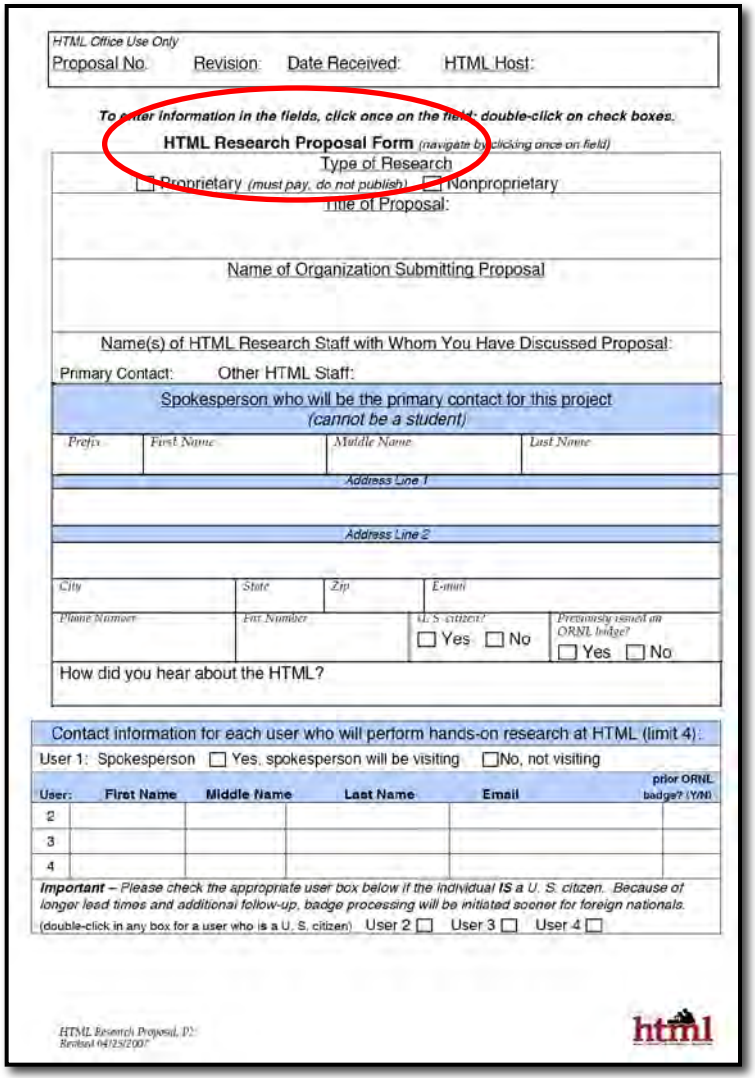


Residual Stresses

Thermography & Thermophysical Properties

Tribology Research

Approach: Access to the HTML



HTML Office Use Only
Proposal No. Revision: Date Received: HTML Host:

To enter information in the fields, click once on the field; double-click on check boxes.

HTML Research Proposal Form (navigate by clicking once on field)

Type of Research
☐ Proprietary (must pay, do not publish) ☐ Nonproprietary

Title of Proposal:

Name of Organization Submitting Proposal

Name(s) of HTML Research Staff with Whom You Have Discussed Proposal:

Primary Contact: Other HTML Staff:

Spokesperson who will be the primary contact for this project (cannot be a student)

Prefix	First Name	Middle Name	Last Name

Address Line 1

Address Line 2

City	State	Zip	E-mail

Phone Number	Fax Number	U.S. citizen?	Previously issued an ORNL badge?
		☐ Yes ☐ No	☐ Yes ☐ No

How did you hear about the HTML?

Contact information for each user who will perform hands-on research at HTML (limit 4):

User 1: Spokesperson ☐ Yes, spokesperson will be visiting ☐ No, not visiting

User:	First Name	Middle Name	Last Name	Email	prior ORNL badge? (Y/N)
2					
3					
4					

Important *– Please check the appropriate user box below if the individual* ***IS*** *a U. S. citizen. Because of longer lead times and additional follow-up, badge processing will be initiated sooner for foreign nationals.*

(double-click in any box for a user who is a U. S. citizen) User 2 ☐ User 3 ☐ User 4 ☐

