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Insights on the Synthesis, Crystal and Electronic Structures, and Optical and Thermoelectric Properties of Sr_{1-x}Sb_xHfSe₃ **Orthorhombic Perovskite**

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ABSTRACT: Single-phase polycrystalline powders of $Sr_{1-x}Sb_xHfSe_3$ (x = 0, 0.005, 0.01), a new member of the chalcogenide perovskites, were synthesized using a combination of high temperature solid-state reaction and mechanical alloying approaches. Structural analysis using single-crystal as well as powder X-ray diffraction revealed that the synthesized materials are isostructural with SrZrSe₃₁ crystallizing in the orthorhombic space group Pnma (#62) with lattice parameters a = 8.901(2) Å; b = 3.943(1) Å; c = 14.480(3) Å; and Z = 4 for the x = 0 composition. Thermal conductivity data of SrHfSe₃ revealed low values ranging from 0.9 to 1.3 W m^{-1} K⁻¹ from



300 to 700 K, which is further lowered to 0.77 W m⁻¹ K⁻¹ by doping with 1 mol % Sb for Sr. Electronic property measurements indicate that the compound is quite insulating with an electrical conductivity of 2.9 S/cm at 873 K, which was improved to 6.7 S/ cm by 0.5 mol % Sb doping. Thermopower data revealed that SrHfSe₃ is a p-type semiconductor with thermopower values reaching a maximum of 287 μ V/K at 873 K for the 1.0 mol % Sb sample. The optical band gap of Sr_{1-x}Sb_xHfSe₃ samples, as determined by density functional theory calculations and the diffuse reflectance method, is ~ 1.00 eV and increases with Sb concentration to 1.15 eV. Careful analysis of the partial densities of states (PDOS) indicates that the band gap in SrHfSe₃ is essentially determined by the Se-4p and Hf-5d orbitals with little to no contribution from Sr atoms. Typically, band edges of pand d-character are a good indication of potentially strong absorption coefficient due to the high density of states of the localized p and d orbitals. This points to potential application of SrHfSe₃ as absorbing layer in photovoltaic devices.

INTRODUCTION

Ternary transition metal chalcogenides have garnered a great deal of attention within the materials research community as they have the potential to offer advanced and unique thermal,¹⁻⁵ electronic,⁶⁻¹¹ and magnetic properties,¹²⁻²⁶ as well as interesting optical responses.^{27–33} Their wide range of crystal structure types and chemical composition allows for creative systematic structural engineering that has produced some of the most well-known photovoltaic and thermoelectric materials, such as $CuInSe_2^{34-36}$ and $CuAgSe^{37-41}$. The flexibility and ease with which these materials have been synthesized spurs the need to investigate new chalcogenidebased crystal structures, potentially offering novel properties and transport mechanisms and adding to the general understanding of how to engineer these materials to power our future.

Ternary transition metal chalcogenides with perovskite structure have been notably absent from recent literature concerning this important material family. The perovskite structure, named for Russian mineralogist Lev Perovski, is

based on the prototype crystal of CaTiO₃, formula $XIIA^{2+VI}B^{4+}X^{2-}_{3}$, forming in the orthorhombic *Pnma* symmetry. In the idealized cubic system, the A cation is stationed at Wyckoff position 4a (0, 0, 0), while B cations populate the body-center 4a site (1/2, 1/2, 1/2). Many variations of this structure have been investigated, most commonly the distorted orthorhombic, tetragonal, and hexagonal perovskite versions.⁴²⁻⁴⁶ These relatively dense structures offer various interesting physical properties such as superconductivity,^{47,48} colossal magnetoresistance,^{49,50} ultralow thermal conductivity,⁵¹ large dielectric constant,^{52,53} and high optical absorption coefficients.⁵⁴⁻⁵⁷ These unique properties have led to the application of inorganic perovskite materials in photovoltaic solar cells, thermoelectric devices,^{58,59} and even inorganic– organic memory devices,^{60,61} often taking advantage of the specific electronic transport properties the high symmetry structure exhibits, as well as high temperature stability.

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Typically, the perovskite structures require significantly high temperatures and pressures for stable formation. Consequently, this has led to a focus on the production of oxides, which has deterred the creation and elucidation of chalcogenide-based perovskites. To date, of the chalcogenide-based perovskites, only sulfide-based compounds have been studied, specifically $EuZrS_3^{62}$ $EuHfS_3^{62}$ $CaZrS_3^{63}$ $BaZrS_3^{64,65}$ and $BaHfS_3^{63}$ but the electronic and thermal properties of these compounds have not been extensively studied. Recently, Sun et al. published the promising results of a theoretical study on a series of ABX₂ compounds with A = Ca, Sr, and Ba, B = Ti, Zr, and Hf, and X = S and Se, predicting the photovoltaic behavior of the distorted perovskite, needlelike, and hexagonal phases.⁶⁶ Results of this research predicted that the distorted perovskite phase of $ABSe_3$, where A = Ca, Sr, and Ba and B = Hf and Zr, exhibits band gaps between 1.3 and 1.7 eV, suggesting excellent potential for high efficiency photovoltaic devices. Furthermore, needle-like (orthorhombic) phases were predicted to possess band gaps of 0.75-1.0 eV, which can be quite useful for thermoelectric applications. More recently, Meng et al. calculated the electrical and optical properties of BaZrS₃ from density functional theory (DFT) calculations and were able to determine that $BaZr_{0.9}Ti_{0.1}S_3$ could exhibit a band gap of 1.46 eV, ideal for single- or multijunction solar cells, and potentially obtain >20% photovoltaic conversion efficiency.⁶⁷ Though the synthesis was challenging, they were also able to create BaZrS₃ with distorted-perovskite structure and confirm that the band gap of 1.85 eV matches that of the calculations.

