Phase Width of Kinetically Stable $([\text{PbSe}]_{1+\delta})_1(\text{TiSe}_2)_1$ Ferecrystals and the Effect of Precursor Composition on Electrical Properties

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Abstract

Synthesis and transport properties of $([\text{PbSe}]_{1+\delta})_1(\text{TiSe}_2)_1$ ferecrystals made from several precursors of different compositions are reported. C-lattice parameters of crystallized compounds vary by under 0.01 Å though relative cation compositions normalized to selenium content are shown to vary by over 30%. Even with a deliberate wide-range of starting precursor compositions crystallized under kinetic conditions, the variation in electrical properties of ferecrystals is less than in similar compounds grown under equilibrium conditions. The growth process of a ferecrystal appears to push impurities of excess starting material in the precursor to the surface, until impurity density becomes too high and defects are incorporated as inclusions, replacing small domains within the layered structure. Transport properties of the many compounds formed cluster into regions, with samples deposited during the same deposition cycle showing less variation.

Keywords: Thin films, Crystal growth, Vapor deposition, Electrical transport, X-ray diffraction

1. Introduction

The high temperatures and long times used in most solid state reactions lead to equilibrium products and an equilibrium distribution of impurity atoms[1, 2]. This leads to the common practice of reporting the properties of a new compound based on the measurement of a single sample, ideally a single crystal that has been structurally characterized. For metallic compounds with a narrow phase width, subsequent reports usually agree with the initial report, as metallic properties are usually not significantly affected by small changes in the concentration of defects or impurities except for at low temperatures[3]. For semiconducting compounds properties often vary significantly between preparations, especially preparations from different groups and even when using near

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equilibrium synthesis conditions, as small differences in impurity levels and/or defects can significantly vary carrier concentration[3]. An especially large variation in properties is observed when there is a range of compositions within which compounds are stable[4]. As the number of elements within a compound is increased or the structure becomes more complicated, obtaining agreement on properties becomes even more difficult due to the varying distributions of the elements within the ideal composition, impurity atoms, and defects of different crystallographic sites.

The challenges in determining the base properties of ternary intergrowth compounds is especially difficult. An example of this is ternary misfit layer compounds of the form $([\text{MX}]_{1+\delta})(\text{TX}_2)_n$, which consists of an intergrowth of a rock salt structure, MX, where M = Sn, Pb, Bi, or RE, and a transition metal dichalcogenide, TX_2 where T = Ti, V, Cr, Nb, or Ta[5]. The chalcogen, X, is either S or Se. The misfit parameter, δ , represents the difference in area per cation of the two different structures, which is required to accurately describe these compounds since the individual MX and TX_2 layers will not necessarily have the same in-plane area per formula unit. The integer n ($n = 1, 2$) may be included to express compounds with multiple TX_2 layers per MX. Electrical properties for nominally the same compound vary considerably from group to group, even for metallic samples. For example, the resistivity of single crystals of $([\text{PbS}]_{1.18})(\text{TiS}_2)$ as reported from different groups[6, 7] differs by a factor of 5 and the resistivity of $([\text{SmS}]_{1.18})(\text{TaS}_2)$ as reported from different groups[8, 9] varies by a factor of 7. The differences in properties of these misfit layer compound crystals is thought to be a consequence of different growth conditions used during vapor transport leading to different amounts of incorporated iodine, other impurities, and/or defects, as has been widely reported for binary constituents[5, 10, 11]. Recently a new synthesis approach was shown capable of preparing intergrowth compounds $([\text{MX}]_{1+\delta})_m(\text{TX}_2)_n$, where m and n , which respectively denote the integer number of rock salt bilayers and dichalcogenide trilayers, can be systematically controlled by design of a precursor[12]. The structures are different from misfit layer compounds in that there is rotational (turbostratic) disorder between basal planes of the constituents and hence no systematic cooperative structural distortion of the constituent layers. The synthesis route to these compounds is kinetically controlled and the kinetics of the formation reaction should determine the concentration and distribution of defects and impurity atoms.

