Grupo de Química Teórica y Computacional de Materiales

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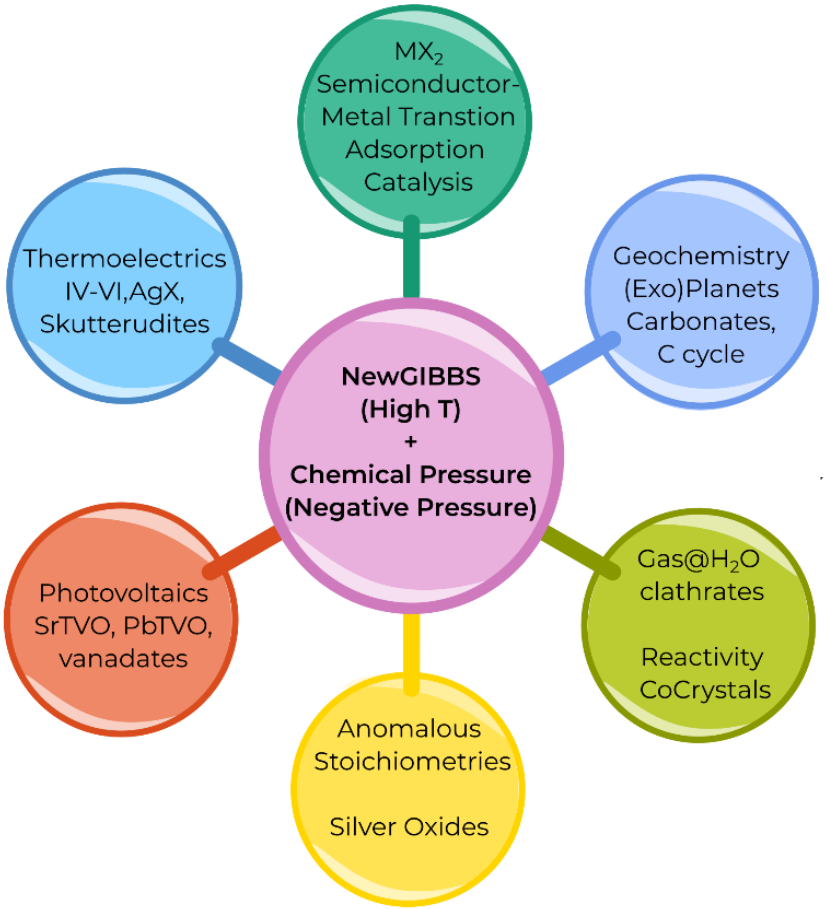
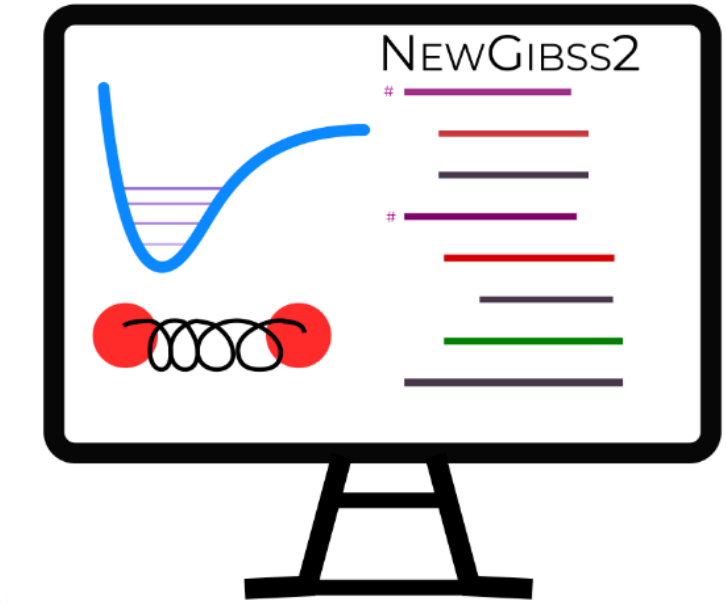
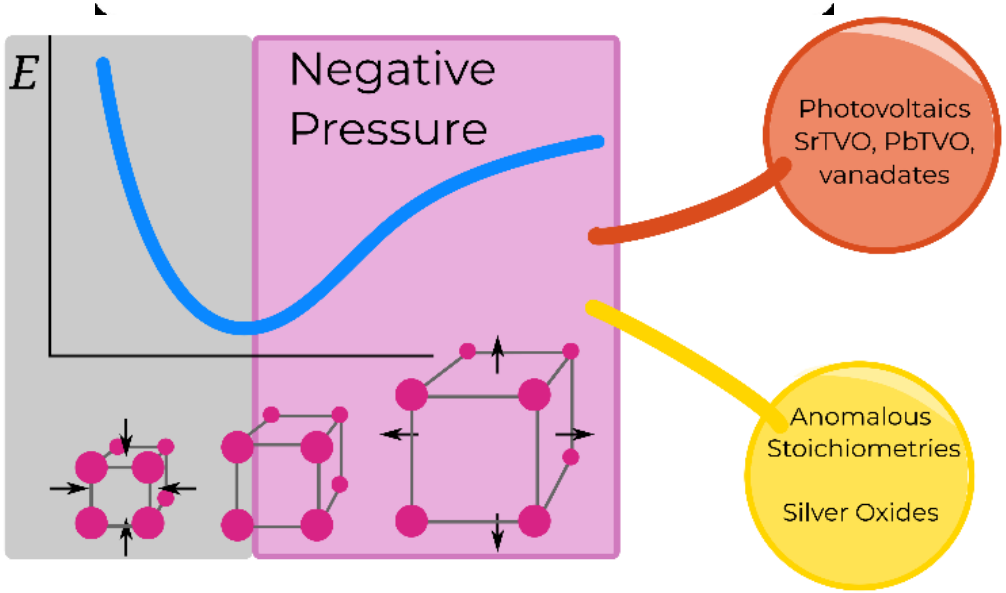
MECHANOCHEMISTRY UNDER CONTROLLED CONDITIONS OF PRESSURE: HIGH TEMPERATURES AND NEGATIVE PRESSURES







