SAND2008-7821C

Office of Nonproliferation Research and Development

Overview
Radiation Detection Materials Development
Sandia National Laboratories

John Goldsmith

Manager, Radiation & Nuclear Detection Materials & Analysis Department

(Livermore, California)

(See me regarding detection systems and/or active interrogation)

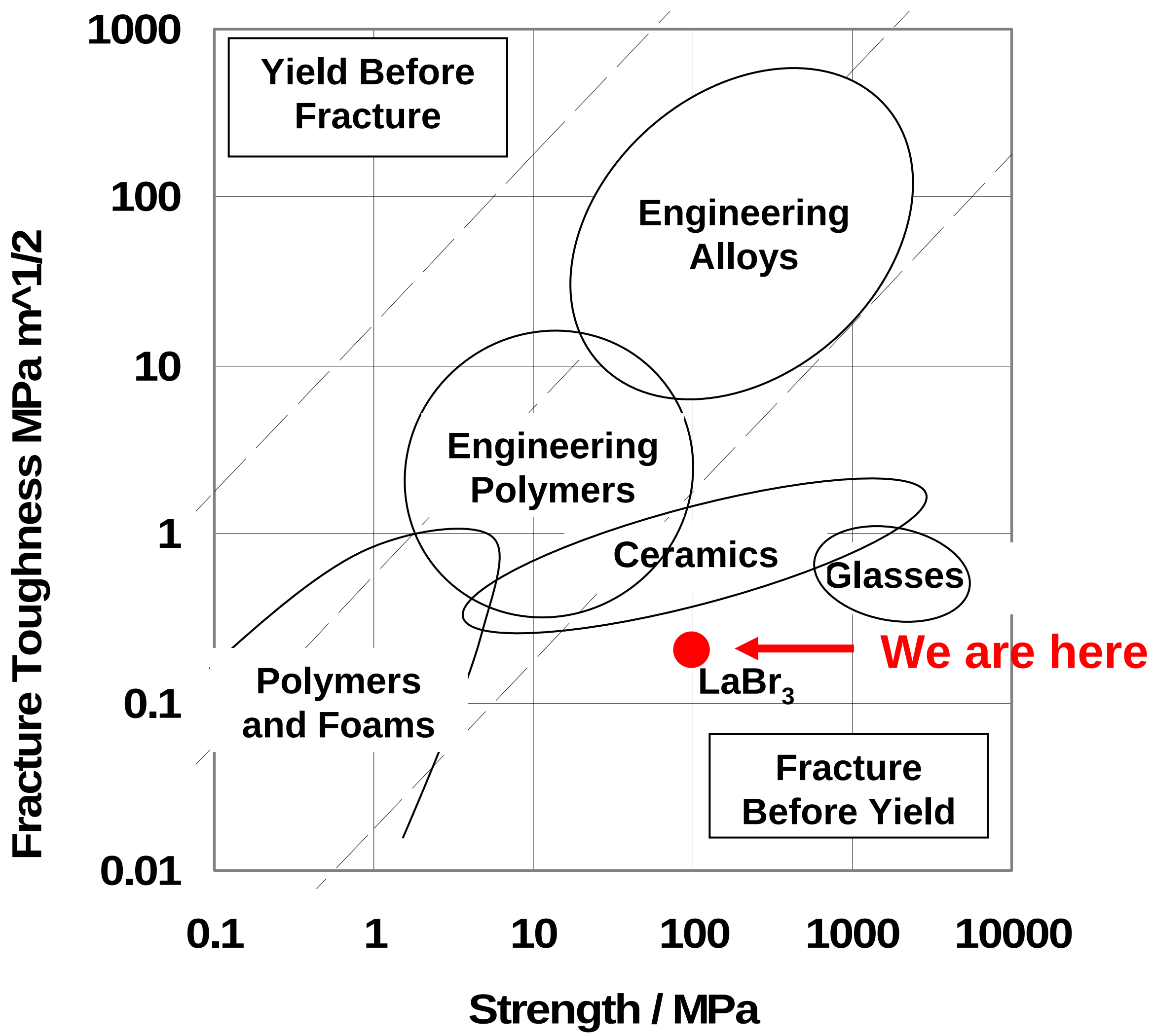
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000.

