Structural and Electrical Properties of a New $([\text{SnSe}]_{1.16})_1(\text{NbSe}_2)_1$ Polytype

Matti B. Alemayehu[†], Matthias Falmbigl[†], Corinna Grosse[‡], Kim Ta[†], Saskia F. Fischer[‡], and David C. Johnson[†]

[†]Department of Chemistry, University of Oregon, 1253 University of Oregon, Eugene, Oregon 97403, United States

[‡]Institut für Physik, Humboldt-Universität zu Berlin, Newtonstrasse 15, 12489 Berlin, Germany

Abstract

A new polytype of the misfit layer compound $([\text{SnSe}]_{1.16})_1(\text{NbSe}_2)_1$ with extensive rotational disorder was prepared from designed modulated elemental reactants. This polytype, previously referred to as a ferecrystal due to the extensive rotational disorder, formed over a range of compositions and precursor thicknesses and the resulting c -axis lattice parameters ranged from 1.2210(4) to 1.2360(4) nm. These values bracket the value published for the crystalline misfit compound prepared at high temperature. The a - and b -axis in-plane lattice parameters of both the SnSe and NbSe₂ constituents were incommensurate, which differs from the misfit layered compound formed via high temperature reaction that has a common b -axis lattice parameter for the two constituents. The in-plane area per unit cell of the ferecrystal is 1-2% larger than the compound formed at high temperature. The ferecrystalline $([\text{SnSe}]_{1.16})_1(\text{NbSe}_2)_1$ compound is 1.6 times more conductive than the misfit layer compound. Hall effect measurements indicate that the ferecrystal is a p -type metal and that the higher conductivity is a consequence of higher mobility of carriers in the ferecrystalline compound.

Keywords: thin films; vapor deposition; electrical transport; X-ray diffraction

Introduction

The existence and unusual structure of misfit layer compounds have challenged conventional wisdom by having non-integer stoichiometry, incommensurate structures, and abrupt structural discontinuities between constituents [1]. There remains a lack of understanding of why these compounds form and what stabilizes them relative to a mixture of the constituents [2]. They provide a unique opportunity to investigate the interplay between interfaces, charge transfer between constituents, and the effect of finite layer thickness on structure and physical properties [3]. Misfit layer compounds (MLCs) are described by the general formula $[(\text{MX})_{1+\delta}]_m(\text{TX}_2)_n$, in which a transition metal dichalcogenide layer with formula TX₂ alternates with a rock salt layer with formula MX along the c -axis. The factor $1+\delta$ accounts for the difference in the area per cation in the different structures. The in-plane lattice parameter mismatch generally leads to distortion of the rock salt structure, and for materials prepared at high temperature there is a common in-plane lattice parameter between the constituents [4]. The subscripts m and n correspond to the number of rock salt and transition metal dichalcogenide layers, respectively, in the repeat unit. The $m = n = 1$ compound is by far the most frequently reported structure formed via traditional, high temperature solid-state and vapor-phase transport reactions [1,5]. These high-temperature reactions only allow access to compounds that are thermodynamically stable.

By using modulated elemental reactants as precursors, it has been shown that many new misfit layered compounds can be formed with both new constituents as layers or through kinetically trapping compounds with specific values of m and n larger than 1 [6,7]. The compounds are often only kinetically stable and the design of the precursor determines the specific m and n values of the compound that self assembles [8]. The term ferecrystal, from the Latin root *fere-* meaning almost, has been used to describe these new compounds because they exhibit extensive rotational disorder between subsequent layers of subsystems (Figure 1) [7]. This disorder inhibits the structural distortions in the layers that result in common in-plane lattice parameters in misfit layer compounds and these structural differences result in properties that are not observed in misfit layer compounds, such as charge density waves [9] and extremely low cross-plane thermal conductivities for fully dense materials [6,10,11].

There have been relatively few comparisons of misfit layer compounds and ferecrystals, but when investigated there have been significant differences between both the structures and the properties of different polytypes [12,13]. This prompted us to prepare the $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$ ferecrystal, and here we compare its structure and properties to the $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$ misfit layer compound. Previously, X-ray powder diffraction was used to determine the structure of the misfit layer compound using a model containing the typical structural features expected for these compounds [14]. Wiegers *et al.* also reported electrical resistivity and Hall effect measurements on a powder compact which indicated metallic behavior [14]. Herein, we provide a detailed structural and property analysis of the ferecrystalline form of $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$ using Rietveld refinement, in-plane and out-of-plane X-ray diffraction, HAADF-STEM, electron diffraction, electrical resistivity and Hall effect measurements. The ferecrystal was most ordered along the c -axis when an excess of SnSe was included in the precursor. The discontinuity observed in the electrical properties of the misfit layered compound was not found in the ferecrystal, and the ferecrystalline film was found to be 1.6 times more conductive due to a higher mobility of the carriers.

Material and methods

The ferecrystals investigated in this study were synthesized via physical vapor deposition using a custom-built high-vacuum system [15] evacuated to a base pressure of 10^{-7} Torr. Elemental sources, Sn (99.999 % purity), Nb (99.999 % purity) and Se (99.999 % purity), were obtained from Alfa Aesar. The precursor films were deposited onto (100) oriented silicon wafers with total thickness values of 47.3(2) nm, 45.2(1) nm, 46.9(3), and 50.6(2) nm for samples A, B, C and D respectively (see table 1). A LabView program controlled the opening and closing of pneumatic shutters to control layer thickness and the deposition sequence of the elemental layers. Se, Sn and Nb were deposited at the rate of 0.05 nm/s, 0.04 nm/s and 0.02 nm/s respectively. Atomic ratio and thickness calibrations of the precursors, for the formation of desired stoichiometric compounds, were performed as described previously [16]. The compositions of the precursors and the self-assembled compounds were determined via electron microprobe analysis (EPMA) as described by Donovan *et al* [17]. A Cameca SX-100 was used for the compositional analysis of these compounds.