It is important to understand the reproducibility of the kinetically controlled synthesis of these turbostratically disordered misfit layer compounds, or ferecrystals, before considering the difference between compounds with different stacking sequences, because small deviations in the product could potentially cause the properties to vary more within different preparations of the same compound relative to compounds with different m and n values. Here we investigate two sets of $([\text{PbSe}]_{1+\delta})_1(\text{TiSe}_2)_1$ samples prepared during different equipment (deposition) cycles from a range of starting precursors. Although a large variation of precursor composition was used, we find that they crystallize to nominally the same product, with a small range of c-axis lattice parameters (defined to

be along the stacking direction of the intergrowth). It is difficult to determine the precise composition of the majority compound as different trace amounts of secondary phases may form, and so the $1+\delta$ nomenclature is used to discuss compounds synthesized as part of the current contribution. We find that electrical behavior in the form of resistivity values, Seebeck coefficients, and carrier densities vary from sample to sample and cluster into discrete regions within deposition cycles. The changes in electrical properties correlate with changes in overall composition. There is a narrower distribution in both the composition and the transport properties of compounds formed from precursors deposited in the same equipment cycle. To minimize contribution from repeatability limitations, the most meaningful comparisons of trends in ferecrystal properties as m or n are varied can be made with precursors from the same deposition cycle.

2. Materials and methods

Thin films of the amorphous precursor were deposited on silicon and quartz substrates using a custom built physical vapor deposition system[13]. Selenium was deposited using a Knudsen effusion cell, whereas lead and titanium were deposited using electron beam guns. The thickness of each elemental layer was monitored using quartz crystal microbalances. Background pressure inside the chamber during film deposition was maintained between 5×10^{-8} and 5×10^{-7} torr for all reported samples. The first set of depositions produced thin films that were approximately 50 nm thick, which consisted of repetitions of the layer sequence Ti – Se – Pb – Se. A second set of samples, prepared much later than the first set, was made with a total thickness of 35 nm. The precursors were calibrated to contain an excess of 2% Se, as this has previously been shown to produce samples with more intense diffraction patterns[12]. The thickness of each layer in the repeating sequence was calibrated via a method described previously such that each layer self assembles into a $([\text{PbSe}]_{1+\delta})_1(\text{TiSe}_2)_1$ unit cell upon annealing[14]. Samples were annealed on a hot plate at 350°C in a nitrogen atmosphere. Electron-probe microanalysis (EPMA) was used to determine the composition of the thin film samples[15]. Specular X-ray diffraction data were collected using a Bruker D8 Discover diffractometer with Cu $K\alpha$ radiation.

Cross-section specimens for high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) investigations were prepared with in-situ lift-out and gallium focused ion beam (FIB) milling methods on an FEI Helios 600 Nanolab. All specimens were thinned to 300nm using wedge pre-milling methods[16] with a 30kV accelerating voltage. The subsequent thinning process was done at 5kV until 100 nm thick, followed by thinning at 2kV to 40 nm thick, with final thinning at 1kV to a final thickness of 20 nm. HAADF-STEM was carried out on an FEI Titan 80-300 using a 50um condenser aperture, 300kV accelerating voltage, 0.050 nA of current, and a 240 mm camera length.

Thin film specimens for electrical transport properties were deposited on insulating fused silica substrates in order to minimize the influence of the substrate. Films were deposited through a shadow mask in a cross geometry, as well as a rectangle. Four-probe electrical resistivity (ρ) was measured from 20