Sandia National Laboratories

Lanthanide Halide Scintillators

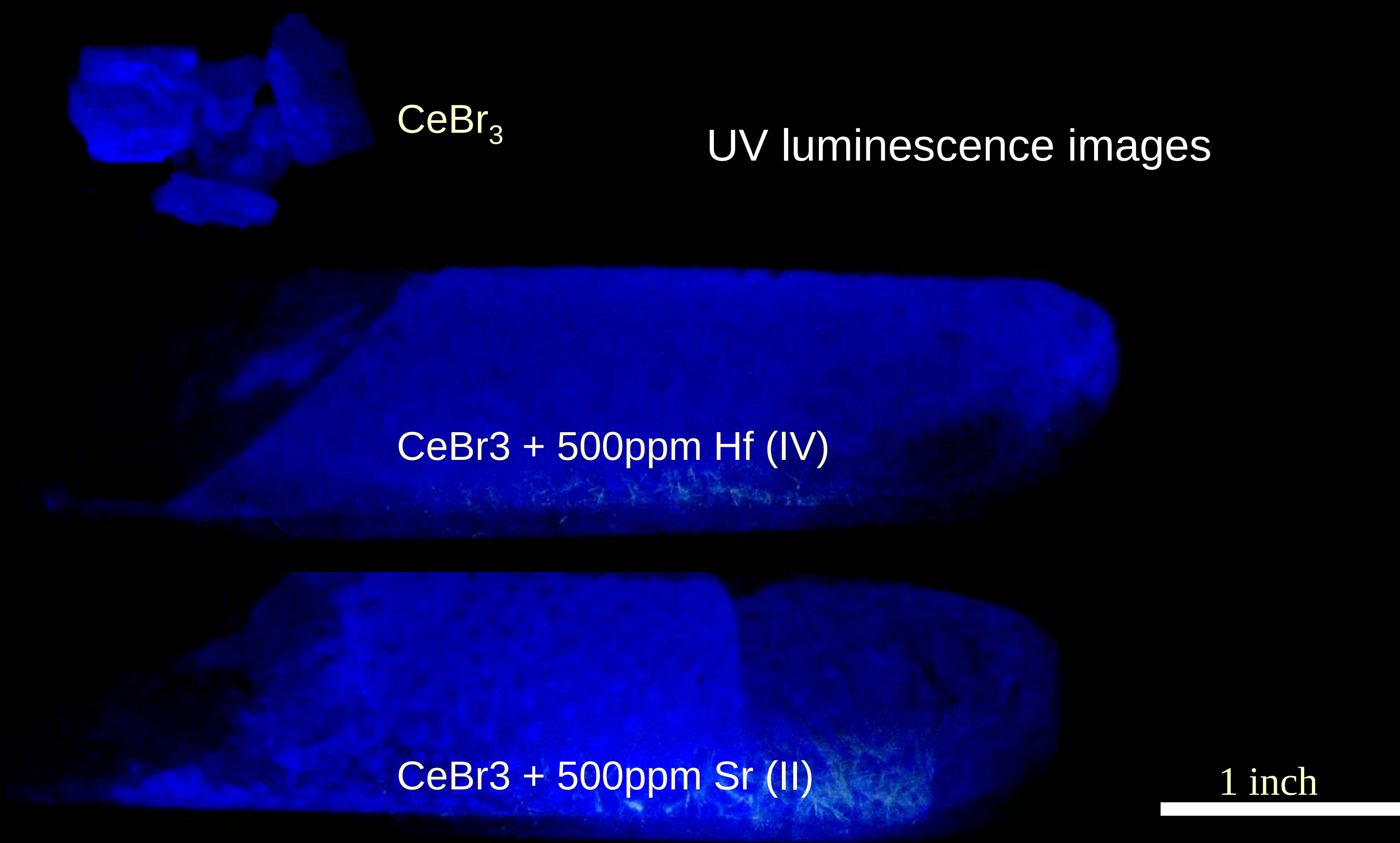
- **Principal Investigator: Patrick Doty**
- **Collaborators:**
  - Xiaowang Zhou, Pin Yang, Paul Allison (MSU graduate student intern), Sandia
  - Mark Harrison / Doug McGregor, Kansas State University
  - Shawn Kilpatrick / David Bahr, (previously at) Washington State University
  - Raulf Polichar, SAIC
- **Goal: overcome the barriers to production of sensitive gamma ray scintillation spectrometers, through a coordinated program of structure/property analyses, modeling and crystal growth**
- **Funding: Advanced Materials Portfolio, NA-22 (Bob Mayo)**

Lanthanum Bromide



- Failure mechanism initiated by slip on prismatic fracture planes
- 3.7:1 anisotropy in coefficient of thermal expansion
- One solution: aliovalent hardening

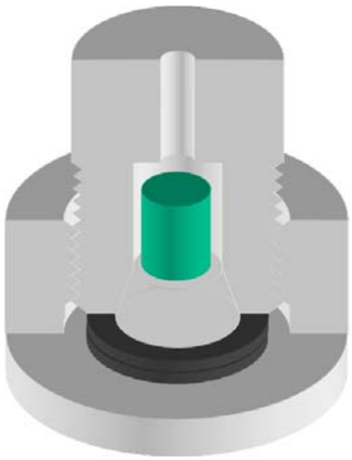
Strengthening agents increased unfractured size from ≤1 centimeter to several inches