Chemical Pressure

❑ Operative definition. Chemical pressure maps

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
J. Am. Chem. Soc. 2012, 134, 5991−5999
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DFT-Chemical Pressure Analysis: Visualizing the Role of Atomic Size in Shaping the Structures of Inorganic Materials

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CHEMISTRY OF MATERIALS
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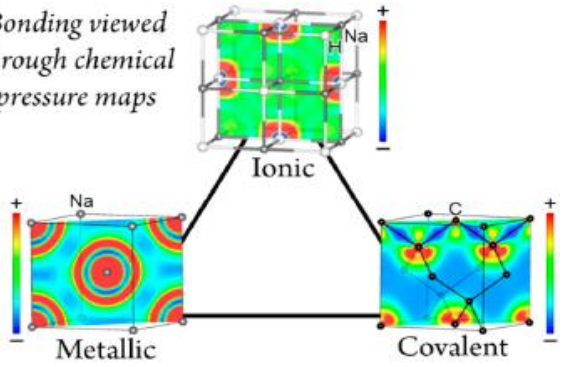
Chemical Pressure Schemes for the Prediction of Soft Phonon Modes: A Chemist's Guide to the Vibrations of Solid State Materials

Joshua Engelkemier, and Daniel C. Fredrickson

Chem. Mater., **Just Accepted Manuscript** • DOI: 10.1021/acs.chemmater.6b00917 • Publication Date (Web): 06 Apr 2016

Bonding viewed through chemical pressure maps



JCTC Journal of Chemical Theory and Computation
Article
Cite This: J. Chem. Theory Comput. 2018, 14, 104−114
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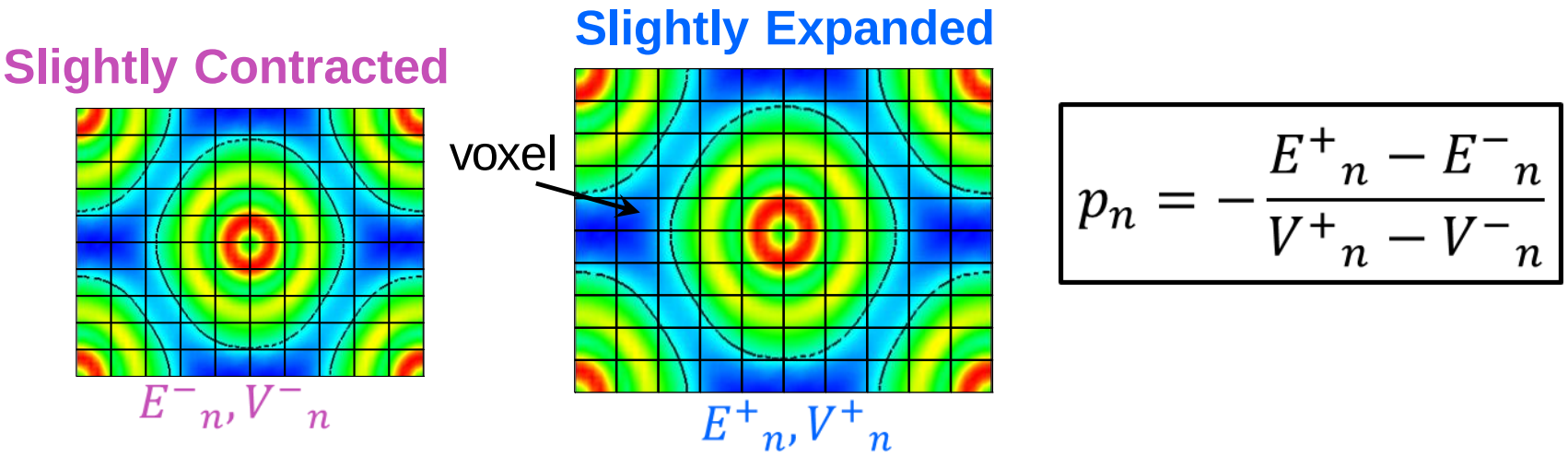
Chemical Pressure Maps of Molecules and Materials: Merging the Visual and Physical in Bonding Analysis

Hussien H. Osman,[†,§] Miguel A. Salvadó,[†] Pilar Pertierra,[†] Joshua Engelkemier,[‡] Daniel C. Fredrickson,[*,‡] and J. Manuel Recio[*,†,‡]

