Synthesis, Characterization and Chemical Stability of Silicon Dichalcogenides, $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$

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ABSTRACT

Silicon dichalcogenides have an intriguing crystal structure consisting of long tetrahedral chains held together by van der Waals forces but the electronic and optical properties have been less explored. In the present work, bulk SiSe_2 , SiS_2 , and $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$ were synthesized by the congruent melt growth method and characterized by Raman spectroscopy, X-ray Diffraction and UV/visible/IR transmission measurements supported by first-principles calculations. First-principles calculations reveal a nearly linear decrease of band gap energy in $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$ with increasing Se content, i.e., from SiS_2 to SiSe_2 which corresponds with a blue-shift in the transmission spectra from bulk SiSe_2 to $\text{Si}(\text{Se}_{0.6}\text{S}_{0.4})_2$, and to SiS_2 . Air stability tests demonstrate the formation of toxic $\text{H}_2\text{Se}/\text{H}_2\text{S}$ gas from sample oxidation at room temperature upon exposure to ambient air, and great care should be paid when handling these materials.

KEYWORDS

A1. Characterization, A1. Computer simulation, A2. Growth from melt, B1. Sulfides, B3. Solar cells,

1. INTRODUCTION

Silicon is a ubiquitous material in modern technology, forming the backbone of integrated circuits and photovoltaic devices. This is due partially to its ability to form large high purity crystals and wafers as well as a variety of Si-based compounds such as SiO_2 and Si_3N_4 which play an integral role in device processing and performance. Recently, there has been increasing interest in layered semiconductors such as the transition metal dichalcogenides (TMDs, for example MoS_2 and WSe_2) due to the unique properties of monolayer and a few-layered films [1][2]. The TMDs are comprised of two-dimensional sheets of covalently-bonded atoms which are held together by van der Waals forces. The silicon-based dichalcogenides e.g. bulk SiSe_2 and SiS_2 , in contrast, consist of long edge-sharing chains of SiSe_4 and SiS_4 tetrahedrons, which are held together via van der Waals forces [3][4] (see Figure 1) but their syntheses and properties are relatively less explored. The ternary alloy system $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$ is believed to possess an indirect band gap ranging from approximately 1.73 ± 0.05 eV (experimental value [5]) for SiSe_2 up to 2.44 eV (prediction [6]) or 5.0 eV (prediction [7]) for SiS_2 (note that the experimental band gap is absent in the literature for SiS_2). The range of band gaps is very interesting for a variety of optoelectronic devices. For example, the lower end of the band gap range is ideal for the top absorber cell of a tandem photovoltaic device based on a monocrystalline silicon bottom cell. A two-junction tandem cell of this type has a theoretical efficiency up to 45% (neglecting Auger losses) [8].

Initial studies of $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$ were carried out in the 1980s with the focus being on the synthesis and structural characterization of the binary compounds SiSe_2 and SiS_2 . Single crystal SiSe_2 was prepared by melt growth using Si and Se powders in a sealed quartz ampoule [9]. The glassy form of $\text{Si}_x\text{Se}_{1-x}$ was synthesized by quenching the ampoule with the molten alloy in water [10]. Bletskan[11] reviewed the melt and gas phase methods to fabricate single crystals of SiSe_2 , SiS_2 and the related $\text{A}^{\text{IV}}\text{B}^{\text{VI}}$ materials. In 1985, Tenhover *et al.* [12] synthesized a series of the glassy $\text{Si}(\text{S}_x\text{Se}_{1-x})_2$ alloys and studied their vibrational properties using Raman spectroscopy. It should be mentioned that discrepancies exist in the literature concerning the color of as-synthesized SiSe_2 . Hauschild *et al.* [5] reported single crystalline SiSe_2 in the form of dark red rods of 1 cm

to 1.5cm in length, while Peter *et al.* [9] described needle-shaped and colorless single crystal SiSe₂. Griffiths *et al.* [13], however, reported fibrous white crystals of SiSe₂. Additionally, optical transmission measurement by Hauschild *et al.* [5], indicated that the single crystal SiSe₂ is an indirect band gap semiconductor with a band gap energy $\leq 1.73 \pm 0.05$ eV. Furthermore, SiSe₂ (also true for SiS₂) was found to react readily with H₂O upon exposure to the moist air, resulting in the formation of toxic H₂Se gas [13], since the chemical reaction (eqn. 1) possesses a negative reaction enthalpy (-47 kJ/mole-atom at room temperature based on SGTE data [14] and [15]).

