

SYNTHESIS OF MULTIPLE CONSTITUENT FERECRYSTAL
HETEROSTRUCTURES

by

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DISSERTATION ABSTRACT

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Title: Synthesis of Multiple Constituent Ferecrystal Heterostructures

The ability to form multiple component heterostructures of two-dimensional materials promises to provide access to hybrid materials with tunable properties different from those of the bulk materials or two-dimensional constituents. By taking advantage of the unique properties of different constituents, numerous applications are possible for which none of the individual components are viable. The synthesis of multiple component heterostructures, however, is nontrivial, relying on either the cleaving and stacking of bulk materials in a “scotch tape” type technique or finding coincidentally favorable growth conditions which allow layers to be grown epitaxially on each other in any order. In addition, alloying of miscible materials occurs when the modulation wavelength is small. These synthetic challenges have limited the ability of scientists to fully utilize the potential of multiple component heterostructures. An alternative synthetic route to multiple component heterostructures may be found through expansion of the modulated elemental reactant technique which allows access to metastable products, known as ferecrystals, which are otherwise inaccessible.

This work focuses on the expansion of the modulated elemental reactants technique for the formation of ferecrystals containing multiple constituents. As a starting point, the synthesis of the first alloy ferecrystals $(\text{SnSe})_{1.16-1.09}([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)$ will be

discussed. The structural and electrical characterization of these compounds will then be used to determine the intermixing of the first three component ferecrystal heterojunction $([\text{SnSe}]_{1+\delta})([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})([\text{SnSe}]_{1+\delta})(\{\text{Nb}_y\text{Mo}_{1-y}\}\text{Se}_2)$. Then, by synthesizing $([\text{SnSe}]_{1+\delta})_m([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ ($m = 0 - 4$) compounds with increasing thicknesses of SnSe, the interdiffusion of miscible constituents in ferecrystals will be studied. In addition, by comparison of the $([\text{SnSe}]_{1+\delta})_m$ $([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ ($m = 0 - 4$) compounds to the $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ ($m = 1 - 8$) compounds the electronic interactions of the MoSe_2 and NbSe_2 layers will be determined. Finally, the effects of different alloying strategies and the interdiffusion of miscible constituents will be further examined by the synthesis of ordered $([\text{SnSe}]_{1.15})_1([\text{Ta}_x\text{V}_{1-x}]\text{Se}_2)_1([\text{SnSe}]_{1.15})_1([\text{V}_y\text{Ta}_{1-y}]\text{Se}_2)_1$ and $([\text{SnSe}]_{1+\delta})([\text{Ta}_x\text{V}_{1-x}]\text{Se}_2)$ compounds with the effect of isoelectric doping on the charge density wave transition in $(\text{SnSe})_{1.15}(\text{VSe}_2)$ also being explored.

This work contains previously published and unpublished co-authored material.

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CHAPTER I

INTRODUCTION

I.1. Authorship Statement

Chapter I contains material published in the *Journal of Solid State Chemistry* in 2015, doi:10.1016/j.jssc.2015.08.018 ahead of print. Co-author Ryan A. Atkins and Dr. Matthias Falmbigl assisted in the synthesis of some of the initial compounds. Co-author Jeffrey J. Ditto performed microscopy measurements. Dr. Dr. David C. Johnson is my advisor and I am the primary author of the manuscript.

I.2. Background

New synthetic methods have been critical both to advance scientific understanding as well as to advance technology. Traditional approaches have historically focused on using thermodynamic control to make desired products, for example growing doped silicon crystals from a melt of fixed composition. Phase diagrams were determined to understand the thermodynamic relationships between compounds. Kinetic control, typically achieved by controlling temperature as a function of time, was used to influence the microstructure. The search for new materials focused on finding reaction conditions where new compounds would be thermodynamically stable. High temperature synthesis and the growth of new materials from melts were commonly used to overcome slow solid state diffusion rates and to form single crystals for structure determination. New compounds and new phenomena are discovered whenever new approaches are developed, such as vapor transport reactions in the 1960's,^{1,2} or new adaptations, such as the use of low temperature fluxes,^{3,4} are explored. A grand challenge in the field of materials discovery is the development of approaches to predict new structures and the

properties associated with specific compositions, and the development of approaches that will enable their synthesis. Historically, serendipity played a significant role in most new discoveries as unexpected compounds formed in reaction mixtures.

An example of a new crystal growth technique that has significantly advanced both scientific understanding and technology is the development of molecular beam epitaxy (MBE). In the 1960's there was much interest in producing new semiconducting materials with specific compositions and specific doping profiles required for new devices. The development of MBE by Arthur and Cho,⁵⁻¹⁰ was a significant breakthrough because it enabled new materials to be created with known structure and designed composition modulations. The MBE process involves directing a flux of the respective elements at a heated substrate with the goal of controlling the surface equilibrium. The temperature of the substrate controls the surface diffusion rates, such that atoms can find favorable surface sites, and the desorption rates of different species. The relative fluxes of the sources to the surface control the surface composition by balancing the arrival rates with the desorption rates. Done correctly, and when the lattice mismatch between the film and the substrate is slight, the process results in the growth of solids with the structure of the substrate but composition controlled by the fluxes of reactants. Composition gradients can be kinetically trapped via the epitaxial growth process, because the volume diffusion rates at the temperatures used are small compared to the surface diffusion rates. MBE growth has yielded new materials with exceptional properties, as materials with designed structural sequences can be prepared with very low defect levels due to low growth temperatures. An example of an exceptional property resulting from MBE growth is very high mobility values produced when dopants are incorporated in a layer that then donates

the resulting carriers to another layer in the grown structure. This process is referred to as modulation doping.¹¹ The lack of dopant atoms in the transport layer, which normally scatter the charge carriers, results in the exceptionally high mobility values. These new materials have led to the discovery of new phenomena including the fractional Hall effect.^{12,13}

The ability to anticipate structures that could be prepared via MBE resulted in theoretical predictions of new phenomena, which resulted in new technologies. Light emitting diodes (LED) are one example where predictions were made about the materials properties and architectures required to observe the emission of light from a diode. Once the phenomenon was observed, predictions were made about how to optimize efficiency and how to produce white light from a LED. MBE practitioners determined how to grow and optimize the predicted structures and the resulting LED technology continues to be enhanced today. An important implication is that synthesis routes that yield materials with predictable structures and compositions enhance synergies between theory and experiment. Starting with reasonable assumptions about structure makes calculations easier and enables extrapolations from existing data, both of which facilitate transforming ideas into technologies.

There is currently significant interest in two-dimensional materials, particularly (2-D) - single structural units that are not epitaxially connected to the structure of the substrate, and the stacking of these layers to make 2-D heterostructures, because of the promise of properties that do not exist in the bulk materials or that are enhanced in the heterostructure relative to the bulk or the individual 2-D constituents. The layer-by-layer design provides clear structural starting points for theory, and the surface states present in

these 2-D layers have resulted in novel classes of materials such as topological insulators - materials that are bulk insulators but whose surfaces contain conducting states. There is a growing list of potential constituents accompanied by criteria to evaluate stability of potential 2-D layers that have yet to be tried. Heterostructures are an ideal class of materials for the materials genome project to explore materials by design because of their defined starting structure.

Approaches to preparing individual 2-D layers have been developing over time. Initially the preparation was based on the effective but technically challenging cleaving of bulk crystals followed by searching for single constituent layers. More recently, recipes have been developed to prepare individual layers on specific substrates by reaction of surface layers or growth from vapor phase precursors. Examples of materials prepared to date via these recipes include MoS_2 ,^{14,15} WS_2 ,¹⁶⁻¹⁷ Silicene¹⁸⁻²⁰ and ZrS_2 ,²¹ all materials with anisotropic structures. Preparing 2-D heterostructures is much more challenging, as the growth techniques developed for individual 2-D layers are typically not compatible with the sequential growth of one constituent on top of another. Indeed the most common approach to making heterostructures has been the cleaving and stacking of individual layers, which has been described as being analogous to building with Lego blocks. While this technique has yielded many new and exciting structures, it is an exacting task only done by a few groups with very low yield²²⁻²⁷ and is limited to small sample areas. It is also limited to those compounds that can be cleaved into a single layer thick 2-D layer and that are stable as an atomically thick layer. Geim has suggested three criteria for stability based on existing data.²⁸ He suggests that 1) the parent 3D structure should have a melting temperature above 1000 °C so that the 2D sheet is stable

at room temperature, 2) the 3D structure must be chemically inert so that no decomposed surface layer forms in air or any other environment, and 3) that insulating and semiconducting 2D-crystals are more likely to be stable compared to metallic ones. There is a need for a flexible synthesis approach that is scalable, enables constituents to be layered without epitaxial relationships between layers, and that is applicable to a wide variety of constituents.

I.3. Modulated Elemental Reactants

The modulated elemental reactant (MER) synthesis approach has been developed over the last two decades at the University of Oregon and is based on controlling local composition and diffusion lengths to control the kinetics of phase formation. The initial concept was that by depositing sequential elemental layers, the layer thicknesses could be reduced such that the layers would mix at low enough temperatures that mixing would be complete before interfacial nucleation could occur. This is illustrated schematically in Figure I.1. The initial ratio of layer thicknesses would control the composition of the amorphous intermediate formed. It was shown that the composition of the amorphous intermediate could control the subsequent nucleation process enabling compounds to be formed kinetically even if they are not thermodynamically stable at the reaction conditions.³⁰ A high level of selectivity can be achieved. By designing precursors that closely mimic the local composition and structure of targeted compounds, diffusion lengths are greatly reduced relative to more traditional synthetic approaches, which allows much lower reaction temperatures and shorter times to be used than conventional methods. The combination of mild annealing conditions and the ability to easily modify

the precursor structure allows numerous metastable compounds to be formed, which cannot be accessed using other techniques.³¹⁻³⁵

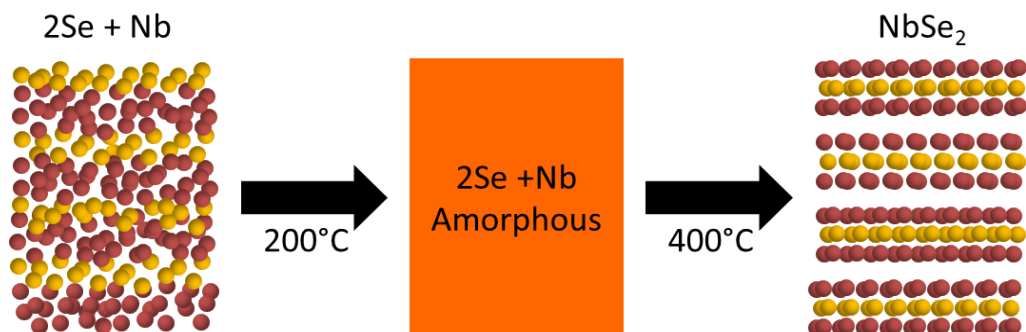


Figure I.1. Schematic of a layered precursor showing the interdiffusion of the layers to form an amorphous intermediate and the subsequent nucleation of the targeted compound.

The structural complexity of products can be increased by adding additional layers with different compositions, leading to the formation of new layered solids containing constituents with different structures. These new compounds can be prepared by combining the precursor layering schemes for single component systems. The structure and composition of each layer is controlled by the composition and thickness of the layer in the precursor. Variations to the layering scheme (nanoarchitecture) of the product can be achieved by simply changing the layering scheme of the precursor. This is illustrated in Figure I.2, where the center structures can be combined to yield three different families of layered structures containing two constituents each. The thickness of each block can be individually controlled as well as the order of the layers, resulting in over 20,000 distinct nanoarchitectures for n and m less than 10.³⁶ The three constituents can also be combined into one heterostructure, either by alloying the constituents that have a common structure,³⁷ to form a random (A,B)C alloy, or by preparing three component heterostructures with distinct layers of each constituent forming an ordered

ABAC alloy. These two possibilities provide access to a large number of new compounds, many more than one would like to make, so the challenge is to understand how properties change as the constituent thicknesses, order, and composition are varied to accelerate the search for the optimum properties for a particular application. In the following sections we outline how this approach can be used to prepare increasingly complex compounds with the structure of the initial precursor controlling the nucleation of individual layers and the resulting nanoarchitecture of the final product.

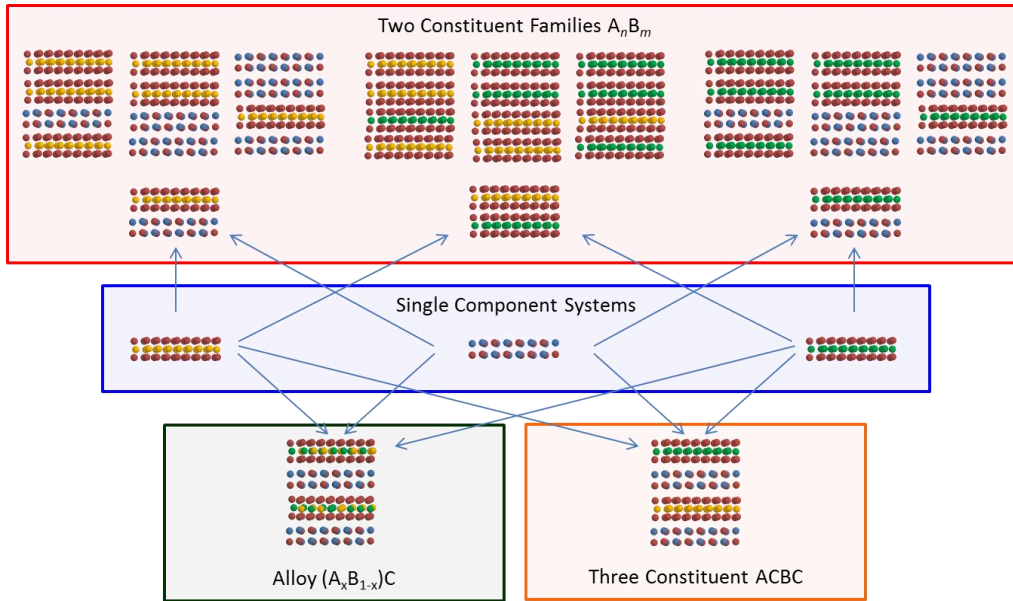


Figure I.2. Synthesis scheme of complex systems built from simpler constituents. The blue box shows the thinnest structural units of three representative binary constituents, the outside two with a transition metal dichalcogenide structure (TSe_2 and $T'Se_2$) and the middle one a rock salt structure (MSe) with two (001) planes. The second row in the red box displays the three simplest binary heterostructures, $(MSe)_1(TSe_2)_1$, $(TSe_2)_1(T'Se_2)_1$ and $(MSe)_1(T'Se_2)_1$. The top row shows the three compounds with the next smallest repeating units, A_1B_2 , A_2B_2 and A_2B_1 , illustrating how the constituents can be assembled with different individual thicknesses and, for thicker repeats, different orders of assembly. The bottom row contains a schematic of compounds where the dichalcogenides have been alloyed to form the compound $(MSe)_1(T_{1-x}T'_xSe_2)_1$ (green box). The thickness of each constituent can be controlled as shown in the top row for the pure dichalcogenides. The image on the bottom left (orange box) shows an ordered alloy, where the three components form the $(MSe)_1(TSe_2)_1(MSe)_1(T'Se_2)_1$ compound. The A, B, and C components can be combined in different thicknesses and sequences to make a very large number of unique nanoarchitectures.

I.3.1. Single Component Systems

The simplest materials to form by MER are compounds containing multiple elements but only one structure or type of material, for example a binary rock salt structure or transition metal dichalcogenide structure. These single constituent systems are the building blocks of the more complex materials to be discussed later. The synthesis of these single constituent systems has provided insights into the formation mechanism as the layered precursor system interdiffuses and ideally nucleates into the desired structures. The interdiffusion of the thin elemental layers in the precursors was shown in the early 1980's to be a low temperature route to amorphous alloys.³⁸ These mechanistic insights are useful in understanding the evolution and resulting structure and properties of more complex systems containing several constituents. The calibration schemes used for these simple component systems are also applied in the design of the precursors required to form more complex materials.

Calibration of the modulated precursors for single component systems consists of two basic steps. The first step is to adjust the relative deposition times of each element to ensure the desired composition. In a binary system, two elements are deposited typically holding the deposition time of one constituent constant while systematically varying the deposition time of the other. For example, in the calibration of NbSe₂ depicted in Figure I.3, the deposition time of Se is held constant while that of the Nb is incrementally changed. Compositional analysis confirms a linear relationship between the atomic ratio of the elements and the ratio of the deposition times, with the slope related to the proportionality factor between the deposition rates measured by the quartz crystal monitors and the actual deposition rates at the sample surface. Scaling deposition times of

all sources equally, yields the same composition but different repeat thicknesses. The graph in Figure I.3 enables the deposition time corresponding to the desired Nb/Se composition ratio to be interpolated, which can then be scaled to deposit a specific thickness of a desired composition. Typically, a 3-5% excess of selenium is used to compensate for losses during annealing of the precursors to transform them into the targeted products.

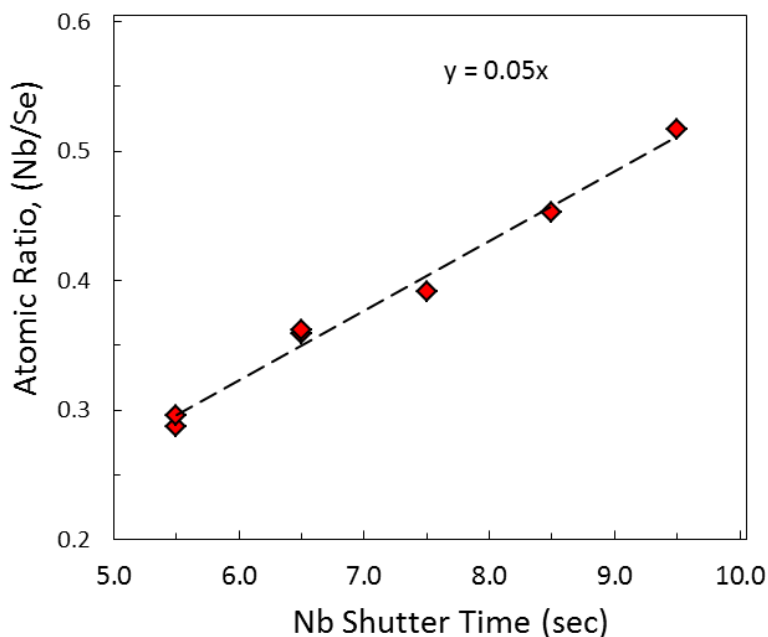


Figure I.3. A graph of the Nb/Se ratio determined from electron probe microanalysis versus the deposition time of niobium, with the deposition time of selenium held constant for all samples. The dashed line is a linear fit through the experimental points.

Once the composition of the precursor is correct, it is crucial that the thickness of the layering is thin enough that the layers interdiffuse before interfacial nucleation occurs. This is the second step in the calibration. Low temperature annealing causes interdiffusion, and if the layers are thin enough this results in an amorphous intermediate with a constant composition. The average composition has a large impact on what

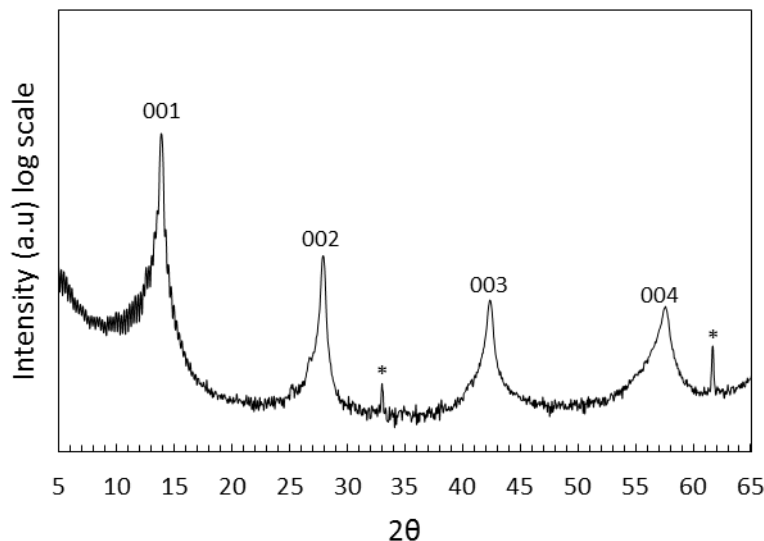


Figure I.4. 00/ diffraction pattern of NbSe₂ formed at 400°C by annealing a precursor containing Nb/Se elemental bilayers. The y axis is log intensity to highlight low intensity diffraction maxima. Only the 00/ reflections are observed due to the textured nature of the product. Substrate peaks are indicated with an asterisk.

crystallizes as nucleation is controlled by local composition. Figure I.4 contains a diffraction pattern of a sample with a composition ratio of one to two of Nb to Se after annealing at 400°C. The intensity of the peaks depends on both the percent of the precursor that has crystallized as well as the extent of preferred alignment of the crystallites. The sharpness of the diffraction peaks reflects the size of coherently scattering crystalline domains. As shown in Figure I.5, the intensity of the peaks of the assembled ferecrystal are sensitive to composition, presumably due to a combination of a reduced amount of product crystalized and the reduced size of the crystallites with increasing deviations of the precursor from the composition corresponding to the stoichiometry of the crystalizing compound. This is presumably caused by the increasing non-stoichiometry at the growing crystallites as the excess element is excluded from the

growing crystal. This variation in intensity provides an additional guide when optimizing the correct composition and thickness of the precursor.

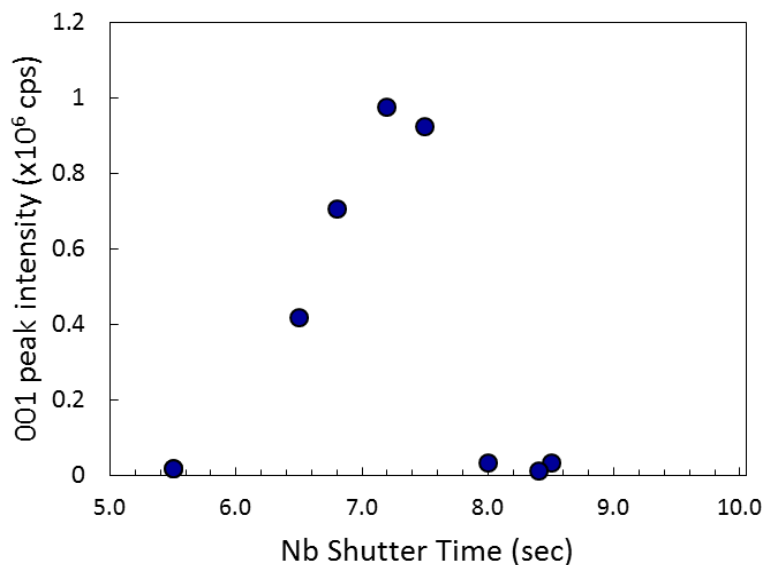


Figure I.5. The intensity of the first observed 00 l reflection of NbSe₂, formed at 400°C, as a function of shutter time depositing Nb at a constant rate. The maximum in the intensity corresponds to the precursor with a 1:2 ratio of Nb to Se.

The goal of the second calibration step is to optimize the thickness of the repeating sequence of elemental layers in a way that each deposited layer evolves into a single structural unit of the targeted constituent, for example, a single Mo/Se bilayer would evolve into one Se-Mo-Se trilayer. The thickness of a single repeating sequence of deposited atomic layers can be determined from an analysis of the X-ray reflectivity (XRR) pattern of the precursor (Figure I.6). The XRR patterns contains Bragg reflections from the repeating sequence of layers and Kiessig fringes, which result from the interference pattern from the front and back of the film and intensity from the incomplete destructive interference of the finite number of layers. A plot of monolayer thickness versus deposition time, as depicted in Figure I.7, allows the deposition times that correspond to a desired repeat thickness to be determined. If the correct repeat thickness

is used, then the number of repeats in the precursor is equal to the number of repeats in the final product.

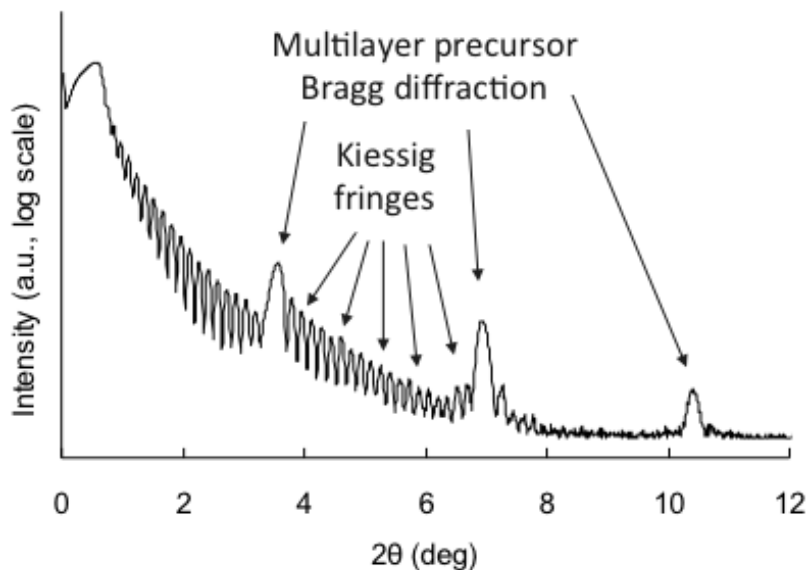


Figure I.6. XRR pattern of an amorphous layered precursor showing Bragg peaks from the multilayer structure and Kiessig fringes from the finite thickness of the sample.

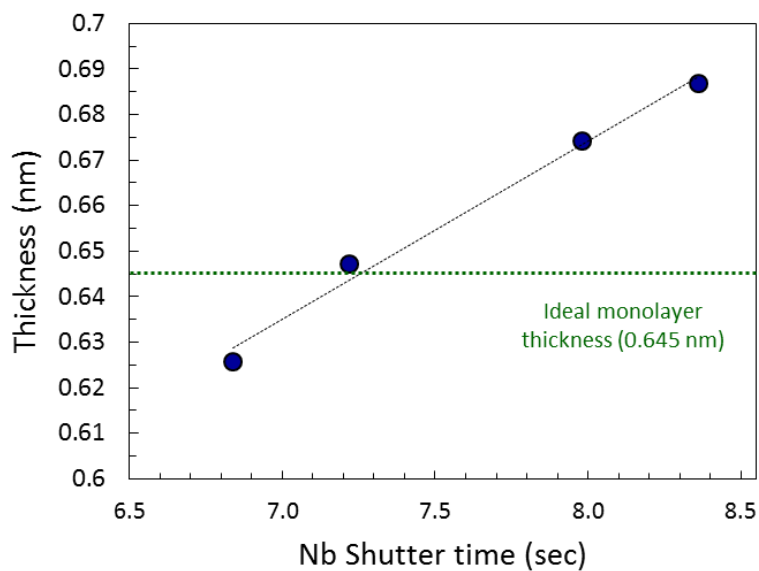


Figure I.7. A plot of the repeating Nb-Se thickness versus the deposition time of the niobium layer. The Se thickness is also being scaled to maintain a constant composition.

For example Figure I.8 contains an NbSe₂ sample in which 58 repeats were deposited giving a product with 58 repeating units by XRR. Having calibrated the thickness in this manner, the number of repeating structural units in the crystalline sample is precisely controlled by changing the number of repeats in the precursor. Samples containing from 2 to 80 repeating structural units have been prepared using this method.³⁹

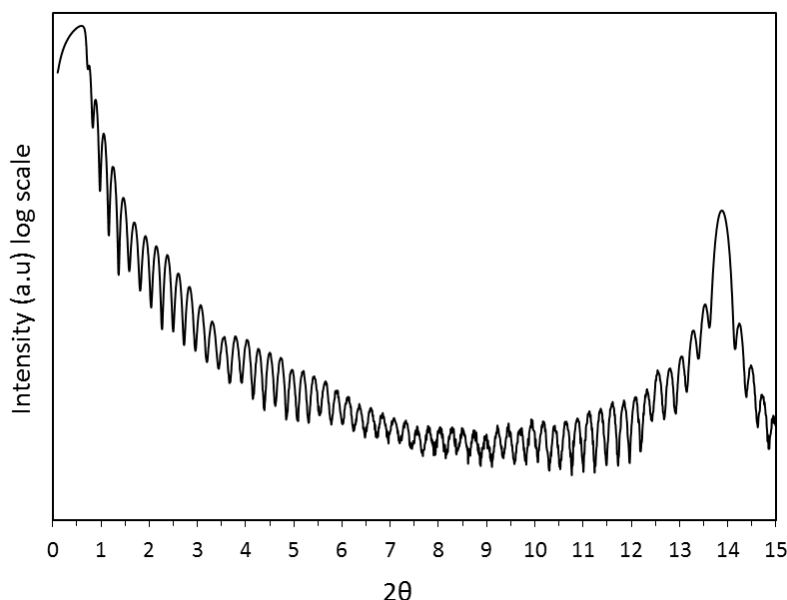


Figure I.8. An XRR pattern of a sample containing 58 repeating NbSe₂ trilayers prepared from a precursor containing 58 repeating Nb-Se bilayers in the repeating precursor.

The preparation of metastable crystalline compounds is a challenge and requires control of both nucleation and growth of the targeted compound. The preparation method described above has turned out to be effective for the synthesis of metastable crystalline samples with varying chemical compositions that cannot be obtained applying classical approaches.⁴⁰⁻⁴³ The key for the success of the method is a drastic reduction of the diffusion length to some nm or even down to few Å. As a consequence interdiffusion,

nucleation and crystallization occur at low temperatures compared to classic approaches of preparing of inorganic solids.⁴⁴⁻⁴⁶

In order to form more complex systems, the calibration procedure needs to be repeated for each single component system. The calibration of multiple-component systems then made much easier if the single component calibrations are available, as discussed next.

I.3.2. Two Component Systems

The calibration of a precursor designed to form a two-component compound follows the same logical process used for the single component precursor, but the additional constituent adds additional elements that need to be calibrated, requiring more steps. The calibration of the relative compositions and thicknesses of all of the layers in the repeating sequence of elemental layers for two component systems is made easier if the deposition parameters for each of the constituents have already been independently calibrated. In this case, the first step in the calibration is to adjust the relative amount of each of the constituents. The relative amounts depends on the different entities being layered, as there will be a misfit in area between the constituents that depends on the crystal faces of the constituents that are adjacent to one another and the unit cell parameters. This results in a factor $1 + \delta$, where δ is the so called misfit parameter, reflecting the differences, or mismatch, of the lattice parameters of the adjacent planes at the interface between the two constituents giving rise to different numbers of formula units per area. When making derivatives of known compounds containing two different constituents, the desired ratio is simply the reported misfit parameter for the two constituents. When attempting to create new compounds between two constituents that

have not been layered before, assumptions about the adjacent crystal phases are made and the bulk lattice parameters are used to calculate misfits. The second step in the calibration is to prepare samples at the desired composition ratios by holding the deposition times of one constituent constant while those of the other are systematically scaled. Plotting the composition ratio versus the deposition time of the varied constituent yields a calibration curve from which the deposition time yielding the desired atomic ratio for the elements can be determined. The third step is to scale thickness of two constituents so that the layers deposited for each constituent yields a single crystallographic unit.

The following example illustrates the process. In the calibration of the SnSe - NbSe₂ system, the difference in area between the (001) planes of SnSe and the (001) planes of NbSe₂ is 1.16 obtained either from the known misfit compound or by using the lattice parameters of the bulk compounds as an estimate. To find the ratio of deposition times to obtain this Sn/Nb ratio, the Nb and Se deposition times of the NbSe₂ constituent are held constant while the deposition times of the Sn and Se precursor layers for the SnSe component are systematically scaled. A plot of the Sn/Nb ratio vs the amount of time the Sn shutter is open results in a linear relationship, shown in Figure I.9, for the specific deposition rates and geometry used. This experimental relationship enables the deposition time that gives a Sn/Nb ratio equal to the known misfit parameter for this compound to be determined. After the appropriate composition is achieved, scaling the deposition times of all elements together to achieve the thickness such that layers in the precursor evolve into single structural units of each constituent completes the calibration. If the thicknesses were correct for each of the single component systems, the thickness

after scaling the compositions are usually pretty close for the two component system, which simplifies this step.

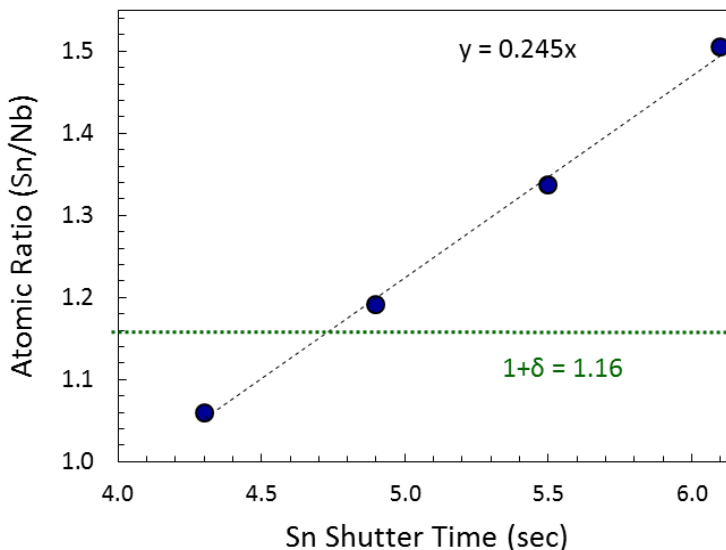


Figure I.9. The variation in the atomic Sn/Nb ratio as a function of the amount of time the Sn shutter is opened. The dotted green line shows the misfit ratio for the SnSe - NbSe₂ system, so the Sn shutter needs to be opened for 4.7 seconds to obtain a Sn/Nb ratio of 1.16.

Using different single component systems as building blocks, a variety of two component systems can quickly be calibrated, precursors prepared, and precursors annealed to form targeted compounds. For example, Figure I.10 contains the specular diffraction patterns for four different $([\text{SnSe}]_{1+\delta})_1(\text{TSe}_2)_1$ compounds with $\text{T} = \text{V}, \text{Nb}, \text{Mo}$ and Ta . The specular diffraction patterns for all of these compounds are similar, but the intensities of the $00l$ reflections vary mainly due to the different scattering factors for the transition metals in the dichalcogenide component. The c -axis lattice parameters of all of the compounds are similar and can be thought of as the sum of the thickness of two (001) planes of SnSe and a Se-T-Se trilayer. Figure I.11 contains the in-plane X-ray diffraction patterns of the same four $([\text{SnSe}]_{1+\delta})_1(\text{TSe}_2)_1$ compounds with $\text{T} = \text{V}, \text{Nb}, \text{Mo}$ and Ta .

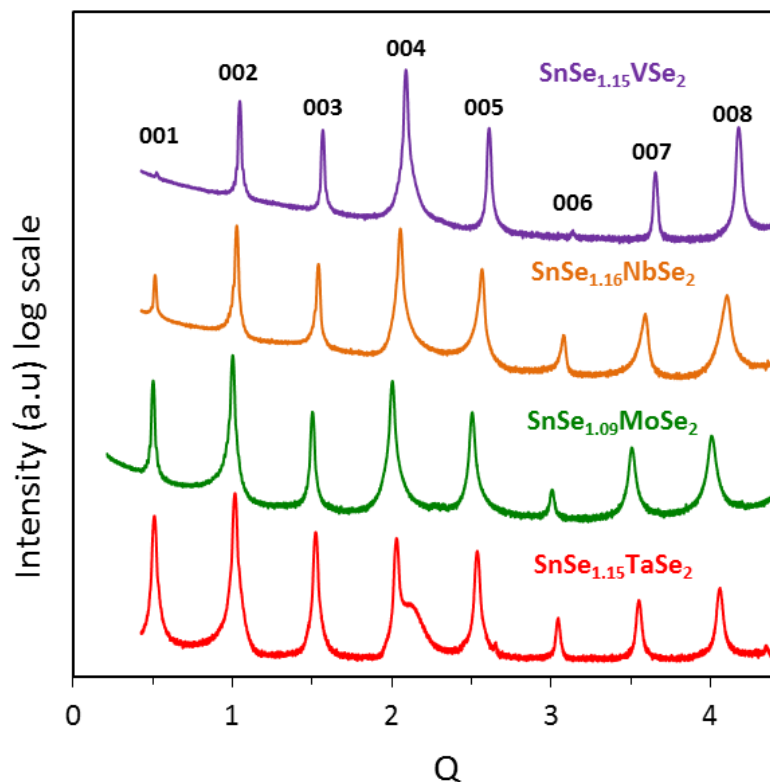


Figure I.10. Specular diffraction scans of $([\text{SnSe}]_{1.15})_1(\text{VSe}_2)_1$, $([\text{SnSe}]_{1.16})_1(\text{NbSe}_2)_1$, $([\text{SnSe}]_{1.09})_1(\text{MoSe}_2)_1$, and $([\text{SnSe}]_{1.15})_1(\text{TaSe}_2)_1$. All of the diffraction peaks are 00 l reflections, and the indices for each reflection are indicated above the scan of the $([\text{SnSe}]_{1.15})_1(\text{VSe}_2)_1$ sample. All samples were annealed at 400°C for 20 minutes.

