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Theoretical investigation of structural, mechanical, elastic and vibrational properties of advanced materials under extreme conditions

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Abstract

One of the recent trends in materials science and technology is the research of the behavior of the materials under the extreme conditions both on the theoretical and experimental basis. There are limitations of the experimental methods, however, theoretical approach can be used as a supplement to the experimental results. As a consequence, in the last two decades a vast number of structure prediction calculations have been performed on chemical systems, focusing on the high-pressure and high temperature phases. In this work, we would like to present several computational studies and their connection to the actual synthesis routes: lead sulfide (PbS), barium sulfide (BaS), and aluminum nitride (AlN). The investigated compounds were calculated on *ab initio* level using the most advanced tools in quantum chemistry and computational material science including Hartree-Fock Theory, Density Functional Theory (DFT) and Hybrid (B3LYP) Approximation. Their structural, mechanical, elastic and vibrational properties have been investigated and in addition, we show structure candidates as the function of size, pressure and temperature and not previously observed in any of the investigated materials thus creating new possibilities for synthesis of advanced materials with improved physical, chemical, and/or mechanical properties.

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Keywords: ab initio ; properties ; advanced materials ; extreme conditions.

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1. Introduction

If we consider the needs of industry over the last decades, there is an enormous demand for new materials, or/and new applications of already existing materials, especially accessible via high pressure/high temperature synthesis, leading to the study of materials under high pressure and/or high temperature, using both theoretical and experimental methods. (Zurek et al. (2015), Zagorac et al. (2014), Djukic et al. (2015), Lukovic et al. (2017)) Great number of theoretical and experimental studies have been performed on chemical systems, focusing on the high-pressure and high temperature phases or/and investigation of their properties (Zhang et al. (2017), Zagorac and Schoen et al. (2014), Matovic et al. (2016), Rosic et al. (2016), Djukic et al. (2016), Cebela et al (2017)).

In this study, we would like to present several computational studies and their connection to the experimental results: lead sulfide (PbS), barium sulfide (BaS), and aluminum nitride (AlN). The investigated compounds were calculated on *ab initio* level using the most advanced tools in quantum chemistry and computational material science. Furthermore, structural, mechanical, elastic and vibrational properties have been investigated in great detail. Finally, we show some additional structure candidates not previously observed in any of the investigated materials.

2. Theoretical Methods

Quantum mechanical calculations were performed using *ab initio* CRYSTAL17 code (Dovesi et al. (2018)) based on a linear combination of atomic orbitals (LCAO). Local optimizations were performed using the Hartree-Fock (HF), Density Functional Theory (DFT), and the hybrid B3LYP (Becke_s three parameter functional (Becke (1993)) in combination with the correlation functional of Lee, Yang, and Parr) methods. In particular, a local density approximation (LDA) with the correlation functional by Perdew and Zunger (PZ), and the Generalized Gradient Approximation (GGA) with the PBE (Perdew, Burke and Ernzerhof) functional were used from DFT methods in this study (Perdew et al. (1996)). Fock/Kohn-Sham matrix mixing of 50% has been used in order to stabilize the total energy value of the calculated structures. Tolerances for the convergence on total energy are set to $1.0\times10-7$ eV per atom in each structural, electronic, elastic and mechanical properties calculations. A k-point meshes of 8 x 8 x 8 Monkhorst-Pack scheme have been used. (Dovesi et al. (2018))

A supercell technique was used to obtain the frequency-dependent dispersion, as implemented in the CRYSTAL17 release. In order to achieve maximum computational efficiency and to keep the calculations tractable, selected supercells for the various directions were used. The LO-TO splitting at the G point was calculated by using the dielectric function, which was computed within the framework of the coupled perturbed Kohn – Sham method. For the calculations in the PbS system, basis sets for Pb and S were used as in reference (Zagorac et al. (2011), Zagorac et al. (2012)). In the case of the BaS system, we used the same basis set for Ba and S as in reference (Zagorac and Doll et al. (2017)). For the calculations in the AlN compound, we have used basis sets from Al and N as in references (Zagorac and Zagorac et al. (2017), Zagorac et al. (2018)). Structure analysis and visualization was performed using the KPLOT and the VESTA programs. A fully automated procedure to calculate second-order elastic constants (SOEC) has been used as implemented in the CRYSTAL17 code. The bulk modulus (B), is obtained from the compliance matrix elements, and from computed data, other elastic properties such as shear modulus (K), Young's modulus (E), Poisson's ratio (v) and quantities derived from the Voigt–Reuss–Hill approximation were easily obtained. Full elastic tensor has been generated by using keyword ELASTCON. (Dovesi et al. (2018))

