Computational Studies of Physical Properties of Boron Carbide

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Outline

- ❑ Motivation
- ❑ Goal
- ❑ Theoretical Methods
- ❑ Progress
- ❑ Future work

Why Boron Carbide

- **Attractive physics properties for energy applications:**
  - *Light & Hard*
  - *High melting temperature, chemical inertness*
  - *High efficiency direct thermoelectric conversion*
  - *High neutron absorption cross section*

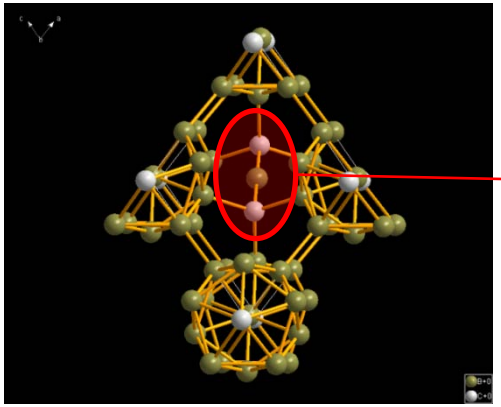
- **Theoretical interests:**
  - *Controversial structure*
  - *Conflicting spectroscopic finger prints*
  - *Mysterious structure-properties relation*

Structure of Boron Carbide

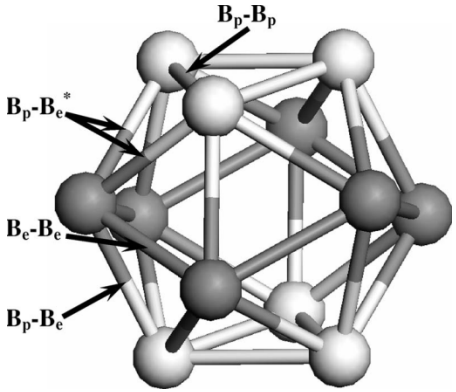
- **Structure types**
  - *Crystal*
  - *Amorphous*
  - *Polycrystal*

- **Crystal structures**
  - *Non-stoichiometric composition* $B_{12+x}C_{3-x}$ *(0.06?<x<0.17)*
  - *Orthorhombic* ***R-3m*** *lattice*
  - *Hexagonal close packed icosahedrons*
  - *Carbon disorder*

- **Local structures**
  - *$(B,C)_{12}$ icosahedra: B_{12} , $B_{11}C$, $B_{10}C_2$…*
  - *$(B,C, \square)_3$ chain: C-B-C,C-B-B,B- □-B…*
  - *(B,C)-(B-C) bond between icosahedra*



Chain: ***Interstitial octahedral sites between $(B,C)_{12}$ icosahedral clusters***



Structure Models

- **Commonly accepted: R-3m lattice**

- **Controversial: carbon distribution in boron carbide**
  - *Carbon site preference*
    - *icosahedron > chain: X-ray*
    - *icosahedron < chain: neutron, IR/Raman*
  - *Vacancy site preference*
  - *Interstitial defect?*

- **Others:**
  - *Disorders in boron carbide: $(B,C)_{12}$ icosahedron vacancy?*
  - *Structure of amorphous boron carbide?*

Puzzles in Boron Carbide

- **Physical properties indifferent to carbon concentration**
  - *Lattice structure remains the same*
  - *Semiconductor for wide range of carbon concentration*
  - *Similar mechanic properties*

- **Bonding in boron carbide**
  - *boron bonding in the chain: is the boron strongly bonded or space constrained?*
  - *bonding strength in the icosahedron and the chain: is the icosahedron softer?*
  - *Finger prints from different technologies used to obtain local structure are often giving conflicting conclusions*

