

Thermoelectric Properties of Undoped High Purity Higher Manganese Silicides Grown by Chemical Vapor Transport

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Schematic of CVT Reaction Setup and Sample Images

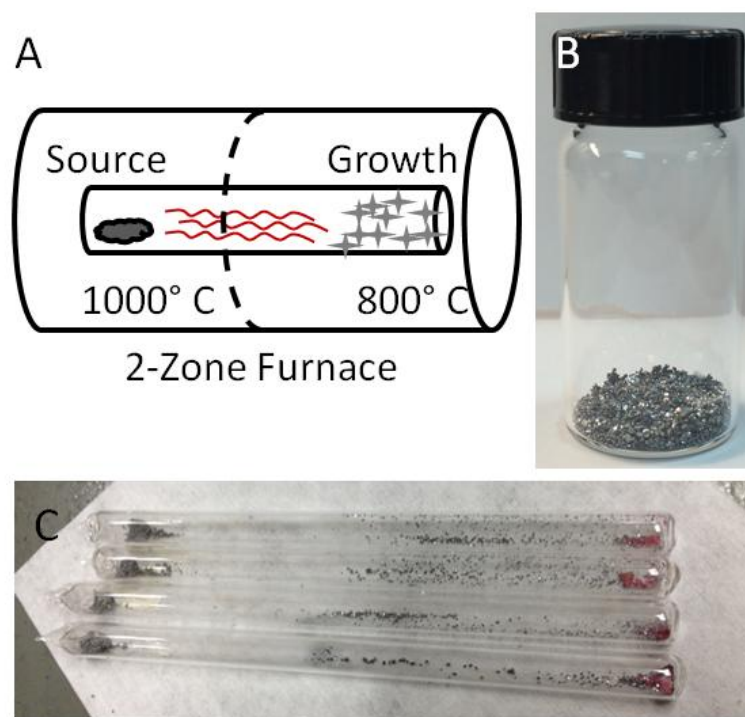


Figure S1. A) Schematic of chemical vapor transport (CVT) reaction setup, B) a collection of ~5 g of CVT grown higher manganese silicide (HMS) crystals for SPS processing, and C) Four representative CVT reaction ampoules.

Assessment of Metal Halide Transport Agents in this Study

Table S1. CVT results of differing metal halide transport agents used in this study.

transport agent	HMS starting mass, g	starting transport agent mass, g	source mass, g	product mass, g	metal chloride product	Crystallite Morphology
CuCl ₂	0.4068	0.0503	0.2245	0.2013	MnCl ₂	Semi-spherical Crystals 0.1-0.5 mm
FeCl ₂	0.4061	0.0535	0.252	0.1781	MnCl ₂	Semi-spherical Crystals ~0.1-0.5 mm
MnCl ₂	0.407	0.0526	0.3633	0.0663	MnCl ₂	Round, Plate-like and wire-like crystals, 0.1-3 mm
ZnCl ₂	0.4004	0.0553	0.0354	0.3784	ZnCl ₂	Dendritic Crystal chunks, 0.1 mm
AlCl ₃	0.4013	0.0499	0.3432	0.0885	AlCl ₃ , MnCl ₂	Semi-spherical crystals, <0.1 mm
SnCl ₂	0.4074	0.0528	0.2316	0.2066	MnCl ₂	Semi-spherical crystals, 0.1-0.5 mm
CrCl ₂	0.4053	0.0521	0.3771	0.0623	MnCl ₂	Semi-spherical crystals, 0.1 mm
MnI ₂	0.403	0.059	N/A	N/A	N/A	Only very small crystals <<0.1 mm
FeI ₂	0.399	0.0485	N/A	N/A	N/A	Only very small crystals <<0.1 mm

* Of those studied, CuCl₂ and FeCl₂ transport agents led to the highest yield and largest crystals. In the case of ZnCl₂ and SnCl₂, we observed the incorporation of Sn and Zn within and throughout the HMS product crystals.

Elemental Analysis of CVT Grown HMS Crystals using ICP-AES

The metal impurity compositions of the HMS crystals synthesized via CVT using CuCl₂ and FeCl₂ transport agents were analyzed using a Perkin Elmer Optima 2000 inductively coupled plasma atomic emission spectroscopy (ICP-AES) Instrument. In each case, 15 mg of crystals were weighed using an analytical balance and digested in 5 ml of a 70/30 hydrofluoric acid/nitric acid mixture overnight. The resulting solution was then diluted appropriately using 18 MΩ nanopure deionized water to obtain a final concentration of 1.5 mg of MnSi_{1.73}/L. The sample

solutions were analyzed using a nebulizer flowing at 0.6 L/min calibrated using 18 MΩ deionized water. Mn, Fe, and Cu standards were utilized at a concentration of 10 mg/L to determine the relative concentrations of analytes in the samples.

