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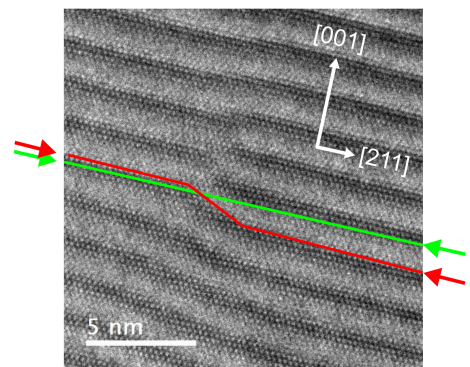
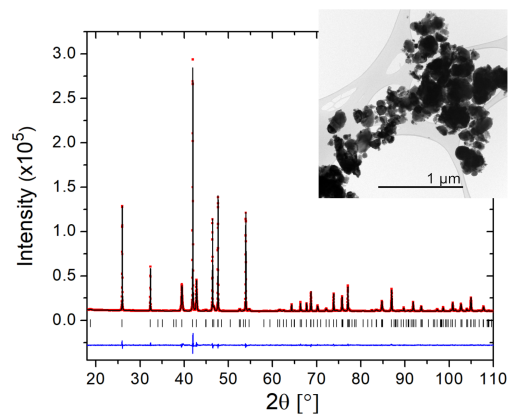
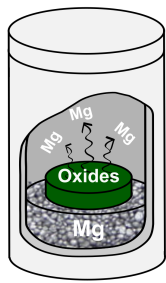
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Mesostructure - thermoelectric properties relationships in $V_xMn_{1-x}Si_{1.74}$ ($x = 0, 0.04$) Higher Manganese Silicides prepared by magnesiothermy

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Abstract

The synthesis of pure pristine and vanadium-doped $MnSi_\gamma$ ($\gamma = 1.74$) powder by a relatively fast, 'low temperature' and high yield magnesiothermy process is described. The powder obtained by this innovative route is composed of well crystallized grains with sizes ranging from 20 to 500 nm and free from any $MnSi$ precipitates. Mesostructured densified pellets with average grain sizes as small as 550 nm are obtained by spark plasma sintering (SPS). Detailed structural and microstructural characterization of the samples were realized at every stage of the process, highlighting a high concentration of defects such as orientational or spacing anomalies of the Nowotny phase, γ variations within a single grain and dislocations. Accordingly a significant decrease of the lattice thermal conductivity is evidenced in comparison to conventionally synthesized (arc-melting/SPS) samples having similar density and (V/)Mn/Si stoichiometry. The thermoelectric properties of these materials are discussed in regard of their complex microstructure.

Keywords: Intermetallics, thermoelectric materials, chemical synthesis, crystal structure, transmission electron microscopy

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1. Introduction

Thermoelectric (TE) materials are being extensively investigated for their potential of energy-saving and dynamical energy harvesting through solid state conversion of heat into electricity [1, 2]. Higher Manganese Silicides (HMS) with chemical formula MnSi_γ ($1.72 < \gamma < 1.75$) are widely considered as a promising thermoelectrical material because of their potential in industrial application. Indeed, HMS are low density materials composed of non-hazardous and inexpensive elements and they possess very good mechanical properties and oxidation resistance. HMS are currently used as *p*-type material for industrial thermoelectric generator (TEG) prototypes operating at mid-temperature [3, 4]. However, a large scale industrial implementation of such materials is limited by their moderate thermoelectric properties usually evaluated by the figure-of-merit ZT defined as:

$$ZT = \frac{\alpha^2}{\rho(\kappa_L + \kappa_e)} T \quad (1)$$

where α is the Seebeck coefficient, ρ the electrical resistivity, κ_L and κ_e the lattice and electronic contribution to the total thermal conductivity κ and T the operating temperature.

Improvement of their TE properties can be achieved through various strategies enhancing ZT [5, 6]. Many studies have been focused on chemical doping of MnSi_γ to increase the power factor $PF = \alpha^2/\rho$ [7, 8] or on fabrication of elaborated microstructures with the aim to decrease κ_L via synthesis routes such as ball-milling [9], melt-spinning [10, 11], fast combustion [12] or reactive sintering [13, 14]. For example, ZT_{max} exceeding unity has been obtained for Re supersaturated HMS realized by liquid quenching [15, 16] at the expense of industrial scalability and elevated price of Re.

Investigation of HMS is rather difficult because these materials are characterized by a high structural, microstructural and synthesis complexity. This

28 includes (i) the difficulty to obtain pure samples due to the incongruent melt-
29 ing of MnSi_γ [17] and the high vapor pressure of Mn at elevated temperature
30 [18], (ii) the formation of metallic MnSi precipitates inside HMS grains which
31 can severely affect the TE [19, 20] and mechanical [21] properties, (iii) the
32 incommensurate chimney-ladder crystal structure which is often unsatisfacto-
33 rily described as a series of commensurate Mn_ySi_x structures (x, y are natural
34 numbers) [22], and (iv) the anisotropic transport properties which can bias the
35 comparison of performances in the case of crystallographically textured samples
36 [23].

37 Recently, we reported on the synthesis of high purity mesostructured TE
38 skutterudites by magnesio-reduction of oxides [24]. This scalable process based
39 on cheap and air-stable oxides leads to the formation at moderate temperature
40 of well crystallized submicronic powders with elevated TE properties. Simi-
41 lar process was attempted to obtain HMS powders by Girard *et al.* [25] starting
42 from nanosilica and MnO_2 in molten salt fluxes but the information on such pro-
43 cess is limited to a single conference abstract and, to the best of our knowledge,
44 no peer-review article has ever been published. We have thus applied a flux-free
45 magnesio-reduction process employing MnO and Si as reactants for the synthesis
46 of pure and vanadium doped $\text{MnSi}_{1.74}$. The structural and microstructural char-
47 acterizations, using X-ray diffraction Rietveld refinements in a composite crystal
48 structure model, electron backscattering diffraction and scanning/transmission
49 electron microscopy on both as-synthesized powders and spark plasma sintered
50 pellets are presented thereafter. The thermal dependence of the electrical resis-
51 tivity, Seebeck coefficient and thermal conductivity have been measured in the
52 temperature range 300-800 K and subsequent thermoelectric performances are
53 discussed in terms of structure-microstructure-properties relationships. These
54 results are compared to equivalent HMS prepared by conventional melting-
55 solidification-annealing method.

2. Experimental procedure

For the magnesio-reduction (MR) synthesis of $\text{MnSi}_{1.74}$ and $\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$, precursor mixtures first need to be prepared by ball-milling of V_2O_5 (Merck, 99 %), MnO (Alfa Aesar, 99 %) and Si (Ventron, 99.9 %) with a molar ratio of 0 : 1 : 1.74 and 0.02 : 0.96 : 1.74, respectively, under air in a planetary mill (Retsch PM100) for 3 h at 650 rpm in a WC vial filled with \varnothing 10 mm WC balls (fig. 1a). A small ball-to-powder ratio of 5 : 1 is used in order to avoid contamination by WC during the milling process. The obtained precursor mixture is cold-pressed at 65 MPa into \varnothing 10 mm pellets with about 4 mm height. Each pellet is placed in a Mo-crucible with Mg turnings (Strem Chemicals, \geq 99 %) equally distributed under and on top of the pellet (fig. 1b). Such distribution of Mg helps to maximize the surface contact between Mg and the pellets in order to promote a homogeneous reduction and was found compulsory to avoid the presence of Mg_2Si by-product. A 25 % excess Mg is empirically needed to complete the magnesio-reduction reaction:



A graphite seal is inserted between the crucible and the lid and the system is held tight with a clamping system. This set-up is placed in an Inconel tube filled with Ar to avoid the Mo-crucible oxidization. The whole is heated up to 1173 K at a rate of 60 K h^{-1} in a tubular furnace and held at this temperature for 8 h before being cooled down by switching off the furnace (fig. 1c). At the end of the reaction the product still in the shape of a pellet can be easily separated from loose MgO powder (fig. 1d). A black powder composed of MnSi_γ is obtained by softly crushing the pellet in an agate mortar. The MgO by-product is removed by soaking the as-synthesized powder twice in diluted hydrochloric acid (2 wt.%) for 5 - 10 minutes and washing three times with distilled water and once more with ethanol before being dried at 353 K overnight (fig. 1e). The washed MnSi_γ

83 powder is then densified by spark plasma sintering (SPS) in \varnothing 10 mm graphite
 84 dies at 1273 K and 75 MPa for 20 min with 100 K min^{-1} heating/cooling rates
 85 using a FCT HP-D-10 apparatus.