Chemical Pressure Formalism. Chemical Meaning

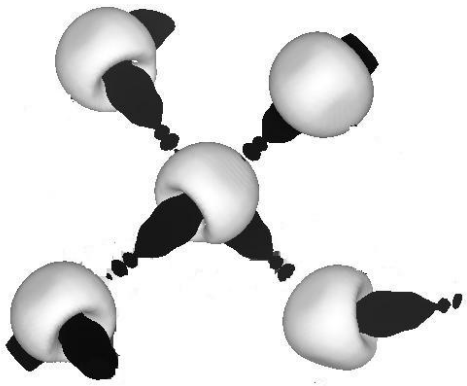
- The unit cell is divided in N_v voxels of volume V_v where the energy density function is evaluated
- **Positive CP** values are associated with non-bonding and antibonding regions. Electron density would like to expand in order to lower the energy of the system.
- **Negative CP** values are associated with bonding regions. Electron density would like to be accumulated (compressed) in order to lower the energy of the system.
- CP analysis gives a global picture of chemical interactions

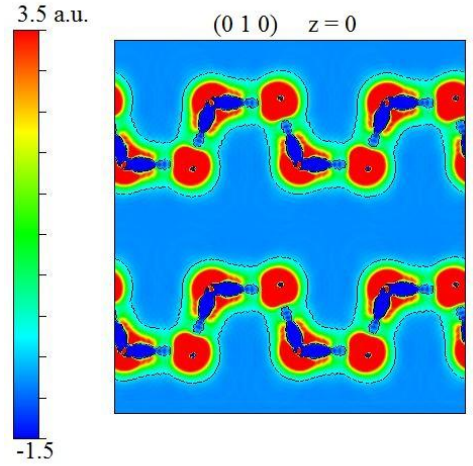


$$p_n = -\frac{E^+_n - E^-_n}{V^+_n - V^-_n}$$

Chemical Pressure Formalism Chemical Bonding

H_2O-I_H





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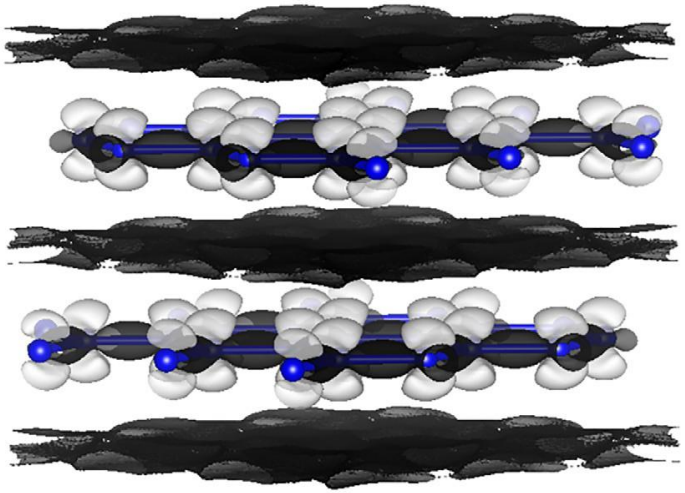
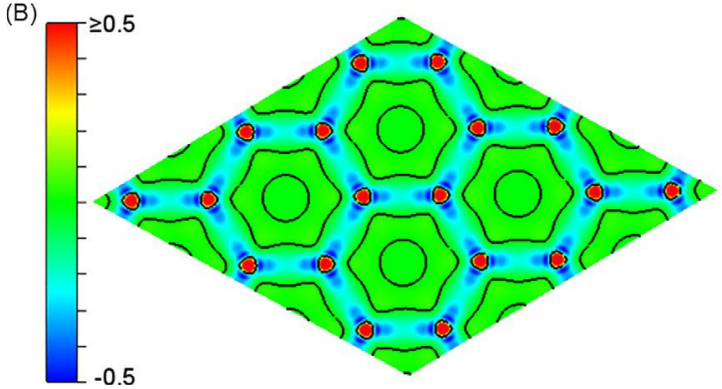
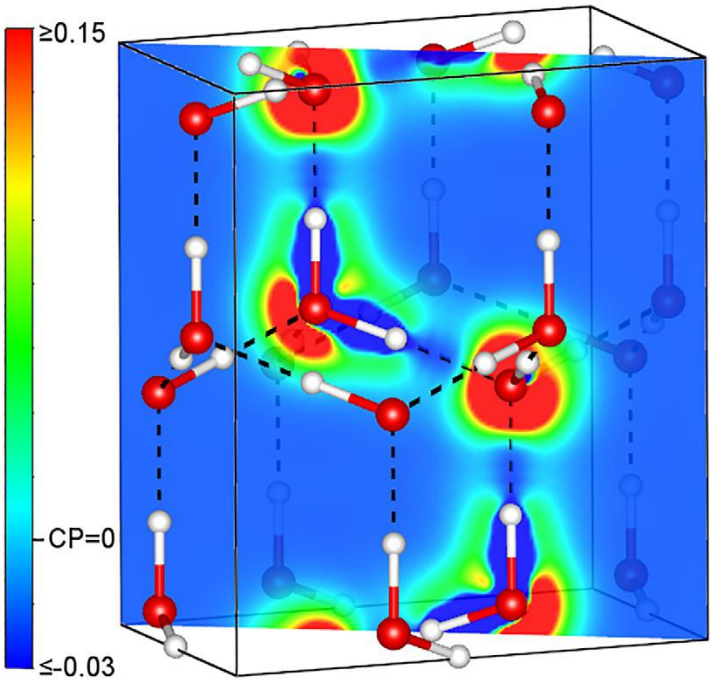
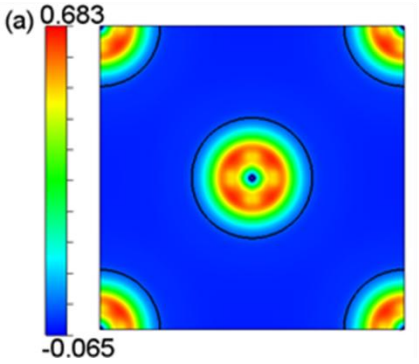