Sample	c-lattice parameter (nm)	295K resistivity (m Ω -cm)	Carrier density (10 ²¹ cm ⁻³)	Composition		
				Pb/Ti	Pb/Se	Ti/Se
a1	1.2181	0.93	2.12	0.95	0.36	0.38
a2	1.2173	1.32	1.76	1.05	0.39	0.37
a3	1.2181	0.83	2.04	0.88	0.33	0.38
a4	1.2167	1.41	1.72	1.10	0.38	0.35
a5	1.2169	1.21	1.71	0.99	0.37	0.37
a6	1.2181	1.45	1.72	1.07	0.38	0.36
a7	1.2170	1.18	1.82	0.96	0.36	0.37
a8	1.2176	1.78	1.86	0.95	0.37	0.38
a9	1.2173	1.14	2.1	0.98	0.36	0.36
b1	1.2188	1.97	1.44	0.92	0.40	0.44
b2	1.2193	3.3	1.07	1.16	0.46	0.40
b3	1.2199	3.01	1.16	1.08	0.43	0.40
b4	1.2194	2.15	1.29	0.91	0.40	0.43
Moore 1:1	1.2174	3.00	2.10	1.16	0.37	0.32

Table 1: Summary of all samples as well as data from the previously reported 1:1 compound[14] (labelled Moore 1:1). Samples from the first deposition cycle, set A, were deposited in order from a1 to a9. Samples from the second deposition cycle, set B, were deposited in order from b1 to b4.

K to 300 K in a custom closed-cycle He cryo-system using the van der Pauw technique on the cross[17]. Electrical leads were attached using pressed Indium contacts. The Seebeck coefficient was measured on the rectangular portion. One half of the sample was cooled slightly below room temperature ($\Delta T < 2K$) and voltages were measured through thermocouples at each side as the temperature equilibrates. The Seebeck coefficient is determined from the slope of applied measured voltage difference as a function of temperature difference, corrected for the Seebeck coefficients of the copper-constantan thermocouple leads. All reported electrical data correspond to the in-plane direction.

3. Results and discussion

3.1. Structural characterization

Sample precursors were prepared in two deposition cycles to synthesize a precursor which yields a sample after annealing that is crystallographically and compositionally in agreement with the previously reported turbostratically disordered $[\text{PbSe}_{1.16}]_1(\text{TiSe}_2)_1$ [14]. Once a parameter-space close to optimal was found, the depositions were fine-tuned by varying the elemental layer thicknesses of the precursor, which also changes the compositions of the precursors. The full width at half maximum of the (002) Bragg reflection was used between depositions as a fast indicator of 1:1 sample quality. Data collected on the samples prepared for this study that formed the 1:1 compound, as well as the previously reported sample, are summarized in Table 1.

Low angle specular diffraction patterns are shown in Figure 1 and indicate little variation is present within deposition cycles. The small variation of critical angle from 0.62 to 0.67 degrees in 2-theta shows little change in density and no correlation was able to be drawn between small shifts in critical angle and composition. Fitting of the high-frequency Kiessig oscillations to the Bragg equation modified for refractive contributions results in film thicknesses within 2.5 nm of the targeted values of 50 nm for set A and 35 nm for set B. The angle at which the Kiessig fringes can no longer be resolved is an indicator of the roughness of the films. The increased smoothness seen in the second set of samples is due to diffraction data being collected from samples on a Si substrate as opposed to fused quartz. The changes in rate of decay of the Kiessig fringes between samples is most-likely due to a variance in different substrate's native oxide thicknesses. The first Bragg Peak is seen in all low-angle scans. The peak centers of gravity vary little from 7.27 degrees, corresponding to a d-spacing of 12.15 Å and the (001) reflection of the 1:1 ferecrystal.

Figure 1: Low-angle diffraction patterns collected from samples. Data from the previously reported 1:1 compound[14] (labelled Moore 1:1) is shown as the bottom curve in each pane. (a) Set A. The first loss of intensity near the critical angle is a substrate artifact. The critical angle is taken from the second loss. (b) Set B. The apparent amplitude difference is due to the stacking. The range of normalized data is comparable for all samples.