To date, the only previously known structures of the series of perovskite materials of the type $ABSe_3$ where A = Ca, Sr, and Ba and B = Zr and Hf are SrZrSe₃, which was successfully synthesized as phase pure by Tranchitella et al. in 1997,⁶⁸ and BaZrSe₃, synthesized in 1964 by Aslanov.^{69,70} However, it was found that both compounds do not adopt the anticipated distorted perovskite structure. SrZrSe₃ crystallizes in a new orthorhombic needlelike structure,⁶⁸ whereas BaZrSe₃ forms in the hexagonal CsNiCl₃ structure (space group P63/mmc #194).^{69,70} Tranchitella's approach to the creation of selenide-based perovskites with the GdFeO₃ structure type is notable in that relatively low-pressure synthesis techniques were employed (<1 GPa). This work follows a similar approach while incorporating mechanical alloying (high energy ballmilling) to produce a novel series of ABSe₃ materials, maintaining an approach that requires less instrumental sophistication than typical perovskite synthesis at high temperature (>1273 K) and pressure (>1 GPa). Hence, we report in this study the synthesis and crystal structure of SrHfSe₃, which adopts the needle-like (orthorhombic) SrZrSe₃type structure, and their thermoelectric and optical properties. Substitutional doping of Sr by Sb in SrHfSe₃ is also investigated in order to probe the effects on the electronic and thermal transport properties as well as the optical band gap.

EXPERIMENTAL DETAILS

Synthesis and Processing. *Synthesis.* Stoichiometric amounts of Sr granules (Alfa-Aesar, 99%, 19 mm long granules), Hf powder (American Elements, 99.5%), Sb powder (Alfa Aesar, 99%), and Se powder (Sigma-Aldrich, 99.5%) were weighed in a glovebox under Ar atmosphere and added to hardened steel jars with hardened steel ball bearings and sealed. 2.5 g of total reactants were added to each jar with 25 g of ball bearings. The jars were mounted on a SPEX 8000D mill and processed for 30 min in order to ensure complete mixing of the reactants. The jars were then transferred to the glovebox, and the contents were transferred to a graphite crucible with a lid (diameter 7

mm × 55 mm), which was placed inside a silica tube. The 8-in. tube was flame-sealed under residual pressure of 10^{-4} Torr. The tube was then heated to 1073 K in 24 h, held for 120 h, and then cooled to room temperature in 24 h. This process was successful in creating >98% phase pure SrHfSe₃ and Sb-doped SrHfSe₃ samples, based on X-ray diffraction (XRD) data. However, attempts to synthesize Ba and Ca compounds were not successful. Further processing of Ba and Ca compounds by cold-pressing the products of the first reaction at ~300 MPa into 13 mm diameter discs and reheating the pellets at 1073 and 1173 K for an additional 120 h did not complete the reaction. Binary compounds such as CaSe and BaSe constituted a majority of the products.

Single Crystal Growth. Single crystals of SrHfSe₃ suitable for X-ray structural analysis were successfully grown by annealing approximately 0.25 g of the presynthesized SrHfSe₃ polycrystalline powder. The powder was flame-sealed into a 7 mm diameter \times 12-in.-long silica tube under residual pressure of 10⁻⁴ Torr. The tube was heated to 1373 K in 24 h and held for 240 h and then cooled to room temperature in 24 h. Lustrous black crystals were harvested from the products. Attempts to produce single crystals of BaHfSe₃ and other compounds failed but did consistently create crystals, which were too small for characterization by single crystal X-ray diffraction methods.

