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Structure prediction and behavior of (un)known materials in extreme conditions

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Introduction:

Over the years scientists have begun research to invent materials sustainable under extreme conditions. Furthermore, such innovative materials explored at high pressures, under high magnetic and electric fields, over a wide range of temperatures, radiation conditions, corrosive environments, under extreme mechanical loads, and non-equilibrium thermodynamic conditions are applicable not only in e.g. deep ocean explorations or space travel but become increasingly relevant in our daily life, such as in applications to energy production and conversion, maintenance of the water supply, or the stability of the computer infrastructure under coronal mass ejections. In that respect, we show the results of well-known barium sulfide (BaS) compound, where novel predicted and previously synthesized BaS phases have been calculated and subjected to extreme pressures up to 100GPa. The structure-property relationship and in particular metalization of BaS has been investigated in detail [1,2]. Boron suboxide, B_6O is the third hardest material after diamond and c-BN and the hardest known oxide. Here, we present structure prediction, high-pressure effect, and properties investigation of superhard B_6O [3,4]. Finally, we present one unknown Cr_2SiN_4 compound calculated using a combination of Density-functional theory (DFT), data mining (DM), global optimization (GO), as well as the newly developed Primitive Cell approach for Atom Exchange (PCAE) method [5]. Moreover, the behavior of the predicted Cr_2SiN_4 compound under high pressure has been investigated.

Barium sulfide, BaS

In the recent years, barium chalcogenides based materials have attracted great scientific and industrial interest due to their potential technological applications e.g. in microelectronics and magneto-optical devices. Furthermore, due to their strong ionic character and metallization behaviour under high pressures these compounds are promising candidates for various electrical and optical devices in the future. Here, the complete study of the structural, electronic and mechanical properties of barium sulphide has been presented, including experimentally observed modifications, as well as predicted (not-yet synthesized) BaS phases and their behaviour in the high pressure regime calculated with high precision DFT functionals.[1,2]

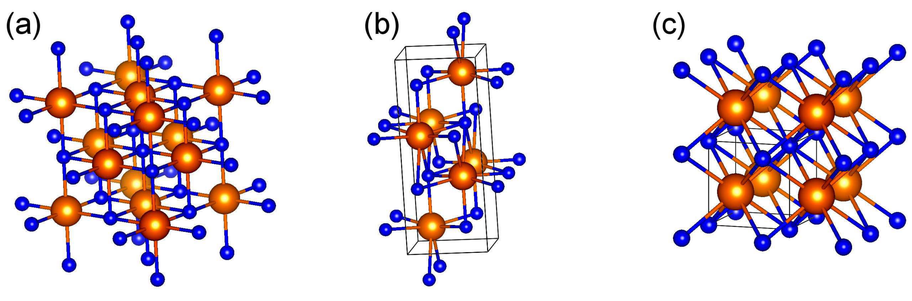
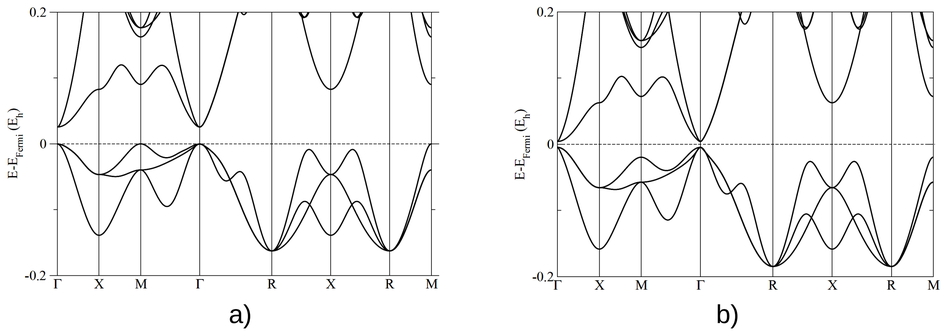
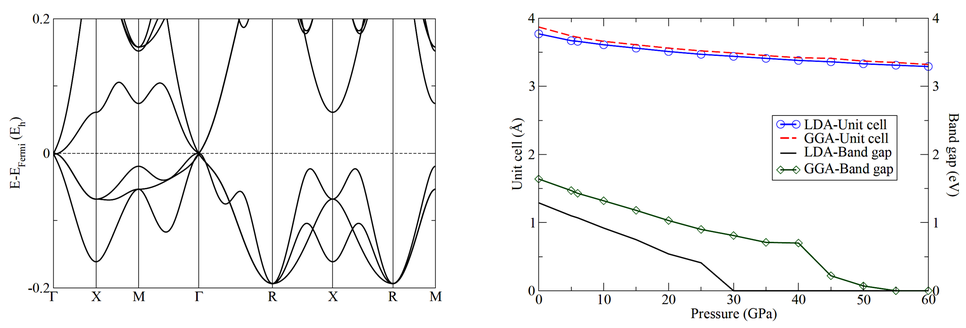