High angle coupled $\theta - 2\theta$ diffraction patterns collected normal to the film surface (Figure 2) also show little variation between samples or deposition cycles. The c-lattice parameters of all samples are within 0.01 Å of the average value and within 0.25% of the previously reported value for the $([\text{PbSe}]_{1.16})_1(\text{TiSe}_2)_1$ ferecrystal. This small change in c-lattice parameter correlates weakly with composition changes, trending with the measured metal (Pb, Ti) to Se ratio. The increased FWHM of the samples from the second deposition cycle is due to fewer layers in the (00l) direction in which the crystallite size is limited by the thickness of the film. The lack of any (hkl) reflections with $h, k \neq 0$ in a coupled out-of-plane geometry is characteristic of ferecrystal samples due to the crystallographic alignment of the samples with the substrate. The similarity of the diffraction patterns suggests a similar average structure for all of the samples. There is some variation in the relative intensities of peaks throughout both sets of samples, with the largest variations occurring on odd (00l) peaks in Pb-rich samples shrinking about 50% from the average relative intensity. These

changes in relative intensity suggest a variation in the occupancy of specific locations reflecting the different compositions of the precursors.

Figure 2: High angle specular diffraction patterns collected from samples in (a) set A and (b) set B. Data from the previously reported 1:1 compound[14] (labelled Moore 1:1) is shown for comparison as the bottom curve in each pane. The apparent difference in scales is due to a reduced range in the pane with fewer curves.

3.2. Electrical characterization

Electrical measurements are more sensitive to impurity phases or local crystalline defects than x-ray measurements. Prior literature suggests charge transport occurs mainly in the conduction band of the transition metal dichalcogenide constituent[14]. We expect changes in impurity and defect concentration would alter the carrier density of the semimetallic TiSe_2 . Table 1 contains the room temperature resistivity of the samples. The composition and resistivity data from both sets of samples cluster in nearby but discrete regions of parameter space, distinct also from the previously published compound. The variation of the extrema from the average value is $\pm 40\%$ within sample set A and $\pm 30\%$ within sample set B. There is a factor of 2 difference between the averages of the resistivity values of the two data sets, with the extrema from the entire experiment spanning a 400% change. The resistivity values were found to trend with the Pb/Se ratio, as shown in Figure 3. The variation in room temperature resistivity (400%), however, is smaller than that reported for different single crystals of misfit layer compounds (500-700%). This is somewhat surprising, as the misfit layer compound crystals were grown under nearly equilibrium conditions while the self-assembly of our precursors is a kinetic process. This suggests that in the self-assembly, the excess material is incorporated as inclusions rather than being dispersed as local defects throughout the film. The larger variation between depositions also suggests that it would be better to make samples with different m and n in the same set to correlate nanoarchitecture with properties.

Temperature dependent resistivity data, collected for most of the compounds from set A, are shown in Figure 4. The temperature dependence is very similar for all samples and indicates metallic behavior. The temperature dependence of the electrical resistivity can be modeled using the Bloch-Grüneisen equation for a metal where scattering of carriers is by phonons,

Figure 3: Sample resistivities and carrier concentrations. Values cluster in two regions for the two sample sets and loosely trend with the overall Pb/Se ratio measured by EPMA, which is at best only proportional to the composition of the ferecrystal. The lines are provided as a guide to the eye.

$$\rho(T) = \rho_0 + \Re \left(\frac{T}{\theta_D} \right)^5 \int_0^{\frac{\theta_D}{T}} \frac{z^5}{(e^z - 1)(1 - e^{-z})} dz$$

where ρ_0 is the residual resistivity, $\Re$ is the electron-phonon interaction constant, and θ_D is the debye temperature. Two of the fits (for a1 and a2) are shown alongside the data in Figure 4 with good agreement to the data. The closest comparison of temperature-dependent resistivity we can make is to the recently reported $([\text{PbSe}]_{1.16})(\text{TiSe}_2)_2$ misfit layer compound analog[18]. The 1:2 misfit layer compound was previously reported to have a room-temperature to residual resistivity ratio of 18.8 whereas our 1:1 ferecrystals are all below 1.8. The very weak temperature dependence indicates a small electron phonon interaction, reflecting the lack of long range order found for compounds prepared by self-assembling designed precursors. This disorder, and the resultant lack of phonons, is responsible for the low lattice thermal conductivity of ferecrystals. The variation of the residual resistivity with both sample set and composition is similar to that of the room temperature values, discussed above. There is evidence for a slight upturn in the resistivity at the lowest temperatures measured, but this upturn is smaller than previously reported[14].