Densification. Polycrystalline single-phase powder of SrHfSe3 and Sb-doped SrHfSe3 samples were consolidated into pellets using the hot-press method. Approximately 1 g of powder sample was added to a 10 mm diameter graphite die and pressed between graphite anvils. Densification of pellets was conducted under flowing Ar gas at 40 mL/ min, a pressing temperature of 1123 K for 2 h, and an applied pressure of 100 MPa with a ramp up and down rate of 225 K/h. The pellets were then removed from the graphite dies and polished to mirror finishes with SiC polishing paper, up to 1200 grit. The densities of the pellets were determined by both the geometric method (measured mass/measured volume) and the "true" density measurement using a He gas Quantachrome Micro Ultrapyc 1200e pycnometer, and they were compared to the theoretical density of SrHfSe₃, 6.58 g/cm³, obtained from the crystal structure refinement. All Sr1-,Sb,HfSe3 pellets yielded both a geometric and true density that were greater than 97% of the theoretical density. The pellets were then dissected into prismatic bars roughly 3 mm × 2 mm × 8 mm using a wire saw and a cutting solution consisting of a mixture of water, glycerin, and silicon carbide 300 mesh powder. The prismatic bars were again polished with metallographic paper to 1200 grit in order to perform electronic transport measurements. The excellent match of the peak intensities on the XRD patterns of the samples prior to and after densification indicates little to no preferred orientation, suggesting isotropic response of the transport properties of the material.

Characterization. Single Crystal X-ray Diffraction. A needleshape single crystal of SrHfSe₃ was harvested from an annealed sample and examined by X-ray diffraction. Intensity data was recorded at 300 K on a STOE IPDS-2T diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 50 kV and 40 mA. The diffraction data were indexed in the orthorhombic crystal system with lattice parameters a = 8.901(2) Å; b = 3.943(1) Å; c = 14.480(3) Å; and Z =4. The structure solution was obtained by direct methods in the space group Pnma (#62) and refined by full-matrix least-squares techniques using the SHELTXL package.⁷¹ The asymmetric unit cell contains two crystallographically independent metal positions: the M1 (4c) site, which is located in an octahedral environment of six Se atoms, and the M2 (4c) site, which is surrounded by nine Se atoms in a tricapped trigonal prismatic geometry; and three Se-atom positions (Se1-Se3), which are all located at Wyckoff site 4c. In the initial refinement model, the smaller Hf atom was located at the M1 site, whereas the Sr atom was located at the M2 site. The refinement of this model yielded $R_1 =$ 7% with reasonable atomic displacement parameters for all atoms except the Sr atom, which showed thermal displacement parameters twice that of Hf and all Se atoms. Nevertheless, bond valence sum (BVS)⁷² calculation results also fully supported the above-mentioned occupation of each metal site (Table 1). The final refinement of this model, while including a secondary extinction correction and anisotropic displacement parameter for all atoms, resulted in the

Table 1. Bond Valence Sum (BVS) Calculations for SrHfSe₃ at 300 K

Atom position	BVS	Oxidation state
Sr1	2.11	2+
Hf1	4.03	4+
Se1	2.16	2-
Se2	2.27	2-
Se3	2.14	2-

final value, $R_1 \sim 3\%$. The final charge balanced composition of the crystal obtained from the refinement was $(Sr^{2+})(Hf^{4+})(Se^{2-})_3$. A summary of the crystallographic data is given in Table 2. The atomic

Table 2. Selected Crystallographic Data for SrHfSe₃ at 300 K

Crystal system	Orthorhombic
Space group	Pnma (#62)
Formula weight (g/mol)	502.99
Calculated density (g/cm ³)	6.576
Lattice parameters (Å)	
<i>a</i> =	8.901(2)
<i>b</i> =	3.943(1)
<i>c</i> =	14.480(3)
$V(Å^3); Z$	508.07(2); 4
Radiation (Å)	λ (Mo K α) = 0.71073
$\mu (\mathrm{cm}^{-1})$	522
2θ range	$7^{\circ} \leq 2\theta \leq 67^{\circ}$
index range	$-13 \le h \le 13$
	$-5 \le k \le 5$
	$-21 \leq l \leq 21$
Transmission factors	0.029-0.198
Diff. elec. density [eÅ ⁻³]	+3.32 to -2.77
$R_1 (F_o > 4\sigma(F_o))^a$	0.029
wR_2 (all) ^b	0.065
GOF	1.148
${}^{a}R_{1} = \sum F_{o} - F_{c} / \sum F_{o} . {}^{b}wR_{1}$	$_{2} = \left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}\right]^{1/2}$

coordinates and isotropic displacement parameters of all atoms are listed in Table 3. Selected interatomic distances are gathered in Table

Table 3. Wyckoff Positions (WP), Atomic Coordinates, and Equivalent Isotropic Displacement Parameters $(U_{eq}/10^{-4} \text{ Å}^2)$ for All Atoms in the Asymmetric Unit Cell of SrHfSe₃ at 300 K

Atom	WP	x	у	z	$U_{\rm eq}^{\ a}$
Hf1	4c	0.8308(6)	1/4	0.4431(3)	80(2)
Sr1	4c	0.5628(2)	3/4	0.6779(8)	112(3)
Se1	4c	0.6611(2)	1/4	0.5120(8)	73(2)
Se2	4c	0.9792(2)	1/4	0.6073(6)	59(2)
Se3	4c	0.7093(2)	1/4	0.2829(7)	78(3)
$^{a}U_{eq}$ is	defined	as one-third of	the trace	of the orthogo	onalized U _i

tensor

4. The software Diamond⁷³ was utilized to create the graphic representation of the crystal structure with ellipsoid representations (98% probability level) for all atoms. Detailed crystallographic data can be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax +49-7247-808-666; e-mail crysdata@fiz.karlsruhe.de), on quoting the depository number CSD-434309.

