

Article

Synthesis, Crystal Structure, and Optical Properties of α -SrHfS₃

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Abstract

Metal-chalcogenide compounds with perovskite-type compositions have drawn increasing attention for their optical properties for solar energy conversion. Herein, a new α -type polymorph of the ternary sulfide SrHfS₃ is described, crystallizing in the NH₄CdCl₃ structure type. The yellow-colored plate-shaped crystals were synthesized at 1173 K using an elemental tin flux in an evacuated sealed tube. Its crystal structure was characterized at room temperature using single crystal X-ray diffraction to form in the orthorhombic *Pnma* space group, with the refined cell parameters of $a = 8.5041(4)$ Å, $b = 3.8004(2)$ Å, $c = 13.8935(6)$ Å, and $V = 449.02(4)$ Å³. The structure comprises five independent crystallographic sites, having one Sr, one Hf, and three S sites. The structure can be described as containing one-dimensional chains of distorted HfS₆ octahedra extending down the *b*-axis to form ${}_{\infty}^1[\text{HfS}_3]^{2-}$ strips of edge-sharing octahedra. The Sr atoms act as charge-balancing space fillers in the structure. High-purity bulk samples of α -SrHfS₃ could be prepared for measurement of its bandgap by optical diffuse-reflectance spectroscopy, showing a direct bandgap of 2.1(1) eV. Results of electronic structure calculations are consistent with this bandgap and type. The conduction and valence band edges stem from the respective empty Hf *d*-orbitals and the filled S *p*-orbital states. In summary, crystal growth of the α -type polymorph of SrHfS₃ has been demonstrated using a Sn flux approach, which can facilitate future broader synthetic explorations at lower temperatures.

Keywords: metal chalcogenides; crystal structure; optical properties; electronic structure calculations

1. Introduction

Metal chalcogenides (MCs) have been the focus of extensive research over the past few decades due to their diverse crystal structures and unique physical properties [1–4]. These compounds, composed of metals and chalcogen elements such as sulfur, selenium, or tellurium, exhibit tunable optical and electronic characteristics, making them suitable for broad range of applications, such as photovoltaics [5,6], photoluminescence [7,8], photocatalysis [9,10], second-order nonlinear optics [3,11], solar cells [12,13], and other optoelectronic applications [14,15]. The chemistry of MCs is often complex due to multidimensional bonding, which leads to the formation of structures with tunable dimensionalities of their underlying structure connectivity [1,16]. The MC compounds are primarily bonded covalently with a variety of potential structures, mostly adopting trigonal or octahedral coordination geometries, depending on the transition-metal cations and the choice of synthetic method. Evidently, a broad range of MCs has been developed, which can be categorized into binary, ternary, and quaternary systems. The structural diversity and potential properties of MCs continue to inspire the exploration of novel compounds and



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innovative synthetic strategies aimed at developing enhanced or entirely new properties through controlled crystal growth and compositional tuning [17].

A prominent class of MCs crystallizes in the AMX_3 structure, where A and M metal cations together have a total valence of 6. The A site is usually occupied by Group-IIA elements such as Ba, Ca, or Sr, while the M-sites typically include group-IVB elements like Hf, Zr, or Ti. The X-site is generally a chalcogen, such as S, Se, or Te. A few examples of the chalcogenide complexes belonging to the AMX_3 family are $CaZrS_3$, $SrZrS_3$, $BaZrS_3$, $BaUS_3$, $CaHfS_3$, $BaHfS_3$, $EuZrS_3$, $EuHfS_3$, $EuHfSe_3$, etc., [18–20]. The AMX_3 type complexes are known to crystallize in the $GdFeO_3$, with a three-dimensional distorted perovskite structure, or the NH_4CdCl_3 , having one-dimensional chains, structure types [21,22]. In AMX_3 compositions, the corner and edge-sharing nature of octahedra leads to more delocalized bands and functional carrier mobilities. MCs with the AMX_3 formula show interesting optical properties, similar to metal halide perovskites (e.g., $CsPbBr_3$) [23,24]. Additionally, these MCs exhibit exceptionally high absorption coefficients, further underscoring their potential in solar energy conversion applications.

