Ab Initio Discovery of Novel Crystal Structure in Barium and Sodium-Calcium Compounds Under Pressure using DFT

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Overview

- *Ab initio* computational study at high pressures
  - Elemental barium
  - Immiscible sodium-calcium binary alloy
- Used density functional theory with a genetic algorithm
- Predicted ground state structures of barium *a priori*
  - Determined ground state transition pressures and phase stability
  - Discovered new ground state phase at moderate pressures
  - Examined complex Ba-IV phase in detail
- Demonstrated feasibility of methods with binary alloy
  - No stable compounds found, but promising results

Proposed vs. Actual Outcomes

Proposed

- Elemental studies
  - Barium, Beryllium, and Magnesium
  - Full structural and electronic characterization of each
  - Time permitting, superconductivity calculations
- Na-Ca Binary Alloy
  - Application of genetic algorithm

Actual

- Elemental studies
  - Barium only!
    - Implemented and tested genetic algorithm
    - Phase stability calculations
    - Discovered new phase and investigated complex phase
    - No electronic analysis
- Na-Ca Binary Alloy
  - Initial results from genetic algorithm

Motivation

- Why study high pressures?
  - Superconductivity!
    - We still don't really know why [1]
  - Incredible material properties
  - Unexpected structural changes
  - Electronic transitions
- Elemental Barium
  - Interesting phase space
  - Significant test of our method
- Sodium-Calcium Binary Alloy
  - Independent elements display remarkable properties
  - Composition space search

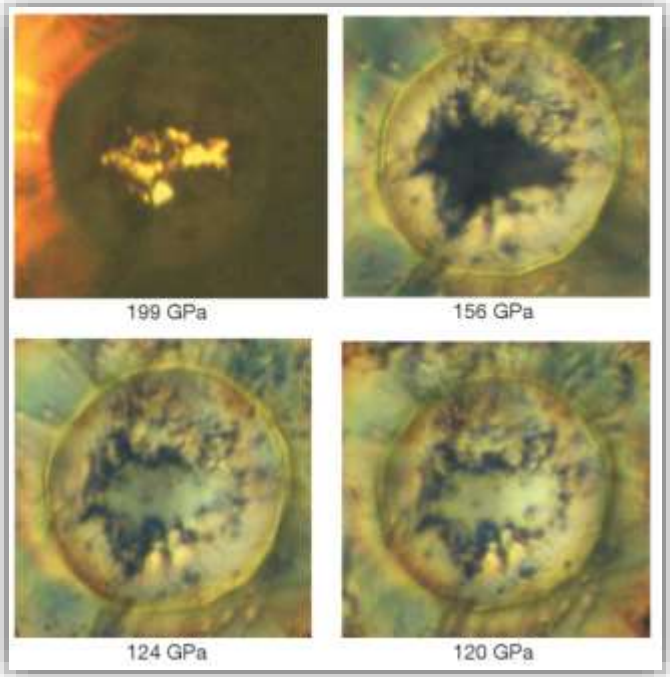


Figure 1: Example of unexpected electronic/optical transition in sodium at high pressure. [2]

Brief Overview of Methods

- Density Functional Theory (DFT)
  - Implemented with VASP
  - Functionals of charge density → ground state energy
  - Accurate, and easier than experimental studies
- Genetic Algorithm (GA) Search
  - Developed by Will Tipton [3]
  - Optimizes randomly generated structures based on evolutionary techniques
  - Minimizes either enthalpy/atom or distance from a convex hull

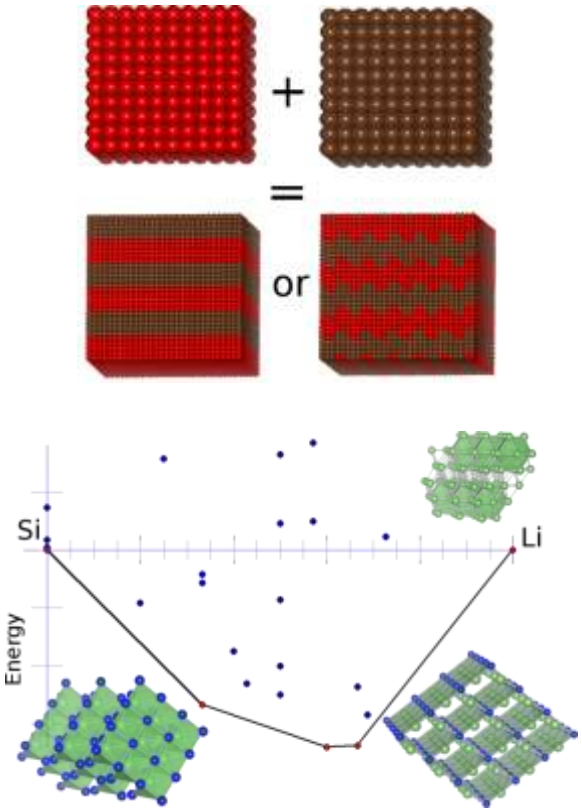


Figure 2: Example of slicing crossover and convex hull [3].

