Atomistic Models for Scintillator Discovery

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Two Problems of Current Interests

ELPASOLITES:

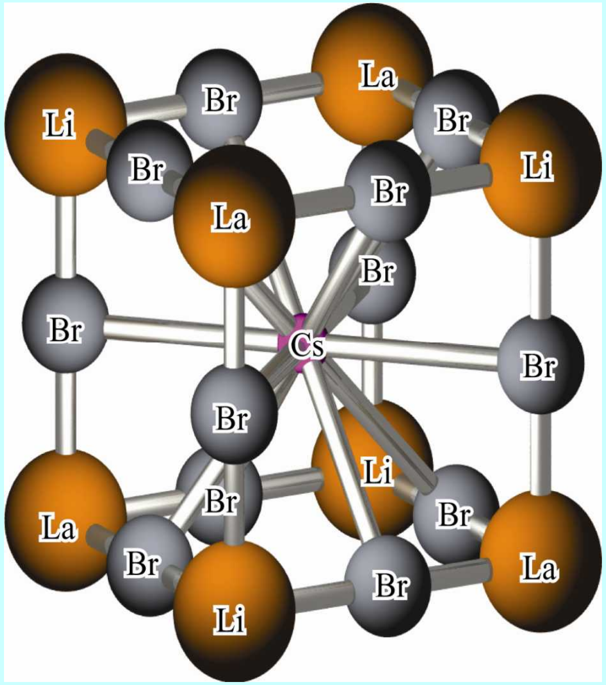
A_2BLnX_6: A, B: alkali; Ln: lanthanide; X: halogen.
Cubic crystals have good properties and low cost.
But how to design materials that have cubic crystals?

LANTHANIDE (e.g., $LaBr_3$):

Extremely brittle, high cost, fracture in the field.
What is the deformation mechanisms and can it be strengthened?

Electronegativity Effect

Double Perovskite $Cs_2LiLaBr_6$



[1]. P. Yang, M. A. Rodriguez, F. P. Doty, X. Zhou, M. R. Sanchez, and K. S. Shah, submitted.

[2]. X. W. Zhou, and F. P. Doty, *Phys. Rev. B*, **78**, 224307 (2008).

Observations:

1. Lattice constant of $Cs_2LiLaBr_6$ is $a = 2r_{LiLa} = 11.289$ Å[1], i.e., $r_{LaLa} = 7.983$ Å.
2. fcc La has a lattice constant $a = 5.307$ Å and a cohesive energy $E_c = -4.446$ eV/atom[2]. In fcc La, $r_{LaLa} = 3.753$ Å.
3. It is difficult to for a potential to be transferrable to both $Cs_2LiLaBr_6$ and La.

Solution:

The electronegativity difference-induced ionization can increase the bond length and reduce the bond strength.

Embedded Ion Method (EIM)

$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=i_1}^{i_N}\phi_{ij}\left(r_{ij}\right) + \sum_{i=1}^{N} E_i\left(q_i,\sigma_i\right)$$

system total energy

$$E_i\left(q_i,\sigma_i\right) = \frac{1}{2} q_i \cdot \sigma_i \, *$$

embedding energy at i

$$q_i = \sum_{j=i_1}^{i_N}\eta_{ji}\left(r_{ij}\right)$$

charge on atom i

$$\sigma_i = \sum_{j=i_1}^{i_N} q_j \cdot \varphi_{ij}\left(r_{ij}\right)$$

electrical potential (in voltage) at i

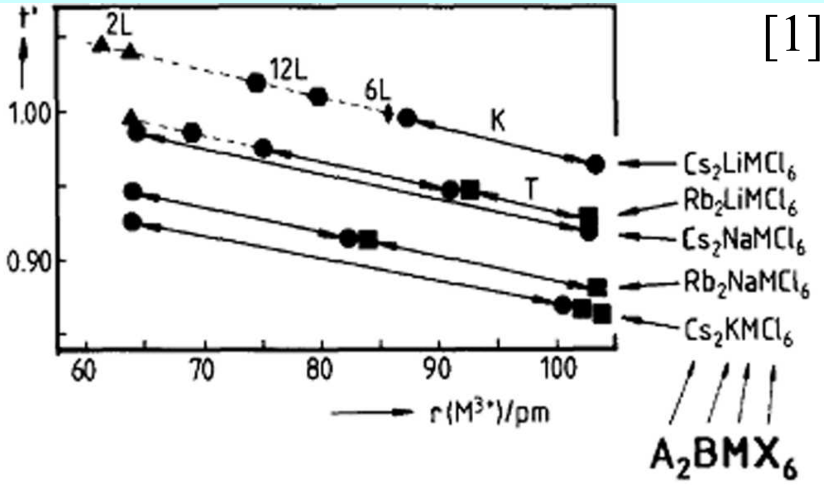
$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=i_1}^{i_N}\phi_{ij}\left(r_{ij}\right) + \sum_{i=1}^{N}\left\{\left(\sum_{j=i_1}^{i_N}\eta_{ji}\left(r_{ij}\right)\right)\cdot\sum_{j=i_1}^{i_N}\left[\left(\sum_{k=j_1}^{j_N}\eta_{kj}\left(r_{jk}\right)\right)\cdot\varphi\left(r_{ij}\right)\right]\right\}$$