Powder X-ray Diffraction and Rietveld Refinement. Phase analysis and the crystal structure identification of various $Sr_{1-x}Sb_xHfSe_3$ compositions in both powder and pellet form were performed by

Table 4. Selected Interatomic Distances (Å) in SrHfSe₃ at 300 K^{*a*}

Bond type	Distance [Å]	Bond type	Distance [Å]				
Hf1—Se3	2.559(2)	Sr1—Se(3 ^v ,3 ^{vi})	3.174(2)				
$Hf1$ — $Se(1,1^i)$	2.676(9)	Sr1—Se2 ^{vii}	3.198(2)				
$Hf1$ — $Se(2^{ii},2^{iii})$	2.698(8)	Sr1—Se3 ^{viii} ,3 ^{ix})	3.212(2)				
Hf1—Se2	2.720(9)	Sr1—Se(1,1 ^{iv})	3.229(2)				
		Sr1—Se1 ^v	3.395(2)				
		Sr1—Se2 ^{iv}	3.844(2)				
^{<i>a</i>} Operators for generating equivalent atoms: (i) x , 1 + y , z ; (ii) 1 – x , 1							
-y, $1 - z$; (iii) $1 - x$, $-y$, $1 - z$; (iv) x , $y - 1$, z ; (v) $1 - x$, $-1 - y$, 1							
-z; (vi) $1 - x$, $-y$, $1 - z$; (vii) $-1/2 + x$, $-1 + y$, $3/2 - z$; (viii) $3/2$							
-x, -y, 1/2 + z; (ix) $3/2 - x, -1 - y, 1/2 + z;$ (x) $1/2 + x, 1 + y, 3/2$							

powder X-ray diffraction (XRD) techniques. XRD data were collected using a graphite monochromated Cu K α (λ = 1.54056 Å) on a Rigaku Miniflex 600 operating at 40 kV and 15 mA and a Rigaku Ultima with rotating arm anode operating at 40 kV and 100 mA. Rietveld refinement pattern fitting was performed on the diffraction patterns of the pellet samples of SrHfSe₃ using the FullProf software package in order to determine the lattice constants and unit cell volume using the single crystal structure data of SrHfSe₃ as a starting model.⁷⁴

-z; (xi) 3/2 - x, 1 - y, 1/2 + z; (xii) 3/2 - x, -y, -1/2 + z; (xiii) 3/2 - x, -1 - y, -1/2 + z; (xiv) 3/2 - x, 1 - y, -1/2 + z.

Wavelength Dispersive X-ray Fluorescence (WDXRF). Powder samples of SrHfSe₃ and Sb-doped SrHfSe₃ were loaded into plastic boats with Prolene film bottoms. Samples were then characterized with a Rigaku Supermini 200 emitting radiation from a Pd source at 50 kV and 4 mA to determine the concentration of each constituent element and the overall chemical composition.

Differential Scanning Calorimetry (DSC). DSC was performed using a Netzsch DSC404 F1, by placing approximately 25 mg of pellet material in a platinum crucible with lid. An empty platinum crucible was used as a reference. The measurement was performed under flowing nitrogen gas, 20 mL/min, from room temperature to 1300 K in order to determine phase purity and to identify thermal events associated with phase changes, such as melting and crystallization of the compound.

X-ray Photoelectron Spectroscopy (XPS). XPS was used to assess the oxidation state of various metal atoms in the samples. Powder samples of each composition were hand pressed into 3 mm diameter pellets under ambient conditions using a Pike Technologies press. XPS spectra were collected for each pellet using a Kratos Axis Ultra XPS equipped with a monochromatic Al source (15 kV, 10 mA). Specimens were loaded into the transfer chamber and allowed to evacuate for a 12 h period reaching less than 5×10^{-7} Torr. The analysis chamber was kept at approximately 10^{-9} Torr during measurement. Wide scans were acquired using an analyzer pass energy of 160 at 1 eV steps. Selected regions were scanned using a pass energy of 20 at 0.02 eV steps. Postprocessing analysis was performed using Casa XPS.

Thermal Transport Measurement. Thermal diffusivity and heat capacity (C_p) data for each pelletized sample was measured using the laser flash method on a Linseis LFA 1000 in order to calculate the thermal conductivity. Pellets were cleaned with acetone and lightly coated with graphite spray; then thermal diffusivity was measured from 300 to 723 K under flowing N₂ gas (>30 mL/min). The data collected was compared with a reference Pyroceram 9606 sample, and the accuracy of the data was determined to be within 2%, with machine precision of ±3%.