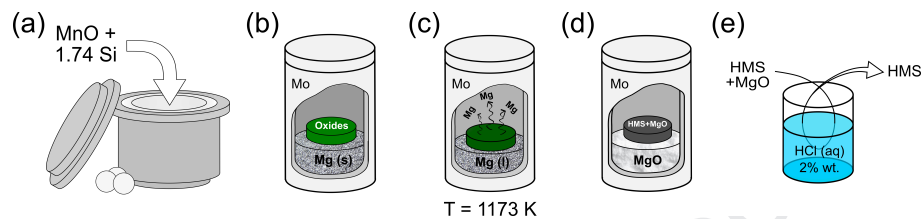


Figure 1: Main steps of the magnesio-reduction synthesis: (a) MnO and Si are ball-milled in WC vial; (b) pellets of MnO/Si mixture are sealed with the adequate amount of Mg in a Mo crucible; (c) Mg vapor reduces the oxides during the heat treatment at 1173 K ; (d) the reduction is completed after 8 h at 1173 K ; (e) MgO is removed from the product by soaking the powder in diluted HCl .

86 In order to investigate how magnesiothermy synthetic route affects the final
 87 thermoelectric properties, $\text{MnSi}_{1.74}$ has also been synthesized by conventional
 88 fusion solidification method. Stoichiometric amounts of the elements are arc-
 89 melted (AM) three times to ensure homogenization and the obtained ingot was
 90 annealed for 100 h at 1273 K in evacuated silica tubes. The annealed ingot
 91 was finely ground in an agate mortar and the powder was densified by SPS in
 92 \varnothing 10 mm graphite dies at 1238 K and 80 MPa for 5 min.

93 The crystal structure and purity of the samples were checked by powder X-
 94 ray diffraction (PXRD) using a Bruker D8 Advance diffractometer in the Bragg-
 95 Brentano geometry working with a monochromatized $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$)
 96 and equipped with a LynxEye detector. Structural parameters were determined
 97 by Rietveld refinement of the PXRD patterns using JANA2006 [26]. Scanning
 98 electron microscopy (SEM) images, energy dispersive spectroscopy (EDS) and
 99 electron backscattering diffraction (EBSD) were performed using a JEOL JSM
 100 7100F microscope equipped with an Oxford EDS SDD X-Max spectrometer and
 101 an EBSD HKL Advanced Nordlys Nano detector. TEM analyses were performed
 102 on a JEOL 2100 LaB₆ instrument operating at 200 kV and equipped with an
 103 Oxford EDS SDD 80 mm^2 spectrometer and high resolution Gatan US1000 and
 104 Orius 200D cameras. Preparation of the powder samples for SEM analyses con-

105 sisted in their deposition on carbon tape followed by metallization with car-
 106 bon. For transmission electron microscopy (TEM), a small amount of powder
 107 was sonicated in absolute ethanol and deposited for drying on a carbon coated
 108 copper grid. For EBSD and EDS analyses, densified pellets were consecutively
 109 mirror polished with 320 down to 1200 grit SiC papers, diamond paste (3 and
 110 1 μm) and colloidal silica. EBSD mappings were analyzed using the *Channel*
 111 *5* software (HKL Technology). Thin foils of densified pellet for TEM analyses
 112 were obtained by dimpling a 100 μm thick pellet down to 10 μm with diamond
 113 paste (3 and 1 μm) followed by Ar-ion milling using a Fischione Ion Mill 1010
 114 operating at 4.5 kV and 4.5 mA.

115 The thermal diffusivity (D) has been measured by the laser flash method on
 116 \varnothing 10 mm and 2 mm thick samples coated with graphite using a Netzsch LFA 467
 117 HyperFlash equipment under N_2 atmosphere. The thermal conductivity could
 118 be calculated by the $\kappa = DC_p d$ relation with C_p the specific heat of the sample
 119 determined thanks to a Netzsch Pyroceram reference sample and d the density
 120 measured by the Archimede method. The Seebeck coefficient and electrical
 121 resistivity were measured simultaneously on $6 \times 2 \times 2$ mm bars using a ZEM3
 122 device (ULVAC-RIKO Inc., Yokohama, Japan) under He atmosphere.

123 3. Results and discussion

124 3.1. Magnesio-reduction synthesis

125 The XRD pattern of the precursor mixture obtained by high energy ball-milling
 126 of MnO and Si is shown in fig. 2. Interestingly, MnSi and MnSi_7 readily start
 127 to form in the milling vial indicating the reduction of manganese. According to
 128 the Ellingham diagram [27, 28] the reduction of MnO by Si :



129 is thermodynamically possible. The activation energy for this reaction is prob-

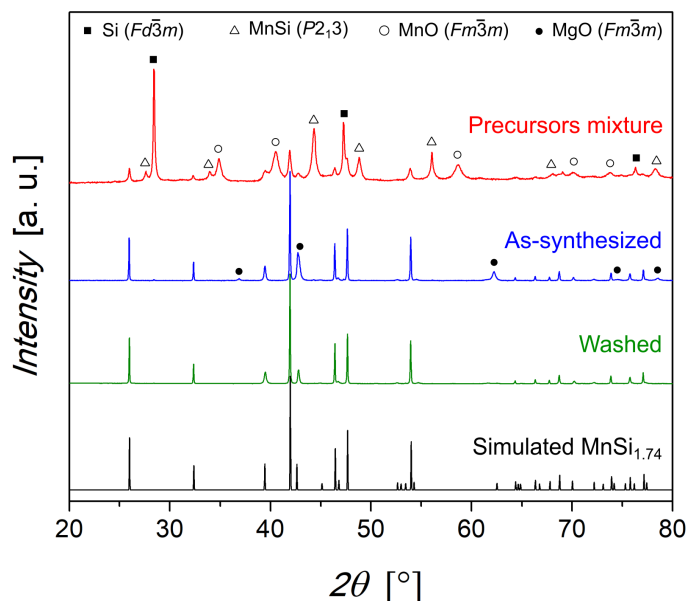
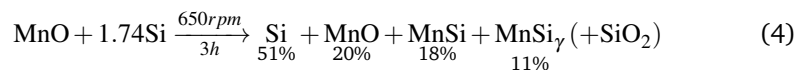


Figure 2: XRD patterns of the precursors mixture (red), as-synthesized HMS powder (blue), HCl washed HMS powder (green) and simulated pattern for $\text{MnSi}_{1.74}$ with first order satellite peaks [22] (black). Some weak intensity satellite reflections in the simulated pattern might not be visible in the experimental ones because of their large broadening (see text for details).

ably overcome locally in the milling vial when highly energetic shocks occur.
 Upon further milling, metallic Mn would then react with unreacted Si to form
 MnSi_γ and MnSi as already reported by different groups [29, 30, 31]. SiO_2 must
 be present in the mixture but could not be detected by XRD due to its probable
 amorphous nature. At the end of the milling step, a very intimate mixture of
 Mn- and Si-containing species is produced according to:

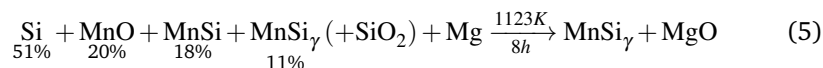


136

where the molar concentrations are determined from Rietveld refinement (see
 fig. SI.1 and tables SI 1,2,3,4).

138

139 The precursors mixture is then reacted with Mg according to:



140

141 and XRD on the as-synthesized powders (fig. 2, blue curve) confirms that the
142 product is only composed of MnSi_γ and MgO.

143 Magnesio-reduction was attempted at several temperatures and a lower limit
144 of 1073 K has been found to initiate this reaction. The high vapor pressure of Mg
145 at these elevated temperatures is expected to easily penetrate inside the pellet
146 to induce the reduction of the oxides and subsequent interdiffusion of native
147 metals to form the targeted silicide. Additionally, the reduction of MnO and SiO₂
148 by Mg is highly exothermic at 1123 K with ΔH_r = - 346.9 and - 344.0 kJ mol⁻¹
149 respectively [27, 28]. The heat released locally inside the pellet may accelerate
150 the reaction and a scenario close to a combustion synthesis [32, 33] cannot be
151 ruled out.