*when $\varphi_{ij}(r) \sim r^{-1}$, the embedding energy reduces to Coulomb interactions between i and its neighbors:

$$E_i\left(q_i,\sigma_i\right) = \frac{1}{2}\sum_{j=i_1}^{i_N}\frac{q_i \cdot q_j}{r_{ij}}$$

The 1st Problem: Crystal Prediction

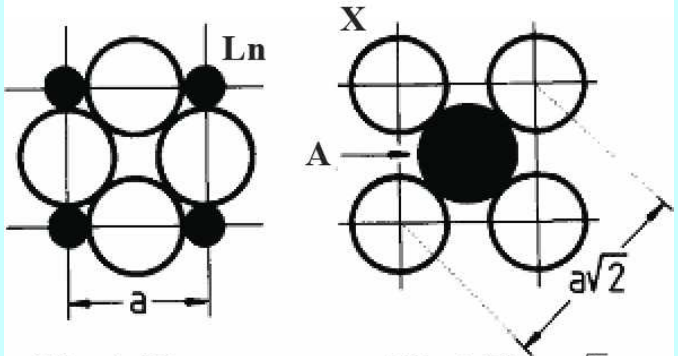
A_2BLnX_6: A, B: alkali; Ln: lanthanide; X: halogen.



[1]

Fig. 11. The derivation of Goldschmidt's tolerance factor t' (above) and its (useless) application to chloro-epasolites

[1]. G. Meyer, *Prog. Solid St. Chem.*, **14**, 141 (1982).



$2R_{Ln} + 2R_X = a$

$2R_A + 2R_X = \sqrt{2}\,a$

$$t' = \frac{R_A + R_X}{\sqrt{2}\left(\frac{R_B + R_{Ln}}{2} + R_X\right)}$$

Two Notions

1. Goldschmidt criterion[1,2] (hard sphere model) constrains bond length r to ionic radii R: $r_{AA} = 2R_A$, $r_{BB} = 2R_B$, $r_{AB} = R_A + R_B$, … Our model treats all bond lengths as independent parameters.

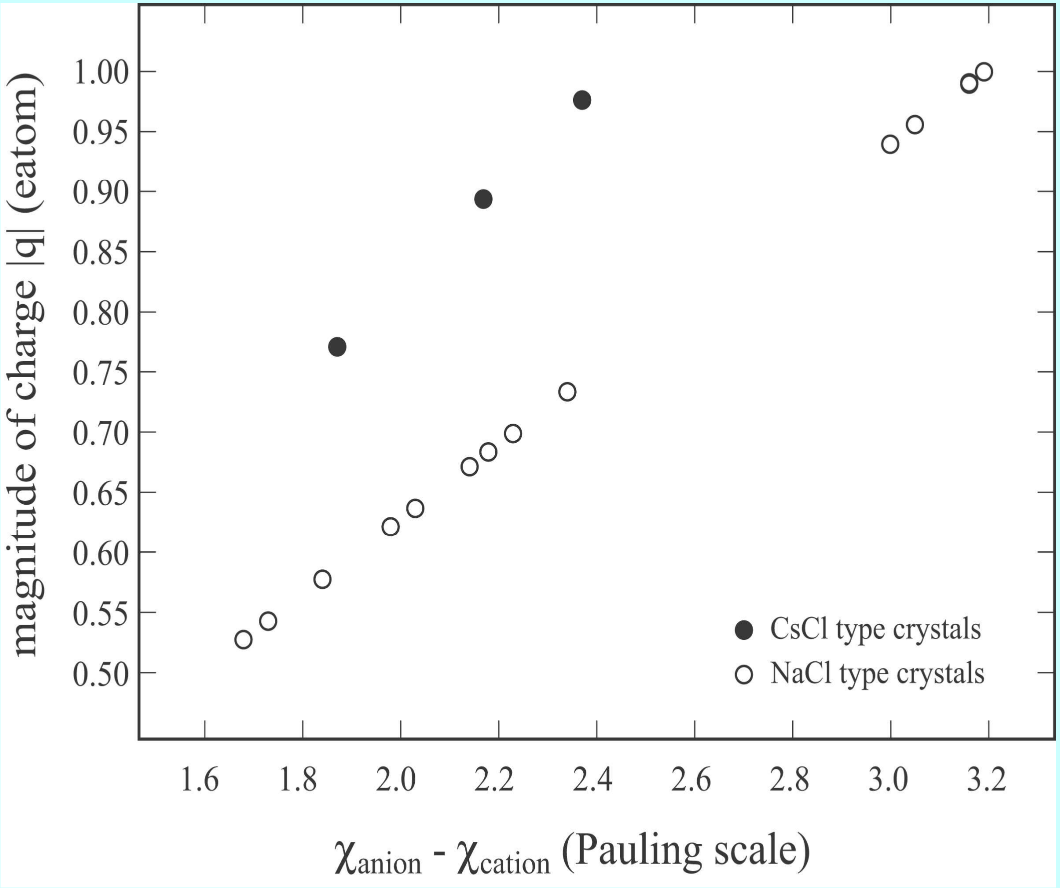
2. We model alkali halides as a first step because elpasolites are composed of alkali, halogen, and lanthanide elements.