Electronic Transport Measurements. Prismatic bars of each composition were cut from the pellets, polished to a mirror finish, and mounted into a ULVAC-RIKO ZEM-3. The thermopower and electrical resistivity of each sample were measured simultaneously from room temperature to 723 K under a low pressure of He. The instrument precision on the electrical resistivity and Seebeck coefficient data is $\pm 4\%$.

Hall-Effect Measurements. Prismatic bars of each composition with approximate size $3 \times 3 \times 8$ mm were polished to a mirror finish, and

room temperature Hall coefficients, R_{H} , were measured using the AC 4-probe setup in a Quantum Design Physical Properties Measurement System (PPMS) under a magnetic field of ± 1 T and using an excitation current of 0.1 mA. The carrier concentration was then calculated as $n_H = (R_H^* e)^{-1}$, where e is the electronic charge.

Optical Band Gap Measurements. A Varian Cary 5000 spectrometer, equipped with a Harrick Praying Mantis diffuse reflectance accessory, was used to collect the optical diffuse reflectance spectra of the compounds over the ultraviolet, visible, and near-infrared spectral regions (UV/vis/NIR). Each sample was ground and placed in a sample holder to a depth of 3 mm. Barium sulfate (Fisher, 99.92%) was used as a 100% reflectance standard. The measurement was conducted at a scan rate of 600 nm/min. The optical band gaps of the samples were estimated from the UV/vis/NIR spectra by extrapolation of the absorption edge to the baseline. The absorption spectra were calculated from the reflectance spectra via the Kubelka–Munk equation.⁷⁵ The direct allowed transmission model was used to fit each set of data in order to produce Tauc plots to estimate the optical band gap.

First-Principles Calculations. DFT calculations were performed using the Vienna *Ab Initio* Simulation Package (VASP),^{76–79} with projector augmented wave pseudopotentials,^{80,81} including 10, 10, and 6 valence electrons for Sr, Hf, and Se, respectively. The band structure without spin–orbit coupling effects was calculated utilizing the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06)^{82,83} in conjunction with interpolation based on maximally localized Wannier functions as implemented in the wannier90 code.⁸⁴ The functional of Perdew–Burke–Ernzerhof (PBE)⁸⁵ was used to evaluate the magnitude of spin–orbit coupling. The plane wave basis set cutoff was set at 400 eV. Gamma-centered grids of $4 \times 8 \times 3$ were used to sample the first Brillouin zone for all calculations.

RESULTS AND DISCUSSION

Synthesis and Crystal Structure. Single-phase fine black powders of Sr_{1-x}Sb_xHfSe₃ phases were synthesized by mechanical alloying of a stoichiometric mixture of high purity elements followed by solid state reaction at moderate temperatures. A comparison of the X-ray diffraction patterns of the synthesized compounds with that of GdFeO₃ reveals sharp differences, meaning that the compounds do not adopt a distorted Perovskite structure. However, striking similarity was observed when comparing the XRD data of the $\mathrm{Sr}_{1-x}\mathrm{Sb}_x\mathrm{HfSe}_3$ phases to that of SrZrSe₃, suggesting that they crystallize in the orthorhombic structure with space group Pnma (#12) (Figure 1A). The observed deviation from the perovskite structure type could be anticipated from the rather low Goldschmidt tolerance factor of t = 0.82, calculated using the formula $t = (r_A + r_0)/\sqrt{2}(r_B + r_0)$, where r_A is the ionic radius of the A-cation (Sr), r_B is the ionic radius of the B-cation (Hf), and r_0 is the ionic radius of the anion (Se).⁸⁶ Composition analysis of the synthesized powder of SrHfSe3 using the wavelength dispersive X-ray florescence (WDXRF) technique showed a slightly Sr-rich composition, Sr_{1.16}Hf_{0.90}Se₃. This structure remained consistent through hot-pressing, signaling that the synthesized compound is single phase and is thermally stable. A similar synthesis approach was also used to synthesize high purity Sb-doped samples of SrHfSe₃. Attempts to synthesize $Sr_{1-x}Sb_xHfSe_3$ phases exclusively by mechanical alloying were not successful in creating pure needle-like or distorted perovskite structure after 100 h of high-energy ballmilling. XRD patterns of the resulting products revealed a mixture of binary impurity compounds, such as HfSe₃, Hf_{1.35}Se₂, and HfSe₂. For example, the small peak at 15 deg on the XRD patterns of Sb-doped samples (Figure 1A) can be associated with the binary phase, HfSe₂ (P-3m space group P-



Figure 1. (a) X-ray diffraction patterns of polycrystalline samples of $Sr_{1-x}Sb_xHfSe_3$ phases synthesized using solid-state reactions of the elements compared to the theoretical pattern calculated using single crystal structure data. (b) Differential scanning calorimetry (DSC) curves for SrHfSe_3 showing a single endothermic peak of melting at 1273 K and a single peak of crystallization at similar temperature. The small peak indicated with (*) on the XRD patterns of Sb- doped samples can be associated with HfSe_2 binary impurity phase.