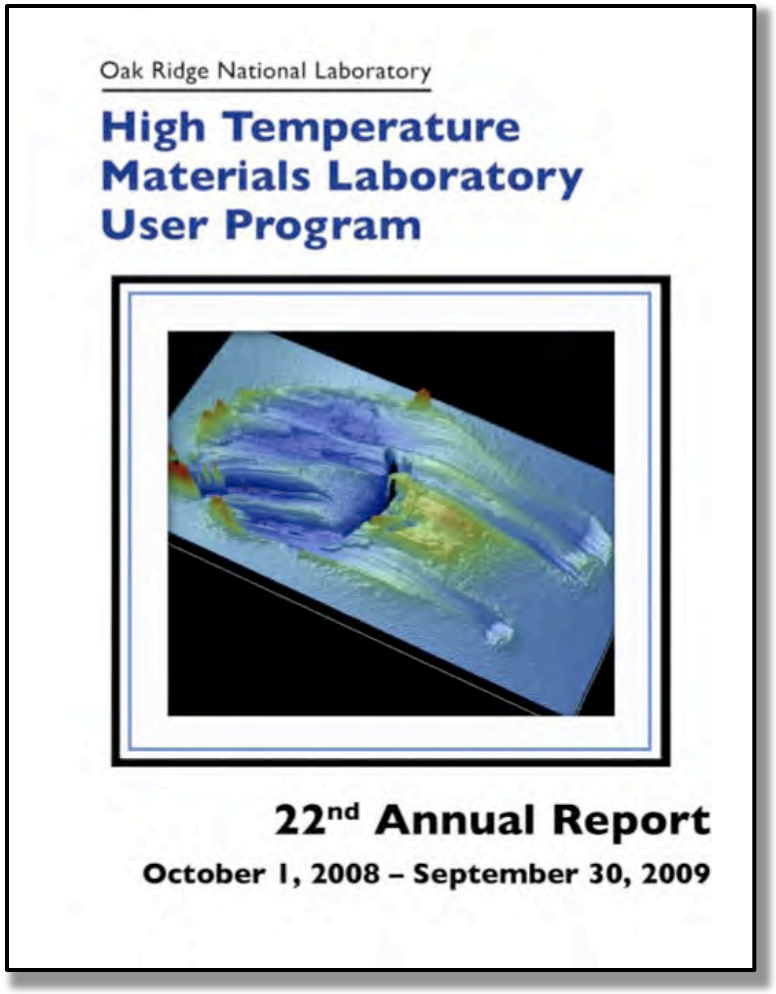
HTML Research Proposal, P2:
Revised 04/25/2007

html

- Access to the HTML User Program is provided through a formal proposal process. Proposals are reviewed by an internal review committee and evaluated based on
  - Technical merit
  - Relevance of the proposed research to the mission of the Vehicle Technologies Program
  - Non-competition with the private sector
  - Organizations based in the U.S.
- Research is completed within 24 months, and it involves one or more user visits to the HTML.

A user agreement (proprietary or non-proprietary) is required prior to starting a user project.

The HTML User Program - Accomplishments



HTML User Program FY2009 Annual Report

A copy of the annual report was provided to reviewers

OAK RIDGE National Laboratory

The HTML User Program - Accomplishments

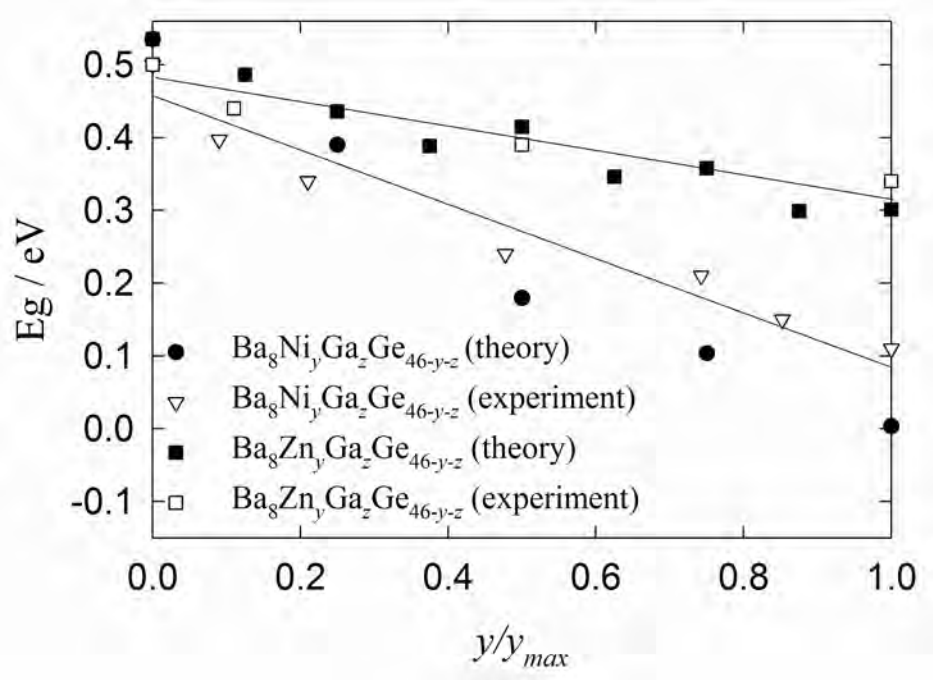
Examples of User Projects

General Motors R&D Center User Project:
"Thermoelectric properties of clathrates through a systematic cross-substitution of framework elements"

