Thermodynamic and thermoelastic properties of wurtzite-ZnS by density functional theory

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ABSTRACT

In the present paper, we provide a detailed theoretical investigation on fundamental thermodynamic, thermomechanical, and electronic properties of wurtzite ZnS between 0–20 GPa and 0–2000 K, obtained by ab initio density functional theory and the B3LYP functional. Several properties, such as phonon dispersion relations, elastic and piezoelectric constants, and thermodynamic and thermoelastic behaviors were calculated and reported. The analysis of the data via volume-integrated third-order Birch-Murnaghan fitting resulted in \( K_0 = 72.17(4) \) GPa, \( K' = 3.87(1) \), and \( V_0 = 85.781(1) \AA^3 \) at \( T = 0 \) K. The Born criteria for the mechanical stability of the mineral phase showed that wurtzite is unstable above about 19 GPa in static conditions. We calculated a direct bandgap for wz-ZnS of 4.86 eV at zero compression, which became an indirect one by increasing pressure above 17 GPa. The results are in good agreement with the experimental and theoretical ones reported in the literature, and further extend the knowledge of an important zinc sulfide phase, for both geological and industrial applications.

Keywords: Wurtzite ZnS, thermodynamic properties, elastic properties, electronic properties, density functional theory, quasi-harmonic approximation

INTRODUCTION

Zinc sulfide ZnS belongs to the important family of the zinc monochalogenides whose general formula is ZnX, with X = S, O, Se, Te, or Cd. All the ZnX phases are isosctructural and, from the mineralogical point of view, zinc sulfide is commonly found either as zinc-blende (zb-ZnS, mineralogical name sphalerite) or wurtzite (wz-ZnS). Both of them have a closed-packed structure, but sphalerite belongs to the cubic system, with space group \( Fm\overline{3}m \) and cubic close packing (3C) with ABC sequence along \(<111>\) direction, whereas wz-ZnS has an hexagonal unit cell (2H) related to the space group \( P\overline{6}_3m \) (Fig. 1) with AB stacking along the [001] direction (Frey et al. 1986). In both zb- and wz-ZnS phases, each ion, either Zn\(^{2+}\) or S\(^{-}\), has a tetrahedral coordination. The structural difference between the two polymorphs is attributed to the stacking order of crystal planes along one of the \( C_3 \) axes and, according to Cardona et al. (2010), explains their very small difference of the enthalpies of formation. In addition, wurtzite is a high-temperature phase with respect to sphalerite, with a two-step 3C \( \rightarrow 2H \) transition at a temperature of about 1280–1300 K (Frey et al. 1986). There exists a third, high-pressure polymorph of ZnS, characterized by a halite-like structure (NaCl), with octahedral coordination of the ions, which is called rock salt (rs) ZnS (space group \( Fm\overline{3}m \)).

In a very recent work we investigated in details by ab initio density functional theory (DFT) simulations the thermodynamic and thermoelastic behavior of both cubic polymorphs of ZnS, finding that the zinc-blende to rock-salt phase transition occurs at 14.3 GPa at \( \sim 300 \) K (Ulian and Valdré 2019b), which was in very good agreement with the experimental result of Ono and Kikegawa (2018) in the same temperature condition (13.4 GPa).

The aim of the present paper is to extend the knowledge on the zinc sulfide polymorphs by providing thermodynamic, thermoelastic, and electronic properties of the wurtzite ZnS phase. Indeed, there is a continuous and still growing interest in its various and manifold applications. For example, zinc sulfide is an ore mineral, which is smelted to obtain zinc, and it is searched in the Earth crust by employing different approaches (Kowalczik et al. 2018). One of them, which is increasingly used at a global scale, is based on three-dimensional reflection seismic methods that provide high-resolution (order of meters to tens of meters) deep-penetration data from about 300 m to 4 km (Malehmir et al. 2012; Bellefleur et al. 2015). A successful application of these methods requires detailed knowledge of the seismic wave propagation in the mineral structure, data that can be calculated from the elastic constant tensor.

In addition, wz-ZnS is the first discovered semiconductor and has very important and interesting electric/electrodynamic, mechanical, and thermodynamic properties for applications in optoelectronic devices (e.g., displays, photodetectors) and in micro- and nanoelectromechanical systems (Özgür et al. 2005; Sang et al. 2013; Wang et al. 2017; Kandpal and Gupta 2018; Ossai and Raghavan 2018; Sinha et al. 2018; Xu et al. 2018). It is then not a surprise that wurtzite shares its name to all isostructural semiconductors of II-IV type. The remarkable chemical and physical features of this mineral phase, e.g., a wide bandgap of about 3.87 eV (region of UV light), high optical transmittance of visible light, polar surfaces, piezoelectric behaviors, and good thermal stability, make wurtzite ZnS a highly valuable material (Cline et al. 1967; Adachi 2005; Xu et al. 2018).

For all these reasons, it is crucial to carefully investigate the