Barium Structure Search

Pressure [Gpa]	Structures			
0	α-U	$P2_1/m$-6	BCC	$C2/m$-5
	FCC	BCT	Simple Hex.	
10	HCP	α-U	*Imm2*-4	C2/m-5
30	HCP	*Pnma*-4	FCC	
60	α-Sm	HCP	α-U	$P\bar{3}m1$-5
100	HCP	α-Sm	FCC	
200	HCP	α-Sm	FCC	
300	HCP	α-Sm	FCC	

Table I: Results of barium genetic algorithm search.

- Structure search at seven pressures
- Discovered every experimental phase (except Ba-IV)
- Discovered a number of symmetry broken and transition structures
- New α-Samarium phase
- Condensation of phase space at high pressures

Barium Phase Stability

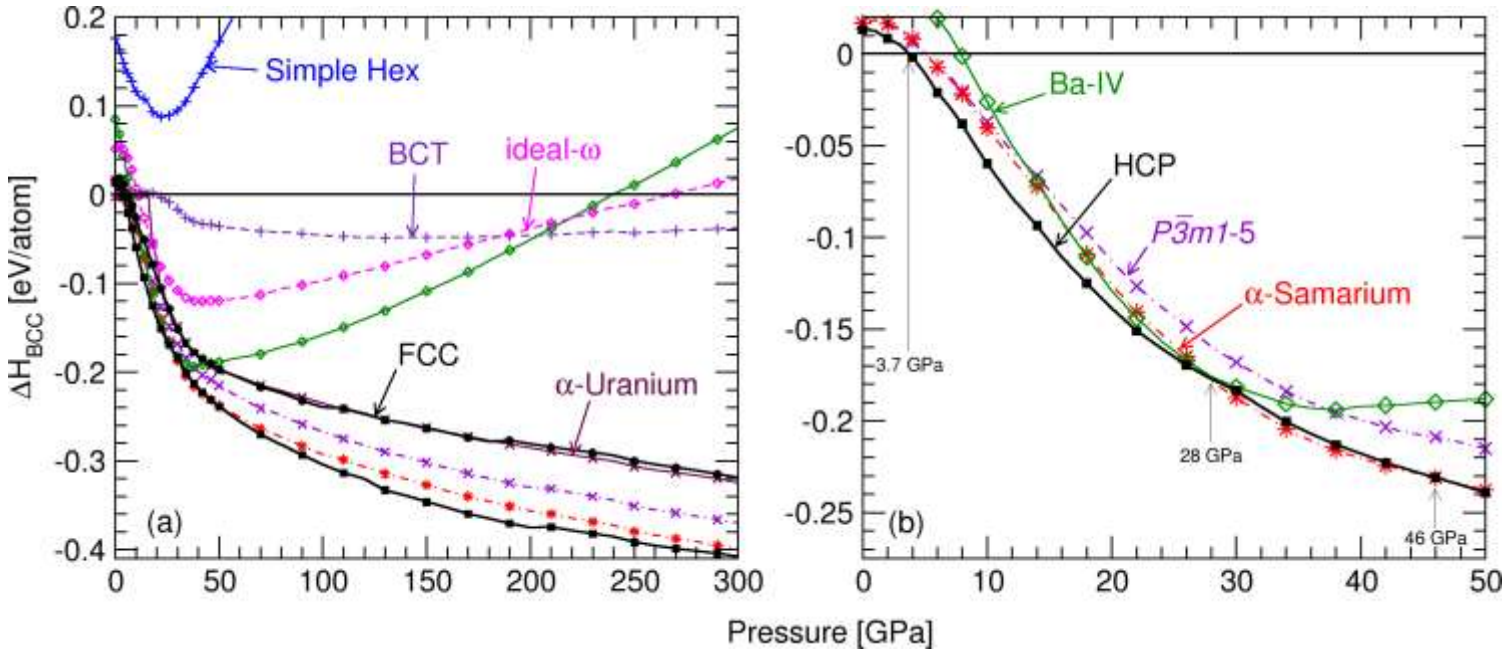


Figure 3: Calculated enthalpy vs. pressure curves for barium, relative to BCC phase.

bcc (Ba–I) $\xrightarrow{5.5}$ hcp (Ba–II) $\xrightarrow{12.6}$ incommens. (Ba–IV) $\xrightarrow{45.0}$ hcp (Ba–V)

Table II: Experimentally observed pressure-induced phase transformations at room temperature, in GPa [4].

