Influence of interstitial V on structure and properties of ferecrystalline **$([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ for $n = 1, 2, 3, 4, 5$, and 6**

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Abstract

A series of ferecrystalline compounds $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ with $n = 1 - 6$ and a thin film $\text{V}_{1+x}\text{Se}_2$ were synthesized utilizing the modulated elemental reactant technique. The effect of interstitial V-atoms ranging from $0.13 \leq x \leq 0.42$ in different compounds on structure and electrical properties of these intergrowth compounds is reported. The presence of the interstitial V-atoms for $n > 1$ was confirmed by Rietveld refinements as well as HAADF-STEM cross sections. The off-stoichiometry in the thin film $\text{V}_{1.13}\text{Se}_2$ causes a suppression of the charge density wave, similar to the effect of non-stoichiometry observed for the bulk compound. The charge density wave of $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_1$, however, is not affected by the non-stoichiometry due to its incorporation as volume inclusions or due to the quasi 2-dimensionality of the isolated VSe_2 layer. In the compounds $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ with $n = 2 - 6$, the temperature dependence of the electrical resistivity approaches bulk-like behavior.

KEYWORDS: ferecrystals; charge density wave; dimensionality; interstitials; intercalation

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1. Introduction

Layered transition metal dichalcogenides (TMD) TX_2 with T being transition metals of group 14, 15, 16 or Sn and X = S or Se are well known to form intercalation compounds. Within the TX_2 sandwiches strong ionic and/or covalent bonding between the metal and chalcogen atoms is present, but only weak van der Waals like cohesive forces hold the individual TX_2 units together. Hence, intercalation of various species such as monoatomic cations, molecular ions and even neutral molecules is possible [1]. A special class of intercalated TMDs are misfit layer compounds, where bilayers of rocksalt-like structured monochalcogenides (MX) are inserted into the van der Waals gap of the dichalcogenide, resulting in a general formula of $([\text{MX}]_{1+\delta})_m(\text{TX}_2)_n$ [2]. The TX_2 layer in these intergrowth compounds as well as locations between the TX_2 and MX layers can also serve as intercalation hosts and especially Li can be incorporated chemically or electrochemically [3-7]. Whereas Li readily intercalates into vacant positions between the MX and TX_2 layer in $([\text{MX}]_{1+\delta})_1(\text{TX}_2)_1$ and $([\text{MX}]_{1+\delta})_1(\text{TX}_2)_2$ as well as between the two dichalcogenide layers in $([\text{MX}]_{1+\delta})_1(\text{TX}_2)_2$, Na was successfully intercalated only into the van der Waals gap between the dichalcogenide layers of

$([MX]_{1+\delta})_1(TX_2)_2$ compounds [1]. Recently, it was demonstrated that addition of small amounts of Cu promotes the formation of $Cu_x(BiSe)_{1+\delta}(TiSe_2)_2$, presumably due to a stabilization of the structure from Cu occupying cavities between the two $TiSe_2$ layers [8].

For VSe_2 the tendency to form self intercalated compounds $V_{1+x}Se_2$ is well known. The dependency of the lattice parameters of the $1T$ -structure (CdI_2 -type) with c decreasing and a increasing as a function of x [9] is different, however, from the expected behavior of other intercalated TMDs where the c -lattice parameter increases on intercalation [1]. The charge density wave (CDW) transition in VSe_2 at 100 K [10] is rapidly suppressed in off-stoichiometric compounds due to additional electrons from the interstitial vanadium atoms populating the conduction band [9]. Recently, a CDW transition in $([SnSe]_{1.15})_1(VSe_2)_1$ was observed [11] and it was demonstrated that increasing the number of VSe_2 layers in the series $([SnSe]_{1.15})_1(VSe_2)_n$ suppresses this transition, suggesting that it is due to the quasi-2 dimensional nature of the independent VSe_2 layer in the ferecrystal $([SnSe]_{1.15})_1(VSe_2)_1$ [12]. Increasing the separation of the single VSe_2 layer by increasing the thickness of SnSe by preparing $([SnSe]_{1.15})_m(VSe_2)_1$ compounds increased the transition temperature, supporting the importance of the quasi-2 dimensional nature of the independent VSe_2 layer [13].