152 3.2. Microstructure of the magnesio-reduced MnSi_γ powders

153 Fig. 3a and 3b show secondary electron SEM images of an as-synthesized MR
154 HMS powder containing MnSi_γ and MgO. It is composed of grains with sizes
155 ranging from about 50 nm to several hundreds of nm, some of them forming
156 aggregates with micrometric sizes. According to EDS elemental analyses, MgO
157 constitute 60 at.% of the as-synthesized powder. Moreover, they give a Si/Mn
158 metal ratio of about 1.7 which is in agreement with the targeted MnSi_{1.74} com-
159 position (fig. SI.2a).

160 The HMS + MgO composite microstructure has been investigated by TEM. A
161 typical brightfield image of the as-synthesized HMS powder is shown in fig. 4a.
162 EDS analyses and selected area electron diffraction realized on several areas of
163 the sample assign the electron-opaque grains to MnSi_γ while the more electron-
164 transparent matrix is mainly composed of much smaller MgO crystals. These
165 observations are consistent with the much broader XRD Bragg peaks ascribed

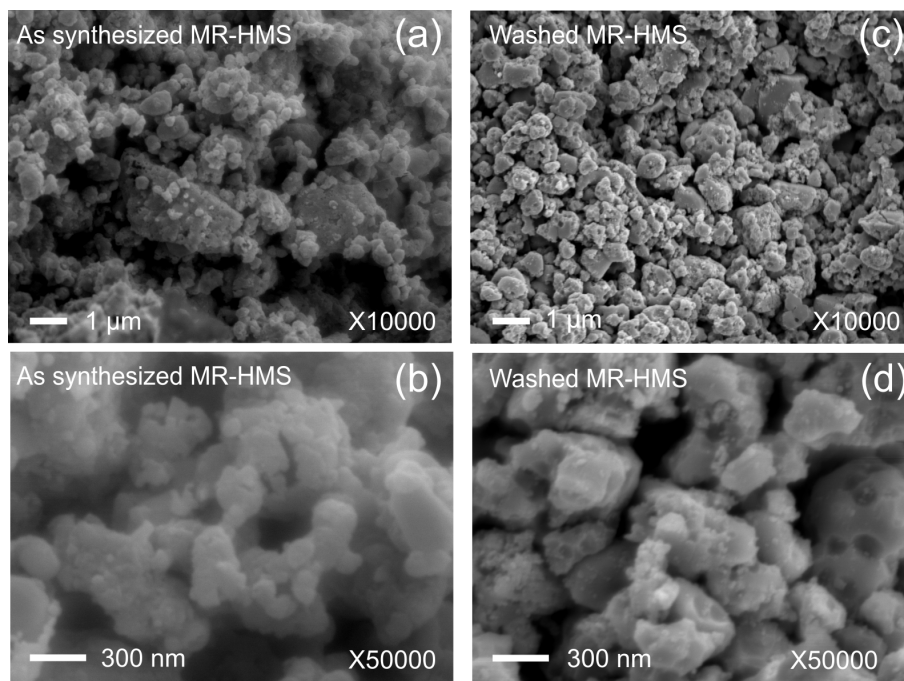


Figure 3: Secondary electron SEM images of (a)(b) as-synthesized MR HMS powder composed of $\text{MnSi}_{1.74}$ and MgO and (c)(d) MR HMS powder after acidic washing containing only $\text{MnSi}_{1.74}$, at two different magnifications.

166 to MgO compared to those of HMS (fig. 2). We hypothesize here that the MgO
 167 matrix formed during the MR reaction and surrounding the MnSi_y grains plays
 168 a significant role by limiting the silicide particle growth at the rather elevated
 169 reaction temperature and thus helps stabilizing the powder submicronic size.

170 After acidic washing, powder XRD (fig. 2) shows that MgO is eliminated,
 171 at least down to the detection limit of the technique. The absence of Mg K_α
 172 emission line on SEM-EDS analyses and the detection of only traces of Mg on
 173 TEM-EDS confirm that MgO was almost entirely removed from the sample (fig.
 174 SI.2). Without the surrounding MgO matrix, the morphology of the HMS grains
 175 is fully revealed and typical SEM and TEM images are shown in fig. 3c,d and
 176 4b, respectively. The grains have relatively isotropic shapes with sizes ranging
 177 from about 50 to few hundreds of nm. Based on their relatively faceted shape,
 178 most of the grains look single crystalline. Interestingly, high resolution trans-

179 mission electron microscopy (HRTEM) does not reveal any MnSi precipitates
 180 inside the grains as is usually seen in samples obtained by crystallization from
 181 a liquid melt. It should also be noticed that HRTEM observations of the sur-
 182 face of the grains before and after the acidic washing (not shown here) do not
 183 reveal any trace of chemical erosion of the grains by the acid. Electron diffrac-
 184 tion patterns (fig. 4c) can be fully indexed using 4 Miller indices $hk\ell m$ with the
 185 MnSi_γ composite crystal structure described in details in the next section. No-
 186 ticeable orientation and spacing anomalies as already reported and described
 187 by Ye and Amelinckx [34] are clearly visible along the $[00\ell]$ rows and will be
 188 further discussed in section 3.4.

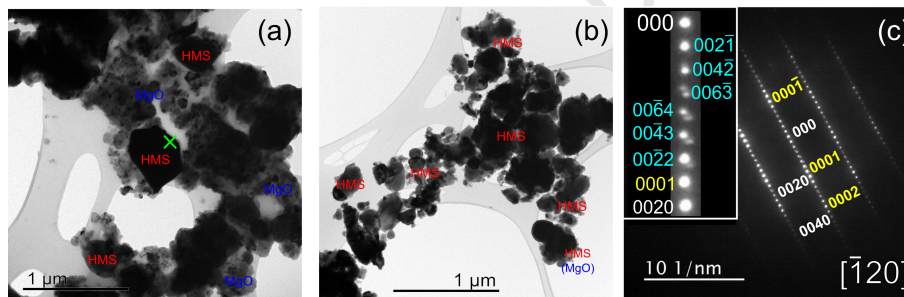


Figure 4: TEM brightfield images of the (a) as-synthesized MR- MnSi_γ + MgO powder and (b) HCl-washed MnSi_γ powder. Annotations on the images correspond to the main phase deduced from EDS analyses performed on different spots of the observed area. (c) Selected area electron diffraction patterns taken at the green cross in (a) and indexed with the composite crystal structure of $\text{MnSi}_{1.74}$ described in section 3.3 and pictured in fig.5. For clarity reason, only strong reflections corresponding to the two basic subsystems are indicated along the $[001]$ row but all satellite reflections could be indexed with $00\ell m$ indices. $hk\ell 0$ (white), $hk0m$ (yellow) and $hk\ell m$ (blue) Miller indices correspond to the Mn-, Si-subsystems and satellite reflections, respectively. The inset shows a close-up view of the orientation anomaly along the $[001]$ direction.

189 3.3. Structural analysis of the MR- MnSi_γ powders

190 MnSi_γ crystallizes in a composite tetragonal ‘Chimney-Ladder’ structure-type
 191 - also known as Nowotny phase - in which a ‘ladder’ subsystem of Si-atoms
 192 ($P4/nnc$, no. 126) is penetrating a ‘chimney’ subsystem of Mn ($I4_1/amd$, no. 141)
 193 [35, 36, 37] (fig. 5).

194 As mentioned above, HMS were originally described as a large family of
 195 stoichiometric compositions with formula Mn_ySi_x where x and y are natural

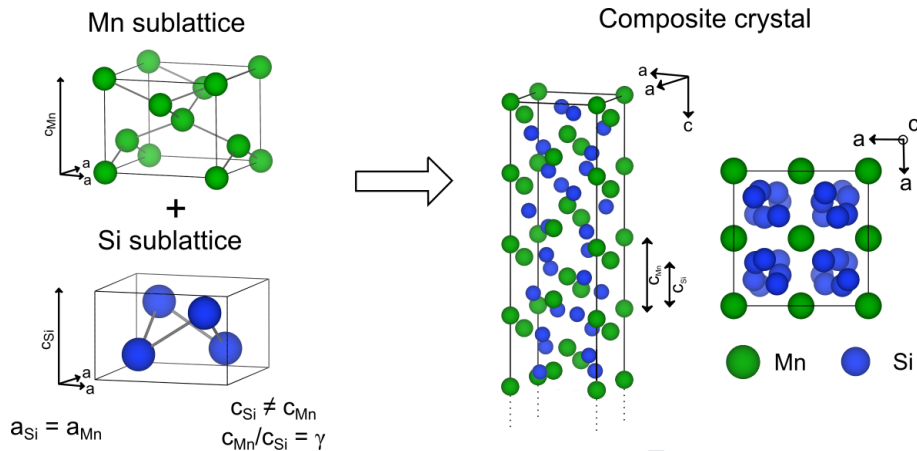


Figure 5: Crystal structure description of MnSi_γ showing the interpenetrating tetragonal Mn- and Si-subsystems with identical a - but different c -lattice parameters (left). The interaction between the two subsystems leads to a composite MnSi_γ unit-cell (right) where $\gamma = c_{\text{Mn}}/c_{\text{Si}}$.