X-ray reflection (XRR) and diffraction (XRD) were performed on a Bruker D8 AXS diffractometer equipped with a Cu K α (0.154 nm) radiation source operated at 40 kV and 40 mA, a Göbel mirror, and Bragg-Brentano optics geometry. Locked coupled θ - 2θ scans were collected from (0-10°) and (6-65°) 2θ for XRR and XRD respectively. Repeat layer thicknesses, total film thicknesses and c -lattice parameters were extracted from the two different X-ray experiments.

In-plane X-ray diffraction scans were collected at Beamline 33BM at the Advanced Photon Source at Argonne National Lab. The experimental setup used a small incident beam angle and a detector with a scanning range parallel to the substrate. The incident X-ray beam had a wavelength of 0.1127 nm. The in-plane lattice parameters were refined from least squares fits to the position of the indexed Bragg- [reflections](#).

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and selected-area electron diffraction were performed at a TEM/STEM JEOL JEM2200FS operated at 200 keV. The sample investigated was from the same batch and on the same substrate material as the sample for the resistivity and Hall measurements that were performed at Humboldt-Universität zu Berlin. A Si(100) wafer with 300 nm silicon oxide on top was used as a substrate. The sample was prepared for TEM using a cross-sectional preparation technique which includes cleaving the sample, gluing it face-to-face, gluing it into a ceramics cylinder, sawing, grinding, dimple grinding and ion milling using Ar ions with energies down to 1.4 kV. The selected-area electron diffraction pattern was taken at the same sample area as the STEM images. A selected-area aperture with a diameter of 130 nm was used.

Temperature-dependent electrical resistivity and Hall measurements were performed using the Van der Pauw method at the University of Oregon and at the Humboldt-Universität zu Berlin. The sample measured at the Humboldt-Universität zu Berlin was deposited on 300 nm thick silicon oxide on Si(100) with a shape of a 5 mm × 5 mm clover leaf. Four contacts were made using thin gold wires that were attached to the samples via indium. The measurements were performed in a flow-cryostat in helium atmosphere between 1.4 K and 300 K. For the Hall measurements magnetic fields up to 0.7 T and a current of 150 μ A were used.

At the University of Oregon, for electrical and Hall effect measurements, copper wires were mounted onto the van der Pauw cross patterns with indium. Measurements were carried out between 20 K and 295 K using a closed cycle He cryostat. Hall effect measurements were conducted using magnetic fields ranging between 0 – 1.6 T at a constant current of 100 mA. In the resistivity measurements, different currents were used to induce the corresponding potential difference. Current was injected through two of the cross arms using a programmable current source. The potential difference between the remaining arms was measured through Keithley 2181A nanovoltmeter. The slope of the current-voltage curve was used to determine the sheet resistance. The average sheet resistance ($R_{\text{Avg Sheet}}$) was then converted to resistivity using the following relationship:

$$\rho = \frac{\pi d}{\ln(2)} R_{\text{Avg Sheet}} f \quad (1)$$

where ρ is resistivity, d is the total thickness of the film and f is the symmetry of the sample.

The magnetic field versus the voltage perpendicular to the current was used to determine the Hall coefficient at a constant current. The slope of the voltage versus field was used to determine the Hall coefficient (R_H). The carrier concentration was determined from the Hall coefficient assuming a single band model using equation 2:

$$p = \frac{1}{eR_H} \quad (2)$$

where p is carrier concentration in cm^{-3} and e is elemental charge.

Results and Discussion

The procedure to form designed precursors has been described in detail previously [15,16]. Briefly, the desired precursor is deposited by physical vapor deposition of the elements to create two layers in the repeat unit, each of which has the composition of a constituent and contains the number of atoms required to form a structural unit. The first step is the calibration of each of the layers so they have the composition of the respective binary compounds. The Se shutter time was kept constant while the shutter times for Nb and Sn were varied. Graphs of shutter time at fixed deposition rates versus atomic ratios for the two different binary samples were determined by EPMA and interpolated to find the ratio of shutter times that yielded the desired stoichiometric ratios of Nb:2Se and Sn:Se. Holding the Nb:2Se and Sn:Se shutter ratios constant, a series of precursors were then prepared by holding the thickness of the Nb:2Se bilayer fixed and varying the thickness of the Sn:Se bilayer. Graphing the Sn/Nb atomic ratio versus the shutter time for the Sn layer gave a linear fit from which the ratio of Sn to Nb shutter times that yielded the predicted misfit value was determined. This yields the ratio of deposition times required to prepare a precursor with the ideal composition for the formation of the desired structure. Finally the overall thickness of the Sn:Se:Nb:Se sequence of layers was scaled, holding all the shutter time ratios constant, to obtain a precursor where each Sn:Se:Nb:Se repeat contains the number of atoms required, to form one crystallographic unit of the target compound $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$. A slight excess selenium (3-5 %) was deposited in each of the layers to compensate for selenium vapor lost during annealing.