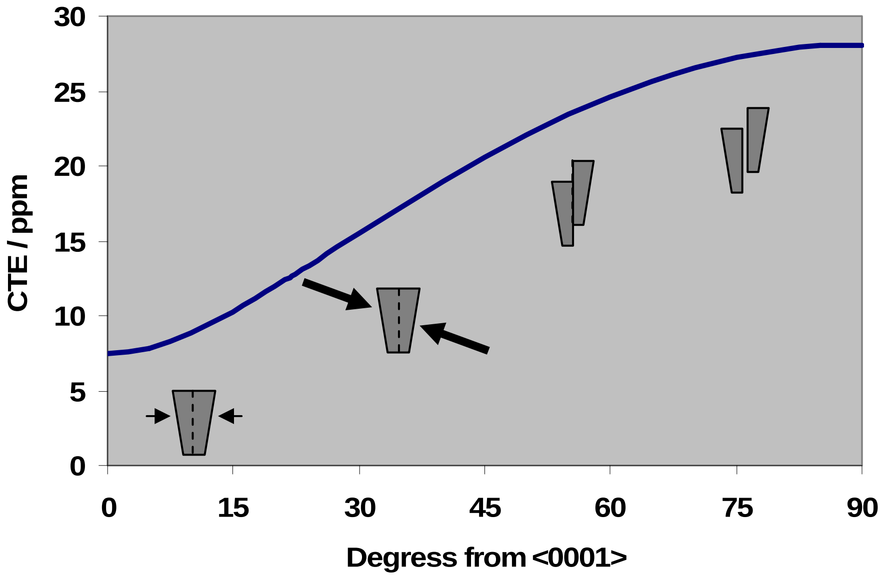


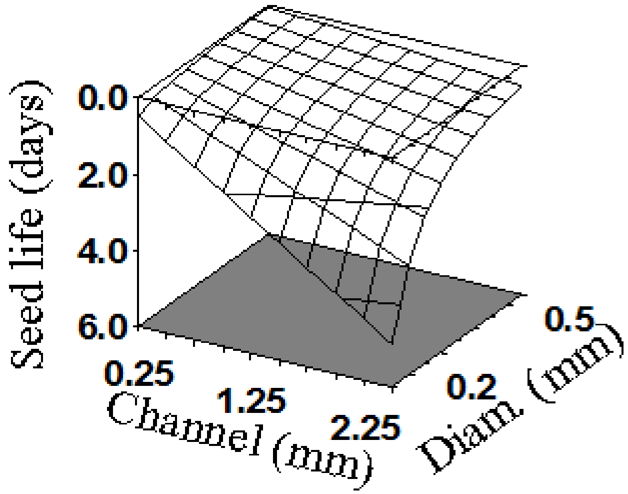
Another approach: seeded growth

Problem: ***Large anisotropy of thermal expansion results in shear force on cleavage planes if gradient is not aligned with c-axis***

- Pure compression for c-axis growth
- Both magnitude and orientation of stress increase rapidly for off-axis growth







Model development

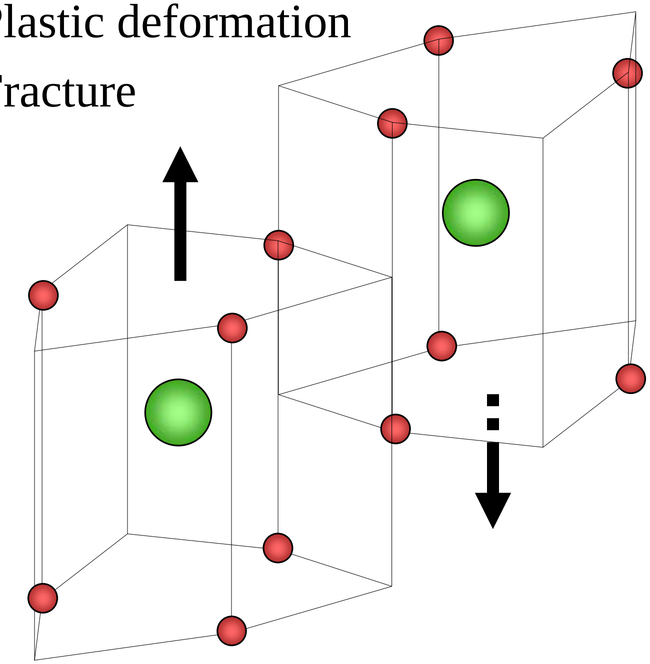
Problem: Develop modeling approach to simulate mechanics of LnX_3 crystals

•Thermal stress during growth

•Slip systems and dislocation reactions

•Plastic deformation

•Fracture



Slip and Fracture in LnX_3

1st generation ionic potentials: Fixed Charge

- Overestimates cohesive energy by factor of four!
- Stoichiometric compositions ONLY
- Can not treat defects

2nd generation: Variable Charge

- Charges solved by minimizing potential for each δt
- *Computationally VERY expensive*.
- Energy is not rigorously conserved!

3rd generation: This Work

The embedded ion method that we are developing solves these problems

- Equilibrium charges are analytically integrated:
- No energy minimization is required
- Energy is rigorously conserved

100 ns time scale, 1,000,000 atoms

.

