



The crystal and electronic band structure of the diamond-like semiconductor $\text{Ag}_2\text{ZnSiS}_4$

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ABSTRACT

Single crystals of the new diamond-like semiconductor $\text{Ag}_2\text{ZnSiS}_4$ have been synthesized using high-temperature, solid state synthesis at 800 °C. The compound crystallizes in the monoclinic, non-centrosymmetric space group Pn with $a=6.4052(1)\text{Å}$, $b=6.5484(1)\text{Å}$, $c=7.9340(1)\text{Å}$, $\beta=90.455(1)^\circ$ and $R1$ (for all data) = 2.42%. The electronic band structure and density of states were calculated using density functional theory (DFT) and the full potential linearized augmented plane wave (LAPW) method within the Wien2k program suite. The calculated band structure suggests that $\text{Ag}_2\text{ZnSiS}_4$ is a direct band gap semiconductor with a calculated band gap of 1.88 eV at the Γ -point. The calculated density of states of $\text{Ag}_2\text{ZnSiS}_4$ is compared with that of AgGaS_2 . The band gap of $\text{Ag}_2\text{ZnSiS}_4$ was also determined experimentally as 3.28 eV via optical diffuse reflectance spectroscopy.

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1. Introduction

Over the past few years, multi-cation diamond-like semiconductors (DLSs) have received increased attention for their promising physical properties. A work by Shi et al. showed that $\text{Cu}_2\text{Sn}_{1-x}\text{In}_x\text{Se}_3$ possess an impressive thermoelectric figure of merit, ZT, of 1.14 at 850 K [1] indicating its potential use in thermoelectric applications. A recent work on the compound $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) has shown that the substitution of In for Sn increases ZT from 0.28 in the native compound to 0.95 in the 10% In substituted phase [2]. Another work by Steinhagen et al. has demonstrated that $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) can be synthesized as nanocrystals in the kesterite structure which can be used as a cheaper route for the production of photovoltaic devices [3]. Furthermore in 2009, Lekse et al. reported that $\text{Li}_2\text{CdSnS}_4$ exhibits a second harmonic generation (SHG) response 100× that of α -quartz and is phase matchable [4]. They suggest that quaternary DLSs with larger band gaps should possess increased laser damage thresholds as compared to the commercially available ternary DLSs that are currently used in non-linear optical devices [5,6]. While these recent studies focus on the technologically useful properties of multication DLSs, one of the

key elements in understanding these materials as a class is the correlation between these desirable attributes and crystal structure.

The above compounds are all diamond-like, i.e. they have a structure that resembles either cubic or hexagonal diamond [7,8] as shown in Fig. 1. These materials follow a set of guidelines that includes, (i) each atom must have an average valence electron concentration of 4, (ii) the average concentration of valence electrons for each anion must be 8 [7,8], (iii) each atom must have a tetrahedral coordination, and (iv) the octet of each anion must be satisfied by its nearest neighbors [7–9]. These guidelines can be used not only to classify the known compounds but also to predict new compounds. Furthermore, combining these rules with an understanding of how the structure of these materials relates to the physical properties could prove useful in predicting properties of yet to be discovered materials.

This work presents the crystal structure, electronic band structure, and density of states (DOS) of the DLS $\text{Ag}_2\text{ZnSiS}_4$ as well as the experimentally determined band gap. $\text{Ag}_2\text{ZnSiS}_4$ is a quaternary DLS of the formula $\text{I}_2\text{-II-IV-VI}_4$, which can be derived from that of the I-III-VI₂ family, with AgGaS_2 being its closest ternary relative. The structure of $\text{Ag}_2\text{ZnSiS}_4$ can be obtained from AgGaS_2 by replacing every two Ga atoms in a doubled structure of AgGaS_2 with one Zn and one Si in an ordered fashion (see Fig. 1). Therefore the band structure and DOS of $\text{Ag}_2\text{ZnSiS}_4$ are compared with that of AgGaS_2 computed using the same method [10].