The reflections in the in-plane diffraction scans of these compounds can be indexed as two families of reflections, each arising from one of the constituents. The in-plane lattice parameters of SnSe do not vary as much as the in-plane a -axis lattice parameter of the transition metal dichalcogenides, leading to the different misfit parameters. In contrast to the crystalline misfit compounds prepared at high temperature, which typically have one commensurate in-plane axis, the in-plane lattice parameters of the constituents in the compounds prepared using the MER approach remain incommensurate. Figure I.12 contains a representative high angle annular dark field scanning transmission microscopy (HAADF-STEM) image of $([\text{SnSe}]_{1.15})_1(\text{VSe}_2)_1$. The image shows the regular stacking of

the two constituent layers and the random rotational disorder between layers. Due to this extensive random rotational disorder found in all the misfit layer compounds prepared using the MER approach, the term "ferecrystal", from the Latin "fere" meaning almost, has been created to describe them.

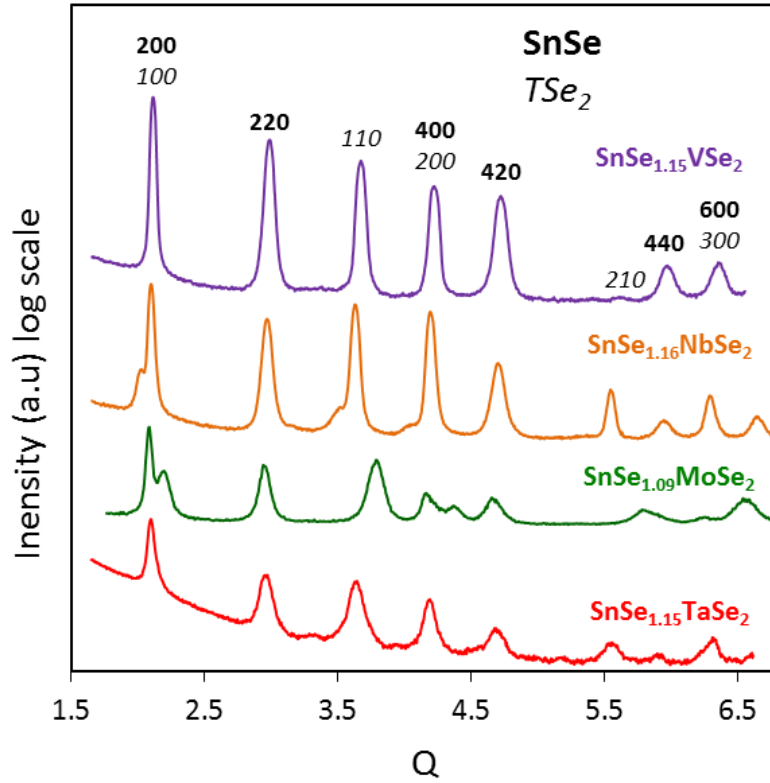


Figure I.11. In-plane diffraction scans of $([\text{SnSe}]_{1.15})_1(\text{VSe}_2)_1$, $([\text{SnSe}]_{1.16})_1(\text{NbSe}_2)_1$, $([\text{SnSe}]_{1.09})_1(\text{MoSe}_2)_1$, and $([\text{SnSe}]_{1.15})_1(\text{TaSe}_2)_1$. All of the diffraction peaks can be indexed as $(hk0)$ reflections of the two constituents. The indices for each reflection are indicated above the scan of the $([\text{SnSe}]_{1.15})_1(\text{VSe}_2)_1$ sample.

In addition to these four compounds, many other members of these $([\text{SnSe}]_{1+\delta})_m(\text{TSe}_2)_n$ families compounds have been prepared as well as quite a few additional families as summarized in Table I.1. Several ferecrystals containing two different dichalcogenides have been prepared, although the extent of intermixing of the transition metals was not determined, because it is very difficult to experimentally determine the

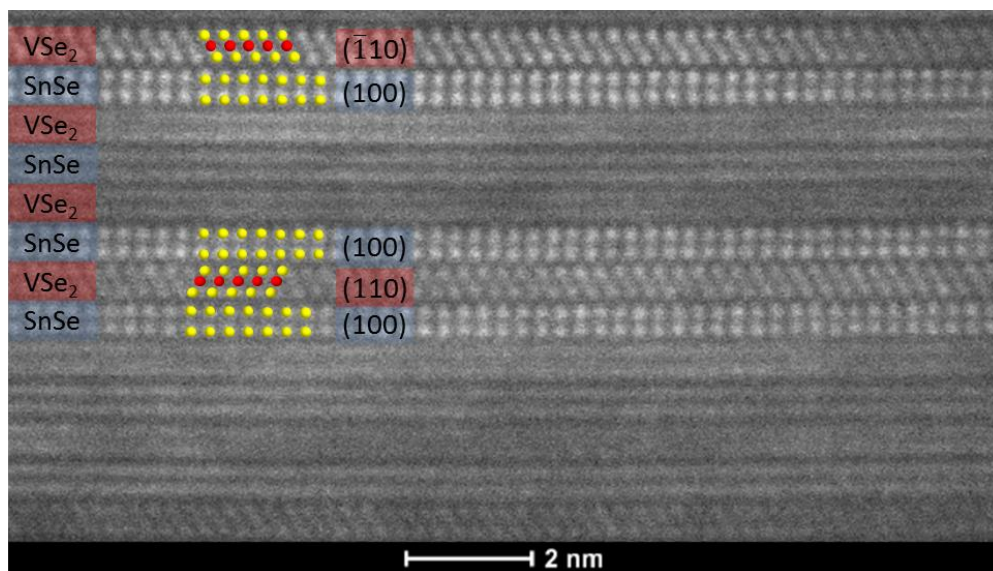


Figure I.12. Cross sectional HAADF STEM image of $([\text{SnSe}]_{1.15})_1(\text{VSe}_2)_1$.

extent of alloying. Two different dichalcogenide- M_2Te_3 systems have been investigated to date, with a large range of different thicknesses of the two constituents. There is an atomically abrupt structural change between the constituents, and the chemical difference between the two structures results in an abrupt composition change as well. The same is true for the dichalcogenide-rock salt compounds, for which the largest number of compounds have been prepared and the most extensive structural studies have been conducted. To our knowledge, this approach has not been tried on other constituents, except for one report of the formation of intergrowths of CoSb_3 and IrSb_3 . While a superlattice was observed, it was not crystallographically aligned with the substrate, making structural characterization challenging. The data suggests that this synthesis approach provides a promising avenue to prepare ferecrystalline materials with a wide variety of different structures.

For any intergrowth of two constituents, there is a large number of compounds that can be formed by varying the layer sequence. For example, there are two distinct

Table I.1. A summary of the different families of compounds that have been prepared utilizing the MER technique.

Compounds	References
Dichalcogenide-Dichalcogenide	
$[(\text{TiSe}_2)_{1+\delta}](\text{NbSe}_2)$	48-51
$\{[(\text{VSe}_2)_n]_{1.06}(\text{TaSe}_2)_m\}_z$	52,53
Dichalcogenide-M_2Te_3	
$[(\text{TiTe}_2)_{1.36}]_x[\text{Bi}_2\text{Te}_3]_y$	54,55
$[(\text{TiTe}_2)_{1+\delta}]_x[\text{Sb}_2\text{Te}_3]_y$	56-58
$\text{M}_2\text{Te}_3 - \text{M}'_2\text{Te}_3$	
$[\text{Sb}_2\text{Te}_3/(\text{Bi,Sb})_2\text{Te}_3]$	59-61
Rock salt - Dichalcogenide	
$[(\text{SnSe})_{1.15}]_m(\text{VSe}_2)_n$	62-65
$[(\text{SnSe})_{1.16}]_m(\text{NbSe}_2)_n$	66-71
$[(\text{SnSe})_{1.09}]_m(\text{MoSe}_2)_n$	72-75
$[(\text{SnSe})_{1.15}]_m(\text{TaSe}_2)_n$	76,77
$[(\text{SnSe})_{1.20}]_m(\text{TiSe}_2)_n$	78,79
$[(\text{PbSe})_{1.15}]_m(\text{TiSe}_2)_n$	80-82
$[(\text{PbSe})_{1.10}]_m(\text{NbSe}_2)_n$	83,84
$[(\text{PbSe})_{1.00}]_m(\text{MoSe}_2)_n$	85-89
$[(\text{PbSe})_{1.12}]_m(\text{TaSe}_2)_n$	90
$[(\text{PbSe})_{0.99}]_m(\text{WSe}_2)_n$	91-93
$[(\text{BiSe})_{1.15}]_m(\text{TiSe}_2)_n$	94
$[(\text{BiSe})_{1.10}]_m(\text{NbSe}_2)_n$	95
$[(\text{CeSe})_{1.14}]_m(\text{NbSe}_2)_n$	95
$[(\text{PbTe})_{1.17}]_m(\text{TiTe}_2)_n$	96

structural isomers that contain three layers of each constituent A_3B_3 and $\text{A}_2\text{B}_2\text{A}_1\text{B}_1$. Both of these compounds will have the same overall composition and approximately the same c -axis lattice parameter, but different superstructures. When there are three layers of one constituent and two of another, there are also two distinct isomers, A_3B_2 and $\text{A}_2\text{B}_1\text{A}_1\text{B}_1$. As the number of layers increases, so does the number of potential structural isomers.

When there are four layers of each constituent, there are 6 distinct structural isomers, A_4B_4 , $A_3B_3A_1B_1$, $A_3B_2A_1B_2$, $A_2B_3A_2B_1$, $A_2B_2A_1B_1A_1B_1$, and $A_2B_1A_1B_2A_1B_1$. When there are 10 layers of each constituent, there are over 4700 possible distinct structural isomers. As illustrated in Figure I.13, for n and m both equal to ten or less, there are over 20,000 distinct structural isomers that can be formed that might be expected to have different physical properties.

$m \backslash n$	1	2	3	4	5	6	7	8	9	10
1	1	1	1	1	1	1	1	1	1	1
2	1	1	2	2	3	3	4	4	5	5
3	1	2	2	4	5	6	8	10	11	14
4	1	2	4	6	10	14	20	26	35	44
5	1	3	5	10	15	26	38	57	79	110
6	1	3	6	14	26	46	76	122	183	275
7	1	4	8	20	38	76	132	232	375	600
8	1	4	10	26	57	122	232	432	750	1272
9	1	5	11	35	79	183	375	750	1384	2494
10	1	5	14	44	110	275	600	1272	2494	4735

Figure I.13. The number of possible structural isomers for a given A_mB_n stoichiometry are given in each of the boxes. The shading of the boxes reflects the rapid increase in the number of isomers as m and n increase.

I.4. Adding Additional Complexity

There are several ways to add complexity beyond that found with two binary constituents. One approach is to alloy one or both of the constituents. Another would be to layer three different constituents, two of which have the same structure to form an ordered intergrowth. A third approach would be to layer three constituents all of which have different structures. In each of these cases, the composition and structure of each constituent and the interaction between constituents will affect physical properties. The

following sections discuss strategies to prepare the required precursors for each of these approaches with experimental examples.

I.4.1. Preparing Random Alloys

Alloying a particular constituent within a multilayer containing two or more compounds in the repeating structure is based on controlling local composition in the specific layer within the precursor that will evolve into the constituent being alloyed.³⁷

The composition control is accomplished via calibrations similar to what was discussed earlier. There are at least two different approaches based on the number of sources used.

The elements to be alloyed in the targeted constituent can be deposited from one source, which is an alloy itself, or the elements can be deposited from different sources, and composition changed by increasing the amount of one element deposited while decreasing the other by the same amount.

Preparing an alloyed constituent using an alloy source is straightforward if the elements are miscible and have similar deposition characteristics. Depositing from an (A,B) alloy source can allow (A,B)C alloys to be synthesized with only minor adjustments to the calibrations of the parent compounds discussed earlier. $(\text{SnSe})_z$ $(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloys, which were recently reported, are one example. One complication of this approach is that the vapor and the melt will have different compositions, and the composition of the vapor as a function of the composition of the melt may not be known. This difference in composition also results in the composition being deposited from the alloy source changing with the amount of time the source has been depositing. This is illustrated in Figure I.14 where the composition of $(\text{SnSe})_z(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ samples made by the deposition of Nb/Mo alloy sources results in samples with a lower Nb content than

the deposition source. Subsequent samples made with the same deposition source, shown in Figure I.15, have increasing Nb content as the source becomes depleted in Mo.

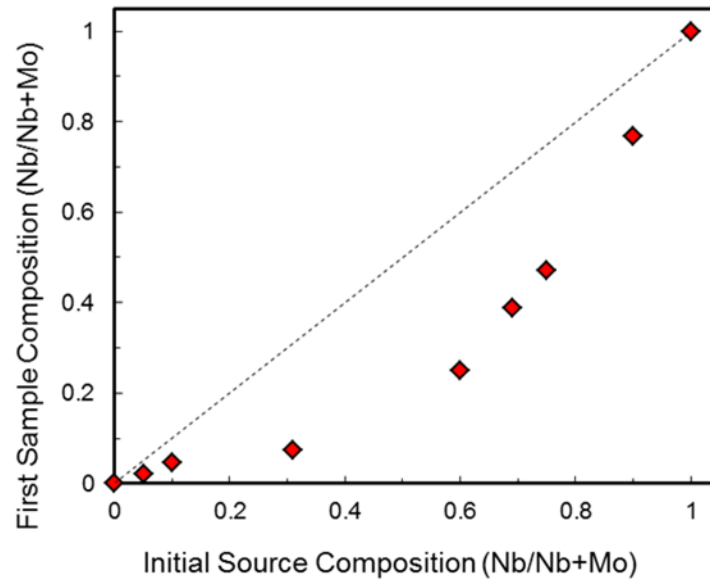


Figure I.14. Plot of the difference between the initial source composition and the composition of the first sample made from that source, showing the preferential deposition of Mo.

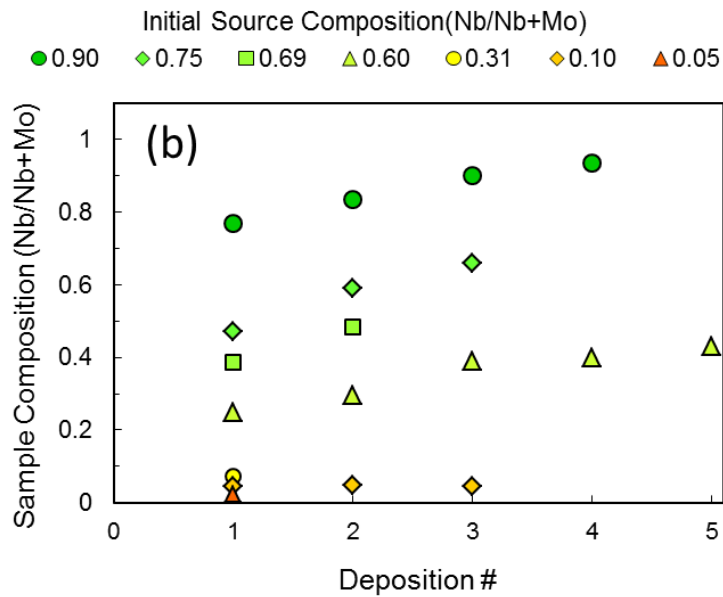


Figure I.15. Plot of the change in the composition of samples as samples are sequentially made from a specific source. The samples become more Nb rich as the source becomes depleted in Mo.

A second approach is using two different deposition sources to create the alloy, which enables alloys to be made of systems where the elements either do not alloy or have vastly different partial pressures over a melted alloy. Depositing fractions of layers using the calibrations of the original components as starting points works even for systems with very different deposition characteristics such as vanadium and tantalum in the alloy system $(\text{SnSe})_{1+\delta}(\text{V}_x\text{Ta}_{1-x})\text{Se}_2$. Holding the non-alloyed constituent constant, the deposition time of the elements in the constituent that are being alloyed are varied as relative fractions of the calibrated parent compounds. As shown in Figure I.16, a linear relationship occurs between relative shutter times and relative compositions of the alloys, allowing the preparation of alloys with precisely controlled compositions.

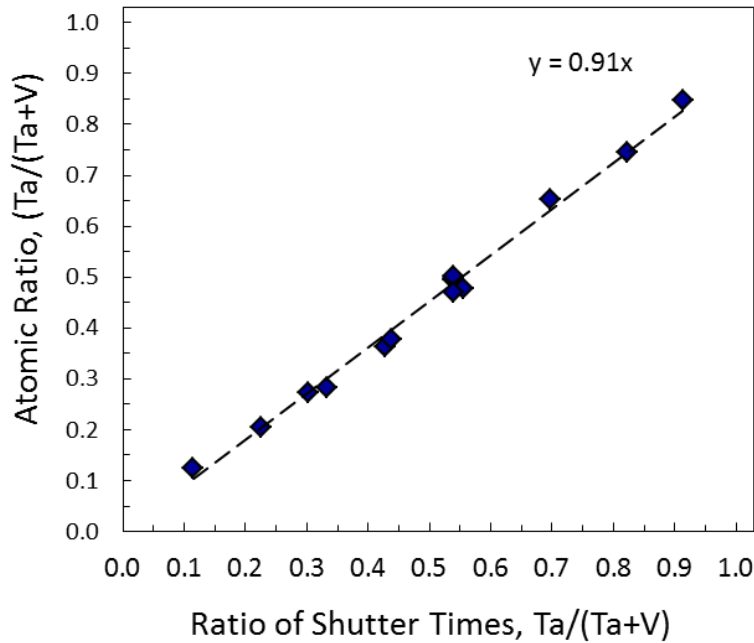


Figure I.16. The change in the atomic percent of Ta in a sample containing an alloyed $(\text{Ta}_{1-x}\text{V}_x)\text{Se}_2$ layer graphed versus the change in the percent of time the shutter of Ta was open divided by the total time that the shutters of Ta and V were opened.

To our knowledge, there have not been any solid solution studies of misfit layered compounds reported due to both difficulties in their synthesis and in the analysis of their diffraction patterns. There are only three systems involving alloying of constituents using the MER approach reported, including that of $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ reported here. The synthesis and properties of $[(\text{TiTe}_2)_{1+\delta}]_x[(\text{Bi}_{2-x}\text{Sb}_x)_2\text{Te}_3]_y$ alloys was reported by Mortensen *et al*,⁹⁸ the rock salt constituent was alloyed in $([\text{Pb}_x\text{Sn}_{1-x}]\text{Se})_z\text{TiSe}_2$,⁹⁹ and the transition metal constituent was alloyed in $(\text{SnSe})_z(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$.³⁷

I.4.2. Ordered ABAC Alloys

Ordered $A_mB_nC_p$ or more complex sequences of three compounds, such as $A_mB_nC_pB_q$, where A, B and C are compounds containing three compositionally different constituents, three structurally different constituents or a mix of these can be prepared expanding the calibration procedure described above. If the calibrated deposition parameters for two component systems containing the constituents are known, the process is straight forward. The desired atomic ratios of the relative layers are based on known or estimated misfit parameters derived from the structures of the constituents. The first step in the calibration is to prepare a sequence of samples with varying amount of the third component while holding the known parameters for the two component system fixed. Interpolating the resulting curve enables the deposition parameters that yield the correct overall stoichiometry to be determined as shown in Figure I. 17 for the $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_n([\text{MoSe}_2]_n)_{1.06}$ system. A second step of scaling of all layers simultaneously may be required to ensure appropriate thickness of the precursor. This is not usually necessary, however, as the calibration of the simpler systems is usually accurate enough to produce the desired precursors. If the disordered alloys have already been made by sequential

deposition, as in the case of $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ described above, then the deposition times giving the appropriate metal ratios are already known and can be used for the disordered alloys.

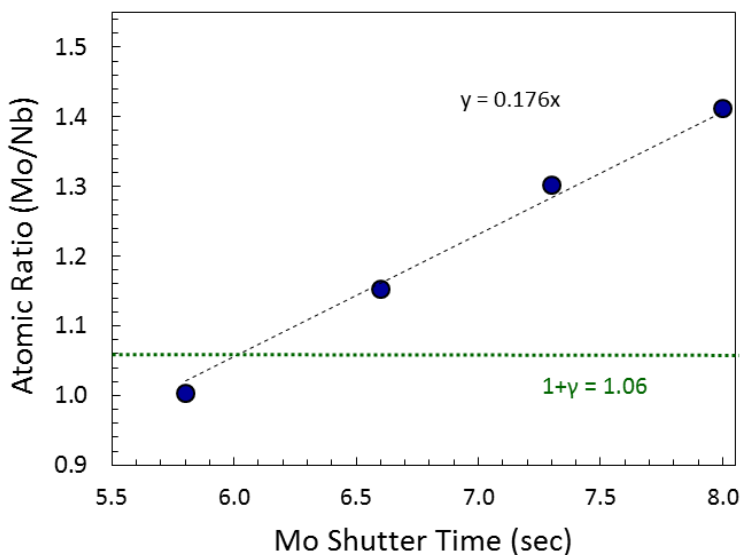


Figure I.17. A graph of the Mo to Nb ratio as a function of the time the Mo shutter was open while the Nb shutter time was held constant. The dotted green line describes the misfit between the NbSe_2 and the MoSe_2 constituents and the intercept with the experimental line provides the time the Mo shutter needs to be held open to achieve this composition.

I.5. Summary and Conclusions

Accessing a homogeneous amorphous state via low temperature annealing of a nanolayered precursor enables metastable compounds to preferentially nucleate, controlled by the composition of the amorphous intermediate. Self-assembly of more complex designed precursors through MER provides a method to systematically design materials with designed nanoarchitecture. Once a targeted intergrowth compound is prepared, additional related compounds with different constituent layer thicknesses and/or different layering sequences can be synthesized simply by changing the layering

scheme in the precursor. This permits structure-function relationships to be systematically tested, as over 20,000 compounds, including structural isomers, can be prepared with each pair of constituents when the thicknesses of the constituents is ten repeat units or less. Adding additional constituents to make more complex systems is straightforward since the synthesis of simpler systems serves as a starting point for the necessary calibrations. The ability to use three or more different components greatly expands the potential complexity of the compounds prepared. For an intergrowth of three or more constituents, the number of additional compounds that can be formed by varying the layer sequence is extremely large.

There is much to understand about the structure of the defined thickness constituent layers and how the layers interact electronically with one another. These interactions will likely control thermal, electronic and magnetic properties. The ability to anticipate the structure of so many potential compounds provides an opportunity for theory to predict both new properties and the nanoarchitectures where optimal performance will be observed. The ability to scale this approach to prepare films over large areas on a variety of substrates will facilitate the development of devices to exploit unique or exceptional properties that are discovered.

I.6. Statement of Problem

This work proposes a method whereby thin-film heterostructures of increasing complexity can be synthesized and understood using simpler systems as models. Methods will be discussed whereby the interdiffusion and electronic interactions of layers in families of complex heterostructures can be determined through comparison to families of related, but simpler ferecrystals.

First the synthesis of the first alloy ferecrystals, $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ (with $x = 0, 0.26, 0.49, 0.83$ and 1), will be discussed (Chapter III). These compounds will be used as models to estimate the interdiffusion of multiple-component ferecrystals discussed in later chapters (Chapters IV and V). This work, Chapter III, was published in *Chemistry of Materials*, volume 26, pages 3443-3449 in 2014 with co-authors Ryan E. Atkins, Jeffrey J. Ditto and David C. Johnson.

Following this study, the synthesis of the first three component ferecrystal, $(\text{SnSe})_{1.16}([\text{Mo}_{0.9}\text{Nb}_{0.1}]\text{Se}_2)_{1.06}(\text{SnSe})_{1.16}([\text{Nb}_{0.9}\text{Mo}_{0.1}]\text{Se}_2)$, will be discussed (Chapter IV). Using the alloys synthesized in chapter III, the interdiffusion of the miscible MoSe_2 and NbSe_2 constituents can be determined. This work, Chapter IV, was published in *Chemistry of Materials*, volume 27, pages 6411-6417 in 2015 with co-authors Jeffrey J. Ditto, Matthias Falmbigl, Zachary L. Hay and David C. Johnson.

In order to control the interdiffusion observed in the three component ferecrystal, discussed in chapter IV, a family of $([\text{SnSe}]_{1+\delta})_m([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ ferecrystals were synthesized. By increasing the number of SnSe layers from 0 to 4, alloying of the miscible constituents could be suppressed. In addition, comparison of the electrical transport properties with those of the $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ ($m = 1 - 8$) family of ferecrystals allowed the electronic interactions of the MoSe_2 and NbSe_2 to be experimentally determined and compared to theoretical calculations. This work, Chapter V, was submitted to the *European Journal of Inorganic Chemistry* in 2015 with co-authors Gavin Mitchson, Jeff Ditto and David C. Johnson.

Although the extent of alloying in the $([\text{SnSe}]_{1+\delta})_m([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1$ $([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ family could be estimated by comparison of the in-plane

lattice constants to those of the $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloys, the similarity of *ab* lattice constants in some systems render this method unviable. Further it should be possible to determine the extent of alloying in multiple component ferecrystals through the use of scanning transmission electron microscopy (STEM) equipped with either energy dispersive X-ray spectroscopy (EDX) or electron energy loss spectroscopy (EELS). Unfortunately, Mo and Nb are ill suited for use in these methods due to overlap of their $K\alpha$ lines and low intensity L lines. The use of Ta and V in the formation of $([\text{SnSe}]_{1+\delta})_I([\text{V}_x\text{Ta}_{1-x}\text{Se}_2]_{1+y})_I([\text{SnSe}]_{1+\delta})_I(\{\text{Ta}_x\text{V}_{1-x}\}\text{Se}_2)_1$ and $(\text{SnSe})_{1.16-1.09}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ alloys should allow the observation of alloying via EDX and/or EELS. This work, chapter VI, is part of an invited article published in *The Journal of Solid State Chemistry* in 2015, ahead of print. The co-authors were Ryan Atkins, Matthias Falmbigl, Jeffery J. Ditto, and David C. Johnson.

Charge density waves (CDW) transitions have been extensively studied in bulk transition metal dichalcogenide (TMD) systems. Prior studies have shown that isoelectric doping of CDW conducting TMDs rapidly suppresses the CDW. Ferecrystals provide an opportunity to study interesting transport phenomenon in structurally independent transition layer dichalcogenide layers due to the lack of epitaxial relationships between the layers. The synthesis of $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ alloys with small amounts of Ta should allow study of the relative stability of ferecrystal CDWs. This work will be submitted to *The Journal of Electronic Materials* in 2015 with co-authors Krista Hill and David C. Johnson.

CHAPTER II

EXPERIMENTAL PROCEDURES

II.1. Synthesis of Modulated Precursors

The synthesis of all ferescystalline compounds in the Dave Johnson lab is accomplished via self-assembly of compositionally modulated precursors. These precursors are formed via physical vapor deposition in custom-built deposition chambers. Figure II.1 is a schematic of the deposition chamber used to synthesize all the samples described in this work. A dual turbo and cryo vacuum system achieved pressures of below 5×10^{-7} torr. Se was deposited using a custom-built Knudsen effusion cell, while elements with lower vapor pressures (Nb, Mo, Ta and V) were deposited using Thermionics 3kW electron beam guns. Deposition rates were monitored using INFICON Xtal quartz crystal monitors. A step motor driven rotating carousel positioned the samples, typically 100 oriented silicon wafers, over the desired source whereupon pneumatically powered shutters would introduce the samples to the elemental flux. The

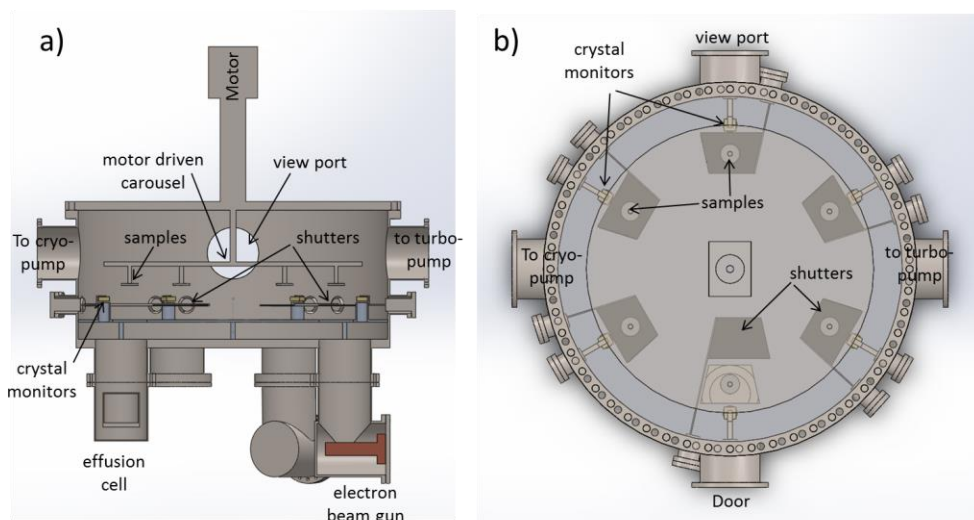


Figure II.1. a) Cutaway schematic of custom-built deposition chamber. b) Top down view.

relationship with the substrate and the film is desired. Control of the pneumatic shutters, the elemental deposition rates and times and the layering sequence was accomplished using a custom-designed labview program. Careful calibration of the compositions and thickness of each layer of the precursor ensures a structure that closely mimics the structure and composition of the desired products. The lack of a structural relationship of the precursor with the substrate allows more complex structures to be formed by combining the calibrated deposition parameters of multiple constituents. An increasingly large number of related compounds can then be made by changing the deposition sequence of the constituents.

II.2. Annealing

Once the modulated precursors have been prepared, self-assembly into ferecrystalline products is accomplished via mild annealing in an N₂ atmosphere drybox (less than 0.7 ppm O₂). Upon annealing, increases in the number and intensity of diffraction maxima indicate nucleation and the formation of the product. Unlike conventional solid state synthesis techniques, which must overcome diffusion barriers in order to form products and often require annealing conditions in excess of 700 C for several days,¹ ferecrystals form rapidly under relatively mild conditions due to the reduced diffusion lengths in the modulated precursor. For example, in the annealing of the (Sn|Se)(Nb|2Se)_z(Sn|Se)(Mo|2Se)_z precursor to become the (SnSe)_{1.16} ([Mo_{0.9}Nb_{0.1}]Se₂)_{1.06}(SnSe)_{1.16}([Nb_{0.9}Mo_{0.1}]Se₂) compound, in-plane (Figure II.1.a) and out-of-plane (Figure II.2.b) X-ray diffraction show that the product is nearly formed after annealing for only 10 seconds at 450 °C. Annealing longer, for 20 min, increased the intensities and sharpens the the 00l reflections, as shown in Figure II.2.b, indicating that

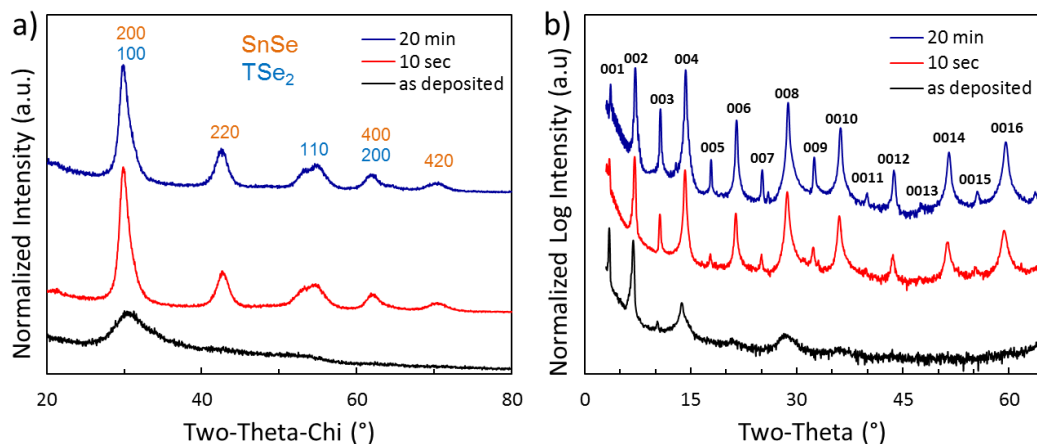


Figure II.2. In-plane (a) and out-of-plane (b) X-ray diffraction patterns for $(\text{Sn}|\text{Se})(\text{Nb}|\text{2Se})_z(\text{Sn}|\text{Se})(\text{Mo}|\text{2Se})_z$ precursor as deposited (black), annealed at 450 °C for 10 seconds (red) and at 450 °C 20 minutes (blue).

additional time increases the quality of the sample. To find the optimal annealing temperatures and times, annealing studies are required for each system studied. For more complex systems, containing multiple components, the most effective annealing conditions are typically similar to those found for the parent compounds. As a result, annealing studies for complex systems can be carried out using the conditions for the parent compounds as a starting point. For example, the annealing conditions for $(\text{SnSe})_{1.16}\text{NbSe}_2$ and $(\text{SnSe})_{1.04}\text{MoSe}_2$ have been reported as 400 °C for 20 min² and 450 °C for 30 min³ respectively. In like manner the optimal annealing conditions for the $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ and $(\text{SnSe})_{1+\delta}([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)$ compounds were found to be 400 °C for 20 min and 450 °C for 30 min as discussed in chapters III and IV respectively. To determine the most effective annealing conditions, precursors are annealed at various temperatures and the number, intensity, full width half maximum and location of each the (00*l*) reflections is monitored by X-ray diffraction. A

representative annealing study of the $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ system is given in Figure II.3.

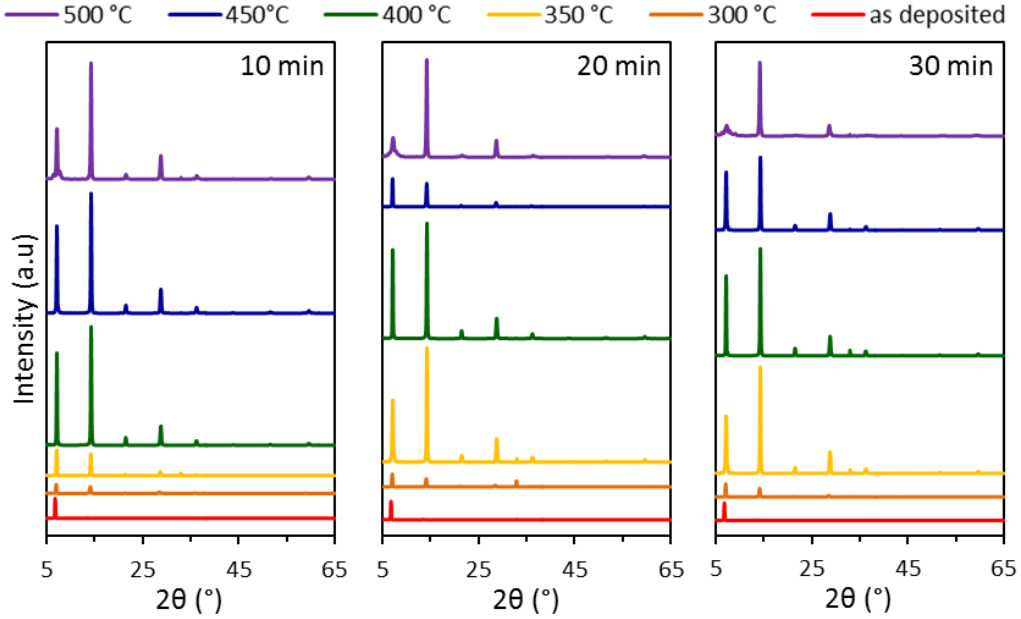


Figure II.3. Out-of-plane X-ray diffraction patterns from an annealing study in the $(\text{SnSe})_{1.13}(\text{Nb}_{0.49}\text{Mo}_{0.51})\text{Se}_2$ compound.