Incommensurate Ba-IV

- What is incommensurate?
  - Two (or more) distinct unit cells in one structure
  - Irrational lattice vector ratio
- Ba-IV (at 12.6 GPa) [4]
  - Experiment – 1.388 ratio
  - Theory – 1.333 ratio
- Computational study by Reed and Ackland [5]
  - Predicted stability of Ba-IV
  - Utilized an unphysical correction:
  - $\Delta E = {}^{V}/_{4} \times C_{33}\left[1 - \frac{2}{3}\,{}^{c_{host}}/_{c_{guest}}\right]^{2}$

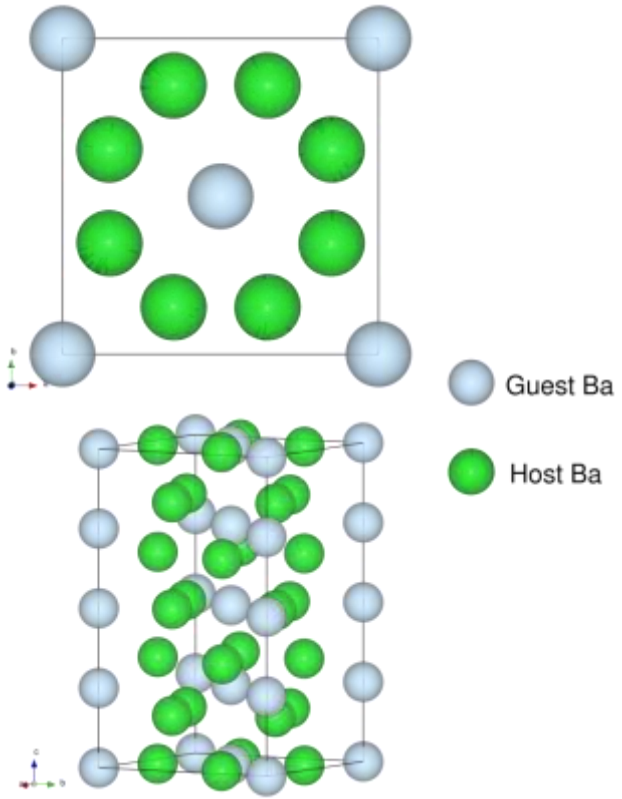
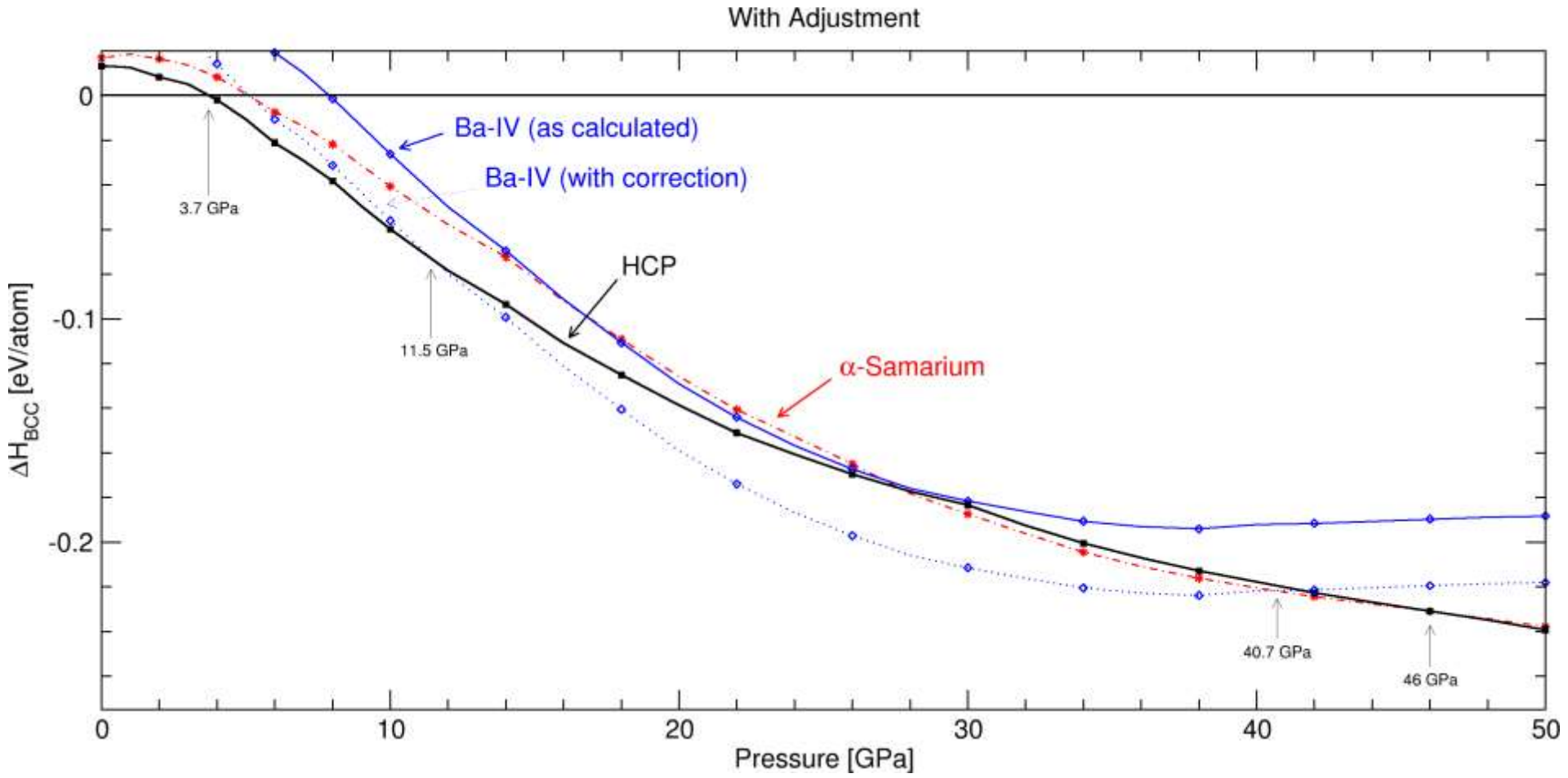


