Lyakhov school on Computational Materials Science
Evolutionary structure prediction using the USPEX code
Guilin, August 3-8, 2013

Computational discovery of novel dielectric materials by evolutionary first principles calculations

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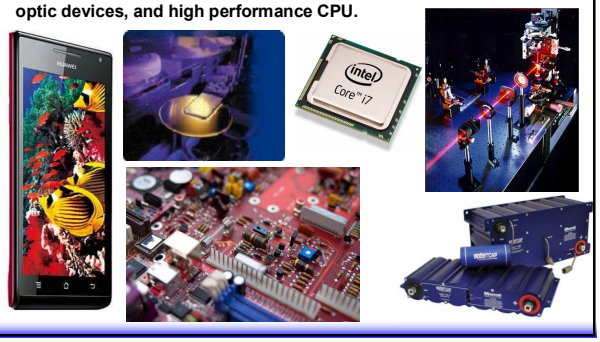
Part I.

INTRODUCTION

Dielectrics

Dielectric ceramics are of importance as components which have been widely used in microwave communications devices, batteries, optic devices, and high performance CPU.



Low-k dielectrics: reduce parasitic capacitance

Permittivity of vacuum 8.854×10^{-12} F/m

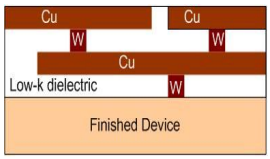
relative permittivity (dimensionless, >1)

Capacitance (F)

Area (m^2)

$$C = \frac{\varepsilon_0 k A}{d}$$

Thickness (m)

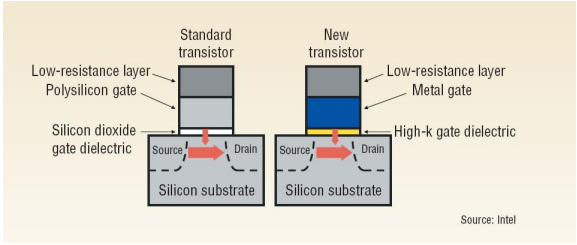


Enabling faster switching speeds and lower heat dissipation

5

High-k dielectrics: reduce gate current leakage

Gate current leakage is resulted by electronic tunneling



Enabling lower power loss and further scaling components/devices

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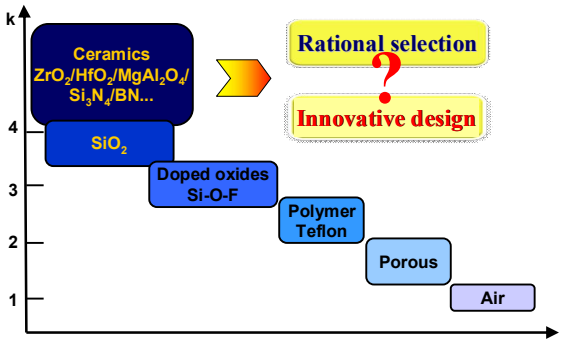
Typical high-k & low-k materials



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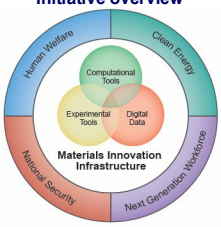
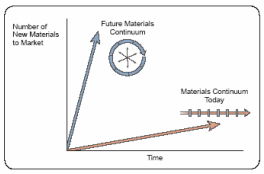
Materials Genome Initiative program

Initiative overview



Initiative acceleration of the materials continuum



The Materials Genome Initiative will develop new integrated computational, experimental, and data informatics tools, which will seamlessly integrate into existing product-design frameworks to enable rapid and holistic engineering design.
----Executive office of the president. Materials Genome Initiative for Global Competitiveness. Washington D.C.: National Science and Technology Council, (2011).

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Dielectrics cover different chemical elements and each compound has many polymorphs

Question

computational, experimental, and/or data informatics tools?