3m; #164). The phase purity and thermal stability of the synthesized $Sr_{1-x}Sb_xHfSe_3$ phases were confirmed by differential scanning calorimetry (DSC) measurements (Figure 1B), which showed a single peak of melting and a single crystallization peak at 1273 K. This indicates that the compound melts congruently and crystallizes without disorder or decomposition. No additional peaks, which would suggest the presence of minor impurity phases, could be detected from the DSC curves.

To confirm the crystal structure of SrHfSe₃, suitable single crystals were successfully grown by annealing polycrystalline powder samples at 1373 K for 10 days, as described in the experimental procedure. Long black needle-like crystals were harvested from the resulting annealed ingots, and analyzed using single crystal X-ray diffraction techniques. Intensity data were indexed in the orthorhombic space group Pnma (#62), with a = 8.9001(18) Å, b = 3.9424(8) Å, and c = 14.480(3) Ű (Table 2). The result suggests that SrHfSe₃ is isostructural with $SrZrSe_3$ (prototype structure NH_4CdCl_3) first developed by Tranchitella et al.⁶⁸ Polyhedral representations of the crystal structures of SrHfSe3 projected along the *b*-axis are shown in Figure 2, along with the connectivity between similar polyhedra. The structure can be divided into two substructures based on the packing arrangement of [HfSe6] or [SrSe9] polyhedra. All metal atoms reside at Wyckoff position 4c, with Hf atoms located in a distorted octahedral geometry [1 + 2 + 2+ 1] and Sr atoms located in a distorted tricapped trigonal prismatic geometry [2 + 1 + 2 + 2 + 1 + 1]. The Hf–Se bond distances range from 2.560(2) Å to 2.720(8) Å, whereas the Sr-Se bond distances range from 3.173(2) Å to 3.395(2) Å with a longer bond of 3.844(2) Å (Table 4). The observed bond distances in SrHfSe3 are comparable to the reported bonding in SrZrSe₃, which is to be expected due to the similarity in the oxidation state (+4) and ionic radius of Zr (230



Figure 2. Projection of the crystal structure of SrHfSe₃ along the *b*-axis highlighting: (a) the octahedral coordination around Hf atoms and (b) the tricapped trigonal prismatic coordination around Sr atoms; (c) double chains of edge-sharing HfSe₆ octahedra running parallel to the *b*-axis; and (d) adjacent SrSe₉ tricapped trigonal prisms sharing edges in all directions to form a 3D network separating adjacent double chains of edge-sharing HfSe₆ octahedra.

pm) and Hf (225 pm). The cell volume of SrHfSe₃, 508.1(2) Å³, is also within 1% of the cell volume of SrZrSe₃, 513.0(4) Å³. Adjacent [HfSe₆] octahedra within the crystal structure of SrHfSe₃ share edges to form isolated double-chains running parallel to the *b*-axis (Figure 2C). The double-chains separated by [SrSe₉] polyhedra are arranged in layers with alternating orientations along the *c*-axis to build the three-dimensional structure (Figure 2A).

Alternatively, the crystal structure of $SrHfSe_3$ can be described as consisting of tricapped trigonal prismatic [$SrSe_9$] polyhedra that share edges (Figure 2D) in all directions to form a three-dimensional framework with channels that are filled by double chains of edge sharing [$HfSe_6$] octahedra.

The accuracy of the structure solution and completeness of the structure refinement were validated by bond valence sum calculations,⁷² X-ray photoelectron spectroscopy (XPS), and comparing the theoretical X-ray powder diffraction pattern created from the single crystal structure solution to experimental XRD patterns from the synthesized Sr_{1-r}Sb_rHfSe₃ phases (Figure 1). Bond valence sum calculations (Table 1) suggest ordering of Hf and Sr atoms within 4c sites with oxidation 4+ and 2+, respectively. To further confirm the assigned oxidation states and chemical environment of Hf and Sr atoms in SrHfSe₃, XPS was performed on selected samples. The spectrum of Sr 3d shell electrons for the pristine SrHfSe₃ sample is shown in Figure 3A along with fitting curves. Two sets of the Sr_3d_{5/2}/ Sr_3d_{3/2} doublet peaks with binding energies 132.2 eV/134 and 136.2 eV/138 eV can be observed, indicating the presence in the polycrystalline sample of Sr atoms with two distinct chemical environments. However, the difference in the binding energies for each set of Sr $3d_{5/2}$ / Sr $3d_{3/2}$ peaks is 1.8 eV, which is consistent with the value reported for Sr²⁺ in SrS (Sr_3d_{5/2}: 132.7 eV).⁸⁷ Since only one crystallographically independent Sr site is observed in the structure of SrHfSe₃, the second doublet may be associated with the presence of a small fraction of Sr-containing impurity phase within the sample. This analysis is consistent with the presence of two sets of the Se_ $3d_{5/2}$ / Se_ $3d_{3/2}$ doublet peaks with binding energies 52 eV/52.9 and 53.7 eV/54.6 eV in the spectrum of Se_3d shell electrons (Figure 3C). The spectrum of Hf 4f shell electrons shows a single Hf $4f_{7/2}$ / Hf $4f_{5/2}$