196 numbers and $\gamma = x/y$ is ranging between ≈ 1.727 and 1.75. Accordingly, they
 197 were described as commensurate structure with c increasing from 17.4 Å for the
 198 simplest Mn_4Si_7 ($\gamma = 1.75$) to $c = 117.9$ Å for $\text{Mn}_{27}\text{Si}_{47}$ ($\gamma \approx 1.741$). Miyazaki
 199 *et al.* have proposed a more general approach, describing MnSi_γ as a composite
 200 structure with a restrained domain of stability for γ [22]. In this approach, the
 201 structure is composed of two incommensurately modulated subsystems, where
 202 the modulation results from interactions between mutually incommensurate,
 203 periodic subsystems [38, 39]. In the case of MnSi_γ , each subsystem is described
 204 by only one atom in the asymmetric unit (four equivalent in the basic cell).
 205 They have identical a lattice parameters of about 5.53 Å, while the c lattice
 206 parameters are different ($c_{\text{Si}} \approx 2.5$ Å and $c_{\text{Mn}} \approx 4.4$ Å) with a non-rational ratio
 207 $\gamma = c_{\text{Mn}}/c_{\text{Si}}$ that corresponds to the Si/Mn stoichiometry of the compound in the
 208 case of full chemical occupancy.

209 In this context, the 3D lattice periodicity is replaced by a 3D+1 one. The
 210 symmetry elements present in the structure are described using a $I4_1/amd(00\gamma)00ss$
 211 superspace group and four $hklm$ Miller indices are required for the complete
 212 indexing of the diffraction patterns [40]. In this superspace description, the re-
 213 ciprocals basis vectors of the Mn and Si-sublattices in MnSi_γ are described from

214 the basis vectors of the composite crystal lattice via the W matrices:

$$W_{Mn} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad W_{Si} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad (6)$$

215

216 In this setting, the diffraction patterns of $MnSi_\gamma$ are composed of $hk00$ -
 217 reflections common to both subsystem, $hkl0$ reflections relative to the basic Mn-
 218 subsystem, $hk0m$ reflections relative to the basic Si-subsystem and $hklm$ satel-
 219 lite reflections with contribution of the incommensurate modulations. In in-
 220 commensurately modulated structures, the displacement vector $u^\mu(x,y,z)$ of the
 221 μ -atom relative to its base structure position $\bar{x}^\mu(x,y,z)$ is described by the mod-
 222 ulation vector function $u^\mu(v_\mu)$. The argument v_μ of the modulation function is
 223 the fourth 3D+1 superspace coordinate of μ in the basic structure. From the
 224 respective W matrices, v_{Mn} and v_{Si} are defined by the relations:

$$\begin{aligned} v_{Mn} &= t + \gamma x_3 \\ v_{Si} &= t + 1/\gamma x_4 \end{aligned} \quad (7)$$

225

226 where t is a real number corresponding to the initial phase of $u^\mu(v_\mu)$.

227

228 As the modulation $u^\mu(v_\mu)$ is periodic in 3D+1 superspace, it can be decom-
 229 posed by Fourier series according to:

$$u^\mu(v_\mu) = \sum_{k=1}^n A_\mu^k \sin(2\pi k v_\mu) + B_\mu^k \cos(2\pi k v_\mu) \quad (8)$$

230 where the amplitudes A_μ^k and B_μ^k are refined to fit to the experimental data.

231 The experimental XRD are satisfactorily fitted by Rietveld refinements using

232 this approach as shown *e.g.* in fig. 6a for a HCl-washed MnSi_γ powder with
 233 refined lattice parameters, modulation vector and atomic displacement param-
 234 eters summarized in Table 1 and 2. The refined γ value of 1.7416(2) is in
 235 agreement with the synthesized and EDS determined compositions, confirming
 236 the ability of the synthesis technique to produce composition controlled materi-
 237 als.

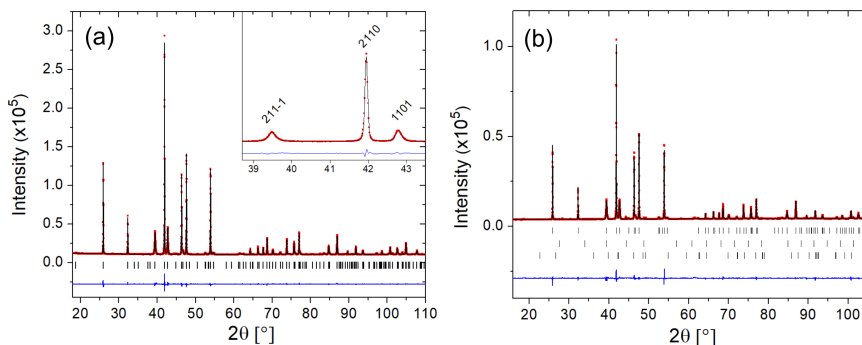


Figure 6: Rietveld refined XRD patterns of (a) washed $\text{MnSi}_{1.74}$, with enlarged view in inset, and (b) $\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$ powders prepared by magnesioreduction. The experimental data are plotted in red symbols, the calculated one in black line and the difference with a blue line. The vertical ticks indicate the theoretical $\text{V}_x\text{Mn}_{1-x}\text{Si}_{1.74}$ ($x = 0, 0.04$) Bragg positions up to the 2nd order satellite reflections. In (b), the second and third rows indicate the theoretical Bragg positions of VSi_2 and MnSi impurities.

238 In the present case, the collected XRD data allowed satellite reflections up
 239 to the 2nd order to be considered in the refinement procedure as many of them
 240 were found to have intensities just above the background level. The modulation
 241 functions were described using Fourier coefficients up to $n = 2$ and $n = 4$ for
 242 Mn and Si subcells, respectively. The large number of refined Fourier coeffi-
 243 cients used to describe the Si modulation is imposed by the crystal symmetry,
 244 the first coefficient describing the z component of the modulation - B^4 - being
 245 non null for $n = 4$. Refined Fourier coefficients are tabulated in Table 2 while
 246 the resulting modulation functions are plotted in fig. 7. On the one hand, the
 247 displacement of Mn around its average position $\bar{x}^{\text{Mn}} = (0,0,0)$ has a small max-
 248 imum amplitude along z of about 0.04 Å while no displacement is found in the
 249 (x,y) plane. On the other hand, Si-atoms at $\bar{x}^{\text{Si}} = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ show much larger

Table 1: Structural parameters obtained by Rietveld refinement of washed $\text{MnSi}_{1.74}$ and $\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$ XRD patterns.

	$\text{MnSi}_{1.74}$	$\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$
$\bar{x}^{\text{Mn}} (x,y,z)$	0 0 0 ¹	0 0 0
a (Å)	5.52908(2)	5.5301(1)
Mn c_{Mn} (Å)	4.36749(4)	4.3696(1)
γ	1.7416(2)	1.7394(2)
U_{iso} (Å ²)	0.0069(8)	0.001(2)
$\bar{x}^{\text{Si}} (x,y,z)$	0.25 0.25 0.25 ¹	0.25 0.25 0.25
a (Å)	5.52908(2)	5.5301(1)
Si c_{Si} (Å)	2.5077(1) ²	2.5121(3)
U_{iso} (Å ²)	0.0033(4)	0.004(2)

¹ Average position coordinates of Mn and Si are constrained

² Calculated as c_{Mn}/γ

250 sinusoidal displacements reaching a maximum of $x = y \approx 0.2$ Å and $z \approx 0.08$ Å.
 251 The large displacement modulations induce the formation of Si-atom helices
 252 around the $(\frac{1}{4}, \frac{1}{4}, z)$ axis as shown in the projection of the crystal structure along
 253 the c -axis (fig. 5). All these refined values are in very good agreement with
 254 those reported by Miyazaki *et al.* obtained on high resolution neutron powder
 255 diffraction data of $\text{MnSi}_{\approx 1.736}$ synthesized by conventional melting/annealing
 256 method [22].