In our recent efforts to synthesize new Sr-based complexes and understand the underlying structural chemistry of these chalcogenides, a new polymorph, α - $SrHfS_3$, has been discovered, belonging to the AMX_3 family with the NH_4CdCl_3 structure type. The β - $SrHfS_3$ phase has been reported earlier [20], and is known to crystallize in the $GdFeO_3$ structure type. The single crystal synthesis of the title compound using an elemental Sn flux facilitated its subsequent structural characterization by single crystal X-ray diffraction. A high-purity, polycrystalline product was obtained for measurements of its optical bandgap by UV-Vis diffuse reflectance spectroscopy. Additionally, electronic structure calculations have been carried out to probe the structural and compositional origins of its band gap and optical absorption.

2. Materials and Methods

2.1. Chemicals Used

Single crystals and polycrystalline phases of a new ternary sulfide, α - $SrHfS_3$ were synthesized using seal tube solid state synthesis method using elemental starting materials of Sr ingot (Alfa Aesar, Haverhill, MA, USA, 99.99% purity), Hf powder (Alfa Aesar, Haverhill, MA, USA, 99.6% purity), S powder (Sigma Aldrich, Milwaukee, WI, USA, 99.999% purity), and Sn powder (Sigma Aldrich, Milwaukee, WI, USA, 99.999% purity). As Sr and Hf are air sensitive, all the starting materials were handled in an Argon-filled dry glovebox.

2.2. Synthesis of α - $SrHfS_3$ Single Crystals

Efforts to synthesize the Sr-based analog of our previously reported compound [25] resulted instead in the initial discovery of yellow, plate-shaped crystals of α - $SrHfS_3$. This reaction utilized a mixture of elemental precursors: Sr (72.6 mg, 0.839 mmol), Hf (49.3 mg, 0.276 mmol), Sn (21.9 mg, 0.184 mmol), and S (56.1 mg, 1.751 mmol). These reagents were massed and loaded into a 6 mm outer diameter (OD) fused-silica tube inside an Ar-filled glove box, targeting the nominal stoichiometry of $Sr_9Hf_3Sn_2S_{19}$. The reaction mixture was sealed after evacuation under a vacuum of approximately 10^{-4} torr for ten minutes. The sealed reaction vessel was then placed inside a programmable muffle furnace (Nabertherm, Lilienthal, Germany) and gradually heated to 773 K in 10 h, where it was annealed for 12 h. The temperature was subsequently raised to 1173 K in 10 h, followed by annealing step at this temperature for 72 h. It was then cooled to 573 K using a cooling rate of 20 K h^{-1} , after which the furnace was powered off to allow the system to return to room temperature. Optical microscopy (Olympus, Center Valley, PA, USA) of the resulting

product was analyzed in an ambient atmosphere revealing the presence of yellow, plate-shaped crystals along with powdered product. Energy dispersive X-ray spectroscopy (EDS) on selected yellow, plate-shaped crystals using a Versa 3D focused ion beam scanning electron microscope (Thermo Fisher Scientific, Hillsboro, OR, USA) shows the presence of Sr, Hf, and S in the ~1:1:3 molar ratio (Figure S2). Given the product distribution, it was hypothesized that the elemental Sn acted as a flux to crystallize the α -SrHfS₃ single crystals. A stoichiometric reaction of elemental starting materials with 200 mg Sn as a flux and the same heating profile was found to reproduce the synthesis of the α -SrHfS₃ single crystals, hence confirming this assumption.

2.3. Synthesis of Bulk, Polycrystalline α -SrHfS₃

A high-purity polycrystalline α -SrHfS₃ sample was synthesized using a two-step solid-state reaction carried out at elevated temperatures. First, the elemental starting materials consisting of Sr (120.9 mg, 1.38 mmol), Hf (246.3 mg, 1.38 mmol), and S (132.8 mg, 4.14 mmol) were loaded into a 10 mm OD fused silica tube inside an Ar-filled glove box. The tube was then evacuated to 10^{−4} torr and sealed using a gas torch. In the first step, the reaction was heated at 1173 K in 10 h, followed by radiative cooling to room temperature. The tube was opened, and the product was crushed into fine powder inside an Ar-filled glove box, followed by compression into an 8 mm cylindrical pellet. The pellet was then resealed under vacuum in a fused-silica tube. In the second step, the reaction was heated in a muffle furnace to 873 K over a period of 6 h, maintained at that temperature for 48 h, and then cooled radiatively to room temperature. The resulting product was opened inside a glovebox and finely ground using a mortar and pestle. The high-purity formation of polycrystalline α -SrHfS₃ was confirmed through powder X-ray diffraction (XRD) characterization using a D6 phaser instrument (Bruker, Karlsruhe, Germany).