[1]. V. M. Goldschmidt, Geochemisce Verterlungsgesetze der Elemente. Norske Videnskap, Oslo, 1927;
[2]. L. Liang, L. Wencong, and C. Nianyi, *J. Phys. Chem. Sol.*, **65**, 855 (2004).

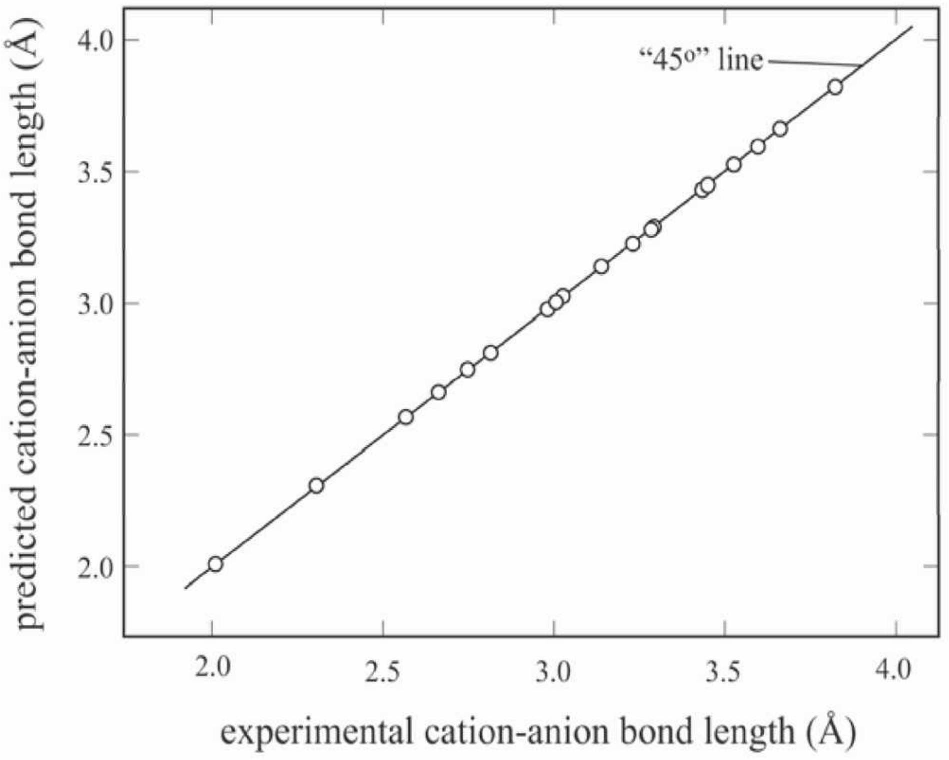
EIM Potential Database

1. contains all nine alkali halide elements (Li, Na, K, Rb, Cs F, Cl, Br, I),
2. focuses on atomic size, but also considers electronegativity and bond energy effects,
3. uses elemental properties directly as model parameters without parameterization, and
4. gives good trend of charge, energy, and bond length predictions.