Goal

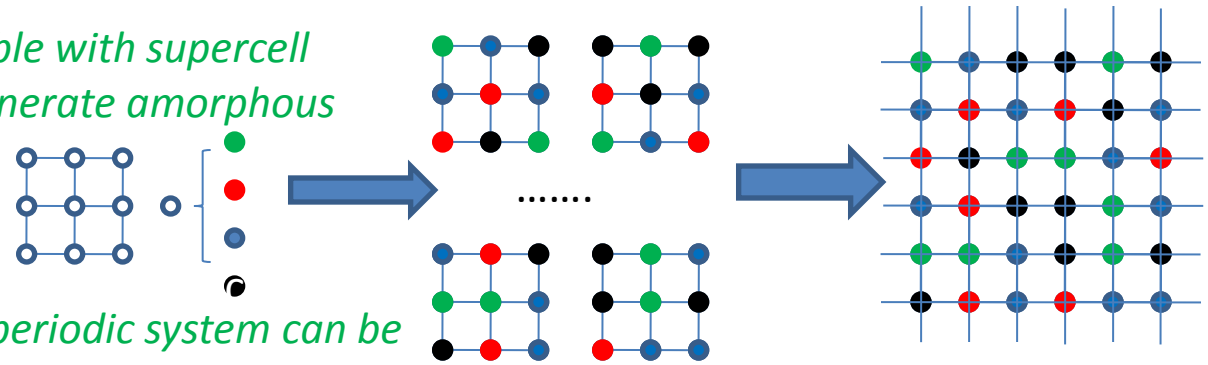
- **To develop a systematic approach for computing physical properties of *disordered system* using *first principles* methods**
  - *Thermodynamic properties: Gibbs free energy, etc.*
  - *Mechanic properties: elastic tensor*
  - *Dielectric properties: dielectric tensor*
  - *Vibrational spectra, XAS/XES spectra*
  - *A portable and scalable software implementation*

- **To resolve the structure and properties puzzles found in boron carbides using the above methods**
  - *Proper structural model for boron carbide.*
  - *Structural-properties relation in boron carbide*
  - *Examining the validity of spectroscopic finger prints*

- **To search for novel structures in boron carbide**

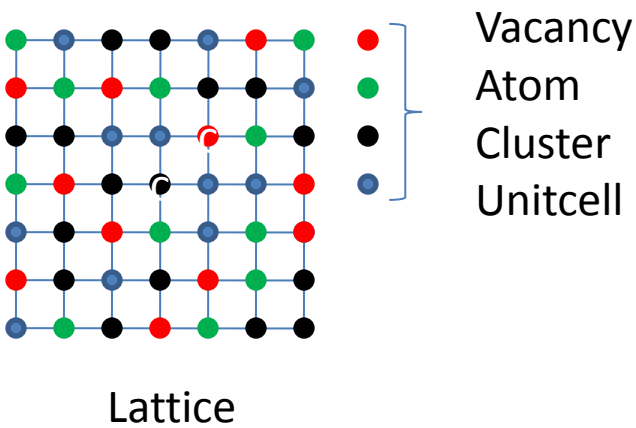
Supercell Approach for Studying Disorder

- **Supercell Approach**
  - *Partial occupation possible with supercell*
  - *Methods available to generate amorphous structure based on it*



- **Advantages**
  - *Methods developed for periodic system can be readily applied*
  - *Larger configuration space for better description of disorder*
  - *Possible to estimate configuration entropy*
  - *Straightforward for phonon and XANES/ELNES calculations*

- **Disadvantages**
  - *May not be suitable for dilute disorder*
  - *Difficult to determine sufficient supercell size*
  - *High computational cost*



Methods: G(P, T) package

- First principles calculation based on DFT
- Born-Oppenheimer approximation
- Quasi-harmonic approximation for lattice dynamics
- Berry phase approach for polarization
- RPA for optical properties

G(P, T) package: Capabilities

- **Phonon**
  - *Zone center phonon modes symmetry assignment*
  - *Phonon dispersion (with/without LO/TO splitting)*
- **Polarization**
  - *Born effective charge*
  - *dielectric properties*
- **Thermodynamic properties**
  - *Helmholtz free energy F(V,T), Gibbs free energy G(P,T)*
  - *Specific heat , thermal expansion, Grüneisen parameter, etc.*
- **Mechanical properties**
  - *Elastic tensor*
  - *T-P dependent elastic properties*
  - *Tensile strength*
  - *Sound velocity*
- **Interface to other programs**
  - *Orthogonalized linear combination of atomic orbitals (OLCAO) method for electronic structure, charge/bonding analysis, XAS/XES spectra.*

G(P, T) package: Implementation

- **Portable implementation: written in bash, Perl and Fortran**

- **Layered toolbox design**
  - *Automation for common tasks*
  - *Service layer:*
    - » *Job management,*
    - » *Input/output processing*
  - *User interface layer:*
    - » *calPhonon, calFVT, calELASTIC, etc.*

- **Queueing module for parallel execution**
  - *Limited scalability of first principles method (VASP ~ 1000 processors)*
  - *Parallelism in G(P,T) algorithms (multiple independent VASP jobs)*

- **Restarting capabilities**

Electronic Structure

- Computing engine: *Vienna ab initio package* (VASP)
- Band structure and density of states
- Charge analysis
- Interface to *OLCAO* for charge and bonding analysis