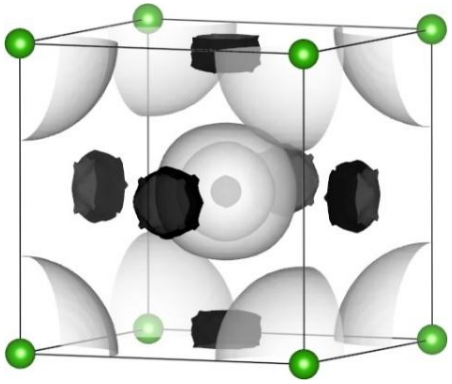


Chemical Pressure. Inorganic crystal structures

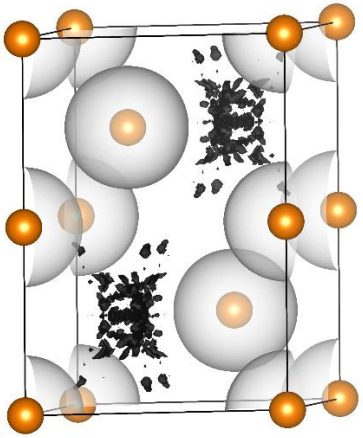
- **Metallic phases:** *fcc* and *sc*-Ca, CsCl-BaSn, *h*P4-K and *fcc*-Na
- **Inorganic crystals:** CaF_2, CaX (X= O, S, Se, Te), $BaSnO_3$, K_2S and NaX (X=F, Cl, Br, I).



Chemical pressure (CP) analysis of *fcc*-Ca at equilibrium conditions. (a) Cross-section along the (001) plane containing the Ca atoms. The CP = 0 contour is shown with a black solid line (b) 3D isosurfaces with CP= +0.001 (white) and CP = – 0.0274 (black). Pressures are given in atomic units.

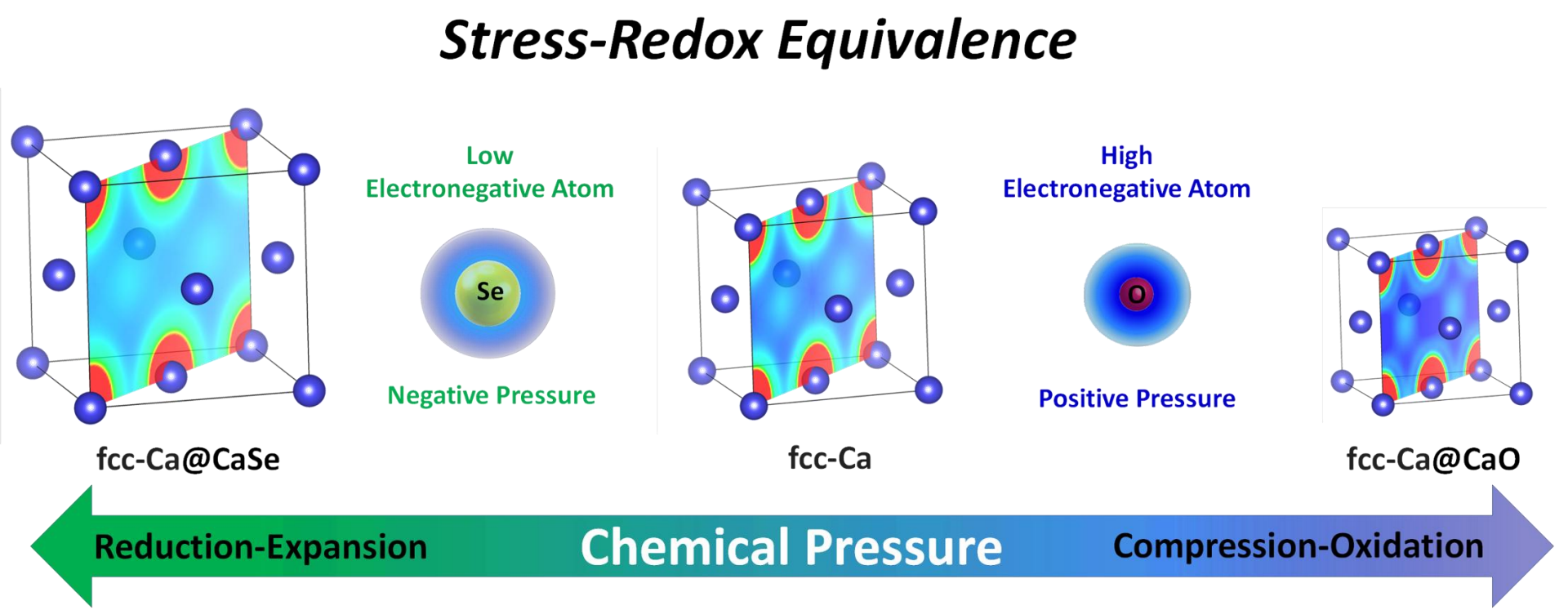


CP isosurfaces of BaSn lattice (Ba = green, Sn = blue) at the equilibrium volume of $BaSnO_3$. White and black isosurfaces are of CP = +0.001 and CP = – 0.0125 au, respectively.