Table 2: Refined coefficients of the modulation functions of Mn (top) and Si (bottom) for washed $\text{MnSi}_{1.74}$ and $\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$

	$\text{MnSi}_{1.74}$			$\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$		
Mn	$x (= x_1)$	$y (= x_2)$	$z (= x_3)$	$x (= x_1)$	$y (= x_2)$	$z (= x_3)$
B^2	0	0	-0.019(1)	0	0	-0.017(3)
Si	$x (= x_1)$	$y (= x_2)$	$z (= x_4)$	$x (= x_1)$	$y (= x_2)$	$z (= x_4)$
A^1	0.0764(3)	0.0764(3)	0	0.0773(4)	0.0773(4)	0
B^1	0.0764(3)	-0.0764(3)	0	0.0773(4)	-0.0773(4)	0
A^3	0.0099(6)	0.0099(6)	0	0.0107(7)	0.0107(7)	0
B^3	-0.0099(6)	0.0099(6)	0	-0.0107(7)	0.0107(7)	0
B^4	0	0	-0.041(3)	0	0	-0.049(4)

257 As illustrated in the inset to fig. 6 with the intense (2110) and (1101) Bragg

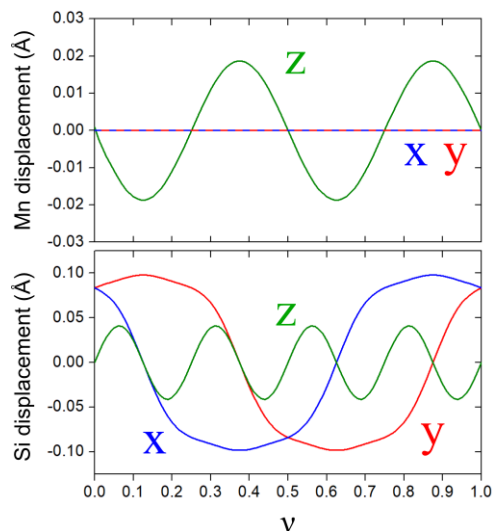


Figure 7: Coordinates of the displacement vector relative to the average position for Mn (top) and Si (bottom) as a function of the fourth space parameter v for washed $\text{MnSi}_{1.74}$

258 peaks, $hk0m$ reflections of the Si subsystem are much broader than the rela-
 259 tively narrow $hkl0$ reflections of the Mn subsystem. From the diffractogram
 260 refinement point of view, this strong peak shape anisotropy between the differ-
 261 ent families of reflections has been managed using a strain tensor implemented
 262 in JANA2006. This could be attributed to higher disorder on the Si subsystem
 263 as confirmed by HRTEM observations that are discussed in next section. This
 264 strain tensor also avoids the implementation of an extra Si-position in the struc-
 265 tural model proposed by Akselrud *et al.* to describe the disordered Si-subsystem
 266 [41].

267 The XRD pattern of washed $\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$ powder was also fitted using
 268 the same approach (fig. 6b, Tables 1 and 2). The lattice parameters are slightly
 269 larger and γ slightly smaller in the case of the V-doped sample. On the other
 270 hand, the Fourier coefficient of the modulation functions remains relatively sim-
 271 ilar. It should be noticed that VSi_2 and MnSi impurities represent 1 and 2 wt.%
 272 of the sample, respectively. The presence of VSi_2 suggest that V was not entirely
 273 inserted in the structure during the magnesio-reduction process.

274 3.4. Microstructure of sintered MnSi_γ pellets

275 $\text{MnSi}_{1.74}$ and $\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$ pellets with densities of 96 % according to the
 276 Archimede weighing were produced by spark plasma sintering. After the sin-
 277 tering step, both samples are single phase according to XRD (fig. 8 and SI.2),
 278 indicating that most of the residual VSi_2 and MnSi reacted during the heat treat-
 279 ment for the doped sample. Accordingly, a significant decrease of γ from about
 280 1.74 for the as-synthesized MR powder to 1.73 for the as-sintered pellet is ob-
 281 tained by Rietveld refinements (fig. SI.3), reaching a value close to the arc-
 282 melted (AM) samples. Generally, the lattice and structural parameters (table
 283 3) of each composition made by both MR and AM synthesis routes are quite
 284 equivalent. Upon V-doping, a moderate increase of a and c_{Mn} is consistent with
 285 the slightly larger vanadium metallic radius ($r_V = 1.346 \text{ \AA}$, $r_{Mn} = 1.264 \text{ \AA}$ [42])
 286 while a much larger increase of c_{Si} from about 2.515 to almost 2.53 \AA is in
 287 agreement with Miyazaki's results [20]. As can be seen from the 2θ shift of the
 288 $(211\bar{1})$ reflection toward low 2θ angles, this increase of c_{Si} is associated to a
 289 significantly smaller γ value for V-doped samples.

290 Interestingly, the $(211\bar{1})$ and (1101) reflections of the AM samples are much
 291 less affected by the broadening than MR samples. In the case of the MR V-doped
 292 sample, the (1101) peak even seems to be composed of three highly convoluted
 293 peaks. This suggests some level of heterogeneity of c_{Si} and thus of γ in the MR
 294 samples, in agreement with similar observations reported by Miyazaki *et al.* in
 295 V- and Ge-doped HMS prepared by conventional methods [20].

296 EDS mapping on polished surfaces of the SPSed pellets (fig. SI.4) con-
 297 firms a homogeneous concentration of Mn and Si (within the resolution of the
 298 technique) on the analyzed areas of the $\text{MnSi}_{1.74}$ sample, while in the case of
 299 $\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$, a few vanadium-rich areas with diameters below 1 μm could
 300 be attributed to small amounts of residual VSi_2 impurity (not visible on XRD
 301 patterns). As a consequence, the V-concentration in this $\text{V}_x\text{Mn}_{1-x}\text{Si}_{1.74}$ may be
 302 slightly below the nominal $x = 0.04$ value.

303 Residual porosity with average size of approximately 100 nm and located at

304 the grain boundaries is visible for samples prepared by MR and AM syntheses
 305 (fig. 9). Similar residual porosity after spark plasma sintering is reported in
 306 samples prepared by other processes such as ball-milling [43], melt-spinning
 307 [10] or solid-state diffusion [44] and seems thus intrinsic to this material den-
 308 sified by SPS.

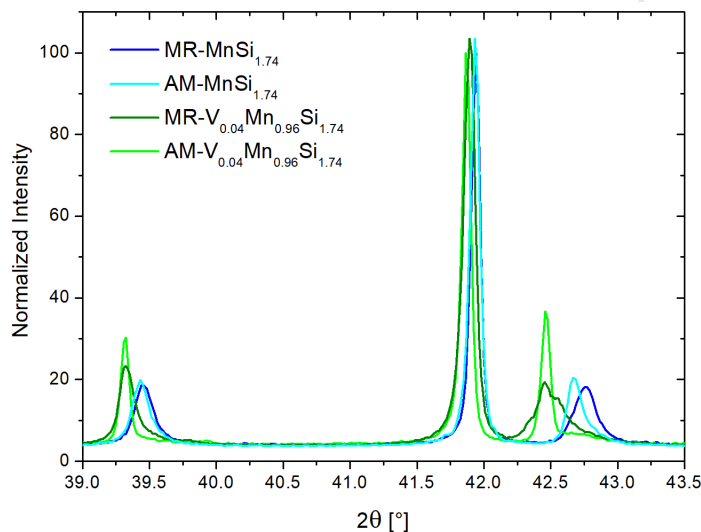


Figure 8: XRD patterns of MR $\text{MnSi}_{1.74}$ (dark blue), MR $\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$ (dark green), AM- $\text{MnSi}_{1.74}$ (bright blue) and AM- $\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$ (bright green) showing the relative peaks shifts among the samples