In summary, limited and even conflicting information exists regarding the optical properties such as the band gap energy of SiS₂ and the color and chemical stability of SiSe₂, SiS₂, and Si(Se_xSi_{1-x})₂.

The present work was aimed at synthesizing a series of bulk SiSe₂, SiS₂, and Si(Se_xSi_{1-x})₂ crystals via the congruent melt growth by varying the stoichiometric ratios of the starting materials. Their structural and optical properties were investigated using Raman spectroscopy, X-ray Diffraction (XRD) and Ultraviolet-Visible-Infrared (UV-VIS-IR) transmission spectroscopy. First-principles calculations were used to predict Raman modes and bandgap energies for SiSe₂ and SiS₂ for comparison to the experimental results.

Figure 1: Crystal structure of SiSe₂ or SiS₂ consisting of needle-like chains of edge-sharing SiSe₄ and SiS₄ tetrahedra bonded via van der Waals forces along the a-axis and b-axis directions.

2. EXPERIMENTAL AND SIMULATION DETAILS

SiSe_2 , SiS_2 , and $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$ crystals were synthesized via congruent melting by varying the stoichiometric ratios of the starting materials. The source materials were powders including 350 mesh 99.999% silicon, 200 mesh 99.999% selenium, and 200 mesh 99.999% sulfur. Stoichiometric amounts of these Si, Se and S powders were weighed and mixed. The quartz tubes used herein were 7 mm inner diameter, 9 mm outer diameter, and 30 cm in length before sealing. Before the sources were introduced into the quartz tubes, the tubes were sealed at one end and rinsed in acetone, 2-propanol, deionized water and were baked to dry.

For melt growth, 1.5 grams of powder was introduced into a quartz tube. A piece of quartz wool was put in the neck of the ampoule in order to prevent the powder from being pumped out during sealing. Then, the tube was evacuated to 10^{-2} to 10^{-3} Torr and sealed by flame heating. The sealed ampoules were then transferred into a tube furnace (LECO® TF-1 Tube Furnace) and annealed at 1100 °C for 8 hours. A small temperature gradient across the ampoule results in vapor transport of the Se and S species from the hotter to the cooler end of the ampoule during growth, which changes the stoichiometry of the original sources. To reduce this effect, the source end of the ampoule was always placed in the cooler end of the heat zone. Step-controlled cooling was used for all samples to further improve the compositional uniformity of the samples. The temperature was decreased in 50 °C increments and held for 3 minutes after each step from 1100 °C to 500 °C. The sample was then allowed to cool naturally to room temperature.

After the melt growth, the SiSe_2 , SiS_2 , and $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$ samples were characterized by Raman spectroscopy and UV-VIS-IR spectroscopy while the samples were still in the sealed ampoules. A WITec® Raman spectroscope with an incident laser beam of 488 nm was used for all sample characterization, and a LAMBDA™ 950 UV-VIS-IR spectrophotometer (Perkin Elmer) with a 150 mm integrating sphere was used to measure the overall transmittance of the samples from 300 to 1100 nm. The transmission spectrum of the quartz ampoule was subtracted from the data. The chemical stability of the samples was tested by cracking the quartz ampoules and exposing the materials to ambient air inside a ventilated hood. A calibrated gas detector (Honeywell Analytics®

SPM Single Point Monitor) was used to measure the concentration of H_2Se and H_2S produced by the samples as a function of distance from the open end of the quartz tube. The detectable gas range for H_2Se and H_2S was 20~150 ppb.