In this study we explore the effect of interstitial V-atoms on the structural and electrical properties of $([SnSe]_{1.15})_1(V_{1+x}Se_2)_n$ with $n = 1 - 6$ and a $V_{1.13}Se_2$ thin film. The thin film $V_{1.13}Se_2$ shows similar structural and electrical property changes as observed for the bulk compound. In contrast to bulk $V_{1+x}Se_2$, an expansion of the c -lattice parameter is observed in the $([SnSe]_{1.15})_1(V_{1+x}Se_2)_n$ samples. The interstitial V-atoms were found to reside only in the van der Waals gap between adjacent VSe_2 layers and not between the SnSe and the VSe_2 . The additional V-atoms have a minor influence on the charge density wave transition in $([SnSe]_{1.15})_1(V_{1+x}Se_2)_1$ presumably because the extra V is incorporated as volume defects rather than as an intercalate. The electrical properties of the $([SnSe]_{1.15})_1(V_{1+x}Se_2)_n$ $n = 2 - 6$ compounds approach that of bulk VSe_2 as n increases, but the Hall coefficient at room temperature is positive, in contrast to the negative Hall coefficient measured for the $V_{1.13}Se_2$ thin film.

2. Material and methods

All thin film samples were synthesized using physical vapor deposition (PVD) in a custom-built vacuum deposition chamber [14] at base pressures as low as 10^{-8} mbar. During the deposition process the low pressure was kept by a cryogenic absorber pump. Se (Alfa Aesar, 99.999 % purity) was evaporated via an effusion cell and electron beam guns were used to evaporate Sn (Alfa Aesar, 99.98 %) and V (Alfa Aesar 99.7 %). The PVD process was carried out on two different substrates, either (100) oriented Si-wafers for structural characterizations or fused silica for the measurement of electrical properties. Details on the operation of the deposition system and the calibration procedure for the initial precursor films of the desired layered samples are described elsewhere [11, 13]. All samples were annealed on a hot plate inside a glove box under nitrogen atmosphere (< 1 ppm/ O_2).

X-ray reflection (XRR) and high-resolution X-ray diffraction (XRD) scans were collected using a Bruker D8 Discover diffractometer equipped with Cu-K α radiation. High quality scans for Rietveld refinement were collected using off-specular conditions (angle offset between θ and 2θ was in all cases 0.2°) to avoid intensity at lower 2θ due to specular reflectivity. The FullProf program package [15] was used for Rietveld refinements. In-plane diffraction of selected samples was performed at the Advanced Photon Source (APS), Argonne National Laboratories, at Beamline 33BM using an incident X-ray beam with $\lambda = 0.11272$ nm. The lattice parameters were calculated performing least squares fits to the peak positions utilizing the WinCSD package [16].

The chemical composition of the thin film samples was determined using a Cameca SX100 Electron Microprobe equipped with 4 wavelength dispersive spectrometers. A thin film technique applying three different acceleration voltages (10, 15, and 20 kV) described in details elsewhere [17] was utilized for precise compositional analysis.

High resolution scanning transmission electron microscopy (HRSTEM) was carried out on a FEI Titan 80-300 TEM/STEM instrument with an objective lens c_s -correction and a high angle annular dark field detector (HAADF). The preparation of selected samples for HRSTEM was performed at the Center for Advanced Materials Characterization in Oregon (CAMCOR) of the University of Oregon (UO) utilizing a FEI Helios Nanolab D600 Dual Beam focused ion beam (FIB). After an in-situ lift out the samples were treated by a thinning technique followed by a low voltage ion beam polishing.