Materials Science of Elpasolite Scintillators

- **Principal Investigator: Patrick Doty**
- **Collaborators:**
  - Xiaowang Zhou, Pin Yang, Sandia
  - Kanai Shah, RMD
- **Goal develop a fundamental understanding of the composition-structure-property relationships for elpasolite family scintillators**
- **Funding: Advanced Materials Portfolio, NA-22 (Bob Mayo)**
  - New start (FY09)

Extending embedded-ion method

Goldschmidt criterion for perovskite

$$0.8 < \frac{R_A + R_X}{\sqrt{2}\left(R_B + R_X\right)} < 0.9$$

Complimentary experimental criteria

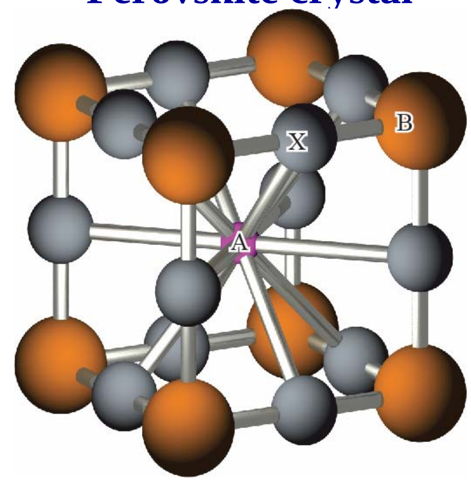
$$0.414 < R_B/R_X < 0.732, \qquad R_B/R_X < 1.203\,R_A/R_X - 0.488, \qquad and$$

$$4.483\left(\chi_X - \chi_B\right)/\left(\chi_X + \chi_B\right) + 17.889 R_B/\left(R_X + R_B\right) - 2.063 R_A/\left(R_X + R_B\right) > 6.088$$

L. Liang, L. Wencong, and C. Nianyi, *J. Phys. Chem. Solids*, **65**, 855(2004).

Here R is atom radius, and χ is electronegativity

Perovskite crystal



Embedded-ion method

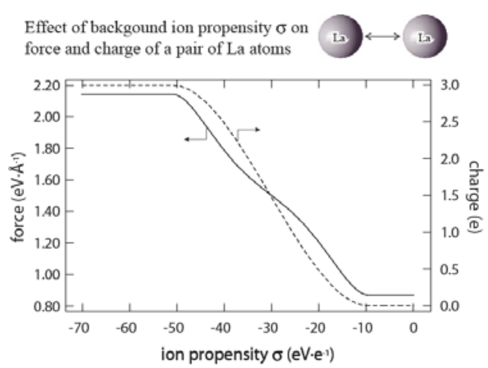
$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ j\neq i}}^{N}\phi_{ij}\left(r_{ij}\right) + \sum_{i=1}^{N} E_{emb,i}\left(\sigma_i\right), \qquad \sigma_i = \sum_{j=1}^{N} F_j\left(\chi_j, J_j, r_{ij}\right)$$

$$\phi_{ij}(r) = \frac{E_{b,ij}\beta_{ij}}{\beta_{ij} - \alpha_{ij}} \exp\left[-\alpha_{ij}\left(r - \frac{R_i + R_j}{2}\right)\right] - \frac{E_{b,ij}\alpha_{ij}}{\beta_{ij} - \alpha_{ij}} \exp\left[-\beta_{ij}\left(r - \frac{R_i + R_j}{2}\right)\right]$$

ϕ: pair energy function; E_{emb}: embedding energy function; σ_i: ion propensity at site i; F: a function characterizing the ionic properties of the atom; χ, J, E_b, α, β, R: parameters.

Note R and χ are input parameters and crystal prediction will be output.

Reactivity incorporated



Correctly predict the ionization of the La atoms and the associated repulsive force at a strong negative ion propensity environment.

Fission Neutron Detection using Heteroepitaxial Chemical Vapor Deposition Diamond

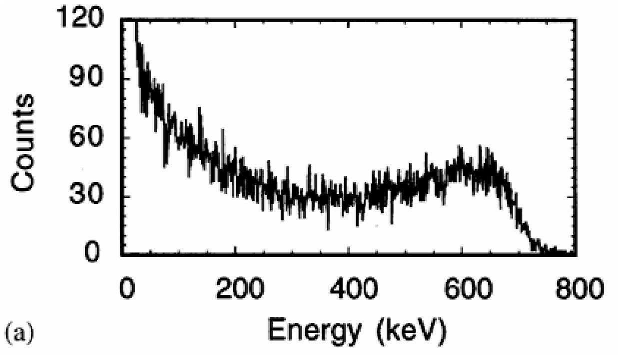
- **Principal Investigator: Richard Anderson**
- **Collaborators:**
  - Brage Golding, Michigan State University
- **Goal: synthesize large-area, defect-free single crystal diamond on low-cost non-diamond substrates (heteroepitaxy)**
- **Funding: DNDO Transformational and Applied Research Directorate**

Note: Brage speaking tomorrow at 8:40 am

Single crystal diamond is the best spectroscopic SNM neutron detector

Efficiency	• Efficient energy transfer to the recoiling diamond nucleus (up to 28%) • Highest scattering efficiency of any material: 6.1% of 0.1 - 1 MeV neutrons lose energy per mm diamond
Semi-conductor Detection Charge Collection is Key	• High mobility* – 4500 cm^2/V-sec electrons – 3800 cm^2/V-sec holes • Long lifetime* - μsec
Linearity	• 4.8 MeV threshold for inelastic scattering
Gamma Insensitive	Yes, Z = 6

*Isberg et al. Science 297 (2002) 1670. : CVD homoepitaxial diamond--room temperature