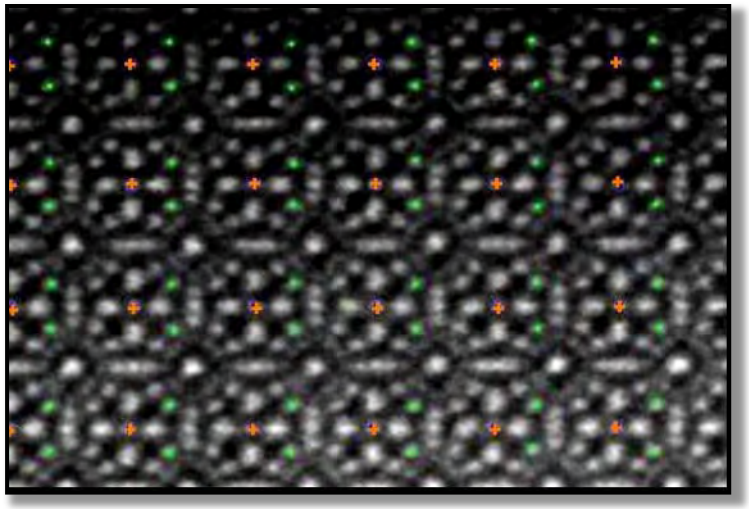
Research problem	Develop fundamental understanding of the structure-property relationships for clathrate thermoelectric materials.
Technical approach	Utilize advanced techniques to characterize the atomic structure of clathrate thermoelectric materials and their transport and electronic properties.
Implications	Thermoelectrics with a high figure of merit will enable the conversion of waste heat from engines into electrical energy to improve overall thermal efficiency and reduce emissions.
Barriers	Scale-up to a practical thermoelectric device, high figure of merit (ZT), and lack of standardized test methods
Collaborators	**GM Users**: Xun Shi, Jihui Yang, James Salvador **HTML Staff**: Hsin Wang, Miaofang Chi

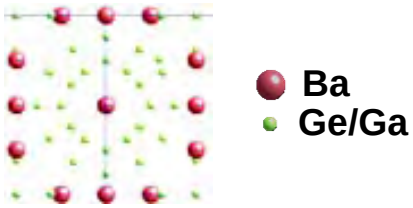
Dr. Xun Shi from General Motors analyzes transport measurement data.

General Motors R&D Center User Project: Accomplishments



- GM designed clathrates with composition that was changed by systematic cross-substitution of elements in the framework structure.
- Experimental measurements verified the ability to "tune" the band gap between 0.1eV and 0.5eV.