2.4. Characterization by X-Ray Diffraction Techniques

Single crystal X-ray diffraction for the α -SrHfS₃ crystals was carried out using the Bruker D8 venture diffractometer operating with a monochromatized Mo K α (λ = 0.71073 Å) radiation source. For data collection, a yellow plate-shaped crystal was selected and mounted on a transparent loop that was then fixed to the goniometer head. After confirming the quality of the crystals using an initial fast scan data collection, a full dataset for the crystal was collected and integrated using the APEX4 software [26]. The absorption correction was applied to the final dataset using the multi-scan method of the SADABS software, version 2008/1 [27]. During the data collection, an operating voltage of 50 kV and a current of 1.4 mA were supplied. The exposure time, detector-to-crystal distance, and frame width were also fixed to 3 s per frame, 50 mm, and 0.5°, respectively.

For the structure solution of α -SrHfS₃, the SHELXTL suite of programs [28] was utilized, where the XPREP program [29] suggested the orthorhombic crystal system with a primitive (*P*) cell. Based on the symmetry and observed extinction conditions, the program suggested two space groups: non-centrosymmetric *Pna*2₁ and centrosymmetric *Pnma*. Based on the statistics of the intensity of reflection value ($|E^2 - 1| = 0.895$), the centrosymmetric space group *Pnma* was chosen. Finally, the structure was solved using the XS program (direct methods) of the SHELXTL suite of programs, followed by the structure refinements [28,30]. A total of five crystallographically independent sites were identified by the program based on their coordination environment and interatomic distances, which were assigned later as one Sr, one Hf, and three S sites in the structure solution. The site occupancy factor for each atomic site was also refined, which confirmed that all the sites were completely occupied and without disorder. This led to a final refined formula of SrHfS₃ for the structure. This structure has been denoted as α -SrHfS₃ throughout the manuscript.

Refinement of atomic positions, scale factors, and atomic displacement parameters was performed using the SHELXL program [30]. Finally, the structure was finalized by verifying the symmetry using the ADDSYM program [31] and standardizing the atomic position using the STRUCTURE TIDY program of PLATON [32]. Additional crystallographic details for the α -SrHfS₃ structure are provided in Tables 1–3, and in the Supporting Information.

Table 1. Crystallographic refinement details for the single crystals of α -SrHfS₃ ^a.

Compound	α -SrHfS ₃
Space group	<i>Pnma</i>
<i>a</i> (Å)	8.5041(4)
<i>b</i> (Å)	3.8004(2)
<i>c</i> (Å)	13.8935(6)
<i>V</i> (Å ³)	449.02(4)
<i>Z</i>	4
ρ (gm.cm ^{−3})	5.359
μ (mm ^{−1})	36.16
<i>R</i> (<i>F</i>) ^b	0.020
<i>R_w</i> (<i>F_o</i> ²) ^c	0.052
<i>S</i>	1.17
δF (e Å ^{−3})	1.18 and −1.21
No. of reflections	12,418
No. of independent reflections	787

^a $\lambda = 0.71073$ Å, $T = 300(2)$ K. ^b $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. ^c $R_w(F_o^2) = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma w F_o^4\}^{1/2}$. For $F_o^2 < 0$, $w = 1/[s^2(F_o^2) + (0.0252P)^2 + 0.0532P]$ where $P = (F_o^2 + 2F_c^2)/3$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Fractional atomic coordinates, site symmetries, Wyckoff positions, and equivalent isotropic displacement parameters (Å²) α -SrHfS₃ crystal structure.

Atom	Wyckoff Position	Site Symmetry	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Hf1	4c	.m.	0.17089(2)	0.250000	0.44296(2)	0.00939(9)
Sr1	4c	.m.	0.43415(6)	0.250000	0.67846(3)	0.01231(12)
S1	4c	.m.	0.01832(14)	0.250000	0.60567(9)	0.0088(2)
S2	4c	.m.	0.16347(13)	0.250000	0.01200(9)	0.0101(2)
S3	4c	.m.	0.29175(16)	0.250000	0.28482(8)	0.0103(2)

Table 3. Selected interatomic distances in the α -SrHfS₃ structure.