Single Pixel Counts vs. energy deposited, 2.5 MeV neutrons in CVD diamond crystal. *G. J. Schmid et al., Nucl. Instr. And Meth. A527 (2004), pp 554-561.*

Problem: Growing diamond on diamond (homoepitaxy) not practical for large-size detectors

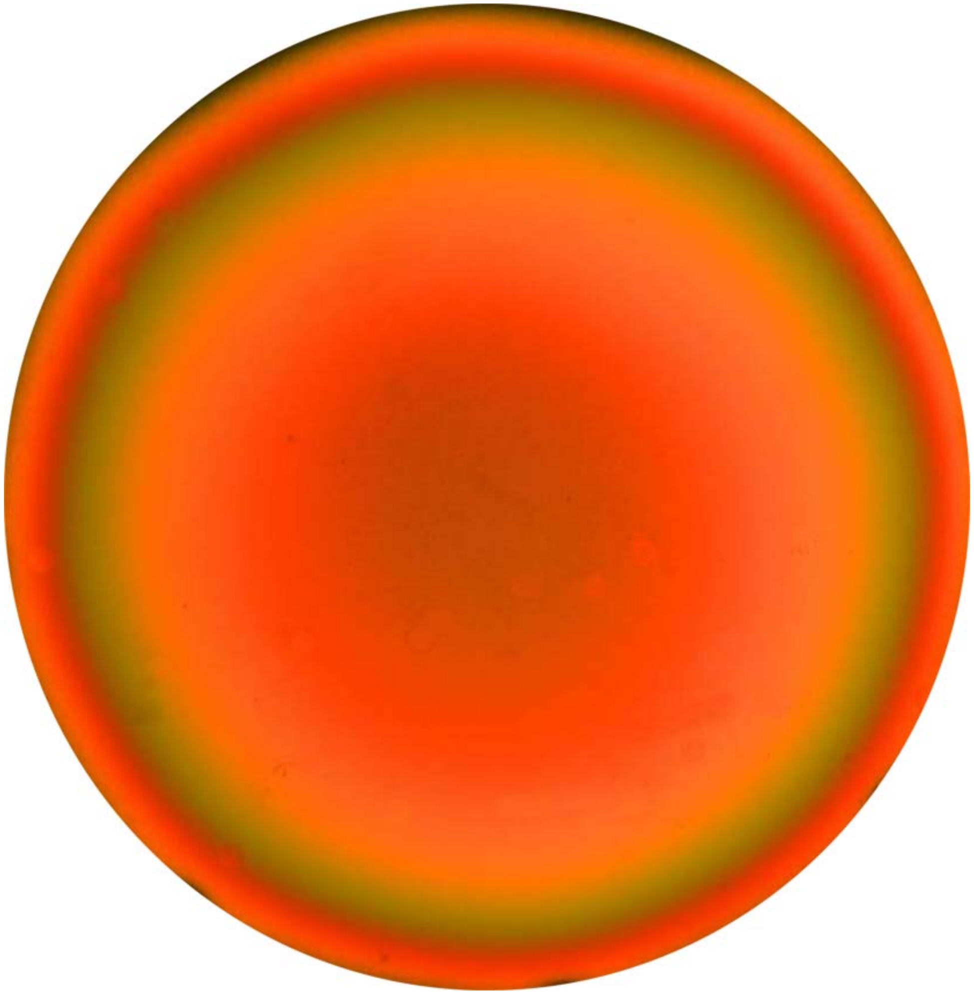
Solution: Scaling by synthesis on non-diamond substrates (heteroepitaxy)

Large, high uniformity diamond grown by heteroepitaxy

600 nm thick single crystal grown by heteroepitaxial CVD

Highly uniform across 8 mm diameter

Will act as "seed" for homoepitaxial growth



8 mm

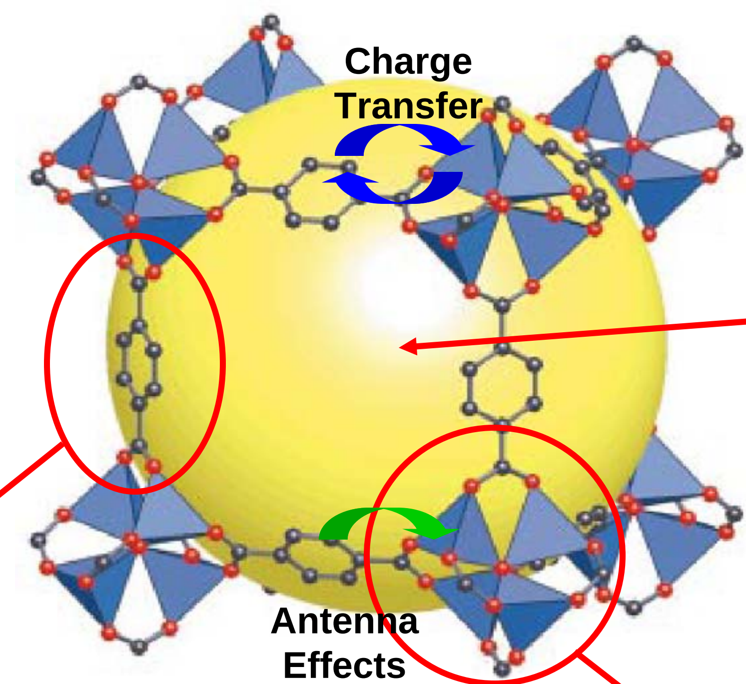
Structural Origins of Scintillation: Metal Organic Frameworks as a Nanolaboratory