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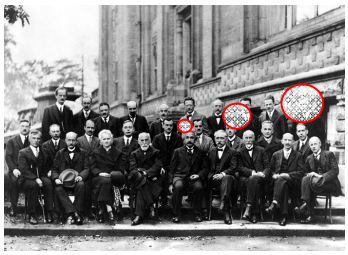
Quantum mechanics is the first principle of other theories

1927 Solvay Conference, Belgian



Dirac: The remaining task of physics is to solve Schrödinger equation

Front Row: I. Langmuir, M. Planck, Mme. Curie, H.A. Lorentz, A. Einstein, P. Langevin, Ch. E. Guye, C.T.R. Wilson, O.W. Richardson
Middle Row: P. Debye, M. Knudsen, W.L. Bragg, H.A. Kramers, P.A.M. Dirac, A.H. Compton, L. de Broglie, M. Born, N. Bohr
Back Row: A. Piccard, E. Henriot, P. Ehrenfest, Ed. Herzen, Th. De Donder, E. Schrödinger, E. Verschaffelt, W. Pauli, W. Heisenberg, R.H. Fowler, L. Brillouin (17/29 Nobel Prize)

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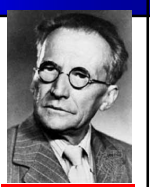
Schrödinger equation

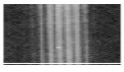
$$-\frac{\hbar}{i}\frac{\partial}{\partial t}\Psi(\vec{r},t)=\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r},t)\right]\Psi(\vec{r},t)$$



1933 Nobel Prize
1925

we know the future W. F. at any time

$|\Psi(r,t)|^2dr$ gives the ***probability*** at time *t* of finding the particle in the region of the *r* axis lying between *r* and *r*+d*r*.



1954 Nobel Prize
1926, Born

DFT

Density Functional Theory

Walter Kohn
1998 Nobel Prize
1964

Hohenberg-Kohn theorem

$$E[\Psi(\vec{r_1},\ldots\vec{r_N})]=E[n(\vec{r})]$$

$$E[\rho]=T_o[\rho]+U[\rho]+E_{xc}[\rho]$$

Kohn-Sham equations

$$\left[\nabla^2+v_{eff}[n(\vec{r})]\right]\varphi_{i,k}(\vec{r})=\varepsilon_{i,k}\varphi_{i,k}(\vec{r})$$

- Exact only for ground state
- Needs approximation to E_{XC}

$$n(\vec{r})=\sum_i f_i\varphi_i^*(\vec{r})\cdot\varphi_i(\vec{r})$$

$$N=\int_\Omega n(\vec{r})d^3r$$

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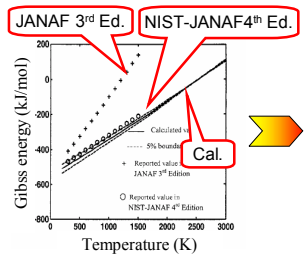
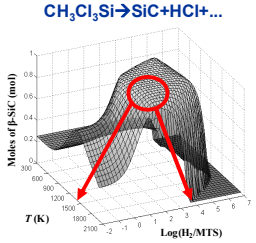
How helpful the first principles

Chemical process planning needs correct thermodynamic data

Evaluation of the thermodynamic data of MTS



$CH_3Cl_3Si \rightarrow SiC+HCl+...$



J Phy Chem Ref Data 35 (2006) 1385-90.

Eur Phys J D 49 (2008) 21–35.

- The calculated thermodynamic data are comparable to the reported data in NIST-JANAF 4th edition. And the calculated temperature & gas ratio for manufacturing SiC are comparable to experiments.

TSCM Science and Technology on Thermostructural Composite Materials Lab 超高温结构复合材料重点实验室

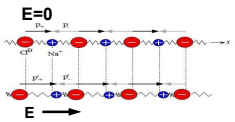
Part II.

MATERIALS BY SELECTION

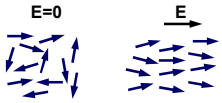
Origination of permittivity: polarization

Electronic polarization

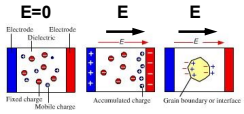
Ionic polarization



Dipolar polarization



Space Charge Polarization



Polarization occurs when an external electric field is applied on the materials and it relates to the frequency of the field.

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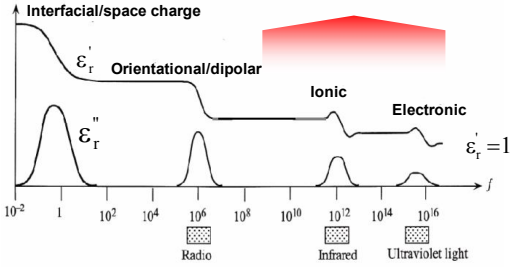
Solvable polarization by first principles