Phonon

❑ Quasi-Harmonic Approximation

$$\omega^2(\mathbf{q})\mathbf{e}_{k_\mu} = \sum_{k',\nu} D_{\mu\nu}\left(\begin{smallmatrix}\mathbf{q}\\ kk'\end{smallmatrix}\right)\mathbf{e}_{k_\mu}$$

$$D_{\mu\nu}\left(\begin{smallmatrix}\mathbf{q}\\ kk'\end{smallmatrix}\right) = \frac{1}{\sqrt{m_\mu m_\nu}}\sum_{l'}\phi_{lk_\mu,l'k'_\nu}\exp[i\mathbf{q}\cdot(\mathbf{r}_{l'k'}-\mathbf{r}_{lk})].$$

$$\phi = \phi_0 + \sum_{lk\mu}\phi_{lk_\mu}u_{lk_\mu} + \frac{1}{2}\sum_{lk\mu,l'k'\nu}\phi_{lk_\mu,l'k'_\nu}u_{lk_\mu}u_{l'k'_\nu} + \cdots$$

❑ Dynamic matrix

- *finite difference approximation*

$$\Phi_{lk_\mu,l'k'_\nu} = -\frac{\partial F_{lk_\mu}}{\partial u_{l'k'_\nu}} \approx -\frac{\Delta F_{lk_\mu}}{\Delta u_{l'k'_\nu}}$$

$$\Phi_{lk,l'k'} = 0 \quad for \quad |r_{lk} - r_{l'k'}| > R_{cutoff}$$

Supercell finite difference approach:

$$\Phi_{lk,l'k'} = 0 \quad for \quad |r_{lk} - r_{l'k'}| > R_{cutoff}$$

Density functional perturbations theory:

$$D_{\mu\nu}\begin{pmatrix} q \\ kk' \end{pmatrix} = \frac{1}{\sqrt{m_\mu m_\nu}}\frac{\partial^2 E}{\partial u^q_{\mu k}\partial u^q_{\nu k'}}$$

❑ LO/TO splitting

- *Born effective charge calculated using Berry phase method*
- *LO/TO splitting calculated using Born effective charge*

Thermodynamic properties

- **Helmholtz free energy** $F(\varepsilon,T)$

  Born-Oppenheimer Approximation: $F(\varepsilon,T) = F_e(\varepsilon,T) + F_v(\varepsilon,T)$

  Electronic free energy: $F_e(\varepsilon,T) \sim E(V)$

  Vibrational free energy:

$$F_v(\varepsilon,T) = \sum\sum\left\{\tfrac{1}{2}\hbar\omega_i(\varepsilon,\vec{q}) + k_B T \ln(1 - e^{-\hbar\omega_i(\varepsilon,\vec{q})/k_B T})\right\}$$

  Thermal stress: $\boldsymbol{\sigma_T}(\varepsilon,T) = \partial F_v(\varepsilon,T) / \partial \varepsilon$

- **Gibbs free energy**

  Legendre transformation: $G(\boldsymbol{\sigma},T) = F(\varepsilon,T) + \boldsymbol{\sigma}\,\varepsilon$

  $\boldsymbol{\sigma}(\varepsilon,T) = \partial F(\varepsilon,T) / \partial \varepsilon$

- **Other thermodynamic properties can be derived from the calculated Helmholtz/Gibbs free energy**

Mechanical properties

- **Elastic tensor**

  No temperature effect: $C(\varepsilon) = -\partial \sigma(\varepsilon) / \partial \varepsilon$

- **Sound velocity**

  Christoffel wave equation: $\rho v^2 u_i = C_{ijklm} l_j l_k u_m$

- **Tensile/compression test**

Spectroscopic properties

- **Electronic:**
  - *ELNES/XANES spectra*

- **Vibrational:**
  - *Phonon dispersion, DOS*
  - *Zone center modes symmetry assignment*
  - *IR spectra*

Extend G(P, T) to disordered systems

❑ Supercell Approach for Disordered Systems

- *Module 1: Supercell sampling*
  - *Model generation: random lattice, genetic algorithm*
  - *Model characterization: RDF, symmetry, etc.*
- *Module 2: Supercell statistics/properties calculations*
  - *Average vibrational properties*
  - *Average elastic properties*
  - *Simple supercell ensemble average*
  - *Cluster expansion method + Monte Carlo simulation for thermodynamic properties*
- *Module 3: Interface to other packages*
  - *Interface to OLCAO for XAS/XES spectra and bonding analysis*