The FWHM of the 004 reflections, given in Figure II.4, show that at lower temperatures (below 400 °C) annealing for 20 minutes leads to a reduced FWHM than annealing for 10 minutes indicating that the sample quality continued to improve at these temperatures after 10 minutes. After 20 minutes, however, the FWHM remains about the same with little or no improvement after 30 minutes. Above a certain temperature, in this case 400 °C, annealing for longer times broadens the peaks indicating sample degradation. A plot of the compositions, determined by EPMA, of the samples annealed for 20 min gives provides insight as to the reason for the degradation (Figure II.5). The compositions of the samples remain constant at temperatures below 400 °C; however at higher temperatures a loss of both Sn and Se is observed by EPMA. The vapor pressure

of Se at 500 °C has been reported as 5 kPa⁴, however, the vapor pressure of Sn at this temperature is much lower ($\approx 1 \times 10^{-9}$ Pa).⁵ The loss of Sn is likely due to a loss of SnSe. Hirayama *et al* measured a vapor pressure for SnSe of 6.14×10^{-2} Pa at 500 °C giving rise to a mass loss of 6 mg from a 5 gram pellet over 3.6 hours.⁶

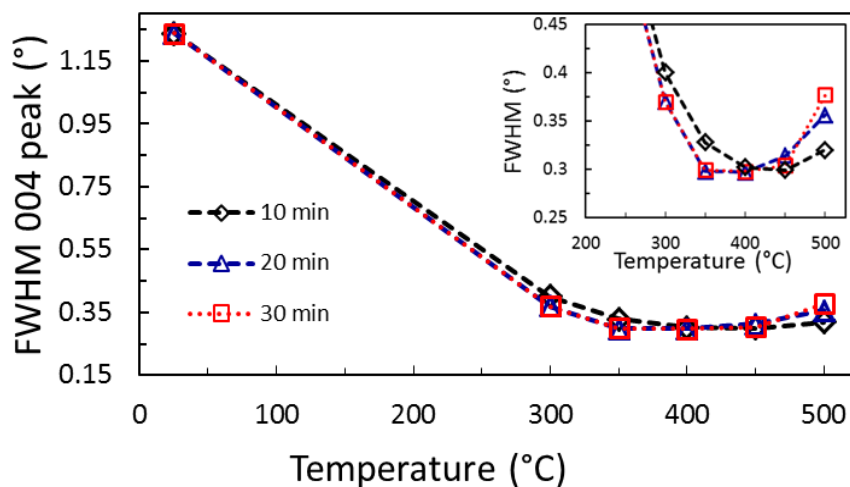


Figure II.4. Full width half maximum of the (002) X-ray diffraction peak from annealing study in the $(\text{SnSe})_{1.13}(\text{Nb}_{0.49}\text{Mo}_{0.51})\text{Se}_2$ compound.

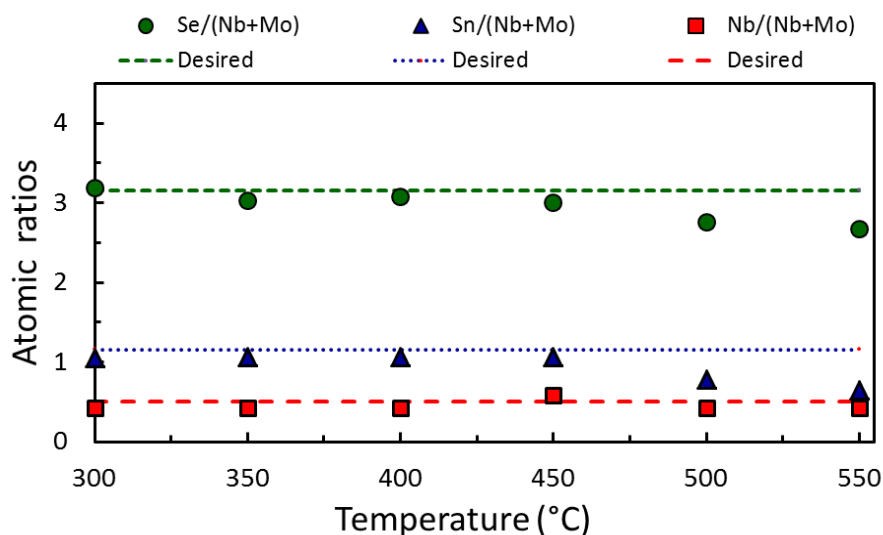


Figure II.5. EPMA atomic ratios vs. annealing temperature from an annealing study on the $(\text{SnSe})_{1.13}(\text{Nb}_{0.49}\text{Mo}_{0.51})\text{Se}_2$ compound.

II.3. X-ray Diffraction and Reflectivity

X-ray diffraction relies on periodic oscillations in intensity caused by constructive and destructive interferences of radiation that is diffracted from repeating regions of electron density. Brag's law given as equation 1, illustrates the relationship between the wavelength of the X-rays (λ), the distance between repeating layers of electron density (d), the number of repeat units (n) and the angles where constructive interferences are observed (θ).

$$n\lambda = 2d\sin(\theta) \quad (1)$$

In the case of ferecrystals, due to the lack of epitaxy between either the layers and the substrate or the layers with each other, individual layers are rotated, more or less randomly, with respect to each other in what is referred to as turbostratic disorder (Figure II.6). Because of turbostratic disorder, there is a short coherence length along the hkl directions which causes streaking of the diffraction peaks corresponding to these directions (Figure II. 6). Nevertheless, long range order is preserved in the $00l$ and $hk0$ directions and scans along these directions produces sharp peaks as indicated in Figure II.6. $00l$ X-ray diffraction provides information along the c -direction including, size of the unit cell, distances and differences between regions of different electron intensity in this direction and provides some qualitative information on the quality of the interfaces along this direction. $hk0$ X-ray diffraction provides information on the identity and of the crystalline constituents by measuring the lattice parameters along the a and b directions.

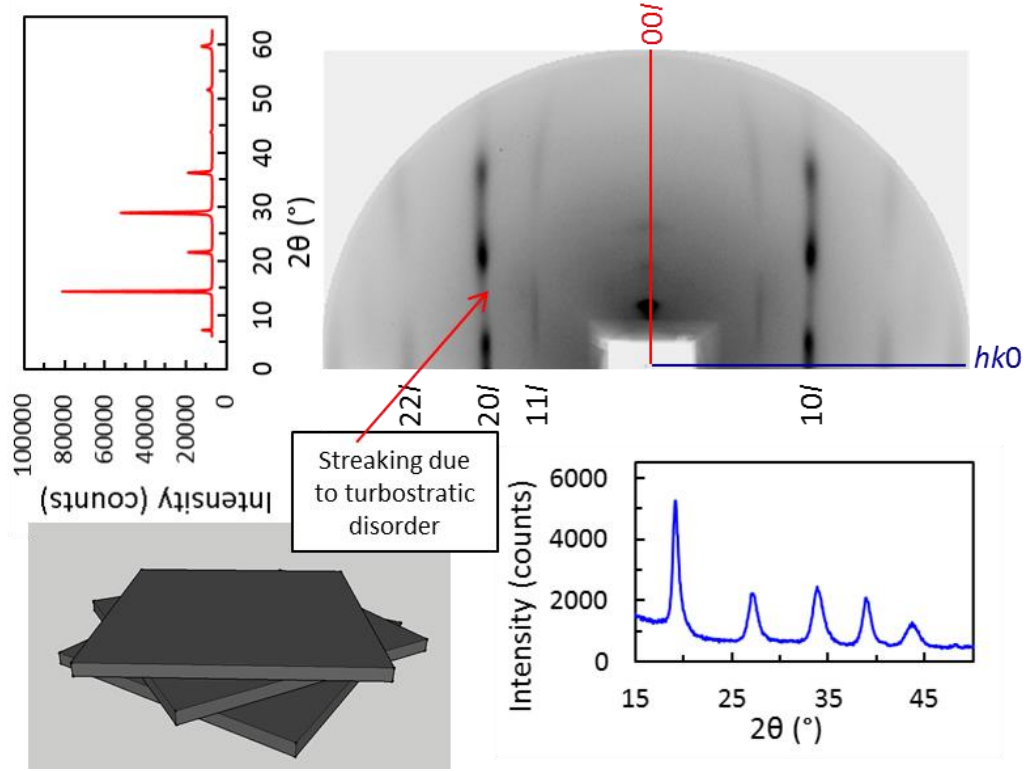


Figure II.6. Schematic illustrating the effect of turbostratic disorder on the X-ray diffraction patterns of a $(\text{SnSe})_{1.13}(\text{Nb}_{0.49}\text{Mo}_{0.51})\text{Se}_2$ ferecrystal. On the bottom left is a cartoon illustrating turbostratic disorder. On the upper left is a $00l$ diffraction pattern. On the upper right a 2D X-ray diffraction pattern and on the lower right a $hk0$ diffraction pattern.

X-ray reflectivity (XRR) allows the calculation of film thickness, surface roughness and electron density and is performed at low angles in the $00l$ direction. XRR measures periodic changes in intensity due to constructive interference of radiation reflected off of substrate-film and film air interfaces. These fringes are called Kiessig fringes and their location and their position is given by the modified Bragg's law, which corrects for the different indexes of refraction of the materials which the X-rays must pass through (Equation 2).

$$n\lambda = 2d\sqrt{\sin^2\theta - \sin^2\theta_c} \quad (2)$$

Out-of-plane (00 l) X-ray diffraction (XRD) and X-ray reflectivity (XRR) measurements were performed on a Bruker D8 AXS diffractometer equipped with a Cu K α radiation source ($\lambda = 0.154$ nm), a Göbel mirror and Bragg-Brentano optics geometry. Grazing incidence in-plane ($hk0$) X-ray diffraction was acquired at the Advanced Photon Source (APS) at Argonne National Laboratory, beamline 33-C or by using a Rigaku Smartlab diffractometer. 2D X-ray diffraction patterns were obtained at APS.

II.4. Scanning Transmission Electron Microscopy

Scanning transmission electron microscopy allowed for mapping of cross sections of samples. This technique uses an incident electron beam which is rastered over the thin-film cross section causing electrons to be diffracted. I, high angular dark field (HAADF) mode incoherently scattered electrons are detected providing Z-contrast as the amount of diffracted electrons depends on the atomic number Z. HAADF-STEM images allowed the turbostratic disorder, coordination of the cations and the quality of the layering of the ferecrystals to be observed.

Cross-section samples for HAADF- STEM were prepared using a FEI Helios Nanolab d600 Dual Beam focused ion beam (FIB). These samples were used for imaging on an FEI Titan 80-300 at the Center for Advanced Materials Characterization in Oregon (CAMCOR) High-Resolution and Nanofabrication Facility, or at the Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory (PNNL).

II.5. Electron Probe Microanalysis

Electron Probe Microanalysis (EPMA) is a technique where an incident electron beam excites X-rays within a sample which are detected by several wavelength dispersive spectrometers (WDS). The composition can be calculated by comparing intensities with

standards of known compositions. By utilizing different electron beam energies the probing depth of the technique can be altered which allows the separation of the film and substrate signal making the technique viable for thin films.⁷

II.6. Electrical Transport Measurements

Samples for electrical transport measurement were deposited onto fused silica substrates in a van der Pauw cross pattern geometry defined by a shadow mask (Figure II.7). Copper wires were attached to the four opposite points of the cross with indium. For resistivity measurements current was sourced through two adjacent contacts while the potential difference was measured through the other two. From the slope of the current-potential curve, the sheet resistance could be calculated. Using the thickness of the film and the resistivity sheet resistance relationship, given in equation 3 allows the resistivity to be calculated. By repeating the measurement for all eight possible geometries the form factor f was iteratively determined, however, by using the cross pattern, the form factor f should be close to 1.⁸

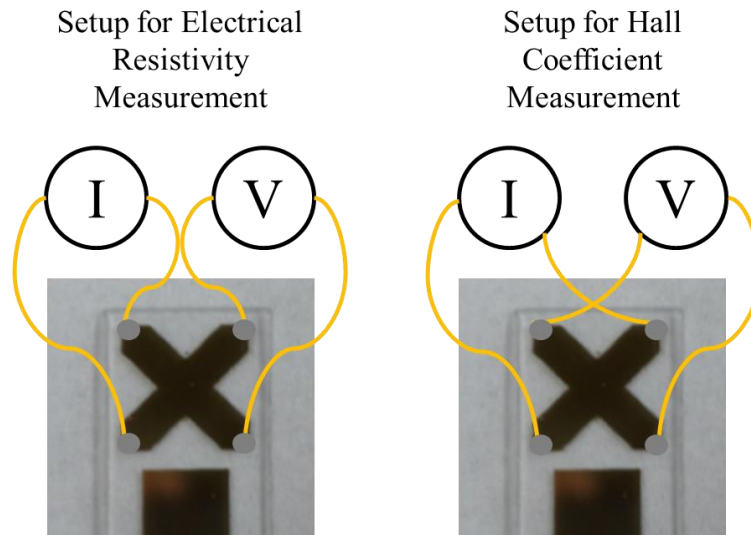


Figure II.7. Schematic illustrating the cross-pattern and contact setup for resistivity and Hall coefficient measurements.

$$\rho = \frac{\pi d}{\ln 2} \frac{R_{AB,CD} + R_{BC,DA}}{2} f \quad (3)$$

Hall coefficient measurements were also performed using van der Pauw geometry.⁸ A magnetic field was created perpendicular to the sample whereupon current was sourced across two opposite ends of the cross. The magnetic field causes carriers in the sample to experience a Lorentz force that separates charges and causes a potential to be built up that was measured the other two opposite ends (Figure II.7). This potential difference is known as the Hall voltage (V_H). If a single band of carriers is assumed, the relationship between V_H , the sample thickness (d), the strength of the magnetic field (B), the current flow (I), the elemental charge (e) and the carrier concentration (n) is given by equation II.4. The measurement of the V_H at different field strengths allows the Hall coefficient R_H and the carrier concentration to be determined from if the sample thickness and the current flow are known.

$$V_H = \frac{IB}{ned} \quad R_H = \frac{V_H d}{IB} \quad n = \frac{1}{R_H e} \quad (5)$$

CHAPTER III

SYNTHESIS OF $([\text{SnSe}]_{1.16-1.09})([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)_1$ FERECRYSTAL ALLOYS

III.1. Authorship Statement

Chapter III was published in *Chemistry of Materials*, volume 26, pages 3443-3449 in 2014. Co-author Ryan A. Atkins assisted in the synthesis of the initial compounds. Co-author Jeffrey J. Ditto performed microscopy measurements. Dr. David C. Johnson is my advisor and I am the primary author of the manuscript.

III.2. Introduction

Virtually all solid state synthesis techniques require elevated temperatures to facilitate diffusion and extended times to achieve homogeneity. As a result, conventional high temperature solid state synthesis techniques are limited by thermodynamics to the formation of only the most stable product(s) of a given elemental composition.¹ As the composition becomes more complex, the number of potential products increases and the synthesis becomes increasingly challenging. For example, the formation of quaternary solid state compounds is very difficult because the product must be more stable than all other possible quaternary configurations as well as all possible configurations involving combinations of ternary compounds, binary compounds and the elements.^{2,3} In addition, there are kinetic challenges arising from the need for n different elements to diffuse to the same location with correct concentrations for the formation of the product.

Misfit layer dichalcogenides are a good example of the limitations of conventional thermodynamic synthesis techniques. Misfit layer dichalcogenides are a subset of layered materials that can be viewed as composite crystals with the generic formula $[(\text{MX})_z]_m(\text{TX}_2)_n$, built from the interleaving of the two independent constituents:

a distorted rocksalt MX (M = Sn, La, Pb, Bi; X = S, Se, Te) and a transition metal dichalcogenide TX₂ (T = Mo, Nb, Ti, V, Ta, and Cr) with z being the extent of the misfit between the constituents in the ab -plane.⁴⁻⁷ Misfit layer dichalcogenides are conventionally synthesized through mixing of the three constituent elements, or a mixture of binary compounds, sometimes with an excess of the chalcogen, followed by annealing at an elevated temperature, typically 850 to 1100 °C, to allow the elements to mix via diffusion.⁷ To obtain single crystals, Schäfer's vapor transport approach is typically used, where a small amount of transport agent is added and the sample is annealed at high temperature with a small gradient in temperature to promote the vapor transport of the elements to a growing crystal.⁸ As a result of the high temperatures, only thermodynamically stable products are likely to be accessible and stable under the reaction conditions, greatly limiting the number of different compounds that can be formed. For example, while one might expect compounds with different values of m and n to be kinetically stable, only compounds where m and n are equal to 1 have been reported, except for a few instances where compounds with n equal to 2 or 3 have been more stable.^{4,9} In addition, while Kalikhman *et al*¹⁰⁻¹² and others^{13,14} have synthesized alloys of several transition metal dichalcogenides, (including (Nb _{x} Mo_{1- x})Se₂, (Ta _{x} Mo_{1- x})Se₂ and (Ta _{x} W_{1- x})Se₂), controlled alloying of misfit layer dichalcogenides has not been reported to our knowledge. The lack of ability to prepare even these simple solid-solution derivatives of known compounds makes developing an understanding of structure-property relationships challenging as concepts cannot be tested.

Recently, our group described a synthetic method by which numerous metastable [(MX) _{z}] _{m} (TX₂) _{n} compounds, known as ferecrystals, could be synthesized. Ferecrystals

are structurally similar to misfit layer dichalcogenides, but lack the long range order of true crystals due to substantial rotational disorder between subsequent layers referred to as turbostratic disorder.¹⁵⁻²³ In the formation of these metastable compounds, physical vapor deposition is used to form an amorphous modulated precursor, as shown in Figure III.1, with local composition and layer thicknesses closely mimicking the desired product. Self-assembly into the desired product is observed upon mild annealing. The use of modulated precursors minimizes diffusion lengths, allowing the formation of kinetically trapped metastable products where the final product contains the nanostructure of the initial precursor. This approach results in a much greater synthetic scope than conventional methods allow, with reports of new $[(MX)_z]_m(TX_2)_n$ compounds in which m and n were independently varied between 1 and 16.

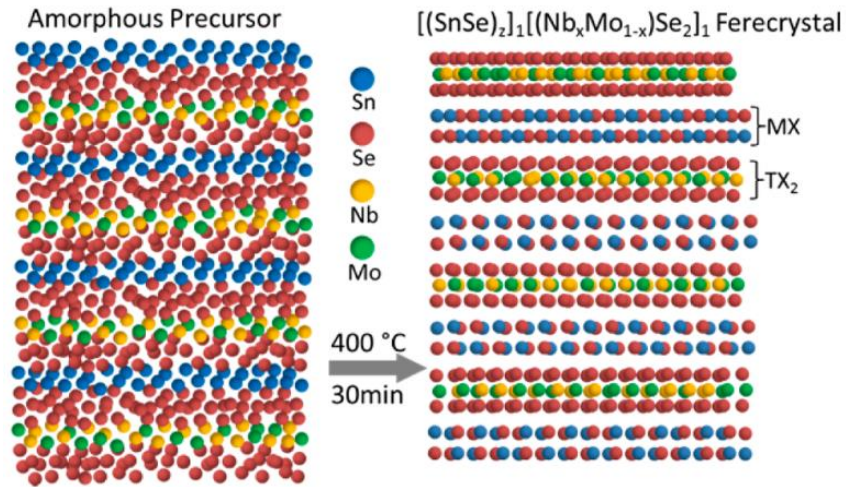


Figure III.1. Schematic of the synthesis scheme for $[(SnSe)_{1.16-1.09}]_1[(Nb_xMo_{1-x})Se_2]_1$ alloy ferecrystals. On the left is the as-deposited amorphous precursor. On the right is the ferecrystal alloy after self-assembly.

The expansion of this method through the formation of modulated precursors with mixed metal layers, as shown in Figure III.1, might allow the synthesis of quaternary $[(MX)_z]_m([T_xT'_{1-x}]X_2)_n$ compounds with controlled compositions. We tested this idea

using Nb and Mo as the transition metals because they are among the most common elements used for dichalcogenide alloys in literature¹⁰⁻¹⁴ and their similarities in size and vapor pressure cause them to behave similarly in physical vapor deposition. In addition, the substitution of Nb acts as a p-type dopant in MoSe₂, allowing the addition of Nb to be tracked electrically as well as structurally and compositionally. We anticipated that this might hold true in our study. Herein we report the first synthesis of (SnSe)_{1.16-1.09}(Nb_xMo_{1-x})Se₂ compounds with x = 0, 0.26, 0.49, 0.83, and 1. Varying Mo/Nb ratios alters the structure of the materials, as shown in X-ray diffraction studies, with lattice parameters of the alloys following linear trends between those of the parent systems as predicted by Vegard's law.^{24,25} Electrical transport properties of alloy materials were seen to trend between the metallic (SnSe)_{1.16}NbSe₂ and semiconducting (SnSe)_{1.09}MoSe₂ parent compounds with each Nb atom providing slightly less than one hole carrier in the MoSe₂ host.

III.3. Experimental

(SnSe)_{1.16-1.09}(Nb_xMo_{1-x})Se₂ with x = 0, 0.26, 0.49, 0.83, and 1 were formed from designed modulated precursors prepared using the modulated elemental reactant technique in a custom built physical vapor deposition vacuum system. A more detailed description of this synthesis technique has been published previously.²³ A dual turbo and cryo pump vacuum system allowed depositions at pressures as low as 10⁻⁸ torr. Mo (99.95% purity), Nb (99.8% purity), Sn (99.999% purity) and Se (99.5% purity) acquired from Alfa Aesar were used as elemental sources. In order to prepare refractive metals for evaporation as received, Mo and Nb pieces were loaded into a custom built, water cooled copper hearth and placed into a hermetically sealed chamber and purged with He at 8

L/min for 20 min. After purging, to remove remaining oxygen, oxophilic Ti was arc-melted by energizing a W electrode to 20 kV for 30 s. Samples were then arc melted to create dense pieces of suitable size. For alloy materials, Nb and Mo were added in desired stoichiometric amounts and then arc-melted.

Compositions of the arc-melted alloy sources and the resulting ferecrystal samples were determined by electron probe micro-analysis (EPMA) on a Cameca SX-100. Accelerated voltages of 10, 15 and 20 keV were used to collect intensities. This technique has been described previously in the literature.²⁶ Composition was then calculated from the film and substrate, or from the alloy source, as a function of accelerating voltage.

Metal sources were evaporated at rates of approximately 0.2 Å/s for Mo and Nb and 0.4 Å/s for Sn, using Thermionics 3 kW electron beam guns. Se was evaporated using a custom built Knudsen effusion cell at a rate of about 0.5 Å/s. Rates were monitored and controlled with quartz crystal monitors. Substrates were mounted on a rotating carousel controlled by a custom designed lab view program, which positioned the sample over the desired source. Pneumatically powered shutters between the elemental sources and the substrates controlled the exposure time of the samples to the elemental flux. Repetition of this process allowed the modulated precursors to be built up layer by layer until reaching a desired thicknesses ranging from of 500 to 600 Å.

Total thickness and repeating unit thickness were monitored by high resolution X-ray reflectivity (XRR) and X-ray diffraction (XRD) performed on a Bruker D8 Discover diffractometer equipped with a Cu K α X-ray source and Göbel mirror optics. Synchrotron X-ray diffraction from the Advanced Photon Source (APS), Argonne

National Laboratory (beamline 33BM) was used to determine the *ab*-plane lattice parameters.

TEM cross section lift out samples were prepared and analyzed at the Center for Advanced Materials Characterization in Oregon (CAMCOR) High-Resolution and Nanofabrication Facility. Scanning Transmission Electron Microscopy (STEM) samples were prepared using an FEI NOVA Nanolab Dual Beam FIB equipped with Side winder ion column and performed on a FEI 80-300 kV Titan equipped with a Fischione Model 3000 Annular Dark Field (ADF) detector.^{28,29} All images were collected at 300 kV.

Samples for electrical measurements were deposited on quartz slides in a 1 x 1 cm cross pattern defined by a shadow mask. Temperature dependent resistivity and Hall effect measurements were performed using the van der Pauw technique.²⁷

III.4. Results and Discussion

The synthesis of $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloy ferecrystals begins with the preparation of a series of compositionally modulated precursors with appropriate compositions and thicknesses to enable self-assembly to the desired products. In order to ensure formation of precursors with stoichiometry and nanoarchitecture analogous to the targeted compounds, careful calibration of the deposition times of the constituent elements is required as described previously.²³ To simplify the procedure for the targeted quaternary compounds, calibrations for the parent ternary $(\text{SnSe})_{1.09}(\text{MoSe}_2)$ and $(\text{SnSe})_{1.16}\text{NbSe}_2$ compounds were used as starting points for the calibrations of the alloy precursors. Briefly, the deposition parameters required to form each binary constituent, SnSe and TSe₂ (where T = Mo, or Nb) were determined by preparing a series of compounds with fixed metal thickness and varying thickness of selenium. Once the ratio

of thicknesses required to obtain the composition of the binary compounds was determined, a series of ternary samples with varying Sn to T ratios were prepared to find the deposition parameters that correspond to the misfit ratio of the desired compound. Finally, the Sn:Se and M:Se thicknesses were scaled simultaneously until the repeat sequence resulted in a single unit cell of the $(\text{SnSe})_y(\text{TSe}_2)_1$ after annealing.

Once the calibrations for the parent $(\text{SnSe})_{1.04}(\text{MoSe}_2)$ and $(\text{SnSe})_{1.16}\text{NbSe}_2$ compounds were complete, substitutions of Mo and Nb allowed the preparation of modulated precursors for the $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloy compounds. This was accomplished by replacing the pure transition metal sources with alloys of various compositions. Transition metal shutter time was calculated as a function of desired Mo/Nb composition assuming a linear trend between the calibrated times of the parent systems. Electron probe micro-analysis of the Mo/Nb ratios of the samples and alloy sources, shown in Figure III.2a, indicate that the samples are consistently lower in Mo content than the source. This is likely because the vapor pressure of Mo is slightly lower than that of Nb,³⁰ resulting in a vapor phase rich in Mo and ultimately in a Mo rich film. In addition, as shown in Figure III.2b, the more times the source is used the higher the Nb content of the sample because the source becomes depleted in Mo. Similar results have been found by other groups for the deposition of alloys using physical vapor deposition.^{31,32}

Once the calibration of the modulated precursors was complete, the annealing conditions were optimized by varying temperature and time and following the evolution of the X-ray diffraction pattern. As shown in Figure III.3a, in the as-deposited sample the (001) diffraction peak is visible but no higher order peaks are observed reflecting the

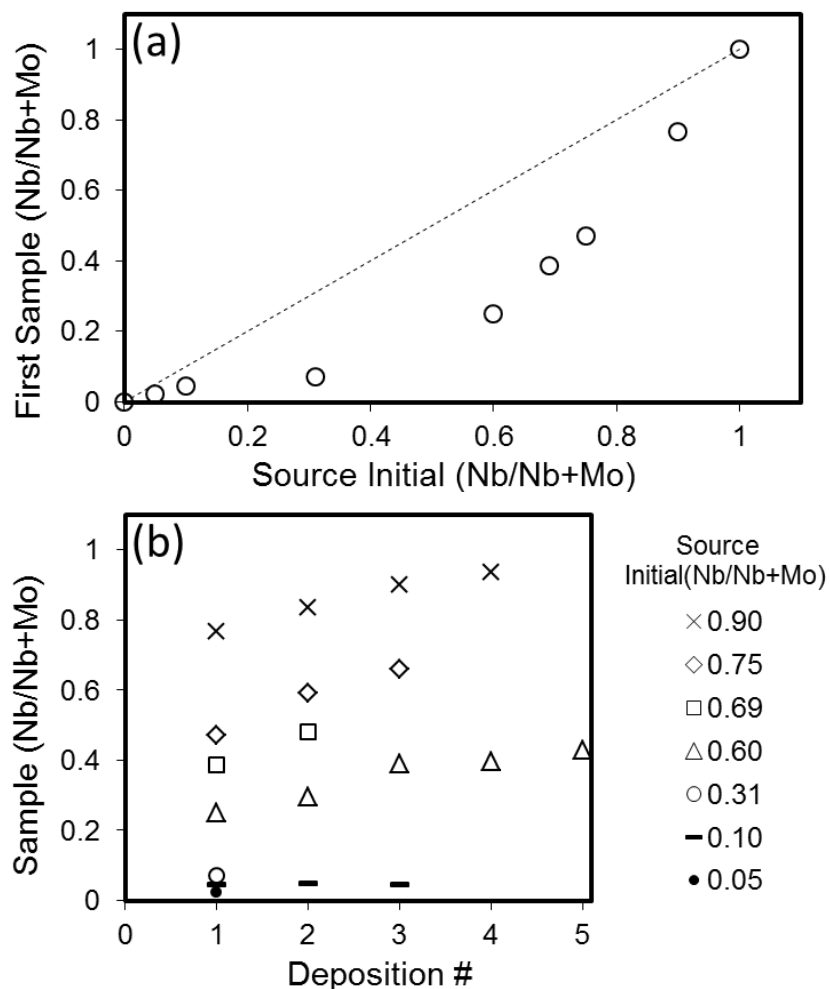


Figure III.2. (a) Nb/Mo ratios of PVD source vs. the first resulting ferecrystal sample. (b) Sample Nb/Mo ratio change vs. number of depositions for PVD sources with different initial Nb content.

disordered state of the as-deposited sample. At 300 °C, peaks that can be indexed as higher order 00 l reflections start to form as the precursor self assembles. Figure III.3b graphs the intensity of the (002) reflection as a function of annealing temperature, showing that the intensity increases until a maximum intensity is reached at 400 °C. Above 400°C, peaks broaden and lose intensity as the targeted compound begins to decompose, indicating the targeted product cannot be prepared via the usual high temperature solid state reaction schemes and that the product is probably metastable. Assuming that the

optimal conditions correspond with the maximum diffraction intensity, 400 °C was chosen as the annealing temperature for the alloys. This is the same temperature determined in previous studies for the parent systems.²²

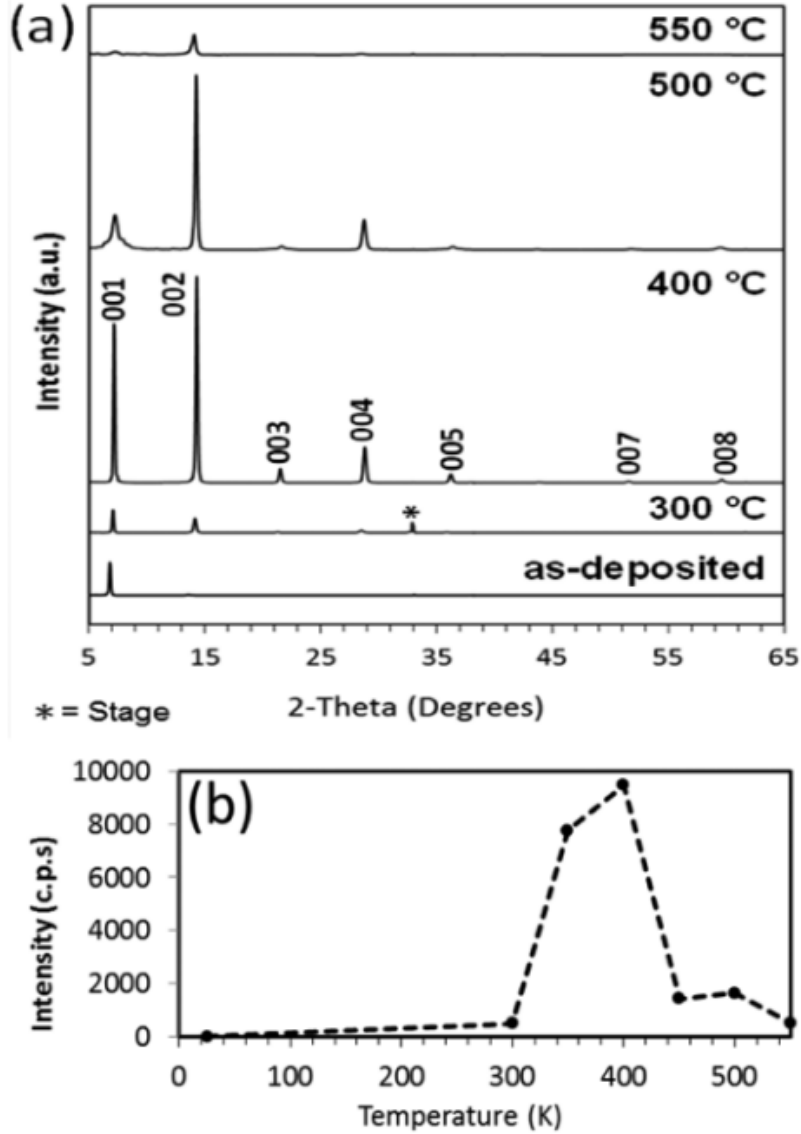


Figure III.3. (a) Grazing incidence XRD patterns of $(\text{SnSe})_{1.13}(\text{Nb}_{0.51}\text{Mo}_{0.49})\text{Se}_2$ annealed at 300, 350, 400, 450, 500, and 550 °C for 20 min. (b) Intensity of the (002) diffraction peaks with temperature.

To determine the structural evolution of the $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloy intergrowths as the Mo/Nb ratio is changed, a number of diffraction experiments were performed. Out-of-plane diffraction patterns, shown in Figure III.4a, of each of the compounds indicated a systematic shift to higher angles of the $00l$ peaks with increasing Nb content. This is caused by linear decrease in the c -lattice parameter of the films as depicted in Figure III.4b. This decrease in c -lattice parameter with increasing Nb occurs despite the fact that Nb is slightly larger than Mo and would be expected to cause an expansion of the lattice parameters as predicted by Vegard's law.^{24,25} Comparison with the

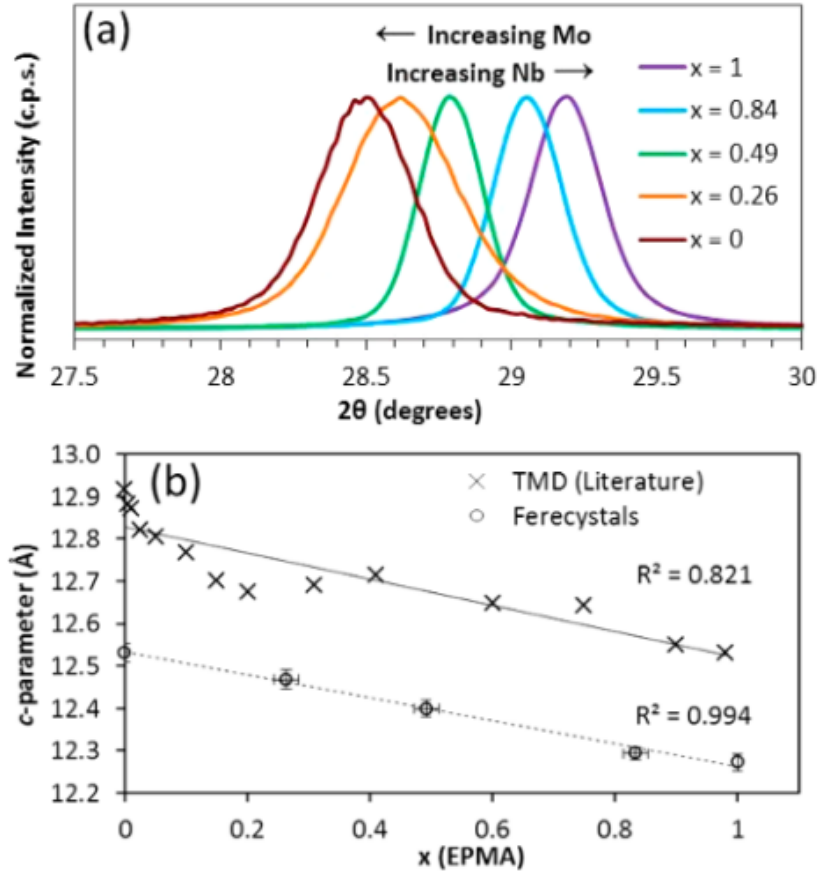


Figure III.4. (a) Out-of-plane X-ray diffraction patterns showing shift in the (004) peak with changes in dichalcogenide composition. (b) Plot of c -lattice parameter vs. x for $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloys.