Quantum mechanics
First principles



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Dielectric spectrum

Dielectric constant along a direction:

$$\varepsilon_{\alpha\beta}(\omega) = \varepsilon_r + i\varepsilon_i = \varepsilon^{\infty}_{\alpha\beta} + \varepsilon^{\infty}_{\alpha\beta}\sum_m \frac{\omega^2_{LO,m} - \omega^2_{TO,m}}{\omega^2_{TO,m} - \omega^2 + i\gamma\omega^2}$$

Electronic polarization

Ionic polarization

Static dielectric constant (LST):

$$\varepsilon_{\alpha\beta}(0) = \varepsilon^{\infty}_{\alpha\beta}\prod_m \frac{\omega^2_{LO,m}}{\omega^2_{TO,m}}$$

Dielectric tensor

$$\varepsilon = \begin{bmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{bmatrix}$$

LO: longitudinal-optical; TO: transverse-optical modes; LST:Lyddane Sachs Teller

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Dielectric spectrum

IR reflectance:

$$R_{\alpha\beta}(\omega) = \left|\frac{\sqrt{\varepsilon_{\alpha\beta}(\omega)} - 1}{\sqrt{\varepsilon_{\alpha\beta}(\omega)} + 1}\right|$$

Refractive index and extinction coefficient:

$$n(\omega) = \sqrt{\frac{1}{2}\left(\sqrt{\varepsilon_r^2 + \varepsilon_i^2} + \varepsilon_r\right)}$$

$$\kappa(\omega) = \sqrt{\frac{1}{2}\left(\sqrt{\varepsilon_r^2 + \varepsilon_i^2} - \varepsilon_r\right)}$$

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Nomenclature of Mulliken symbols

Mulliken Symbols

Symbols used to identify irreducible representations of groups:

A = singly degenerate state which is symmetric with respect to rotation about the principal C_n axis,

B = singly degenerate state which is antisymmetric with respect to rotation about the principal C_n axis,

E = doubly degenerate,

T = triply degenerate,

X_g = (gerade, symmetric) the sign of the wavefunction does not change on inversion through the center of the atom,

X_u = (ungerade, antisymmetric) the sign of the wavefunction changes on inversion through the center of the atom,

X_1 = (on a or b) the sign of the wavefunction does not change upon rotation about the center of the atom,

X_2 = (on a or b) the sign of the wavefunction changes upon rotation about the center of the atom,

' = symmetric with respect to a horizontal symmetry plane σ_h,

'' = antisymmetric with respect to a horizontal symmetry plane σ_h.

Cotton, F. A. *Chemical Applications of Group Theory, 3rd ed.* New York: Wiley, pp. 90-91, 1990.

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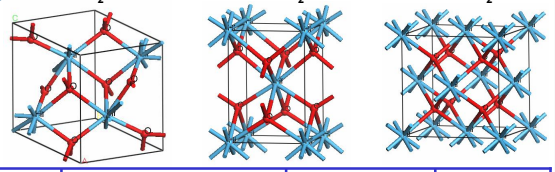
Typical dielectrics

m-HfO_2 t-HfO_2 c-HfO_2



Compound	Accoustic & optic modes	ε_{static}	ε_∞
monoclinic-HfO_2	$2B_u(A)+A_u(A)+7B_u(IR)+8A_u(IR)+9A_g(R)+9B_g(R)$	[20.3 18.3 12.8]	[4.7 4.6 4.3]
tetragonal-HfO_2	$E_u(A)+A_{2u}(A)+2E_u(IR)+2A_{2u}(IR)+3E_g(R)+2B_{2g}(R)+A_{1g}(R)+B_{1u}(S)$	[95.8 95.8 14.5]	[5.1 5.1 4.5]
cubic-HfO_2	$T_{1u}(A)+T_{1u}(IR)+T_{2g}(R)$	[30.9 30.9 30.9]	[4.9 4.9 4.9]

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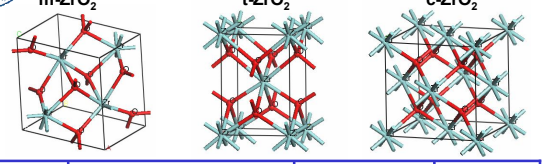
Typical dielectrics (contd)

m-ZrO_2 t-ZrO_2 c-ZrO_2



Compound	Accoustic and optic modes	ε_{static}	ε_∞
monoclinic-ZrO_2	$2B_u(A)+A_u(A)+7B_u(IR)+8A_u(IR)+9A_g(R)+9B_g(R)$	[19.6 18.2 15.1]	[5.7 5.6 5.2]
tetragonal-ZrO_2	$A_{2u}(A)+E_u(A)+2A_{2u}(IR)+2E_u(IR)+3E_g(R)+A_{1g}(R)+2B_{2g}(R)+B_{1u}(S)$	[78.3 78.3 18.9]	[6.2 6.2 5.6]
cubic-ZrO_2	$T_{1u}(A)+T_{1u}(IR)+T_{2g}(R)$	[29.2 29.2 29.2]	[6.2 6.2 6.2]