For the CuCl₂ CVT crystals, the mean Cu concentration is around 0.01 mg/L, or a concentration of 0.7 wt%. For the FeCl₂ CVT crystals, the Fe concentration is negligible. In conjunction with the thermoelectric properties measurements, and in particular the Hall effect data, it is clear that if any Cu or Fe is incorporated within the HMS crystals, there is no effect on the electronic structure of these materials.

Table S2. Individual ICP-AES Analysis Results of CuCl₂ CVT crystals.

Replicate#	Analyte	Net Intensity	Corrected Intensity	Calibrated Conc.	Elemental Concentration, mg/L
1	Fe	238.204	868.4	99.2	0.001
1	Mn	257.61	2440416.8	2437836.4	1.45
1	Cu	327.393	9304.8	4269.2	0.011
2	Fe	238.204	813	43.9	0
2	Mn	257.61	2465006.4	2462425.9	1.47
2	Cu	327.393	9056.4	4020.7	0.01
3	Fe	238.204	764.6	-4.6	0
3	Mn	257.61	2449657.3	2447076.8	1.46
3	Cu	327.393	9048	4012.4	0.01
4	Fe	238.204	798.8	29.6	0
4	Mn	257.61	2496031.4	2493451	1.48
4	Cu	327.393	9070.2	4034.6	0.01

Table S3. Mean ICP-AES Analysis Results of CuCl₂ CVT crystals.

Analyte	Net Intensity	Corrected Intensity	Elemental Concentration, mg/L	Std. Dev.
Fe	238.204	42	0	0.0002
Mn	257.61	2460197.5	1.46	0.015
Cu	327.393	4084.2	0.01	0.0003

Table S4. Individual ICP-AES Analysis Results of FeCl₂ CVT crystals.

Replicate#	Analyte	Net Intensity	Corrected Intensity	Calibrated Conc.	Elemental Concentration, mg/L
1	Fe	238.204	949.3	180.2	0.001
1	Mn	257.61	2727997	2725417	1.62
1	Cu	327.393	7279.9	2244.3	0.006
2	Fe	238.204	798.8	29.7	0
2	Mn	257.61	2665147	2662567	1.58
2	Cu	327.393	7208.3	2172.7	0.006
3	Fe	238.204	803.1	33.9	0
3	Mn	257.61	2740168	2737588	1.63
3	Cu	327.393	7151.8	2116.2	0.005
4	Fe	238.204	756.4	-12.8	0
4	Mn	257.61	2800473	2797893	1.67
4	Cu	327.393	7122.6	2087	0.005

Table S5. Mean ICP-AES analysis results of FeCl₂ CVT crystals.

Analyte	Net Intensity	Corrected Intensity	Elemental Concentration, mg/L	Std. Dev.
Fe	238.204	57.8	0	0.0005
Mn	257.61	2730866	1.63	0.033
Cu	327.393	2155.1	0.005	0.0002

Energy Dispersive Spectroscopy (EDS) Analysis of the Lamellae

CVT crystals and samples prepared by SPS were analyzed by EDS in an SEM operating at 15 kV with a working distance of 10 mm. The randomly-oriented CVT crystals were embedded within epoxy on the sample puck and finely polished using SiC sandpaper up to 1200 grit. The samples prepared by SPS were polished in the same manner, but without embedding in epoxy as they were large enough to manipulate by hand. EDS spectra were collected in both point-and-shoot mode as well as linescan mode, and quantification was accomplished using Noran System 6 software. Representative EDS analysis is shown in Figure S3. The quantification of the matrix composition shows MnSi_{1.64}, within a 5% relative error to the

nominal composition of $\text{MnSi}_{1.73}$. We found that there is indeed a decrease in the Si content across the lamellae (Figure S3D), but the very small size of the feature prevents accurate quantitative analysis of the lamellae composition. When comparing the spots analyzed from the MnSi lamellae, the composition is always Si rich (Figure S3B), indicating a relative error of ~15-30%. We attribute this error to the large interaction volume, which will excite a region larger than the lamellae thickness; therefore, the X-rays obtained are originating from the surrounding HMS matrix and quantitative EDS of these samples is not possible.