An annealing study was conducted to determine the temperature and time required for the self-assembly of the target compound from the designed precursor. Pieces of the same 1:1 precursor were annealed at temperatures ranging from 200 °C to 500 °C for 20 minutes at each temperature. Figure 2 shows diffraction patterns after annealing at each temperature. The X-ray pattern of the as deposited sample at low angles revealed layering of the as-deposited precursors, while at high angles the appearance of weak 00 l maxima suggests a limited amount of long-range order. With increasing annealing temperature, the 00 l reflections in the XRR move to higher angles, indicating that the layers in the sample become thinner. An increasing number of additional 00 l reflections appear in the diffraction patterns, indicating increasing order as the targeted compound crystallizes. The full width at half maximum (FWHM) of the reflections decreases as annealing temperature increases, reaching a minimum at 400 °C, which was taken to be the optimal temperature for forming the targeted compound, $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$. All the Bragg maxima observed can be indexed as 00 l reflections, indicating that the sample is crystallographically aligned with the c -axis perpendicular to the substrate (see Figure 2 and 3).

A number of different precursors were prepared and surprisingly most of them formed $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$ even if the repeating period of the precursor and the composition were significantly different than the final ferecrystal reflecting the stability of the misfit compound in the bulk phase diagram. Impurity phases were not observed in the diffraction patterns due to the large intensity of the 00 l reflections that results from the crystallographic alignment of the ferecrystal. Table 1 contains the repeat period of the precursors that formed the targeted compound, the composition of the samples, the FWHM after annealing at 400 °C and the c -axis lattice parameters obtained from the position of the 00 l diffraction maxima in the specular diffraction patterns. The calculated c -axis lattice parameters ranged 1.2221(4) to 1.2360(4) nm. The c -axis lattice parameter reported for the misfit layer compound $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$ is

1.2282(2) nm [14], which falls within the range of lattice parameters found for different preparations of the ferecrystal. Since the samples formed over a surprisingly large range of compositions, the FWHM was used as a guide to the quality of the samples that formed. A composition ratio of Sn/Nb of 1.25 and a repeat thickness 1.2226(4) nm gave the narrowest FWHM.

Table 1. The precursor period, Sn/Nb atomic ratio, FWHM of the (002) reflection of the compound formed after annealing a precursor for 20 minutes at 400 °C, and the *c*-axis lattice parameter for the samples prepared in this study that formed $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$. *Note: further characterizations were performed on sample C.*

Sample	Repeating period of precursor	Sn/Nb atomic ratio	FWHM (°) of (002) reflection	<i>c</i> -axis lattice parameter (nm)
A	1.3061	1.14(1)	0.321(1)	1.2221(4)
B	1.3116	1.21(1)	0.246(1)	1.2225(4)
C	1.3159	1.25(1)	0.219(1)	1.2226(4)
D	1.5488	1.33(1)	0.422(1)	1.2360(4)

The FullProf program package [18] was used for Rietveld refinement of the 00*l* diffraction pattern of sample C, which gave the sharpest reflections, to obtain the positions of the atomic planes along the *c*-axis. The refinement was carried out on a high quality 00*l*-scan and the results along with a schematic of the structure with the inter plane distances are shown in Figure 3. The model converged to low R-values and the positions of the atomic planes along the *c*-direction and occupancies are given in Table 2. The average distance between the Sn-Se layers within the rock salt structure was found to be 0.2711(1) nm which is similar to the Sn-Se distance reported for the misfit layered compound [14]. The SnSe layers show a puckering of 0.045(1) nm which is slightly smaller than found in the analogous misfit layer compound (0.049 nm) [14]. This puckering results from the Sn atoms interacting with the Se of the dichalcogenide layer and the longer distance between the SnSe and the dichalcogenide Se layers in the ferecrystal (0.2906 nm) compared with the misfit layer compound (0.2873 nm) is consistent with a weaker interaction between the constituents. The Nb-Se inter plane distance within the dichalcogenide constituent was found to be slightly smaller in the ferecrystal, 0.1644(2) nm, relative to that reported for the misfit layer compound (0.167 nm) [14]. The refinement yielded an occupancy of 0.92 for the Nb and Se positions in the dichalcogenide subunit, agreeing within error with the tin to niobium ratio determined from EPMA for this sample (1.25(1)).

Table 2. Rietveld refinement results from room temperature XRD-data. Space group: $P\bar{3}m1$. *Due to the limited amount of Bragg reflections, the B_{iso} for all atoms was fixed to 0.005 nm².*

Parameter/Compound	
Composition from refinement	$[(\text{SnSe})_{1.16}](\text{NbSe}_2)_{0.92}$
Radiation	Bruker D8, Cu K α
2 θ range (degrees)	$6 \leq 2\theta \leq 65$
<i>c</i> (nm)	1.22627(4)
Reflections in refinement	8
Number of variables	13
$R_F = \sum F_o - F_c / \sum F_o$	0.0344
$R_I = \sum I_o - I_c / \sum I_o$	0.0730
$R_{wp} = [\sum w_i y_{oi} - y_{ci} ^2 / \sum w_i y_{oi} ^2]^{1/2}$	0.122
$R_P = \sum y_{oi} - y_{ci} / \sum y_{oi} $	0.0959
$R_e = [(N - P + C) / (\sum w_i y_{oi}^2)]^{1/2}$	0.0218

$\chi^2 = (R_{wp}/R_e)^2$	31.1
Atom parameters	
Nb in $1a(0)$	
Occ.	0.92(1)
Se1 in $2c(z), z$	0.1341(1)
Occ.	1.84(1)
Sn in $2c(z), z$	0.3711(2)
Occ.	1.16
Se2 in $2c(z), z$	0.4078(2)
Occ.	1.16