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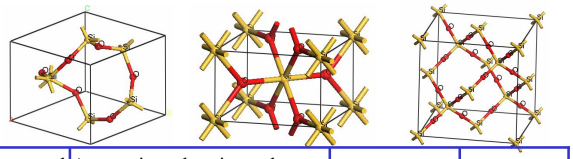
Typical dielectrics (contd)

quartz stishovite cristobalite



Compound	Accoustic and optic modes	ε_{static}	ε_∞
trigonal-SiO_2	$A_2(A)+E(A)+4A_2(IR)+8E(IR,R)+4A_1(R)$	[4.4 4.4 4.3]	[2.3 2.3 2.3]
tetragonal-SiO_2	$A_{2u}(A)+E_u(A)+A_{2u}(IR)+3E_u(IR)+B_{2g}(R)+2B_{2u}(S)+E_g(R)+A_{2g}(S)+A_{1g}(R)+B_{1g}(R)$	[11.3 11.3 9.0]	[3.4 3.4 3.5]
cubic-SiO_2	$T_{1u}(A)+2T_{1u}(IR)+T_{2g}(R)+T_{2u}(S)+E_u(S)+A_{2u}(S)$	[3.7 3.7 3.7]	[2.1 2.1 2.1]

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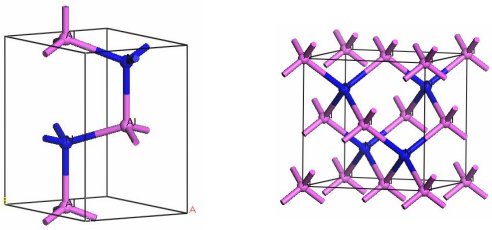
Typical dielectrics (contd)

w-AlN c-AlN



Compound	Accoustic and optic modes	ε_{static}	ε_∞
wurtzite-AlN	$A_1(A)+E_1(A)+A_1(IR,R)+E_1(IR,R)+2E_2(R)+2B_2(S)$	[7.9 7.9 9.2]	[4.4 4.4 4.6]
cubic-AlN	$T_2(A)+T_2(IR,R)$	[11.5 11.5 11.5]	[5.7 5.7 5.7]

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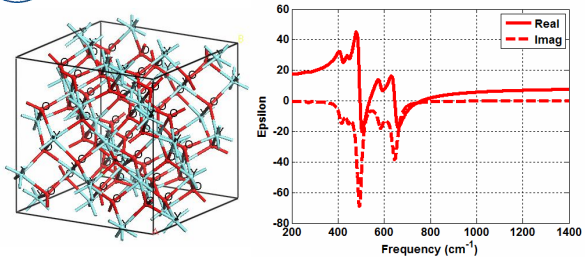
Typical dielectrics (contd)



Compound	Accoustic and optic modes	ε_{static}	ε_∞
cubic-Y_2O_3	$T_u(A)+16T_u(IR)+4A_g(R)+4E_g(R)+14T_g(R)+5A_u(S)+5E_u(S)$	[8.8 8.8 8.8]	[4.1 4.1 4.1]

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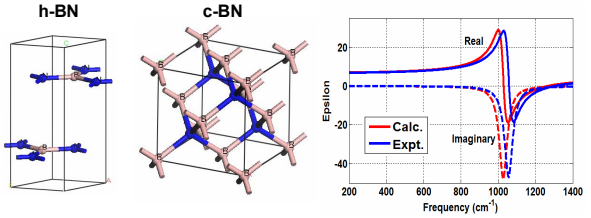
Typical dielectrics (contd)

h-BN c-BN



Compound	Accoustic and optic modes	ε_{static}	ε_{∞}
hexagonal-BN	$A_{2u}(A)+E_{1u}(A)+A_{2u}(IR)+E_{1u}(IR)+2E_{2g}(R)+2B_{2g}(S)$	[6.3 6.3 2.8]	[4.6 4.6 2.5]
cubic-BN	$T_2(A)+T_2(R, IR)$	[6.9 6.9 6.9]	[4.4 4.4 4.4]