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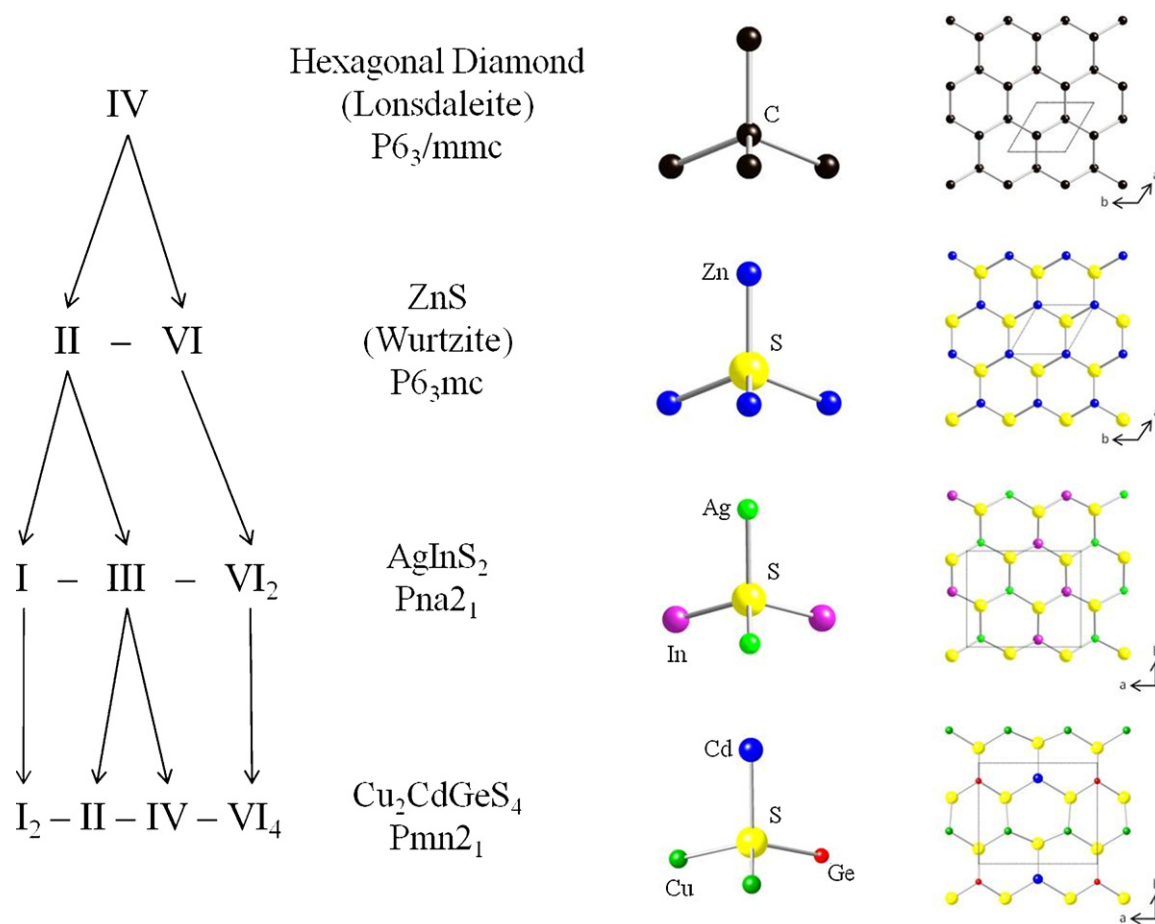


Fig. 1. Structural progression of the hexagonal family of DLs, showing the most common space groups at each level.

2. Experimental

2.1. Reagents

Chemicals used in this work were utilized as obtained unless otherwise noted: (1) silver powder, ~325 mesh, 99.99%, Cerac Milwaukee, WI; (2) zinc powder, 99.999%, Strem, Newburyport, MA; (3) silicon powder, 99.999%, Strem, Newburyport, MA; (4) sulfur powder, sublimed, 99.5%, Fisher Scientific, Pittsburgh, PA.

2.2. Synthetic procedure, Ag₂ZnSiS₄

Single crystals of Ag₂ZnSiS₄ were produced by weighing 4 mmol of Ag, 2 mmol of Zn, 2 mmol of Si, and 8 mmol of S in an argon-filled glove box. These reagents were combined using an agate mortar and pestle until the sample appeared homogeneous (~20 min). The mixed powder was then transferred to a graphite crucible which was placed into a 12 mm O.D. fused-silica tube. The tube was flame-sealed under a vacuum of approximately 10⁻³ mbar and placed in a programmable muffle furnace. The reactants were heated to 800 °C over 12 h and held at that temperature for 96 h. After which the sample was slow-cooled to 500 °C at 5 °C/h (60 h) and then allowed to cool radiatively to ambient temperature.

The product was a gray colored ingot with colorless needle-like crystals slightly tinted green protruding from the surface. Energy dispersive spectroscopy (EDS) showed the presence of all four elements in the translucent crystals.

2.3. Physical property measurements

2.3.1. Scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS)

SEM/EDS was performed on a Hitachi S-3400N scanning electron microscope equipped with a Bruker Quantax model 400 energy dispersive spectrometer using an XFlash[®] 5010 EDS detector with a 129 eV resolution. Samples were mounted on double-sided carbon tape affixed to an aluminum specimen holder. Images were taken at a working distance of 10 mm with an accelerating voltage of 15 kV. EDS spectra were also collected under the same conditions for 2 min live time.

2.3.2. Single-crystal X-ray diffraction data collection and reduction

A Bruker SMART Apex 2 CCD single crystal X-ray diffractometer employing graphite monochromatized molybdenum K_{α} radiation with a wavelength of 0.7107 Å and operating with a tube power of 50 kV and 30 mA was used to collect the data for 40 s/frame at ambient temperature. A total of 4283 measured reflections were collected with 1456 unique. The program SAINT was used to integrate the data and SADABS was employed to perform the absorption correction [11,12]. XPREP was used for space group determination and to create files for SHELXTL. Based on systematic absences, two space groups were initially considered, Pn and $P2/n$. The space group Pn (No. 7) was selected because all DLs are noncentrosymmetric due to all of the tetrahedra pointing in the same direction along a crystallographic axis.

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