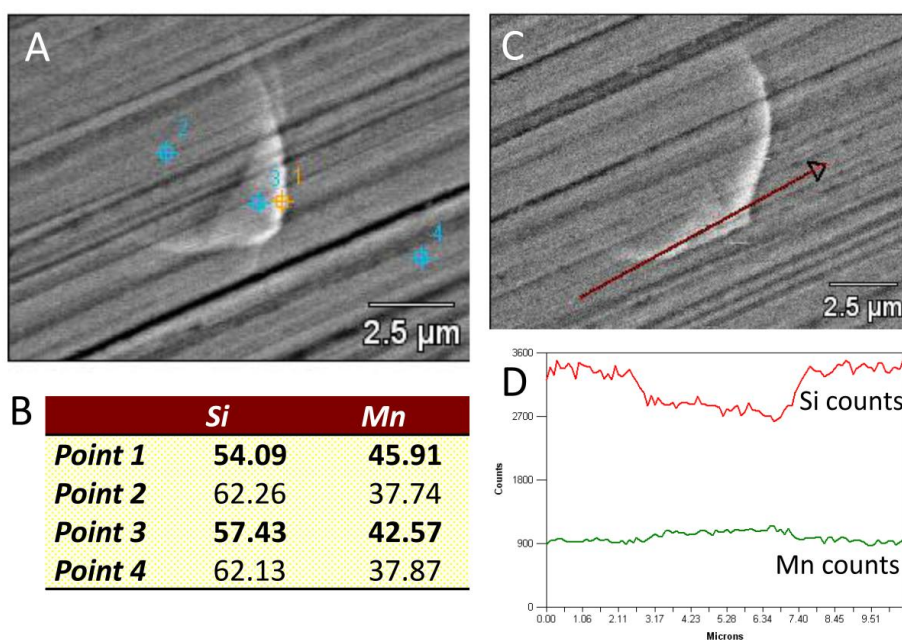


Figure S2. EDS analysis of a CuCl_2 CVT crystal analyzed using the point-and-shoot (A and B) and linescan (C and D) methods. Error associated with the interaction volume results in significant error in analyzing the quantitative composition of the lamellae (B, points 1 and 3 in bold), but the MnSi lamellae are revealed to be Si deficient (D).

Minor HMS Reflections Observed by HRPXRD

The HRPXRD experiments conducted revealed a number of minor HMS reflections not normally observed using a lower-resolution laboratory XRD instrument. In order to verify that these minor reflections belong to the HMS phases, in Figure S3 we compare the obtained HRPXRD diffractogram of the FeCl_2 CVT sample with PXRD patterns calculated from the known experimentally reported HMS single crystal structures, namely Mn_4Si_7 , $\text{Mn}_{11}\text{Si}_{19}$, $\text{Mn}_{15}\text{Si}_{26}$, and $\text{Mn}_{27}\text{Si}_{47}$. We find excellent agreement between the minor reflections observed in HRPXRD and the calculated reflections from these HMS phases.