- **Principal Investigator: Patrick Doty**
- **Collaborators:**
  - Mark Allendorf, Ron Houk, Rago Bhakta, Ida Nielsen, George Vizkelethy, and Barney Doyle, Sandia
- **Goal: develop tools and techniques that elucidate fundamental processes in organic scintillators through studies of metal organic framework materials (MOFs), and enable the characterization and control of the growth and synthesis processes for fast neutron scintillators and other potential sensor materials**
- **Funding: DTRA Basic and Applied Sciences Directorate**

Sandia National Laboratories

Why are MOFs interesting for sensing applications?

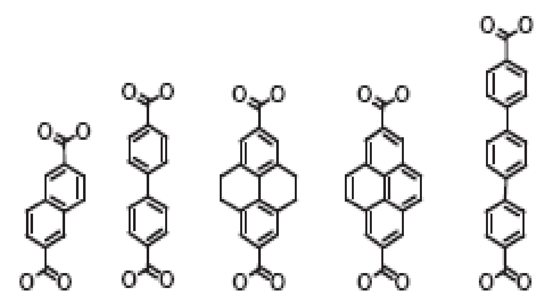
- Strong bonding
- Tailor structure for application



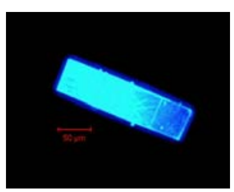
Guest emission:
- Dyes
- Nanoparticles
- Metal clusters