3D CP isosurfaces in the *h*P4 phase of metallic K at the volume of K_2S compound. White and black isosurfaces are of CP = +0.001 and CP = –0.043 au, respectively.

Generalized stress-redox equivalence



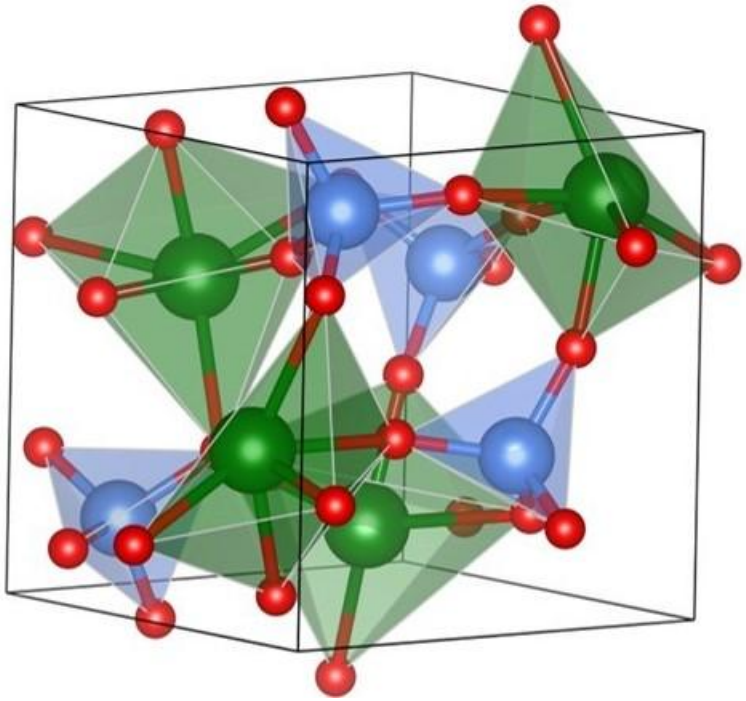
Electronegativity and equalization principle

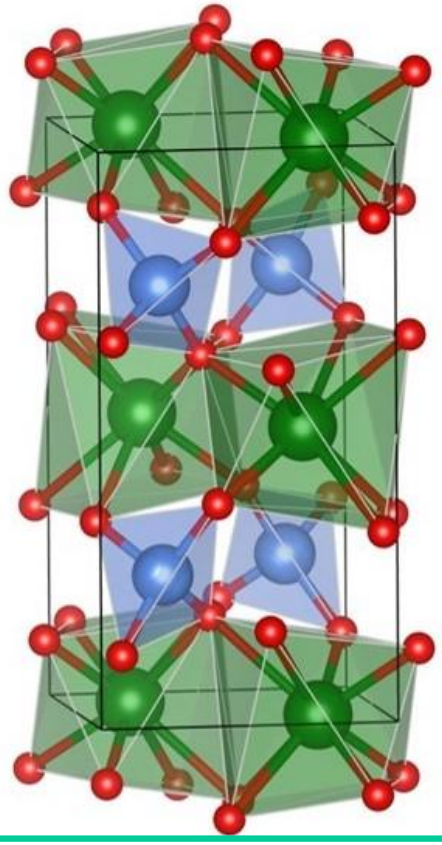
KEY-LOCK PRINCIPLE

Upon crystal formation, the metallic subarray adjust its size either reducing or increasing its volume just to match the electronegativity of the non-metallic element.

Only non-metallic elements with the electronegativity corresponding to the CP mínimum value of the metallic lattice can enter in those positions and form the inorganic crystal.