In order to perform in-plane electrical resistivity and Hall measurements a shadow mask creating a cross pattern was used on fused silica substrates. The total film thickness used to calculate the sheet resistivity and the Hall-coefficient was evaluated from XRR data and for all samples was about 50 nm. Small indium pieces were used to electrically contact the sample to Cu-wires. All measurements were carried out in a temperature range between 20 and 300 K and for the Hall measurements magnetic fields up to 1.6 T were applied.

3. Results and discussion

3.1 Structure and composition

The modulated elemental reactant (MER) method [18] allows synthesizing nanolaminate precursors, which resemble the intended product closely in layering sequence and composition. To create the desired precursor, a multi-step calibration of the deposition parameters to define stoichiometric ratios between the involved elements and to find the correct total amount of material in each elemental layer condensed onto the substrate is required [11]. In the present study a Sn/V ratio of ~ 0.95 rather than the ideal ratio of 1.15 was chosen in order to synthesize V-rich compounds. Here, the number of VSe₂-layers (n) in ([SnSe]_{1.15})₁(V_{1+x}Se₂)_n (short hand notation (1, n)) is consecutively increased from 1 to 6 and in addition a thin film sample V_{1+x}Se₂ was synthesized in a similar manner.

A short annealing duration at moderate temperatures is required to self assemble the desired metastable intergrowth compounds from the precursors. In an earlier investigation the ideal annealing conditions for ([SnSe]_{1.15})₁(VSe₂)₁ were found to be 400 °C for 20 min [11]. As

these conditions to form the intended product might depend on the Sn/V ratio, an annealing study for the sample $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_3$ was carried out. A sample deposited on a Si wafer was cleaved into several pieces, which were annealed at different temperatures for a duration of 20 min each. Specular diffraction scans were performed for all samples in order to elucidate under which conditions the self-assembly into the superstructure is promoted best. The resulting patterns are plotted in Fig. 1a. The Bragg reflections belonging to binary 1T-VSe₂ [19] although very broad are clearly visible already after the deposition process suggesting that there is already order in the VSe₂ blocks of the targeted $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_3$ compound. Only at temperatures ≥ 300 °C the superstructure peaks start to grow, indicating a registry between the VSe₂ blocks. The intensity increases at the same time as the full width at half maximum (FWHM) decreases until 400 °C. At higher temperatures the compound starts to decompose. The Bragg reflections shift with increasing temperature to higher angles indicating a shrinking of the unit cell. This reduction in size indicating the formation of the final product up to 400 °C is accompanied by a slight decrease in Se-content as observed by EPMA and displayed in Fig. 1b. Above 400 °C the oxygen content increases significantly and the Se content drops. The Sn/V ratio remains essentially constant until 450 °C, however, at higher temperatures the Sn-content rapidly decreases to 0. This most likely arises from the formation of tin(II)oxide, which sublimates under the open annealing conditions [20]. The peak at 33.0° in 2 θ , which is observed in the diffraction pattern collected after the heat treatment at 500 °C, can be attributed to the formation of V₂O₃ [21]. Backscattered images of the sample annealed at 600 °C combined with EDX-spectra clearly show the presence of V and O in the film with small islands where V, Se and a smaller amount of O are still present. This observation is corroborated by the diffraction pattern of the sample annealed at 500 °C, where the (00 l) peaks of 1T-VSe₂ together with the impurity peak can be observed (see Fig. 1a). Based on these results, an annealing time of 20 min at 400 °C was used to form the final intergrowth compounds discussed herein.

Fig. 1. a) High-angle X-ray diffraction patterns of $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_3$ collected at different temperatures. Selected Bragg reflections for the sample annealed at 400 °C are provided. The asterisk marks stage or substrate peaks. b) EPMA results as a function of temperature for $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_3$. Please note that the data points plotted at 0 °C correspond to the as deposited precursor.