Coordinating Metal:
- Transition metals
- Lanthanides
- Open coordination sites

Fluorescent Linkers



2,6-NDC BPDC HPDC PDC TPDC

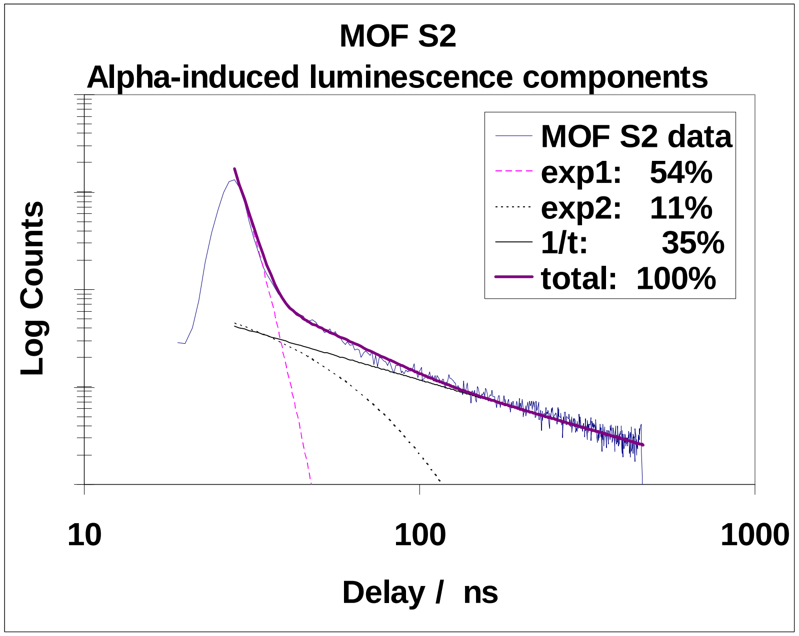


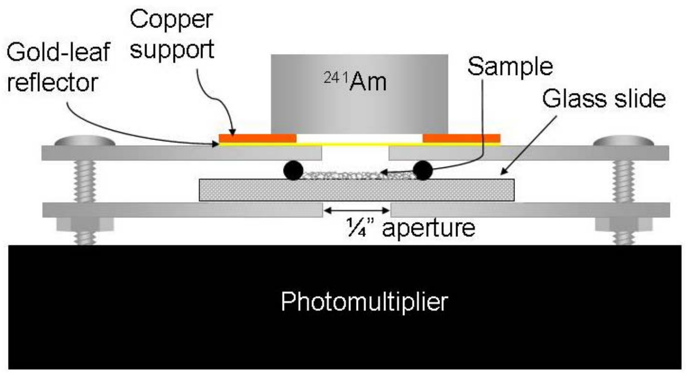
Sandia National Laboratories

Local MOF environment controls scintillation timing

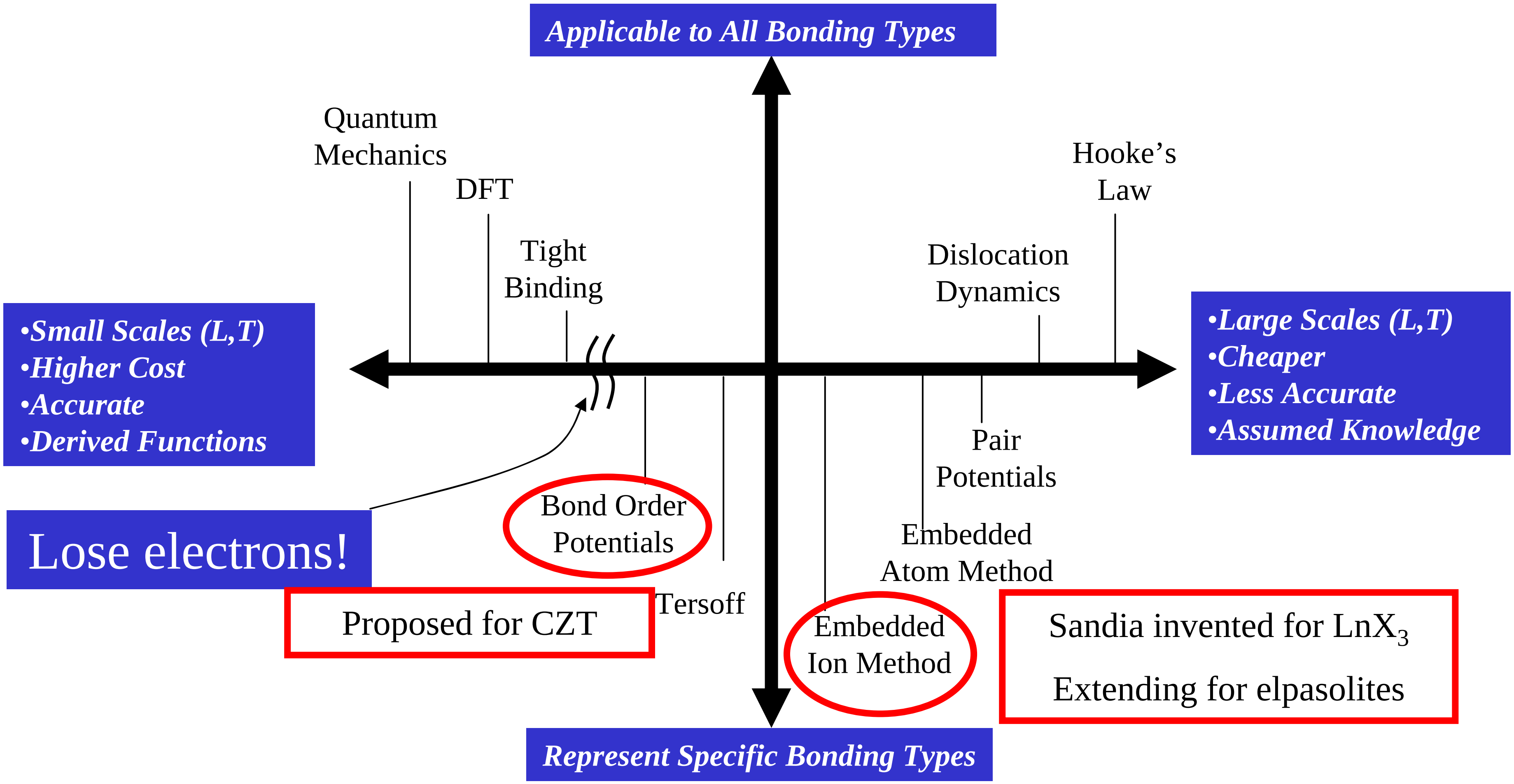
- **Timing data obtained by exposure to α particles**
- **MOF-S1: Exponential decay of fast component**
- **MOF-S2: Scintillation pulses observed on two different time scales:**
  - Fast (< 1 μs): biexponential decay
  - Slow (>>1 μs): 1/t
- **Slow component may be the result of electron tunneling**

Pulse-shape discrimination may be controllable via MOF crystal structure



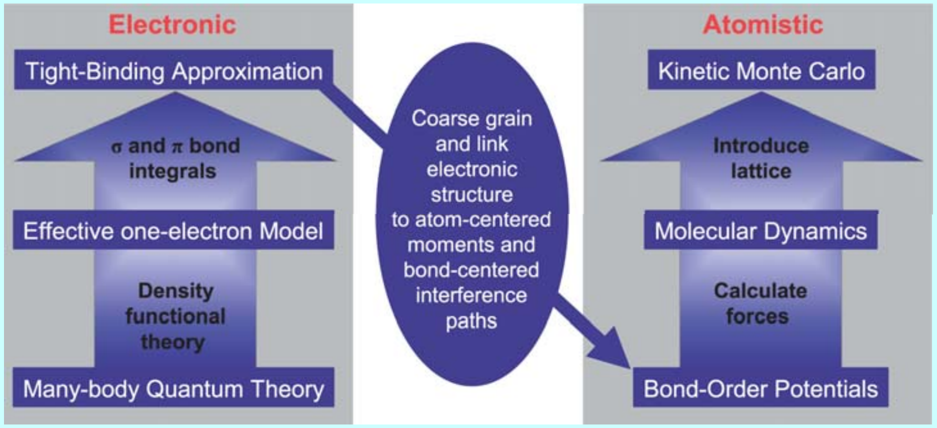


Modeling approaches (halides)