Solid State Solutions. $SnMo_{(1-x)}W_xO_4$





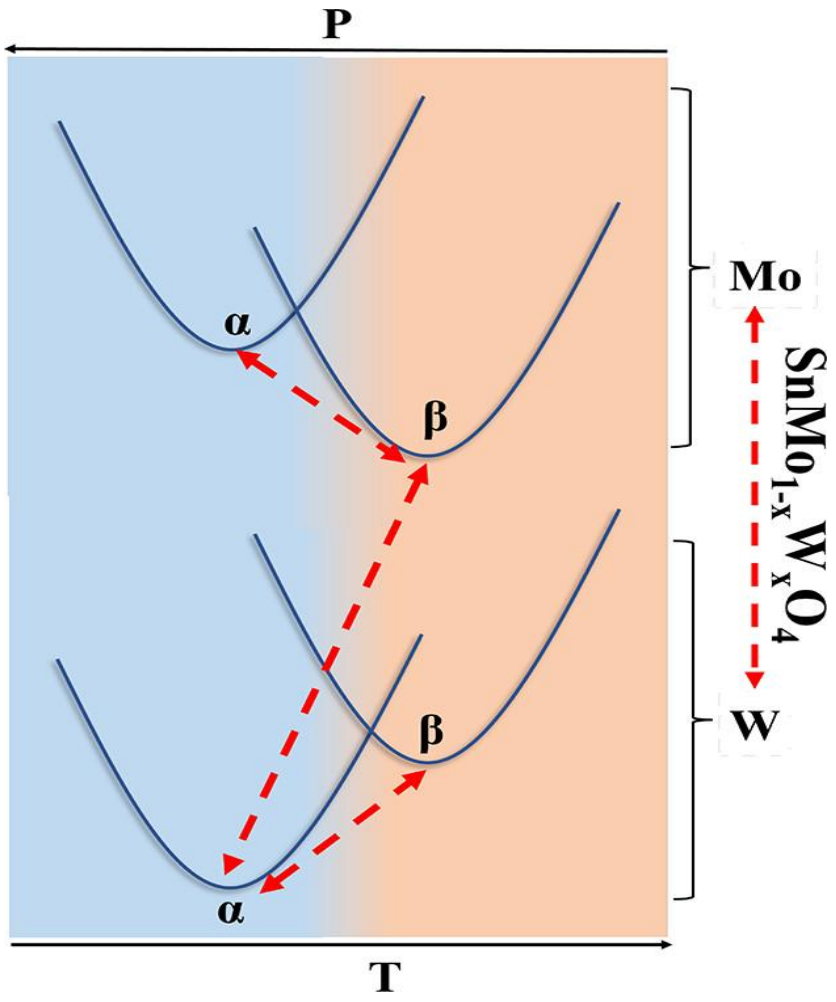
Beta-phase. Cubic

- SnMoO4 at RCs. V = 90.9 $Å^3$
- SnWO4 at high T (p<0). V = 88.5 $Å^3$
- Direct gap
- r(Mo^{6+}) ~ 0.41 Å

Alpha-phase. Orthorhombic

- SnWO4 at RCs. V = 81.5 $Å^3$
- SnMoO4 at high p (p>0). V = 81.3 $Å^3$
- Indirect gap
- r(W^{6+}) ~ 0.42 Å

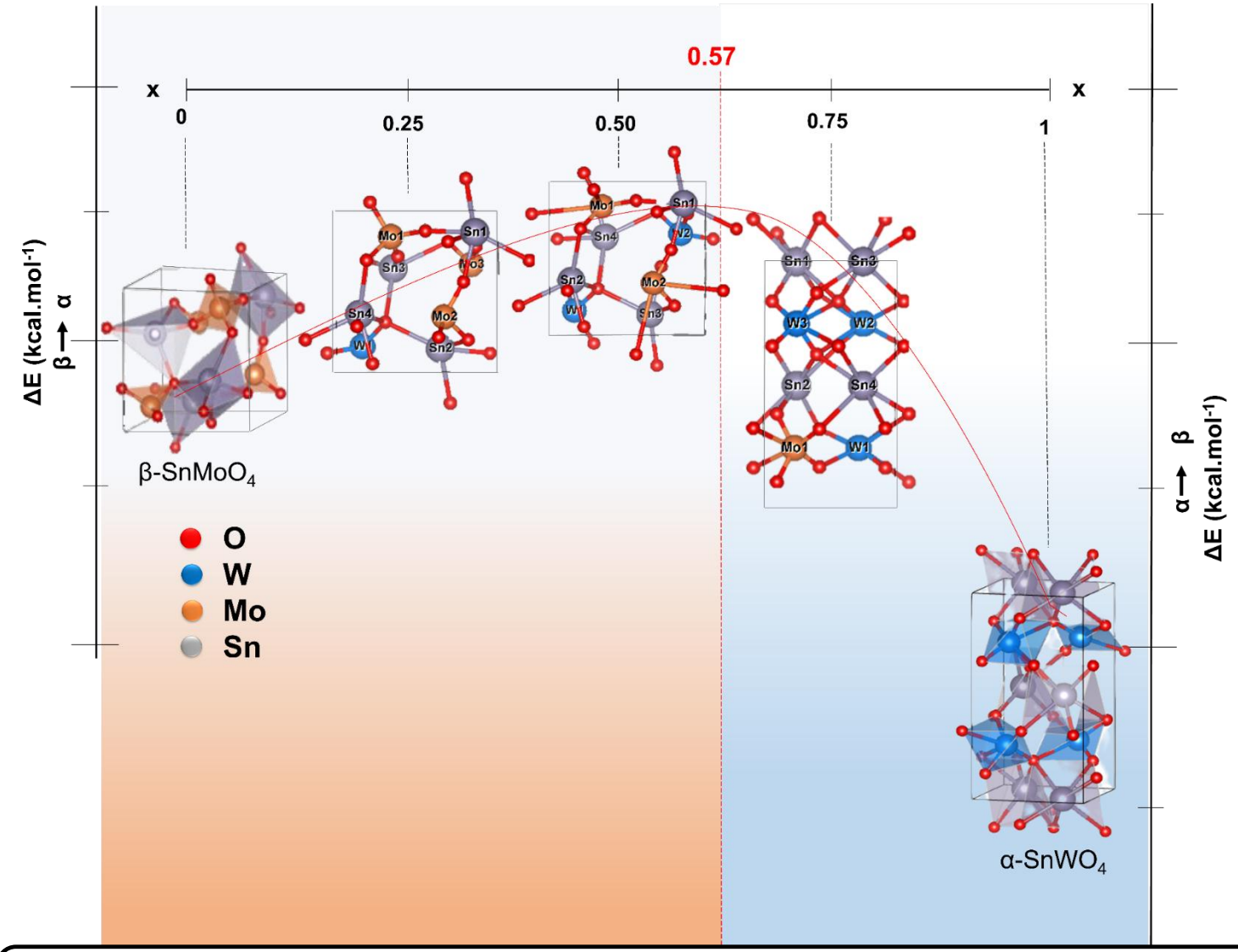
CP-PP Equivalence in $SnMo_{1-x}W_xO_4$



- Candidates to improve photocatalysis in hydrogen economy.
- $SnWO_4$ orthorhombic *α* phase. Small and indirect band gap.
- $SnMoO_4$ cubic β phase with a direct band gap around 1.5 eV higher than *α*-$SnWO_4$.
- Chemical doping controls the stable structure