Module 1: Supercell Sampling

❑ Model generation

- *Importance sampling method to minimize supercell set*
- *Method 1: Fixed lattice of atoms for substitutional disorder*
  - *Random placing atoms based on partial occupation*
- *Method 2: Fixed lattice of clusters*
  - *Random placing clusters based local structure distribution*
  - *Seeds for generating amorphous models*
- *Method 3: Genetic algorithm*
  - *Global search algorithm to locate energy minimal*
  - *Finding new structures*

Module 2: Supercell Statistics

- **Monte Carlo:**
  - *All first principles energy evaluations*
    - *Use electronic total energy of the supercell*
    - *Use Helmholtz free energy of the supercell*
  - *Cluster expansion:*
    - *Genetic algorithm to generate a small modeling set*
    - *Small model sampling -> empirical cluster interaction parameters*
    - *Monte Carlo simulation using empirical cluster parameters*

Phase I: method and program development

Year 1 progress (04/01/2009-03/31/2010)

- **Module 1: Supercell Sampling**
  - *Implemented*
  - *Method 3 genetic algorithm still under test*

- **Module 2: Supercell Statistics/Properties Calculation**
  - *Implemented, under test*

- **Module 3: Interface to OLCAO method**
  - *Implemented and passed tests.*

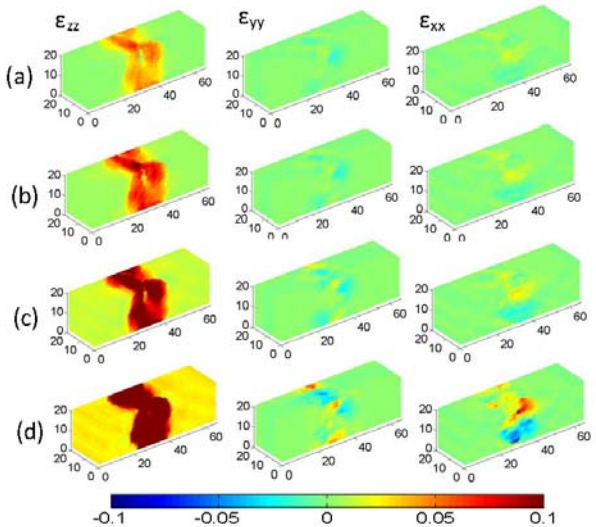
Phase I: Other Developments

Year 1 progress

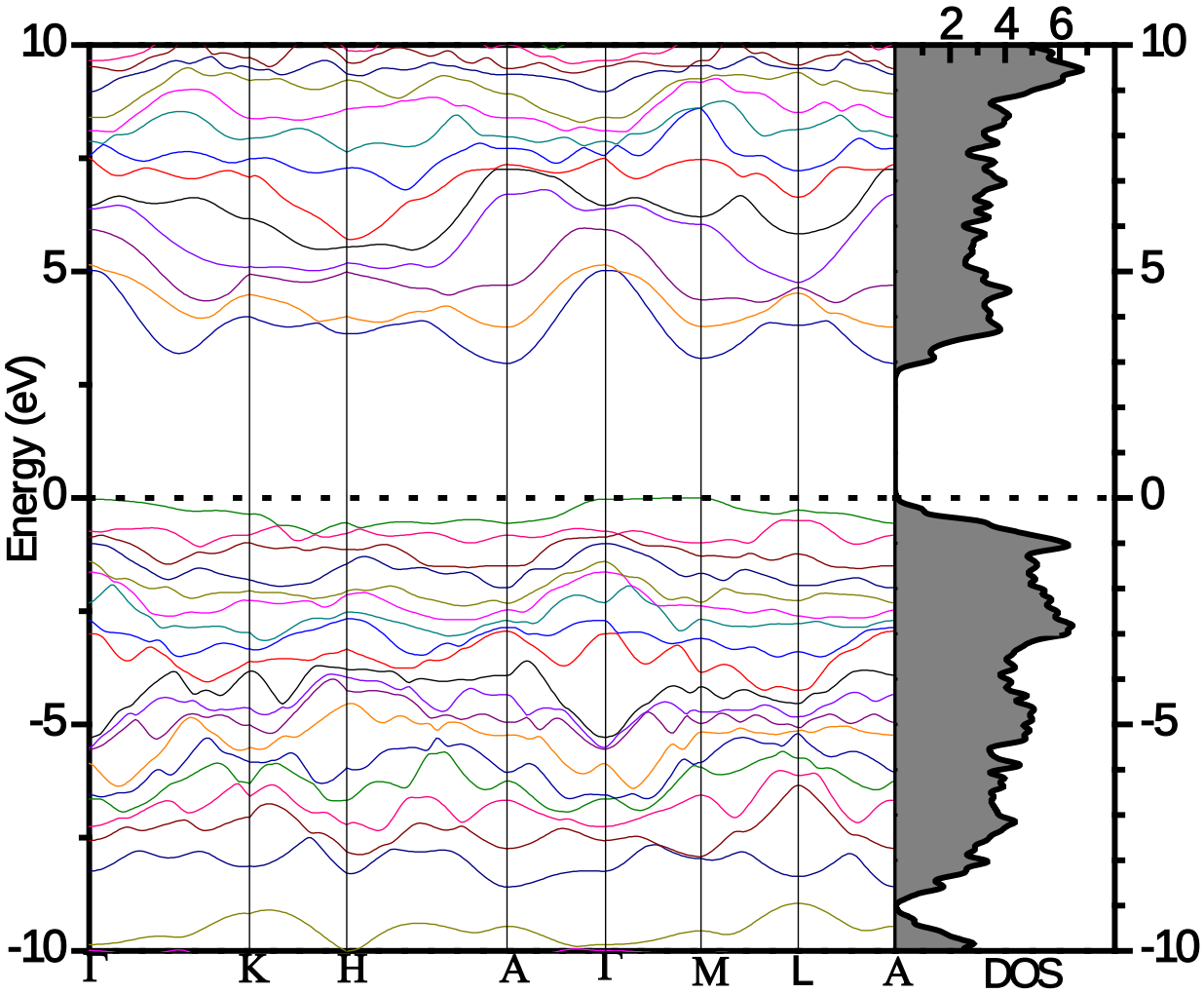
- **Temperature dependent elastic tensor**

