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# Improvement of Thermoelectric Properties via Texturation using a Magnetic Slip Casting Process – the Illustrative Case of $\text{CrSi}_2$

Sylvain Le Tonquesse,<sup>\*,†</sup> Wenhao Zhang,<sup>‡,¶</sup> Bhuvanesh Srinivasan,<sup>†</sup>  
Bruno Fontaine,<sup>§</sup> Takanobu Hiroto,<sup>||</sup> Takao Mori,<sup>‡,¶</sup> Jean-François Halet,<sup>†</sup>  
David Berthebaud,<sup>\*,†</sup> and Tohru S. Suzuki<sup>\*,||</sup>

<sup>†</sup>*CNRS-Saint-Gobain-NIMS, IRL 3629, Laboratory for Innovative Key Materials and Structures (LINK), National Institute for Materials Science, Tsukuba 305-0044, Japan*

<sup>‡</sup>*National Institute for Materials Science (NIMS), WPI-MANA, 1-1-1 Namiki, Tsukuba 305-0044, Japan*

<sup>¶</sup>*Graduate School of Pure and Applied Science, University of Tsukuba, Tsukuba, Ibaraki 305-8671 Japan*

<sup>§</sup>*Univ Rennes, CNRS, Ecole Nationale Supérieure de Chimie de Rennes, ISCR-UMR6226, F-35000, Rennes, France*

<sup>||</sup>*National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047, Japan*

E-mail: Sylvain.LETONQUESSE@cnrs.fr; David.BERTHEBAUD@cnrs.fr;  
SUZUKI.Tohru@nims.go.jp

## Abstract

Transition metal silicides constitute a promising class of inexpensive and non-toxic thermoelectric materials showing competitive properties. This article reports an ef-

4 efficient process to synthesize highly textured poly-crystalline CrSi<sub>2</sub> by performing slip  
5 casting under a strong magnetic field. The crystallographic texture of spark plasma  
6 sintered samples, characterized by electron back-scattered and X-ray diffraction tech-  
7 niques showed a fiber texture symmetry with the *c*-axis of hexagonal CrSi<sub>2</sub> aligning  
8 preferentially along the magnetic field direction. The thermoelectric properties mea-  
9 sured both parallel and perpendicular to the *c*-axis texture direction showed a large  
10 anisotropy. In particular, a significantly higher Seebeck coefficient was measured  $\parallel c$   
11 reaching a maximum value of 200  $\mu\text{V K}^{-1}$  at 650 K, inducing a power factor  $\parallel c$  twice  
12 higher than  $\perp c$  with an average value of 2.2  $\text{mW m}^{-1} \text{K}^{-2}$ . Density functional theory  
13 and transport property calculations revealed that an anisotropic two-band model can  
14 explain the higher thermoelectric property along the *c*-axis direction, which can be  
15 traced to Cr-Cr bonding interactions along this direction. The estimated thermoelec-  
16 tric figure of merit  $ZT_{\parallel c}$  was improved to 0.20 at 773 K. This is 50 % higher than that  
17 measured for randomly oriented samples and comparable to that observed for single  
18 crystals. Such a performance boost can certainly be reiterated for other types of ther-  
19 moelectric materials using the efficient magnetic slip-casting process reported in this  
20 article.

## 21 **1 Introduction**

22 Thermoelectric (TE) materials, which enable the conversion of waste heat into electricity,  
23 have been the object of extensive investigations over the past, with the aim to increase  
24 the efficiency of current fossil fuel combustion technology. The conversion efficiency of TE  
25 materials is directly linked to their figure of merit  $ZT$  given by:

$$26 \quad ZT = \frac{\alpha^2 T}{\rho \kappa} \quad (1)$$

27 with  $\alpha$  the Seebeck coefficient,  $\rho$  the electrical resistivity,  $\kappa$  the thermal conductivity  
28 and  $T$  the absolute temperature. In the last decade, mid-temperatures (600 - 800 K) ther-  
moelectrics such as PbTe<sup>1</sup>, GeTe<sup>2,3</sup>, SnTe<sup>4</sup>, CoSb<sub>3</sub>-based skutterudites<sup>5,6</sup> and SnSe<sup>7,8</sup> with