Grazing incidence in-plane diffraction geometry was used to obtain the *ab*-plane diffraction pattern, which is shown in Figure 4. All observed reflections could be attributed to the two independent crystal lattices of the SnSe and the NbSe₂ subsystems. The reflections corresponding to the SnSe phase can be indexed using a square basal plane based on a 3D-rock salt structure and result in an *a*-lattice parameter of 0.599(1) nm. The observed *a*-axis lattice parameter for SnSe falls within the previously reported range (0.5935(4) - 0.6050(9) nm) for SnSe based ferecrystals [8]. A close inspection reveals slightly larger peak widths for reflections where $h \neq k$ relative to $h = k$ reflections. Following the work of Beekman *et al* [19], the symmetry was reduced from a square to a rectangular in the plane. Using the axes convention from the bulk structure of SnSe [20] resulting in an *a*-axis lattice parameter of 0.422(2) nm and a *b*-axis lattice parameter of 0.426(2) nm. Converting the unit cell settings to one comparable to that reported for the [(SnSe)_{1.16}]₁(NbSe₂)₁ misfit layer compound, *a*-axis and *b*-axis lattice parameters of 0.597(2) nm and 0.602(2) nm were obtained. The misfit layered compound was reported to have an *a*-axis lattice parameter of 0.5928(1) nm and a *b*-axis lattice parameter of 0.5971(2) nm, so the ferecrystal has an *ab*-plane area that is 1.6% larger, with the difference reflecting the more extensive structural distortions present in the misfit layered compound analog. Compared to bulk SnSe (3.692 nm²) [20], both the ferecrystal and the MLC *ab*-plane areas are both significantly smaller: 3.594 nm² and 3.540 nm² respectively. The smaller areas are consequences of the distortion of the ferecrystal and the MLC towards a square plane and reflect both the effect of charge transfer between the layers and distortions in the misfit layer compound to obtain a commensurate *b*-axis lattice parameter between constituents. The Bragg maxima corresponding to the NbSe₂ constituent can be indexed as *hk*0 reflections using a hexagonal basal plane, resulting in an *a*-axis lattice parameter of 0.3462(1) nm. This is slightly larger than the *a*-axis lattice parameter of the NbSe₂ in the misfit layered compound, 0.3441(1) nm. The calculated *a*-axis lattice parameter of the ferecrystal is slightly smaller than the *a*-axis lattice parameter range reported for a 1*T*-NbSe₂ (0.353(1) nm) polytype, larger than the 2*H*-NbSe₂ polytype (0.3449-0.3460(1) nm), and is within the range reported for the 4*H*-NbSe₂ polytype (0.3439-0.3800(2) nm) [21–24]. Knowing the in-plane lattice parameters of both constituents of the ferecrystal enables the calculation of the crystallographic misfit parameter, $\delta = 0.16$, which is identical to that determined in this manner for the MLC-counterpart.

The HAADF-STEM images in Figure 5 show the layered structure of the ferecrystal with SnSe double layers alternately stacked with NbSe₂ triple layers. The total ferecrystal film thickness indicated in Figure 5a) is in agreement with the thickness determined by XRR. The STEM image in Figure 5b) shows the very uniform stacking sequence of the constituents. The continuously increasing intensity from the top to the bottom of the image can be ascribed to the wedge-shape of the sample due to the TEM sample preparation. In the part of the ferecrystal

shown in Figure 5c) several crystal orientations of SnSe and NbSe₂ could be indexed. These projections agree with the crystal structures reported for binary SnSe and NbSe₂. The turbostratic disorder of the ferecrystal can be seen in the HAADF-STEM images. In Figure 5c) several SnSe and NbSe₂ layers are oriented with low-indexed zone axes parallel to the electron beam, while

neighboring layers show different $[uv0]$ crystal orientations. In the overview image in Figure 5a) several parts of the ferecrystal appear abruptly brighter than the neighboring sample regions. This can also be ascribed to the turbostratic disorder of the ferecrystal. The atomic number contrast of the HAADF-STEM images ($Z_{\text{Sn}} = 50$ and $Z_{\text{Nb}} = 41$) mostly results in brighter SnSe layers and darker NbSe₂ layers. However, if the atom density parallel to the electron beam is high in some NbSe₂ layers due to their crystal orientation they can also appear brighter than the SnSe layers. An in-plane lateral grain size of 15 nm – 40 nm was estimated from the HAADF-STEM images.

The selected-area electron diffraction (SAED) pattern in Figure 6 shows a pronounced streaking along the c -axis direction, which can be attributed to the short coherence lengths along this direction due to the turbostratic disorder in the sample. From the distance between the 00/ reflections in the pattern, a repeat unit thickness of 1.23(1) nm was determined, which is consistent with the X-ray diffraction scans. The hkl reflections were indexed separately for the SnSe and the NbSe₂ subsystem. The positions of the SnSe family of reflections agree with the almost square in-plane unit cell of SnSe which was found for the SnSe part in this ferecrystal by in-plane X-ray diffraction. The distortion from the orthorhombic room temperature structure of bulk SnSe is clear, as separate $h \neq k$ reflections, which would be expected from the large difference between the in-plane a - and b - parameter, are not present in the SAED pattern.