3. Results and Discussion

3.1. Lead Sulfide (PbS)

Lead sulfide is an inorganic compound, appearing as mineral galena in nature, which is the principal ore and important compound of lead. PbS has great number of applications from semiconductors to infrared sensors and photo-optical industry.(Wang et al (2013), Trejo et al. (2015)) Recently it has attracted great attention in nanotechnologies, where different morphologies e.g. nanocrystals, nanorods, nanotubes, etc., can play important roles in their properties (Karami et al. (2013), Rempel et al. (2013), Khan et al. (2017)). One of the important application of PbS is found in friction industry for enhancing heat conduction and regulating friction coefficient. In this study we have investigated

structural, mechanical, elastic and vibrational properties of PbS which might greatly extend or open new applications of lead sulfide.

The experimentally known modification of PbS crystallizes in the NaCl structure at standard conditions. With the increase of pressure the PbS undergoes a phase transition from the rock-salt modification to an intermediate orthorhombic phase (TlI (B33) structure) at about 2.2 GPa and with further pressure increase to about 21.5 GPa, the orthorhombic TlI phase is transformed to the CsCl type (Zagorac et al. (2011), Demiray et al. (2013), Li et al. (2014)). The starting points of this study were the results of the global and local optimizations of the energy landscape in the PbS system on the *ab initio* level by using Hartree–Fock and DFT. (Zagorac et al. (2011), Zagorac and Schoen et al. (2011), (Zagorac et al. (2012)) Besides the experimentally known modification exhibiting the rock salt structure, we had observed a second minimum, showing the low-temperature α-GeTe-type structure. Here, we show vibrational properties of the PbS represented by the phonon spectra of the NaCl type modification computed with Hartree–Fock and DFT-LDA methods (Fig. 1). The results for the NaCl modification are in good agreement with the experiment and previous calculations. Although the NaCl structure is kinetically stable at equilibrium, it is already unstable at at the HF level of theory calculated for the equilibrium volume (Zagorac et al. (2012)). We note that our vibrational properties and phonon calculations have experimental and theoretical conformation with forefront X-ray scattering techniques and DFT calculations, where Bertolotti et al. (2016) have identified that, PbS and PbSe QDs undergo a lattice distortion with displacement of the Pb sublattice, driven by ligand-induced tensile strain at nanoscale level.

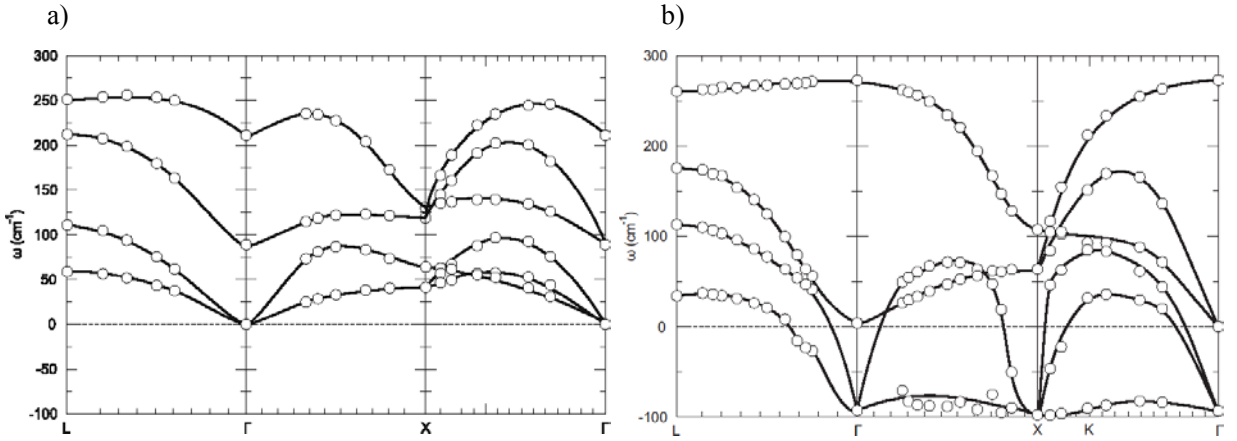

Fig. 1. Vibrational properties of the lead sulfide represented with phonon calculations: a) the NaCl-type modification calculated using LDA method; b) the rock salt type calculated using the Hartree-Fock approximation at equilibrium volume. We note that the rock salt modification appears to be unstable at HF level of theory. (Zagorac et al. (2012))