309 Further microstructural characterization of the sintered pellets was realized
 310 by electron back-scattering diffraction (EBSD, fig.9). EBSD maps have been
 311 obtained by scanning the area with a 50 nm step and by indexing the Kikuchi
 312 lines using the commensurate Mn_4Si_7 structure ($P\bar{4}c2$, $a = 5.52 \text{ \AA}$, $c = 17.46 \text{ \AA}$).
 313 Orientation analysis of the maps do not reveal any crystallographic texturation
 314 of the pellets which could have been caused by the uniaxial pressing during the
 315 sintering process [23]. TE properties of the pellets will thus be considered as
 316 isotropic. The grain size distributions (fig. 9) have been obtained from EBSD
 317 maps by considering all diffracting domains containing at least 12 pixels (*i.e.*
 318 $\sim 0.03 \mu\text{m}^2$). It follows a log-normal law with average values of 580 nm and
 319 606 nm for the sintered undoped and V-doped MR samples, respectively. Such

Table 3: Main structural and microstructural characteristics of the SPSeD MR and AM $V_xMn_{1-x}Si_{1.74}$ ($x = 0$ and 0.04) samples used for the TE characterizations

		MR $MnSi_{1.74}$	AM $MnSi_{1.74}$	MR $V_{0.04}Mn_{0.96}Si_{1.74}$	AM $V_{0.04}Mn_{0.96}Si_{1.74}$
	a (Å)	5.5295(3)	5.52954(6)	5.5308(4)	5.5319(1)
	c_{Mn} (Å)	4.3696(3)	4.36834(8)	4.3710(3)	4.3746(1)
	c_{Si} (Å)	2.5156(3)	2.5110	2.5265	2.5291
	γ	1.7370(3)	1.7397(3)	1.7300(6)	1.7297(1)
Si	$A^1(x)$	0.0768(8)	0.0769(8)	0.0758(8)	0.0753(6)
	$A^2(x)$	0.010(1)	0.013(1)	0.012(1)	0.014(1)
	$A^3(z)$	-0.049(8)	-0.064(7)	-0.042(7)	-0.050(6)
	$U_{iso}^{(2)}$	0.004(3)	0.008(2)	0.001(2)	0.007(2)
Mn	$A^2(z)$	-0.017(4)	-0.009(5)	-0.013(4)	-0.009(3)
	$U_{iso}^{(2)}$	0.001(2)	0.001(1)	0.001(1)	0.001(1)
Impurity (wt. %)	Si	/	2	/	1
	MnSi	/	1	/	1

320 small grain sizes logically lead to a much higher density of grain boundaries
 321 than a conventionally synthesized AM sample with average grain size estimated
 322 at $13 \mu m$ using the same procedure. Enhanced scattering of the phonons at the
 323 grain boundaries and reduced lattice thermal conductivity are expected from
 324 such microstructure.

325 Fig. 10a shows a typical low magnification brightfield TEM image of the
 326 MR $MnSi_{1.74}$ densified sample. The shape and size distribution of the grains
 327 are in good agreement with the EBSD analysis. The residual porosity due to
 328 incomplete densification is confirmed at the grain boundaries. As for the as-
 329 synthesized powder, no MnSi precipitates are observed inside the grains after
 330 sintering.

331 As shown on the HRTEM images (fig 10b,c), the great majority of the grain
 332 boundaries looks well crystalline and free of amorphous layer. Proper sintering
 333 of nanometric powders can be quite challenging because of oxidation layers or
 334 residual absorbed species at the surface of the particles which often result in
 335 much higher electrical resistivity compared to bulk [45]. In the present case,
 336 the good crystallinity of the grain boundaries is expected to prevent exceed-

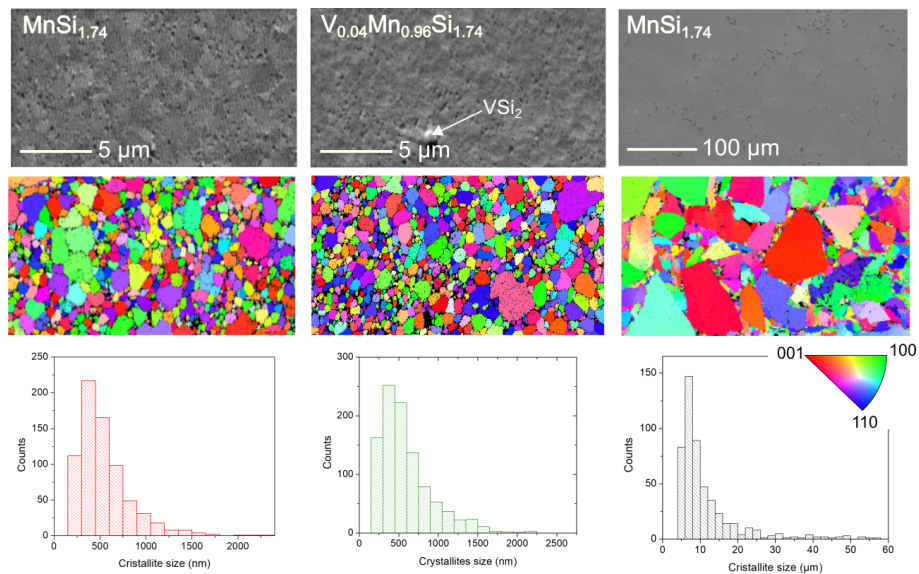


Figure 9: EBSD microstructural analyses of SPSed pellets of MR $\text{MnSi}_{1.74}$ (left), MR $\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$ (middle), and AM $\text{MnSi}_{1.74}$ (right). The top, middle and bottom rows correspond to backscattered electron images of the analyzed areas, EBSD maps and histograms of the grain size distribution, respectively

337 ingly large decrease of the charge carriers transport while still acting as efficient
 338 phonon scattering centers.

339 Typical electron diffraction patterns along the $[\bar{1}20]$ zone axis obtained on
 340 a MR $\text{MnSi}_{1.74}$ sintered pellet (fig. 10d) are significantly different than those
 341 obtained on the as-synthesized powder (fig. 4c). The ‘orientation’ anomalies
 342 affecting the Si and satellite rows of reflections are no more visible. This evolu-
 343 tion is attributed to the heat treatment during the sintering and seems correlated
 344 to the variation of the modulation vector observed by XRD. Such influence of
 345 the temperature on the microstructural properties of MnSi_γ have already been
 346 reported, *e.g.* by Kikuchi *et al.* who reported a linear decrease of γ with tem-
 347 perature above 770 K associated to a VEC change [46]. In addition, careful
 348 examination of the diffraction pattern obtained on several areas of the sample
 349 reveals some degree of structural heterogeneity between different crystals. As
 350 an example, fig. 10e and 10f are diffraction patterns taken along the $[\bar{1}10]$ zone
 351 axis on two different crystals. While in fig. 10e the arrangement of the satellite

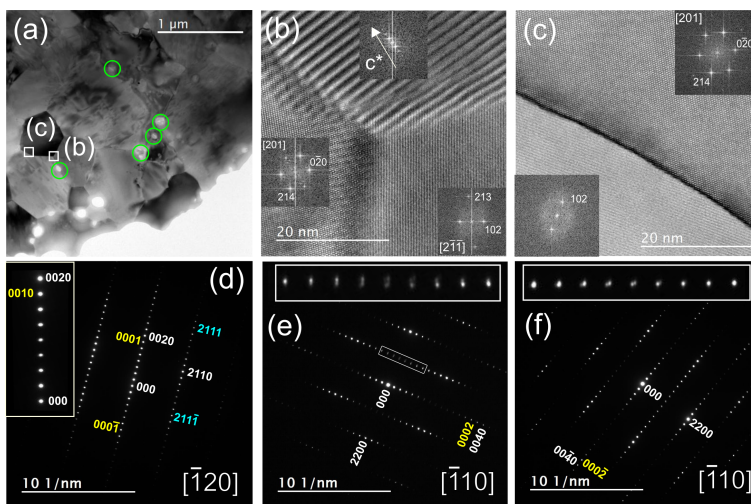


Figure 10: Low magnification brightfield TEM images of typical thinned undoped $\text{MnSi}_{1.74}$ pellet showing (a) the residual porosity (encircled in green) and the areas chosen for (b) and (c) HRTEM images showing the high crystallinity of the grain boundaries. FFT in insets indicate the crystal orientation of the grains. (d) Typical electron diffraction pattern taken along the $[\bar{1}20]$ zone axis. (e) and (f) Electron diffraction patterns obtained on two different crystals along the $[\bar{1}10]$ zone axis showing different anomalies.