Electrical transport measurements on different $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$ samples were conducted at the University of Oregon (UO) and the Institut für Physik at the Humboldt-Universität zu Berlin (HU). The data agreed to within 3%, and the temperature dependences were the same within error. The electrical resistivity as a function of temperature for the ferecrystalline compound is compared with the misfit layer compound [14] and single crystalline NbSe₂ [27] in Figure 7. NbSe₂ is metallic [27–30] with room temperature ab -plane resistivity values between 1.5 $\mu\Omega\text{-m}$ – 36 $\mu\Omega\text{-m}$ reported [27–29]. As a binary, SnSe is a p -type semiconductor [31] with significantly higher room temperature resistivity values of $4 \times 10^4 \mu\Omega\text{-m}$ – $1.8 \times 10^6 \mu\Omega\text{-m}$ for bulk samples [32] and $1.0 \times 10^5 \mu\Omega\text{-m}$ – $2.0 \times 10^6 \mu\Omega\text{-m}$ for polycrystalline thin films [33][34]. The simplest approximation is to assume that only the NbSe₂ layer conducts, as was done previously for the MLC. Using this approximation, the ferecrystal and the MLC should exhibit approximately double the resistivity of bulk NbSe₂. The room temperature resistivity of the ferecrystal (3.7 $\mu\Omega\text{-m}$) is higher than the NbSe₂ by a factor of 2.45 while the resistivity of the misfit layer compound is higher by a factor of 3.75. The deviation from this simple model indicates a more complex scenario with the presence of interlayer interactions that are different in the ferecrystal and the misfit layer compound. The ferecrystal has a lower resistivity than the misfit layer compound at all temperatures and does not exhibit the change in slope at 150 K observed in the misfit layer compound. This change in slope was not discussed further in the report of the MLC compound [14]. The lower resistivity in the ferecrystal is a consequence of either the form of the sample used (crystallographically aligned film versus a pressed powder), a higher mobility and/or a higher carrier concentration.

A superconducting transition temperature (T_c) of 7 K was reported for the NbSe₂ single crystal [27]. In the inset of Figure 7, the superconductivity transition temperature for the

ferecrystalline compound is displayed to be 1.7 K. Upon applying a magnetic field of 660 mT, the transition temperature is no longer observed in the measured temperature range. In the misfit layer compound within a measurement range of 4.2 K – 300 K no superconducting transition was reported [14]. A prior study of the influence of crystal thickness of NbSe₂ on the superconducting transition temperature revealed a reduction in T_c with decreasing thickness. For a single layer NbSe₂, a T_c of 3.8 K was predicted [28]. The T_c observed in the ferecrystal can be considered as a single layer NbSe₂ transition temperature due to the separation of each layer by SnSe. However, the effect of interlayer interaction (discussed below) also influences the transition temperature.

The temperature dependence of the resistivity of the ferecrystal can be modeled using the Bloch-Grüneisen model above the superconducting transition temperature to ambient temperature. The model describes the temperature dependent charge carrier-phonon interaction in metallic compounds, where the phonon density of states is based on the Debye model:

$$\rho(T) = \rho_o + \Re \left(\frac{T}{\theta_D} \right)^5 \int_0^{\frac{\theta_D}{T}} \frac{z^5}{(e^z - 1)(1 - e^{-z})} dz \quad (3)$$

Where ρ_o is the residual resistivity, $\Re$ the electron-phonon interaction constant, and θ_D the Debye temperature. For the MLC compound [14], the data were fitted below 150 K, where a change in slope is observed. As reported by Rouxel *et al*, MLCs containing NbX₂ and TaX₂ display a Debye temperature around 200 K [35]. The ferecrystalline ([SnSe]_{1.16})₁(NbSe₂)₁ exhibits a Debye temperature of 239 K while its MLC analog has a Debye temperature of 147 K (results of fits listed in Table 3). From this fit, the electron-phonon interaction was observed to be lower in the ferecrystal compound. Both of these differences may be a consequence of the turbostratic disorder present in the ferecrystal, which reduces the lattice thermal conductivity by a factor of ten or more [36], and also results in different in-plane lattice parameters for the constituent layers. Another reason for the observed difference in the resistivity might arise from the presence of in-plane and cross-plane resistivity in the MLC powder compact as opposed to the ferecrystal film where only in-plane resistivity is measured.

Table 3. Residual (T = 20 K), room temperature resistivity (T = 295 K) and Debye temperature (Bloch-Grüneisen fit) of the misfit layer compounds and ferecrystals of formula ([MX]_δ)_m(TX₂)_n: (M= Sn, X= Se and T= Nb)

Compound	T_c (K)	ρ_o (T = 0 K) ($\mu\Omega$ m)	ρ (T = 295K) ($\mu\Omega$ m)	θ_D (K)
([SnSe] _{1.16}) ₁ (NbSe ₂) ₁ –MLC [14]	-	2.80(1)	5.72(1)	147(2)
([SnSe] _{1.16}) ₁ (NbSe ₂) ₁ (UO)	-	2.20(1)	3.70(1)	239(2)
([SnSe] _{1.16}) ₁ (NbSe ₂) ₁ (HU)	1.7	2.10(1)	3.80(1)	241(2)

Figure 8 shows an overlaid Hall coefficient plot of the misfit layer compound, the ferecrystal compound and the single crystalline NbSe₂. Both the misfit layer compound and the ferecrystal sample have positive Hall coefficients in the investigated temperature range, indicating *p*-type (hole) conduction. Bulk NbSe₂ has a positive Hall coefficient for temperatures down to about 25 K and a negative Hall coefficient below [27,37,38]. This change in Hall

coefficient has been proposed to be accompanied by the formation of a charge density wave at this temperature [29,37,38]. A similar change in Hall coefficient is not observed for the ferecrystals for temperatures down to 10 K. Table 4 contains the room temperature carrier concentrations calculated from the Hall coefficients, assuming a single band model, and the calculated carrier concentration, assuming one hole per Nb-atom, using the given unit cell dimensions for $2H$ -NbSe₂, the misfit layer compound, and the ferecrystal. The number of holes per niobium atom is slightly less than one, presumably due to defects such as a small concentration of niobium atoms in the van der Waals gap that makes the niobium d band contain slightly more than one electron per niobium atom. The misfit layer compound has a number of carriers per niobium that is larger than the one which was not discussed in the original publication [14]. The ferecrystalline compound contains 0.85 holes/Nb, presumable due to charge transfer from the SnSe to the NbSe₂ [39].