$(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ TMD alloys, measured by Kalikhman,¹⁰ shows a similar overall trend and slope. The contraction in the c-lattice parameter of the TMD alloys was attributed by Moussa Bougouma *et al*¹⁴ to a reduction of electron density with added Nb causing changes in electrostatic repulsions between the selenium atoms and the transition metal atom. Deviations from linearity in the $(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ TMD systems was attributed, by Kalikhman, to regions of mixed 3R and 2H-TSe₂ phases. The addition of the SnSe layer in the ferecrystals between TSe₂ layers removes this effect, resulting in a more linear trend.

The in-plane ($hk0$) structure of the alloys was investigated from X-ray diffraction scans obtained at the Advanced Photon Source (APS). Figure III.5 shows a representative in-plane diffraction pattern for the sample $(\text{SnSe})_{1.13}(\text{Nb}_{0.51}\text{Mo}_{0.49})\text{Se}_2$. The diffraction maxima can be indexed as a mixture of cubic SnSe and hexagonal $\text{Nb}_{0.51}\text{Mo}_{0.49}\text{Se}_2$. The

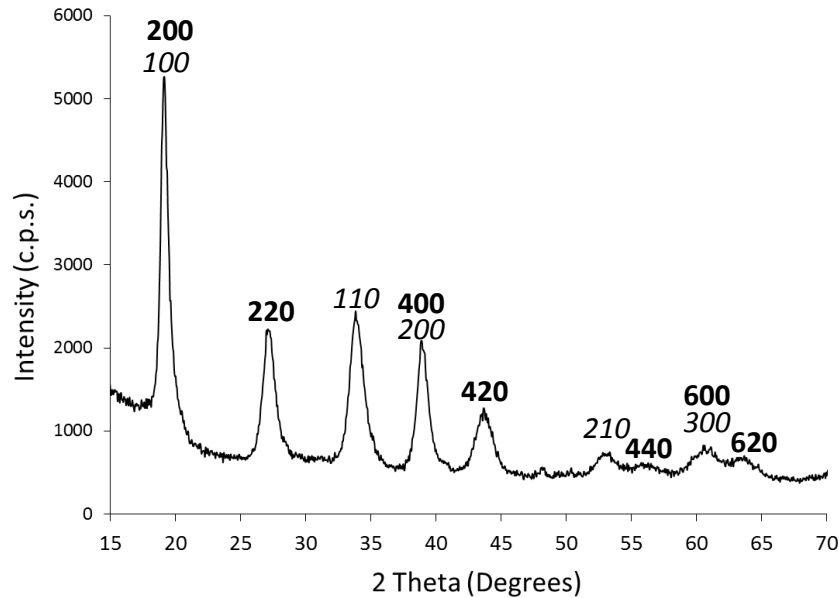


Figure III.5. In-plane ($hk0$) X-ray diffraction pattern of $(\text{SnSe})_{1.13}(\text{Nb}_{0.51}\text{Mo}_{0.49})\text{Se}_2$. Indices for the cubic SnSe are given in bold, while those of the hexagonal $(\text{Nb}_{0.51}\text{Mo}_{0.49})\text{Se}_2$ are given in italic.

values for the $(\text{SnSe})_{1.09}\text{MoSe}_2$ ²² and $(\text{SnSe})_{1.16}\text{NbSe}_2$ ⁶ parent compounds of 6.003(1) Å and 5.928(1) Å respectively. The a -lattice parameter of the $\text{Nb}_{0.51}\text{Mo}_{0.49}\text{Se}_2$ was found to be 3.398(4) Å which is also between the literature values for the parent compounds of 3.320(1) Å for the $(\text{SnSe})_{1.06}(\text{MoSe}_2)$ and 3.441(1) Å for the $(\text{SnSe})_{1.16}\text{NbSe}_2$. Based on the unit cell parameters of the rocksalt and dichalcogenide components, the structural misfit was calculated to be $z = 1.13$ also falling between the published values of the parent $(\text{SnSe})_{1.09}(\text{MoSe}_2)$ and $(\text{SnSe})_{1.16}\text{NbSe}_2$ systems.

In-plane diffraction patterns of the ferecystals, shown in Figure III.6a, exhibit a shift to lower angles of the (110) peaks of the dichalcogenide constituent with increasing Nb content. This is caused by a linear increase in the dichalcogenide a -lattice parameter that is very similar to Kalikhman's findings for the $(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ TMD systems, as shown in Figure III.6b. While increasing the Nb content of the alloys causes a decrease in the c -lattice parameter of the film, it increases the a -lattice parameter of the dichalcogenide constituent. The result is an overall decrease in the c/a ratio of the unit cell with increased Nb content. Moussa Bougouma *et al*¹⁴ attributed this decrease in c/a ratio with increased Nb to a decrease in electron density in the $4dz^2$ of the transition metal. They postulated that this leads to a less pronounced repulsion of the selenium atoms by this non-bonding orbital and a decrease in the c -lattice parameter. Further, they attribute the increase in a -lattice parameter to changes in inner shell repulsion with the repulsion of the selenium $3p_x$ and $3p_y$ orbitals stronger than the repulsion of the $3p_z$ orbitals. Structural rearrangement takes place to reduce repulsion of the $3p_x$ and $3p_y$ orbitals resulting in an increase in a -lattice parameter and a decrease in c -lattice parameter as the Nb/Mo ratio

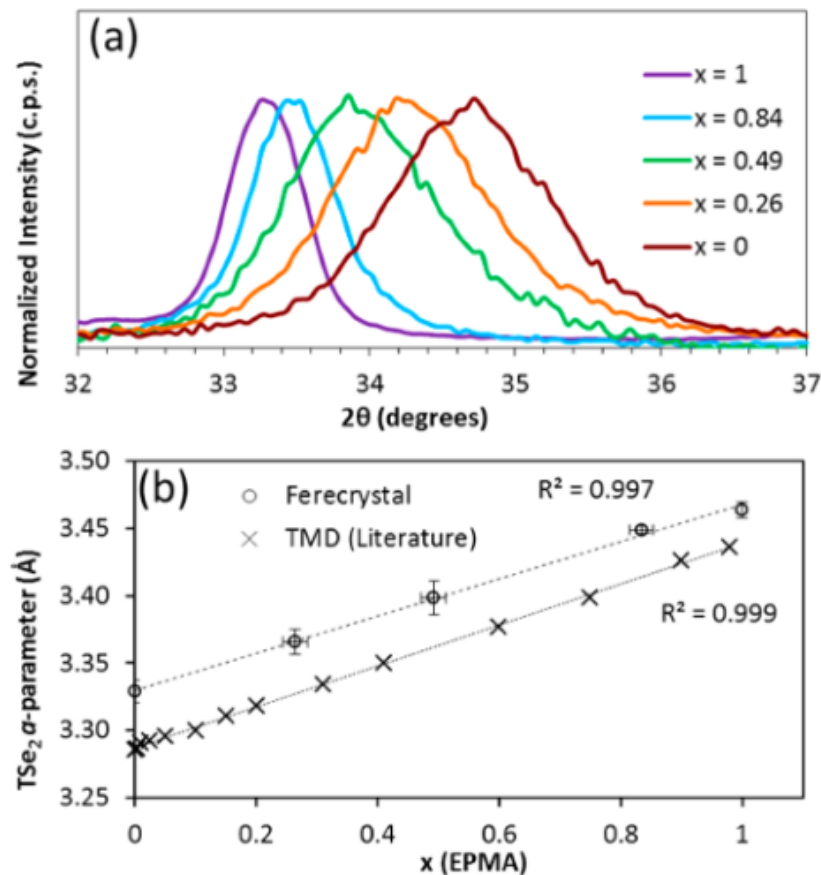


Figure III.6. (a) In-plane X-ray diffraction patterns showing shift in the (110) peak of the dichalcogenide with changes in Mo/Nb ratio. (b) Plot of dichalcogenide a -lattice parameter vs. x for $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloys.

increases. While the a -lattice parameter of the dichalcogenide increases with Nb content, the rock salt a -lattice parameter, as shown in Figure III.7a, does not change within error. This supports the view that the substitution of Nb into $(\text{SnSe})_{1.09}(\text{MoSe}_2)$ takes place exclusively in the dichalcogenide layer leaving the structure of the rock salt largely unchanged. Changes in the relative a -parameters of the dichalcogenide and rock salt layers leads to a linear change in the misfit parameter of the $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloys as a function of x , varying from 1.09 at $x = 0$ to 1.16 at $x = 1$, as shown in Figure III.7b.

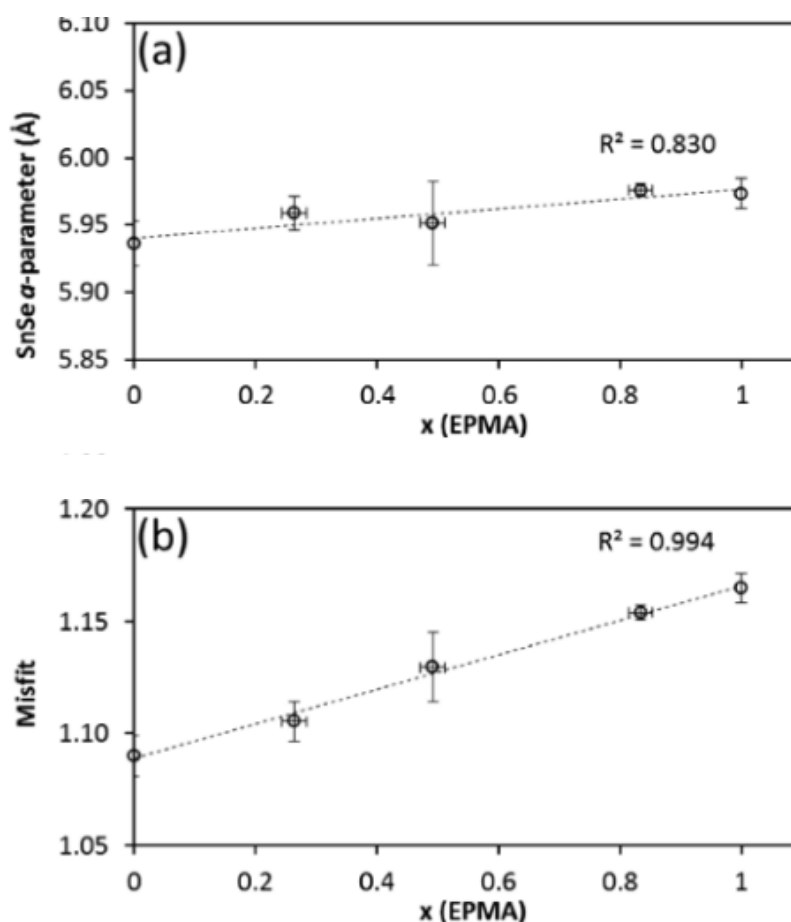


Figure III.7. (a) Plot of rock salt a -parameter vs. x for $(\text{SnSe})_z(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloys. (b) Misfit parameter (z) vs. x for $(\text{SnSe})_z(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloys.

High-angle annular dark-field (HAADF) STEM was used to further investigate the structure of the ferecrystal alloys. A Z-contrast STEM image of the $([\text{SnSe}]_{1.13})_1(\text{Nb}_{0.49}\text{Mo}_{0.51}\text{Se}_2)_1$ ferecrystal is shown in Figure III.8. The coordination of the transition metal is clearly trigonal prismatic as can be seen from the chevron structure in the expanded region of Figure III.8. Distinct alternating parallel layering of SnSe bilayers with $\text{Nb}_{0.49}\text{Mo}_{0.51}\text{Se}_2$ monolayers is observed as expected based on $00l$ X-ray diffraction measurements. While several different crystal orientations of the constituent layers can be seen in the image without any relationship between them, a degree of short range order

can be seen in the upper left corner of the image, with adjacent SnSe and dichalcogenide layers showing the same orientation in adjacent layers.

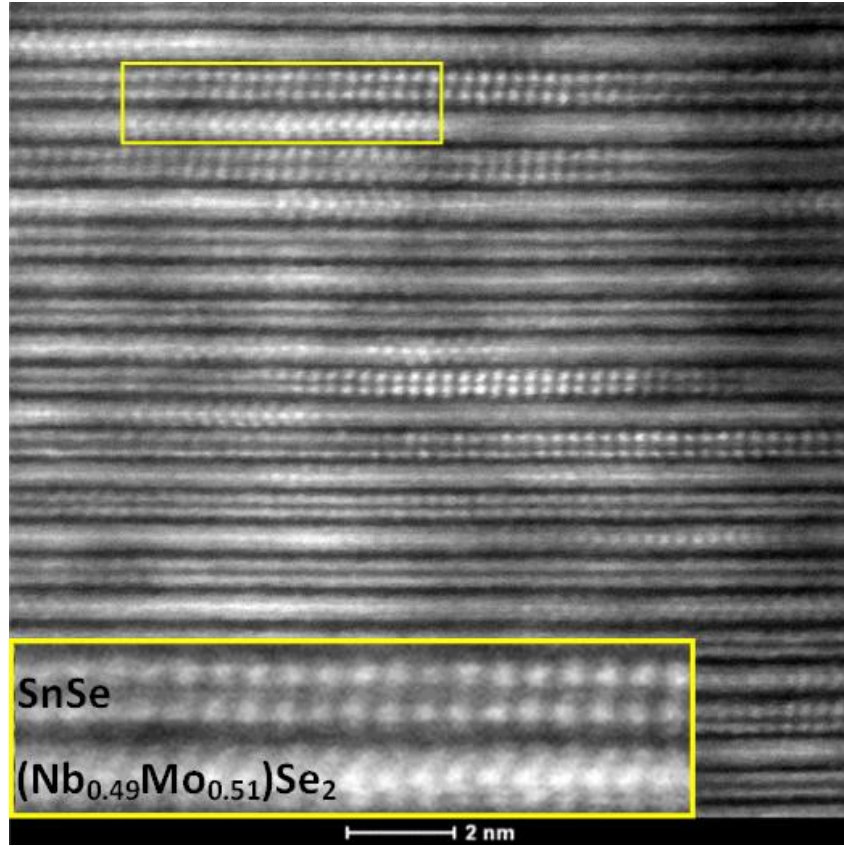


Figure III.8. STEM image of $(\text{SnSe})_{1.13}\text{Nb}_{0.51}\text{Mo}_{0.49}\text{Se}_2$

In order to further investigate the long range order of the $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloys, area X-ray patterns were obtained at the Advanced Photon Source (APS). A representative image of the $(\text{SnSe})_{1.13}(\text{Nb}_{0.49}\text{Mo}_{0.51})\text{Se}_2$ ferecrystal is shown in Figure III.9. Significant broadening of the reflections along the c -direction is indicative of a short coherence length in this direction. The lack of long range coherent scattering from the layered constituents is indicative of turbostratic disorder and confirms that only short range order exists between the layers as seen in the STEM image in Figure III.8.

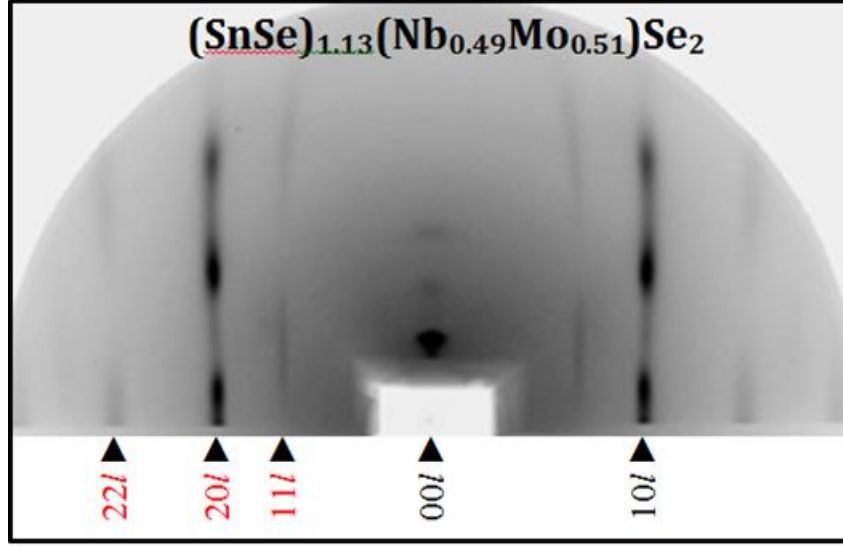


Figure III.9. 2D X-ray diffraction pattern of $(\text{SnSe})_{1.13}\text{Nb}_{0.51}\text{Mo}_{0.49}\text{Se}_2$ ferecrystal.

To measure electrical transport properties, $(\text{SnSe})_{1.16-1.09}\text{Nb}_x\text{Mo}_{1-x}\text{Se}_2$ ferecrystals with $x = 0, 0.35, 0.54, 0.76$ and 1 were deposited on quartz slides. X-ray and EPMA analysis confirmed these samples had the same diffraction patterns and compositions as the samples deposited on silicon wafers and discussed earlier. The $(\text{SnSe})_{1.09}\text{MoSe}_2$ showed semiconducting resistivity vs. temperature behavior, as shown in Figure III.10, with a room temperature resistivity $\rho = 220 \text{ m}\Omega\text{-cm}$. This is similar to previously published values for the $(\text{SnSe})_{1.09}\text{MoSe}_2$ ferecrystal of $\rho = 140 \text{ m}\Omega\text{-cm}$.²² The $(\text{SnSe})_{1.16}\text{NbSe}_2$ ferecrystal showed metallic resistivity vs. temperature behavior with $\rho = 0.35 \text{ m}\Omega\text{-cm}$ at 300K dropping slightly to $0.14 \text{ m}\Omega\text{-cm}$ at 20K . This is a slightly lower resistivity than was reported by Wiegiers *et al* for the crystalline misfit layer compound analog.⁶ Wiegiers reported a $\rho = 0.58 \text{ m}\Omega\text{-cm}$ at 300K which dropped to $0.28 \text{ m}\Omega\text{-cm}$ at 4K . The lower resistivity measured for the ferecrystal is surprising, given the extent of turbostratic disorder. This suggests that the rotational disorder is not an effective scatter of the charge carriers. Electrical resistivity vs. temperature behavior of the

(SnSe)_zNb_xMo_{1-x}Se₂ alloy ferecrystals, shown in Figure III.10, was consistent with heavily doped semiconductors becoming more metallic with increased x.

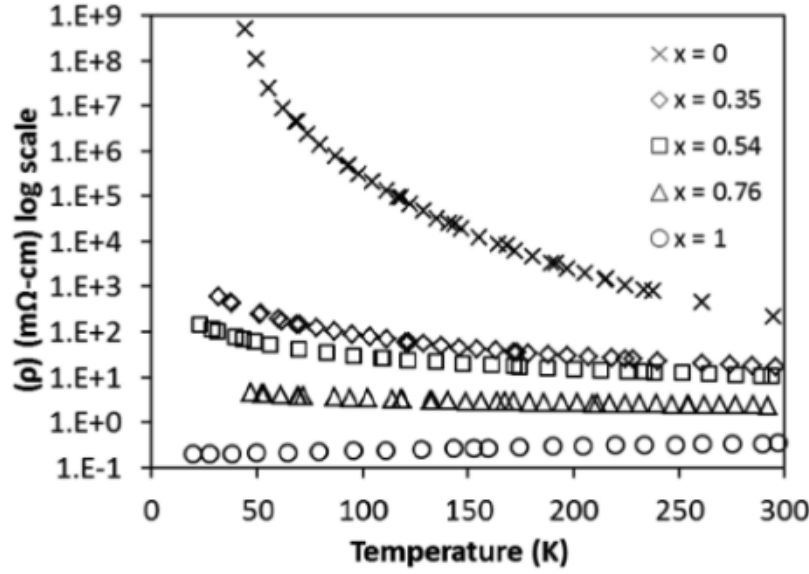


Figure III.10. Resistivity vs. temperature for (SnSe)_{1.16-1.09}(Nb_xMo_{1-x})Se₂ ferecrystals with x = 0, 0.35, 0.54, 0.76 and 1.

The room temperature electrical transport properties of the (SnSe)_{1.16-1.09}(Nb_xMo_{1-x})Se₂ alloy ferecrystals exhibit electrical transport properties between those of the (SnSe)_{1.09}MoSe₂ and (SnSe)_{1.16}NbSe₂ ferecrystals. Electrical conductivity, shown in Figure III.11a, increases slowly for x between 0 and 0.54, increasing more rapidly as x approaches 1. This is similar to results from the (Nb_xMo_{1-x})Se₂ TMD system where Kalikhman¹² attributed it to formation of deep impurity bands which reduce the number of carriers added per Nb to less than 1 for Mo rich (Nb_xMo_{1-x})Se₂ alloys. This is supported by the room temperature carrier concentration vs. x of the (SnSe)_{1.16-1.09}Nb_xMo_{1-x}Se₂ ferecrystals, calculated from measured Hall coefficients using the single band model.

Figure III.11b shows that carrier concentrations are consistently lower than the linear slope expected by the addition of a single hole per added Nb atom. Calculations based on unit cell size and the number of Nb atoms per unit cell indicates that the number of holes per Nb drops with additional Mo from 0.98 hole/Nb at $x = 1$ to 0.25 hole/Nb at $x = 0.35$.

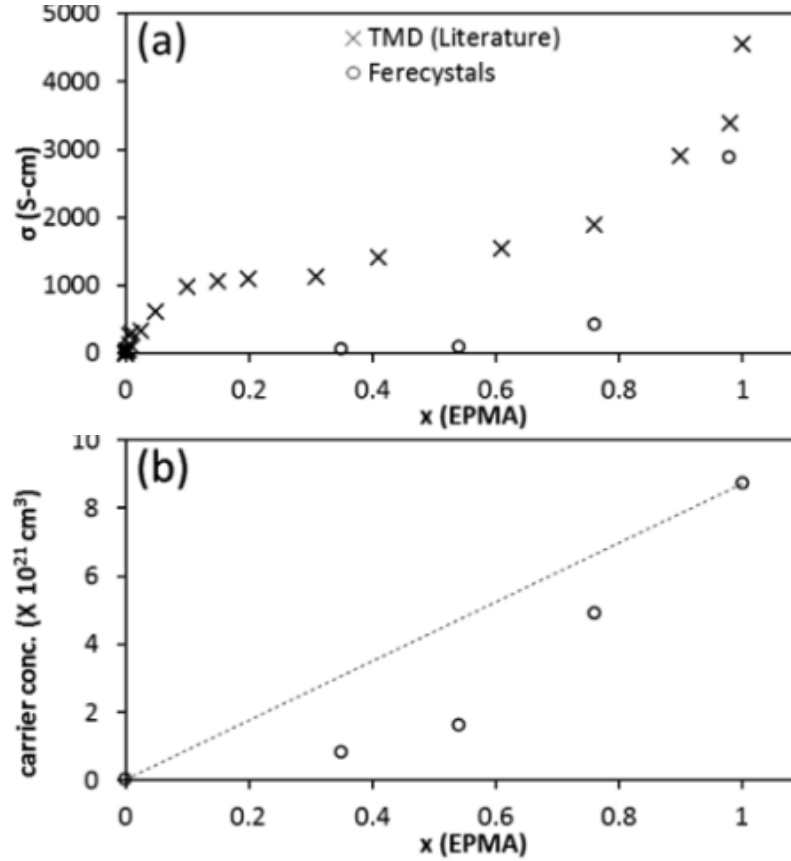


Figure III.11. (a) Room Temperature conductivity vs. x for $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloys compared to literature values for $(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ TMD alloys. (b) Room Temperature carrier concentration vs. x for $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloys.

III.5. Conclusion

The mixed-metal ferecystal compounds, $(\text{SnSe})_{1.16-1.09}\text{Nb}_x\text{Mo}_{1-x}\text{Se}_2$ with $x = 0$, 0.26, 0.49, 0.83, and 1, were successfully produced via adaptation of the modulated elemental reactant method. To our knowledge, this is the first report of a systematic solid

solution in misfit compounds and was enabled by the structure and short diffusion lengths in the designed precursors. Structural changes observed in the alloys, as a function of metallic ratios, were similar to literature observations for the $\text{Nb}_x\text{Mo}_{1-x}\text{Se}_2$ system. A linear decrease in the c -lattice parameters was observed from 12.53(2) Å for $(\text{SnSe})_{1.09}\text{MoSe}_2$, to 12.27(2) Å for $(\text{SnSe})_{1.16}\text{NbSe}_2$. A linear increase in the a -parameters of the dichalcogenide constituent was observed from 3.329(8) Å for $(\text{SnSe})_{1.09}\text{MoSe}_2$, to 3.461(4) Å for $(\text{SnSe})_{1.16}\text{NbSe}_2$. Very little change was observed in the a -lattice parameter of the rocksalt constituent leading to a linear increase in misfit parameter of the alloys with increased Nb content. STEM imaging and 2D-Xray diffraction confirm structural characteristics similar to misfit layer compounds but also show turbostratic disorder indicative of ferecrystals. Electrical transport properties of these $(\text{SnSe})_{1.16-1.09}\text{Nb}_x\text{Mo}_{1-x}\text{Se}_2$ ferecrystals were found to be between those of the semiconducting $(\text{SnSe})_{1.09}\text{MoSe}_2$ and metallic $(\text{SnSe})_{1.16}\text{NbSe}_2$ parent compounds but with carrier concentrations and conductivity consistently lower than expected by the addition of a single hole per added Nb atom.

III.6. Bridge

The ability to use kinetic control in modulated elemental reactants allows the ability to form many compounds that do not exist on phase diagrams. The synthesis of multiple constituent systems should be possible via this technique by interleaving the structures together. A small amount of alloying is expected if miscible constituents with similar structures are used. The determination of the extent of alloying in a multiple constituent system is requires meaningful standards for comparison.

The following chapter describes the synthesis of the first three component ferecrystal $(\text{SnSe})_{1.16}([\text{Mo}_{0.9}\text{Nb}_{0.1}]\text{Se}_2)_{1.06}(\text{SnSe})_{1.16}([\text{Nb}_{0.9}\text{Mo}_{0.1}]\text{Se}_2)$. The synthesis of $(\text{SnSe})_{1.16-1.09}\text{Nb}_x\text{Mo}_{1-x}\text{Se}_2$ ferecrystal alloys in Chapter III provides standards whereby alloying of the miscible NbSe_2 and MoSe_2 constituents can be determined.

CHAPTER IV

SYNTHESIS AND CHARACTERIZATION OF QUATERNARY MONOLAYER

THICK MoSe₂/SnSe/NbSe₂/SnSe HETEROJUNCTION SUPERLATTICES

IV.1. Authorship Statement

Chapter IV was published in *Chemistry of Materials*, volume 27, pages 6411-6417 in 2015. Co-author Jeffrey J. Ditto performed microscopy measurements. Co-author Dr. Matthias Falmbigl assisted in structural refinements. Co-author Zachary L. Hay assisted in the annealing study and diffraction experiments. Dr. David C. Johnson is my advisor and I am the primary author of the manuscript.

IV.2. Introduction

Heterostructures containing different layers of 2-D crystals interleaved with one another in defined order have attracted considerable interest as they provide a potentially broad platform where ideas for exceptional performance or new functionalities can be theoretically tested with reasonable assumptions about structure.¹⁻¹² A key driver for this interest is the high probability that it will be possible to experimentally verify predictions. While initially the focus was on graphene-based heterostructures, there is increasing interest in preparing systems using other 2-D materials such as hexagonal BN and transition metal dichalcogenides (TMDs). Recent work includes the prediction that van der Waals crystals, containing alternate layers of MoS₂ and WS₂, will have optical and electronic properties distinct from its individual components⁸ and the prediction of piezoelectricity in systems where different 2-D constituents are layered.⁹ The use of TMD nanostructures such as ultra-thin films or nanoparticles has recently improved the properties of TMDs dramatically. Semiconducting TMDs, such as MoS₂ and MoSe₂, are

currently being investigated for numerous applications (electrochemical sensors,¹⁰ supercapacitors,¹¹ photovoltaics,¹² and as catalysts for water splitting reactions).¹³⁻¹⁴ While bulk MoS₂ shows limited utility as a hydrogen evolution reaction (HER) catalyst- due to low conductivity and high onset voltage¹³ -its performance is greatly improved by incorporating MoS₂ nanoparticles onto the surface of reduced graphene oxide sheets.¹⁴ The observation that the properties of 2-D materials often differ from those of the bulk compounds will continue to be an important motivation to synthesize and study heterostructures.

While techniques exist for the synthesis of heterostructures, their preparation remains a challenge. One approach has been the cleaving and stacking of individual layers. While this technique has led to the formation of many new and exciting structures, it is an exacting task only done by a few groups with very low yield.¹⁻⁷ Additionally, metallic layers have generally been found to be unstable in ambient atmosphere.¹ Epitaxy provides another approach for the synthesis of heterostructures. Koma has shown that it is possible to grow TMD superlattices via MBE, coining the term van der Waals epitaxy due to the weak bonding between constituent layers.¹⁵⁻¹⁷ While this technique has produced films of exceptional quality, van der Waals epitaxy of superlattices is challenging for several reasons. The weak interlayer attraction tends to the formation of island structures rather than coherent monolayers. MBE becomes increasingly difficult as the number of constituents increases, requiring separate sets of growth conditions for each. Frequently it is not possible to grow both B on A and A on B. In addition, if the two constituents are thermodynamically miscible, increased interdiffusion occurs as the modulation wavelength of the superlattice decreases.¹⁸⁻¹⁹ Significant analytical challenges

arise when attempting to determine the extent of interdiffusion as precise compositional analysis of single layers is non-trivial. Preparing multi constituent heterostructures is experimentally challenging.

Here we demonstrate that the modulated elemental reactant (MER) method is viable for the formation of ordered systems containing three different structural constituents. To the best of our knowledge, there have been no reports of crystalline misfit layer compounds with three distinct constituents. The compound with a formula of $(\text{SnSe})_{1+\delta}(\text{MoSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}(\text{NbSe}_2)_1$ was targeted from a precursor with an initial structure containing a repeating sequence of elemental layers in the order Sn|Se|Mo|Se|Sn|Se|Nb|Se, as illustrated in Figure IV.1. The targeted compound is a "worst case" synthetic challenge because compounds with alloyed transition metal dichalcogenide layers, $(\text{SnSe})_{1+\delta}(\text{Nb}_{1-y}\text{Mo}_y)\text{Se}_2$, readily form²⁰ and the single bilayer-thick SnSe layer is only a 0.6 nm barrier to the mixing of the transition metals during self-assembly of the precursor into the desired superstructure. Due to the interdiffusion of miscible heterostructures synthesized by both normal and van der Waals epitaxy, and the reported miscibility of NbSe₂ and MoSe₂,²¹ interdiffusion of the dichalcogenides is difficult to avoid. The extent of the interdiffusion was evaluated by comparing structural as well as electrical properties to the $(\text{SnSe})_{1+\delta}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ ferecrystal alloys reported previously.²⁰ We estimate a stoichiometry of $(\text{SnSe})_{1.16}([\text{Mo}_{0.9}\text{Nb}_{0.1}]\text{Se}_2)_{1.06}(\text{SnSe})_{1.16}([\text{Nb}_{0.9}\text{Mo}_{0.1}]\text{Se}_2)$ for the prepared compound. This suggests that MER provides a general route to the synthesis of van der Waals heterostructures. The ability of MER to prepare heterostructures with several constituents in designed arrangements greatly expands the range of theoretical predictions which can be experimentally tested.

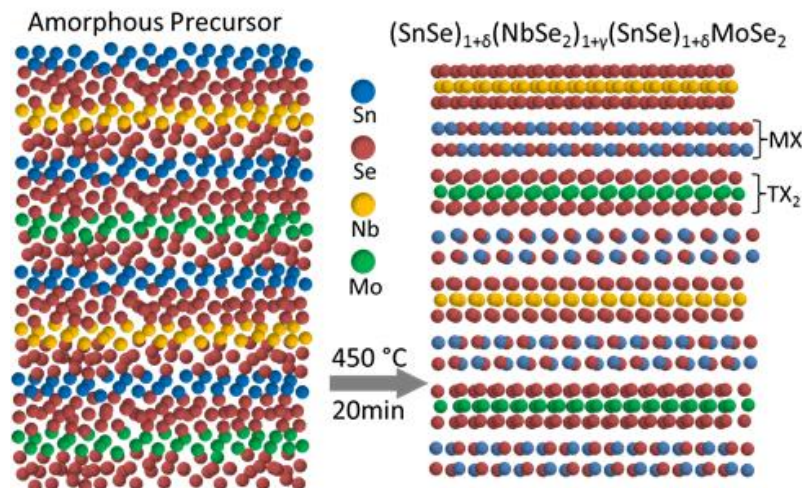


Figure IV.1. (a) Synthesis schematic for $(\text{SnSe})_{1+\delta}(\text{MoSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}(\text{NbSe}_2)_1$. The as deposited precursor is depicted on the left with the self-assembled ferecystal on the right.

IV.3. Experimental

The $(\text{SnSe})_{1+\delta}(\text{MoSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}(\text{NbSe}_2)_1$ samples were self-assembled from carefully designed modulated precursors prepared using a custom-built physical vapor deposition system.²² A vacuum system with dual turbo and cryo pumps allowed depositions at pressures as low as 10^{-8} torr. Mo (99.95% purity), Nb (99.8% purity), Sn (99.999% purity) and Se (99.5% purity) acquired from Alfa Aesar were used as elemental sources. Metal sources were evaporated at rates of approximately 0.2 Å/s for Mo and Nb and 0.4 Å/s for Sn, using Thermionics 3 kW electron beam guns. Se was evaporated using a custom built Knudsen effusion cell at a rate of about 0.5 Å/s. Deposition rates were monitored with INFICON Xtal quartz microbalance monitors. Substrates were mounted on a rotating carousel controlled by a custom designed LabVIEW program, which positioned the sample over the desired source. Pneumatically powered shutters between the elemental sources and the substrates controlled the exposure time of the samples to the elemental flux. Repetition of this process allowed the modulated

precursors to be built up layer-by-layer until reaching a desired thickness between 500 and 600 Å. This thickness was chosen for convenience. Films thicker than ~300 nm become less crystallographically aligned due to cumulative roughness. Films containing a single repeating unit are difficult to characterize. The precursors were annealed on a hotplate under inert conditions with $O_2 < 0.6$ ppm in a N_2 drybox.

Compositions of the modulated precursors and ferecrystal samples were determined by electron probe micro-analysis (EPMA) on a Cameca SX-100. Acceleration voltages of 7, 12, and 17 keV were used to collect intensities. Composition was then calculated from the film and substrate as a function of acceleration voltage as described previously.²³

Total thickness and repeating unit thickness were monitored by high resolution X-ray reflectivity (XRR) and X-ray diffraction (XRD) performed on a Bruker D8 Discover diffractometer, equipped with a $Cu K_\alpha$ X-ray source and Göbel mirror optics. *ab*-plane lattice parameters were determined from in-plane Synchrotron X-ray diffraction performed at the Advanced Photon Source (APS), Argonne National Laboratory (beamline 33BM).

Transmission electron microscopy (TEM) cross-section, lift-out samples were prepared and analyzed at the Center for Advanced Materials Characterization in Oregon (CAMCOR) High-Resolution and Nanofabrication Facility. Scanning transmission electron microscopy (STEM) samples were prepared using an FEI NOVA Nanolab Dual Beam FIB equipped with Side winder ion column and performed on a FEI 80-300 kV Titan equipped with a Fischione Model 3000 Annular Dark Field (ADF) detector. All images were collected at 300 kV.