Atom Pair	Distance in Å	Atom Pair	Distance in Å
Hf1-S3	2.426(1)	Sr1-S3	3.050(1) × 2
Hf1-S2	2.5525(8) × 2	Sr1-S3	3.080(1) × 2
Hf1-S1	2.5800(8) × 2	Sr1-S1	3.084(1)
Hf1-S1	2.607(1)	Sr1-S2	3.106(1) × 2
S··S	3.4321(5)	Sr1-S2	3.287(1)
Sr1··Sr1	3.8004(2)		

The bulk polycrystalline powder of α -SrHfS₃ was characterized by powder X-ray diffraction (XRD) collected at room temperature using a PANalytical Empyrean diffractometer with Cu K α radiation ($\lambda = 1.54$ Å). The data were recorded over a 2θ range of 5° to 75°, with a step size of 0.013°.

2.5. Characterization by UV-Vis Diffuse Reflectance Spectroscopy

Room temperature solid-state diffuse reflectance spectra for a polycrystalline sample of α -SrHfS₃ were obtained using a Shimadzu UV3600 spectrophotometer (Kyoto, Japan). Barium sulfate (BaSO₄), previously dried, served as the reference standard for the reflectance measurements across the wavelength range of 2400 nm (0.5 eV) to 350 nm (3.5 eV). The Kubelka–Munk equation ($\alpha/S = (1 - R^2)/2R$) was employed to convert the reflectance data into corresponding absorption values. Here R , S , and α are reflectance, scattering coefficients, and absorption coefficients, respectively [33]. The optical bandgap of the polycrystalline α -SrHfS₃ sample was subsequently determined through analysis using a Tauc plot:

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

Here, E_g , h , A , and ν correspond to the bandgap, Planck's constant, proportionality constant, and the frequency of incident light, respectively. The exponent n indicates the type of electronic transition, with $n = 2$ representing a direct band gap and $n = 1/2$ corresponding to an indirect band gap [34].

2.6. Electronic Structure Calculations

Density functional theory (DFT) calculations of the electronic structures of both the α and β polymorphs of SrHfS₃ were performed using the Projector Augmented Wave (PAW) method of the Vienna Ab initio simulation package (VASP) [35,36]. The exchange-correlation functionals were treated using the generalized gradient approximation method [37]. The energy cut-off threshold of 300 eV was used in consistent with the respective PAW pseudopotentials for Sr_sv, Hf_pv, and S. The energy convergence criteria for the geometry relaxation calculations were set to 10^{-8} eV for reaching self-consistency. The geometry relaxed structures for both the α and β polymorphs of SrHfS₃ were achieved using a Γ -centered k -point mesh of $3 \times 6 \times 2$ and $4 \times 3 \times 4$, respectively. The individual atomic contributions were projected out, and the total density of states (DOS) were calculated. For both the crystal structures, the k -point path of Γ -X-S-Y- Γ -Z-U-R-T-Z | X-U | Y-T | S-R was followed within the Brillouin zone, including eight intersections along each high symmetry direction for a total of 96 k points [38].

3. Results and Discussion

3.1. Synthesis and Structural Description

Initial attempts to synthesize the sulfur and strontium-containing analog of Ba₉Hf₃Sn₂Se₁₉ resulted in the successful synthesis of the new ternary phase α -SrHfS₃. However, its synthesis could subsequently be attained in high purity from a stoichiometric reaction at high reaction temperatures, as shown in Figure 1 by comparison of the simulated versus experimental powder XRD plots. The synthesis of the polycrystalline α -SrHfS₃ phase was always accompanied by a SrS impurity. A reaction temperature of 1173 K was found to yield the highest product purity after synthetic attempts over a range of reaction temperatures. By comparison, an alternate β -SrHfS₃ polymorph is synthesized at a higher reaction temperature of 1373 K [20], possessing a structure type that is an orthorhombic distortion of the perovskite-type structure. Thus, the addition of an elemental Sn flux was necessary to grow single crystals of the α -SrHfS₃ polymorph at the lower reaction temperature and to characterize its structure by single crystal XRD.