Bond order potential for covalent systems

BOP Is a Quantum-mechanically Derived Potential



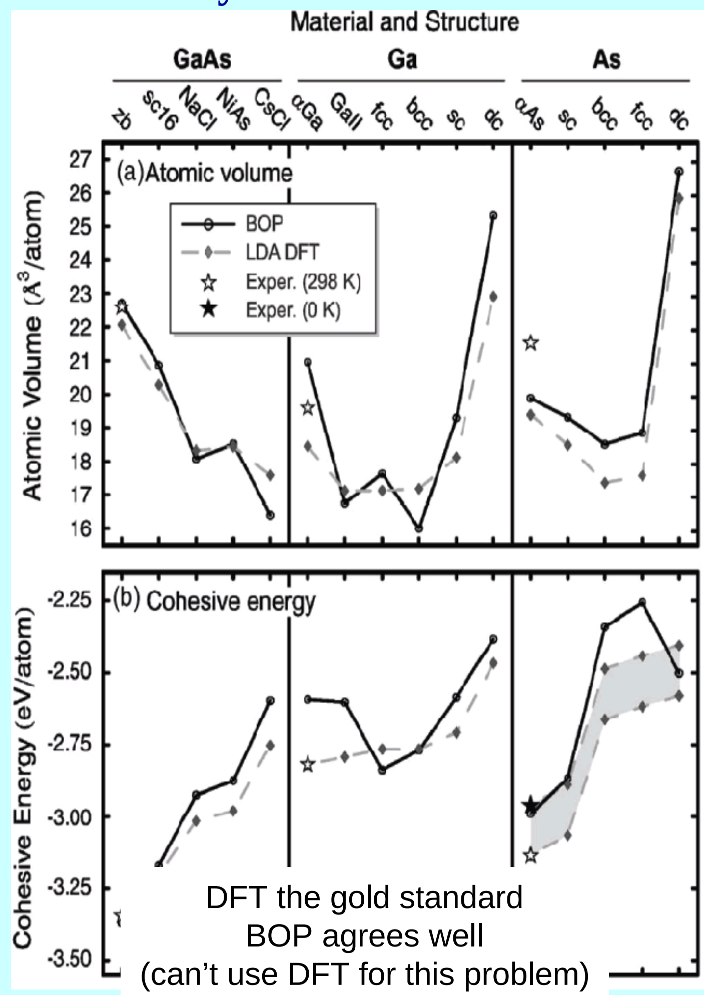
Can incorporate: σ bonding, π bonding, promotion energy, environment dependence, dihedral angle, and more...

Defect types	DFT	BOP
V_{Ga}	3.15	3.28
V_{As}	3.10	2.93
Ga_{As}	2.12	2.03
As_{Ga}	2.48	2.50
Ga_i (tetrahedral)	2.98	2.66
		4.14
As_i (tetrahedral)	5.04	4.47
		3.32
Ga_i (⟨110⟩ dumbbell)	3.53	4.97
As_i (⟨110⟩ dumbbell)	4.07	3.82
Ga_i (⟨100⟩ dumbbell)	-	3.86
As_i (⟨100⟩ dumbbell)	-	4.68

The Only Predictive Potential for Defects

- D. G. Pettifor, Phys. Rev. Lett., 63, 2480 (1989).
- D. G. Pettifor, and I. I. Oleinik, Phys. Rev. B, 59, 8487 (1999).
- D. G. Pettifor, and I. I. Oleinik, Phys. Rev. B, 65, 172103 (2002).
- I. I. Oleinik, and D. G. Pettifor, Phys. Rev. B, 59, 8500 (1999).
- D. G. Pettifor, and I. I. Oleinik, Phys. Rev. Lett., 84, 4124 (2000).
- D. A. Murdick, X. W. Zhou, H. N. G. Wadley, D. Nguyen-Manh, R. Drautz, and D. G. Pettifor, Phys. Rev. B, 73, 45206(2006).
- D. A. Murdick, H. N. G. Wadley, and X. W. Zhou, Phys. Rev. B, 75, 125318(2007).

The Only Transferrable Potential



DFT the gold standard
BOP agrees well
(can't use DFT for this problem)

Not currently active:

- Organic scintillators for neutron spectroscopy (former DNDO project)
- Ceramic lanthanum halide scintillators (former DNDO project)
- Organic semiconductors for neutron counting (LDRD)
- Modeling of trapping mechanisms in CZT (proposed)

Materials capabilities at Sandia

- **Computational Materials Science**
- **X-ray powder diffraction and structure analysis of hygroscopic materials**
- **X-ray single crystal rocking curves**
- **Electron microscopy and microanalysis**
- **Thermal analysis techniques**
- **Thermomechanical property evaluation**
- **Microhardness and fracture strength**
- **Spectroscopic evaluations including fluorimetry and time correlated radioluminescnce characterization**
- **Electronic measurements of solid-state detector materials including current-voltage, capacitance-voltage, photoconductivity, mobility and trapping time**
- **Low temperature studies including photoluminescence and thermally-stimulated current**
- **Organic and inorganic synthesis**

jgold@sandia.gov

fpdoty@sandia.gov

User facility: http://www.sandia.gov/bus-ops/partnerships/tech-access/facilities/radiation.html