A set of precursors $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ with $n = 1$ to 6 was synthesized and subsequently annealed at 400 °C for 20 min. The XRD patterns after annealing contain sharp Bragg-reflections, which can all be indexed to (00 l) reflections of the targeted compounds as shown

in Fig. 2a. The presence of only (00 l)-reflections results from the strong preferred orientation of the superstructures parallel to the Si-substrate surface. The c -lattice parameters of all $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ compounds in as deposited state as well as after annealing are plotted vs. the number of VSe_2 -layers in Fig. 2b (see also Table 1). The slope for the as deposited samples reveals an average thickness per $\text{V}:\text{Se}_2$ -layer of 0.667(5) nm, which shrinks upon annealing to 0.605(1) nm corresponding to the thickness of a single VSe_2 layer. Interestingly, this value is significantly larger than the previously reported VSe_2 layer thickness of 0.596(1) nm for the stoichiometric series of $([\text{SnSe}]_{1.15})_1(\text{VSe}_2)_n$ [12]. This difference can be attributed to the presence of a significant amount of interstitial vanadium atoms in the present compounds ranging from $x = 0.14$ to 0.42 as determined by EPMA (Table 1). This expansion along the c -axis is contrary to the behavior of bulk $\text{V}_{1+x}\text{Se}_2$, where the c -lattice parameter decreases from 0.611 to 0.596 nm for $x = 0$ to 0.18 [9] and for $x = 0.13$ has a value of 0.600 nm. For the thin film $\text{V}_{1.13}\text{Se}_2$ a c -lattice parameter of 0.60795(1) nm, which is close to the bulk value, was observed. For the $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ compounds the intercept of the linear fit of the c -lattice parameters as a function of n reveals a thickness for the SnSe constituent of 0.592(5) nm, which is slightly thicker than 0.576(2) nm reported for the series of $([\text{SnSe}]_{1.15})_m(\text{VSe}_2)_1$ [13]. This difference results from the larger distance between SnSe and VSe_2 constituents compared to the distance between two consecutive SnSe-layers [12, 13].

Fig. 2. a) High-angle X-ray diffraction patterns of $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ with $n = 1 - 6$ and a VSe_2 thin film. Selected Bragg reflections for all compounds are provided. The asterisk marks a substrate peak. b) c -lattice parameter for $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ as a function of the number of VSe_2 -layers (n) for as deposited and annealed (400 °C, 20 min) compounds.

Table 1. a -lattice parameters of the constituents, misfit parameter (δ), c -lattice parameter of the superlattice, c/a -ratio (a -lattice of the $\text{V}_{1+x}\text{Se}_2$ constituent), Sn/V-ratio (EPMA, normalized to a (1,1) composition) and off-stoichiometry (x) of $\text{V}_{1+x}\text{Se}_2$ calculated from EPMA results for a thin film $\text{V}_{1+x}\text{Se}_2$ and the ferecrystalline compounds $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ with $n = 1 - 6$.

compound	a -lattice parameter (SnSe), nm	a -lattice parameter ($\text{V}_{1+x}\text{Se}_2$), nm	Misfit parameter δ	c -lattice parameter, nm	c/a -ratio	Sn/V-ratio	$\text{V}_{1+x}\text{Se}_2$, x

(0,1)	n.a.	0.3376(3)	n.a.	0.60795(1)	1.80	n.a.	0.13
(1,1)	0.59273(4)	0.34082(8)	0.15	1.2030(1)	1.78	0.97	0.23
(1,2)	0.59419(5)	0.34240(3)	0.15	1.8014(1)	1.76	0.97	0.14
(1,3)	0.59514(4)	0.34335(3)	0.15	2.400(1)	1.76	0.93	0.22
(1,4)	0.5917(1)	0.34037(9)	0.15	3.012(1)	1.78	0.91	0.42
(1,5)	0.5908(1)	0.33985(9)	0.15	3.618(1)	1.78	0.93	0.38
(1,6)	0.59412(5)	0.34273(4)	0.15	4.228(1)	1.77	0.90	0.28