Figure 3. (a) XPS spectrum and curve-fitting analysis of Sr²⁺ in SrHfSe₃. Two sets of doublet peaks indicate possible Sr-based impurity in small amounts. (b) XPS spectrum and curve-fitting analysis of Hf⁴⁺ in SrHfSe₃. (c) XPS spectrum and curve-fitting analysis of Se²⁻ in SrHfSe₃.

doublet (Figure 3B) with binding energies 15.3 eV/16.9 eV, similar to the values (16.1 eV/17.8 eV) reported for Hf⁴⁺ in HfS₂.^{88,89} No indication of any Hf-based impurity phase could be detected. One can conclude based on XPS data that the oxidation states of Sr, Hf, and Se atoms in SrHfSe₃ are 2+, 4+, and 2–, respectively.

Optical Properties. The optical band gap of each material was determined by collecting the diffuse reflectance of each sample over the near-IR and UV–visible light spectra. Tauc plots of the response of $Sr_{1-x}Sb_xHfSe_3$ samples are shown in Figure 4. The direct transmission model is applied to all samples as direct band gaps were estimated from the density functional theory analysis performed by Sun et al. associated with SrHfSe₃ and BaHfSe₃.⁹⁰ For $Sr_{1-x}Sb_xHfSe_3$ samples, the band gap is estimated at 1.02 eV for the undoped sample, and increasing to 1.06 and 1.15 eV for the 0.5 and 1.0 mol %



Figure 4. Optical band gaps of $Sr_{1-x}Sb_xHfSe_3$ showing increasing band gap with increasing Sb content.

samples, respectively. The observed increase in band gap offers evidence that Sb doping significantly changes the electronic structure of the system in addition to raising the Fermi level. This is an intriguing result as it identifies a possible avenue for engineering the band gap of the material for photovoltaic applications. The ideal direct band gap for photovoltaic applications is expected to be between 1.1 and 1.6 eV, corresponding to efficiencies eclipsing 28%. Thus, Sb-doped needle-like SrHfSe₃ appears to provide a promising opportunity for further development in photovoltaics.⁹¹

Electronic Structure. DFT calculations using the HSE06 functional were performed to investigate the band structure (Figure 5) and the partial density of states (PDOS) (Figure 6)



Figure 5. Band structure of $SrHfSe_3$ calculated using the HSE06 functional. Energies are referenced to the valence band maximum. The compound is a direct gap material with a calculated gap of 0.88 eV.



Figure 6. Calculated partial density of states (PDOS) of SrHfSe₃. The valence band has primarily Se-p character, and the conduction band primarily Hf-d character.

of SrHfSe₃. The band structure calculated along high-symmetry directions of the first Brillouin zone shows that both the conduction band (CB) minimum and the valence band (VB) maximum are located at the Γ point, indicating that SrHfSe₃ is a direct gap semiconductor with a band gap of 0.88 eV (Figure 5). This result does not include the effects of spin orbit coupling. Calculations with the PBE functional showed that spin—orbit coupling effects on the gap are minor, narrowing the gap by approximately 50 meV. Interestingly, the band gap obtained from our calculation is similar to the value previously

anticipated for the hypothetical needle-like structure of $SrHfSe_{3}$,⁹⁰ and is close to the experimental value of 1.02 eV obtained from diffuse reflectance measurements (Figure 4). Both experimental and theoretical values of the band gap are consistent with the black color of the SrHfSe₃ polycrystalline powder sample.

Careful analysis of the partial densities of states (PDOS) indicates that the highest occupied valence band (or HOMO) primarily consists of Se-4p orbitals, whereas the lowest unoccupied conduction band (or LUMO) is mainly composed of Hf-5d orbitals (Figure 6). This implies that the optical absorption of SrHfSe₃ can be mainly ascribed to the promotion of carriers from the Se-4p to the Hf-5d orbitals. The valence bands between -5 and 0 eV (referenced to the HOMO) mostly consist of Se-4p orbitals, whereas the conduction bands from 0.88 to 5 eV are dominated by Hf-5d states. Therefore, the band gap in SrHfSe₃ is essentially determined by the Se-4p and Hf-5d orbitals with little to no contribution from Sr atoms. Typically, band edges of p- and d-characters are a good indication of a potentially strong absorption coefficient due to the high density of states of the localized p and d orbitals. This points to a potential application of SrHfSe₃ as an absorbing layer in photovoltaic devices. However, significant d-character of the conduction band could result in large carrier effective masses and low carrier concentration, which can lead to low intrinsic carrier mobility and low overall electrical conductivity.