29 high  $ZT > 1.5$  have been reported. Despite this recent breakthrough, the use of these  
30 materials for large-scale industrialization remains impracticable as they are composed of  
31 rare, expensive or toxic constituting elements<sup>9</sup>. Moreover, the requirement for good me-  
32 chanical properties, chemical and thermal stability and low density reduces even more  
33 the number of possible candidates. Transition metal silicides (TMS) such as  $\text{CrSi}_2$ , the  
34 low-temperature phase  $\beta\text{-FeSi}_2$  and  $\text{MnSi}_{1.74}$ , extensively studied nowadays both in the  
35 academics<sup>10-12</sup> and the industry<sup>13-15</sup> constitute viable alternatives. TMS are character-  
36 ized by high power factors  $PF = \alpha^2/\rho$  but their maximum  $ZT$  remain moderate (0.13 for  
37  $\text{CrSi}_2$ <sup>16</sup>, 0.20 for doped  $\beta\text{-FeSi}_2$ <sup>17</sup> and 0.45 for  $\text{MnSi}_{1.74}$ <sup>18</sup>) due to high thermal conduc-  
38 tivities<sup>19</sup>. For these reasons, the majority of published works related to TMS focused on  
39 reducing  $\kappa$  using common strategies such as alloying<sup>20-22</sup>, nanostructuring<sup>23,24</sup>, thin  
40 films<sup>25</sup>, and composite synthesis<sup>26-30</sup>. Employing these strategies, enhanced maximum  $ZT$   
41  $\approx 1$  (+ 150 %) for Re-doped  $\text{MnSi}_{1.74}$ <sup>31,32</sup> or  $ZT = 0.25$  (+ 70 %) for Ge-doped  $\text{CrSi}_2$ <sup>20</sup>  
42 were achieved for instance. However, these promising results were often obtained at the  
43 expense of increased cost or reduced thermal stability.

44 An alternative approach to enhance  $ZT$  consists in the texturation of bulk polycrystalline  
45 TMS along preferential crystallographic directions. Most thermoelectric TMS are known  
46 to exhibit intrinsically large anisotropy of their TE properties<sup>33</sup>. For example,  $\text{MnSi}_{1.74}$   
47 (tetragonal) and  $\text{CrSi}_2$  (hexagonal) single crystals show  $PF$  that are about 40 % higher  
48 along the  $a$ - and  $c$ -axes, respectively, mostly due to higher Seebeck coefficients<sup>34,35</sup>. Induc-  
49 ing large texturation in polycrystalline materials should result in macroscopic properties  
50 comparable to single crystals without the inherent high processing cost of the latter which  
51 strongly reduces potential industrial applications. Texturation processes reported for TMS  
52 mostly consist in sintering pellet or ribbon shaped particles under uniaxial pressure, the  
53 particle morphology being produced by cleaving large crystals along preferential crystallo-  
54 graphic planes<sup>34,36</sup> or by melt-spinning process<sup>37</sup>. However, the properties remain close to  
55 randomly oriented materials due to the relatively small texturation strength. The crystal-

56 lization of an Mn-Si melt under a magnetic field of 3 T was also used to produce textured  
57 MnSi<sub>1.74</sub> polycrystalline ingots<sup>38</sup>. According to the authors, the electrical resistivity  $\perp c$   
58 was twice lower than for randomly oriented samples synthesized without magnetic field.  
59 However, the resulting *PF* of 0.2 mW m<sup>-1</sup> K<sup>-2</sup> is about five times lower than reference  
60 samples from the literature due to a large amount of a secondary phase. Other thermome-  
61 chanical processes such as rolling or hot-extrusion, which have been successfully used for  
62 other TE materials such as Bi<sub>2</sub>Te<sub>3</sub><sup>39</sup>, oxides<sup>40</sup> and oxi-chalcogenides<sup>41</sup>, are not applicable  
63 to TMS due to their purely elastic mechanical behaviors. These literature results show  
64 that inducing high texturation of TMS samples is a promising method to increase their TE  
65 performances but also that appropriate texture processes remain to be developed.