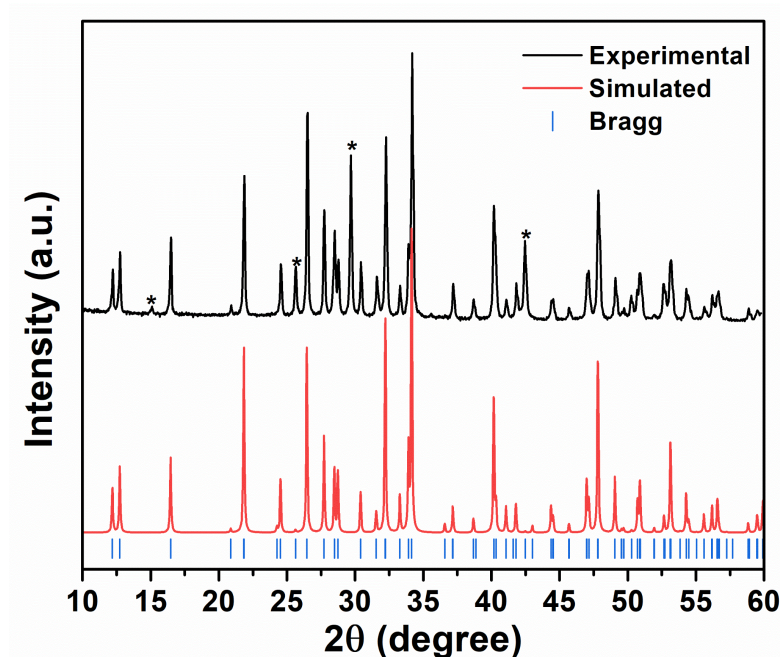


Figure 1. Comparison of the experimental powder XRD of polycrystalline α -SrHfS₃ versus the simulated pattern obtained from the single crystal refinement results. The blue line and the (*) symbol represent the Bragg positions and a SrS impurity phase [39].

The yellow-colored crystals of α -SrHfS₃ were characterized at room temperature by single crystal XRD to crystallize in the orthorhombic crystal system and space group *Pnma* ($a = 8.5041(4)$ Å, $b = 3.8004(2)$ Å, $c = 13.8935(6)$ Å and $V = 449.02(4)$ Å³). The structure consists of five independent crystallographic sites (one Sr, one Hf, and three S sites) with four formula units per unit cell ($Z = 4$). All atomic sites were refined as fully occupied, with the atomic coordinates, site symmetries, and Wyckoff position listed in Table 2. The crystal structure of the α -SrHfS₃ compound is represented in Figure 2a. The structure extends along the *b*-axis, where the Hf atoms are connected to each other via edge sharing. Each Hf atom is connected to six S atoms and forms a distorted octahedra geometry in the crystal. These octahedra share two of the S atoms with each other along the *a*-axis, which further extends infinitely along the *b*-axis, forming ${}_{\infty}^1[\text{HfS}_3]^{2-}$ strips having two edge-sharing chains of octahedra, as shown in Figures 2a and 3a. The extended view of the Sr coordination in the crystal structure is condensed into a three-dimensional net of ${}_{\infty}^3[\text{SrS}_3]^{4-}$. Each Sr cation is connected to eight S anions, forming a distorted bicapped trigonal prismatic type geometry shown in Figure 3b. The Sr polyhedra extend along the *a*-axis via face sharing with the other Sr polyhedra. These polyhedra also extend along the *c*-axis via edge sharing, given in Figure S1 in the Supporting Information.

The Hf-S distances in the α -SrHfS₃ structure occur in the range of 2.426(1) Å to 2.607(1) Å. These distances are consistent with those in related metal chalcogenide compounds, such as Rb₄Hf₃S₁₄ (2.426(2) Å to 2.683(2) Å) [40], Ba₆Hf₅S₁₆ (2.470(2) Å to 2.530(2) Å) [41] and Rb₂HfS₄ (2.472(1) Å to 2.576(1) Å) [42]. The Sr-S interatomic distances fall in the range of 3.050(1) Å to 3.287(1) Å. These bond distances can be compared with previously reported compounds such as Sr₂GeS₄ (2.934(4) Å to 3.354(5) Å) [20], SrSc₂S₄ (2.980(7) Å to 3.154(9) Å) [43], and SrU₂S₅ (2.965(1) Å to 3.589(1) Å) [44]. Additionally, calculated bond valence sums, Table S3 in the Supporting Information, are consistent with a charge-balanced formula which can be written as (Sr⁺²) (Hf⁺⁴) (S⁻²)₃.