Electrical measurements were obtained from samples deposited on quartz slides in a 1 x 1 cm cross-pattern defined by a shadow mask. Temperature dependent resistivity and Hall effect measurements were performed using the van der Pauw technique as described previously.²⁴

IV.4. Results and Discussion

The targeted compounds were prepared from compositionally modulated precursors with appropriate compositions, layering sequence, and layer thicknesses which were subsequently annealed to self-assemble the desired structure. The calibrations for the parent ternary compounds, $(\text{SnSe})_{1.04}\text{MoSe}_2$ and $(\text{SnSe})_{1.16}\text{NbSe}_2$ have been previously reported,^{25,26} and were used as a starting point to form the initial quaternary $(\text{SnSe})_{1+\delta}(\text{MoSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}(\text{NbSe}_2)_1$ ferecrystal. The calibration process for the quaternary $(\text{SnSe})(\text{NbSe}_2)_z(\text{SnSe})(\text{MoSe}_2)_z$ precursor involved scaling the precursor for $(\text{SnSe})_{1.04}\text{MoSe}_2$ to compensate for the misfit between the ternary compounds. The procedure followed was similar to that described previously for two-constituent systems.²⁴

The annealing conditions required to form the $(\text{SnSe})_{1+\delta}([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}$ $(\text{SnSe})_{1+\delta}([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)$ ferecrystal were determined by annealing the precursor at temperatures ranging from 300 to 500 °C for 20 min in 50 °C increments. The resulting diffraction scans are shown in Figure IV.2. In the as-deposited sample, the first few diffraction peaks are visible but there is considerable broadening of the higher order peaks (Figure IV.2a). This indicates that the as-deposited sample lacks long-range order. At 300°C, additional (00l) reflections are apparent and increase in intensity with

increased annealing temperature. A maximum intensity with minimum full width at half maximum (FWHM) is reached at 450°C, as shown in Figures IV.3a and IV.3b. Above

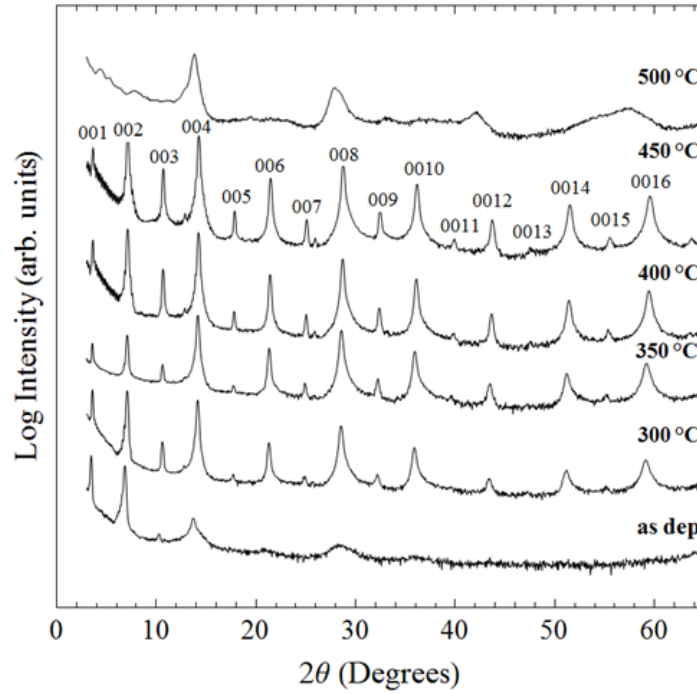


Figure IV.2. Specular XRD patterns of $(\text{SnSe})_{1+\delta}([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}$ ($[\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2$) annealed at temperatures ranging from 300 to 500 °C. The (00 l) indices are shown above the scan taken after annealing at 450°C.

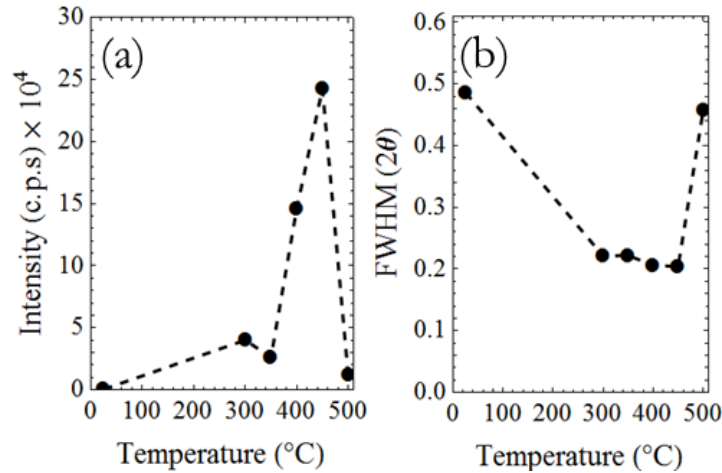


Figure IV.3. (a) Change in the intensity of the (004) reflection with temperature. (b) Change in the FWHM of the (004) reflection with temperature.

450°C, peaks broaden and lose intensity due to the metastable nature of the product.

Consequently, 450°C was chosen as the annealing temperature for this system.

The amorphous $(\text{Sn|Se})(\text{Nb|2Se})_z(\text{Sn|Se})(\text{Mo|2Se})_z$ precursor clearly self-assembles into the ferecrystalline product; however, interdiffusion of the dichalcogenide metals across the SnSe may occur resulting in a structure better described by $(\text{SnSe})_{1+\delta}(\text{Nb}_x\text{Mo}_{1-x}\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}(\text{Mo}_x\text{Nb}_{1-x}\text{Se}_2)$, where x represents the extent of intermixing between the resulting Nb-rich and Mo-rich dichalcogenide constituents. This interdiffusion is often seen in superlattices with miscible constituents and increases as the superlattice period decreases.¹⁸⁻¹⁹ It is analytically difficult to determine the exact composition of individual layers within the structure. The specular X-ray diffraction pattern of $(\text{SnSe})_{1+\delta}([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)$, shown in Figure IV.4,

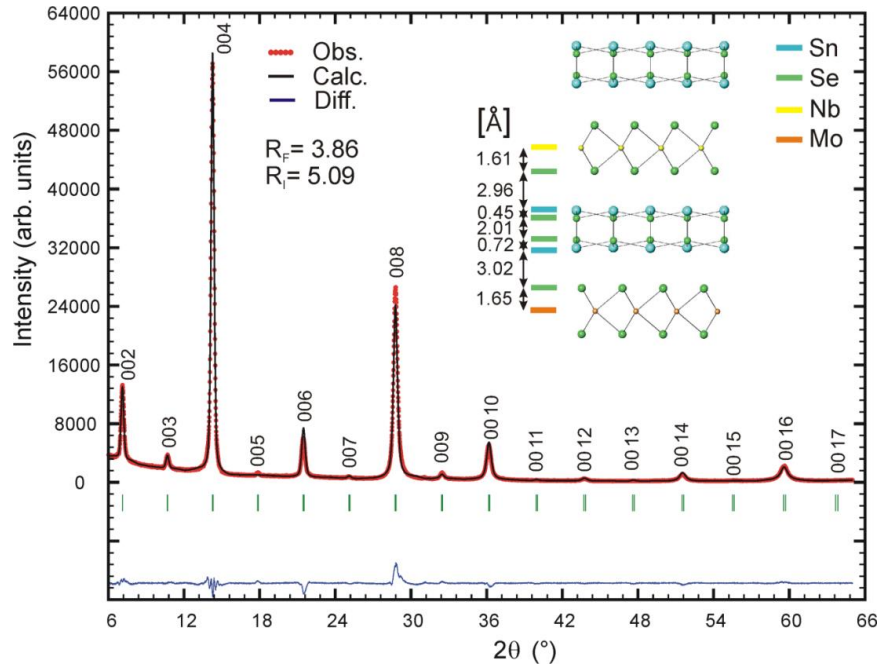


Figure IV.4. Rietveld refinement of the $(\text{SnSe})_{1+\delta}([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)$. Experimental data are in black and the fit to the data in red with the residuals below in blue. The inset shows the structure and distances obtained from the fit.

contains (00 l) superlattice peaks not seen in the X-ray pattern of the (SnSe)_{1.13}(Nb_{0.51}Mo_{0.49})Se₂ alloy ferecrystal published previously,²⁰ indicating that the c-axis lattice parameter has approximately doubled in size. This implies that the sample has Nb-rich and Mo-rich regions as described by the above formula. Figure IV.4 also shows the Rietveld refinement of the 00 l data, which gives the positions of the planes of atoms along the c direction. The c-lattice parameter obtained is 2.484(2) nm, which is close to that expected from the sum of the two parent compounds, (SnSe)_{1.04}MoSe₂ and (SnSe)_{1.16}NbSe₂.^{25,26} As the electron density differences between Mo and Nb are slight, only differing by a single electron, the extent of intermixing cannot rigorously be determined using this method, but a best fit was obtained assuming a negligible amount of interdiffusion. The distances between the plane of transition metal atoms and the planes of selenium atoms in the Se-T-Se trilayers were determined to be 1.65(2) and 1.61(2) Å, which match well with the published values of 0.16(1) and 0.1644(2) nm for the (SnSe)_{1.04}MoSe₂ and (SnSe)_{1.16}NbSe₂ parent ferecrystals.^{25,26} The distance between the dichalcogenide selenium atoms and the neighboring rock salt atoms were determined to be 0.302(2) and 0.296(2) nm, which also match well with the published values for the (SnSe)_{1.04}MoSe₂ and (SnSe)_{1.16}NbSe₂ parent compounds of 0.31(1) and 0.2906(1) nm respectively. The total thickness of the rock salt bilayer, 0.318 nm, is close to that found in the parent compounds 0.30(2) nm for (SnSe)_{1.04}MoSe₂ and 0.316(1) nm for (SnSe)_{1.16}NbSe₂). The Rietveld refinement also revealed information regarding the puckering of the rock salt layers arising from interlayer attraction. During the refinement, however, we found that the puckering values were unstable, varying greatly with changes in the composition or misfit parameter used in the fit. While the puckering of the rock salt

on the NbSe₂ side was found to be 0.05(2) nm, closely matching the value of 0.045(1) nm found for the (SnSe)_{1.16}NbSe₂ parent compound, the puckering of the SnSe on the MoSe₂ side was 0.07(2) nm. This is somewhat larger than that found in typical ferecrystals and may be indicative of stronger interlayer interaction, but also could be due to defects.

To gain additional structural information about the (SnSe)_{1+δ}[(Mo_xNb_{1-x})Se₂]_{1+γ}(SnSe)_{1+δ}[(Nb_xMo_{1-x})Se₂] films, high-angle annular dark-field (HAADF) STEM images were obtained. Figure IV.5a illustrates the long-range order and precise layering in the sample that result in the sharp diffraction pattern shown in Figure IV.4. The alternating layering of SnSe bilayers with the dichalcogenide regions can be clearly seen. The coordination of the various atoms can be clearly seen in the Z-contrast STEM image expansions provided in Figure IV.5b. The chevron structure observed in the dichalcogenide

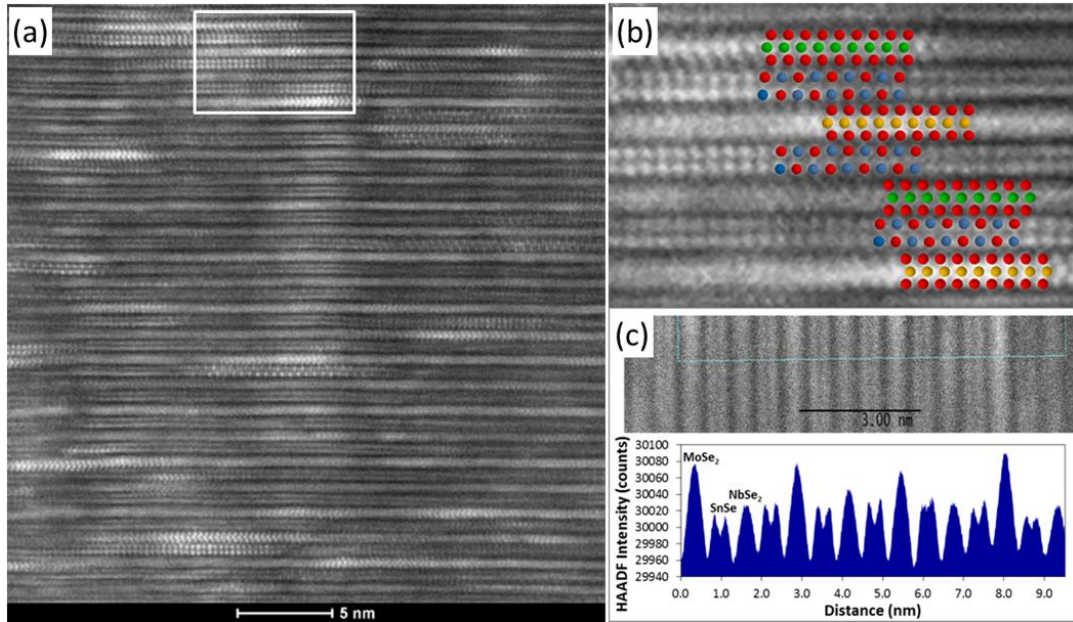


Figure IV.5. (a) STEM image of (SnSe)_{1+δ}[(Mo_xNb_{1-x})Se₂]_{1+γ}(SnSe)_{1+δ}[(Nb_xMo_{1-x})Se₂]. (b) Expansions of different layers within part a showing the local coordination of the layers. (c) HAADF Intensity line profile for (SnSe)_{1+δ}[(Mo_xNb_{1-x})Se₂]_{1+γ}(SnSe)_{1+δ}[(Nb_xMo_{1-x})Se₂] film.

regions indicates trigonal prismatic coordination for the transition metals, while a rock salt structure is observed for the SnSe constituents. In Figure IV.5a, the Z-contrast is insufficient to distinguish between the MoSe₂ and the NbSe₂ layers. Increasing the electron current and reducing the camera length allowed the Z-contrast of the image to be further improved, but with a loss of atomic resolution. A HAADF intensity line profile, given in Figure IV.5c, clearly shows a difference in intensity for the two dichalcogenide layers. The contrast results from the slightly increased Z-value of Mo, as well as a reduced a-lattice parameter of MoSe₂ compared to NbSe₂, which increases the density of the MoSe₂ layer.

To further identify the different layers within the (SnSe)_{1+δ}([Mo_xNb_{1-x}]Se₂)_{1+γ}(SnSe)_{1+δ}([Nb_xMo_{1-x}]Se₂) film, EDX line scans were also performed (Figure IV.6). While the separation of the Mo, Nb, and Sn into distinct layers was observed, quantifying the

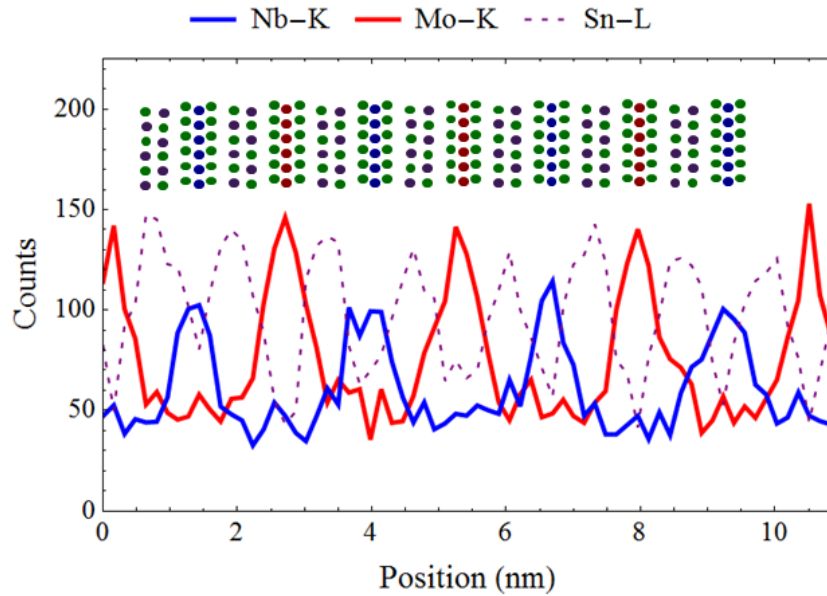


Figure IV.6. EDX line scan of (SnSe)_{1+δ}([Mo_xNb_{1-x}]Se₂)_{1+γ}(SnSe)_{1+δ}([Nb_xMo_{1-x}]Se₂). The Mo-K line (red), Nb-K line (blue) and the Sn-L line (purple dashed) are shown. Selenium omitted for clarity.

amount of interdiffusion is difficult using EDX as it requires accurate measurement of the background signal of the instrument. The peak widths of the EDX signals are determined by the excitation volume of the electron beam, resulting in widths that are broader than the 0.6 nm thicknesses of the individual layers. This limits our ability to determine the extent of mixing between adjacent layers.

In order to study the in-plane structure of $(\text{SnSe})_{1+\delta}([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)$, the $hk0$ diffraction pattern of the ferecrystal was collected and compared to those of the parent compounds (Figure IV.7). $hk0$ diffraction scans, shown in Figure IV.7a, exhibit diffraction maxima that can be attributed to a single SnSe rock salt structured constituent and the dichalcogenide structured constituents. The splitting of the dichalcogenide peaks indicates the presence of two distinct dichalcogenides. The dichalcogenide 110 reflection, expanded in Figure IV.7b, shows diffraction maxima for

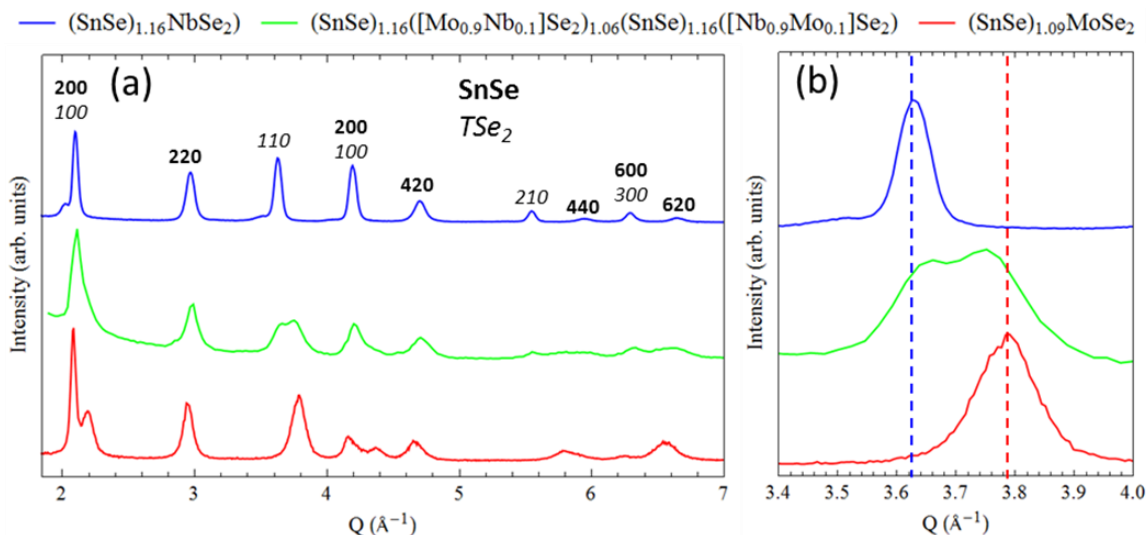


Figure IV.7. (a) In-plane ($hk0$) XRD pattern of $(\text{SnSe})_{1+\delta}([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)$ compared to the $(\text{SnSe})_{1.16}\text{NbSe}_2$ and $(\text{SnSe})_{1.09}\text{MoSe}_2$ parent compounds. Indices for the SnSe are given in bold, while those of the TSe_2 (where $\text{T} = \text{Mo}$ and/or Nb) are given in italics. (b) Expansion of the TSe_2 110 region.

the $(\text{SnSe})_{1+\delta}([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)$ at positions between those of the $(\text{SnSe})_{1.16}\text{NbSe}_2$ and $(\text{SnSe})_{1.09}\text{MoSe}_2$ parent compounds. This change in the a-axis lattice parameters could be a result of the different compositions of the dichalcogenides, electron transfer, or templating of the dichalcogenide layers through the rock salt. If different compositions are assumed to be the dominant cause for the splitting, the maximum extent of the interdiffusion in the $(\text{SnSe})_{1+\delta}([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)$ can be estimated. As expected from Vegard's law, a linear relationship between composition and in-plane lattice parameter was found previously in a study of $(\text{SnSe})_z(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ ferecrystal alloys.²⁰ Using this data, we estimate a maximum value for the amount of interdiffusion of $12 \pm 2\%$, which agrees with our estimate from the Rietveld refinement and is comparable to MBE grown epitaxial superlattices with periods in this range.¹⁸⁻¹⁹ This would give a formula of $(\text{SnSe})_{1.16}([\text{Mo}_{0.9}\text{Nb}_{0.1}]\text{Se}_2)_{1.06}(\text{SnSe})_{1.16}([\text{Nb}_{0.9}\text{Mo}_{0.1}]\text{Se}_2)$ for the compound.

Electrical resistivity vs. temperature for the $(\text{SnSe})_{1.16}([\text{Mo}_{0.9}\text{Nb}_{0.1}]\text{Se}_2)_{1.06}(\text{SnSe})_{1.16}([\text{Nb}_{0.9}\text{Mo}_{0.1}]\text{Se}_2)$ ferecrystal shows that it is metallic with an order of magnitude higher resistivity than that of $(\text{SnSe})_{1.16}\text{NbSe}_2$ and two orders of magnitude lower than $(\text{SnSe})_{1.09}\text{MoSe}_2$ (Figure IV8a). The resistivity shows a slight increase with decreasing temperature previously observed in Nb-rich $(\text{SnSe})_{1+\delta}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ ferecrystal alloys. Since the SnSe rock salt and Mo-rich dichalcogenide layers are expected to be semiconducting, the majority of charge conduction is expected to be through the Nb-rich dichalcogenide layers. By assuming all of the current travels in the Nb rich layer, the resistivity of the $(\text{SnSe})_{1.16}([\text{Mo}_{0.9}\text{Nb}_{0.1}]\text{Se}_2)_{1.06}(\text{SnSe})_{1.16}([\text{Nb}_{0.9}\text{Mo}_{0.1}]\text{Se}_2)$ ferecrystal can be used to estimate the degree of intermixing.

The $(\text{SnSe})_{1.16}([\text{Mo}_{0.9}\text{Nb}_{0.1}]\text{Se}_2)_{1.06}(\text{SnSe})_{1.16}([\text{Nb}_{0.9}\text{Mo}_{0.1}]\text{Se}_2)$ ferecrystal has fewer Nb-rich dichalcogenide layers than the $(\text{SnSe})_{1+\delta}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ ferecrystal alloys which must be accounted for in comparing the resistivity's. Normalization of the resistivity by multiplying by the amount of the c-axis lattice parameter of the unit cell contributed by the Nb-rich dichalcogenide layer allows these numbers to be compared. Figure IV.8b shows the linear relationships of the normalized room temperature and low temperature (45K) resistivity vs x for the Nb-rich $(\text{SnSe})_{1+\delta}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ ferecrystal alloys with x = 0.76, 0.81, and 1. Assuming the change in resistivity is primarily a result of interdiffusion, rather than charge transfer, the normalized electrical resistivity of the $(\text{SnSe})_{1+\delta}([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)$ ferecrystal should follow this same relationship. This allows a second, independent estimate of the interdiffusion in addition to the value obtained by diffraction. Fitting the room temperature and low temperature

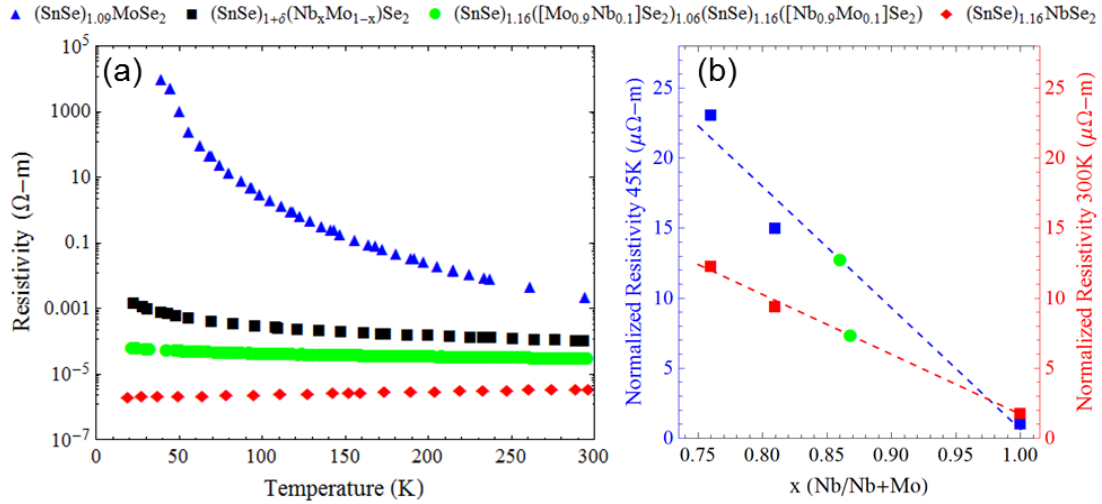


Figure IV.8. (a) Electrical resistivity vs. temperature of $(\text{SnSe})_{1.16}([\text{Mo}_{0.9}\text{Nb}_{0.1}]\text{Se}_2)_{1.06}$ $(\text{SnSe})_{1.16}([\text{Nb}_{0.9}\text{Mo}_{0.1}]\text{Se}_2)$ (green circles), $(\text{SnSe})_{1.03}\text{MoSe}_2$ (blue triangles), $(\text{SnSe})_{1.13}([\text{Nb}_{0.5}\text{Mo}_{0.5}]\text{Se}_2)$ (black squares) and $(\text{SnSe})_{1.16}\text{NbSe}_2$ (red diamonds). (b) Normalized room temperature (red squares) and 45K (blue squares) resistivity vs. x for the $(\text{SnSe})_z(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ ferecrystal alloys compared to the $(\text{SnSe})_{1+\delta}([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)$ (green circles).

resistivity of the $(\text{SnSe})_{1+\delta}([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)$ compound to the lines given by the alloys (Figure IV.8b) gives interdiffusion estimates of $13 \pm 2\%$ and $14 \pm 4\%$ respectively. These are in close agreement to the interdiffusion estimate of $12 \pm 2\%$ obtained from diffraction. Charge transfer, which may be occurring, would cause these numbers to be overestimated, making them a reasonable upper limit to the amount of interdiffusion occurring.

To investigate the extent of the possible charge transfer, Hall coefficient measurements of the $(\text{SnSe})_{1+\delta}([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)$ compound were performed. A positive Hall coefficient of $3.2(1) \times 10^{-3} \text{ cm}^3\text{C}^{-1}$ was measured, indicating that holes are the majority carrier. Using a single band model results in a calculated carrier concentration of $2.0(1) \times 10^{21} \text{ cm}^{-3}$, or 0.6 holes per Nb atom in the compound. This is significantly less than the nearly one hole per Nb atom reported for $([\text{SnSe}]_{1.16})_1(\text{NbSe}_2)_1$, but very close to the 0.6 holes per Nb reported for $([\text{SnSe}]_{1.16})_2(\text{NbSe}_2)_1$.²⁷ The additional SnSe layer in $([\text{SnSe}]_{1.16})_2(\text{NbSe}_2)_1$ relative to $([\text{SnSe}]_{1.16})_1(\text{NbSe}_2)_1$ results in a significantly reduced number of carriers per Nb atom, presumably due to increased charge transfer from the SnSe. The similarity between the Hall coefficient of $([\text{SnSe}]_{1.16})_2(\text{NbSe}_2)_1$ and $(\text{SnSe})_{1+\delta}([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)$ suggests that charge transfer is also occurring between SnSe and the dichalcogenide layers.

IV.5. Conclusion

We have successfully prepared the compound $(\text{SnSe})_{1.16}([\text{Mo}_{0.9}\text{Nb}_{0.1}]\text{Se}_2)_{1.06}(\text{SnSe})_{1.16}([\text{Nb}_{0.9}\text{Mo}_{0.1}]\text{Se}_2)$ through the self-assembly of a layered precursor of the formula $\text{Sn}|\text{Se}|\text{Mo}|\text{Se}|\text{Sn}|\text{Se}|\text{Nb}|\text{Se}$. Analysis by XRD and STEM indicates distinct Mo

and Nb rich dichalcogenide layers with interleaved SnSe between them. This represents the first example of a three component ferecrystal and illustrates the utility of the MER technique in the preparation multiple component heterostructures. The ability to control local composition through the use of designed precursors allowed the interdiffusion of the two dichalcogenide constituents to be evaluated by comparison of structural and electrical properties to the $(\text{SnSe})_{1+\delta}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ random alloys. It is expected that the amount of interdiffusion will decrease as the SnSe layer thickness is increased. The ability to form multiple component thin films via the MER method greatly increases the number of compounds that can be prepared, and will enable theoretical predictions and proposed thin film device strategies to be tested.

IV.6. Bridge

Having observed the slight alloying of miscible constituents in multiple-component thin films synthesized via MER and having demonstrated the ability to determine intermixing using simpler systems as standards, control of the intermixing and an understanding of the electronic interactions of the layers is desirable. The ability to form families of related structures via MER by changing the layering scheme of the precursor provides a powerful tool for systematically changing interlayer distances allowing interdiffusion to be controlled. Comparison to families of simpler systems should allow the electronic interactions on more complicated systems to be determined.

The following chapter describes the synthesis of a family of $([\text{SnSe}]_{1+\delta})_m$ $([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ ferecrystals (with $m = 0, 1, 2, 3$ and 4). By increasing the thickness of the SnSe layer, the alloying of the miscible NbSe₂ and MoSe₂ can be controlled. In addition, comparison of the electrical transport properties to

the $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ ($m = 1 - 8$) compounds should allow the electronic interactions of the MoSe_2 and NbSe_2 constituents to be determined.

CHAPTER V

SYNTHESIS OF A FAMILY OF $([\text{SnSe}]_{1+\delta})_m([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1$

$([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ HETEROJUNCTION SUPERLATTICES

(WHERE $m = 0, 1, 2, 3$ AND 4)

V.1. Authorship Statement

Chapter V was submitted to the *European Journal of Inorganic Chemistry* in November of 2015. The co-authors are Gavin Mitchson, Jeffery J. Ditto, and David C. Johnson. Co-author Gavin Mitchson assisted in the synthesis and characterization of the $m = 0$ compound. Co-author Jeffery J. Ditto performed microscopy measurements. Dr. David C. Johnson is my advisor and I am the primary author of the manuscript.

V.2. Introduction

Since the isolation of graphene in 2004¹ there has been great interest in two-dimensional materials which often exhibit different properties than in the bulk compound.^{2,3} In recent years, researchers have prepared two-dimensional heterostructures by stacking different two-dimensional materials.⁴⁻¹⁰ The layering of different two-dimensional materials to form heterostructures provides the ability to optimize properties by taking advantage of the qualities of each material. It also allows properties to be systematically tuned by varying the nanoarchitecture. Numerous applications have been suggested, including electrical sensors,¹¹ supercapacitors,¹² photovoltaics¹³ and water splitting reactions.^{14,15} Despite their enormous potential, however, systematic studies of the properties of multi-component heterostructures are hindered by synthetic challenges.

The synthesis of two-dimensional heterostructures is often accomplished through the cleaving of bulk crystals, followed by the physical stacking of individual layers.

While this process has led to films with exciting properties, it is a tedious and difficult technique.⁵⁻⁹ Additionally, the requirement that films be stable as monolayers limits the number of two-dimensional materials that can be stacked using this technique. Metallic monolayers are thought to be generally unstable under ambient conditions.⁴ In addition to physical stacking, synthesis of heterostructures can also be accomplished through epitaxy. Koma and coworkers demonstrated epitaxial growth of transition metal dichalcogenide (TMD) superlattices, coining the term van der Waals epitaxy due to weak interlayer bonding.^{16,17} Epitaxy, however, becomes increasingly difficult as the number of constituents increases because new and mutually compatible growth conditions must be found for each additional constituent. It is often not possible to find mutually compatible conditions to grow both B on A as well as A on B. In addition, interdiffusion occurs during growth if layers are miscible.^{18,19} Another method for the formation of two-dimensional heterostructures is the modulated elemental reactants (MER) technique. This approach has been used to prepare families of related structures, allowing systematic studies of properties as a function of nanoarchitecture.²⁰ Rather than epitaxy, MER relies on a diffusion constrained self-assembly of compositionally modulated amorphous precursors to form kinetically stable films. Families of related compounds are prepared by changing the layering scheme of the precursors.^{21, 22}

Herein we report the synthesis of a family of related $([\text{SnSe}]_{1+\delta})_m([\text{NbSe}_2]_{1+\gamma})_1$ $([\text{SnSe}]_{1+\delta})_m(\text{MoSe}_2)_1$ heterojunction superlattices (with $m = 0 - 4$), whose structures are schematically illustrated in Figure V.1. Systematically increasing the thickness of the SnSe layers interleaved between MoSe_2 and NbSe_2 constituents decreases the extent of

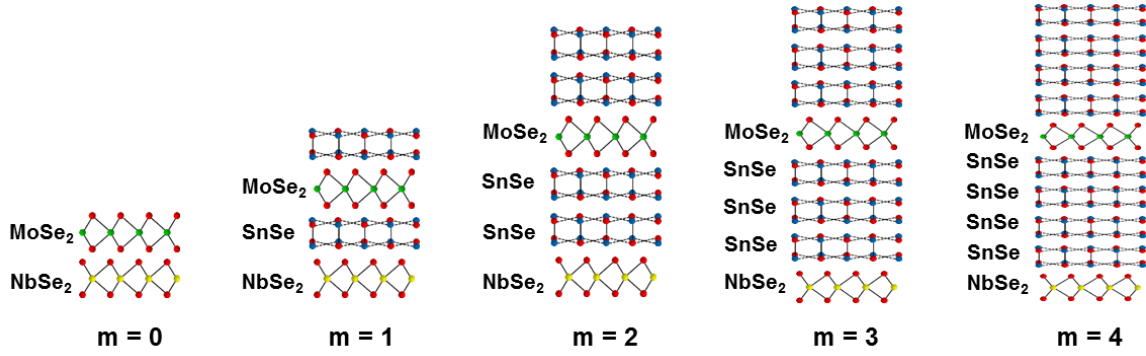


Figure V.1. Illustration of the change in the dichalcogenide separation through modification of the stacking sequence of $([\text{SnSe}]_{1+\delta})_m([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)_{1+\gamma}([\text{SnSe}]_{1+\delta})_m([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)_1$ ferecrystals (with $m = 0 - 4$).

interdiffusion of the miscible dichalcogenide layers. When $m = 0$ the miscible dichalcogenide layers interdiffused leading to about 20% alloying. When $m = 1$, approximately 10% of the transition metals diffused into the neighboring layer, forming $(\text{SnSe})_{1.16}([\text{Mo}_{0.9}\text{Nb}_{0.1}]\text{Se}_2)_{1.06}(\text{SnSe})_{1.16}([\text{Nb}_{0.9}\text{Mo}_{0.1}]\text{Se}_2)$ rather than the targeted compound $(\text{SnSe})_{1.16}(\text{MoSe}_2)_{1.06}(\text{SnSe})_{1.16}(\text{NbSe}_2)$.²³ Herein we show that increasing m to 2 reduces the alloying to about 5% and the extent of alloying became less than our experimental approaches could determine (less than 1%) when $m = 3$ or 4. The electrical transport properties of the $([\text{SnSe}]_{1+\delta})_m([\text{NbSe}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\text{MoSe}_2)_1$ ($m = 0 - 4$) compounds show evidence of reduced alloying with increased m as well as charge transfer from the SnSe layers previously observed in the $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ ($m = 1 - 8$) compounds.²⁰ Comparison of the electrical transport properties with the $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ ($m = 1 - 8$) compounds also provides insight into the electronic interactions between the MoSe_2 and NbSe_2 constituents, indicating little to no charge transfer occurs. The ability to prepare 3-component quaternary heterojunctions with designed structures greatly expands the number of parameters that can be used to understand how

nanoarchitecture affects both structure and properties, which increases the ability to tune and optimize properties.

V.3. Experimental

The compositionally modulated amorphous precursors were formed in a custom-built physical vapor deposition system. A dual turbo and cryo vacuum pump system allowed depositions at pressures of 10^{-7} torr. Tin (99.999 % purity), niobium (99.8 % purity) and molybdenum (99.95 % purity) obtained from Alpha Aesar were deposited using Thermionics 3kW electron beam guns. Se (99.5 % purity) was deposited using a custom-built Knudsen effusion cell. Precursors were built-up layer by layer following a designed layering scheme until a thickness of about 42 nm was reached. Thickness and deposition rates were monitored and controlled using quartz crystal microbalances. Following formation of the precursors sample were annealed in a nitrogen atmosphere ($O_2 < 0.6$ ppm) at 450 C for 20 min to ensure self-assembly into the ferecrystalline products.