Thermoelectric Properties. To probe the thermoelectric behavior of SrHfSe₃, high-density pellets of pristine and Sb-doped SrHfSe₃ samples were fabricated and their thermal conductivity, electrical conductivity, and thermopower in the midtemperature range, 300-700 K, were measured. Thermal conductivity results indicate that SrHfSe₃ exhibits relatively low values ranging from 1.3 W/mK at 300 K to 0.9 W/mK at 700 K, which is suitable for thermoelectric applications (Figure 7C). The substitution of 0.5 mol % and 1 mol % Sb for Sr reduces the thermal conductivity further to 0.77 W/mK at 700 K. At temperatures below 673 K, 1 mol % Sb yields the lowest thermal conductivity, which can be expected due to mass



Figure 7. Thermoelectric properties of $Sr_{1-x}Sb_xHfSe_3$ samples. (a) electrical conductivity; (b) thermopower; (c) thermal conductivity; and (d) figure of merit, ZT.

fluctuation phonon scattering since the atomic mass of Sb is nearly 1.5 times greater than that of Sr. Above 673 K, there appears to be little difference in the thermal conductivity of 0.5 and 1 mol % Sb samples.

Electronic transport data showed that the synthesized pristine SrHfSe₃ sample is a poor metal with very low values of the electrical conductivity (~0.5 S/cm) and thermopower $(\sim 7 \ \mu V/K)$ at 300 K (Figures 7A and 7B). Hall effect measurements indicate that SrHfSe₃ is a high p-type semiconductor with carrier concentration of 1.05×10^{19} cm⁻³ at 300 K. Upon increasing the temperature, both the electrical conductivity and thermopower surprisingly rapidly increase simultaneously, reaching maximum values (2.5 S/cm and ~260 μ V/K) at 700 K and remain constant with further increase in temperature to 800 K. The trend suggests the presence of impurity donor states within the band gap of the synthesized ptype SrHfSe₃ sample. Such states upon thermal excitation of extrinsic carriers to the conduction band (CB) become donor states leading to bipolar conduction where thermally activated extrinsic carriers from impurity states gradually compensate intrinsic holes. Partial substitution of Sr atoms in SrHfSe3 by electron richer Sb atoms results in a large suppression of hole concentration around 300 K, leading to a large increase in the thermopower value at 300 K from $\sim 7 \mu V/K$ for the pristine sample to 135 μ V/K for the sample containing 0.5 mol % Sb. Upon increasing the temperature, the thermopower and electrical conductivity of the Sb-doped samples rapidly increase, reaching maximum values of 6.7 S/cm and 284 μ V/K at 873 K for the sample containing 0.5 mol % Sb. Another alternative explanation for this simultaneous increase in both electrical conductivity and thermopower of SrHfSe3 upon Sb-doping is that the added electrons resulting from the n-type doping move the Fermi level toward the conduction band, resulting in bipolar conduction where extrinsic electrons counter intrinsic holes, increasing both the carriers effective mass and mobility. While the overall thermoelectric performance of this material is not impressive, Sb-doping did substantially improve both the maximum power factor, 0.522 μ W/cm K² for 0.5 mol % doped at 798 K compared to 0.182 μ W/cm K² at 698 K for SrHfSe₃, and the figure of merit, 0.046 for 0.5 mol % doped at 698 K compared to 0.014 at 698 K for SrHfSe₃.

CONCLUSION

In summary, we have synthesized the ternary chalcogenide perovskite SrHfSe3 through solid-state reaction of the elements and investigated its crystal structure as well as the optical and thermoelectric properties. We found that the compound crystallizes with the SrZrSe₃ structure type rather than the distorted orthorhombic perovskite structure reported for SrHfS₃. Optical spectroscopy data indicate that SrHfSe₃ is a semiconductor with band gap of ~ 1 eV. The band gap for SrHfSe₃ is in good agreement with our theoretical study as well as the predicted value from DFT calculations.⁶⁶ Interestingly, partial substitution of Sb at Sr sites led to a significant increase in the optical band gap to 1.06 and 1.15 eV for the samples containing 0.5 mol % and 1.0 mol % Sb, respectively. Further doping could provide the ability to tune the band gap of the orthorhombic structure of SrHfSe₃ within the energy range 1.1 to 1.4 eV, suitable for practical solar energy conversion materials. Electronic transport data suggest that the pristine p-type SrHfSe3 sample is a poor metal with a large concentration of extrinsic carriers at 300 K. Interestingly, both the thermopower and electrical conductivity increase

rapidly with rising temperature, which is attributed to bipolar conduction arising from thermal excitation of extrinsic electrons to the conduction band.

ASSOCIATED CONTENT

Accession Codes

CCDC 1837976 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

NAM synthesized the samples and carried out structural characterization, performed high temperature electronic and thermal conductivity measurements, performed data analysis, and cowrote the manuscript. CB helped in the synthesis and carried out structural characterization. LW and EK performed theoretical studies and cowrote the manuscript. AO, JC, AP, TB, and CU performed high temperature electronic and thermal conductivity measurements, performed data analysis, and coedited the manuscript. AW, SS, and JA performed optical properties measurements and coedited the manuscript. P.F.P.P. conceived the experiment, performed data analysis, and cowrote the manuscript.

Notes

The authors declare no competing financial interest.

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