STEM image along the [100] direction for $Ba_8Ni_yGa_zGe_{46-y-z}$

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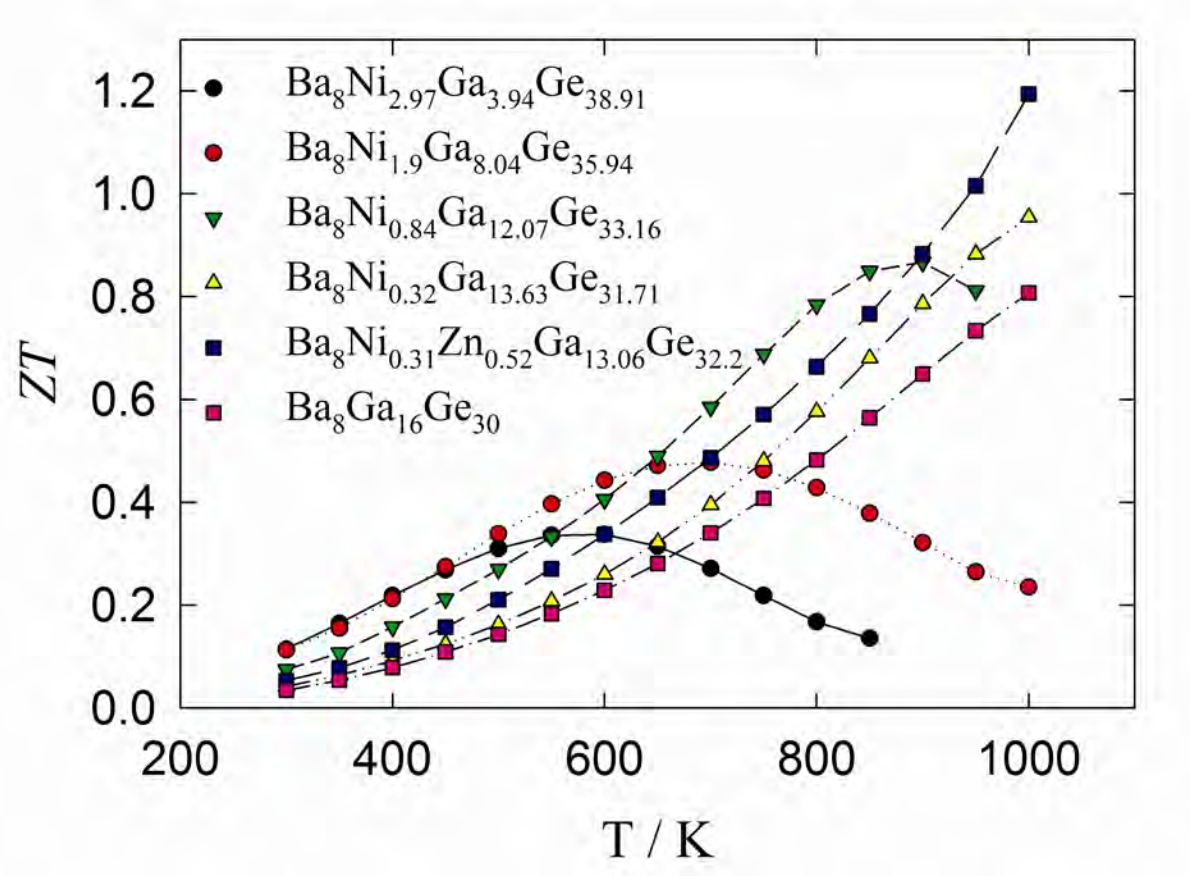
General Motors R&D Center User Project: Accomplishments

Temperature dependence of ZT for transition metal-substituted $Ba_8Ga_{16}Ge_{30}$. Maximum ZT is 1.2 near 1000K.



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University of Michigan/Ford Research

"Characterization of Alumina-Supported Pt and Pt-Pd Alloy NO Oxidation Catalysts with Advanced Electron Microscopy"

Research problem	To determine the relative efficacy of Pt/alumina vs. bimetallic Pt-Pd/alumina materials for the catalytic after-treatment of exhaust emissions in lean-burn gasoline and diesel engines.
Technical approach	Utilize the unique capabilities at the HTML for characterization of experimental Pt and Pt-Pd on alumina catalytic materials to obtain chemical and structural information at the atomic level, via aberration-corrected electron microscopy techniques.
Implications	Development of cost-effective, durable catalysts for emission control.
Barriers	Cost, Durability, Fundamentals of Catalysis
Collaborators	**Users**: X. Pan and O. Ezekoye (U. of Michigan) and A. Drews and G. Graham (Ford) **HTML Staff**: Larry Allard

University of Michigan Ph.D. student Obi Ezekoye at controls of the HTML User Program's ACEM at ORNL.

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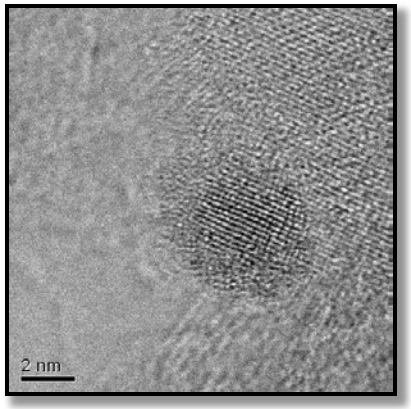
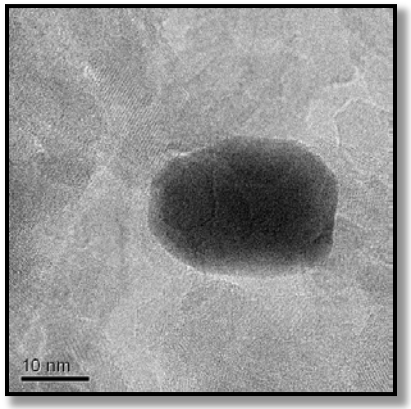
University of Michigan/Ford Research User Project



500° C Aging
particle size ~5nm



900° C Aging
particle size ~25nm

- Application of advanced electron microscopy techniques to characterization of alumina-supported Pt and Pt-Pd bimetallic catalysts has allowed us to understand the relation between alloying and particle coarsening aging under lean conditions .
- Some direct association between Pt and Pd was observed at the initial stage of bimetallic catalyst synthesis, but there is clearly a strong tendency for alloying to proceed *in situ* during the course of lean aging. This has a positive influence on limiting the growth of anomalously large particles typically found in pure Pt catalysts that have been harshly aged under lean conditions.
- We have also demonstrated that replacement of moderate amounts of Pt with Pd can be done with little or no loss of activity for NO oxidation. Further, standard catalyst precursors and synthesis methods have been shown to suffice.
- The use of Pd to both increase catalyst durability and decrease Pt loading in Pt-based catalysts for lean-burn engine exhaust-gas treatment thus appears even more favorable than before.