X-ray diffraction and reflectivity measurements, performed on a Bruker D8 Discover ($CuK\alpha$ radiation), were used to determine repeating unit and total film thickness respectively. Grazing incidence in-plane ($hk0$) X-ray diffraction, performed on a Rigaku Smartlab X-ray diffractometer with $CuK\alpha$ radiation ($\lambda = 0.15418$ nm), was used to characterize the in-plane structure of the films.

Samples for high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging were prepared at the Center for Advanced Materials Characterization in Oregon (CAMCOR) High-Resolution and Nanofabrication Facility.

Samples were prepared using an FEI NOVA Nanolab Dual Beam FIB equipped with Side winder ion column. (HAADF-STEM) images were obtained at the Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory (PNNL).

Compositions of the modulated precursors and ferecrystal samples were measured by electron probe micro-analysis (EPMA) on a Cameca SX-100. Intensities were collected at acceleration voltages of 7, 12, and 17 keV allowing composition to be calculated from the film and substrate as a function of acceleration voltage using a previously described approach.²⁹

Samples for electrical transport measurements were deposited on quartz slides in a 1 x 1 cross pattern defined by a shadow mask. Electrical resistivity and hall coefficient measurements were performed using a van der Pauw geometry as previously described.³⁰

V.4. Results and Discussion

The synthesis of compounds via MER relies on the formation of compositionally modulated amorphous precursors, which closely mimic the stoichiometry and structure of the desired products, resulting in self-assembly upon mild annealing. Careful calibration of the deposition parameters used in the formation of the precursors is required to ensure formation of the desired product as has been previously described.²³ For the synthesis of the $([\text{SnSe}]_{1+\delta})_m([\text{NbSe}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\text{MoSe}_2)_1$ ($m = 0 - 4$) the deposition parameters determined previously for the $m = 1$ compound were used as a starting point for the compounds with $m = 0, 2, 3$, and 4 .²⁴ Precursors for the compounds $([\text{SnSe}]_{1+\delta})_m([\text{NbSe}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\text{MoSe}_2)_1$ ($m = 0 - 4$) were prepared by depositing a repeating sequence of elemental layers $m \times [\text{Sn}|\text{Se}][\text{Mo}|\text{Se}]\{m \times [\text{Sn}|\text{Se}]\}|\text{Nb}|\text{Se}$ onto silicon wafers

(Table V.1). Each layer sequence was repeated until the total thickness of the film reached about 42nm. X-ray reflectivity patterns of the precursors showed the expected systematic increase in the repeating thickness as m was increased.

Table V.1. The precursor structure, targeted structure and elemental ratios, both targeted and measured, of the $([\text{SnSe}]_{1+\delta})_m([\text{MoSe}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ compounds.

Precursor Structure	Targeted Structure	Se/(Sn+Mo+Nb)		Sn/(Mo+Nb)		Mo/Nb	
		Target	Found	Target	Found	Target	Found
Mo-Se + Nb-Se	$([\text{MoSe}_2]_{1.06})_1(\text{NbSe}_2)_1$	2.00	2.0(1)	0.00	0.00	1.08	1.1(1)
1(Sn-Se) + Mo-Se + 1(Sn-Se) + Nb-Se	$([\text{SnSe}]_{1.17})_1([\text{MoSe}_2]_{1.06})_1$ $([\text{SnSe}]_{1.17})_1(\text{NbSe}_2)_1$	1.47	1.4(1)	1.13	1.2(1)	1.08	1.1(1)
2(Sn-Se) + Mo-Se + 2(Sn-Se) + Nb-Se	$([\text{SnSe}]_{1.17})_2([\text{MoSe}_2]_{1.06})_1$ $([\text{SnSe}]_{1.17})_2(\text{NbSe}_2)_1$	1.31	1.3(1)	2.23	2.3(1)	1.08	1.1(1)
3(Sn-Se) + Mo-Se + 3(Sn-Se) + Nb-Se	$([\text{SnSe}]_{1.17})_3([\text{MoSe}_2]_{1.06})_1$ $([\text{SnSe}]_{1.17})_3(\text{NbSe}_2)_1$	1.23	1.2(1)	3.35	3.4(1)	1.08	1.2(1)
4(Sn-Se) + Mo-Se + 4(Sn-Se) + Nb-Se	$([\text{SnSe}]_{1.17})_4([\text{MoSe}_2]_{1.06})_1$ $([\text{SnSe}]_{1.17})_4(\text{NbSe}_2)_1$	1.18	1.2(1)	4.46	4.5(1)	1.08	1.2(1)

Annealing these amorphous precursors for 20 minutes at 450°C in an N_2 atmosphere²³ resulted in an increase in both the number of specular (00 l) XRD reflections and their intensity. An increasing number of Bragg reflections were observed for samples with increasing numbers of SnSe layers, indicating the unit cell size increased (Figure V.2). For each sample, all maxima could be indexed as (00 l) reflections, indicating that the samples are crystallographically aligned to the substrate. The c -axis lattice parameters, given in Table V.2, increase linearly as m is increased. The slope yields an average thickness of a single SnSe bilayer of 0.580(1) nm. This is consistent with the literature values of SnSe bilayer thicknesses in 1:1 misfit layer compounds, which range between 0.578 and 0.599 nm.²⁷ The slope is also consistent with changes in the c -axis lattice parameter with SnSe thickness observed in previous studies of the ferecrystal families $([\text{SnSe}]_{1.16})_m(\text{NbSe}_2)_1$ and $([\text{SnSe}]_{1.04})_m(\text{MoSe}_2)_1$ (0.577(5)²⁰ and 0.589(1)²⁸ respectively).

This suggests that the $([\text{SnSe}]_{1+\delta})_m([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ compounds which share a similar structure. The measured atomic compositions of the ferecrystals, given in Table V.1, are similar to the stoichiometry's of the targeted compounds and systematically vary as expected from the layer sequences of the precursors.

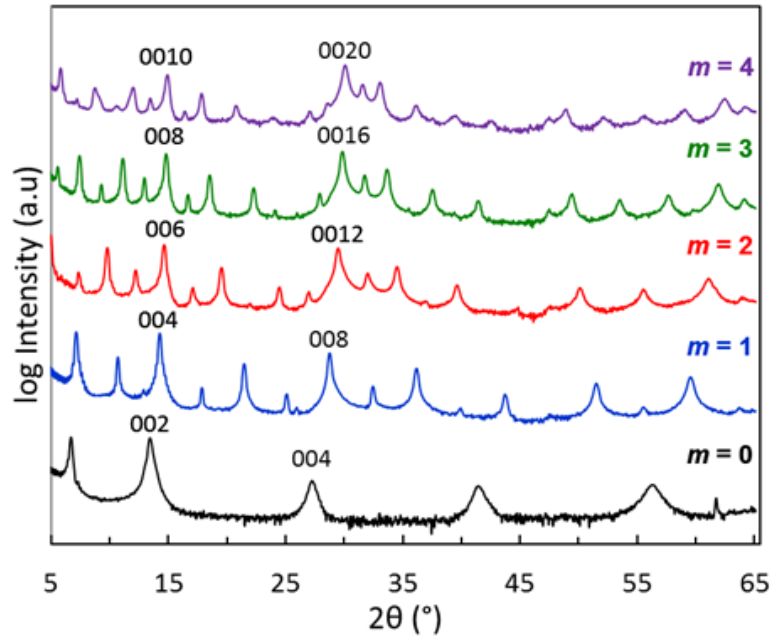


Figure V.2. Locked-coupled (00 l) XRD patterns of $([\text{SnSe}]_{1+\delta})_m([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ ferecrystals (with $m = 0 - 4$).

Further insight into the structure of the $([\text{SnSe}]_{1+\delta})_m([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ ferecrystals was obtained from high-angle annular dark-field scanning transmission microscopy (HAADF STEM) images. Figure V.3 shows a representative image of the sample with $m = 2$. The image agrees with the interpretation of the specular diffraction patterns. All of the zone axes imaged reflect trigonal prismatic coordination of the metal in the dichalcogenide layers with each dichalcogenide layer

interleaved with two rock salt bilayers. The individual layers are distinct and parallel and exhibit the turbostratic disorder typical of ferecrystals.

Table V.2. The lattice parameters and formulas estimated from in-plane X-ray diffraction for the $([\text{SnSe}]_{1+\delta})_m([\text{MoSe}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ compounds.

m	c-axis lattice parameters (nm)	a-b axis lattice parameters (nm)				Formula predicted from $hk0$ X-ray diffraction
		SnSe (a)	SnSe (b)	NbSe ₂	MoSe ₂	
0	1.311(1)	-	-	0.343(1)	0.334(1)	$([\{\text{Mo}_{0.9}\text{Nb}_{0.1}\}\text{Se}_2]_{1.06})_1$ $(\{\text{Nb}_{0.8}\text{Mo}_{0.2}\}\text{Se}_2)_1$
1	2.476(1)	0.4225(1)	0.4222(1)	0.3447(5)	0.3342(5)	$([\text{SnSe}]_{1.16})_1([\{\text{Mo}_{0.90}\text{Nb}_{0.10}\}\text{Se}_2]_{1.06})_1$ $([\text{SnSe}]_{1.16})_1(\{\text{Nb}_{0.87}\text{Mo}_{0.13}\}\text{Se}_2)_1$
2	3.637(1)	0.4279(1)	0.4239(1)	0.3458(5)	0.3343(5)	$([\text{SnSe}]_{1.17})_2([\{\text{Mo}_{0.89}\text{Nb}_{0.11}\}\text{Se}_2]_{1.07})_1$ $([\text{SnSe}]_{1.17})_2(\{\text{Nb}_{0.95}\text{Mo}_{0.05}\}\text{Se}_2)_1$
3	4.791(1)	0.4292(1)	0.4238(1)	0.3462(5)	0.3334(5)	$([\text{SnSe}]_{1.17})_3([\text{MoSe}_2]_{1.08})_1$ $([\text{SnSe}]_{1.17})_3(\text{NbSe}_2)_1$
4	5.951(1)	0.4302(1)	0.4233(1)	0.3458(5)	0.3329(5)	$([\text{SnSe}]_{1.17})_4([\text{MoSe}_2]_{1.08})_1$ $([\text{SnSe}]_{1.17})_4(\text{NbSe}_2)_1$

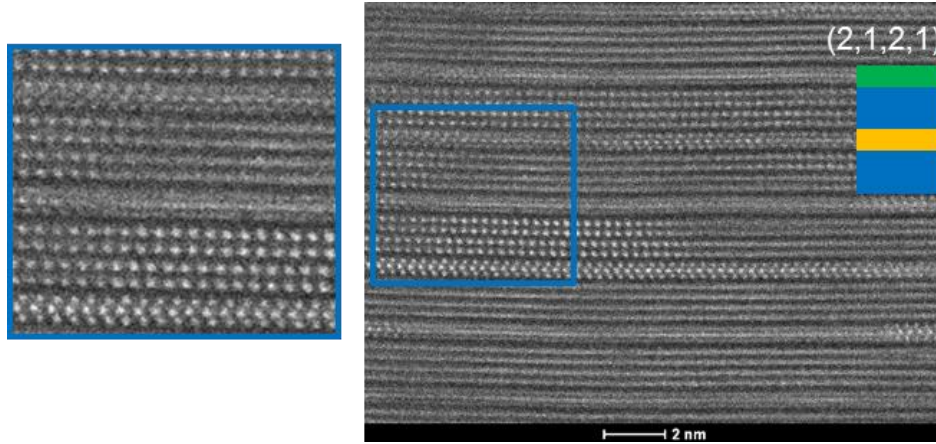


Figure V.3. HAADF-STEM images of $([\text{SnSe}]_{1+\delta})_m([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1$ $([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ samples with $m = 2$ and 4. Se_2 Different orientations of the individual constituents are highlighted.

In-plane diffraction patterns were collected to determine the in-plane structure of the reported compounds. All maxima can be indexed as $(hk0)$ reflections of the respective SnSe, NbSe₂ and MoSe₂ constituents. The SnSe reflections show a slight broadening with increasing thickness of the SnSe layers (see the inset of Figure V.4) indicating a symmetry reduction to a rectangular in-plane unit cell similar to that observed previously

in $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ ($m = 1 - 8$) compounds.²⁰ Rectangular in-plane lattice constants are given in Table V.2 and range from 0.422 to 0.430 nm, matching well the magnitude and following the same trend as those found for the $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ compounds. Dichalcogenide ($hk0$) reflections for both the NbSe_2 and MoSe_2 constituents can be observed in all samples, as can be clearly seen in the inset expansion of the (110) reflection in Figure V.4). The a -axis lattice parameters (Table V.2) all lie between those of the $([\text{SnSe}]_{1.16})_1(\text{NbSe}_2)_1$ and $([\text{SnSe}]_{1.09})_1(\text{MoSe}_2)_1$ parent compounds of 0.3462(1)²⁰ and 0.3320(1) nm²⁸ respectively. For the $m = 0$ compound the dichalcogenide peaks are closer

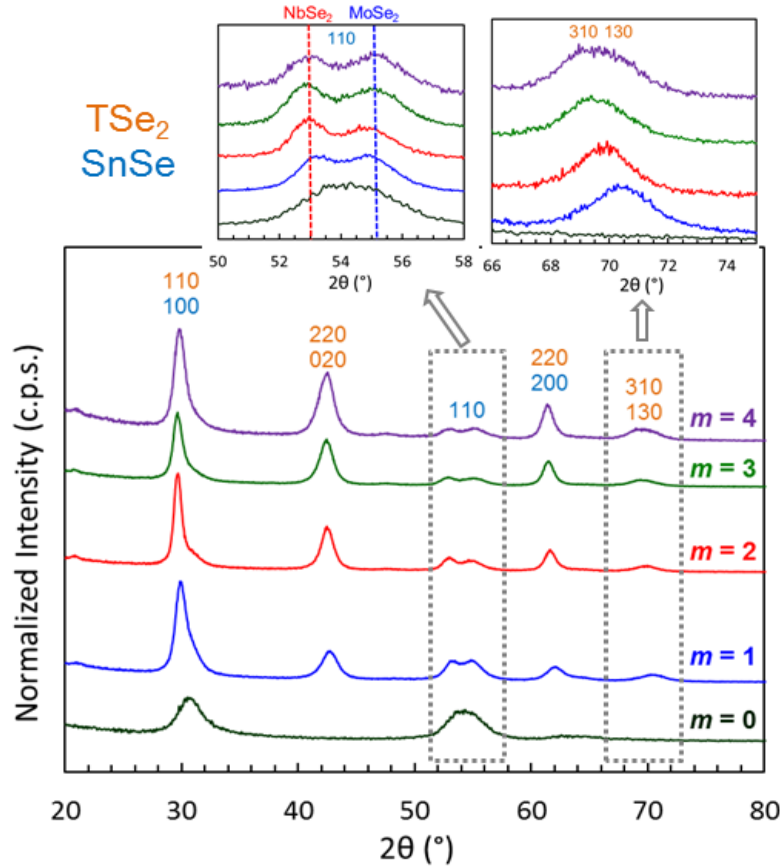


Figure V.4. In-Plane ($hk0$) XRD $([\text{SnSe}]_{1+\delta})_m([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)$ ferecrystals (with $m =$ to 0-4) compared to the $([\text{SnSe}]_{1.16})_1(\text{NbSe}_2)_1$ and $([\text{SnSe}]_{1.09})_1(\text{MoSe}_2)_1$ parent compounds. Insets show the expansion of the TSe_2 110 and SnSe 310/130 regions.

together, resulting in considerable overlap between dichalcogenide peaks. This is likely due to alloying between the miscible constituents. With the addition of increasing numbers of SnSe layers the dichalcogenide ($hk0$) reflections separate and become closer to the positions of the parent compounds (Figure V.4). Using the Vegard's law relationship determined previously for the $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloys²⁹ allows us to estimate the alloying between the dichalcogenides. This yields a stoichiometry of $([\text{Mo}_{0.9}\text{Nb}_{0.1}]\text{Se}_2)_{1.06}([\text{Nb}_{0.8}\text{Mo}_{0.2}]\text{Se}_2)_1$ for the $m = 0$ compound. The a -axis lattice parameters approach those of the parent compounds as the number of SnSe layers is increased, indicating a decrease in the amount of alloying (Figure V.5). Samples with one and two SnSe layers give estimates for the interdiffusion from Vegard's law of about 10%. Addition of three or more SnSe layers causes the estimated interdiffusion to be lowered below detectable limits. Estimated formulas for each compound are given in Table V.2.

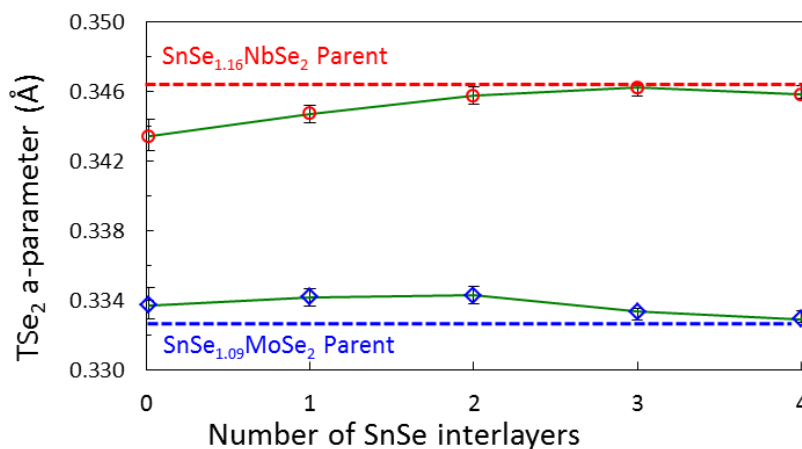


Figure V.5. TSe₂ a -axis lattice parameter is graphed versus the number of SnSe bilayers. The Mo-rich constituent is given by blue triangles, the Nb-rich constituent by red circles. The red and blue horizontal lines depict the a -parameters of the SnSe_{1.16}NbSe₂ and SnSe_{1.09}MoSe₂ parent compounds respectively.

The electrical transport properties of the $([\text{SnSe}]_{1+\delta})_m([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1$ $([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ ferecrystals is dominated by the conductivity of the Nb-rich TSe_2 constituent, similar to previously investigated $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ ²⁰ compounds and Nb-rich $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloys.²⁹ The resistivity vs. temperature behavior (Figure V.6) shows an increase in resistivity with decreasing temperature with the $\rho/\rho_{300\text{K}}$ value rising with m to reach a value of 2.8 for the $m = 4$ compound. This effect was also observed for the Nb-rich $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloys²⁹ and $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ compounds²⁰ with m greater than 6. For the $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ compounds, this effect was attributed to charge transfer from the

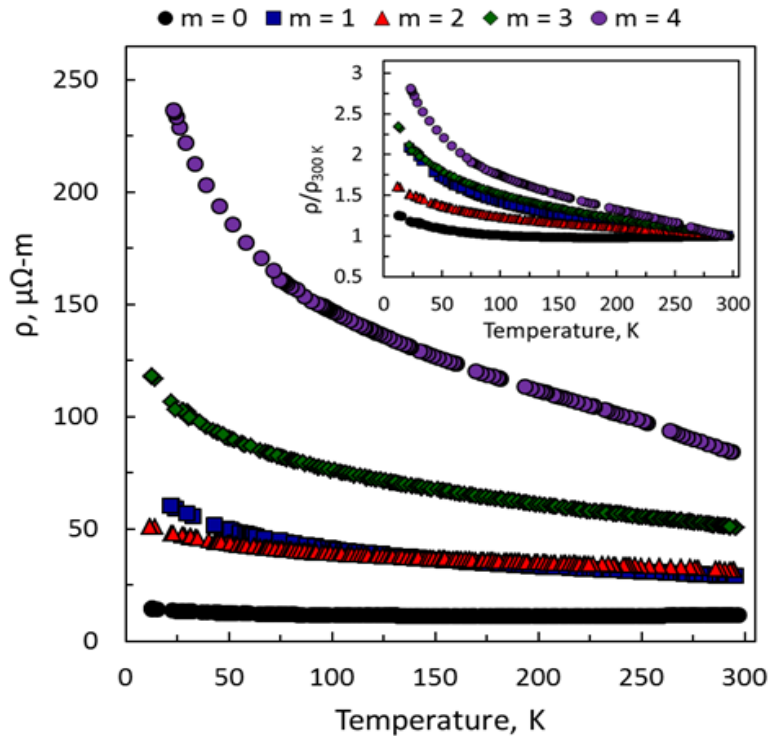


Figure V.6. Resistivity vs. temperature for the $([\text{SnSe}]_{1+\delta})_m([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1$ $([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ compounds with $m = 0-4$. The inset shows the resistivity ratio $\rho/\rho_{295\text{K}}$.

SnSe layers into the NbSe₂ layers. Its onset at lower m values in the $([\text{SnSe}]_{1+\delta})_m$ $([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ ferecrystals may be evidence of alloying of the dichalcogenides with small numbers of SnSe interlayers. This is supported by the resistivity behavior of the $([\{\text{Mo}_{0.9}\text{Nb}_{0.1}\}\text{Se}_2]_{1.06})_1(\{\text{Nb}_{0.8}\text{Mo}_{0.2}\}\text{Se}_2)_1$ ($m = 0$) compound which shows similar behavior to the $(\text{SnSe})_{1.16-1.09}(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ ($x = 0.76$) compound previously reported.²⁹ The localization of carriers appears to be related to the separation of the conducting NbSe₂ rich layers by semiconducting layers of either SnSe or MoSe₂, and increases as this thickness is increased.

The room temperature resistivity (Figure V.7a) shows a gradual increase with increasing SnSe layers as a result of an increased contribution of the semiconducting SnSe. If the majority of charge conduction occurs through the conducting NbSe₂ layers, we can extract the resistance of this conducting layer by assuming that it is in parallel with high resistance layers of SnSe/MoSe₂ (Figure V.7b). The reduction in the normalized room temperature resistivity with increasing thickness of SnSe from $m = 0$ to 2, results from the decrease in alloying of the dichalcogenide layers. The increase in room temperature normalized resistivity observed for the $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ compounds from $m = 2$ to $m = 4$, is thought to result from increased charge transfer from the SnSe.

Temperature dependent Hall measurements, shown in Figure V.8, reveal positive Hall coefficients for all samples, indicating that holes are the majority carriers. There is a systematic increase in the Hall coefficient with increased m suggesting that average carrier concentration is decreasing as the thickness of SnSe increases. The Hall coefficient decreases with temperature for $m = 0$. The Hall coefficient increases with

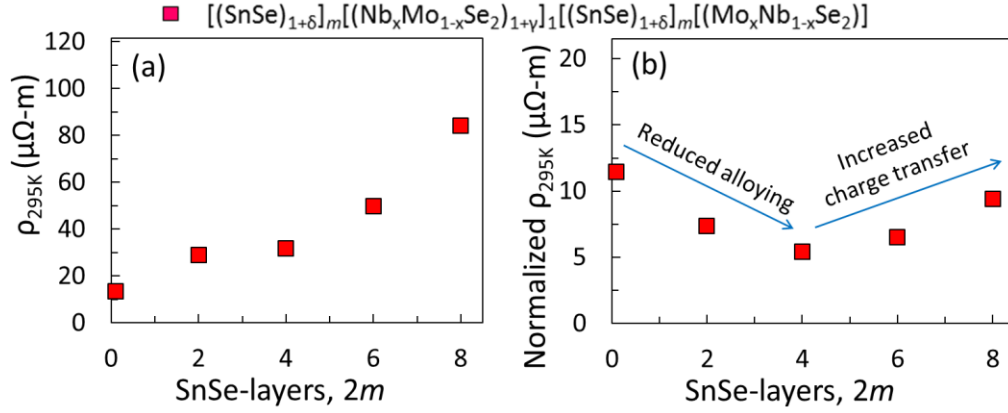


Figure V.7. (a) Room temperature resistivity and normalized room temperature resistivity (b) vs. the number of SnSe layers in $[(\text{SnSe})_{1+\delta}]_m[(\text{Mo}_x\text{Nb}_{1-x}\text{Se}_2)_{1+\gamma}]_1[(\text{SnSe})_{1+\delta}]_m[(\text{Nb}_x\text{Mo}_{1-x}\text{Se}_2)]_1$ compounds with $m = 0$ to 4. (b) Normalized room temperature resistivity (red squares).

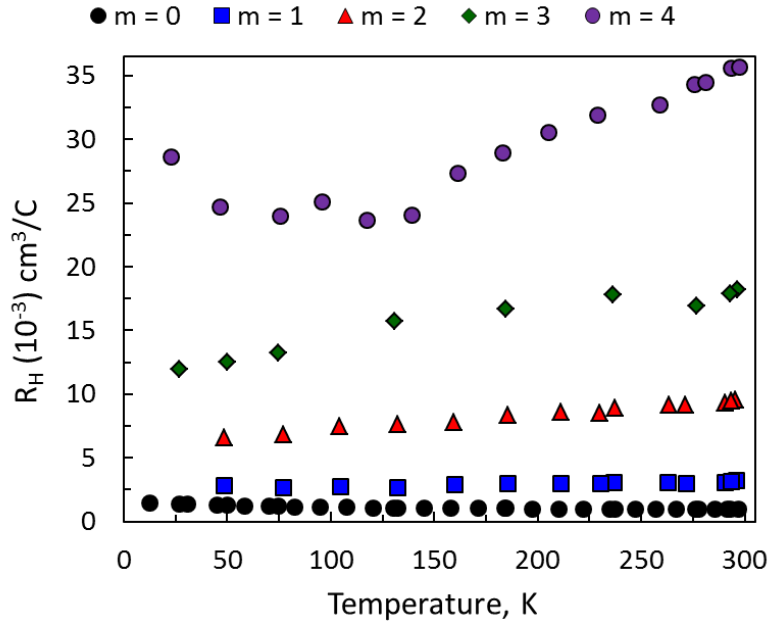


Figure V.8. Temperature dependent Hall coefficients measured for the $[(\text{SnSe})_{1+\delta}]_m[(\text{Mo}_x\text{Nb}_{1-x}\text{Se}_2)_{1+\gamma}]_1[(\text{SnSe})_{1+\delta}]_m[(\text{Nb}_x\text{Mo}_{1-x}\text{Se}_2)]_1$ compounds with $m = 0$ to 4.

temperature for $m = 1 - 3$, as observed previously for the $[(\text{SnSe})_{1+\delta}]_m(\text{NbSe}_2)_1$ compounds.²⁰ The Hall coefficient for the $m = 4$ compound decreases at low temperatures followed by an increase above 100K. This complex behavior suggests that multiple bands

are likely involved and that the interaction between the constituents changes as a function of nanoarchitecture.

A rough estimate of the temperature dependent carrier concentrations can be obtained from the Hall coefficients using the single-band approximation (Figure V.9). A reduction in the carrier concentration is observed for increasing m as a result of the increased proportion of semiconducting SnSe layers in the samples. A slight increase in carrier concentration vs. temperature is observed for samples with $m = 1-4$, which was also observed in the $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ system²⁰ and was attributed to possible limitations of the single band model, energy dependence of the Hall scattering factor, or a change in charge transfer between constituents with temperature.

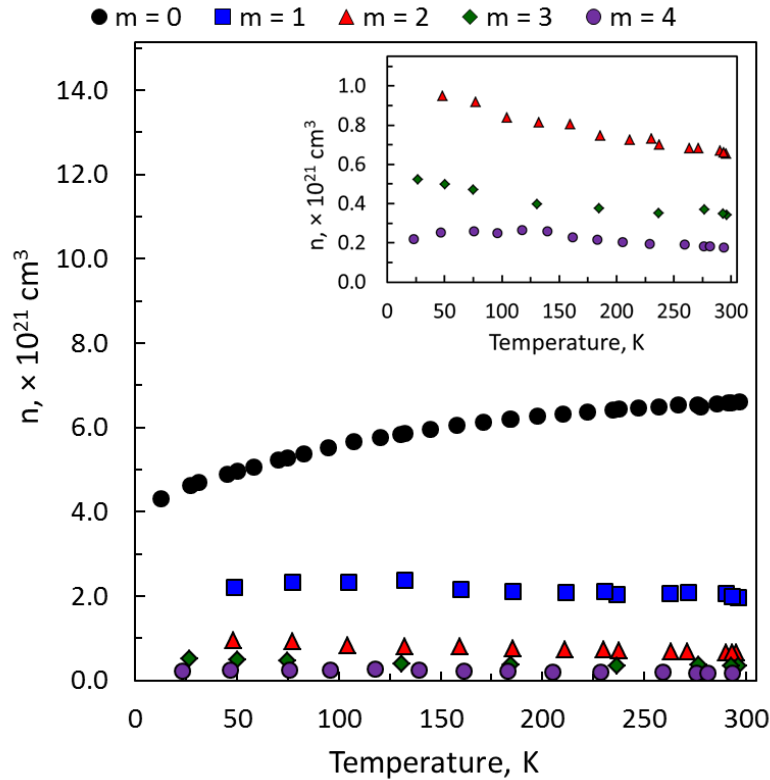


Figure V.9. Temperature dependent carrier concentrations calculated using a single band model for the $([\text{SnSe}]_{1+\delta})_m([\text{Mo}_x\text{Nb}_{1-x}\text{Se}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\text{Nb}_x\text{Mo}_{1-x}\text{Se}_2)_1$ compounds.

Temperature dependent mobility values calculated assuming a single band model for the $m = 0$ compound decrease slightly with temperature as expected for a metallic-type sample. For the $m = 1-4$ compounds, however, the mobility increases with temperature, suggesting carriers are localized as the temperature is decreased. The absolute values of the room temperature mobility for the $([\text{SnSe}]_{1+\delta})_m$ ($([\text{Mo}_x\text{Nb}_{1-x}\text{Se}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\text{Se}_2)_1$ compounds increase with increasing m and are lower than those found for the $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ compounds.²⁰ The lower values for the mobility for small m values are probably a consequence of increased scattering due to Mo alloying with the NbSe_2 layers.

Assuming the transport is dominated by the niobium rich layer, we can calculate the number of carriers per niobium atom in the $\text{Mo}_x\text{Nb}_{1-x}\text{Se}_2$ layer by assuming all the carriers are in this layer and dividing by the number of calculated Nb atoms per cm^3 (Figure V.10). Charge transfer from the Se 4p band of the SnSe into the half-filled band formed by the Nb d_z^2 orbitals is thought to decrease the number of holes as m increases.²⁸ Comparing the number of carriers per Nb atom in the $\text{Mo}_x\text{Nb}_{1-x}\text{Se}_2$ layer with data for previously reported $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ compounds containing the same number of SnSe layers per NbSe_2 layer suggests that there is little or no charge transfer between the NbSe_2 and MoSe_2 constituents.

A proposed band alignment diagram for NbSe_2 , SnSe, and MoSe_2 is given in Figure V.11. Charge transfer from the SnSe layer to the NbSe_2 layer observed in the $([\text{SnSe}]_{1+\delta})_m(\text{NbSe}_2)_1$ compounds²⁰ has been proposed to occur due to the Se 4p band of the SnSe layer, which lies at a higher energy than the half-filled Nb $4d_z^2$ band. The lack

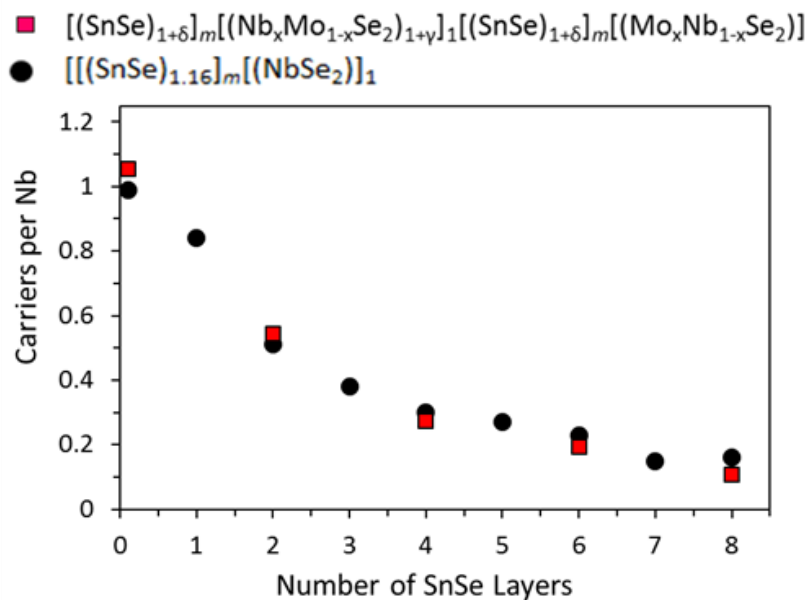


Figure V.10. Holes per Nb with increasing numbers of SnSe layers for the $[(\text{SnSe})_{1+\delta}]_m[(\text{Mo}_x\text{Nb}_{1-x}\text{Se}_2)_{1+\gamma}]_1[(\text{SnSe})_{1+\delta}]_m[(\text{Nb}_x\text{Mo}_{1-x}\text{Se}_2)]_1$ (red squares) compared to the $[(\text{SnSe})_{1.16}]_m(\text{NbSe}_2)_1$ (black circles).

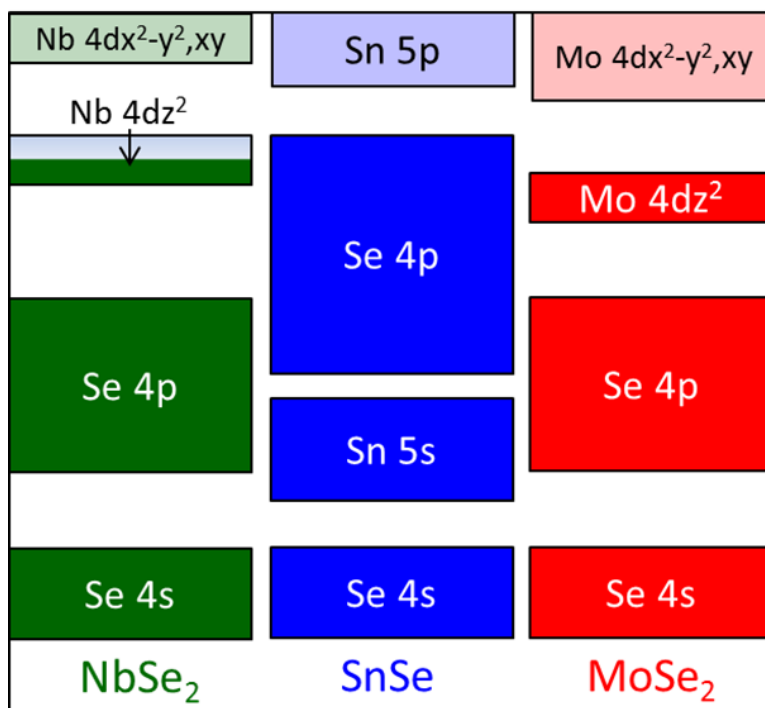


Figure V.11. Band alignment diagram of the NbSe_2 (green), SnSe (blue), and MoSe_2 (red) systems.

of charge transfer between the MoSe₂ and NbSe₂ layers may be due to the filled Mo 4d² being at lower energy than the corresponding Nb 4d² band. The Fermi level would then reside within the Nb 4dz² band and within the band gap of the MoSe₂ layer.

V.5. Conclusion

We have reported the successful synthesis of a family of ([SnSe]_{1+δ})_m ([{Mo_xNb_{1-x}}Se₂]_{1+γ})₁([SnSe]_{1+δ})_m([Nb_xMo_{1-x}}Se₂)₁ heterojunction superlattices with $m = 0 - 4$. Characterization of the compounds by XRD and HAADF-STEM confirmed the formation of individual dichalcogenide layers, which are distinct and parallel, interleaved with a systematically increasing number of distorted rock salt bilayers. Comparison of the in-plane X-ray diffraction patterns to those of the (SnSe)_{1.16-1.09}(Nb_xMo_{1-x})Se₂ alloys allowed the extent of alloying between the miscible MoSe₂ and NbSe₂ constituents to be estimated. Alloying, which was about 20% at $m = 0$, is systematically reduced to less than 1% as m is increased to 3 and 4. Electrical transport measurements of the ([SnSe]_{1+δ})_m ([{Mo_xNb_{1-x}}Se₂]_{1+γ})₁([SnSe]_{1+δ})_m([Nb_xMo_{1-x}}Se₂)₁ compounds with $m = 0 - 4$ is consistent with the extent of dichalcogenide alloying decreasing with increasing m . Comparison of the electrical transport properties to those of the ([SnSe]_{1+δ})_m(NbSe₂)₁ ($m = 1 - 8$) compounds suggests that there is little or no charge transfer between the MoSe₂ and NbSe₂ layers. The ability to form families of related three component heterostructure thin films greatly expands the number of compounds that can be created, allowing systematic study of complex interlayer interactions.