- β-$SnMoO_4$ → α-$SnMoO_4$ **(1 GPa) /** β-$SnMoO_4$ → α-$SnMo_{0.57}$**$W_{0.43}$**O_4
- α-$SnWO_4$ → β-$SnWO_4$ **(1200 K (-3 GPa) /** α-$SnWO_4$ → β-Sn**$Mo_{0.57}$**$W_{0.43}O_4$

Polymorphism in $SnMo_{(1-x)}W_xO_4$

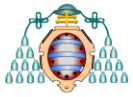


Polymorphism induced by chemical pressure

First Si+C+O mineral

EHPRG51 European High Pressure Research Group International Meeting

search Group International Meeting (EHPRG 51)
1-6 September 2013
Queen Mary University of London, UK



Prediction of a novel stable SiCO crystal structure

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www.malta-consolider.com CONSOLIDER 2010 MALTA Matter at High Pressure

Introduction

Although CO_2 and SiO_2 do not react at ambient conditions, their structural analogies at high pressure raise the question whether any Si-C-O crystalline phase may exist. An interface consisting of unknown SiCO compounds has been in fact proposed for the oxidized silicon carbide. Also, recent experiments performed by Santoro et al. at 18-26 GPa and 600-980 K by reacting silicalite, a microporous zeolite, and molecular CO_2 filling the pores claimed the synthesis of a silicon carbonate phase with CO_2 units.

It opens the way for a new class of stable carbonate compounds at pressures close to the Earth's mantle conditions, with possible implications in the understanding of the deep carbon cycle and the carbon storage. We present here results from extensive structural searches of crystalline systems containing just silicon, carbon and oxygen atoms.

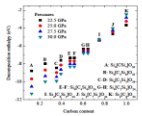
Method

- Structural searches were performed with the USPEX code according to the chemical reaction $xSiO_2+ySiO_2 \rightarrow Si_xC_yO_{(2x+2y)}$.
- x,y varying between 1 and 3, up to 4 formula units, pressures from 15 to 150 GPa.
- Underlying DFT *ab-initio* calculations were performed with the VASP code.
  - PBE exchange-correlation functional and PAW description of the electron-ion-core interaction.
  - Lowest enthalpy structures were reoptimized with more stringent accuracy (cut-off energy: 600 eV), k-point grid spacing $2\pi x0.03$ Å^{-1}.
- Phonon frequencies were calculated using density-functional perturbation theory as implemented in the ESPRESSO package.
  - Full phonon dispersion curves obtained by Fourier transformation matrices computed on (4,4,4) regular q-point grids.

Is there any SiCO compound compatible with crystal-chemistry?

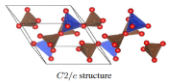
From database analysis, we found a candidate structure: UB_2O_6 ($C2/c$, Z=4). It has the correct $Si_{1-x}C_xO_2$ stoichiometry & carbonate (CO_3) units when substituing U and B for Si and C, respectively. After optimization at 28 GPa, it shows distorted SiO_6 and CO_4 units, and it is unstable vs. decomposition into CO_2-III and SiO_2-stishovite.

We analized the relationship between carbon content and stability. Different SiCO configurations were generated replacing U and B' for Si, and B for C in the conventional reference structure $U_4[B_nB'_{8-n}]O_{24}$ (n=1-8).



Decomposition enthalpy vs carbon content for different SiCO isomers.

- Evolving influence of pressure over the decomposition reaction as C content increases.
- $|\Delta H|$ decreases when C content increases for a given pressure.
- SiC_2O_6 is the most plausible stoichiometry.

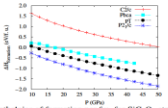


$C2/c$ structure

- Z = 1,2,3,4. Pressures: 20, 24, 28, 32 GPa.
- Lowest enthalpy structure $P2_1/c$, Z= 2.

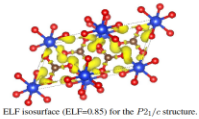
SiO_6
d(Si-O)$_{av}$ = 1.74 Å
CO_3
d(C-O)$_{av}$ = 1.27 Å

$P2_1/c$ structure at 28 GPa.



Enthalpies of formation per f.u. for SiC_2O_6 structures.

- The $C2/c$ structure is clearly unstable.
- The most stable structures found in the searches present SiO_6 octahedra corner-connected through almost-planar CO_3 units.



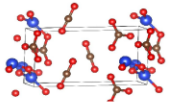
ELF isosurface (ELF=0.85) for the $P2_1/c$ structure.

- Covalent bond basin associated to the C-O bond.
- Ionic character of the Si-O bonds.

Evolution with pressure of SiC_2O_6 compounds

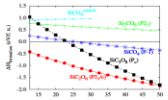
Searches at 0.5, 5, 15, 50, 65, 80,100 and 150 GPa

At pressures lower than 15 GPa



- The searches signal the decomposition into molecular units. Although the $P2_1/c$ structure is unstable versus decomposition into CO_2 and SiO_2, it is still dynamically stable.

Searches on other stoichiometries

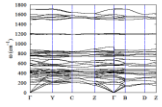


Enthalpies of formation per f.u. for $Si_xC_yO_{(2x+2y)}$ isomers.