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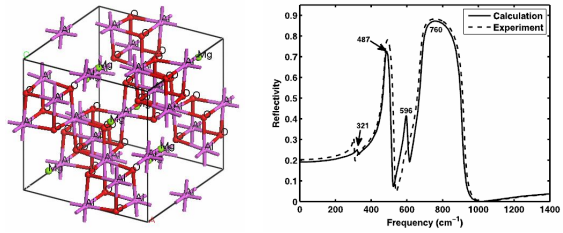
Typical dielectrics (contd)



Compound	Accoustic and optic modes	ε_{static}	ε_{∞}
cubic-$MgAl_2O_4$	$T_{1u}(A)+4T_{1u}(IR)+A_{1g}(R)+E_g(R)+3T_{2g}(R)+T_{1g}(S)+2A_{2u}(S)+2E_u(S)+2T_{2u}(S)$	[7.7 7.7 7.7]	[3.1 3.1 3.1]

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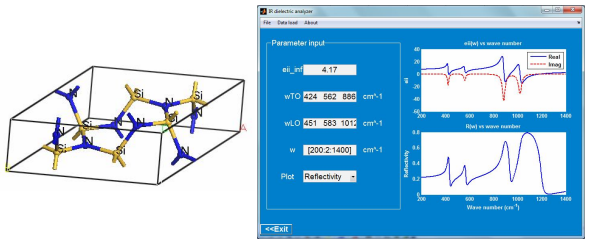
Typical dielectrics (contd)



Compound	Accoustic and optic modes	ε_{static}	ε_{∞}
hexagonal-Si_3N_4	$A_u(A)+E_{1u}(A)+4A_g(R)+2E_{1g}(R)+5E_{2g}(R)+2A_u(IR)+4E_{1u}(IR)+3B_g(S)+2E_{2u}(S)$	[8.0 8.0 7.9]	[4.0 4.0 4.1]

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If we do not know the crystal structure models

Question

How to perform the computations?

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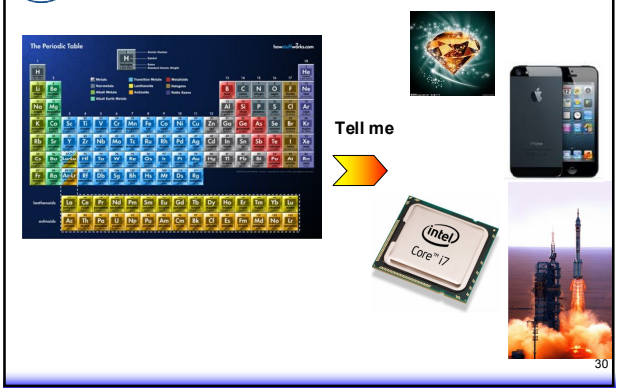
Part III.

MATERIALS BY DESIGN

I have a dream ...



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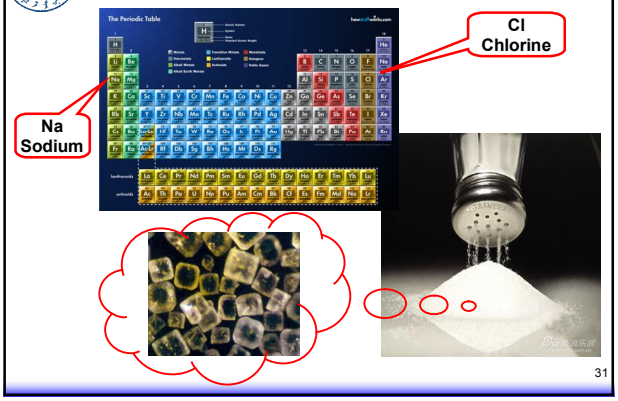
A very common but important material: salt!



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Questions

- Why it is cubic (isotropic)!
- Can we see how Na bonds with Cl?