Table 4. Predicted and actual carrier concentration of NbSe₂ [27], the misfit layer compound prepared by Wieggers, [14] and the ferecrystal $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$ at room temperature. The calculated carrier concentration assumes one carrier per niobium atom and uses the lattice parameters of the indicated compound [40]. For the misfit layer compound and the ferecrystal, we assumed that all of the carriers are localized in the NbSe₂ constituent. The actual carrier concentrations were calculated from the measured room temperature Hall coefficients assuming a single band model and also assuming all the carriers were in the NbSe₂ layer. The final column contains the number of carriers (holes) per niobium atom.

Compound	calculated p (10^{22} cm^{-3})	actual p (10^{22} cm^{-3})	holes/Nb
$2H$ -NbSe ₂	1.47	1.36	0.93
$[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$ (UO)	0.79	0.67	0.85
$[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$ (HU)	0.79	0.61	0.77
$[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$ MLC	0.79	0.83	1.05

The ferecrystal has a larger Hall coefficient than the misfit layer compound at room temperature and both of these compounds show an increasing Hall coefficient with decreasing temperature. At $T \sim 50$ K, the Hall coefficient of the misfit layered compound becomes larger than that of the ferecrystal. Assuming a single band model, this suggests that the carrier concentration in the ferecrystal is less than that in the misfit layer compound analog at room temperature and that the carrier concentration decreases as temperature is decreased. The ferecrystal also has a lower resistivity than the misfit layered compound, so the Hall data implies that the mobility also must be higher. This might be inherent to the structural differences between the two different [polytypes](#) or a consequence of the form of the samples measured - thin film versus powder compact, or a combination of both. To gain additional insight, we compared the ferecrystal data with that reported for a single crystal of NbSe₂, which was also presented in Figures 7 and 8. The resistivity of the ferecrystal is about twice that of NbSe₂ and the Hall coefficient of both are positive with the magnitude of the Hall coefficient of the ferecrystal about double that of NbSe₂. This suggests that the ferecrystal has half the carrier density of NbSe₂, presumably due to negligible carrier concentration of the SnSe constituent layer. If we assume that the SnSe does not contribute to the carrier concentration or resistivity, then the isolated single layers of NbSe₂ in the ferecrystal have about the same carrier concentration and conductivity as the bulk single crystal at room temperature.

Figure 9 contains the mobility of NbSe₂, the misfit layer compound and the analogous ferecrystal, which was calculated from the relationship $\sigma = p\mu e$ assuming a single-band model, where σ is electrical conductivity, p is the hole concentration, μ is mobility and e is the

elementary charge. The lower resistivity in the ferecrystal relative to the misfit layer compound results from its higher mobility, reflecting its crystallographic alignment relative to the randomly oriented powder compact measured by Wiegers [14]. The mobility of the ferecrystal compound exhibits a $T^{-1/2}$ dependence within the reported temperature range, which perhaps suggests predominant optical phonon scattering [41]. Interestingly, the mobility of the ferecrystal and the bulk NbSe₂ exhibit similar values at room temperature indicating no additional charge carrier scattering was introduced by the SnSe interfaces.

Conclusions

The rotational disorder in the ferecrystal [polytype](#) of ([SnSe]_{1.16})₁(NbSe₂)₁ results in a less distorted *ab*-plane of SnSe compared to bulk SnSe than observed in the crystalline misfit layered compound. The ferecrystalline ([SnSe]_{1.16})₁(NbSe₂)₁ was found to be more conductive than the MLC compound at all temperatures. We conclude that the higher conductivity is due to the higher carrier mobility in the ferecrystalline compound. A superconducting transition was observed at 1.7 K. If one assumes all of the electrical transport properties arise from the NbSe₂ layer of the ferecrystal, the resistivity, carrier concentration and mobility of the single NbSe₂ layer in the ferecrystal is very close to that measured for single crystals of bulk NbSe₂.

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Reference

- [1] J. Rouxel, A. Meerschaut, G. a. Wiegers, Chalcogenide misfit layer compounds, J. Alloys Compd. 229 (1995) 144–157.
- [2] M. Kalläne, K. Rosnagel, M. Marczyński-Bühlöw, L. Kipp, H. Starnberg, S. Stoltz, Stabilization of the Misfit Layer Compound (PbS)_{1.13}TaS₂ by Metal Cross Substitution, Phys. Rev. Lett. 100 (2008) 065502.
- [3] G. A. Wiegers, Charge transfer between layers in misfit layer compounds, J. Alloys Compd. 219 (1995) 152–156.
- [4] G.A. Wiegers, Misfit layer compounds: structures and physical properties, Prog. Solid State Chem. 24 (1996) 1 – 139.
- [5] G. Wiegers, R. Haange, Electrical transport and magnetic properties of the misfit layer compound (LaS)_{1.14}NbS₂, J. Phys. Condens. Matter. 455 (1990). 455-463.
- [6] Q. Lin, M. Smeller, C.L. Heideman, P. Zschack, M. Koyano, M.D. Anderson, [D.C Johnson](#), Rational Synthesis and Characterization of a New Family of Low Thermal Conductivity Misfit Layer Compounds [(PbSe)_{0.99}]_m(WSe₂)_n, Chem. Mater. 22 (2010) 1002–1009.