$$C(\varepsilon, T) = -\partial \sigma(\varepsilon, T) / \partial \varepsilon$$

- **Tensile program**
  - *Uniaxial tensile/compression test*
    - *Poisson ratio = 0*
    - *Poisson ratio = const.*
    - *Poisson ratio adjusted to keep stress in other directions zero*
  - *Add local strain analysis (DefAna) support*

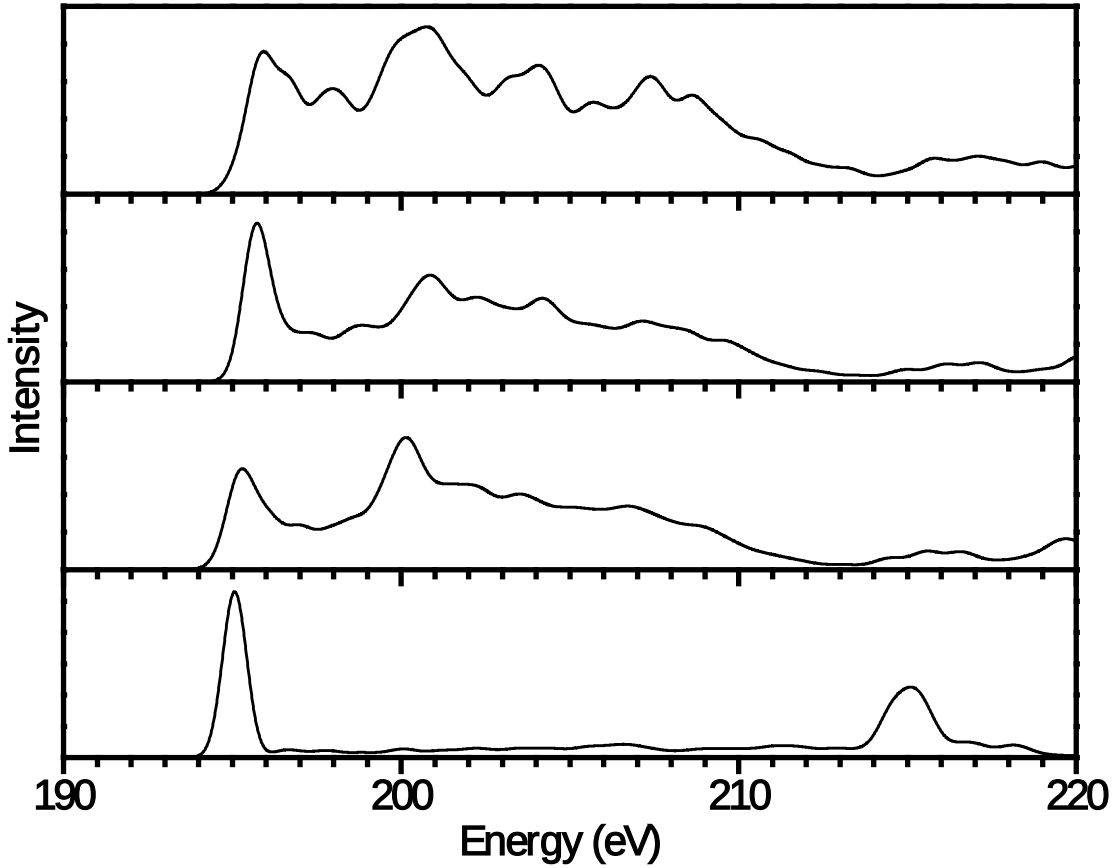


Preliminary Results



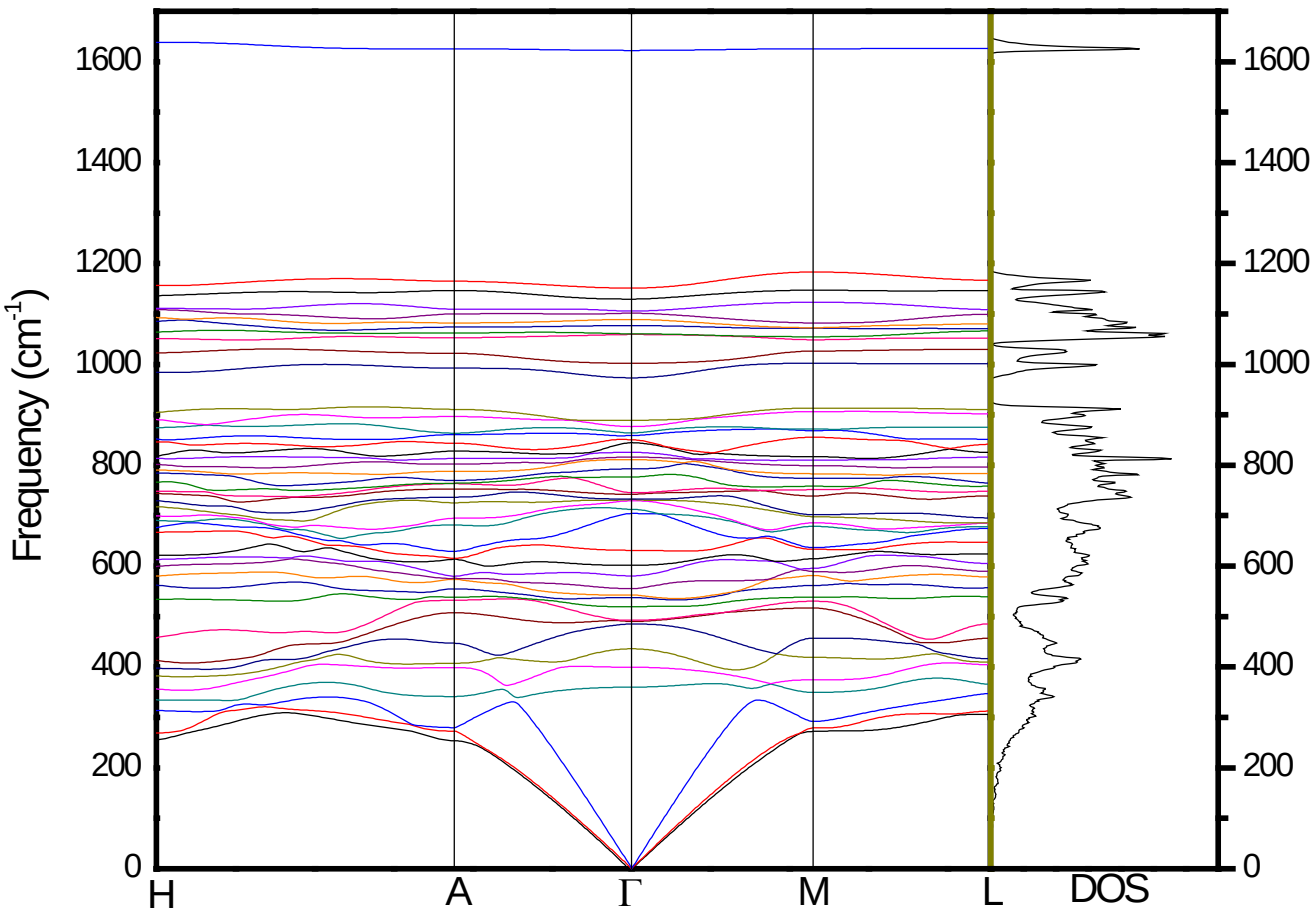
Band structure and density of state of boron carbide $B_{12}C_3$ ($B_{11}C$-CBC model) calculated using the G(P,T) package via the OLCAO interface.