3.2. Barium Sulfide (BaS)

Recently, barium chalcogenides BaX (X = S, Se and Te) has attracted great scientific and industrial interest due to their potential technological applications in microelectronics and magneto-optical devices. (Nakanishi et al. (1993)) Furthermore, their strong ionic character and metallization behavior under high pressures could indicate these compounds as new promising candidates for various electrical and optical devices in the future. (Heng et a. (2000)) Barium sulfide (BaS) is like other barium chalcogenides, a wide-band gap semiconductor with large variety of applications. Although it is commonly used as a precursor to other Ba compounds, it is widely used in electronics, optics, ceramics, paints and additives. (Holeman et al. (2001)) Under normal conditions BaS crystallizes in the rock-salt (NaCl) type of structure. Experimental and theoretical studies has observed a high pressure phase transition from the NaCl to the CsCl type of structure at pressures above 6 GPa (Yamaoka et al. (1980), Zagorac et al. (2017)). Recently, TlI phase has been suggested to occur along the NaCl → CsCl phase transition, as well as possibility of existence of 5-5 and NiAs type of structure in the BaS system (Zagorac et al. (2017)). In addition, There exist several

experimental observations, indicating that with the further increase of pressure above 80 GPa, the CsCl modification of BaS starts to show a metallic character.

In this study we have investigated structural, vibrational, elastic and mechanical properties of the bariuim sulfide compound. Here, we show vibrational properties of the BaS represented by the phonon spectra of the NaCl type modification computed with the hybrid B3LYP approximation (Fig. 2). The vibrational properties for the NaCl modification at equilibrium are in good agreement with the previous experimental and theoretical results for BaS system. Furthermore, we have calculated phonon band structure of NaCl phase in the PbS system using B3LYP approach and compared to the BaS system. We note that the NaCl structure is stable at equilibrium in BaS system, while the optical frequencies in the PbS system are much lower at the Γ-point indicating instability of the equilibrium structure.

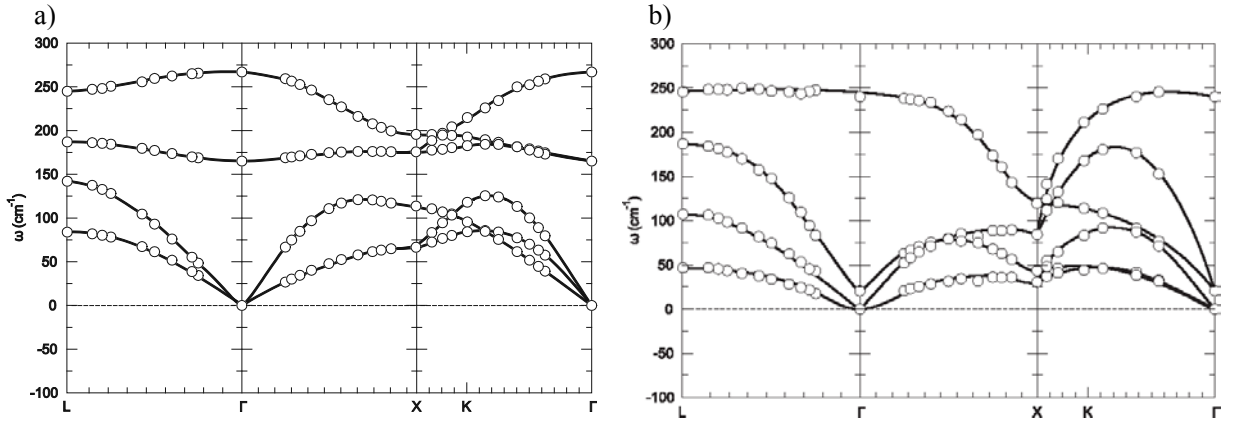

Figure 2. Vibrational properties of the equilibrium rock salt structure represented with phonon calculations calculated using hybrid B3LYP approach: a) In the BaS system, indicating stable strcuture; b) in the PbS system, indicating instability at the Γ-point of the of the Brillouin zone.