OAK RIDGE National Laboratory

Pacific Northwest National Laboratory

"Morphological and Electronic Structure of Pt-Re Nanoparticles Supported on Carbon under Activation and Reaction Conditions for Aqueous-Phase Reforming of Bioliquid"

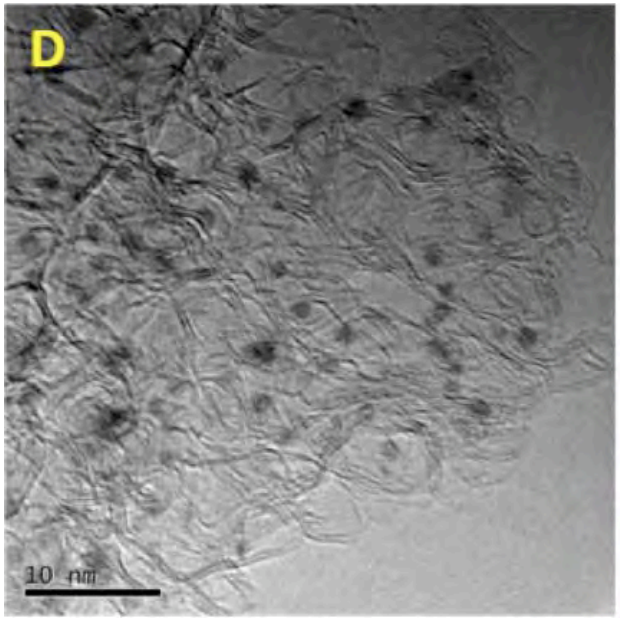
Research problem	To understand the mechanisms by which Re enhances the activity of Pt/activated carbon catalysts for aqueous phase reforming (APR) of oxygenated hydrocarbons for production of hydrogen and biofuels.
Technical approach	Characterize experimental Pt and Pt-Re on "real" activated carbon supports and on "model" thin film carbon supports, to obtain chemical and structural information at the atomic level, via aberration-corrected electron microscopy techniques
Implications	Development of cost-effective, durable catalysts for hydrogen and biofuel production.
Barriers	Cost, Durability, Fundamentals of Catalysis
Collaborators	**PNNL Users**: Liang Zhang and Yong Wang **HTML Staff**: Larry Allard

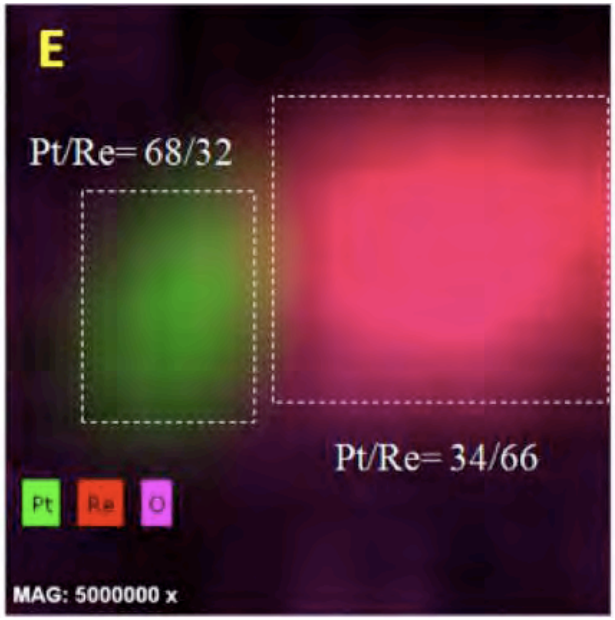
Dr. Liang Zhang at controls of the HTML User Program's ACEM at ORNL