V.6. Bridge

Having demonstrated the formation of ordered (ABAC) and disordered A(B,C) ferecrystal alloys through the synthesis of ([SnSe]_{1+δ})_m([{Mo_xNb_{1-x}}Se₂]_{1+γ})₁([SnSe]_{1+δ})_m

$(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ and $([\text{SnSe}]_{1+\delta})([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)$ alloys, a study on the effects of these two doping strategies on different families of ferecrystals is desirable. Due to the known miscibility of TaSe_2 and VSe_2 , synthesis of the $([\text{SnSe}]_{1.15})([\text{Ta}_x\text{V}_{1-x}]\text{Se}_2)$ and $([\text{SnSe}]_{1+\delta})([\{\text{Ta}_x\text{V}_{1-x}\}\text{Se}_2]_{1+\gamma})([\text{SnSe}]_{1+\delta})_m(\{\text{V}_x\text{Ta}_{1-x}\}\text{Se}_2)$ compounds should be possible. Although the extent of alloying in $([\text{SnSe}]_{1+\delta})_m([\{\text{Mo}_x\text{Nb}_{1-x}\}\text{Se}_2]_{1+\gamma})_1([\text{SnSe}]_{1+\delta})_m(\{\text{Nb}_x\text{Mo}_{1-x}\}\text{Se}_2)_1$ can be estimated by comparing the in-plane lattice constants to the $([\text{SnSe}]_{1+\delta})([\text{Mo}_x\text{Nb}_{1-x}]\text{Se}_2)$ alloys. It should also be possible to estimate interdiffusion from EDX; however, the K-lines for Mo and Nb overlap and their L-lines are too weak. The K-lines of V and Ta are such that the formation of ordered (ABAC) and disordered A(B,C) $\text{SnSe}/\text{TaSe}_2/\text{VSe}_2$ alloys should allow the interdiffusion of the dichalcogenide constituents to be observed by EDX. In addition, the effect on the charge density wave of the $(\text{SnSe})_{1.15}\text{VSe}_2$ by two different doping styles can also be observed.

CHAPTER VI

SYNTHESIS OF ORDERED (ABAC) and DISORDERED A(B,C) SnSe/TaSe₂/VSe₂

FERECRYSTAL ALLOYS

VI.1. Authorship Statement

Chapter VI describes material published in *The Journal of Solid State Chemistry* in 2015, doi:10.1016/j.jssc.2015.08.018, ahead of print. The co-authors were Ryan Atkins, Matthias Falmbigl, Jeffery J. Ditto, and David C. Johnson. Ryan Atkins and Matthias Falmbigl assisted in the synthesis of some of the initial compounds. Co-author Jeffrey J. Ditto performed microscopy measurements. David C. Johnson is my advisor and I am the primary author of the manuscript.

VI.2. Introduction

The stacking of two-dimensional materials to form heterostructures has generated considerable interest in recent years due to the promise of properties that either do not exist in bulk materials or the 2-D constituents, or that can be enhanced by joining the materials in the formation of heterostructures.¹⁻¹² The preparation of 2-D heterostructures remain a challenge as compatible growth techniques for the individual constituents are often not compatible with the growth of constituents on top of each other. In addition alloying of adjacent layers is observed if constituents are thermodynamically miscible.^{13,14} As a result, the formation of most heterostructures thus far has been accomplished via the cleaving and stacking of individual layers.¹⁻⁷ While many films with exciting properties have been synthesized, difficulty in scaling the technique coupled with the requirement that layers be stable as monolayers limits the utility of this method. There is a need for a scalable synthesis approach whereby 2-D materials can be layered

without epitaxial relationships between constituents and that is widely applicable for a variety of different materials.

Over the last several years a new synthetic approach has been developed at the University of Oregon known as modulated elemental reactants (MER).¹⁵⁻²⁰ Formation of products via MER is accomplished by the self-assembly of amorphous precursors, deposited by physical vapor deposition, which closely match the local composition of the desired products. The formation of amorphous precursors minimizes diffusion lengths allowing products to be formed at much lower temperatures and with much shorter times than conventional techniques. It has been shown that the composition of the amorphous precursor can control subsequent nucleation, allowing compounds to be formed kinetically that are not thermodynamically stable at reaction conditions.¹⁵ Further, deposition is performed on unheated substrates as epitaxial relationships between film and film and between film and substrate are not desired. The lack of interlayer epitaxial relationships greatly increases synthetic scope, allowing heterostructures of multiple constituents to be formed, as compatible growth conditions are not required. As observed in epitaxial films, the alloying of miscible constituents is still expected in multiple constituent heterostructures synthesized via MER.

We report the synthesis of several new compounds, the random alloys $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ and the ordered alloy $[(\text{SnSe})_{1.15}]_1[(\text{Ta}_x\text{V}_{1-x})\text{Se}_2]_1[(\text{SnSe})_{1.15}]_1$ $([\text{V}_y\text{Ta}_{1-y}]\text{Se}_2)_1$, are used to illustrate the challenges in the synthesis of multiple component systems with miscible constituents. These systems were chosen because the transition metal dichalcogenide alloy $(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ compounds with x up to 0.6 were previously reported and are thermodynamically stable.²¹ The extent of the alloying of the

miscible TaSe₂ and VSe₂ layers was estimated from energy dispersive X-ray spectroscopy (EDX) line scans in giving an estimated formula of (SnSe)_{1.15}]₁[(Ta_{0.7}V_{0.3}]Se₂)₁ [(SnSe)_{1.15}]₁[(V_{0.7}Ta_{0.3}]Se₂)₁ for the compound. In addition to presenting the synthesis and structure, we report electrical properties, which systematically change with x in (SnSe)_{1+δ}(Ta_xV_{1-x})Se₂ compounds. The resistivity of the ordered alloy can be modeled as the two parent compounds [(SnSe)_{1.15}]₁[(Ta_xV_{1-x}]Se₂)₁ and [(SnSe)_{1.15}]₁[(V_yTa_{1-y}]Se₂)₁ in parallel.

VI.3. Experimental

The synthesis of (SnSe)_{1.15}(V_{1-x}Ta_x)Se₂ and [(SnSe)_{1.15}]₁[(Ta_xV_{1-x}]Se₂)₁ [(SnSe)_{1.15}]₁[(V_yTa_{1-y}]Se₂)₁ ferecrystals was accomplished from self-assembly from compositionally modulated precursors using methods described above.

VI.3. Results and Discussion

The synthesis of ferecrystal begins with the preparation of compositionally modulated precursors which, upon mild annealing, undergo self-assembly to the desired ferecrystalline compounds as discussed previously. The optimal annealing conditions to form SnSe/TaSe₂/VSe₂ alloys were determined from by annealing the precursor designed to form the (SnSe)_{1.15}[(V_{1-x}Ta_x]Se₂) at temperatures ranging from 300 to 500 °C for 20 minutes in 50 °C increments (Figure VI.1). As shown from the diffraction scans in Figure VI.1a, as the sample is annealed, there is an increase in the number, intensity and sharpness of the reflections. A maximum intensity and minimum full width half maximum (FWHM) is reached at 400 C Figures VI.1b and VI.1c). Above 450 C broadening of the reflections is seen indicating decomposition of the sample.

Consequently, 400 °C was chosen as the optimal annealing temperature for these compounds.

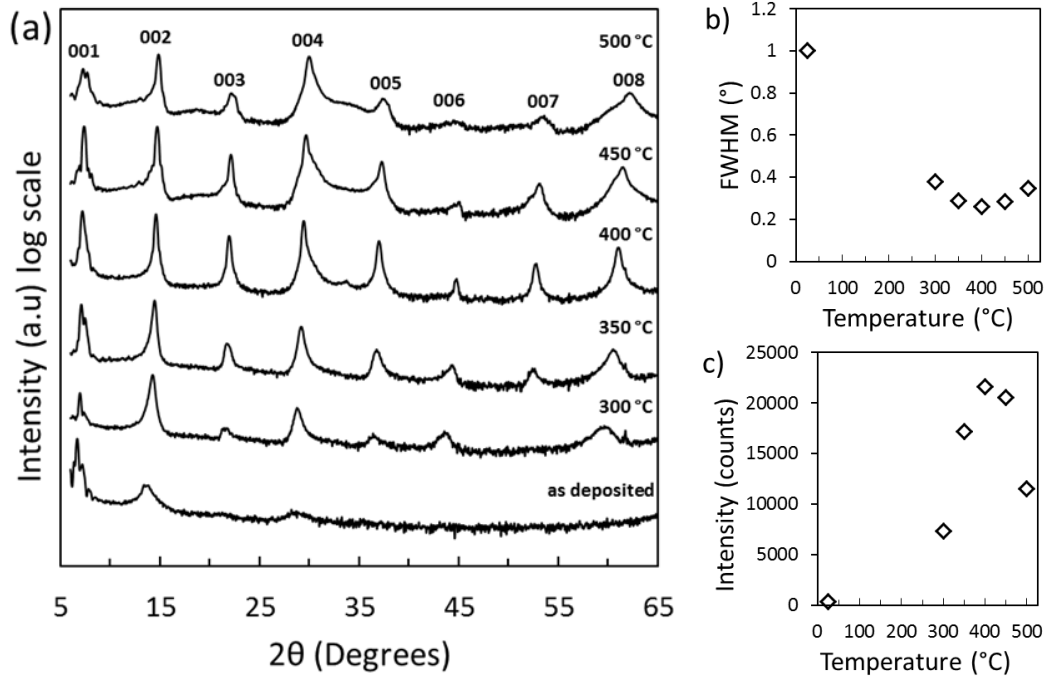


Figure VI.1. (a) Specular XRD patterns of $(\text{SnSe})_{1.15}([\text{V}_{0.5}\text{Ta}_{0.5}]\text{Se}_2)$ annealed at temperatures ranging from 300 to 500 °C. The (00*l*) indices are shown above. (b) Change in the intensity of the (002) reflection with temperature. (c) Change in the FWHM of the (004) reflection with temperature.

Detecting that one constituent has been alloyed and determining the composition of the alloyed layer is an experimental challenge. Specular XRD of the $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ system shows systematic changes in relative peak intensities (Figure VI.2) and in the position of reflections as *x* goes from 0 to 1. The systematic shift to lower angles of the Bragg peaks with increasing substitution of V by Ta indicates an increase in the lattice parameter in the *c* direction. As shown in Figure VI.3, the *c*-axis lattice parameter increases linearly as the amount of Ta is increased, as expected from Vegard's law due to the larger size of Ta. The *c*-axis lattice parameter, however, is the sum of the

thicknesses of the SnSe and dichalcogenide constituents, so additional data are required to confirm that the alloying is limited to the dichalcogenide layer.

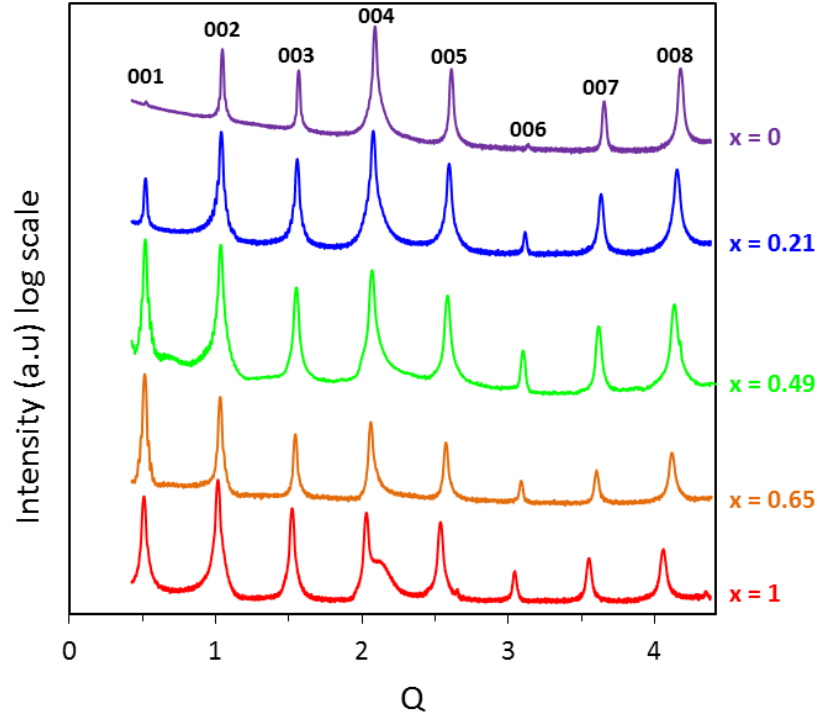


Figure VI.2. Specular X-ray diffraction scans of a series of $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ compounds formed at 400°C . The diffraction peaks shift slightly to lower angles as x is increased, indicating an increase in the c -axis lattice parameter. The $00l$ indices are shown above the top diffraction scan.

In-plane XRD scans of the $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ compounds, shown in Figure VI.4, provide information about in-plane structure of both constituents, enabling us to determine how the structure of each constituent changes as a function of x . The relative intensities of the $hk0$ reflections change as the vanadium content increases. For example, the intensity of the (210) reflection of the dichalcogenide decreases relative to the (110) reflection. The relative positions of the peaks also change as a function of x , indicating changing in-plane lattice parameters of both the SnSe and $(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ constituents.

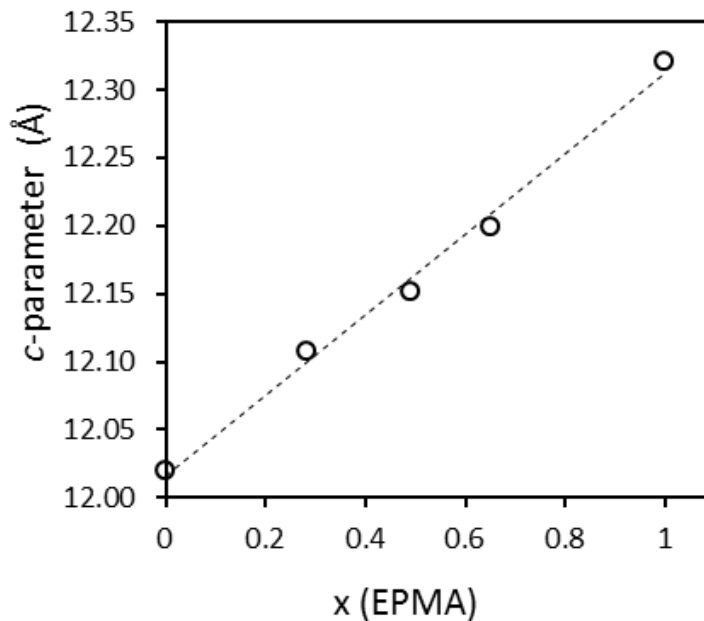


Figure VI.3. The calculated *c*-axis lattice parameter for a series of $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ compounds plotted as a function of *x*. The linear increase in the *c*-axis lattice parameter with increasing *x* is expected from Vegard's law.

Figures VI.5 and VI.6 show the change in the *a*-axis lattice parameters of SnSe and $\text{Ta}_x\text{V}_{1-x}\text{Se}_2$ respectively. The *a*-axis lattice parameters of both compounds increase linearly as *x* increases to 0.65. The *a*-axis lattice parameters for *x*=1, the $(\text{SnSe})_{1.15}\text{TaSe}_2$ sample, are smaller than expected from the trends observed as *x* increases, due to a change in the coordination of the transition metal in the dichalcogenide from octahedral for the V rich samples to trigonal prismatic coordination for Ta in TaSe_2 . This is consistent with prior results reported for alloying of VSe_2 and TaSe_2 . The change in the lattice parameter of SnSe is likely due to changes in charge transfer with the dichalcogenide as the coordination changes. Changes in the lattice parameter of SnSe have been observed both as a function of the thickness of the SnSe layer, and as the dichalcogenide constituent has been varied.²²

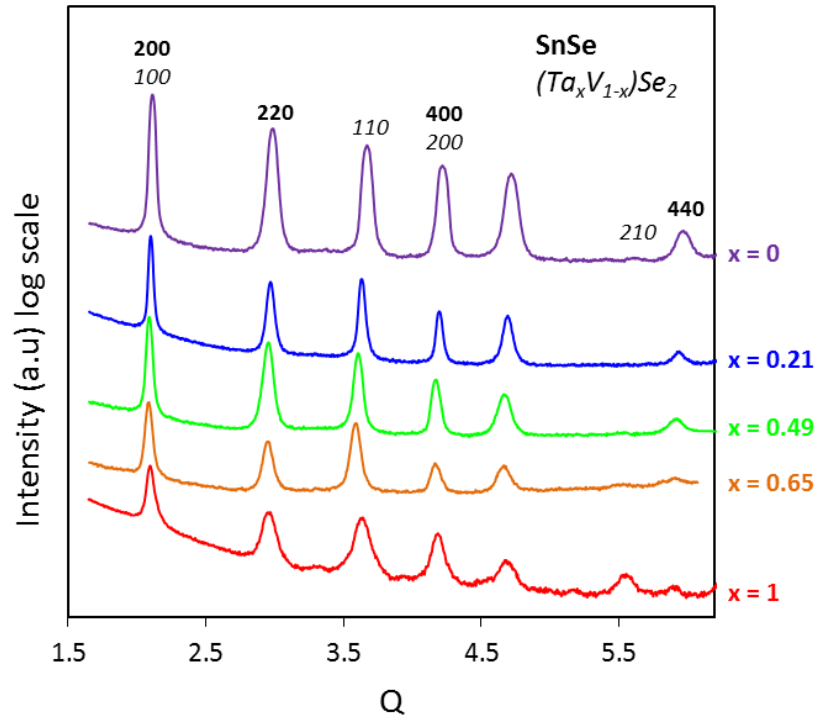


Figure VI.4. In-plane X-ray diffraction scans of a series of $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ compounds formed at 400°C . The diffraction peaks shift as x is increased, indicating changes in the a -axis lattice parameter of both constituents. The $(hk0)$ indices are shown above the top diffraction scan with the indices for SnSe indicated in bold.

By changing the layering scheme of the precursor, depositing Ta and V in separate layers, ordered ABAC alloys can be formed. The formation of an ordered alloy can be seen from the additional $00l$ reflections in the specular diffraction pattern due to the increased size of the unit cell. Figure VI.7 compares the specular diffraction patterns of the $(\text{SnSe})_{1+\delta}(\text{Ta}_{0.5}\text{V}_{0.5})\text{Se}_2$ random alloy and the ordered compound $(\text{SnSe})_{1+\delta}(\text{VSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}\text{TaSe}_2$. A total of 80 layers were used for the compounds, 40 repeat units for the A(B,C) random alloys and 20 repeat units for the ABAC alloys, making both films approximately 50nm thick. A doubling of the unit cell compared to the $(\text{SnSe})_{1+\delta}(\text{Ta}_{0.5}\text{V}_{0.5})\text{Se}_2$ is indicative of the formation of an ordered $\text{A}_m\text{B}_n\text{C}_p\text{B}_q$ alloy with the

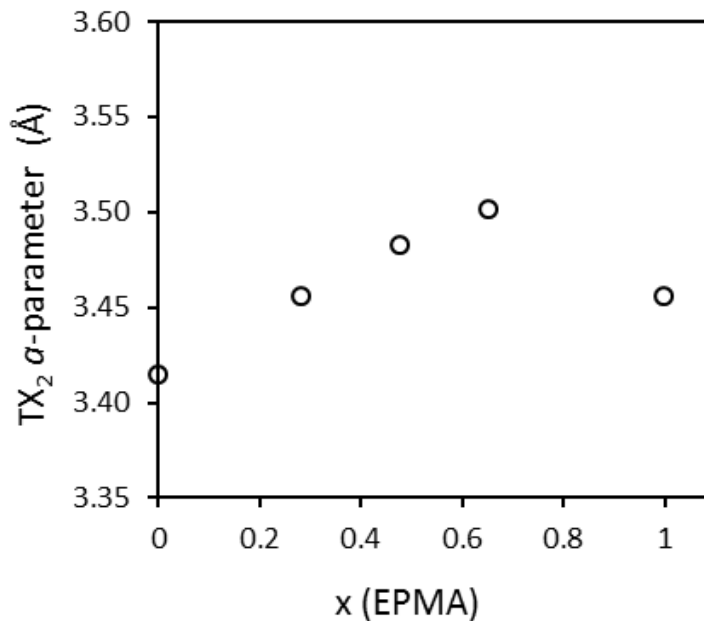


Figure VI.5. The calculated a -axis lattice parameter for the $(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ constituent plotted as a function of x . The linear increase in the a -axis lattice parameter with increasing x is expected from Vegard's law due to the larger size of Ta relative to V. The small a -axis lattice parameter for $x = 1$ results from a change from octahedral coordination for $x=0.8$ to trigonal prismatic coordination when $x = 1$.

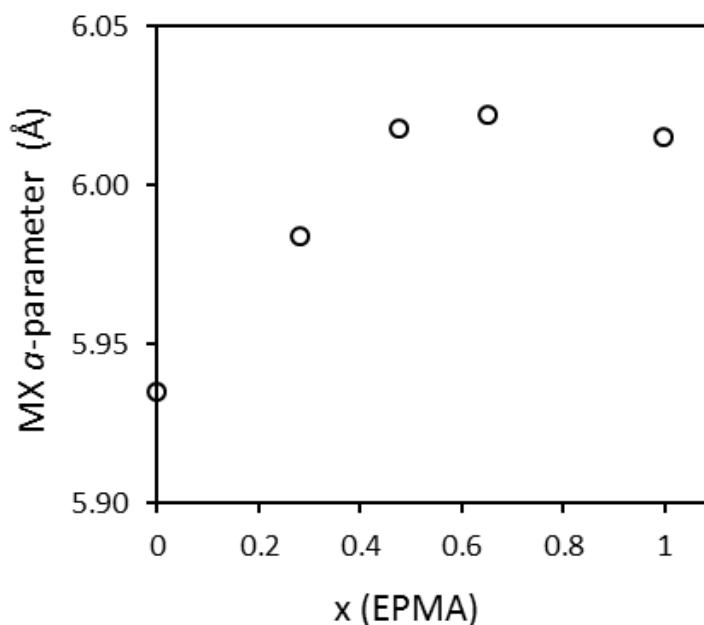


Figure VI.6. The calculated a -axis lattice parameter for the SnSe constituent plotted as a function of x .

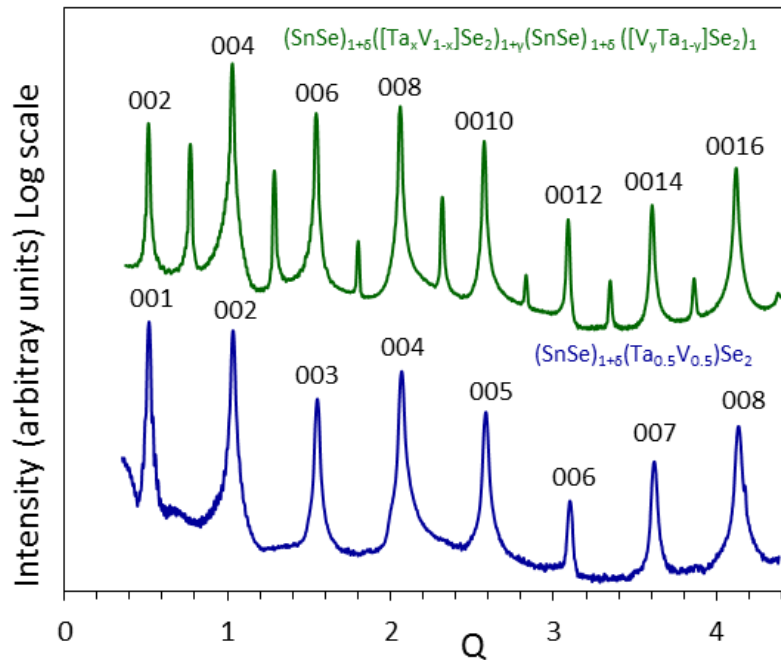


Figure VI.7. A comparison of the diffraction patterns of $(\text{SnSe})_{1+\delta}(\text{Ta}_{0.5}\text{V}_{0.5})\text{Se}_2$ and $(\text{SnSe})_{1+\delta}(\text{VSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}\text{TaSe}_2$ formed at 400°C . The doubling of the number of reflections results from a doubling of the c -axis lattice parameter.

general formula of $(\text{SnSe})_{1+\delta}([\text{Ta}_x\text{V}_{1-x}]\text{Se}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}([\text{V}_\gamma\text{Ta}_{1-\gamma}]\text{Se}_2)_1$ where the degree of intermixing of the dichalcogenide layers must be determined before the formula for the new compound is known.

The extent of intermixing between the dichalcogenide layers is difficult to determine experimentally. One estimate of the extent of intermixing can be obtained from the in-plane lattice parameters of the constituents. Figure.VI.8 contains the in-plane X-ray diffraction pattern of the nominally $(\text{SnSe})_{1+\delta}(\text{VSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}\text{TaSe}_2$ compound. The splitting of the dichalcogenide peaks, which would be expected for pure VSe_2 and TaSe_2 constituents, is not observed. This suggests that the mixing is significant, larger than 20%

from the line widths of the reflections and the change in the lattice parameters of the $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ alloys discussed above.

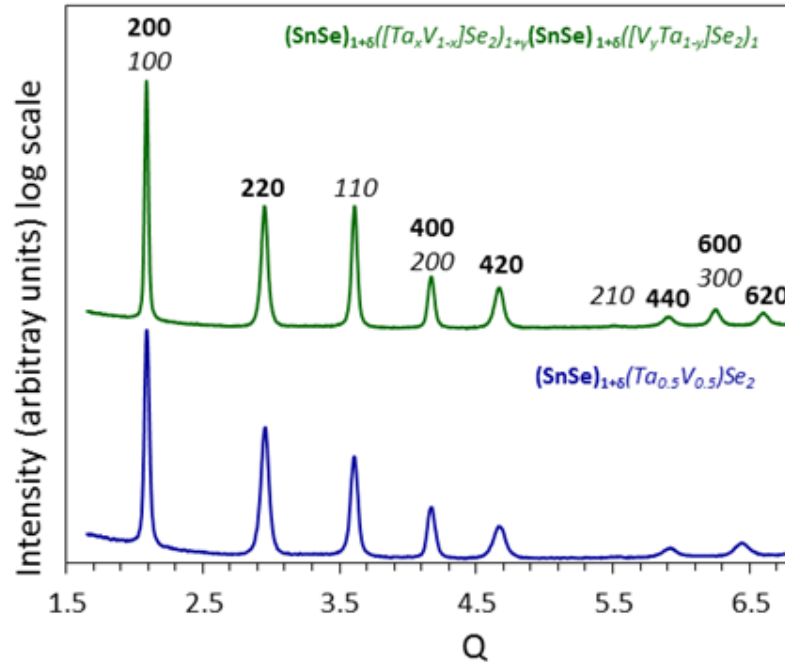


Figure VI.8. In-plane diffraction of the nominally $(\text{SnSe})_{1+\delta}(\text{VSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}\text{TaSe}_2$ compound (green) to determine the extent of intermixing. The indices of the $(hk0)$ reflections are given above the top diffraction scan, with those in bold the indices for SnSe reflections and those in *italic* for the dichalcogenide constituents. The pattern of the $(\text{SnSe})_{1+\delta}(\text{Ta}_{0.5}\text{V}_{0.5})\text{Se}_2$ (blue) is provided for comparison.

To obtain additional information on the structure, HAADF-STEM images were collected and shown in Figure VI.9. The structure consists of alternating layers of a dichalcogenide and rock salt structure in distinct parallel layers. Multiple orientations of each constituent can be seen due to the turbostratic disorder between layers. The coordination of the dichalcogenide atoms in both layers is octahedral, which agrees with what would be expected if the TaSe_2 layer contains at least 20% vanadium. If there was

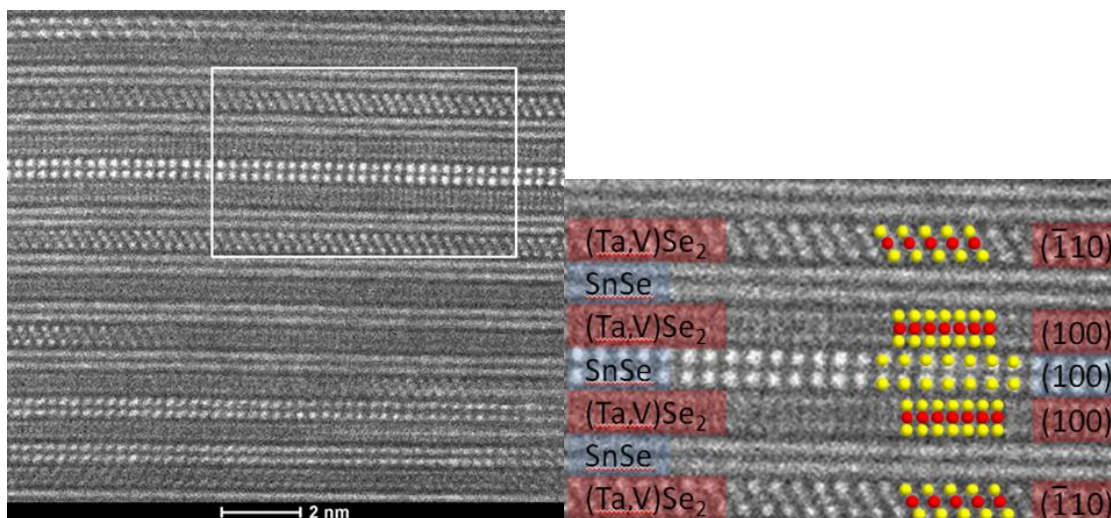


Figure VI.9. High Resolution HAADF STEM image of the nominal $(\text{SnSe})_{1+\delta}(\text{VSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}\text{TaSe}_2$ compound shows the local structure. The different zone axes in different layers result from rotational disorder which is typical for layered compounds prepared using the MER technique.

no alloying between the layers, the TaSe_2 layer would be expected to have trigonal prismatic coordination. An intensity difference would be expected between the VSe_2 and TaSe_2 layers due to the difference between the atomic numbers of the transition metals, but only a small intensity difference is observed. This, combined with the observed octahedral coordination and the X-ray diffraction results indicates significant intermixing of the dichalcogenide layers. The data suggests that a more accurate representation of the nominally $(\text{SnSe})_{1+\delta}(\text{VSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}\text{TaSe}_2$ compound is $[(\text{SnSe})_{1.15}]_1([\text{Ta}_x\text{V}_{1-x}]\text{Se}_2)_1$ $[(\text{SnSe})_{1.15}]_1([\text{V}_y\text{Ta}_{1-y}]\text{Se}_2)_1$ to account for intermixing and alloying of the dichalcogenide layers. A more direct measure of the distribution of the V and Ta atoms between the dichalcogenide layers was obtained via EDX maps of the $(\text{SnSe})_{1.15}([\text{Ta}_x\text{V}_{1-x}]\text{Se}_2)_1$ $(\text{SnSe})_{1.15}([\text{V}_y\text{Ta}_{1-y}]\text{Se}_2)_1$ compound, which are shown in Figure VI.10. The EDX images show alternating regions of brighter and lesser intensity for the V and Ta regions

indicating Ta-rich and V-rich dichalcogenide regions, which is consistent with the specular diffraction data.

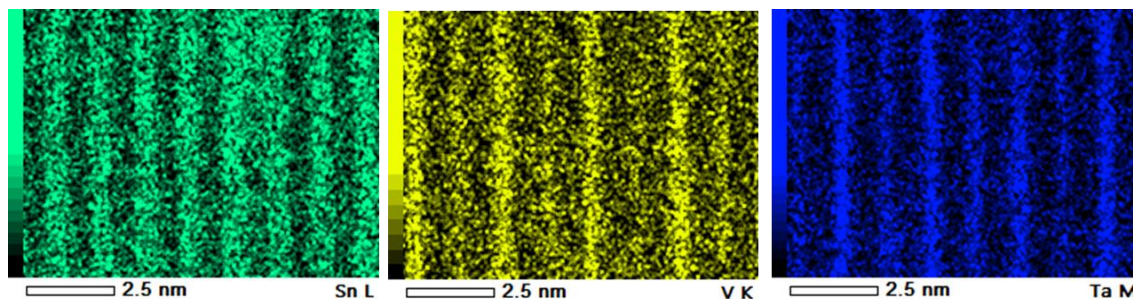


Figure VI.10. EDX maps of a region the $([\text{SnSe}]_{1.15})_1([\text{Ta}_x\text{V}_{1-x}]\text{Se}_2)_1([\text{SnSe}])_{1.15})_1$ $([\text{V}_y\text{Ta}_{1-y}]\text{Se}_2)_1$ compound. The data is consistent with the HAADF STEM images, with alternating layers of SnSe and the transition metal dichalcogenide. The vanadium and tantalum intensities oscillate out of phase with one another, suggesting alternating layers of a tantalum rich and a vanadium rich dichalcogenide.

EDX line scans (Figure VI.11) of $([\text{SnSe}]_{1.15})_1([\text{Ta}_x\text{V}_{1-x}]\text{Se}_2)_1([\text{SnSe}]_{1.15})_1$

$([\text{V}_y\text{Ta}_{1-y}]\text{Se}_2)_1$ allow the extent of interdiffusion to be estimated. If x is equal to y , then the ratio of the areas of the V peaks in the V-rich layer and the Ta-rich layer should equal the ratio of the Ta peak areas. With this assumption, x can be calculated from the V peak area in the V rich layer divided by the sum of the areas of the V peaks in both layers. The same calculation can be done using the Ta signal, giving an estimate of the error and the validity of the assumption. Calculating the areas of the peaks using Gaussian fits, a value for x of 0.68(5) was obtained. The relatively large uncertainty comes from the difficulty of choosing a value for the background signal for both of the EDX energies. The quantification is consistent with estimates from the other approaches discussed above.

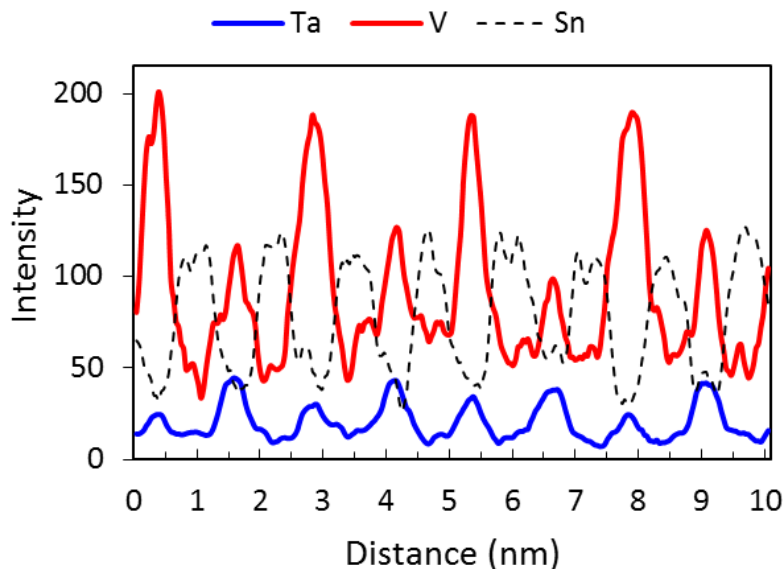


Figure VI.11. EDX line scans of $([\text{SnSe}]_{1.15})_1([\text{Ta}_x\text{V}_{1-x}]\text{Se}_2)_1([\text{SnSe}]_{1.15})_1([\text{V}_y\text{Ta}_{1-y}]\text{Se}_2)_1$ compound. The out of phase oscillation of the Ta and V layers indicates alternating V and Ta rich dichalcogenide layers.