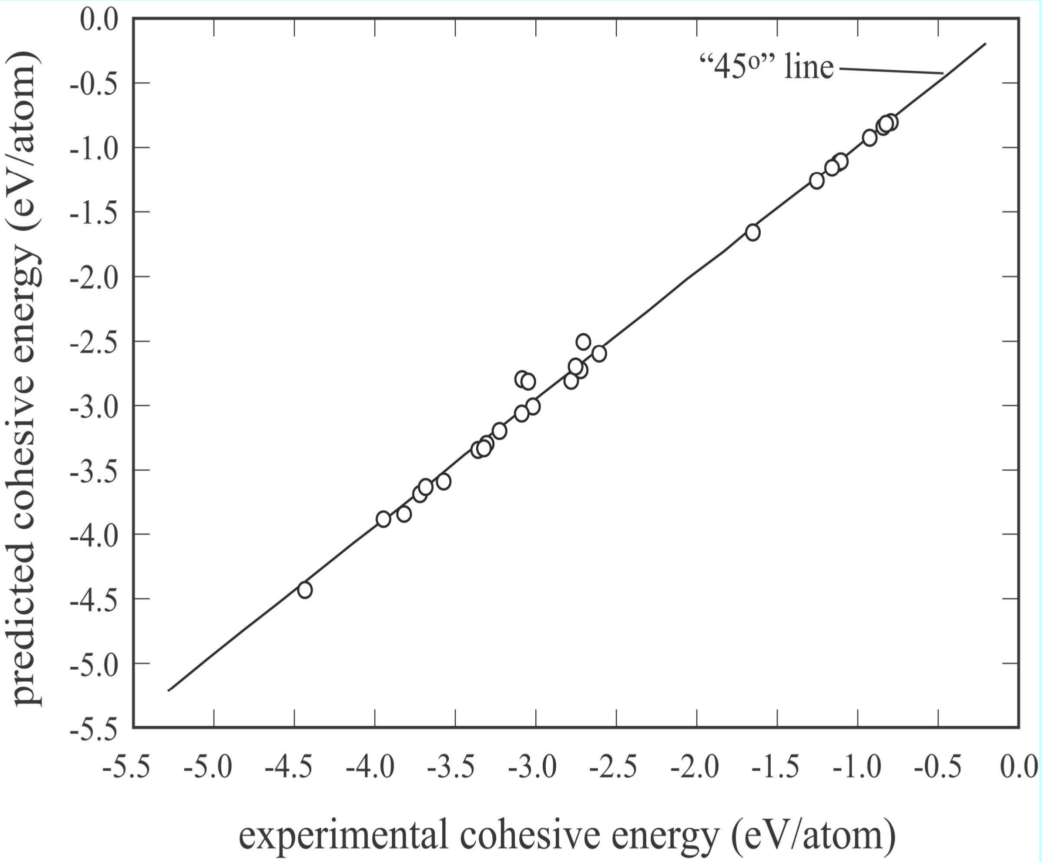
Charge vs. Electronegativity



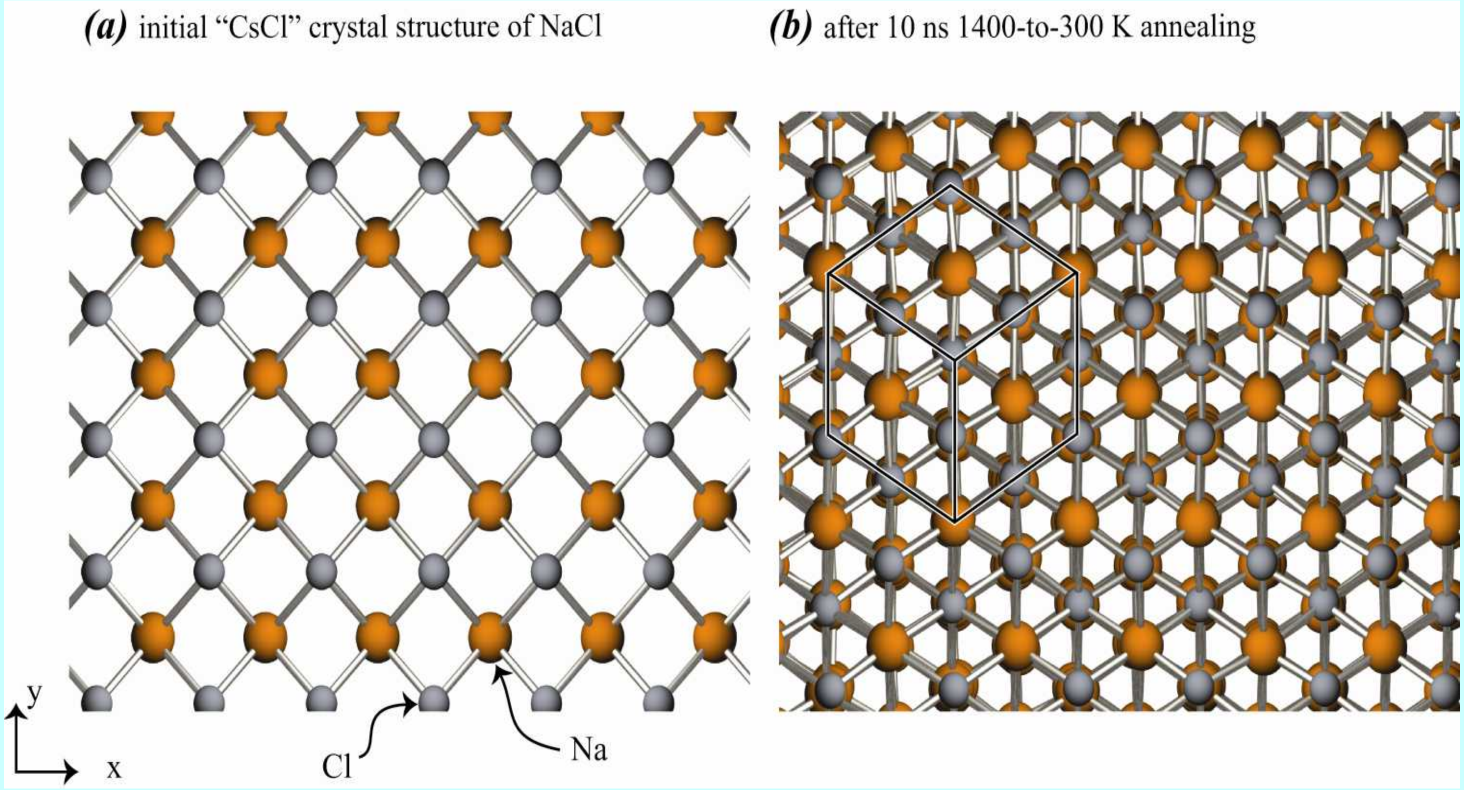
Lattice Constant Prediction



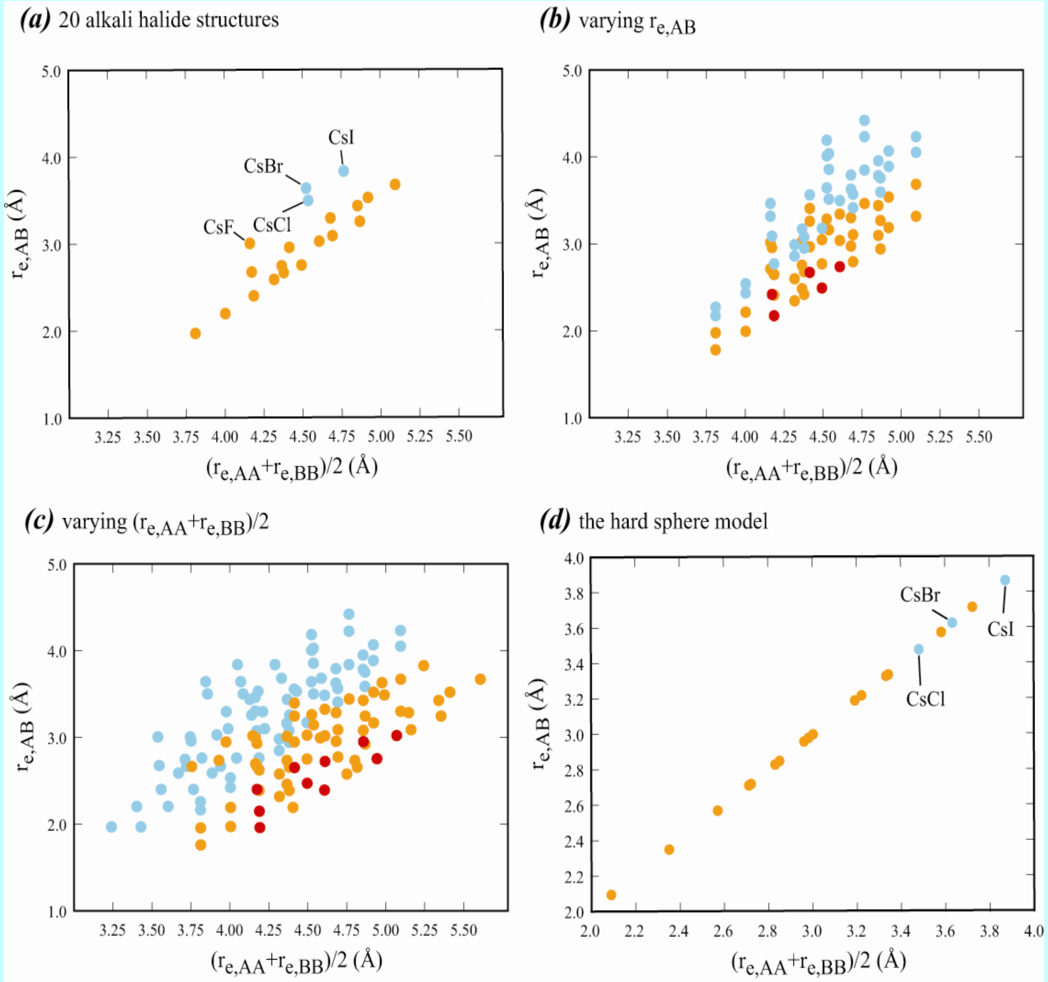
Cohesive Energy Prediction