To gain further information on the electrical properties, Hall coefficients were measured at room temperature for all samples. All samples exhibit a negative Hall coefficient indicating conduction via electrons, which is consistent with prior suggestions of charge donation to TiSe_2 from PbSe . Following prior literature reports, the Hall coefficients were converted to carrier concentration assuming a single band model[6]. Carrier concentrations are reported for all

Figure 4: Variable temperature resistivity data for select ferecrystal samples from set A. Solid lines are from Bloch-Grüneisen fits of samples a1 and a3 and show the samples follow a metallic behavior.

samples in Figure 3 and in Table 1, and are shown as a function of temperature on a subset of samples (Figure 5). Room temperature carrier concentration for each deposition varies by 15% from the average value and there is a factor of 1.5 between sets. Room temperature carrier concentration has a linear downward trend with cation impurity (Figure 3), suggesting reduced donation of charge into the dichalcogenide layer. The variation of the carrier concentration with temperature may be a consequence of assuming a single band model to calculate carrier concentrations. A change in charge transfer with temperature would be expected and lead to the observed weak temperature dependence.

Hall mobilities calculated from carrier concentration and resistivity measurements vary between 1.8 and 3.8 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. The mobility increases with carrier concentration, which is unusual for doping because dopant atoms usually cause scattering. However, this is consistent with charge donation from PbSe to TiSe_2 , where conduction occurs in a location spatially separated from the dopant. The mobility decreases as the Pb/Se ratio increases, perhaps due to defects in the dichalcogenide layer from the excess rock-salt cation acting as scattering centers.

Seebeck coefficients were all negative, consistent with Hall coefficient in indicating that electrons are the majority carrier. The magnitude of the Seebeck coefficients vary by about $2.5 \mu\text{V K}^{-1}$ within a set of samples. The average values of each set were ca. $5 \mu\text{V K}^{-1}$ apart. As expected, the magnitude of the Seebeck coefficient increases as carrier density is reduced. If conduction from a single parabolic band with acoustic scattering is assumed, the carrier effective

Figure 5: Carrier concentration as a function of temperature for a subset of samples.

mass can be determined from the Pisarenko relationship[19],

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{\frac{3}{2}}$$

Where α is the Seebeck voltage, k_B is the Boltzmann constant, e is the elementary charge, h is Planck's constant, m^* is the effective mass, T is the absolute temperature, and n is the carrier concentration. The average carrier mass was found to be $4.4 m_e$ and $3.6 m_e$ for sets A and B respectively, both lower than calculated from data on the previously reported 1:1 compound ($5.5 m_e$). The variations in m^* indicate the band assumptions are imperfect in describing the ferecrystal as we change precursor composition. However, the relative insensitivity of the Seebeck coefficient to changes in carrier concentration from compositional modulation may bode well for future studies of using dopants to influence ferecrystal transport properties, for example the thermoelectric power factor[20]. Coupled with the inherent tunability due to flexibility in synthetic control of the MER synthesis method for ferecrystals[21], this could offer an additional degree of freedom in controlling the transport properties of these compounds. Figure 6 graphs the correlation between the effective mass as calculated from the Pisarenko equation as a function of the cation concentrations measured for each sample. The lowest effective masses correspond to samples with a high cation (Pb, Ti)/Se ratio, as expected from their reduction in carrier density. The Seebeck coefficient is relatively insensitive to changes in the carrier concentration, as shown by the inset in Figure 6. The data from both set A and set B once again cluster into discrete regions, with the single data point from the previously published compound[14] in a different space as well. Moore also

reported Seebeck measurements from three other data points with magnitudes of 66-69 $\mu\text{V K}^{-1}$, though no carrier concentration data was provided for these samples[14]. This once again reinforces that systematic studies of ferecrystal compound stacking sequences would be best done within a deposition cycle.