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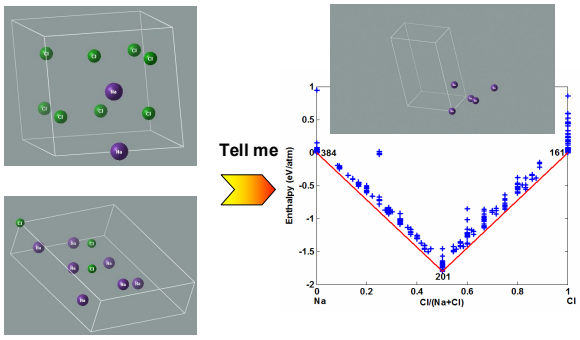
Evolutionary first principles calculations



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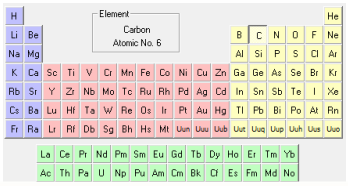
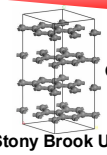
Energy surface of the materials

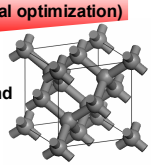
Universal Structure Predictor: Evolutionary Xtallography



Quantum mechanics (local optimization)
+Evolutionary algorithms (Global optimization)



Graphite, diamond
.....



Prof. Artem Oganov, Stony Brook Univ. , New York
http://han.ess.sunysb.edu/~USPEX/

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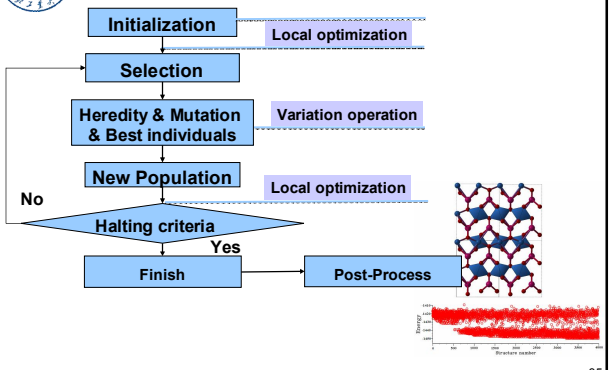
Predict crystals by evolution



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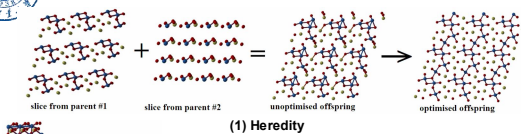
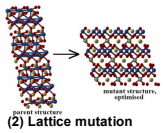
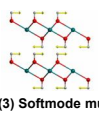
Evolutionary operators



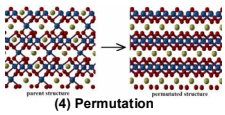
(1) Heredity



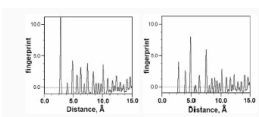
(2) Lattice mutation



(3) Softmode mutation



(4) Permutation



Fingerprint is related to the pair correlation function

$$F_{AB}(R) = \sum_{A_i \in cell} \sum_{B_j} \frac{\delta(R - R_{ij})}{4\pi R_{ij}^2 \frac{N_A N_B}{V} \Delta} - 1 = g_{AB}(R) - 1$$

Difference between 2 structures is given by „distance", e.g.: $dist(i,j) = \left(\sum_p \left| fp_{i_k} - fp_{j_k} \right|^p \right)^{\frac{1}{p}}$

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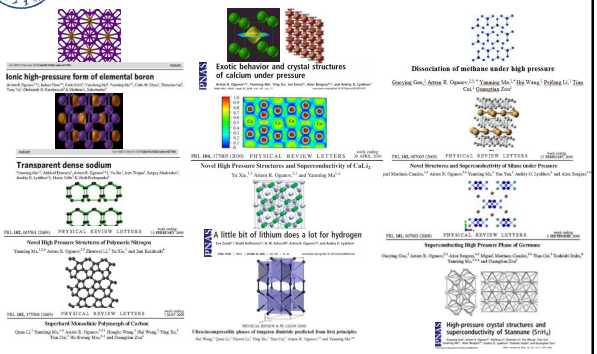
Many Applications



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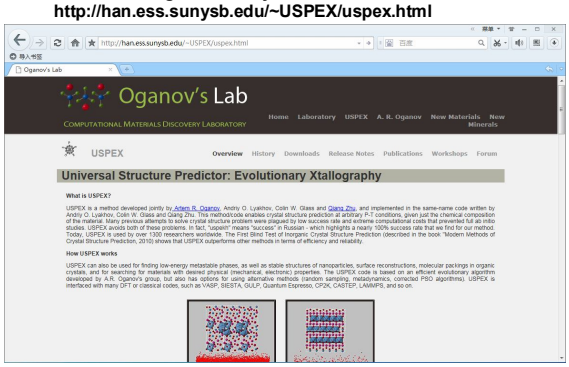
Visit the website for more information on USPEX