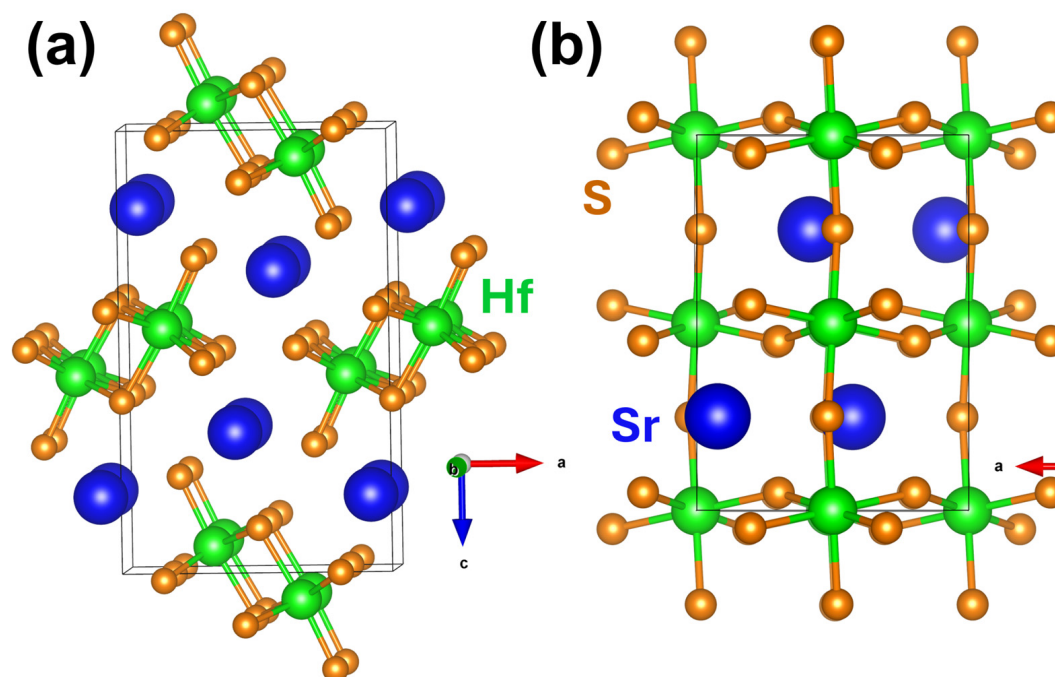


Figure 2. Unit cell views of the α -SrHfS₃ structure (a), and the previously reported β -SrHfS₃ structure (b) [20].

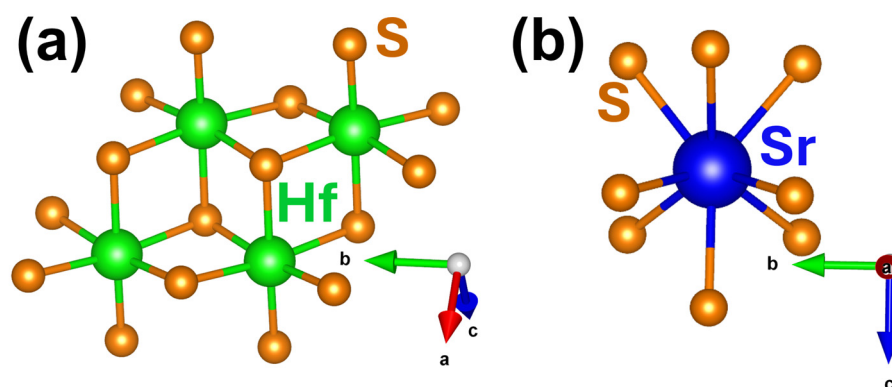


Figure 3. The coordination environment for (a) Hf atoms and (b) Sr atoms in the α -SrHfS₃ structure.

The crystal structure of the α -SrHfS₃ polymorph is markedly different than the previously reported β -SrHfS₃ structure, illustrated in Figure 2b [20]. The earlier reported compound, β -SrHfS₃, adopts the GdFeO₃ structure type. This structure type is an orthorhombic distortion of the ideal cubic perovskite type, consisting of a 3D network of vertex-sharing HfS₆ octahedra. By comparison, the α -SrHfS₃ structure adopts the NH₄CdCl₃ structure type, consisting of chains of edge-shared HfS₆ octahedra. Previous reviews covering a wider range of metal–chalcogenide semiconductors, specifically possessing perovskite-type compositions, have highlighted the structural factors that determine which of these two main structure types form in different chemical systems [45]. For example, the analogous Ba-containing BaHfS₃ and BaZrS₃ can be synthesized in only the GdFeO₃ structure type. However, the Zr-version of the title compound, SrZrS₃, can similarly be prepared in both the GdFeO₃ and the NH₄CdCl₃ structure types [18,46]. The latter represents the higher temperature structure above 1253 K, similar to the temperature dependence of SrHfS₃. It has been recently postulated that EuHfS₃ and SrHfS₃ could potentially form in the NH₄CdCl₃ structure type at lower reaction temperatures [45]. Thus, the present study is the first experimental validation of its formation at a reaction temperature of 1173 K.