First-principle calculations were used to examine the phonon frequencies at Γ point and band gaps in $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$ with space group *Ibam* (No. 72) [9]. All first-principles calculations in the present work were carried out using the Vienna Ab-initio Simulation Package (VASP 5.3.5) [16][17], together with the ion-electron interaction described by the projector augmented wave method (PAW) [18]. The selected exchange-correlation (X-C) functionals were mainly based on our previous tests on α -sulfur and sulfur-containing material [19], i.e., the van der Waals correction (the D3 method [20] employed herein) together with the generalized gradient approximation (GGA-PBE [21]) and the improved GGA of PBEsol [22]. In addition, ancillary calculations were also performed using the X-C functional of the local density approximation (LDA) [23]. To gain accurate band gaps, we employed the hybrid X-C functional of Heyd-Scuseria-Ernzerhof (HSE)[24][25] with a range of separation parameter μ . For the example of the GGA-PBE, the μ value switches the X-C functional from PBE0 ($\mu = 0$), HSE06 ($\mu = 0.2$), HSE03 ($\mu = 0.3$), to PBE ($\mu = \text{infinitely large}$). Concerning the valence configuration, six electrons ($3s^23p^4$) were treated as valence electrons for sulfur (S), six ($4s^24p^4$) for Se, and four ($3s^23p^2$) for Si. During VASP calculations for the 12-atom $\text{Si}(\text{S,Se})_2$, in general we used a plane wave energy cutoff of 360 eV and a k -point mesh of $7 \times 11 \times 11$ (or $4 \times 7 \times 7$ for the time-consuming HSE calculations). The reciprocal-space energy integration was performed using the Gauss smearing method for structural relaxations and phonon calculations. Final calculations of total energies and band gaps were performed by the tetrahedron method incorporating a Blöchl correction [26]. The self-consistency of total energy was converged to better than 10^{-6} eV/atom.

Phonon calculations of SiS_2 and SiSe_2 were performed using the direct method in terms of a 48-atom $1 \times 2 \times 2$ supercell. Force constants were calculated directly using the VASP code with the k -points mesh of $5 \times 5 \times 5$. Phonon properties were predicted using the mixed-space approach [27] as implemented in the YPHON code [28]. Note that the mixed-space approach was recently developed with force constants computed from the

real space and the long-range dipole-dipole interactions computed from the reciprocal space, and it works well for both polar and nonpolar materials [27]. In the present work, the long-range dipole-dipole interactions including properties of the Born effective charge tensor and dielectric tensor, which result in the longitudinal optical-transverse optical (LO-TO) splitting, were calculated from the linear response method.

3. RESULTS & DISCUSSION

Prior to annealing, the source powder mixtures are black in the quartz ampoules as shown in Fig. 2(a). After annealing at 1100 °C for 8 hours and step-cooling, the sample color changes from white for SiS_2 , to orange for $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$, and to dark red for SiSe_2 , as shown in Fig. 2(b-f), demonstrating a clear color gradient with increasing Se content. The sample color varies from some of the reports in the literature. For example, Peter *et al.* [9] reported a colorless single crystal SiS_2 prepared in a sealed quartz-glass tube at 1420 K by reacting Al_2S_3 and SiO_2 in a dry N_2 stream. In the case of crystal SiSe_2 , it was reported to be white and needle-like [29], dark red rods [5], needle-shaped and colorless [9], and reddish brown [30]. The reason for the reported color variations is unclear; however, the dark red/reddish brown color of SiSe_2 obtained in this study is consistent with a bandgap energy in the range of 1.6-1.8 eV.

Figure 2: Photos of samples in sealed quartz ampoule before (a) and after annealing for starting stoichiometries of: (b) SiS_2 , (c)-(e): $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$, with $x=0.25, 0.5, 0.75$ in source, and (f) SiSe_2 .

Raman spectroscopy measurements were used for phase identification of SiSe_2 , SiS_2 and $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$ alloys. A complete list of the 18 phonon modes for SiS_2 and SiSe_2 (space group *Ibam* with 6 atoms in the primitive cell) was given by Griffiths *et al.* [13],

$$\Gamma = 2A_g^{(R)} + 3B_{1g}^{(R)} + 2B_{2g}^{(R)} + 2B_{3g}^{(R)} + A_u + 2B_{1u}^{(IR)} + 3B_{2u}^{(IR)} + 3B_{3u}^{(IR)} \quad (2)$$

where the superscripts *R* and *IR* indicate the Raman and infrared active modes. A_u is an inactive mode and the three acoustic modes are B_{1u} , B_{2u} , and B_{3u} . Prior studies of SiSe_2 and SiS_2 attributed these modes to the crystalline forms of SiSe_2 and SiS_2 , respectively [13][3], as shown in Table 1 with the calculated and experimental phonon frequencies at the Γ point of SiS_2 and SiSe_2 [3, 29, 31, 7, 4, 13].