The in-plane diffraction patterns of all compounds are displayed in Fig. 3. The VSe_2 thin film exhibits only $hk0$ reflections consistent with the trigonal structure of bulk VSe_2 [19] and has the smallest a -lattice parameter. However, the value is significantly smaller than expected from the bulk lattice parameter of $a = 0.342$ nm for nonstoichiometric $\text{V}_{1.13}\text{Se}_2$ [9]. For all ferecrystalline compounds $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ with $n = 1$ to 6 independent lattice parameters for both constituents are observed. The Bragg reflections corresponding to the SnSe constituent can be indexed to a square basal plane and all a -lattice parameters are close to the values reported for stoichiometric $([\text{SnSe}]_{1.15})_m(\text{VSe}_2)_1$ ferecrystals [13]. For bulk $\text{V}_{1+x}\text{Se}_2$ the a -lattice parameter increases with increasing x [9]. However, for the present intergrowth compounds no clear trend is observed. The significantly smaller a -lattice parameters of the dichalcogenide constituents for the (1,4) and the (1,5) sample correlates with the larger off-stoichiometry in the VSe_2 layer (see Table 1). Interestingly, the SnSe in-plane area adjusts to the smaller area of the $\text{V}_{1+x}\text{Se}_2$ constituent to keep the misfit for all the compounds at 0.15. This flexibility of the monochalcogenide in-plane area as the dichalcogenide varies its thickness and its area is a general characteristic of ferecrystalline compounds, and reflects the varying amounts of charge transfer between constituents and the dependence of interface energies on surface structure [22]. The intensities of the SnSe reflections compared to the $\text{V}_{1+x}\text{Se}_2$ reflections decrease as expected for increasing n in the $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ compounds.

Fig. 3. In-plane X-ray diffraction patterns of $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ with $n = 1 - 6$ and a $\text{V}_{1+x}\text{Se}_2$ thin film. The Bragg reflections for the SnSe and the $\text{V}_{1+x}\text{Se}_2$ constituent are provided for the (1,1) compound and the (0,1) compound, respectively.

Rietveld refinements of the $(00l)$ patterns were conducted for three compounds, the (0,1), (1,2) and (1,3) compound, to unveil the effect of the interstitial V-atoms on the structure along the superlattice direction. For the thin film $\text{V}_{1+x}\text{Se}_2$ the refinement resulted in a composition of $\text{V}_{1.12(1)}\text{Se}_2$ in excellent agreement with the EPMA result (Table 1). Similar to the bulk structure [19] the Se-atoms shift away from the center position between the V-layers closer to the interstitial V-atoms by 3 %. (see also SI). For the ferecrystalline compounds $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ with $n = 2$ and 3, the refined occupancy of the interstitial V-atoms also matches the EPMA results (Fig. 4 and Table 1). During the simultaneous refinement of occupancy and z -value of the interstitial V, the misfit between the SnSe and the $\text{V}_{1+x}\text{Se}_2$ constituent was fixed to 0.15 extracted from the in-plane diffraction results. All attempts to introduce interstitial V-atoms in-between the SnSe and VSe_2 -layers resulted in slightly negative occupancies. The distance of the interstitial V-atoms to the Se-plane is shorter than the distance between the fully occupied V-position and the Se-layers, which is similar to the behavior observed in the thin film compound and bulk $\text{V}_{1+x}\text{Se}_2$ [19]. For the (1,3) compound the interstitial V-layer resides slightly asymmetric along the superstructure direction as it is shifted closer to the VSe_2 -layer adjacent to the SnSe-layer (see Fig. 4). In both ferecrystalline compounds the VSe_2 -layers exhibit a slight asymmetry, which might affect the transport properties.