3.2. Optical Properties

The metal chalcogenide perovskites have been the subject of intense recent research efforts because of their promising optoelectronic properties for applications involving solar energy conversion [45]. Their optical band gaps typically occur deep within the visible-light energies, with optical absorption coefficients rising to greater than 10^5 cm^{-1} . UV-Vis diffuse reflectance spectroscopy measurements were collected on the yellow-colored crystals of the α -SrHfS₃ polymorph within the wavelength range of 350 nm to 2400 nm. The optical bandgap was analyzed from a Tauc plot of the direct band transition, as depicted in Figure 4. The band transition was estimated from the onset of absorption, occurring at about 2.1(1) eV in the Tauc plot. This value is consistent with its semiconducting properties and yellow-colored crystals. By comparison, the previously reported band gaps (direct) for the related α -SrZrS₃ and β -SrZrS₃ polymorphs occur at about 1.5 and 2.1 eV, respectively [46]. Hence, the relatively smaller direct bandgap for the α -SrHfS₃ polymorph is consistent with these results.

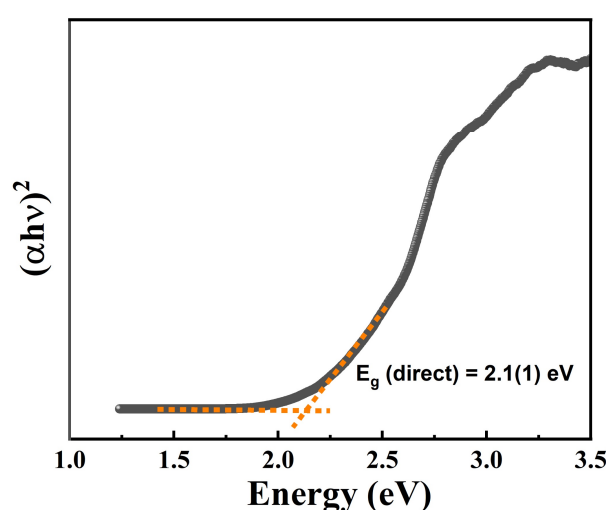


Figure 4. Tauc plot of α -SrHfS₃ polycrystalline sample. The black line represents the direct bandgap plot.

3.3. Electronic Structure Calculations

The electronic structures of both α -SrHfS₃ and β -SrHfS₃ were calculated using density functional theory methods to probe the structural origins and trends in their band gaps. After a full geometry relaxation, the total energy was calculated to be -33.0261 eV per formula for α -SrHfS₃ and a relatively higher -33.0199 eV per formula for β -SrHfS₃. The difference in total energies of about 6.2 meV per formula is negligible and consistent with the capability to synthesize either polymorph as a sensitive function of the reaction conditions, such as by varying temperature or using a Sn-flux reagent. Next, the density-of-states (DOS) and band structures were calculated and plotted, as shown in Figure 5. The partial DOS showing each of the atomic orbital contributions has been projected for Sr, Hf, and S, with the total DOS shown as the black line and the Fermi level (E_f), the vertical dashed line. Both DOS plots show a valence band (VB) and conduction band (CB) predominantly comprising S *p*-orbital (green line) and Hf *d*-orbital (brown line) states, respectively. On comparing their band gaps in Figure 5a,b, the band gap for the β -SrHfS₃ polymorph is larger by about 0.8 eV. The band structures of α - and β -SrHfS₃ are given in Figure S3 and Figure S4, respectively, in the Supporting Information. Band structure calculations demonstrate that both polymorphs have the closest energy separation of their VB and CB edges located at the Γ *k*-points, with direct band gaps of 0.70 eV for α -SrHfS₃ and 1.50 eV for β -SrHfS₃. Compared to the experimental value of 2.1(1) eV for α -SrHfS₃, this underestimation of its bandgap by about 1.4 eV is the result of well-documented issues

accompanying density functional theory calculations on solids. This trend in their band gaps is also consistent with other chalcogenide semiconductors, which exhibit both the α and β polymorphs. For example, the related SrZrS_3 exhibits both polymorphs, with optical measurements finding that the β - SrZrS_3 shows a larger bandgap by about 0.6 eV.