Figure 1. Visualization of the calculated structure types in barium sulphide: a) NaCl type, experimentally observed at standard conditions, b) TlI type, predicted at high pressures and c) CsCl type, observed at high pressures (small (blue) and large (orange) spheres correspond to S and Ba atoms, respectively)



a) b)

Figure 2. Band structure of the CsCl (B2) structure at: a) 40GPa showing indirect band gap, b) 45GPa showing direct band gap (calculation performed using GGA-PBE)



a) b)

Figure 3. a) Band structure of the CsCl (B2) structure at: a) 55GPa exhibiting metallic properties (calculation performed using GGA-PBE) b) Calculated size of the band gap in the CsCl modification in the BaS compound at elevated pressures up to 60GPa (calculations performed using LDA-PZ and GGA-PBE functional)

Boron suboxide, B_6O

Boron suboxide is the hardest known oxide and the third hardest material after diamond and cubic boron nitride, with reported values of hardness between 30 and 45 GPa. Additionally, B_6O has high thermal stability, high chemical inertness and high melting temperature, making it applicable for cutting, grinding, drilling and coatings. Its advantage among other superhard materials is thermodynamic stability already at ambient conditions, while most of the superhard materials must be synthesized at high pressure (HP). Here, we present structure prediction, high-pressure effect, and properties investigation of superhard B_6O [3,4].

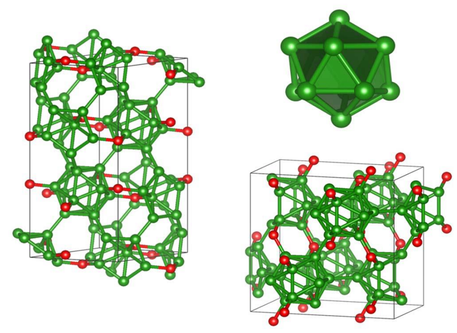
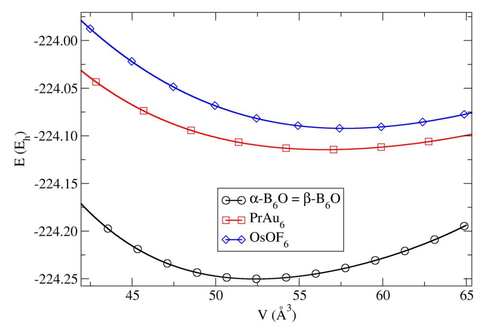
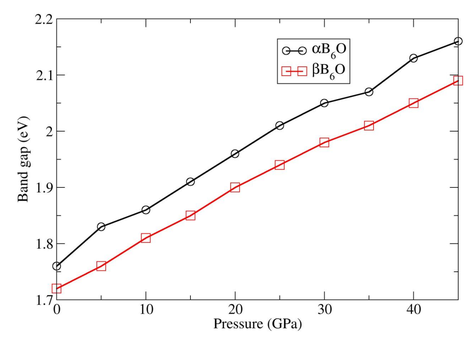


Figure 1. Crystal structures of (a) α-B_6O; (b) B_{12} icosahedra; (c) β-B_6O. Green and red spheres denote boron and oxygen atoms, respectively.
Figure 2. Energy versus volume *E(V)* curves of B_6O calculated using GGA-PBE functional of the energetically favorable α-B_6O, β-B_6O, $PrAu_6$ and $OsOF_5$ predicted structures.
Figure 3. Band gaps in the α- and β-B_6O modifications at the high pressure (HP) regime calculated using GGA-PBE functional.[3,4]