Fig. 4. Rietveld refinement results for $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ with $n = 2$ and 3 . The interlayer distances along the c -axis are provided (the dashed lines indicate mirror planes present in the space group $P\bar{3}m1$ at the origin and at 0.5 along the c -direction). The error for all distances is < 0.001 nm. The structural schematics show full occupation of the interstitial V-position.

In an earlier report on ferecrystalline compounds it was demonstrated that off-stoichiometry can result in the formation of stacking faults and/or partial replacement of one layer by the other without interrupting the surrounding layers [23]. In order to confirm the results from

Rietveld refinements and rule out the formation of stacking defects for compounds with $n > 1$, HAADF-STEM images were collected. In Fig. 5a a cross section of the $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_6$ is displayed revealing abrupt interfaces and the intended layering sequence of blocks of 6 consecutive dichalcogenide layers separated by one layer of the SnSe constituent (see also SI for $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_3$) and no indication for the presence of stacking faults can be found. For the (1,1) compound, defect formation is necessary to accommodate any off-stoichiometry due to excess vanadium [24]. No interstitial V-atoms were found between the SnSe and VSe_2 layers in the STEM-cross section of $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_1$. The off-stoichiometry presumably results from volume inclusions or a very small number of stacking faults, because large areas with the expected alternation of SnSe and VSe_2 layers were observed (see SI). Extensive rotational disorder between the constituents, a typical feature of ferecrystalline compounds [25], is observed in all the compounds. Within the VSe_2 blocks the same crystallographic orientation for each layer as expected for a 1T-polytype is observed (see SI). Fig. 5b and c display magnified areas of VSe_2 blocks. In Fig. 5b no interstitial V-atoms are observed, whereas in Fig. 5c bright spots located in the van der Waals gap between two neighboring VSe_2 layers resulting from interstitial V-atoms are clearly present. The inspection of several images suggests the agglomeration of the interstitial V-atoms in distinct areas, most likely due to the requirement of a small lattice expansion to accommodate the additional V-atoms in the structure. The layers displayed in Fig. 5c are comparable to the bulk structure of VSe [26], which is equivalent to a full occupation of the interstitial position in VSe_2 [19], clearly demonstrating the presence of interstitial V-atoms in these compounds.

Fig. 5. HAADF-STEM images of $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_6$. a) An overview displaying the intended layering sequence and highlighting the presence of rotational disorder between the constituents, areas of 6 consecutive layers of $\text{V}_{1+x}\text{Se}_2$, where no interstitial V-atoms (b) and interstitial V-atoms (c) are observed. The stick and ball models of the corresponding VSe_2 and VSe structures [19, 26] with projections along the [110] direction are provided.

3.2 Electrical Properties

The electrical resistivity of all compounds as a function of temperature is displayed in Fig. 6a. The $\text{V}_{1+x}\text{Se}_2$ thin film has a similar room temperature resistivity compared to the bulk single crystalline compound [10]. However, the temperature dependence is less pronounced and the kink at 100 K indicative for the charge density wave transition is hardly visible. This

observation is consistent with reports on the effect of non-stoichiometry on the CDW transition in bulk $V_{1+x}Se_2$, where small amounts of interstitial V-atoms cause a suppression of the CDW state [9]. The c/a -ratio of the thin film compound (1.80) is slightly smaller than the one reported for stoichiometric VSe_2 (1.82) [10]. The $([SnSe]_{1.15})_1(V_{1+x}Se_2)_1$ compound has an abrupt increase in resistivity similar to that reported for stoichiometric $([SnSe]_{1.15})_1(VSe_2)_1$. [11] Increasing the layer thickness of the VSe_2 above $n = 1$ dramatically changes the magnitude of the charge density wave transition (Fig. 6). Interestingly, the $([SnSe]_{1.15})_1(V_{1+x}Se_2)_2$ compound exhibits a higher electrical resistivity than $([SnSe]_{1.15})_1(V_{1+x}Se_2)_1$. Further increase of the VSe_2 -layer thickness results in a continuous decrease in resistivity. All ferecrystalline compounds show a significantly smaller temperature dependence of the electrical resistivity compared to the bulk and thin film compounds (see Table 2), which results directly from the rotational disorder between the constituents and thus a reduced scattering of the charge carriers by phonons. The changes in the resistivity as n is increased are similar to that reported previously for stoichiometric compounds [12].