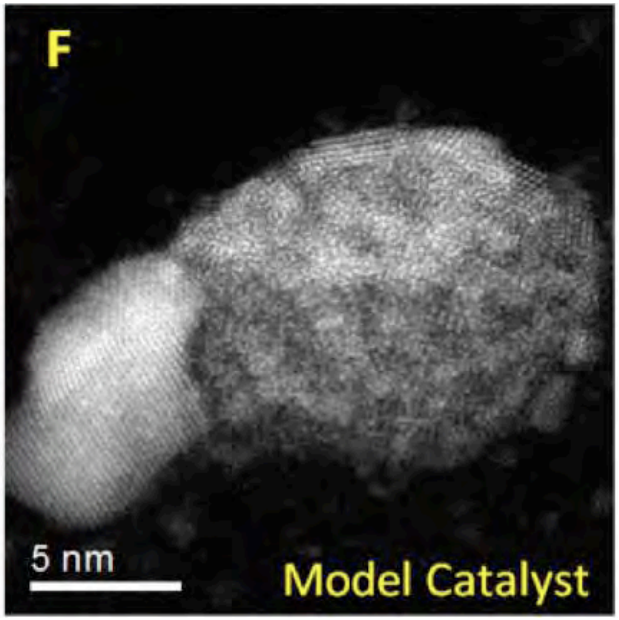
Pacific Northwest National Laboratory User Project

"Real" APR catalyst

"Model" APR catalyst for *in situ* studies







D. PtRe nanoparticles retained in "turbostratic" carbon structure with graphite sheet fragments. EDS showed Pt-rich and Re-rich particles.

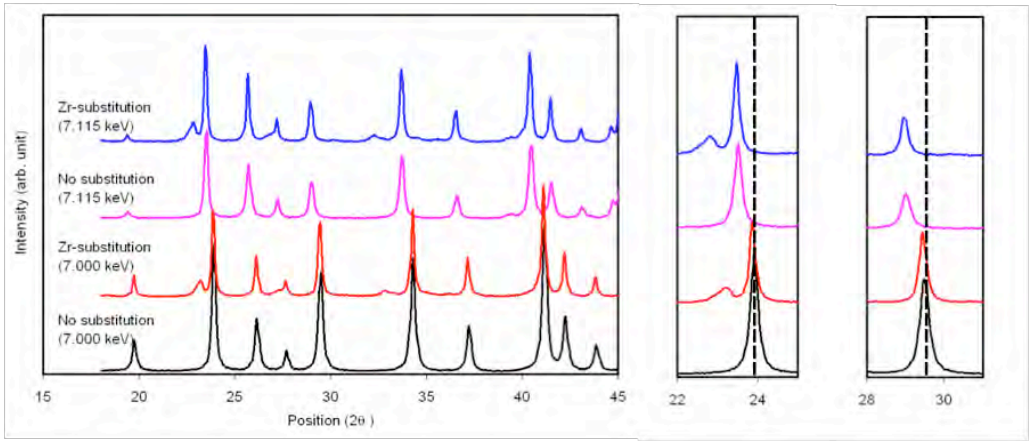
E, F: PtRe nanoparticle structure and chemistry studied by *in situ* heating of particles deposited on thin carbon film. Particle shown has left side with high Pt and right side enriched in Re with oxygen. ReOx phase occurs due to water molecules re-adsorbing dissociatively on the Re surface.

Massachusetts Institute of Technology

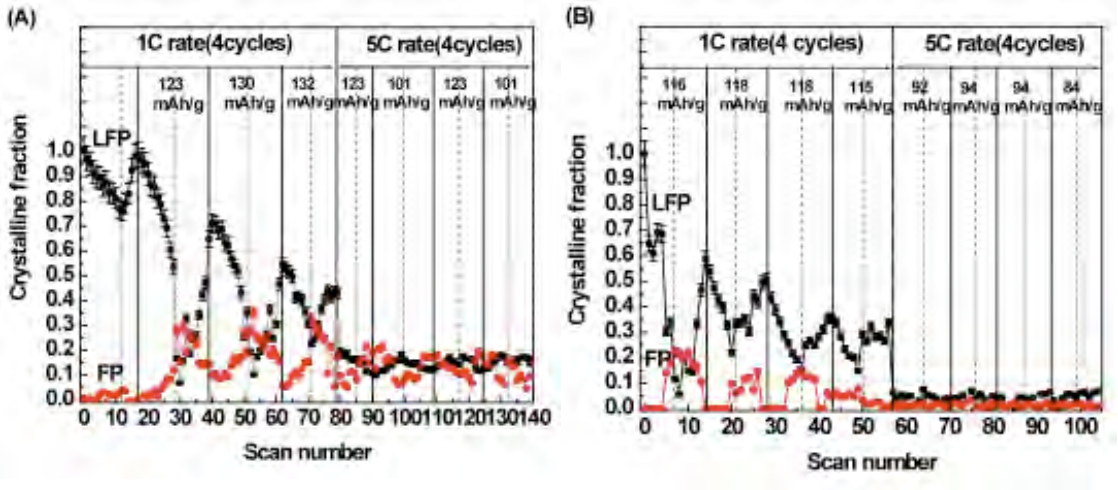
"Structural analyses of battery materials for the electrification of vehicles"