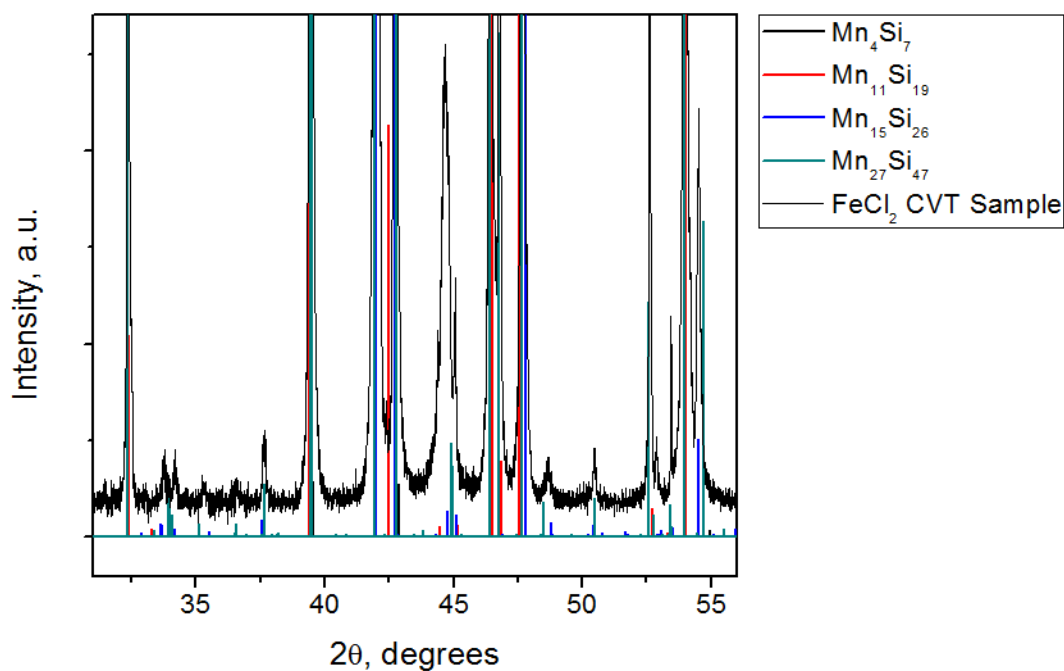


Figure S3. Comparison of minor peaks observed in the HRPXRD of the HMS sample grown by FeCl_2 CVT with theoretical PXRD patterns of Mn_4Si_7 , $\text{Mn}_{11}\text{Si}_{19}$, $\text{Mn}_{15}\text{Si}_{26}$, and $\text{Mn}_{27}\text{Si}_{47}$. The minor reflections observed coincide with expected reflections that are normally not observed using lower resolution PXRD. In particular, the broad peak located at $2\theta = 45^\circ$ can be indexed as belonging to the $(0\ 2\ 2(m-n))$ and $(1\ 2\ (m+n))$ reflections, assuming the formula of $\text{Mn}_n\text{Si}_{2n-m}$.

Electron Diffraction Analysis of the HMS crystals

Finely crushed HMS CVT crystal samples were used for transmission electron microscopy (TEM) characterization. As has been demonstrated previously,^{S1,S2} the positions and numbers of the satellite reflections in the selected area electron diffraction (SAED) pattern of HMS can be used to determine a distinct known commensurate phase of HMS. In this analysis, diffraction is accomplished along the zone axes that are perpendicular to the c axis, i.e. the $\langle 110 \rangle$ and $\langle 120 \rangle$ zone axes (Figure 3a-b in the main text). The spacing between the spots can be determined using Gatan Digital Micrograph digital microanalysis software and correlated to a spacing given by the ratio p/m' , which can be expressed by:

$$\frac{p}{m'} = \frac{2q\left(\frac{1}{c_{Si}}\right) - s\left(\frac{1}{c_{Mn}}\right)}{\left(\frac{1}{c_{Si}}\right)} \quad [S1]$$

where c_{Si} and c_{Mn} are the lattice parameters of the Si and Mn sublattices, q is the number of satellite peaks between adjacent Mn sublattice spots, and s is the vector of the Mn sublattice spacing along the c axis. The lattice spacings $1/c_{Si}$ and $1/c_{Mn}$, as well as the s and q variables, can be determined using SAED, shown more clearly for the hypothetical $\langle 110 \rangle$ zone axis in Figure S4. In our case, the values for the data shown in Figure 3 in the main text and analyzed as shown using Eq. S1 revealed values of $p/m'_{\langle 110 \rangle} = 0.340$ and $p/m'_{\langle 120 \rangle} = 0.185$, neither of which belong to a known commensurate phase of HMS using previously published data for p/m' of various HMS phases.¹ Both values are quite small, indicating either an incommensurate phase or a unknown phase with a long c -axis with a smallest common multiple larger than 39:68.

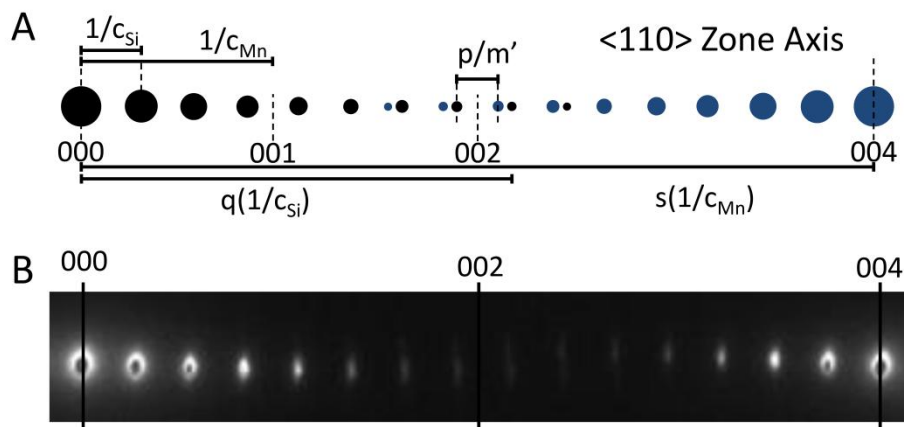


Figure S4. A) Hypothetical $\langle 110 \rangle$ zone axis of HMS, showing the pertinent measurable parameters to identify the specific HMS phase. B) shows a representative pattern along the $\langle 110 \rangle$ zone axis from a HMS crystal grown by CuCl_2 CVT for comparison.