Figure 4: 4/3 commensurate analog of Ba-IV used in our calculations. Its space group is *I4/mcm* and has 32 atoms at Wyckoff positions *4a*, *4c*, *8h* (x=0.35271), and *16l* (x=-0.35011 and z=-0.33503) at 12.6 GPa.

Incommensurate Ba-IV

Vol/atom	C_{33}	c-ratio
31 Å	50 GPa	1.333



A Novel Barium Phase!

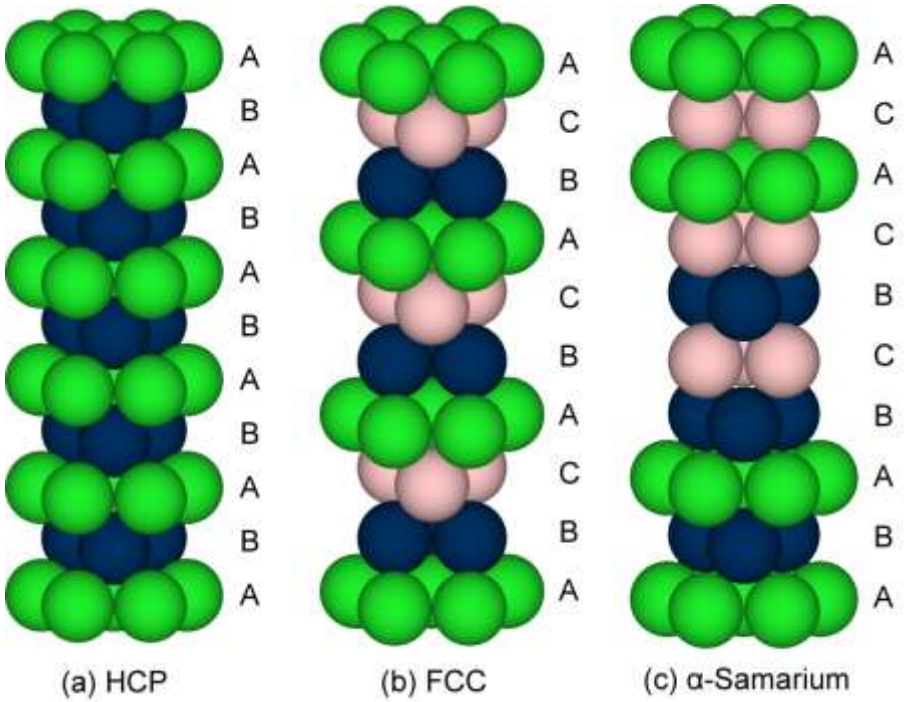


Figure 5: Close packed structures of barium. (a) HCP simple …ABA… stacking; (b) FCC three layer …ABCA… pattern; (c) α-Sm nine-layer …ABABCBCACA… pattern.