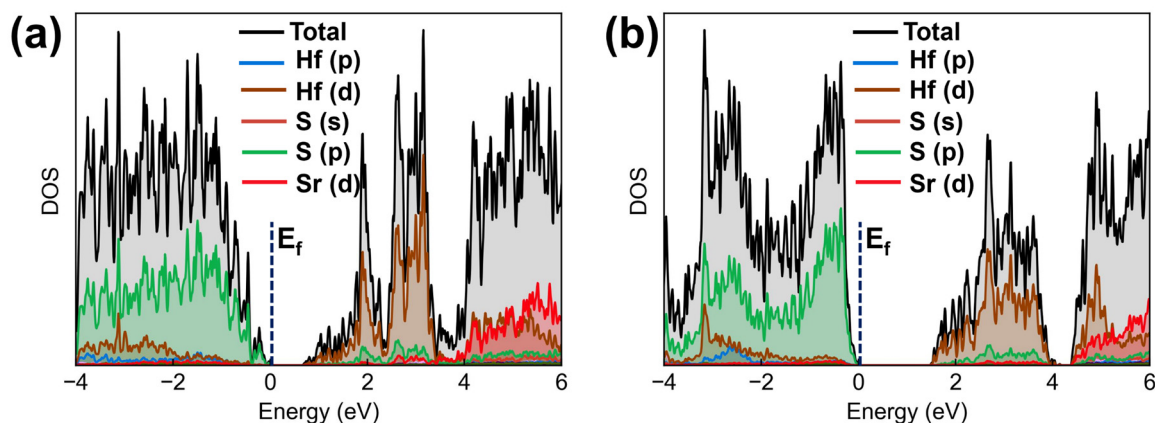


Figure 5. Calculated electronic density-of-state plots for (a) α - SrHfS_3 and (b) β - SrHfS_3 crystal structures. The Fermi energy levels are located at 0 eV, which is shown by blue dashed line.

4. Conclusions

The α -type polymorph of the ternary sulfide SrHfS_3 has been synthesized as a polycrystalline product from solid-state reactions at 1173 K, as well as in the form of yellow single crystals using an excess of elemental Sn as a flux. The compound is found to crystallize in the NH_4CdCl_3 structure type in the orthorhombic $Pnma$ space group, consisting of doubled edge-shared chains of distorted octahedra. It is synthesizable at a relatively lower reaction temperature as compared to the previously reported β - SrHfS_3 polymorph with the GdFeO_3 distorted perovskite structure type. Optical diffuse-reflectance spectroscopy yielded a direct bandgap of 2.1(1) eV. Results of electronic structure calculations are consistent with a direct bandgap occurring at the Γ k -point. The conduction and valence band edges are found to comprise the empty Hf-based d -orbitals and the filled S-based p -orbital states predominantly, respectively. In summary, crystal growth of the α -type polymorph of SrHfS_3 is demonstrated using a Sn flux, providing a synthetic pathway to perovskite-type compositions that receive increasing attention for their applications in solar energy conversion.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/solids7020020/s1>, Figure S1: Unit cell view of α - SrHfS_3 crystal structure, having only Sr polyhedra represented approximately along the b -axis; Figure S2 shows the EDS data of α - SrHfS_3 crystals; Figure S3. Electronic band structure for α - SrHfS_3 ; Figure S4. Electronic band structure for β - SrHfS_3 ; Table S1. Atomic displacement parameters ($\text{\AA}^2$) for α - SrHfS_3 ; Table S2. Geometric parameters ($\text{\AA}$, $^\circ$) for α - SrHfS_3 ; Table S3. Calculated bond valence sums for the ions in α - SrHfS_3 .

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Data Availability Statement: The crystallographic information file (cif) of the α -SrHfS₃ crystal structure is deposited to Cambridge Crystallographic Data Centre (CCDC) with the CCDC number of 2533120, and it can be accessed from <https://www.ccdc.cam.ac.uk/> (accessed on 30 March 2026). Further details of crystal structure, geometric parameters, and electronic structure calculations are provided in the Supporting Information.

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