Room Temperature Physical Properties and Thermal Diffusivity of the SSR and CVT

HMS Samples

Table S6 compares the density and room-temperature electrical transport properties of two HMS samples prepared by SPS processing of CVT grown crystals with a HMS sample prepared by solid-state reaction (SSR) followed by SPS processing. The SSR data is from reference S3. The SPS CVT samples are found to be more than 96% of theoretical density. The electrical conductivity of the SPS CVT samples are higher than the SSR sample which may be due to their slightly higher hole concentration. The percent uncertainty in the thermoelectric properties are as follows: electrical conductivity 5%, Hall coefficient 5%, carrier concentration 6%, and mobility 8%.

Table S6. Room temperature density (ρ), electrical conductivity (σ), Hall coefficient (R_H), hole concentration (p) and mobility (μ_H) of the SSR and CVT HMS samples.

Sample	ρ (g cm ⁻³)	σ (Ω^{-1} cm ⁻¹)	R_H (10 ⁻⁹ m ³ C ⁻¹)	p (10 ²¹ cm ⁻³)	μ_H (cm ² V ⁻¹ s ⁻¹)
SSR	4.87	475	4.05	1.54	1.92
CVT using CuCl ₂	5.03	544	3.46	1.81	1.88
CVT using FeCl ₂	4.99	560	3.69	1.70	2.07

Figure S5 shows the specific heat (C_p) and thermal diffusivity (α) of the SSR and CVT HMS samples. The total thermal conductivity, κ_{tot} , was then calculated by $\kappa_{\text{tot}} = C_p \alpha \rho$. We have used the measured C_p of the SSR sample to calculate the thermal conductivity of all samples since the C_p is not expected to vary considerably among the HMS samples. The uncertainties in the specific heat data is 6%, and thermal diffusivity is 3%.

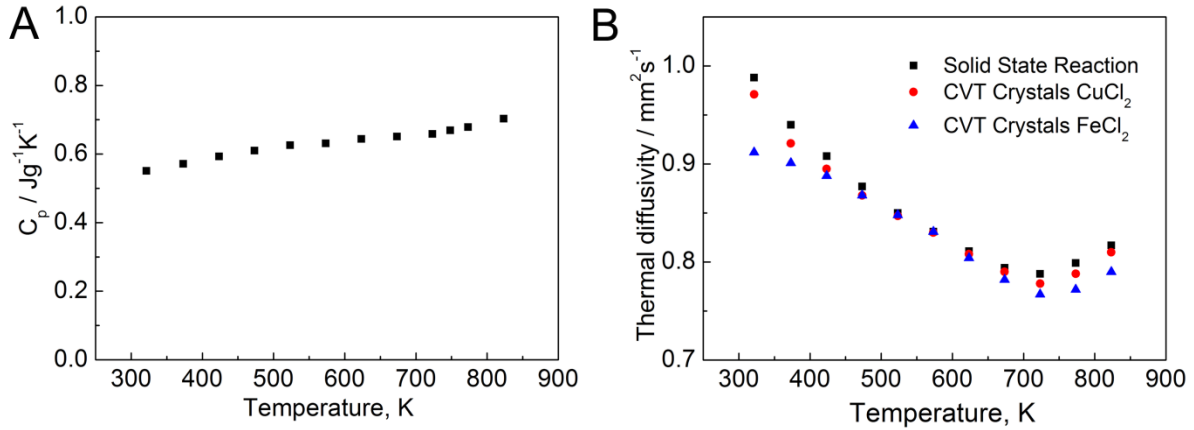


Figure S5. A) Specific heat (C_p) of the SSR HMS sample and B) thermal diffusivity (α) of the SSR and CVT HMS samples.

References

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- S3. Chen, X.; Girard, S. N.; Meng, F.; Lara-Curzio, E.; Jin, S.; 571 Goodenough, J. B.; Zhou, J.; Shi, L. *Adv. Energy Mater.* **2014**, 572 DOI: 10.1002/aenm.201400452.