Research problem	To determine the site occupancy of dopants in the olivine structure, with particular emphasis on identifying site mixing and site vacancies. To determine overpotential effects on phase stability and transformation mechanisms.
Technical approach	Perform resonant x-ray powder diffraction measurements on alivolavent cation (Mg^{2+}, Al^{3+}, Zr^{4+}, Ti^{4+}, Nb^{5+}) substituted olivine powders. Perform *in situ* synchrotron XRD during potentiostatic and galvanostatic cycling.
Implications	Development of safe, durable batteries with high energy and power density.
Barriers	Cost, Battery Fundamentals, Performance, Life
Collaborators	**MIT Users**: Y. M. Chiang, N. Meethong Y.H. Kao **HTML Staff**: Jianming Bai

MIT graduate students Nonglak Meethong (foreground) and Yu-Hua Kao at the HTML's X14A beamline (at the NSLS).



XRD patterns of Zr-substituted samples measured at both wavelengths clearly show shifting of peak positions toward the low angles direction, indicating unit cell dilation due to lattice-doping. A NASICON phase can also be observed for the Zr substituted samples.



Crystalline fraction determined from *in situ* XRD for 113nm (A) and 34nm (B) particle sizes under different charging conditions (four cycles at 1C followed by 4 cycles at 5C). It is the transformed amorphous phase that ends up being cycled.

Massachusetts Institute of Technology:

What we learned and accomplished:

- Resonant synchrotron X-ray diffraction enabled detailed study of aliovalent dopant effects in olivine $Li_{1-x}Fe_{1-y}A_yPO_4$.
- Synchrotron X-ray diffraction performed *in situ* during potentiostatic and galvanostatic cycling, combined with phase-field modeling, revealed a significant dependence of phase transition pathway on overpotential in the model olivine $Li_{1-x}FePO_4$.
- At both low (e.g., <20 mV) and high (>75 mV) overpotentials, a crystal-to-crystal olivine transformation is preferred, whereas at intermediate overpotentials a crystalline-to-amorphous phase transition dominates.
- The overpotential-dependent phase transformation pathways seen in these experiments can be understood as an influence of driving force on nucleation and growth kinetics of competing phase transitions.

University of Florida evaluates synthesis of CIGS absorber layer for photovoltaics

Research problem: To identify pathways and kinetics for Cu-In-Ga-Se (CIGS) absorber formation using *in situ* x-ray diffraction

Implications: Potential cost reduction of photovoltaics from increased production efficiency

Description of Work: As a part of their DOE Solar America Initiative (SAI) project, researchers from the University of Florida are collaborating with the Oak Ridge National Laboratory, the National Institute of Standards and Technology, and four start-up thin-film photovoltaic industries based in California tc understand and optimize the processi ıte input data as well as validation of ıan and the HTML User Progran ıigh-temperature x-ray diffraction exp elated to industrial processes f

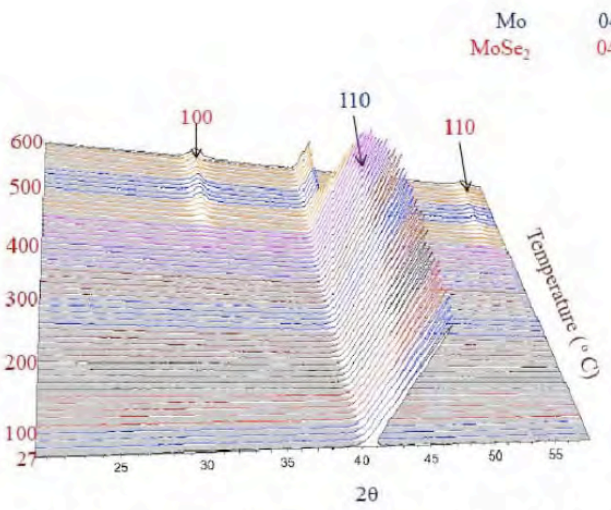
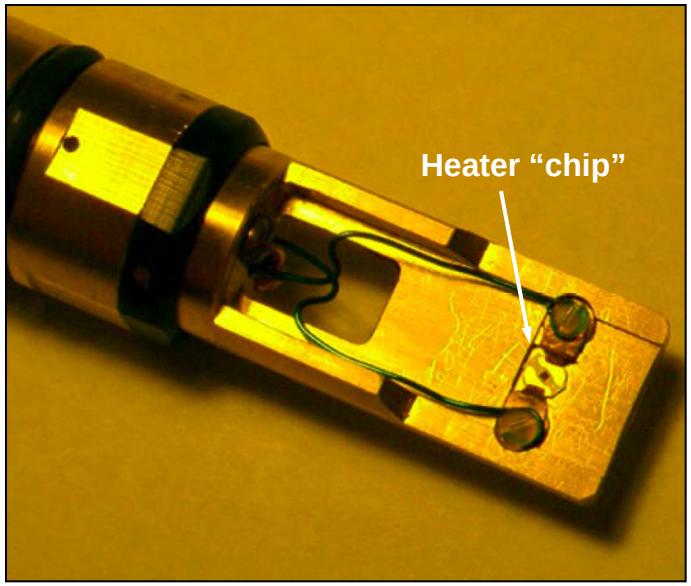