352 peaks is equally spaced but slightly misoriented along the c -axis, fig. 10f shows
 353 on the contrary a split in satellite spot position in agreement with a variation of
 354 the modulation vector. A clear explanation of the origin of such microstructural
 355 effects is not available in literature and moreover out of the scope of the present
 356 work. However it is worth to underline that such effects are not homogeneous
 357 at the micrometer scale throughout the samples and are a characteristic of HMS
 358 that should be taken into account during theoretical modeling of the system.

359 An important contrast inside the crystals can be observed in brightfield mode
 360 (fig. 10a) and are attributed to local deviations from the diffraction condition
 361 due to large lattice distortions. Magnified images of this area are shown in fig.
 362 11a and 11b revealing high concentration of dislocation-like defects propagat-
 363 ing lattice distortion up to a distance of 50 nm in the crystal. A more detailed
 364 study of lattice defects was realized by high resolution imaging on thin crystals
 365 oriented along the $[\bar{1}20]$ zone axis. A defect-free area is shown in fig. 11(c)
 366 revealing two types of structural features: (i) large fringes with approximately

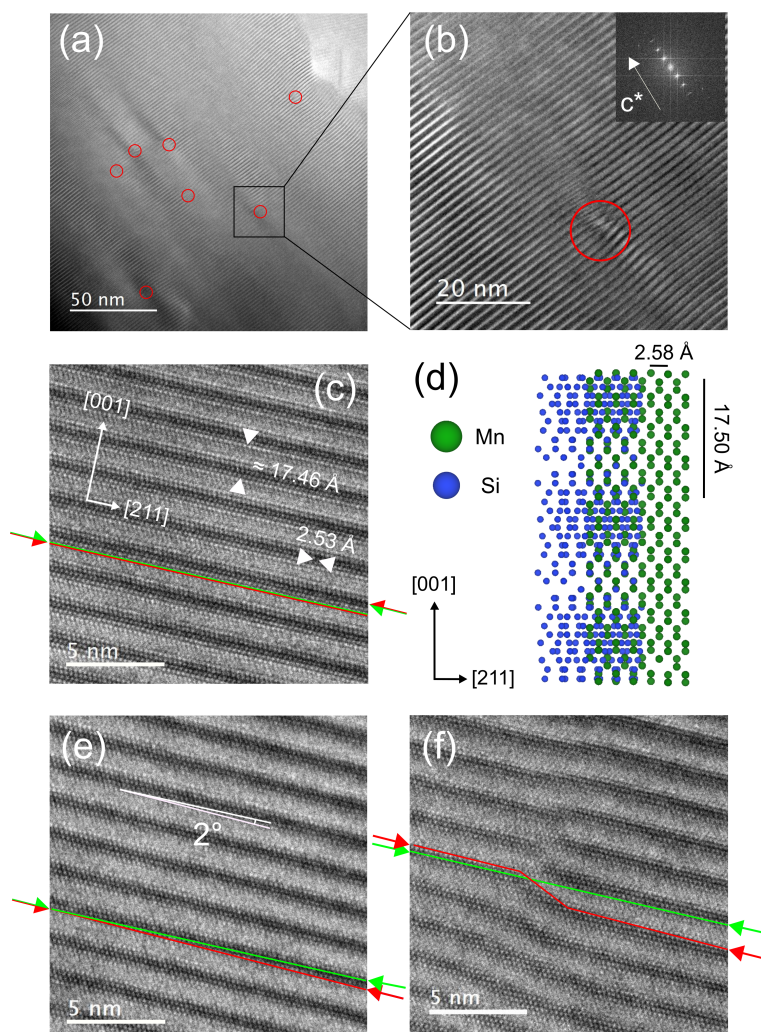


Figure 11: (a) and (b) Brightfield images of MR $\text{MnSi}_{1.74}$ sintered pellet showing dislocation-like defects (encircled in red) at two different magnifications. (c) Typical HRTEM image of a defect-free area of a $\text{MnSi}_{1.74}$ crystal taken along the $[\bar{1}20]$ zone axis with average characteristic distances of the lattice determined from the corresponding FFT image. The orientations of the Moiré fringes and the Mn atomic rows are emphasized on the images with red and green lines, respectively. (d) Scheme of the formation of Moiré-like fringes along the $[\bar{1}20]$ direction by interaction of the Si-sublattice (left side) and Mn-sublattice (right side). (e) and (f) HRTEM images showing the tilting of the Moiré fringes relatively to the $[211]$ direction and a dislocation-like defect, respectively.

367 17.46 Å periodicity along the $[001]$ direction corresponding to the c -axis of the
 368 commensurate structure of Mn_4Si_7 and generated by Moiré interferences be-
 369 tween the two Mn- and Si-subsystems of the composite crystal and (ii) atomic

370 rows spaced by approximately 2.53 Å along the [211] direction and correspond-
371 ing to the Mn-Mn distance in the $[\bar{1}20]$ projection of the structure (fig. 11c).
372 The schematic representation of the crystal structure projection along the $[\bar{1}20]$
373 direction illustrates the formation of the Moiré fringes by interaction of the two
374 sublattices (fig. 11c). As assumed by the structural model, the orientation of the
375 Moiré fringes and the Mn rows are both parallel to the [211] direction because
376 of the existence of lattice translation symmetry in the (001) plane. Surpris-
377 ingly, the situation is somewhat different in fig. 11e taken in a different area
378 of the same crystal, where the Moiré fringes are found to be tilted by about
379 2° with respect to the Mn row itself. Ye and Amelinckx reported similar ob-
380 servations and explained it as a small systematic ‘phase-shift’ of the Si helical
381 arrangement inside the columnar Mn-sublattice resulting in the tilting of the
382 Moiré fringes [34]. According to these authors, the loss of the tetragonal sym-
383 metry in the area of the crystal affected by the Si helices ‘phase-shift’ explains
384 the ‘orientation’ anomalies visible on the electron diffraction patterns. Similar
385 type of images taken on the dislocation-like defects (fig. 11f) reveals that only
386 the Moiré fringes are deformed on these areas of the crystal. As shown by the
387 green line, the Mn rows remains well oriented and defect-free throughout the
388 analyzed area and even close to the lattice defect where severe distortion is ex-
389 pected. From these observations, the Si sublattice can be described as highly
390 deformed by numerous defects while on the contrary the Mn lattice remains
391 well crystallized and less affected by Si sublattice disorder. It should be noticed
392 that this more ‘realistic’ description of the HMS structure is consistent with the
393 peak shape broadening of the Si $hk0m$ reflections clearly visible on the powder
394 XRD patterns and supports the use of the strain tensor applied in our Rietveld
395 refinements.

396 The presence of numerous defects and heterogeneities within the submi-
397 cronous grains of MR $\text{MnSi}_{1.74}$ might act as efficient scattering centers for phonons
398 and thus might strongly influence the thermal conductivity of the materials.
399 In the next section, the thermoelectric properties of pristine and V-doped MR
400 $\text{MnSi}_{1.74}$ are thus presented and compared to conventionally synthesized AM

401 counterparts. The objective is to discuss the effect of the different synthesis
 402 routes and microstructures on the TE properties of comparable polycrystalline
 403 $\text{MnSi}_{1.74}$ samples.

404 **3.5. Thermoelectric properties of MR and AM $\text{MnSi}_{1.74}$ and** 405 **$\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$**

406 The TE properties of $\text{MnSi}_{1.74}$ and $\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$ synthesized by magnesio-
 407 re-duction or arc-melting were measured from room temperature up to 800 K (fig.
 408 12). Measurements of the electronic properties were cycled twice and showed
 409 good reversibility within a time span of few hours at high temperature.