Structure Prediction



Crystal Phase Diagram



(a) 20 alkali halide structures

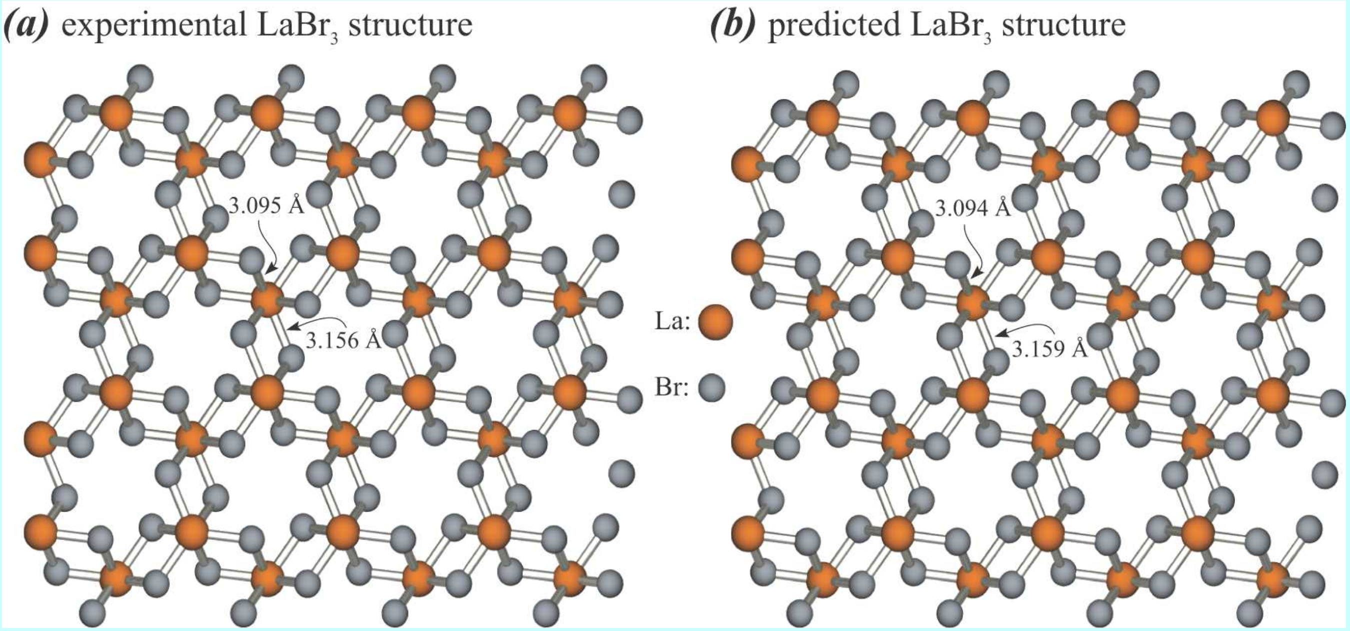
(b) varying $r_{e,AB}$

(c) varying $(r_{e,AA}+r_{e,BB})/2$