66  
67 Here, an efficient texturation process is proposed which consists in slip casting a disper-  
68 sion of CrSi<sub>2</sub> particles under a strong magnetic field (12 T). This process takes advantage of  
69 the diamagnetic anisotropy of the materials to align the freely moving particles in suspen-  
70 sion along their easy magnetization axis<sup>42</sup>. In addition, slip casting processes make pos-  
71 sible the fabrication of large scale near net-shape parts which is of uttermost importance  
72 for efficient industrialization. The oriented green body obtained after slip casting can be  
73 further processed to obtain a fully dense textured sample. Such a process has already been  
74 successfully applied to oxides<sup>43,44</sup>, carbides<sup>45-47</sup>, nitrides<sup>48,49</sup> and borides<sup>50</sup> for instance  
75 but rarely to TMS<sup>51,52</sup>. Indeed, CrSi<sub>2</sub> is a good candidate to demonstrate the usefulness  
76 of this texturation method for TE TMS because to our knowledge, (i) no data is available  
77 in the literature on textured polycrystalline samples, (ii) its congruent melting facilitates  
78 the synthesis of large amount of material prepared by conventional fusion/solidification  
79 processes, and (iii) it has a simple crystal structure compared to others TMS (MnSi<sub>1.74</sub>  
80 has an aperiodic crystal structure<sup>53,54</sup> and  $\beta$ -FeSi<sub>2</sub> presents stacking faults<sup>55</sup>) which make  
81 easier the realization of texture analyses. In this article, the texturation process is first  
82 described in detail and the optimal synthesis conditions are discussed. The texture of the

83 samples were quantitatively analyzed using both electron backscattered diffraction (EBSD)  
84 and X-ray diffraction (XRD) techniques. The directional TE properties were measured and  
85 compared to a randomly oriented reference as well as single crystal data from the litera-  
86 ture. The computed band structure and the transport properties of CrSi<sub>2</sub> are discussed in  
87 order to better understand the origin of the strong anisotropy in this material.

## 88 **2 Experimental procedure**

### 89 **2.1 Synthesis**

90 CrSi<sub>2</sub> was synthesized by arc-melting Cr chips (Aldrich Chemicals, 99.995 %) and Si pieces  
91 (Aldrich Chemicals, 99.95 %) in stoichiometric amount using a home-made furnace appa-  
92 ratus. The furnace chamber was purged three time with Ar and the resulting ingot of  
93 about 1.5 cm<sup>-3</sup> was flipped and remelted four times to ensure good homogenization. The  
94 weight loss was under 0.2 wt.%. The CrSi<sub>2</sub> ingot was then pulverized into powder by wet  
95 ball-milling using a Fritsch Pulverisette 7 and Y-stabilized ZrO<sub>2</sub> jar and balls (Ø= 5 mm).  
96 The ball-to-powder weight ratio was set to 5, the jar was filled with ethanol at 15 vol.%  
97 and the milling was performed at 200 rpm for 8 h. The ball-milled powder was dried  
98 overnight at 373 K. A slurry containing 20 wt.% solid load was prepared by dispersion of  
99 the CrSi<sub>2</sub> powder in absolute ethanol. 0.3 wt.% of polyethylenimine (PEI) dispersing agent  
100 (Sigma Aldrich, average M = 10000 g mol<sup>-1</sup>, linear chains) was added to the slurry and  
101 the acidity was adjusted with 0.1 vol.% of acetic acid to reach an equivalent pH of 5.5.  
102 The breaking of the aggregates was ensured by thoroughly sonicating the slurry. The later  
103 was poured in the slip casting set-up consisting of a cylindrical polyethylene mold (Ø= 12  
104 mm, height = 40 mm) placed on a porous alumina plate (25 % porosity) covered with a  
105 membrane filter (200 nm pores size). The mold containing the slurry was covered with a  
106 plastic film in order to prevent evaporation of ethanol. The slip casting set-up was placed  
107 inside a 12 T superconducting magnet either in vertical or horizontal position. The green  
108 bodies were first densified by cold isostatic pressing (CIP) at 394 MPa for 10 min then by

109 spark plasma sintering (SPS) in a  $\varnothing = 10$  mm graphite die at 1523 K (heating and cooling  
110 rate of  $50 \text{ K min}^{-1}$ ) and 80 MPa for 10 min.