Prof. Artem Oganov, Stony Brook Univ. , New York
http://han.ess.sunysb.edu/~USPEX/uspex.html



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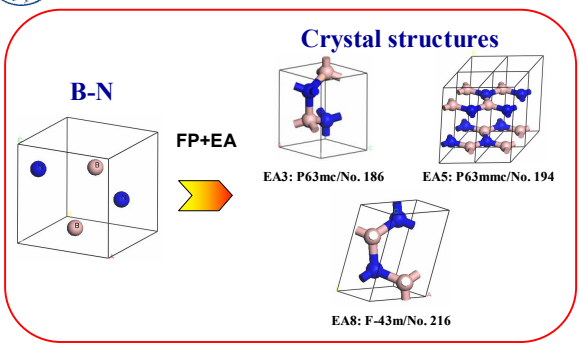
From elements to crystal structures



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From crystal structures to properties

Application by calculation

Dielectric constant tensor: c-BN

$$\varepsilon^0 = \begin{bmatrix} \varepsilon^0_{xx} & & \\ & \varepsilon^0_{xx} & \\ & & \varepsilon^0_{zz} \end{bmatrix} = \begin{bmatrix} 6.9 & 0 & 0 \\ 0 & 6.9 & 0 \\ 0 & 0 & 6.9 \end{bmatrix}$$

$$\bar{\varepsilon} = 6.9$$

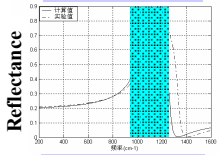
h-BN

$$\varepsilon^0 = \begin{bmatrix} \varepsilon^0_{xy} & & \\ & \varepsilon^0_{xy} & \\ & & \varepsilon^0_{zz} \end{bmatrix} = \begin{bmatrix} 6.3 & 0 & 0 \\ 0 & 6.3 & 0 \\ 0 & 0 & 2.8 \end{bmatrix}$$

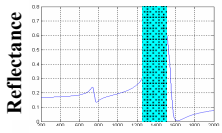
$$\bar{\varepsilon} = 5.1$$

Reflective spectrum

950cm^{-1}-1250cm^{-1}



1300cm^{-1}-1500cm^{-1}



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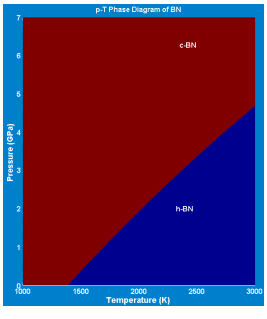
p-T phase diagram of BN

- **Thermodynamic data obtained from first-principles**



$$G = F(T,V) + pV$$

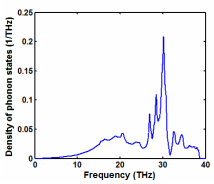
$$F(T,V) = E_0(V) + F_{vib}(T,V) + U_{zero}(V)$$

total electronic energy+vibration energy+zero-point energy

$$F_{vib}(T,V) = \int_\Omega k_B T \ln[1 - \exp(-\hbar\omega / kT)] g(V,\omega) d\omega$$

$$U_{zero}(V) = \frac{1}{2}\int_\Omega \hbar\omega g(V,\omega) d\omega$$

$$p = -(\partial F / \partial V)_T$$



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Mechanical properties of BN

c-BN is isotropic, while h-BN is transverse isotropy

Mechanical properties of cubic-BN

E (GPa)	ν	B (GPa)	C_{ij}			G (GPa)			λ		
			C_{11}	C_{12}	C_{44}	Voigt	Reuss	Hill	Voigt	Reuss	Hill
700.2	0.15	329.0 ±1.0	736.6 ± 1.7	125.2 ±1.2	424.9 ±1.5	377.2	367.6	372.4	77.5	83.9	80.7

Mechanical properties of hexagonal-BN

E (GPa)	ν	B (GPa)	C_{ij}					G (GPa)			λ		
			C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	Voigt	Reuss	Hill	Voigt	Reuss	Hill
844.2 21.5	0.22 4e-3	20.7 ±0.4	885.2 ± 2.0	190.7 ±1.0	0.38 ±0.1	21.5 ±0.5	5.0 ±0.12	178.2	10.7	94.4	122.9	13.6	68.2