(d) the hard sphere model

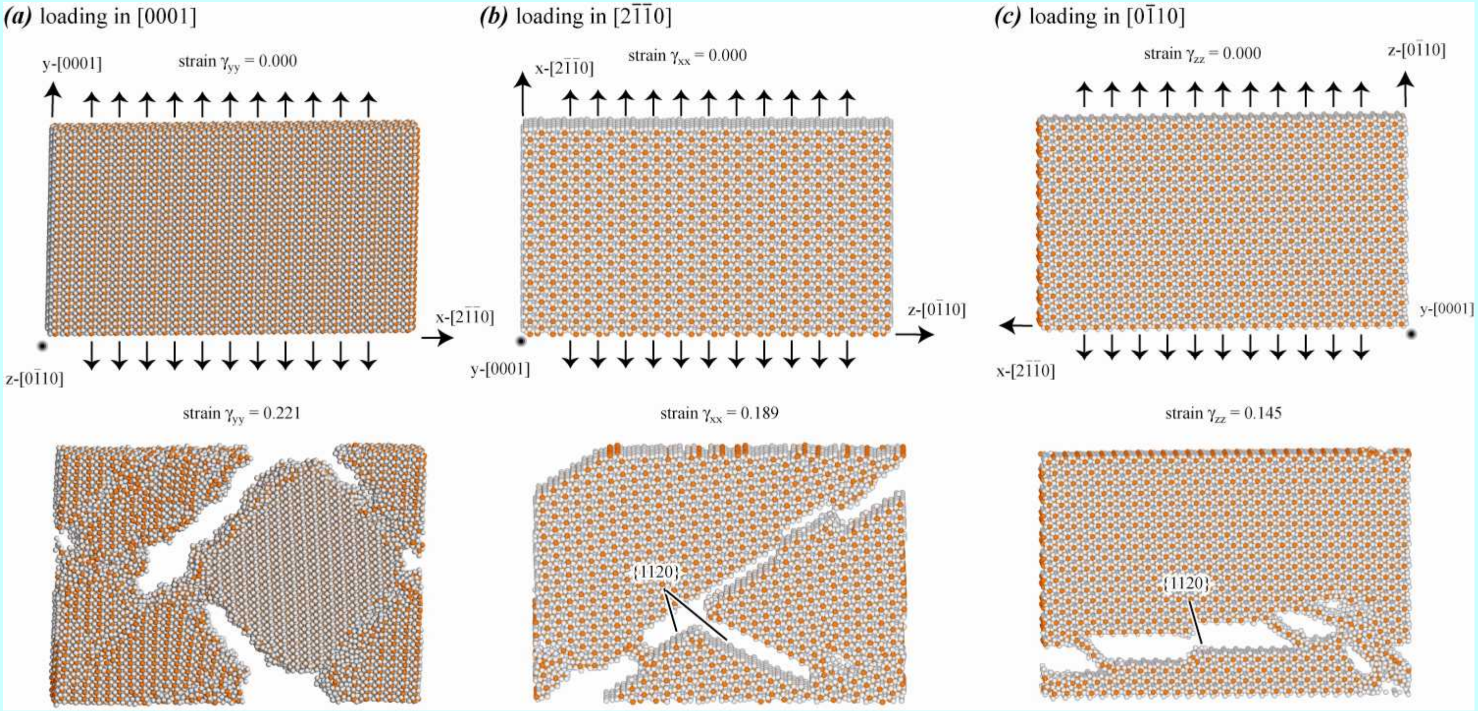
The 2nd Problem: $LaBr_3$ Fracture

(a) c/a ~ 0.57; (b) rotated Br polyhedron; (c) two La-Br bond lengths; and (d) big lattice hollows