Table 1. Calculated and experimental phonon frequencies at Γ point of SiS_2 and SiSe_2 , where *R* and *IR* indicate the Raman and infrared active modes, respectively.

SiX	Method	$A_g^{(R)}$	$A_g^{(R)}$	$B_{1g}^{(R)}$	$B_{1g}^{(R)}$	$B_{1g}^{(R)}$	$B_{2g}^{(R)}$	$B_{2g}^{(R)}$	$B_{3g}^{(R)}$	$B_{3g}^{(R)}$	A_u	$B_{1u}^{(IR)}$	$B_{2u}^{(IR)}$	$B_{2u}^{(IR)}$	$B_{3u}^{(IR)}$	$B_{3u}^{(IR)}$
SiS_2	PBEsol+D3 ^a	421	143	613	333	84	435	165	423	176	359	459 (575)	575 (594)	179 (181)	563 (584)	191 (192)
	PBE+D3 ^a	419	139	607	338	74	422	172	419	179	359	452 (570)	567 (584)	179 (180)	564 (582)	185 (185)
	Expt. ^a	437	143	631	356				181							
	Expt. ^b	430	138	625	351				181	175		590	402		487	
	Expt. ^c											475		188	475	188
	Calc. ^d	445	143	640	363	64	450	181	443	187		485 (610)	608 (624)	191 (192)	596 (624)	191 (192)
SiSe_2	PBEsol+D3 ^a	236	86	494	190	56	333	113	351	105	200	369 (449)	432 (444)	118 (119)	455 (467)	102 (103)
	PBE+D3 ^a	235	87	491	194	56	340	109	331	115	201	363 (447)	448 (458)	104 (104)	437 (448)	114 (114)
	Expt. ^a	244	82	514	204		350	113	350	113						
	Expt. ^b	248	82	512	204		355	122	345	114		492	397		468	
	Expt. ^c	242	68	515	216		350	110	350	110		490	390		460	
	Expt. ^c	237	70	515	213		357	125		125			387		470	
	Expt. ^c	236	70	521	202		358	131		131			380		470	
	Expt. ^f	242	81	516	218	48	367	113		113			399		472	
	Expt. ^g	245	83	515	205	47	357	114	347	120						

^aThe present work by first-principles calculations or experiments.

^b Measurements by Tenhover *et al.* [3][29]

^c Measurements by Begemann *et al.* [31]

^d Predictions using PBE0 as implemented in GRYPAL06 by Zwijnenburget *et al.* [7]

^e Measurements summarized by Arai *et al.* [4]

^f Measurements by Arai *et al.* [4]

^g Measurements by Griffiths *et al.* [13]

The Raman peaks in Fig. 3(a) correspond to crystalline SiSe₂ [13]. The very intense and narrow peak at 244 cm⁻¹ can be assigned to the (ν_1 , A_g) symmetric stretching mode of SiSe₄. The peak at 82 cm⁻¹ is assigned to the (ν_2 , A_g) mode which represents the bending coordinate with motional characteristics. The 350 cm⁻¹ peak is the (ν_8 , B_{3g}) mode which represents the motions of silicon atoms transverse to the axes of the chains in an orthorhombic bridge structure. The 113 cm⁻¹ peak is the (ν_7 , B_{2g}) mode and the 204 cm⁻¹ peak is the (ν_4 , B_{1g}) mode which represents the scissor-like motion involving both bond-stretching and angle-bending motions. It is worth noting that the (ν_4 , B_{1g}) mode is located at 204 cm⁻¹ in crystalline SiSe₂ but at 216 cm⁻¹ in glassy SiSe₂, as pointed out in the literature [29], which further provides evidence of the crystalline form of our synthesized SiSe₂. Fig. 3(b) shows the Raman spectra of our SiS₂ sample. Similar to SiSe₂, the Raman spectra of SiS₂ is also dominated by the normal modes of Si(S_{1/2})₄ tetrahedra unit. According to Tenhover *et al.* [3], the B_{1g} mode in glassy SiS₂ is split into two peaks. Hence the present SiS₂ sample can be verified to be crystalline SiS₂. Figs. 3(c) and (d) show the first-principle phonon frequencies at Γ point for SiSe₂ and SiS₂ in comparison with the present Raman results as well as the measurements in the literature [3, 4, 7, 13, 29, 31], see details in Table 1. In Fig. 3(c) and (d), the PBEsol is an improved generalized gradient approximation (GGA) for solids and their surface [22]. D3 is one kind of van der Waals correction used in the present work [20]. R means Raman spectra, and IR means Infrared. A good agreement is found between the calculations and experiments.