3.3. Aluminum Nitride (AlN)

In the past years, aluminum nitride (AlN) is attracting great interest of the industry and scientific community due to its dielectric properties, high melting point, thermal conductivity, electrical resistivity, mechanical strength, and corrosion resistance (Berger (1997)). In addition, AlN is a wide band gap semiconductor, piezoelectric and ceramic material with a wide range of technological applications, e.g. optoelectronic devices, mobile phones, laser diodes, and optical detectors, as well as for HT-, HP-, HF- devices, steel, metal, and semiconductor manufacturing industry, military applications, etc. (Monemar (1999)). Most of these industrial and technological applications are closely related to the structure-property relationships. At normal conditions aluminum nitride crystallize in the wurtzite structure and is a covalent bonded material. AlN also appears in the cubic form with sphalerite structure type, which converts to the wurtzite structure as the thickness of the film increases. With the increase of pressure up to 22 GPa, a rock-salt (NaCl) type of structure has been observed, both in theory and in the experiment. (Cai et al. (2007), Zagorac and Zagorac et al. (2017)) In addition, there are several other studies dealing with various AlN modifications at high pressures which include orthorhombic, tetragonal and hexagonal phases (Zagorac and Zagorac et al. (2017), Zagorac et al. (2018)).

In the final part of this study we have investigated mechanical properties of the AlN compound, and related structural and elastic properties as function of pressure. The summary of all mechanical properties plotted for each of the investigated modifications of aluminum nitride are presented in the Fig. 3. We observe that most of the mechanical properties have the highest values in the high pressure NaCl structure, while the lowest one are appearing in the *β*-BeO modification, which has been calculated at the effective negative pressures. Furthermore, we note that in the case of the sphalerite or polytype modifications, the mechanical properties of AlN would not change, which could be desirable in some technological applications. Furthermore, we point that our calculations were in a good agreement with available theoretical results when available.

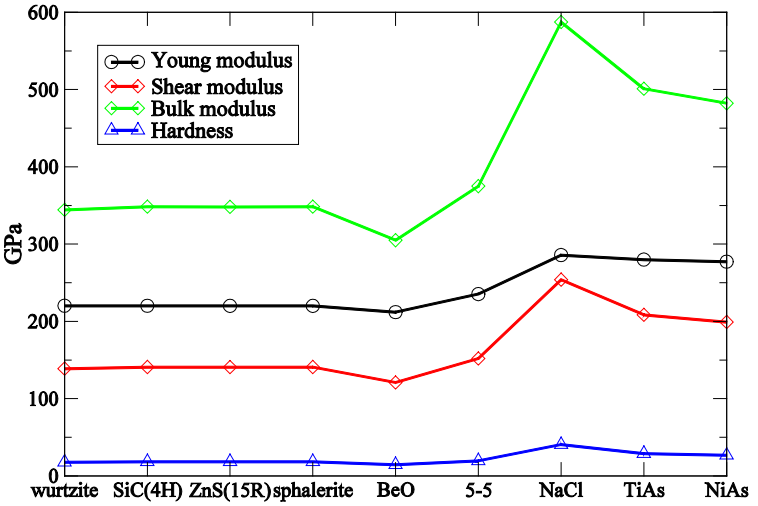

Figure 3. Bulk modulus B, Young's modulus E, shear modulus K and hardness HV for nine AlN modifications. Zagorac et al. (2018)

4. Conclusion

In this work, we show several computational studies including lead sulfide (PbS), barium sulfide (BaS), and aluminum nitride (AlN). In each of the investigated system structural, mechanical, elastic and vibrational properties have been calculated, their connection to the experimental results and related properties. All calculation have been performed on *ab initio* level using Hartree-Fock Theory, Density Functional Theory (DFT) and Hybrid (B3LYP) Approximation. Presented calculations in each of the individual studies were in a good agreement with available experimental and theoretical results. Finally, we show some additional modifications of investigated compounds creating new possibilities for synthesis of advanced materials with improved properties.

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