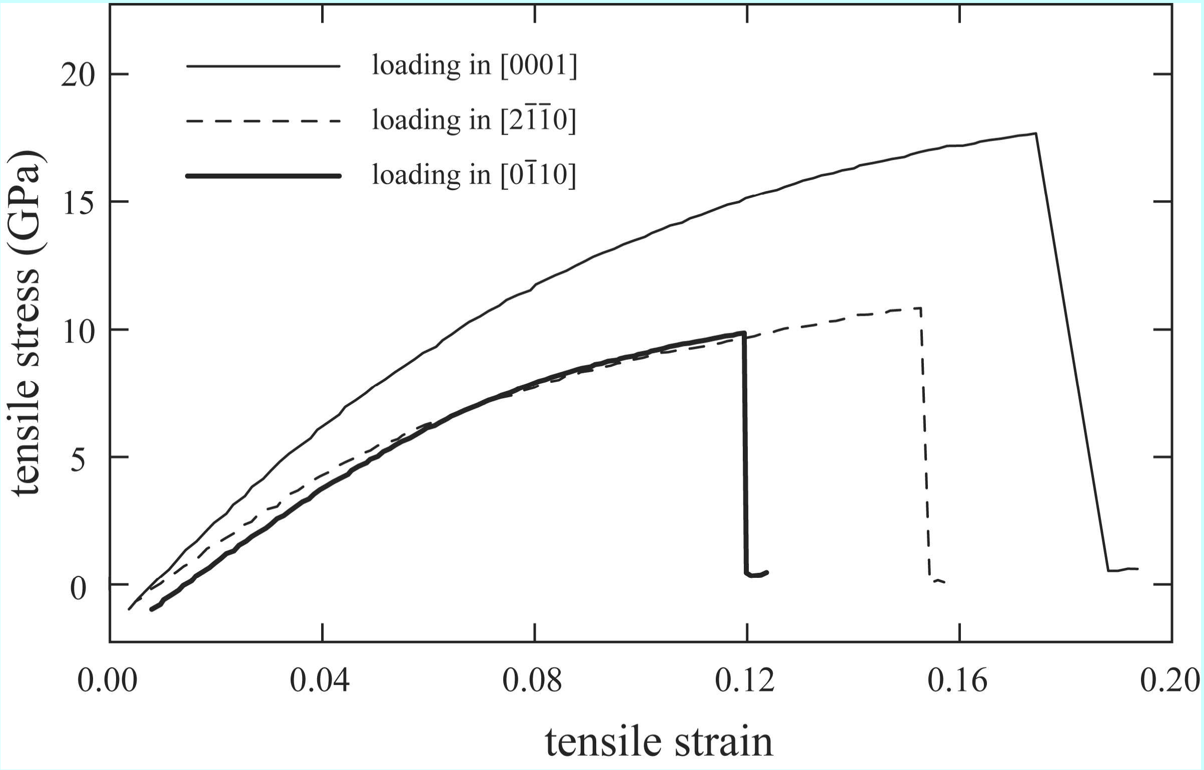


Our $LaBr_3$ EIM captures the structural properties!