- **α-Samarium**
  - Never before seen in barium
  - Proposed true ground state of lithium [6]
  - Close packed
  - Complicated stacking pattern
    - Incomplete electron transfer?
  - Electronic analysis needed

Sodium-Calcium Structure Search

- Composition search takes much longer than elemental structure search
- No stable compounds found yet
- Proved feasibility of method

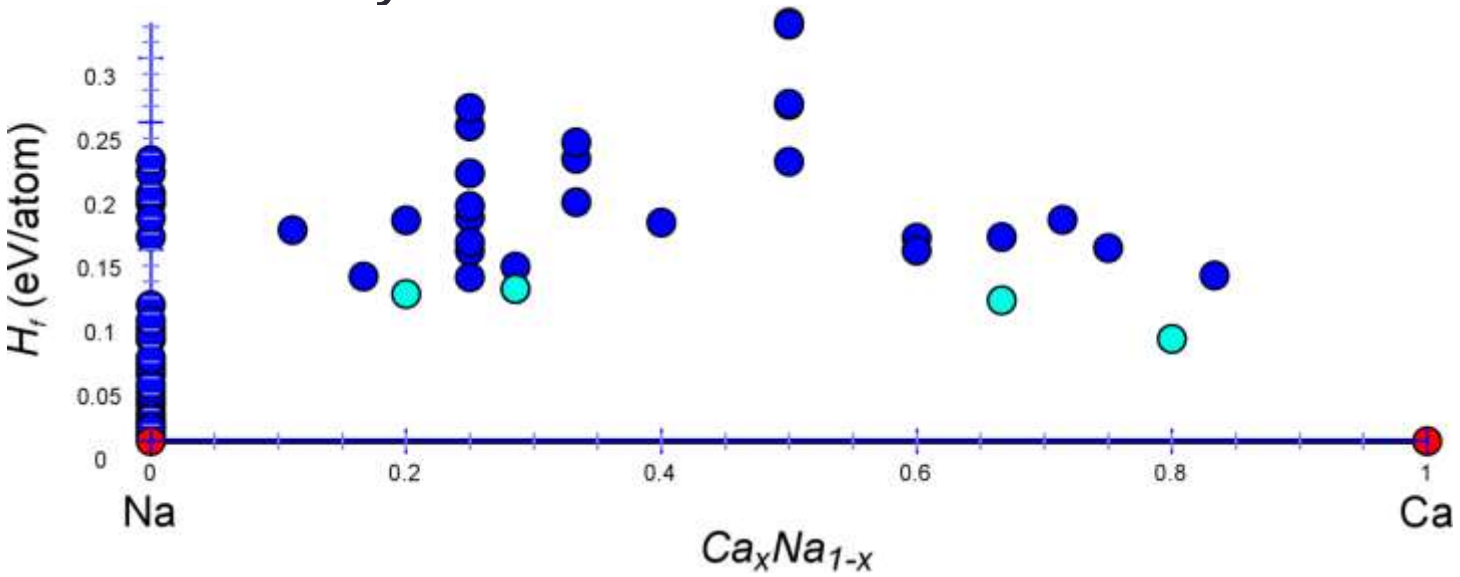


Figure 6: Initial Na-Ca binary search results at 50 GPa. No stable intermediates were discovered. Red structures are stable; cyan deserve more investigation.

Summary

- Performed genetic algorithm structure search on barium
  - Discovered all but one experimentally known phase
  - Discovered new phase (α-Samarium)
- Calculated phase stability as function of pressure
  - Results deviate from experimental observations
  - Predict new α–Sm ground state from 28-46 Gpa
- Characterized commensurate analog of Ba-IV
  - Contest previous results from literature
  - Still not able to predict stability without a significant correction
- Performed initial Na-Ca binary alloy structure search
  - Proved feasibility of methods, but no stable structures found

Future Work

- Elemental materials
  - Investigate larger analogs of Ba-IV
  - Full electronic analysis of new barium phase
  - Search for other close-packed structures in barium
  - Search for α-Samarium structure in similar elements
- Sodium-calcium binary alloy
  - Continue structure search
  - Constrain search to smaller composition space
  - Investigate promising compounds
  - Perform search at more pressures

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