Figure 3: (a) Raman spectra of the synthesized SiSe₂, (b) Raman spectra of the synthesized SiS₂; and first-principle phonon frequencies at Γ point in comparison with the present and other experimental results for (c) SiSe₂ and (d) SiS₂.

In the case of $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$ as shown in Fig. 4(a), the Raman spectra exhibit a clear shift in A_g mode with increasing Se content: 432 cm⁻¹ peak in $\text{Si}(\text{Se}_{0.25}\text{S}_{0.75})_2$, 316 cm⁻¹ in $\text{Si}(\text{Se}_{0.5}\text{S}_{0.5})_2$, and 247 cm⁻¹ in $\text{Si}(\text{Se}_{0.75}\text{S}_{0.25})_2$. In order to determine the final composition in our $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$ alloys, first-principle calculations were carried out in terms of the Raman peak of the (ν_L, A_g) mode as a function of the Se mole fraction, see Fig. 4(b). Based on calculated results of band gap and lattice parameter (volume) as a function of composition, the (ν_L, A_g) peak in Raman spectra should follow roughly a linear variation as a function of Se content. Given the position of the (ν_L, A_g) peak from Raman spectra, the mole fraction of Se in our samples can be estimated. From Fig. 4(b), it is worth noting that the synthesized ternary compounds are $\text{Si}(\text{Se}_{0.03}\text{S}_{0.97})_2$, $\text{Si}(\text{Se}_{0.6}\text{S}_{0.4})_2$, and $\text{Si}(\text{Se}_{0.98}\text{S}_{0.02})_2$.

Figure 4: (a) Raman spectra of the synthesized $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$, and (b) the (ν_1, A_g) peak in Raman spectra as a function of Se content in the final $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$ ternary compounds based on first-principle calculations.

To identify the crystal structure of SiSe_2 , a SiSe_2 ampoule was opened in an inert glove box and the XRD data was collected using a Bruker D8 diffractometer located in the glove box, as shown in Fig. 5(a). The XRD system was setup in the conventional Bragg-Brentano geometry and employed a graphite monochromator. From the XRD data, SiSe_2 was characterized as an orthorhombic structure and is consistent with the ICDD pattern no: 000250756. It was characterized from the sample shown in Fig. 5(b). The photo clearly shows the needle-like fibers in the synthesized SiSe_2 ampoule.

Figure 5: (a) XRD measurement on SiSe₂ and ICDD pattern of the crystalline SiSe₂, (b) Photo of synthesized SiSe₂ sample which shows the needle-like fibers within the ampoule.

The band gaps of SiSe₂, SiS₂, and Si(Se_xS_{1-x})₂ are also predicted by first-principle calculations. Fig. 6(a) illustrates the variation of the band gap in Si(Se_xS_{1-x})₂ from the X-C functionals of PBEsol+D3, PBE+D3, and PBE+D3+Γ (μ = 0.7). Note that the range separation parameter μ = 0.7 is selected based on a comparison of the calculated and measured band gaps for SiSe₂ [5] and the selected PBE+D3 is based on a comparison of the calculated and measured lattice parameters of SiS₂ and SiSe₂ [9]. The more reliable X-C functional is PBE+D3, and the results from PBEsol+D3 are listed for reference. In general, Fig. 6(a) shows that the band gap of Si(Se_xS_{1-x})₂ decreases with increasing Se content, for example from 3.0 eV (413 nm) for SiS₂ to 1.73 eV (716 nm) for SiSe₂ based on the X-C functional of PBE+D3+μ. Moreover, a slightly negative deviation is shown for the band gap of Si(S,Se)₂ as a function of Se content, and even the X-C functional of PBE+D3 can predict a reasonable band gap of Si(Se_xS_{1-x})₂. To compare to these predictions, UV-VIS-IR transmission spectroscopy was carried out on three samples of SiSe₂, Si(Se_{0.6}S_{0.4})₂, and SiS₂, as shown in Fig. 6(b). Since the measurements were performed with the samples inside the sealed quartz ampoules, it was not possible to determine the sample thicknesses and therefore it was not possible to directly determine

the optical band gaps of these samples. For the purposes of comparison, the transmission spectra for each sample were normalized to their maximum values, see Fig. 6(b). A blue shift was observed from SiSe_2 to $\text{Si}(\text{Se}_{0.6}\text{S}_{0.4})_2$ and to SiS_2 , which is consistent with the calculated results about the band gap variation for $\text{Si}(\text{Se}_x\text{S}_{1-x})_2$.