- [7] C. Heideman, N. Nguyen, J. Hanni, Q. Lin, S. Duncombe, D.C. Johnson, The synthesis and characterization of new $[(\text{BiSe})_{1.10}\text{m}(\text{NbSe}_2)_n]$, $[(\text{PbSe})_{1.10}\text{m}(\text{NbSe}_2)_n]$, $[(\text{CeSe})_{1.14}\text{m}(\text{NbSe}_2)_n]$ and $[(\text{PbSe})_{1.12}\text{m}(\text{TaSe}_2)_n]$ misfit layered compounds, *J. Solid State Chem.* 181 (2008) 1701–1706.
- [8] R. Atkins, J. Wilson, P. Zschack, C. Grosse, W. Neumann, D.C. Johnson, Synthesis of $[(\text{SnSe})_{1.15}\text{m}(\text{TaSe}_2)_n]$ Ferecrystals: Structurally Tunable Metallic Compounds, *Chem. Mater.* 24 (2012) 4594–4599.
- [9] R. Atkins, S. Disch, Z. Jones, I. Haeusler, C. Grosse, S.F. Fischer, [D.C Johnson](#), *Journal of Solid State Chemistry Synthesis*, structure and electrical properties of a new tin vanadium selenide, 202 (2013) 128–133.
- [10] A. Mavrokefalos, Q. Lin, M. Beekman, J.H. Seol, Y.J. Lee, H. Kong, [D.C Johnson](#), In-plane thermal and thermoelectric properties of misfit-layered $[(\text{PbSe})_{[0.99]}][\text{x}](\text{WSe}_2)[\text{x}]$ superlattice thin films, *Appl. Phys. Lett.* 96 (2010) 181908.
- [11] C. Chiritescu, D.G. Cahill, C. Heideman, Q. Lin, C. Mortensen, N.T. Nguyen, et al., Low thermal conductivity in nanoscale layered materials synthesized by the method of modulated elemental reactants, *J. Appl. Phys.* 104 (2008) 033533.
- [12] D.R. Merrill, D.B. Moore, M.N. Coffey, A.W. Jansons, M. Falmbigl, D.C. Johnson, Synthesis and characterization of turbostratically disordered $(\text{BiSe})_{1.15}\text{TiSe}_2$, *Semicond. Sci. Technol.* 29 (2014) 064004.
- [13] R. Atkins, D.B. Moore, D.C. Johnson, Insights into the Self-Assembly of Ferecrystalline Compounds from Designed Amorphous Precursors, *Chem. Mater.* 25 (2013) 1744–1750.
- [14] G. Wiegers, W.Y. Zhou, The Misfit Layer Compound SnSeNbSe_2 , *Mat. Res. Bull.* 26 (1991) 879–885.
- [15] L. Fister, D.C. Johnson, Controlling Solid-State Reaction mechanisms using diffusion length ultrathin-film superlattice composite, (1992) 4639–4644.
- [16] R.D. Westover, R.A. Atkins, J. Ditto, D.C. Johnson, Synthesis of $[(\text{SnSe})_{1.16-1.09}]_1[(\text{Nb}_x\text{Mo}_{1-x}\text{Se}_2)]_1$ Ferecrystal Alloys, *Chem. Mater.* 26 (2014) 3443–3449.
- [17] John J. Donovan; Tracy N. Tingle, An Improved Mean Atomic Number Background Correction for Quantitative Microanalysis, *Microsc. Soc. Am.* 2 (1996) 1–7.
- [18] T. Roisnel; J. Rodriguez-Carvajal, A Windows tool for Powder Diffraction Pattern, *Anal. Mater. Sci. Forum.* 118 (2001) 378–381.

- [19] M.Beekman; D. Johnson, Controlling Size-Induced Phase Transformations Using Chemically Designed Nanolaminates†, *Angew. Chem. Int. Ed. Engl.* 52 (2013) 13211–13214.
- [20] H. Krebs, D. Langner, Mischkristallsysteme zwischen halbleitenden Chalcogeniden der vierten Hauptgruppe, *Zeitschrift für Anorg. und Allg. Chemie.* 334 (1964) 37–49.
- [21] A. Meerschaut, C. Deudon, NbSe₂ compounds : correlation between nonstoichiometry and stacking type (σ polytypism), *Mater. Res. Bull.* 36 (2001) 1721–1727.
- [22] F. Kadijk, ON THE POLYMORPHISM OF NIOBIUM DISELENIDE, *J. Less Common Met.* 23 (1971) 437–441.
- [23] L.H. Brixner, Preparation and properties of the single crystalline AB₂-type selenides and tellurides of niobium, tantalum, molybdenum and tungsten, *J. Inorg. Nucl. Chem.* 24 (1962) 257–263.
- [24] F. Kadijk, NIOBIUM AND TANTALUM DISELENIDES, *Recl. Des Trav. Chim. Des Pays-Bas.* 83 (1964) 768–775.
- [25] T. Chattopadhyay, J. Boucherle, Neutron diffraction study on the structural phase transition in GeTe, *J. Phys. C Solid.* 1431 (1987).
- [26] B.E. Brown, D.J. Beerntsen, Layer structure polytypism among niobium and tantalum selenides, *Acta Crystallogr.* 18 (1965) 31–36.
- [27] H.N.S. Lee, The Low-Temperature Transport Properties of NbSe₂, *J. Appl. Phys.* 40 (1969) 602.
- [28] R. Frindt, Superconductivity in Ultrathin NbSe₂ Layers, *Phys. Rev. Lett.* 28 (1972) 5.
- [29] A. LeBlanc, A. Nader, Resistivity anisotropy and charge density wave in 2H - NbSe₂ and 2H - TaSe₂, *Solid State Commun.* 150 (2010) 1346–1349.
- [30] J. Edwards, R. Frindt, ANISOTROPY IN THE RESISTIVITY OF NbSe₂, *J. Phys. Chem. Solids.* 32 (1971) 2217–2221.
- [31] B. Subramanian, T. Mahalingam, Electrodeposition of Sn, Se, SnSe and the material properties of SnSe films, *Thin Solid Films.* 357 (1999) 119–124.
- [32] T. Abraham, C. Juhasz, J. Silver, J.D. Donaldson, M. Road, A TIN-119 Mössbauer and electrical conductivity study of the system Sn_xGe_{1-x}Se (0 $\leq$ x $\leq$ 1), *Solid State Commun.* 27 (1978) 1185–1187.