Fig. 6. Electrical resistivity as a function of temperature for $([SnSe]_{1.15})_1(V_{1+x}Se_2)_n$ with $n = 1 - 6$ and a $V_{1+x}Se_2$ thin film. For comparison the data of single crystalline bulk VSe_2 [10] are plotted.

The temperature dependent Hall coefficient of all compounds corroborates the results from the electrical resistivity (Fig. 7), with the $([SnSe]_{1.15})_1(V_{1+x}Se_2)_1$ sample exhibiting a distinctly different behavior due to quasi 2-dimensionality [12]. The samples with n greater than one show behavior similar to the bulk, perhaps resulting from the crystallographic orientation of the consecutive VSe_2 layers within each block in the 1T-polytype leading to 3 dimensional behavior. This strong dependence on dimensionality might arise from the unique nature of the charge density wave transition in VSe_2 [27, 28]. The similarity of the resistivity anomaly in the (1,1) compound to the stoichiometric (1,1) compound previously published supports the absence of interstitial V-atoms between the SnSe and VSe_2 layers suggested by the diffraction and STEM data. The presence of interstitial V-atoms in the ferecrystalline compounds with $n > 1$ does not significantly alter their transport properties compared to the stoichiometric

compounds either [12]. As the thickness of the VSe_2 constituent increases, the magnitude of the positive Hall coefficient decreases and changes sign at temperatures between 4 - 20 K for $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ with $n = 2$ and 3, and this sign change shifts to 60 K for $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_6$. Similar to the bulk compound, the thin film sample of $\text{V}_{1+x}\text{Se}_2$ is an n-type conductor. However, the kink at the CDW transition temperature is less pronounced compared to the stoichiometric bulk single crystal [10] and stretched out over a wider temperature range.

Fig. 7. Hall coefficient as a function of temperature for $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ with $n = 1 - 6$ and a $\text{V}_{1+x}\text{Se}_2$ thin film. For comparison the data of single crystalline bulk VSe_2 [10] are plotted.

Table 2. Electrical resistivity ratio, carrier concentration at room temperature, carriers/V-atom at RT and RT carrier mobility for $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ with $n = 1 - 6$, a $\text{V}_{1+x}\text{Se}_2$ thin film, and bulk VSe_2 [10].

compound	$\rho_{\text{RT}}/\rho_{150\text{K}}$	$n_{\text{RT}}, *10^{21}$ cm^3	Carriers/V- atom	Carrier mobility μ , $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$
(0,1)	1.8	200	10.6	0.14
(1,1)	1.2	6.4	0.6	3.28
(1,2)	1.1	10.4	0.8	1.63
(1,3)	1.1	15.4	1.0	1.42
(1,4)	1.1	20.3	1.1	1.08
(1,5)	1.1	21.2	1.1	1.06
(1,6)	1.1	25.1	1.3	0.92
VSe_2 [10]	2.0	90	5.4	0.31

Carrier concentrations and mobilities at room temperature were calculated for all compounds assuming a single band approximation and are listed in Table 2. The carrier concentration of the thin film sample of $\text{V}_{1+x}\text{Se}_2$ is higher than that calculated from Bayard's results [10], probably due to the presence of interstitial V-atoms that introduce additional electrons into the conduction band. The number of 10.6 carriers/V-atom is more than double the number reported for stoichiometric bulk VSe_2 (5.4 carriers/V-atom), which cannot be explained by the additional electrons from the 0.13 interstitial V-atoms. For the ferecrystalline compounds the carrier concentration increases systematically as a function of n . However, comparing the carriers/V-atom based on the composition from EPMA results in an almost constant carrier

concentration/V-atom at room temperature for compounds with $n > 2$. Only for the (1,1) and (1,2) compound the carriers/V-atom remain below 1, suggesting charge transfer between the constituent layers [29].