Figure 6: (a) Band gap of silicon dichalcogenides by first-principle predictions using three different X-C functionals. (b) UV/visible/IR transmission spectra for the synthesized samples SiSe_2 , $\text{Si}(\text{Se}_{0.6}\text{S}_{0.4})_2$, and SiS_2 .

Silicon dichalcogenides will hydrolyze when exposed to moist air. For example, SiSe_2 will form SiO_2 and H_2Se gas. H_2Se is a colorless and flammable gas with a very offensive odor and is considered as one of the most toxic selenium compounds. The threshold limit value (TLV) of H_2Se , which represents the maximum recommended exposure for humans, is 50 ppb, and the median lethal concentration, i.e. the LC50 value, is 0.3 ppm (guinea pig, 8 hours) and 5.9 ppm (rat, 1 hour) (According to MSDS of H_2Se). Consequently, extreme care must be taken when handling these materials in air. To further assess the potential safety hazards, a gas detector was used to monitor the concentration of H_2Se produced by the oxidation of SiSe_2 in ambient air at room temperature after the quartz ampoules were broken open. The tests were carried out in the fume hood with a negative pressure. Almost immediately after exposure to air, the H_2Se concentration above the sample reached the upper detection limit (150 ppb). These data indicate that SiSe_2 reacts quickly when exposed to air and produces toxic H_2Se gas. Note that similar results were also obtained with the SiS_2 sample exposed to air, emitting the

H₂S gas due to a negative enthalpy for the reaction similar to Eq. (1), however, a quantitative measurement was not performed for this case.

4. CONCLUSIONS

In the present work, bulk SiSe₂, SiS₂, and Si(Se_xS_{1-x})₂ were synthesized via the congruent melt growth method. First-principle calculations were performed to predict the band gaps and to identify the Raman modes of Si(Se_xS_{1-x})₂. A good agreement was found between calculations and experiments. We show a nearly-linear decrease of band gap in Si(Se_xS_{1-x})₂ with increasing Se content, i.e., from about 3.0 eV for SiS₂ to about 1.7 eV for SiSe₂, and the predicted band gaps are consistent with a blue shift in the UV-VIS-IR transmission spectra. Air stability measurement points out that toxic H₂Se/H₂S gas is readily formed when Si(Se_xS_{1-x})₂ is exposed to moist air, and great care needs to be paid when handling this material.

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REFERENCES

- [1] Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman, M.S. Strano, Electronics and optoelectronics of two-dimensional transition metal dichalcogenides., *Nat. Nanotechnol.* 7 (2012) 699–712. doi:10.1038/nnano.2012.193.
- [2] S.M. Eichfeld, L. Hossain, Y. Lin, A.F. Piasecki, B. Kupp, a G. Birdwell, et al., Highly Scalable , Atomically Thin WSe₂ Grown via Metal Organic Chemical Vapor Deposition, (2015) 2080–2087. doi:10.1021/nn5073286.
- [3] M. Tenhover, M.A. Hazle, R.K. Grasselli, Atomic Structure of SiS₂ and SiSe₂ Glasses, *Phys. Rev. Lett.* 51 (1983) 404–406.
- [4] M. Arai, D.L. Price, S. Susman, K.J. Volin, U. Walter, Network Dynamics of Chalcogenide glasses, II. Silicon diselenide, *Phys. Rev. B.* 37 (1988) 4240–4245.
- [5] E. a. Hauschild, C.R. Kannewurf, Optical transmission in single crystal silicon diselenide, *Solid State Commun.* 6 (1968) viii. doi:10.1016/0038-1098(68)90216-0.
- [6] D.I. Bletskan, V. V. Vakulchak, K.E. Glukhov, Electronic structure of low-pressure and high-pressure phases of silicon disulfide, *Appl. Phys. A.* 117 (2014) 1499–1514. doi:10.1007/s00339-014-8584-z.
- [7] M.A. Zwijnenburg, R.G. Bell, F. Corà, Structure, bonding and physical properties of tetragonal and orthorhombic SiS₂ from (hybrid) DFT calculations, *J. Solid State Chem.* 181 (2008) 2480–2487. doi:10.1016/j.jssc.2008.06.006.
- [8] F. Meillaud, a. Shah, C. Droz, E. Vallat-Sauvain, C. Miazza, Efficiency limits for single-junction and tandem solar cells, *Sol. Energy Mater. Sol. Cells.* 90 (2006) 2952–2959. doi:10.1016/j.solmat.2006.06.002.
- [9] J. Peters, B. Krebs, Silicon disulphide and silicon diselenide: a reinvestigation, *ActaCrystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* 38 (1982) 1270–1272. doi:10.1107/S0567740882005469.
- [10] J.E. Griffiths, M. Malyj, G.P. Espinosa, J.P. Remeika, Nonstoichiometric Selenium Rich SixSe_{1-x} Films, *Solid State Commun.* 53 (1985) 587–590.