410 The electrical resistivity of MR $\text{MnSi}_{1.74}$ (fig. 12a) increases from $23 \mu\Omega\cdot\text{m}$
 411 at 320 K to $39 \mu\Omega\cdot\text{m}$ at 750 K, in agreement with the behavior expected for a
 412 heavily degenerated semiconductor. In the same temperature range, its positive
 413 Seebeck coefficient (fig. 12b) increases accordingly from 135 to $230 \mu\text{V}\cdot\text{K}^{-1}$.
 414 The electronic properties of AM $\text{MnSi}_{1.74}$ were measured in the same conditions:
 415 at room temperature, the electrical resistivity and Seebeck coefficient are found
 416 to be 17 % and 2 % lower for the AM $\text{MnSi}_{1.74}$ sample in comparison to MR
 417 sample. At higher temperature, the difference in electrical resistivity becomes
 418 less and less significant, which is attributed to the apparition of the bipolar effect
 419 arising at slightly lower temperature (700-750 K) in the case of the MR sample.
 420 This effect corresponds to the thermal activation of minor carriers across the
 421 band gap (electrons in this case) leading to the simultaneous decrease of the
 422 electrical resistivity and the Seebeck coefficient. Maximum power factor PF of
 423 $1.3 \text{ mW m}^{-1} \text{ K}^{-2}$ at 740 K and $1.4 \text{ mW m}^{-1} \text{ K}^{-2}$ at 700 K (fig. 12c) are found
 424 for MR and AM $\text{MnSi}_{1.74}$, respectively. This corresponds to a 5 % reduction
 425 of the maximum PF which can be attributed in a large extent to the higher
 426 resistivity of the MR sample. Assuming similar charge carrier concentration in
 427 MR and AM samples from equivalent Seebeck coefficients and γ -value [46], the
 428 higher electrical resistivity in the mesostructured samples could be explained
 429 both by its lower density and possibly by higher scattering of charge carriers at
 430 the numerous grain boundaries.

431 Fig. 12d shows the temperature dependence of the total $\kappa_{tot}(T)$ and lattice
 432 $\kappa_L(T)$ thermal conductivities calculated by subtracting to $\kappa_{tot}(T)$ the electronic
 433 contribution $\kappa_e(T)$ calculated using the Wiedemann-Franz law $\kappa_e(T) = L T/\rho(T)$
 434 with $L = 2.4 \cdot 10^{-8} \text{ W } \Omega \text{ K}^{-2}$. The lattice thermal conductivity of MR $\text{MnSi}_{1.74}$
 435 amounts to $2.3 \text{ W m}^{-1} \text{ K}^{-1}$ at 320 K, which corresponds to a 13 % decrease
 436 compared to AM $\text{MnSi}_{1.74}$ at the same temperature. The beneficial reduction of
 437 the lattice thermal conductivity in MR $\text{MnSi}_{1.74}$ is attributed to the smaller grain
 438 sizes and the high concentration of defects as evidenced by EBSD and TEM
 439 analyses. However, the effect of mesostructuration becomes less and less effi-
 440 cient with increasing temperature and the lattice thermal conductivities of the
 441 two samples ultimately reach similar value at 750 K corresponding to the tem-
 442 perature with the highest PF . Equivalent maximum ZT of about 0.4 is achieved
 443 at 750 K which is in good agreement with the best performances reported for
 444 undoped HMS synthesized by conventional melting/annealing/SPS [47, 48].
 445 No improvement of the ZT could be achieved because the beneficial effect of
 446 the mesostructuration on κ_{tot} is counterbalanced by the deterioration of PF re-
 447 sulting in equivalent ZT values over the whole temperature range. Concordant
 448 experimental results show that highly-densified nanostructured HMS (average
 449 grain size around 200 nm) synthesized by ball milling followed by SPS did not
 450 improve the ZT also because of the drop of the power factor [9]. It suggests that
 451 any attempt to reduce the grain size down to few hundreds of nm is inefficient
 452 to improve ZT in the case of $\text{MnSi}_{1.74}$.

453 Increasing PF of MR-HMS was attempted by partially substituting manganese
 454 with vanadium up to 4 %. Vanadium-doping was reported to effectively im-
 455 proved the power factor of MnSi_γ while employing a relatively abundant el-
 456 ement compared to other commonly used dopant such as Ge or Re [49]. In
 457 addition, V_2O_5 can be reduced relatively easily by Mg in the synthesis condi-
 458 tion unlike other very stable oxides such as Al_2O_3 . As for undoped $\text{MnSi}_{1.74}$, TE
 459 measurements were realized on both MR and AM $\text{V}_{0.04}\text{Mn}_{0.96}\text{Si}_{1.74}$. The elec-
 460 trical resistivity and the Seebeck coefficient of both samples decrease with the
 461 insertion of vanadium in the structure. This is consistent with an increase of

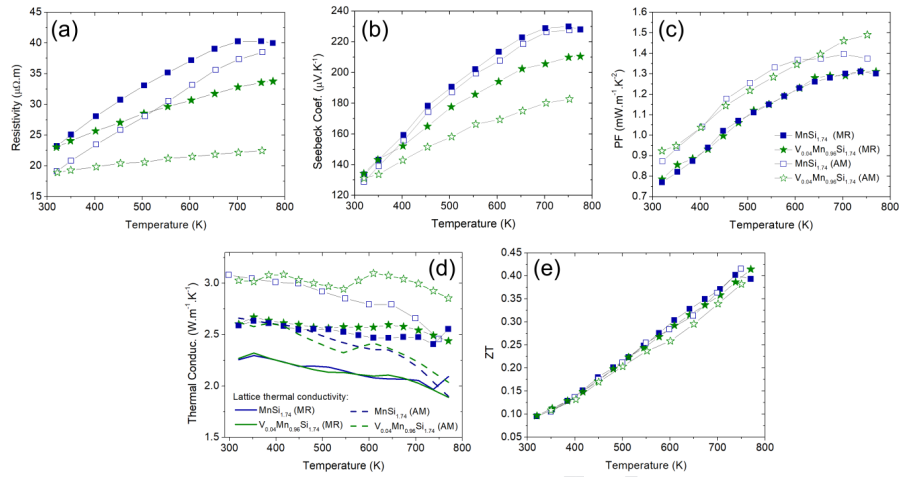


Figure 12: High temperature thermoelectric properties of $MnSi_{1.74}$ (blue squares) and $V_{0.04}Mn_{0.96}Si_{1.74}$ (green stars) synthesized by magnesioreduction (MR, filled symbols) and conventional arc-melting (AM, empty symbols): thermal dependence of (a) electrical resistivity, (b) thermopower, (c) power factor, (d) total (symbols) and lattice (solid lines for MR $MnSi_{1.74}$ and dotted lines for AM $MnSi_{1.74}$) thermal conductivities and (e) resulting figure-of-merit.

462 the holes concentration in the materials resulting from the substitution of Mn
 463 by an electron-poorer element. The less pronounced effect of the doping on the
 464 MR sample could be explained by the probable smaller amount of V effectively
 465 substituting Mn due to the residual VSi_2 precipitates observed by EDS mapping.
 466 Miyazaki *et al.* [49] clearly showed a linear increase of the charge carrier con-
 467 centration with V-doping. Accordingly, a slightly smaller charge carrier density
 468 is expected in the MR-sample, also in agreement with the higher Seebeck co-
 469 efficient of this material. Consequently, doping the MR sample do not improve
 470 PF while for the AM sample it leads only to a small improvement of about 8 %
 471 above 700 K. Similarly, doping do not induce significant improvement of the
 472 lattice thermal conductivity which remain identical to the undoped sample over
 473 the whole temperature range. Neither the mass fluctuation scattering of thermal
 474 phonons at the disordered Mn/V sites, nor the submicrometric VSi_2 precipitates
 475 present in the materials seem to significantly influence κ_L . As a consequence,
 476 no improvement of ZT_{max} has been achieved in our case by vanadium doping.

477 **4. Conclusion**

478 A new magnesio-reduction synthesis for high purity $\text{MnSi}_{1.74}$ is reported. This
479 method offers many advantages over conventional melting/annealing syntheses
480 such as the use of cheap and air-stable precursors (MnO and Si), relatively fast
481 heat treatment at moderate temperature and the possibility to produce doped
482 compounds. Additionally, a finely divided powder is directly obtained, which is
483 suitable for the sintering of mesostructured materials with average grain size of
484 about 500 nm. The influence of the microstructure, investigated by means of
485 EBSD and TEM, on the thermoelectric properties was evaluated by comparison
486 with a sample synthesized by a conventional arc-melting/annealing/sintering
487 process and composed of much larger grains. The thermal conductivity is de-
488 creased by up to 25% at 300 K thanks to the mesostructuring and associated
489 crystal defect density. However, this beneficial effect is counterbalanced by a de-
490 crease of the power factor, resulting eventually in materials with similar $ZT_{max} \simeq$
491 0.4 at 750 K. The present results suggest that microstructure engineering alone
492 might not be a sufficient strategy to improve the TE properties of HMS.

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- Mesosstructured higher manganese silicides are synthesized by magnesioreduction
- Crystal structures are refined in composite-incommensurate unit-cells
- Microstructures are examined by EBSD and TEM
- The decrease in thermal conductivity is correlated to the microstructure

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