The positive sign of the Hall-coefficient indicating holes as the majority carriers at room temperature for all ferecrystals, rather than electrons as observed for the bulk and thin film compounds, along with the changing sign of the Hall coefficient with temperature all point toward a more complex electronic structure. Possible explanations are a different band splitting induced by a change in the c/a -ratio of the VSe_2 constituent (see Table 1) in the intergrowth compounds and/or changes in the relative mobility of different bands. The c/a ratio of the VSe_2 constituent is smaller than for the bulk sample and the thin film sample (see Table 1). Theoretical calculations demonstrated that the band structure of VSe_2 is very sensitive to the c/a -ratio and compared to other 1T-structures is closer to a trigonal prismatic splitting of the d -bands [30], where p-type conduction is reported for isovalent $2H-NbSe_2$ and $2H-TaSe_2$ [31]. Such a band splitting could be induced by the interaction between the two constituents in the $([SnSe]_{1.15})_1(V_{1+x}Se_2)_n$ compounds. The (1,1) sample has a significantly higher mobility again indicating a change in dimensionality has a large effect on the transport properties of the compounds. All ferecrystalline compounds have a higher mobility than the bulk or the thin film sample and the value slightly decreases with increasing VSe_2 thickness. The reduced carrier mobility for the ferecrystalline compounds with $n > 1$ could arise from the slight asymmetry of the VSe_2 constituent along the c -direction as well as the presence of interstitial V-atoms, which decreases the carrier mobility in the thin film compound compared to bulk.

4. Conclusions

A series of ferecrystalline compounds $([SnSe]_{1.15})_1(V_{1+x}Se_2)_n$ with $n = 1 - 6$ and a thin film $V_{1+x}Se_2$ were synthesized utilizing the modulated elemental reactant technique. The presence of interstitial V-atoms ($0.13 \leq x \leq 0.42$) in the thin film sample as well as in the intergrowth compounds with $n > 1$ between two TMD layers was confirmed by Rietveld refinement and inspection of HAADF-STEM cross sections. The interstitial V causes an expansion of the VSe_2 constituent along the superlattice direction and the amount correlates with the in-plane lattice parameters of the dichalcogenide. The area of the SnSe constituent adapts to this change in a way to keep the misfit parameter at 0.15 for all compounds. Compared to bulk $V_{1+x}Se_2$ the trend of the lattice parameters as a function of x is reversed. Similar to off-stoichiometry in bulk compounds, the charge density wave transition in the n-type thin film $V_{1.13}Se_2$ sample is strongly suppressed. In the intergrowth compounds $([SnSe]_{1.15})_1(V_{1+x}Se_2)_n$ with $n = 2 - 6$, the temperature dependence of the electrical resistivity is less than found in VSe_2 . All of the $([SnSe]_{1.15})_1(V_{1+x}Se_2)_n$ samples have a positive Hall coefficient at room temperature. $([SnSe]_{1.15})_1(V_{1+x}Se_2)_1$ has a large anomaly in both resistivity and Hall effect attributed to a charge density wave state, resulting from the quasi 2-dimensionality of the isolated single VSe_2 layer. Interestingly, while the carrier concentration increases with increasing VSe_2 layer thickness, the carrier mobility decreases.

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HAADF-STEM image displaying the presence of interstitial V-atoms in the
ferrecrystalline compounds $([\text{SnSe}]_{1.15})_1(\text{V}_{1+x}\text{Se}_2)_n$ with $n = 1, 2, 3, 4, 5$, and 6.