- [11] D.I. Bletskan, Glass formation in binary and ternary chalcogenide systems, *Chalcogenide Lett.* 3 (2006) 81–119.
- [12] M. Tenhover, J.H. Harris, M.A. Hazle, H. Scher, R.K. Grasselli, Isoelectronic Substitution In $\text{Si}(\text{S}_x, \text{Se}_{1-x})_2$ Glasses, *J. Non. Cryst. Solids.* 69 (1985) 249–259.
- [13] J.E. Griffiths, M. Malyj, G.P. Espinosa, J.P. Remeika, Crystalline SiSe_2 and SixSe_{1-x} glasses: Syntheses, glass formation, structure, phase separation, and Raman spectra, *Phys. Rev. B.* 30 (1984) 6978–6990.
- [14] Scientific Group Thermodata Europe (SGTE), Ed., *Thermodynamic Properties of Inorganic Materials, Landolt-Bornstein, New Series, Group IV, Vol. 19*, Springer, Berlin, 1999.
- [15] M.S. Chandrasekharaiah, J.L. Margrave, Enthalpies of Formation of Solid Silicon Dichalcogenides, *J. Phys. Chem. Ref. Data.* 23 (1994) 499. doi:10.1063/1.555960.
- [16] G. Kresse, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B.* 54 (1996) 11169–11186. doi:10.1103/PhysRevB.54.11169.
- [17] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.* 6 (1996) 15–50. doi:10.1016/0927-0256(96)00008-0.
- [18] G. Kresse, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B.* 59 (1999) 1758–1775. doi:10.1103/PhysRevB.59.1758.
- [19] S. Shang, Y. Wang, P. Guan, W.Y. Wang, H. Fang, T. Anderson, et al., Insight into structural, elastic, phonon, and thermodynamic properties of α -sulfur and energy-related sulfides: a comprehensive first-principles study, *J. Mater. Chem. A.* 3 (2015) 8002–8014. doi:10.1039/C4TA07062C.
- [20] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu., *J. Chem. Phys.* 132 (2010) 154104. doi:10.1063/1.3382344.