(Fig. 1)



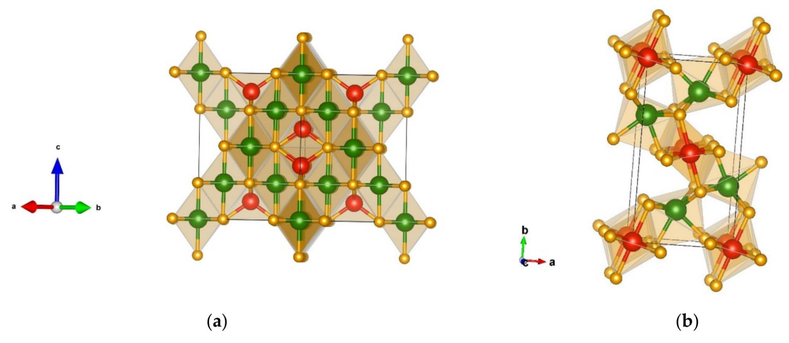
(Fig. 2)



(Fig. 3)

Novel Cr_2SiN_4 compound

A number of studies have indicated that the implementation of Si in CrN can significantly improve its performance as a protective coating. As has been shown, the Cr-Si-N coating is comprised of two phases, where nanocrystalline CrN is embedded in a Si_3N_4 amorphous matrix. However, these earlier experimental studies reported only Cr-Si-N in thin films. Here, we present the first investigation of possible bulk Cr-Si-N phases of composition Cr_2SiN_4. To identify the possible modifications, we performed global explorations of the energy landscape combined with data mining and the Primitive Cell approach for Atom Exchange (PCAE) method. After *ab initio* structural refinement, several promising low energy structure candidates were confirmed on both the GGA-PBE and the LDA-PZ levels of calculation. [5] Special focus of this study is on the structure candidates in the Cr_2SiN_4 system at extreme pressure conditions.



(a) (b)

Figure 1. Visualization of energetically favorable Cr_2SiN_4 modifications: (a) the equlibrium Al_2MgO_4-spinel-type in space group *Fd-3m* (no. 227); and (b) high-pressure Na_2MnCl_4-type that appears in space group *Pbam* (no. 55). Green, red, and yellow spheres denote Cr, Si, and N atoms, respectively.

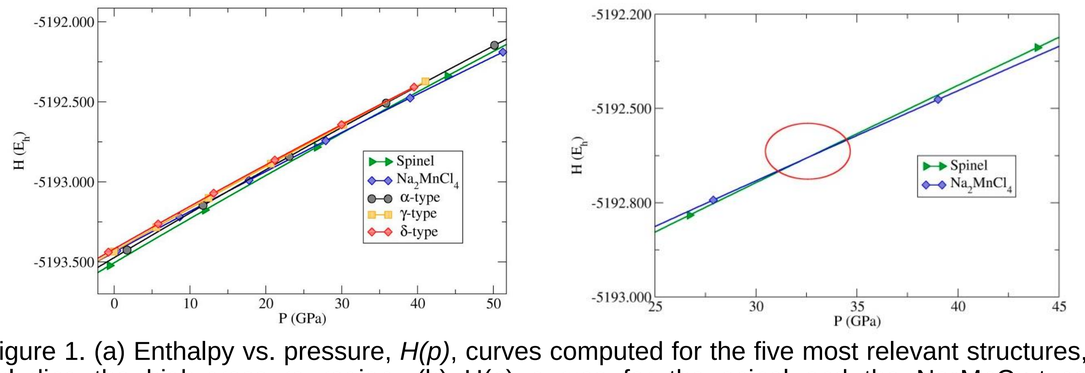


Figure 1. (a) Enthalpy vs. pressure, *H(p)*, curves computed for the five most relevant structures, including the high-pressure region. (b) H(p) curves for the spinel and the Na_2MnCl_4-type (transition pressure was found to be ~33 GPa. Calculations done using GGA-PBE functional. [5]

References:

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[5] T. Škundrić, D. Zagorac, J.C. Schön, M. Pejić, B. Matović, Crystal structure prediction of the novel Cr2SiN4 compound via global optimization, data mining, and the PCAE method, Crystals, 11(8), 891 (2021)

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Република Србија
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