Figure 6: Effective masses determined from the Pisarenko relationship plotted against cation ratios for all samples and the previously reported 1:1 compound[14] (labelled Moore 1:1). A general trend of decreasing effective mass with cation concentrations is apparent. The inset shows the Seebeck coefficient as a function of carrier concentration. Symbol allocation is consistent between the main figure and inset.

3.3. Defect characterization

To gain further insight on any structural changes due to the variation in the composition of the precursors, and how they might influence the electrical properties discussed above, cross sections of two samples were prepared for STEM imaging. From Set A, sample a5 was chosen as its intermediate composition should be representative of the set. From Set B, sample b2 was chosen as it is the most Pb-rich sample in the study. STEM images of the 2 samples are shown in Figure 7. The bright PbSe rock salt layers and dimmer TiSe_2 dichalcogenide layers are visible in both samples. Surprisingly, the a5 sample shows a capping layer of PbSe at the surface, even though the composition from EPMA does not indicate excess Pb relative to the previously published ferecrystal. The excess PbSe appears excluded from the bulk compound and only appears on the surface. The highly Pb-rich b2 sample shows that excess lead is incorporated into the film, replacing the dichalcogenide layer in regions as PbSe inclusions. Unlike sample a5 where excess PbSe is excluded, defects are instead trapped during the growth of the crystal front. Even with the inclusions, the layering

of the ferecrystal is not severely disturbed, hence the narrow range of c-lattice parameters still observed from the lead-rich samples. However, the difference in scattering power of PbSe defect regions relative to the TiSe_2 helps to explain the previously noted changes in diffraction intensity between samples. Crystallization of excess lead first on the surface, then as nanoscale PbSe inclusions within the dichalcogenide layer also offers insight as to why the transport properties are not severely affected by changing the composition of the sample. Following behavior of well-known semimetallic and narrow band gap materials[4, 22], one might expect a highly dispersed defect distribution to cause a severe perturbation to the transport properties of the ferecrystal relative to discrete inclusions of a wider band-gap compound.

The MER deposition method ensures a similar composition throughout the film, so this implies that the buried excess lead is ‘pushed’ towards the surface prior to the formation of the ferecrystal. It remains to be seen if annealing conditions can be used to further promote exclusion of excess rock-salt to the ferecrystal surface, enhancing purity without destroying the bulk metastable structure. Temperature ramps, Se vapor annealing, or excess dwell time are all avenues to explore.

Figure 7: HAADF-STEM images of sample a5 and b2. In both cases, excess PbSe can be seen on the surface. Regular, uninterrupted layering is visible in a5, whereas the highly lead-rich b2 sample shows excess lead incorporates itself as PbSe inclusions rather than dispersed Pb, however the global layering scheme is hardly interrupted.

4. Conclusions

Turbostratically disordered $([\text{PbSe}]_{1+\delta})_1(\text{TiSe}_2)_1$ forms over a range of initial precursor compositions resulting in a very narrow range of c-axis lattice parameters. STEM images showed excess rock salt in a typical sample was excluded from the bulk and instead formed on the surface of the ferecrystals,

and then eventually as nanoscale inclusions when the Pb content became high enough. The resistivity between samples was found to vary by a factor of two, with the change correlating with the Pb/Se ratio. The Seebeck coefficient was consistent within a set of samples prepared in the same deposition cycle. The unusual temperature dependence of the carrier concentration and unusual variation in the effective mass calculated from the Seebeck coefficients and the carrier concentration suggest a more complicated band structure than often assumed. The small change in electrical properties between ferecrystal samples relative to the large difference between reports of single crystals of misfit layer compounds, especially from a set of samples in the same deposition cycle, is encouraging for future experiments that explore how properties vary as compounds with different values of n and m are prepared.

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