- [21] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* 77 (1996) 3865–3868. doi:10.1103/PhysRevLett.77.3865.
- [22] J. Perdew, A. Ruzsinszky, G. Csonka, O. Vydrov, G. Scuseria, L. Constantin, et al., Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces, *Phys. Rev. Lett.* 100 (2008) 136406. doi:10.1103/PhysRevLett.100.136406.
- [23] J.P. Perdew, Self-interaction correction to density-functional approximations for many-electron systems, *Phys. Rev. B.* 23 (1981) 5048–5079. doi:10.1103/PhysRevB.23.5048.
- [24] J. Heyd, G.E. Scuseria, M. Ernzerhof, Erratum: “Hybrid functionals based on a screened Coulomb potential” [*J. Chem. Phys.* 118, 8207 (2003)], *J. Chem. Phys.* 124 (2006) 219906. doi:10.1063/1.2204597.
- [25] J. Heyd, G.E. Scuseria, M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, *J. Chem. Phys.* 118 (2003) 8207. doi:10.1063/1.1564060.
- [26] P.E. Blöchl, O. Jepsen, O.K. Andersen, Improved tetrahedron method for Brillouin-zone integrations, *Phys. Rev. B.* 49 (1994) 16223–16233. doi:10.1103/PhysRevB.49.16223.
- [27] Y. Wang, J.J. Wang, W.Y. Wang, Z.G. Mei, S.L. Shang, L.Q. Chen, et al., A mixed-space approach to first-principles calculations of phonon frequencies for polar materials., *J. Phys. Condens. Matter.* 22 (2010) 202201. doi:10.1088/0953-8984/22/20/202201.
- [28] Y. Wang, L.-Q. Chen, Z.-K. Liu, YPHON: A package for calculating phonons of polar materials, *Comput. Phys. Commun.* 185 (2014) 2950–2968. doi:10.1016/j.cpc.2014.06.023.
- [29] M. Tenhover, R.S. Henderson, D. Lukco, M.A. Hazle, R.K. Grasselli, Vibrational studies of crystalline and glassy SiSe₂, *Solid State Commun.* 51 (1984) 455–459. doi:10.1016/0038-1098(84)91012-3.

- [30] A. Pradel, V. Michel-Lledos, M. Ribes, Two New Polymorphs of SiSe₂ : Structural Investigation by Raman and Si MAS NMR Spectroscopies and Relationship with the Structure of Vitreous SiSe₂, *Chem. Mater.* 2 (1993) 377–380.
- [31] B. Begemann, J. Dorschner, T. Henning, H. Mutschke, Optical Properties of Glassy SiS₂ and the 21 Micron Feature, *Astrophys. J.* 464 (1996) L195–L199.
doi:10.1086/310110.

Table 1. Calculated and experimental phonon frequencies at Γ point of SiS_2 and SiSe_2 , where R and IR indicate the Raman and infrared active modes, respectively.

SiX	Method	$A_g^{(R)}$	$A_g^{(R)}$	$B_{1g}^{(R)}$	$B_{1g}^{(R)}$	$B_{1g}^{(R)}$	$B_{2g}^{(R)}$	$B_{2g}^{(R)}$	$B_{3g}^{(R)}$	$B_{3g}^{(R)}$	A_u	$B_{1u}^{(IR)}$	$B_{2u}^{(IR)}$	$B_{2u}^{(IR)}$	$B_{3u}^{(IR)}$	$B_{3u}^{(IR)}$
SiS_2	PBEsol+D3 ^a	421	143	613	333	84	435	165	423	176	359	459 (575)	575 (594)	179 (181)	563 (584)	191 (192)
	PBE+D3 ^a	419	139	607	338	74	422	172	419	179	359	452 (570)	567 (584)	179 (180)	564 (582)	185 (185)
	Expt. ^a	437	143	631	356			181								
	Expt. ^b	430	138	625	351			181		175		590	402		487	
	Expt. ^c											475		188	475	188
	Calc. ^d	445	143	640	363	64	450	181	443	187		485 (610)	608 (624)	191 (192)	596 (624)	191 (192)
	PBEsol+D3 ^a	236	86	494	190	56	333	113	351	105	200	369 (449)	432 (444)	118 (119)	455 (467)	102 (103)
	PBE+D3 ^a	235	87	491	194	56	340	109	331	115	201	363 (447)	448 (458)	104 (104)	437 (448)	114 (114)
SiSe_2	Expt. ^a	244	82	514	204		350	113	350	113						
	Expt. ^b	248	82	512	204		355	122	345	114		492	397		468	
	Expt. ^c	242	68	515	216		350	110	350	110		490	390		460	
	Expt. ^e	237	70	515	213		357	125		125			387		470	
	Expt. ^e	236	70	521	202		358	131		131			380		470	
	Expt. ^f	242	81	516	218	48	367	113		113			399		472	
	Expt. ^g	245	83	515	205	47	357	114	347	120						

^aThe present work by first-principles calculations or experiments.

^b Measurements by Tenhover *et al.* [3][29]

^c Measurements by Begemann *et al.* [31]

^d Predictions using PBE0 as implemented in GRYPAL06 by Zwijnenburget *et al.* [7]

^e Measurements summarized by Arai *et al.* [4]

^f Measurements by Arai *et al.* [4]

^g Measurements by Griffiths *et al.* [13]