Preliminary Results



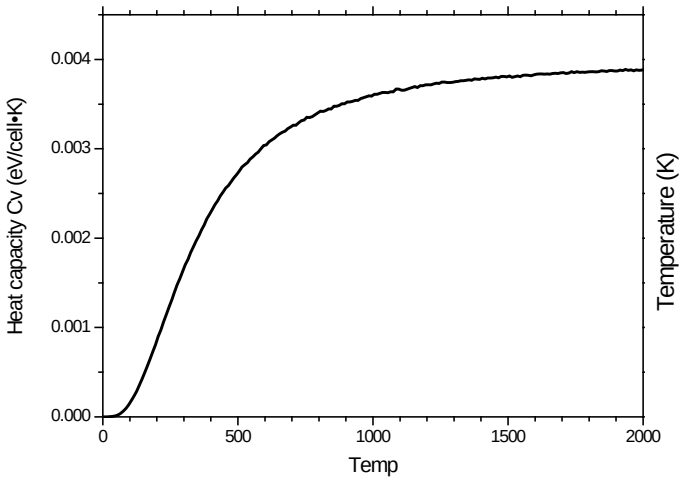
XANES spectra of four distinct boron sites in $B_{12}C_3$ ($B_{11}C$-CBC model) calculated using the G(P,T) package via the OLCAO interface

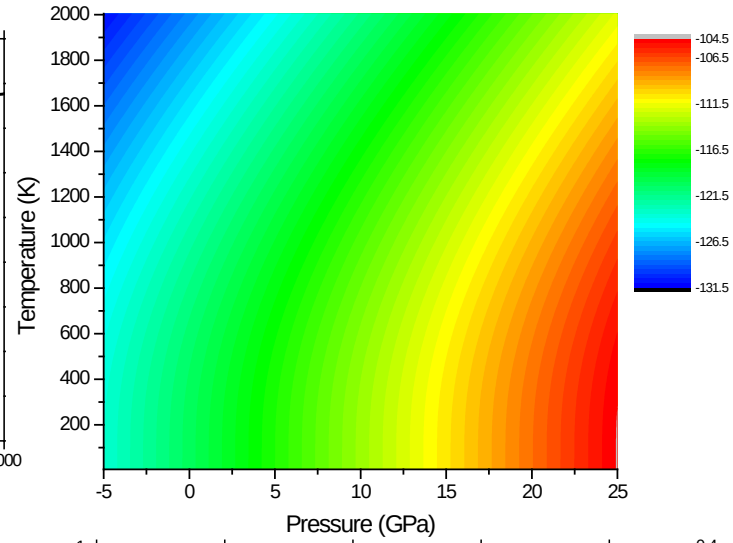
Preliminary Results

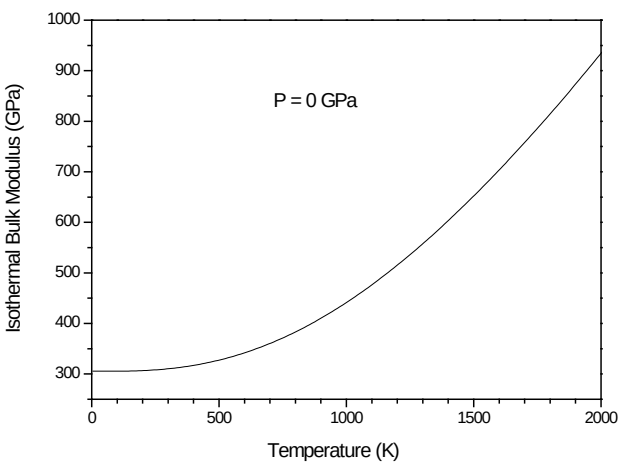


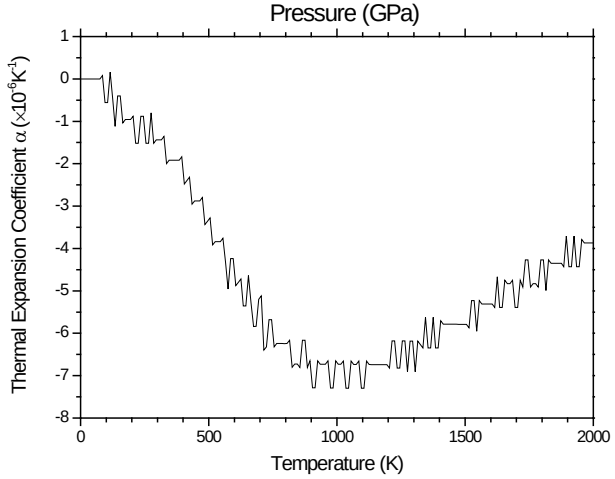
Phonon dispersion and density of state of boron carbide $B_{12}C_3$ ($B_{11}C$-CBC model) calculated using the G(P,T) package.