- [33] D. Quan, Electrical properties and optical absorption of SnSe evaporated thin films, *Phys. Status Solidi*. 421 (1984) 421–426.
- [34] J. Singh, R. Bedi, Electrical properties of flash-evaporated tin selenide films, *Thin Solid Films*. 199 (1991) 3–6.
- [35] J. Rouxel, A. Meerschaut, G.A. Wiegers, Chalcogenide misfit layer compounds, *J. Alloys Compd.* 229 (1995) 144–157.
- [36] C. Chiritescu, D.G. Cahill, N. Nguyen, D. Johnson, A. Bodapati, P. Koblinski, et al., Ultralow thermal conductivity in disordered, layered WSe₂ crystals., *Science*. 315 (2007) 351–3.
- [37] R. Morris, Connection between Charge-Density Waves and Superconductivity in NbSe₂, *Phys. Rev. Lett.* 34 (1975) 1164–1166.
- [38] H. Mutka, N. Housseau, J. Pelissier, R. Ayroles, C. Roucau, Effects of defects on charge density waves in layered dichalcogenides, *Solid State Commun.* 50 (1984) 161–164.
- [39] M.B. Alemayehu, G. Mitchson, B.E. Hanken, M. Asta, D.C. Johnson, Charge Transfer between PbSe and NbSe₂ in [(PbSe)_{1.14}]_m(NbSe₂)₁, *Chem. Mater.* 26 (2014) 1859–1866.
- [40] L.L. Kalikhman, V. L.; Pravoverova, Electrical Properties of Molybdenum Diselenide-Niobium Diselenide and Molybdenum Diselenide-Tantalum Diselenide alloys, *Neorg. Mater.* 10 (1974) 1190–1194.
- [41] H.J. Goldsmid, *Introduction to Thermoelectricity*, Springer, Berlin, 2010. 143.

Figure captions

Figure 1. A schematic representation of the structure of the $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$ misfit layer compound (a) and two grains of the $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$ ferecrystal compound illustrating the extensive rotational disorder between the constituent layers.

Figure 2. (a) X-ray reflectivity patterns collected after annealing a precursor for 20 minutes at the temperatures shown between the graphs. (b) X-ray diffraction patterns collected after annealing a precursor for 20 minutes at the temperatures shown between the graphs. On the 500 °C scan, the diffraction maxima marked with (*) at 22.4° and 46.8° of 2θ correspond to orthorhombic SnO₂. All of the remaining diffraction maxima can be indexed as 00*l* reflections from the targeted ferecrystal, $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$.

Figure 3. The X-ray diffraction pattern, Rietveld refinement, and difference plot for $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$. The inset figure shows the interlayer distances for the different planes of atoms along the *c*-axis of the ferecrystal.

Figure 4. In-plane X-ray diffraction pattern of the $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$ ferecrystal compound. The numbers above the diffraction maxima are the *hk*0 reflections of the constituents.

Figure 5. Cross-sectional HAADF-STEM images of the $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$ ferecrystal compound. (a) Overview of the ferecrystal; (b) enlarged image of the framed area in a); (c) enlarged image of the framed area in b). The structure model of SnSe in c) is given according to the structure of binary SnSe at room temperature

reported by Chattopadhyay *et al* [25] and using space group $Pmcn$. The structure model of $NbSe_2$ is given according to $2H-NbSe_2$ reported by Brown *et al* [26]

Figure 6. Selected-area electron diffraction pattern of the $[(SnSe)_{1.16}]_1(NbSe_2)_1$ ferecrystal compound. On the right hand side of the image brightness and contrast were changed in order to enhance the reflections. The families of reflections given on the left hand side are indexed for the SnSe subsystem and the reflections on the right hand side are indexed for $NbSe_2$. SnSe is indexed according to binary SnSe at room temperature reported by Chattopadhyay *et al* [25], using space group $Pmcn$ and lattice parameters as found by in-plane X-ray diffraction for the $[(SnSe)_{1.16}]_1(NbSe_2)_1$ ferecrystal. The $NbSe_2$ is indexed according to binary $2H-NbSe_2$ as reported by Brown *et al* [26]. The $00l$ ferecrystal reflections in the center of the diffraction pattern result from the ferecrystal stacking sequence.

Figure 7. Electrical resistivity of $[(SnSe)_{1.16}]_1(NbSe_2)_1$ ferecrystal as a function of temperature. For comparison, the electrical resistivities of the MLC counterpart (powder compact) [14] and single crystal $NbSe_2$ [27] are graphed. The dashed lines represent least-squares fits to the Bloch-Grüneisen model. The inset shows the superconductivity transition for the ferecrystalline compound at 1.7 K. The dashed lines in the inset are lines to guide the eye.

Figure 8. Hall Coefficient of $[(SnSe)_{1.16}]_1(NbSe_2)_1$ as a function of temperature. The Hall coefficients of the MLC analog [14] and $NbSe_2$ single crystal [27] are shown for comparison.

Figure 9. Mobility of $[(SnSe)_{1.16}]_1(NbSe_2)_1$ as a function of temperature in comparison to the mobility of the MLC analog [14] and bulk single crystalline $NbSe_2$ [27]. Dashed lines represent $T^{-1/2}$ temperature dependence.

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9