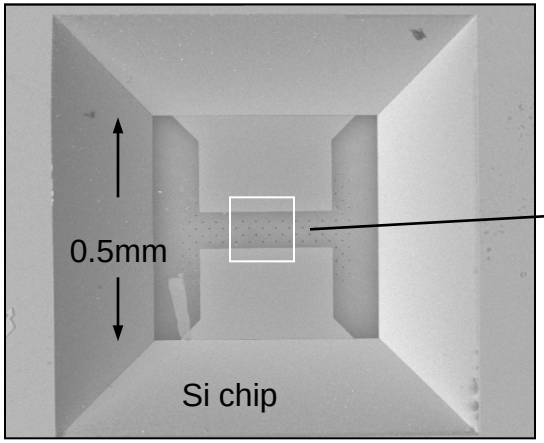
Fig. 62. Temperature ramp selenization of molybdenum.

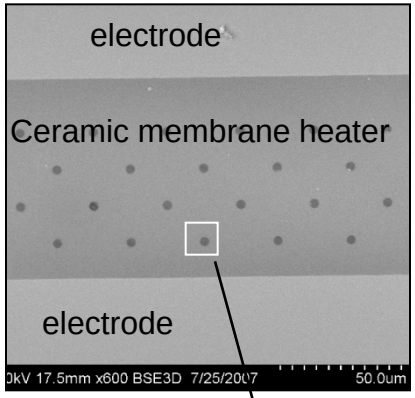
Summary

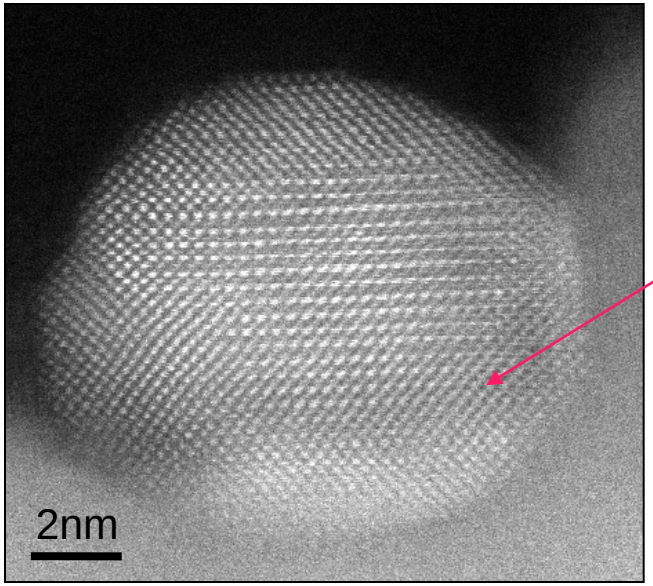
- The HTML is a National User Facility that supports the missions of the Vehicle Technologies Program, in particular by working with industry, universities and other national laboratories to develop energy-efficient technologies that will enable the U.S. to use less petroleum and reduce greenhouse gas emissions.
- The HTML User Program capabilities are also being utilized to support other programmatic activities at ORNL.

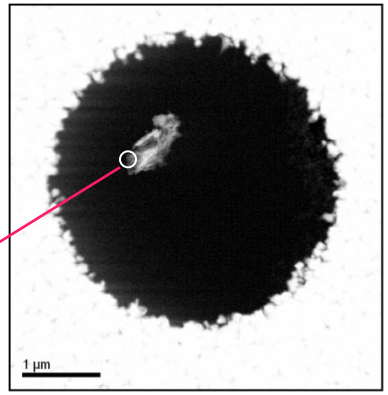
A new paradigm for *in situ* microscopy:
in situ heating with Protochips' MEMS* heater technology











Protochips Co. provides novel heating elements fabricated using semiconductor technology. Thin ceramic membrane can be heated to >1000° C in 1 millisec!

*MEMS = micro-electromechanical system

Ultra-stable operation for sub-Ångström imaging

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