SiC_2O_6 (Pc structure)

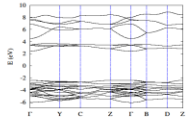
$SiCO_4$ ($P\bar{1}$ structure)

Searches on SiC_2O_6 compounds



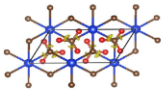
Phonon dispersion curves for the $P2_1/c$ structure at 27.5 GPa.

- Absence of imaginary frequencies → Dynamically stable.



Electronic band structure of the $P2_1/c$ structure at 0 GPa.

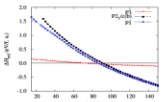
- Insulator (E_g = 4.8 eV) until very high pressures.



ELF isosurface (ELF=0.85) of the SiC_2 matrix.

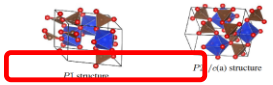
- In spite of its metallic character, it presents 3 ELF attractors of very high ELF value.
- The formation and localization of the oxygen anions can be related to them.

At pressures higher than 15 GPa



Enthalpies relative to the $P2_1/c$ structure vs pressure.

- Symmetrization towards the $P\bar{3}$ structure.
- Appearance of distorted CO_4 tetrahedra in the $P\bar{1}$ and $P2_1/c$(b) structures.



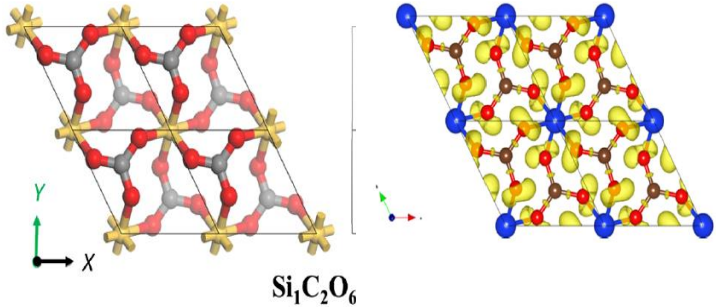
$P\bar{1}$ structure — $P2_1/c$(a) structure

- SiC_2O_6 is the most favourable stoichiometry.
- SiC_2O_6 and $SiCO_4$ are also stable against decomposition.
- The most stable structures consist of SiO_6 octahedra and triangular (CO_3) or tetrahedral (CO_4) units.

PHYSICAL REVIEW X **4,** 011030 (2014)

Unraveling Crystalline Structure of High-Pressure Phase of Silicon Carbonate

Rulong Zhou,[1] Bingyan Qu,[1] Jun Dai,[2] and Xiao Cheng Zeng[2,*]
[1]*School of Science and Engineering of Materials, Hefei University of Technology, Hefei, Anhui 230009, China*
[2]*Department of Chemistry and Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, Lincoln, Nebraska 68588, USA*



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A novel crystalline SiCO compound

Cite this: *Phys. Chem. Chem. Phys.*, 2015, 17, 25055

Miriam Marqués,*[a] Angel Morales-García,[b] José Manuel Menéndez,[c] Valentín G. Baonza[b] and José Manuel Recio[c]

The previously proposed $P\bar{3}$ structure $(Z = 1)$[12] is thermodynamically stable against decomposition in a slightly smaller pressure range than the $P2_1/c$ structure, from 9.4 to 37.3 GPa (see Fig. 4).

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Article

A Chemical Bonding Interpretation of Unusual Compressibility Trends in Hydrated Magnesium Sulfates

Getachew G. Kebede, Ruth Franco, Fernando Izquierdo-Ruiz, Alvaro Lobato,* and J. Manuel Recio*

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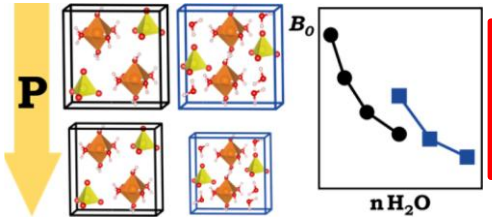

Inorganic Chemistry
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Article

Pressure-Driven Water Release from Magnesium Sulfate Hydrates: Thermodynamic and Mechanistic Insights

Getachew G. Kebede, Ruth Franco, Fernando Izquierdo-Ruiz, Alvaro Lobato,* and J. Manuel Recio*

Cite This: https://doi.org/10.1021/acs.inorgchem.5c03991

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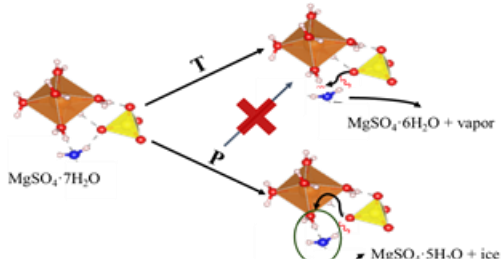

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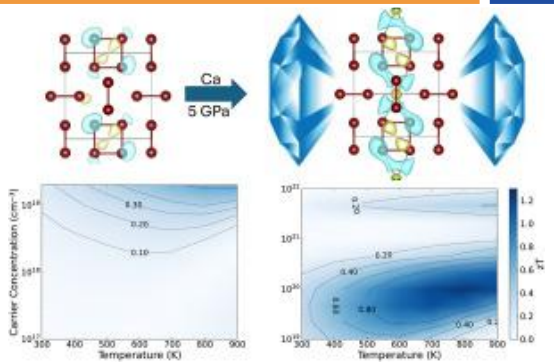

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Decoupling electronic transport properties: A combined physical and chemical pressure approach for boosting thermoelectric performance in skutterudites

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