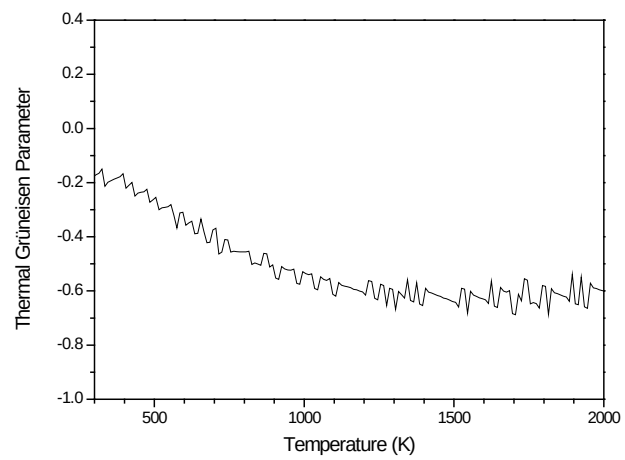
Preliminary Results











Phase II: Application to Boron Carbide

Year 2 plan

- **Task 1: Structure-Properties Relation in Boron Carbide**
  - *Gibbs free energy vs. carbon concentration*
  - *Carbon distribution vs. carbon concentration*
  - *Bonding and charge vs. carbon concentration*

- **Task 2: Spectroscopic Finger Prints of Boron Carbide**
  - *Phonon dispersion, DOS, and IR spectra*
  - *XANES/ELNES spectra*

- **Task 3: Search for New Structure of Boron Carbide**
  - *Use genetic algorithm to locate energy minimum structure*

Future Plan: Continue Development of G(P,T)

- **Add support for linear response method and other first principles package (e.g.,Quantum Espresso, Abinit)**

- **Add support for first principles molecular dynamics to calculate transport properties**

- **Add anharmonic correction to Gibbs free energy**
  - *User higher order term of the interatomic potential energy*

- **Integrate with thermodynamic modeling and phase field simulation**
  - *Supply thermodynamic data and mechanic properties data for large scale simulation*

Publication

Publication

- Sitaram Aryal, Paul Rulis, Lizhi Ouyang, Wai-Yim Ching, "Ab initio calculations of the elastic, thermodynamic, electronic, and spectroscopic properties of $B_{12}O_2$", in revision.
- W. Y. Ching, Paul Rulis, Lizhi Ouyang, Aryal Sitaram, Anil Misra, "*Theoretical study of the elasticity,mechanical behavior, electronic structure, interatomic bonding, and dielectric function of an intergranular glassy film model in prismatic Si_3N_4*", Phys. Rev. B, recommended
- E.A. Petruska, D.V.S. Muthu, S. Carlson, A.M. Krogh Andersen, **L. Ouyang**, M.B. Kruger, "*High-pressure Raman and infrared spectroscopic studies of ZrP2O7*", Solid State Communications 150, 235, 2010
- W. Y. Ching, Paul Rulis, **Lizhi Ouyang**, and A. Misra, "*Ab initio tensile experiment on a model of an intergranular glassy film in β-Si3N4 with prismatic surfaces*", App. Phys. Lett. 94, 051907, 2009

Presentation

- Seminar: Lizhi Ouyang, "Temperature and Pressure Dependent Thermodynamic and Mechanical Properties of Crystals", University of Missouri-KC, Kansas City, Oct. 16, 2009
- Seminar: Lizhi Ouyang, "Modeling of Intergranular Thin Film of Si3N4", Zhejiang University, Hangzhou, July 8, 2009
- Poster: Lizhi Ouyang, etc. "Role of Intergranular Film in the Failure of Ceramics", ISMANAM Beijing, July 5, 2009

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  Mr. Mahmoud Ibrahim, Tennessee State University (Undergraduate)

  Mr. David Lynes, Tennessee State University (Undergraduate)

  Mr. Aryal Sita Rum, University of Missouri-Kansas City (PhD student)