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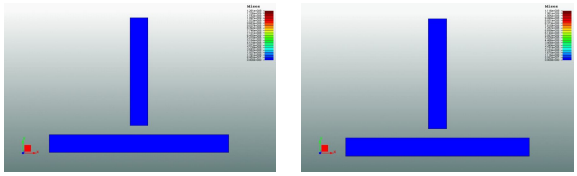
Stress propagation in c-BN/h-BN laminates



c-BN/h-BN
h-BN helps releasing stress in c-BN

h-BN/c-BN
Stress accumulates in c-BN

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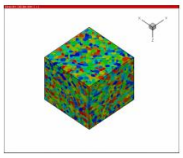
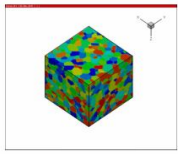
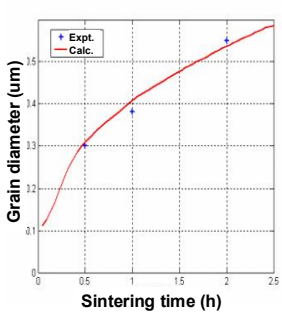
Grain growth by Monte-Carlo simulation



20 MC steps



100MC steps



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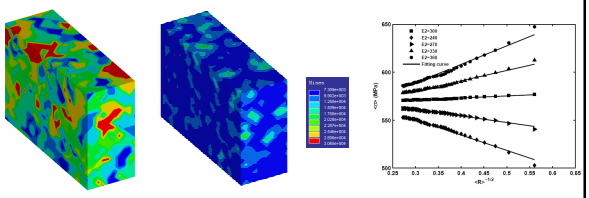
Stress analysis by FEM



Polycrystalline material | Mises stress (MPa) | Stress *vs* <R>$^{-1/2}$

Joint work with Prof. Zhiqiang Feng, Evry Univ., France

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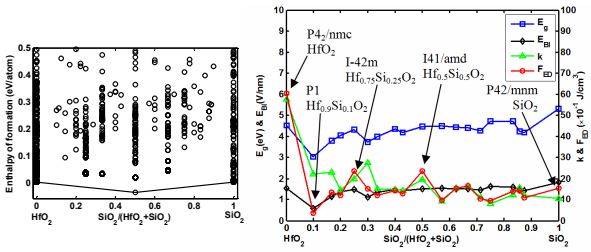
Design for variable compositions



$$\max F_{ED} = \frac{1}{2}\varepsilon_0 k E_{BI}^2 = 8.1882\ \mathrm{J/cm^3} \times k\left(E_g / E_{gc}\right)^{2\alpha}$$

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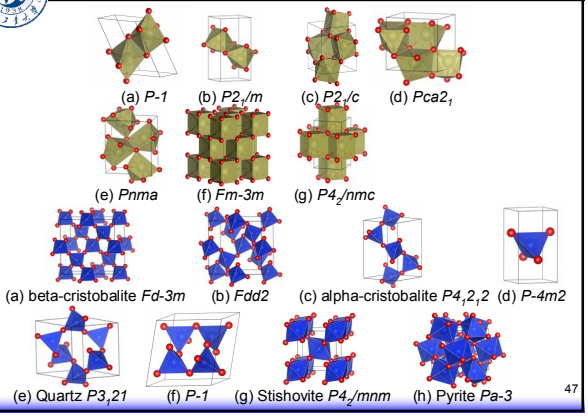
Identify the materials genes



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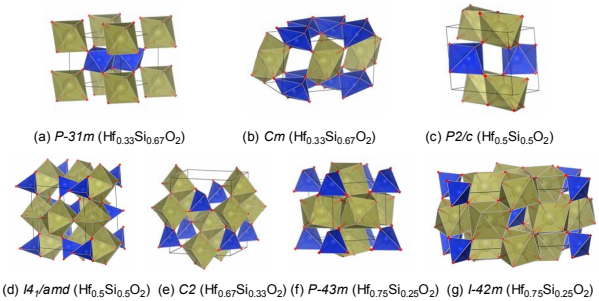
Discovery the materials genome



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Part IV.

CONCLUSION REMARKS

Conclusion remarks

- The dielectric properties of some typical dielectrics and their polymorphs are calculated and compared in the framework of first principles, which helps rational selection for dielectrics.
- The calculated structural data and dielectric properties from first principles based on DFT are comparable to reported data.
- A software package for IR dielectric analysis provides an efficient mean for faster materials selection and application.
- Innovative design for dielectrics can be realized by hybrid first principles and evolutionary algorithms.

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