Adding complexity to the structure of the layered compounds provides an additional avenue to control properties. Figure VI.12a contains electrical resistivity data for the six $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ alloys prepared in this investigation. The absolute values of the room temperature resistivity is that expected for a metal, agreeing with prior reports of the analogous dichalcogenide alloys reported by DiSalvo, *et al.*²¹ but the magnitude of the resistivity is higher due to the interfaces and SnSe bilayer which would not be expected to contribute significantly to the conductivity.²³ Figure VI.12b plots room temperature resistivity vs. x which has a linear relationship up to $x = 0.85$. The resistivity of the $x = 1$ compound is smaller than expected from the extrapolation of this trend, due to the change in coordination of the dichalcogenide from octahedral to trigonal prismatic in the pure TaSe_2 end member. The Temperature dependent resistivity measurements show a suppression of the charge density phenomenon previously reported for

(SnSe)_{1.15}VSe₂ at doping levels above $x = 0.12$. This is in agreement with previously reported findings for the (Ta_{1-x}V_x)Se₂ transition metal dichalcogenide alloys.²¹ The general increase in the resistivity at lower temperatures apparent in the alloys reported here was also observed in the TMD alloys. Temperature dependent Hall coefficient measurements, shown in Figure VI.12c, suggest complex behavior. The charge density wave in (SnSe)_{1.15}VSe₂ is clearly evident with an abrupt increase in the Hall coefficient for this compound. The suppression of the charge density wave with substitution of Ta for V results in essentially temperature independent Hall coefficients for all of the other compounds except the alloy with 0.49. This compound shows a change in the sign of the Hall coefficient changing at 134 K and a continuously decreasing Hall coefficient. Additional studies will be required to understand the complex behavior of this alloy.

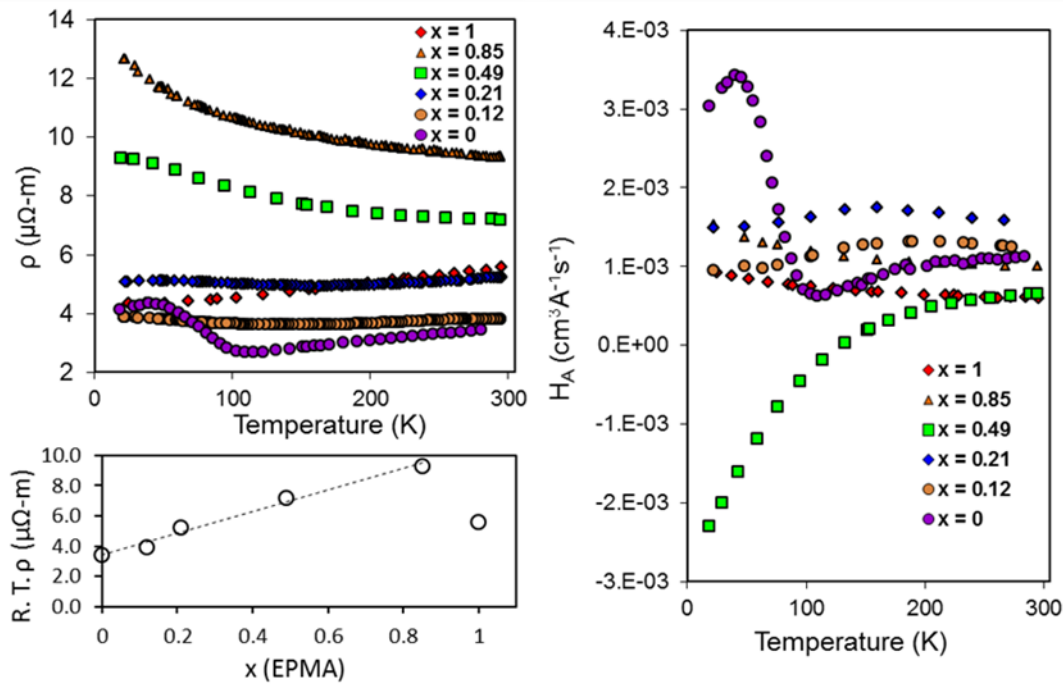


Figure VI.12. Electrical transport properties of the (SnSe)_{1+δ}(Ta_xV_{1-x})Se₂ compounds as a function of x . a) Temperature dependent resistivity. b) Room temperature resistivity as a function of x . c) Temperature dependent Hall coefficient.

Figure VI.13 contains the temperature dependence of the electrical resistivity of the ordered alloy with the targeted composition $([\text{SnSe}]_{1.15})_1(\text{VSe}_2)_1([\text{SnSe}]_{1.15})_1(\text{TaSe}_2)_1$ along with that measured for $([\text{SnSe}]_{1.15})_1(\text{VSe}_2)_1$, $([\text{SnSe}]_{1.15})_1(\text{TaSe}_2)_1$ and $([\text{SnSe}]_{1.15})_1([\text{Ta}_{0.5}\text{V}_{0.5}]\text{Se}_2)_1$. The ordered alloy has a slightly higher resistivity than that of the disordered alloy and similar temperature dependence, consistent with the extensive Interdiffusion of the dichalcogenide constituents discussed earlier. The sharp change in resistivity at low temperature, attributed to a charge density wave in $\text{SeSe}_{1.15}\text{VSe}_2$ is not present in the ordered alloy. Using the compositional results of the EDX scans, both the magnitude and temperature dependence can be modeled by $([\text{SnSe}]_{1.15})_1([\text{Ta}_{0.7}\text{V}_{0.3}]\text{Se}_2)_1$ and $([\text{SnSe}]_{1.15})_1([\text{Ta}_{0.3}\text{V}_{0.7}]\text{Se}_2)_1$ layers in parallel.

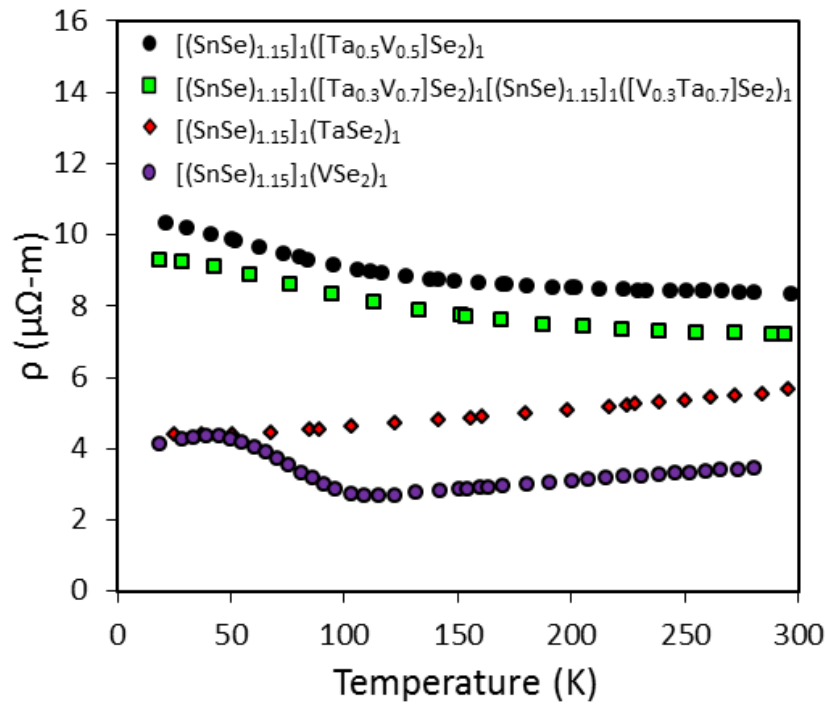


Figure VI.13. Temperature dependent resistivity of the $([\text{SnSe}]_{1.15})_1([\text{Ta}_{0.3}\text{V}_{0.7}]\text{Se}_2)_1$ $([\text{SnSe}]_{1.15})_1([\text{V}_{0.3}\text{Ta}_{0.7}]\text{Se}_2)_1$ compound and the related compounds $([\text{SnSe}]_{1.15})_1(\text{VSe}_2)_1$, $([\text{SnSe}]_{1.15})_1(\text{TaSe}_2)_1$ and $([\text{SnSe}]_{1.15})_1([\text{Ta}_{0.5}\text{V}_{0.5}]\text{Se}_2)_1$.

VI.4. Conclusion

The data collected on the $([\text{SnSe}]_{1.15})_1([\text{Ta}_x\text{V}_{1-x}]\text{Se}_2)_1([\text{SnSe}]_{1.15})_1([\text{V}_y\text{Ta}_{1-y}]\text{Se}_2)_1$ compound illustrates the challenges in limiting the interdiffusion of layers during the self-assembly of the MER precursor into the targeted compound. This case was chosen as a "worst case" scenario, with two metals that form a complete solid solution as dichalcogenides and only a single bilayer of SnSe separating the two of them. One would anticipate a reduction in the amount of mixing of the layers as a result of separating the constituents by thicker rock salt layers and by reducing either the time or temperature of the annealing required to self-assemble the product from the precursor. Changing the identity of the rock salt buffer layer might also reduce the amount of interdiffusion. Choosing components that are less miscible or using three different structural elements would be additional approaches to limit the amount of mixing. More knowledge of the mechanism of the transformation of the precursor to the final product would be useful to identify approaches to better control the final compositions of the constituent layers.

The data collected on the $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ alloys suggest that the a structural change in the TaSe_2 layer from trigonal prismatic to octahedral when small amounts of V are added consistent with previous observations. In addition, the charge density wave transition of the $(\text{SnSe})_{1.15}\text{VSe}_2$ ferecrystal is suppressed upon addition of isoelectric dopants. Further studies are required to investigate the complex electronic transport properties of this system.

VI.5. Bridge

Charge density waves (CDW) transitions are an interesting and complex phenomenon observed in some low dimensional systems and have been extensively

studied in bulk transition metal dichalcogenide (TMD) systems. Prior studies have shown that isoelectric doping of CDW conducting TMDs rapidly suppresses the CDW. Due to the lack of epitaxial relationships between the layers, ferecrystals provide an opportunity to study interesting transport phenomenon in structurally independent transition layer dichalcogenide layers. The synthesis of $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ alloys with small amounts of Ta should allow relative stability of ferecrystal CDWs and bulk CDWs to be better assessed. In the following chapter the CDW transition in $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ ferecrystals will be studied in a series of compounds starting with very low Ta concentrations. The effect of the isoelectric Ta dopants on the CDW transition will be discussed.

CHAPTER VII

SUPPRESSION OF A CHARGE DENSITY WAVE IN $([\text{SnSe}]_{1.15})_1(\text{VSe}_2)_1$

FERECRYSTALS VIA ISOELECTRIC DOPING WITH Ta

VII.1. Authorship Statement

Chapter VII describes material that will be submitted to *The Journal of Electronic Materials* in 2015. The co-authors are Krista Hill and David C. Johnson. Co-author Krista Hill assisted in the characterization of some of the compounds. Dr. David C. Johnson is my advisor and I am the primary author of the manuscript.

VII.2. Introduction

Two-dimensional materials have attracted considerable interest for potential applications due to new and exciting properties not observed in bulk materials. The discovery of unique properties in 2D graphene, not observed in 3D graphite,¹ has stemmed a wide interest in two-dimensional materials, which has grown to include a wide range of materials from boron nitride to transition metal dichalcogenides. The transition metal dichalcogenides (TMD)s are among the two-dimensional materials that have attracted significant attention from the 2-D community²⁻²² because their wide range of interesting bulk properties, such as superconductivity, spin-orbit coupling, intercalation chemistry and charge density waves and their use as catalysts and potential solar cell materials.²³⁻²⁹

The discovery of charge density wave (CDW) transitions in certain TMDs, described by Thorne *et al*²⁷ as “modulation of the conduction electron density in a metal and an associated modulation of the lattice atom positions,” resulted in numerous studies investigating the nature and potential applications of the nonlinear conductivity of these

materials.^{18-22, 26-29} In bulk TMD materials, CDW transitions are typically strongly suppressed by the introduction of defects and impurities.³⁰⁻³³ For example, Di Salvo *et al* showed a decrease in the CDW onset temperature (T_{CDW}) of TaSe₂ with various dopants.³³ There are also a few reports of the T_{CDW} increasing with doping, such as observed by Schneemeyer *et al* in Ve₂ when doped with Nb.³⁰ In either case the CDW transition was rapidly suppressed by the introduction of impurities. Charge density wave transitions have also been investigated in ultrathin dichalcogenides,¹⁸⁻²² VSe₂^{21-22, 26-29} has perhaps been the most investigated, with different studies reporting conflicting observations from samples cleaved from bulk crystals. A CDW transition was observed in the ([SnSe]_{1.15})₁(VSe₂)₁ ferecrystal,³⁴ which is unusually robust with respect to non-stoichiometry³⁵ and modulation doping.³⁶ Increasing the SnSe thickness layers in ([SnSe]_{1.15})_m(VSe₂)₁ increases T_{CDW} ³⁷ while increasing the number of VSe₂ layers changes the carrier type, which suppresses the CDW behavior.³⁸ Interestingly the CDW transition is absent in the ([SnSe]_{1.15})₁(VSe₂)₁ misfit layer compound analog. Wiegiers *et al* suggested that the lack of a CDW is a consequence of the lattice distortions arising from lattice matching of the constituents providing an alternative lower in energy to the CDW state.³⁹ The extensive rotational disorder between the constituents in the ferecrystal, resulting in independent in-plane structures of the constituents, may account for the observation of CDW phenomenon in these materials.

These prior studies lead us to investigate substitutional doping of VSe₂ containing ferecrystals with Ta to compare the stability of the CDW transition in isolated VSe₂ layers to that observed in bulk VSe₂. (SnSe)_{1.15}(V_{1-x}Ta_x)Se₂ alloys with $x = 0, 0.04, 0.06, 0.07$ and 0.09 were synthesized. The lattice parameters change as expected from Vegard's law,

with the a -axis lattice parameter of the dichalcogenide increasing as the Ta percentage is increased. All the compounds are metallic and have an increase in resistivity at low temperature as expected for a charge density wave. The upturn moves to lower temperature and the change in resistivity becomes smaller as the percentage of Ta is increased in the VSe_2 layer. All the compounds have a positive Hall coefficient, in contrast with bulk VSe_2 , which has a negative Hall coefficient. The Hall coefficients decrease as temperature is decreased from room temperature, and then increase at the temperature where there is an upturn in the resistivity, indicating a decrease in carrier concentration. The minimum in the Hall coefficient as a function of temperature decreases systematically as the Ta concentration in the VSe_2 layer is increased. The suppression of the CDW transition in $(\text{SnSe})_{1.15}(\text{V}_{1-x}\text{Ta}_x)\text{Se}_2$ alloys as Ta concentration is increased similar to that observed for bulk VSe_2 , and similar also to substitutions done in other TMDs, which show that CDW transitions are suppressed at about 10% doping levels for isoelectronic dopants.

VII.3. Experimental

The $(\text{SnSe})_{1.15}(\text{V}_{1-x}\text{Ta}_x)\text{Se}_2$ alloys were synthesized from compositionally modulated precursors in a method described previously.²¹ Briefly, the deposition of the precursors was accomplished using a custom-built physical vapor deposition chamber. Se (99.5 % purity) was deposited using a custom-built Knudson effusion cell. Ta (99.95 % purity), V (99.7 % purity) and Sn (99.999 % purity), obtained from Alpha Aesar, were deposited using Thermionics 3kW electron beam guns. The deposition rates and thicknesses were monitored and controlled using quartz crystal microbalances. Self-

assembly of the ferecrystals was accomplished by annealing the prepared precursors at 400 °C for 20 min in a nitrogen atmosphere ($O_2 < 0.6$ ppm).

Out-of-plane X-ray diffraction and X-ray reflectivity measurements were performed on a Bruker D8 Discover X-ray diffractometer ($CuK\alpha$ radiation) and were used to determine the thickness of the films and repeating units and assess the quality of the films. Grazing incidence in-plane X-ray diffraction was performed on a Rigaku Smartlab X-ray diffractometer ($CuK\alpha$ radiation) and was used to characterize the in-plane structure of the films.

Compositions of the ferecrystals were measured by electron probe micro-analysis (EPMA) on a Cameca SX-100. Intensities were collected at acceleration voltages of 7, 12, and 17 keV.

Electrical transport measurements were performed on samples deposited on fused silica slides in a 1 x 1 cross pattern defined by a shadow mask. Electrical resistivity and Hall coefficient measurements were performed using a van der Pauw geometry.

VII.4. Results and Discussion

We sought to synthesize a series of Ta doped $(SnSe)_{1.15}VSe_2$ ferecrystals with low doping levels which would allow the susceptibility of the CDW of isolated VSe_2 layers to isoelectric dopants to be determined. Synthesis via modulated elemental reactants is accomplished through the self-assembly of designed amorphous precursors deposited by physical vapor deposition. The calibration procedure for precursors designed to form $([SnSe]_{1.15})_1(VSe_2)_1$ ferecrystals have been reported previously. The introduction of Ta into the VSe_2 layer of $([SnSe]_{1.15})_1(VSe_2)_1$ was accomplished by depositing increasing amounts of Ta adjacent to the V layers in the precursor. Self-assembly into the $(SnSe)_{1.15}$

(V_{1-x}Ta_x)Se₂ ferecrystals was accomplished by annealing the precursors in a N₂ environment at 400 °C for 20 minutes, the optimal annealing temperature previously determined for the ([SnSe]_{1.15})₁(VSe₂)₁ and (SnSe)_{1.15}(V_{0.5}Ta_{0.5})Se₂ ferecrystals.^{34,40} Locked-coupled out-of-plane X-ray diffraction scans, given in Figure VII.1, show diffraction maxima that can be indexed as (00*l*) reflections with c-axis lattice parameters (Table VII.1) consistent with those of (SnSe)_{1.15}(V_{1-x}Ta_x)Se₂ ferecrystals previously reported.⁴⁰ The observation of only 00*l* reflections confirms that the layers are highly ordered parallel to the substrate. The composition, determined from electron probe micro analysis (EPMA) give Ta/(V+Ta) ratios of 0, 0.04, 0.06, 0.07 and 0.09 for the compounds (Table VII.1).

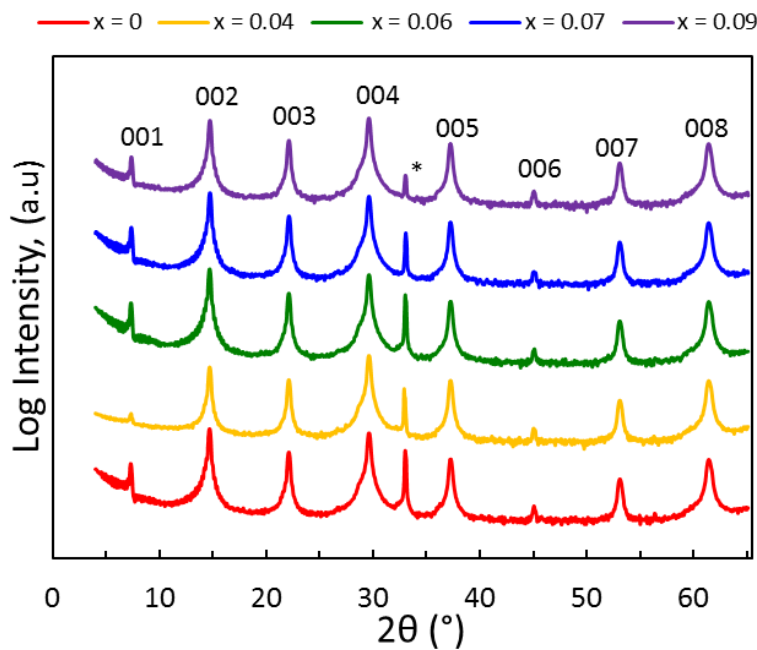


Figure VII.1. Out-of-plane specular X-ray diffraction patterns for (SnSe)_{1+δ}(Ta_xV_{1-x})Se₂ compounds (with x = 0, 0.04, 0.06, 0.07 and 0.09). The (*) designates silicon substrate peaks.

Table VII.1. The Ta/(V+Ta) ratio (x), lattice parameters, room temperature resistivities, temperature of minimum resistivity ($T_{\min}$) and the ρ_{25K}/ρ_{295K} ratio of the $(\text{SnSe})_{1.15}(\text{V}_{1-x}\text{Ta}_x)\text{Se}_2$ compounds.

Ta/(V+Ta) ratio x	c (nm)	a (TSe ₂) (nm)	a (SnSe) (nm)	ρ_{RT} ($\mu\Omega\text{m}$)	ρ_{25K}/ρ_{295K}	$T_{\min}$ (K)
0	1.2059(1)	3.409(1)	5.943(1)	3.67(1)	1.29	120(5)
0.04	1.2064(1)	3.411(1)	5.945(1)	3.85(1)	1.44	112(5)
0.06	1.2062(1)	3.416(1)	5.946(1)	4.86(1)	1.30	105(5)
0.07	1.2063(1)	3.422(1)	5.954(1)	3.89(1)	1.11	76(5)
0.09	1.2065(1)	3.428(1)	5.956(1)	4.31(1)	1.01	70(5)

The ab -plane diffraction patterns were obtained using grazing incidence in-plane X-ray diffraction (Figure VII.2.) All reflections could be indexed as $(hk0)$ reflections of the SnSe and $(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ constituents. The calculated a -axis lattice parameters (Table 1)

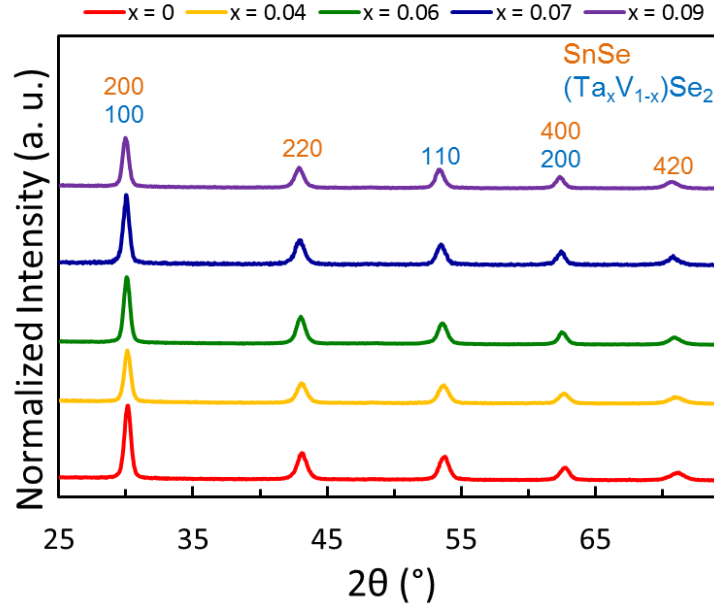


Figure VII.2. Grazing incidence in-plane X-ray diffraction patterns for $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ compounds (with $x = 0, 0.04, 0.06, 0.07$ and 0.09).

increase linearly with x and are consistent with previous results in $(\text{SnSe})_{1.15}(\text{V}_{1-x}\text{Ta}_x)\text{Se}_2$ ferecrystals.⁴⁰ This in-plane diffraction data, combined with the specular diffraction data and previously published diffraction data and STEM images of $([\text{SnSe}]_{1.15})_1(\text{VSe}_2)_1$ support a structure containing alternating layers consisting of a bilayer of SnSe and a single dichalcogenide layer

Temperature dependent in-plane electrical resistivity measurements (given in Figure VII.3) were performed on samples with $x = 0, 0.04, 0.06, 0.07$ and 0.09 . The $x = 0$ compound shows the onset of the CDW transition, observed previously, indicated by a dramatic change in the slope of the resistivity vs. temperature curve below 120 K. The temperature dependence of all of the resistivity curves are similar in form, with a systematic decrease in the high temperature slope as the amount of Ta substitution is increased. The magnitude of the resistivity at room temperature, however, does not vary

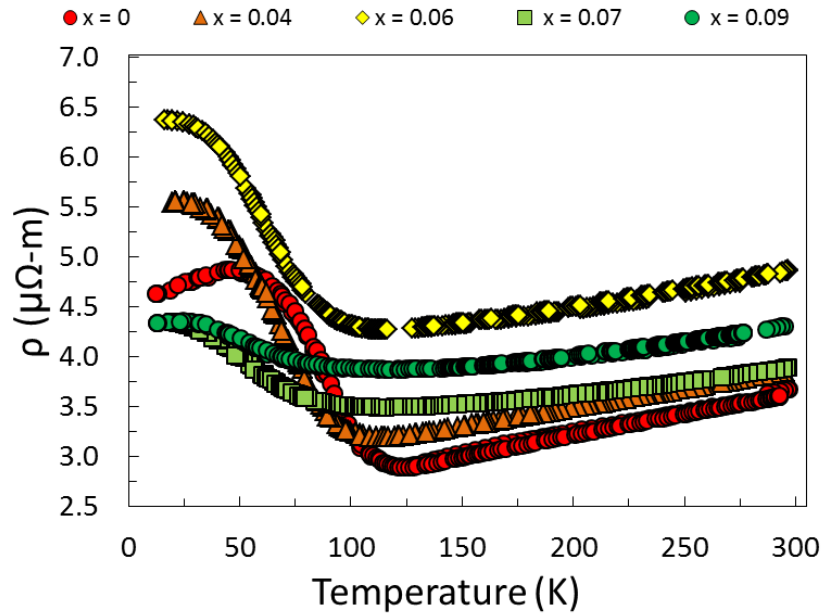


Figure VII.3. Temperature dependent resistivity of the $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ (with $x = 0, 0.04, 0.06, 0.07$ and 0.09).

systematically, (Table VII.1), probably due to slight differences in sample quality.

Normalization of the electrical resistivity by dividing by the room temperature resistivity allows the samples to be more easily compared (Figure VII.4). The increase in resistivity as temperature is decreased below the minimum decreases as the amount of Ta substitution is increased.

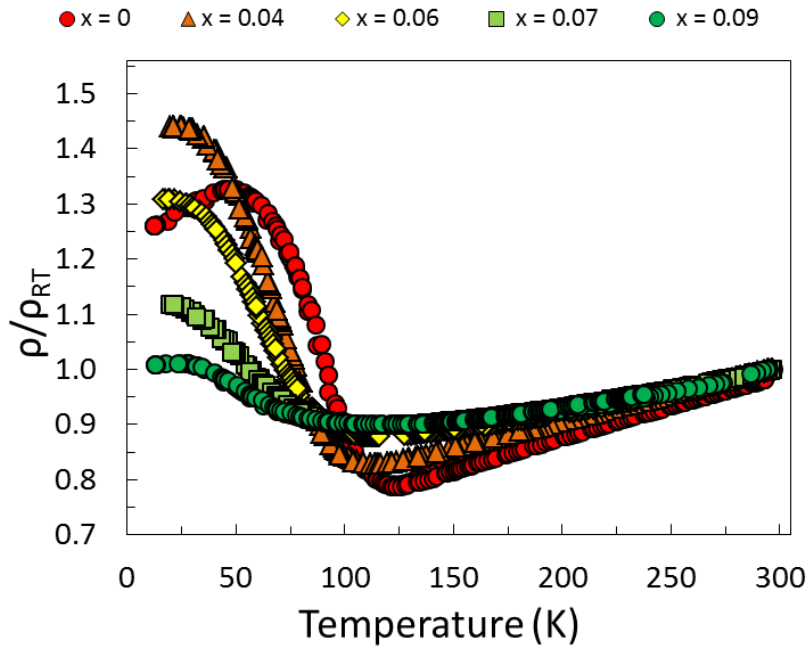


Figure VII.4. ρ/ρ_{RT} vs. temperature of the $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ (with $x = 0, 0.04, 0.06, 0.07$ and 0.09)

Temperature dependent Hall coefficient measurements, given in Figure VII.5, provide additional insight to the unusual temperature dependence of the resistivities. The Hall coefficients for all the samples have similar temperature dependence. Decreasing the temperature from room temperature results in a slowly decreasing Hall coefficient. Below the CDW onset temperature, the Hall coefficient increases. The sharpness of this increase and the magnitude of this increase decreases as the amount of Ta substitution increases.

As can be seen in the expanded inset in Figure VII.5, the minimum in the Hall Coefficient shifts to lower temperature as the amount of Ta substitution is increased (Table VII.1). This data suggests that all of the samples reported here have a CDW transition, but the reduced temperature of the minimum Hall coefficient and the reduction of the magnitude of the change in the Hall coefficient indicates that the addition of Ta to the VSe₂ layer suppresses the CDW.

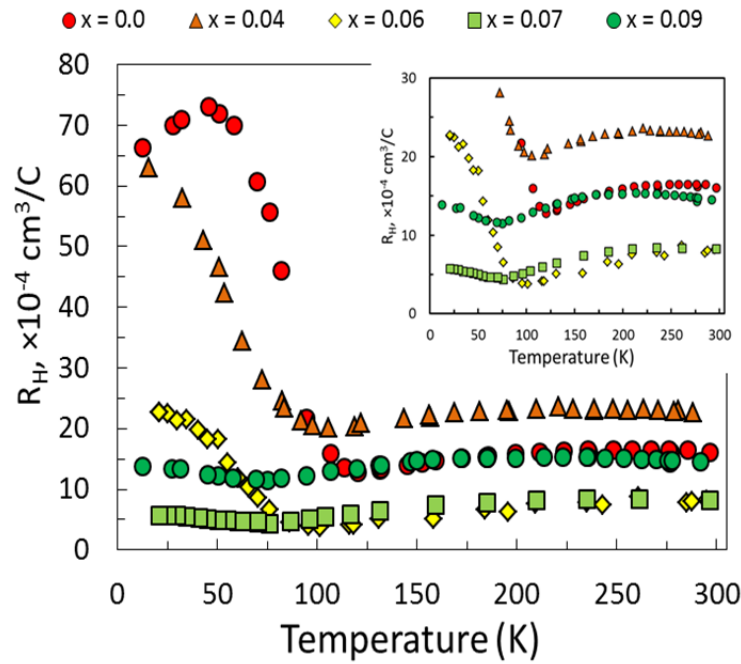


Figure VII.5. Hall coefficient vs. temperature of the (SnSe)_{1+δ}(Ta_xV_{1-x})Se₂ (with x = 0, 0.04, 0.06, 0.07 and 0.09).

CDW transitions in bulk transition metal dichalcogenides are also rapidly suppressed by the addition of dopants. For example, Di Salvo *et al* determined that the charge density wave of bulk TaSe₂ was destabilized at doping concentrations of 10% for many different cations.³⁴ Similar work by Mutka *et al* showed that the charge density wave in VSe₂ was rapidly suppressed by defects induced via electron bombardment. They

found that increased bombardment lowered the CDW onset temperature with the CDW being suppressed at a fraction of displaced metal atoms of less than 0.01.³² The CDW in $([\text{SnSe}]_{1.15})_1(\text{VSe}_2)_1$ was reported to be stable with respect to excess vanadium, but in this system the excess vanadium is incorporated as volume defects rather than as an intercalate.⁴¹ The addition of isoelectric dopants dispersed in the VSe₂ layer suppresses the CDW as was found in bulk materials.

VII.5. Conclusion

The stability of the charge density wave in structurally independent VSe₂ layers to isoelectric dopants was probed by the addition of Ta to $(\text{SnSe})_{1.15}\text{VSe}_2$ ferecrystals forming $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ alloys. The lattice parameters of the alloys systematically change with the amount of Ta, consistent with the formation of single $(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ layers separated by bilayers of SnSe. Electrical resistivity and Hall coefficient measurements show that the charge density wave onset temperature and the magnitude of the increase in resistivity and Hall coefficient below the onset temperature all decrease when the amount of Ta is increased, indicating a destabilization of the charge density wave transition. In contrast to the stability of the CDW transition with respect to volume defects induced by non-stoichiometric films, the CDW in $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ alloys is suppressed by doping at similar concentrations to that found in bulk materials.

CHAPTER VIII

CONCLUSIONS

First, the motivation of 2D materials, particularly 2D heterostructures was put forth. This was followed by a brief overview of the synthetic challenges in the synthesis of multiple component heterostructures by either cleaving of bulk materials or through epitaxial growth. Interesting films of high quality have been produced by either of these methods. However, the lack of scalability, arduousness of the task and the requirement that monolayers be stable under ambient conditions in the cleaving bulk materials coupled with the difficulty of finding growth conditions that allow constituents to be grown on each other, in either order, in epitaxial growth, arouse the need for a deposition technique whereby multiple constituent films can be synthesized without epitaxial relationships between the layers, allowing a large variety of 2D materials to be stacked in any sequence or pattern. Next, a brief overview of the modulated elemental reactants method of forming multiple component thin films by self-assembly of compositionally modulated precursors was undertaken including a discussion of the method whereby systems containing multiple constituents could be designed by combining calibrated precursor schemes of simpler systems.

Following this, the synthesis of the first quaternary system via modulated elemental reactants was put forward; the synthesis of a family of $([\text{SnSe}]_{1.16-1.09})_1$ $([\text{Nb}_x\text{Mo}_{1-x}]\text{Se}_2)_1$ alloy ferecrystals. These materials represent the first synthesis of a series of controlled misfit layer compound alloys. Structural characterization of the materials showed that both in-plane and out-of-plane lattice parameters followed Vegard's law and electrical transport measurements of the alloys observed behavior

between those of the semiconducting MoSe₂ and metallic NbSe₂ parent compounds. Characterization of these alloys would prove useful in the characterization of subsequent compounds.

Next, the synthesis of the first three component ferecrystal heterojunction, (SnSe)_{1.16}([Mo_{0.9}Nb_{0.1}]Se₂)_{1.06}(SnSe)_{1.16}([Nb_{0.9}Mo_{0.1}]Se₂) was discussed. Characterization by XRD, HAADF-STEM and EDX indicated distinct MoSe₂ and NbSe₂ regions. Comparison of the structural and electrical transport properties to those of the ([SnSe]_{1.16-1.09})₁([Nb_xMo_{1-x}]Se₂)₁ alloys allowed the extent of alloying of the miscible NbSe₂ and MoSe₂ to be determined.

This was then followed by a discussion on the synthesis of a family of related heterostructures, the ([SnSe]_{1+δ})_m([Mo_xNb_{1-x}]Se₂)_{1+γ})₁([SnSe]_{1+δ})_m ({Nb_xMo_{1-x}]Se₂)₁ ferecrystals (with $m = 0, 1, 2, 3$ and 4). By increasing the thickness of the interleaved SnSe rocksalt layers the alloying of the miscible dichalcogenides could be controlled and studied. In addition comparison of electrical transport properties to those of the ([SnSe]_{1+δ})_m(NbSe₂)₁ ($m = 1 - 8$) compounds allowed the electrical interactions of the MoSe₂ and NbSe₂ constituents to be determined.

Next, the synthesis and characterization of ([SnSe]_{1+δ})_l([V_xTa_{1-x}]Se₂)_{1+γ})₁ ([SnSe]_{1+δ})_l([Ta_xV_{1-x}]Se₂)₁ and (SnSe)_{1.15}(Ta_xV_{1-x})Se₂ ferecrystals was discussed. The in-plane lattice parameters of the (SnSe)_{1.15}(Ta_xV_{1-x})Se₂ ferecrystals were shown to have a non-Vegard's law relationship with a structural transition from octahedral to trigonal prismatic coordination at high values of x . The overlap of the K α lines of Mo and Nb prevented quantification of the extent of alloying in the ([SnSe]_{1+δ})₁([Mo_xNb_{1-x}]Se₂)_{1+γ})₁ ([SnSe]_{1+δ})₁([Nb_xMo_{1-x}]Se₂)₁ compound. This problem is resolved in the ([SnSe]_{1+δ})_l

$([V_xTa_{1-x}Se_2]_{1+\gamma})_1([SnSe]_{1+\delta})_l(\{Ta_xV_{1-x}\}Se_2)_1$ allowing a formula of for the compound of $([SnSe]_{1+\delta})_l([V_{0.7}Ta_{0.3}Se_2]_{1+\gamma})_1([SnSe]_{1+\delta})_l(\{Ta_{0.7}V_{0.3}\}Se_2)_1$ to be estimated. In addition, both the magnitude and temperature dependence of the electrical transport properties could be modeled by $([SnSe]_{1.15})_1([Ta_{0.7}V_{0.3}]Se_2)_1$ and $([SnSe]_{1.15})_1([Ta_{0.3}V_{0.7}]Se_2)_1$ layers in parallel.

Finally, a discussion of the effect of isoelectric doping on the charge density wave in structurally isolated VSe_2 layers was discussed. Electrical transport measurement on the $(SnSe)_{1+\delta}(Ta_xV_{1-x})Se_2$ alloys (with $x = 0., 0.04, 0.06, 0.07$ and 0.09) indicated that, despite the reported stability of the charge density wave in ferecrystals to structural defects due to non-stoichiometry, the charge density wave is rapidly suppressed at doping concentrations above about 7% in a similar manner to bulk materials.

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