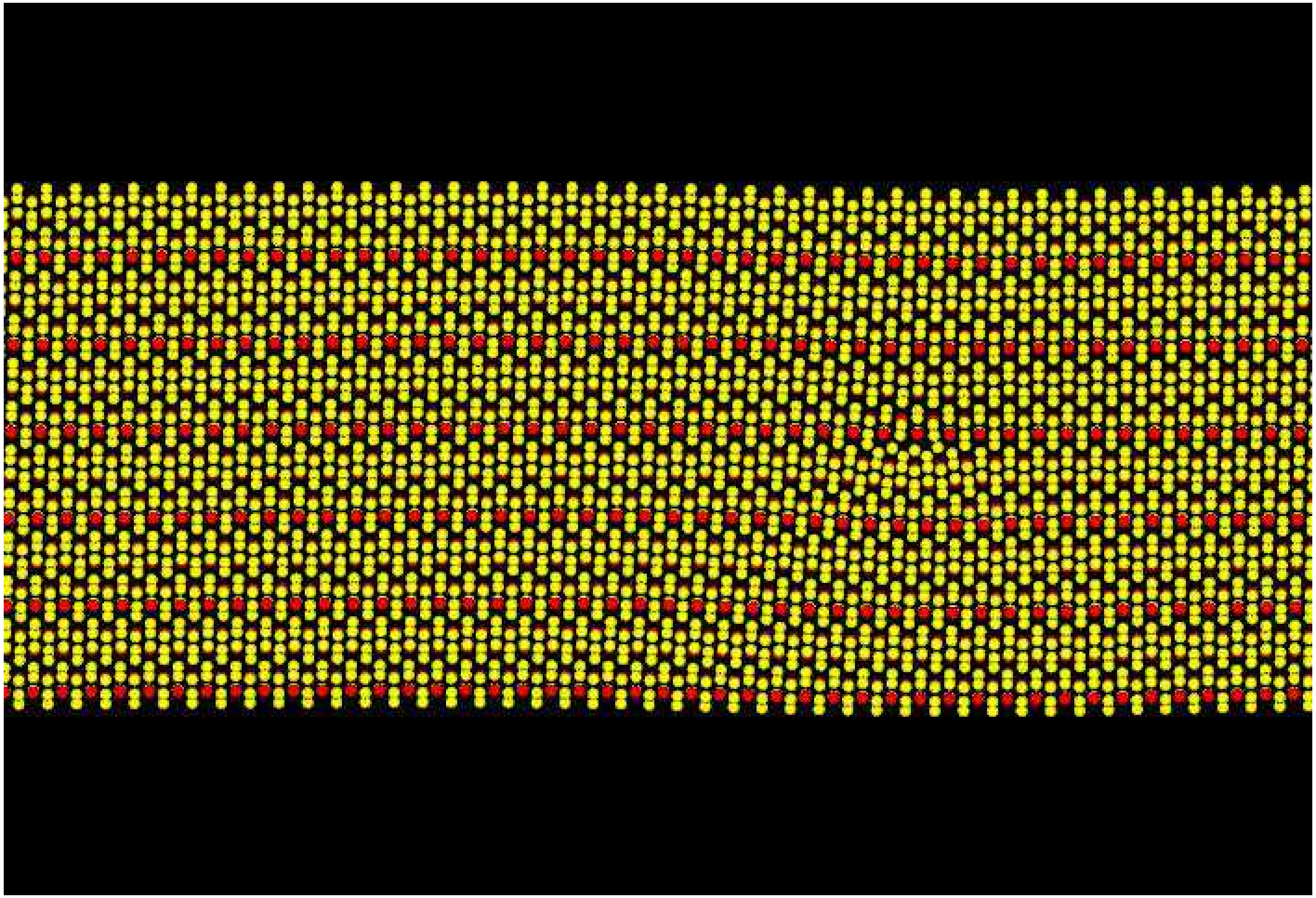
Tensile Fracture vs. Orientation



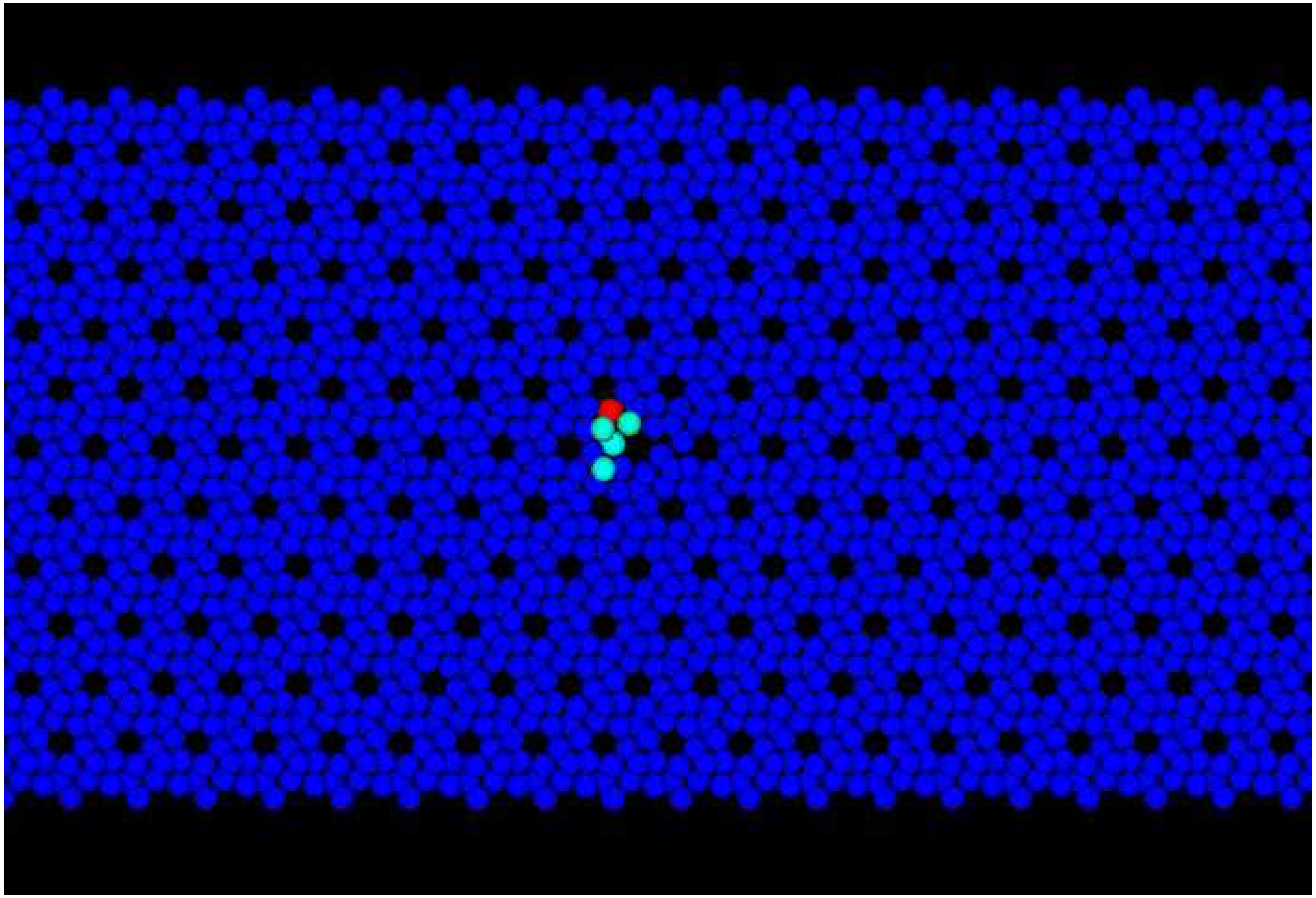
Tensile Stress vs. Strain



[0001] Edge Dislocation under 4GPa at 0 K



[0001] screw dislocation under 3GPa at 0 K



Slip Systems

•The only mobile dislocations in $LaBr_3$ are on the prism planes.

•The material cannot be strain-hardened. Approaches that block dislocation motion on the prism planes must be sought.

Conclusions

- New atomistic simulation methods enable crystal rules to be explored in atomic size-electronegativity-bond energy space.
- A new crystal rule beyond the hard sphere model was discovered for alkali halides.
- The critical stress for the {1120} cleavage is very low in $LaBr_3$.
- The only mobile dislocations in $LaBr_3$ are on the {1120} prism planes.
- $LaBr_3$ cannot be strain-hardened. Approaches that block the dislocations (e.g., solid-solution strengthening) can be used.

Acknowledgement

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