## 111 **2.2 Powder and slurry characterizations**

112 The grain size distribution of the ball-milled powder was determined by the dynamic light  
113 scattering (DLS) technique using a Microtrac Nanotrac ULTRA apparatus. Zeta-potentials  
114 were measured using a Malvern Nano Essentials zetasizer. The viscosity was measured  
115 using a Tokisangyo RE-215L viscometer.

## 116 **2.3 X-ray diffraction analyses**

117 XRD analyses were performed using a Rigaku TTRIII diffractometer equipped with a rotat-  
118 ing Cu anode ( $\lambda_{K\alpha 1} = 1.5406 \text{ \AA}$  and  $\lambda_{K\alpha 2} = 1.5444 \text{ \AA}$  with a ratio  $I_{K\alpha 2}/I_{K\alpha 1}$  of 0.5, 45 kV  
119 and 150 mA) and a D/teX Ultra detector. XRD texture analyses were performed using a  
120 Rigaku SmartLab diffractometer equipped with  $\chi$ - $\phi$  attachment, a rotating Cu X-ray anode  
121 ( $\lambda_{K\alpha 1} = 1.5406 \text{ \AA}$  and  $\lambda_{K\alpha 2} = 1.5444 \text{ \AA}$  with a ratio  $I_{K\alpha 2}/I_{K\alpha 1}$  of 0.5, 45 kV and 200 mA)  
122 and a HyPix-3000 detector. For XRD texture measurements,  $2\theta/\theta$  scans were measured in  
123 the range  $5^\circ - 130^\circ$  with a step size of  $0.02^\circ$ . The  $\chi$  angle was measured in the range  $0^\circ -$   
124  $45^\circ$  with a step size of  $5^\circ$  for all samples and the  $\phi$  angle was measured in the range  $0^\circ -$   
125  $180^\circ$  with a step size of  $5^\circ$  for CrSi<sub>2</sub>-h and kept constant for CrSi<sub>2</sub>-r and CrSi<sub>2</sub>-v. Refinement  
126 of the XRD patterns and texture analyses were performed using the *MAUD* software<sup>56</sup>.

## 127 **2.4 Scanning electron microscopy analyses**

128 Back-scattered electron images and elemental energy dispersive spectroscopy (EDS) anal-  
129 yses of the sintered pellets were performed with a scanning electron microscope (SEM)  
130 Hitachi Tabletop TM3000. Particle morphology and EDBS mapping were realized using a  
131 JEOL JSM7000F SEM microscope equipped with a field-emission electron source. Samples  
132 preparation for EBSD consisted in successive polishings with silicon carbide, diamond and  
133 colloidal silica.

## 134 **2.5 Thermoelectric properties measurements**

135 Thermal diffusivity ( $D$ ) measurement was performed under  $N_2$  atmosphere on  $\emptyset = 10$  mm  
136 and 1 mm thick samples coated with graphite using a laser flash analysis (LFA) apparatus  
137 Netzsch 467 HyperFlash. The thermal conductivity was calculated using the expression  
138  $\kappa = D \cdot C_p \cdot d$  with  $D$  the thermal diffusivity,  $d$  the density and  $C_p$  the specific heat.  $C_p$   
139 was calculated using the Dulong-Petit law  $C_p = 3 \cdot N \cdot R / M = 0.69 \text{ J g}^{-1} \text{ K}^{-1}$  with  $N=3$  the  
140 number of formula per unit cell,  $R$  the ideal gas constant and  $M$  the molar mass.  $d$  was  
141 determined by the Archimede method in absolute ethanol. The Seebeck coefficient and  
142 electrical resistivity were measured simultaneously on  $9 \times 1 \times 2 \text{ mm}^3$  bars using a ZEM5  
143 equipment under partial He atmosphere. The Hall coefficient ( $R_H$ ) was measured in AC  
144 mode using a physical property measurement system (PPMS, Quantum Design) with a  
145 magnetic field sweeping from -5 T to +5 T. The charge carrier concentration  $n$  of the  
146 sample  $\text{CrSi}_{2-r}$  was calculated from the expression  $n = 1/eR_H$  with  $e$  the elementary charge  
147 of the electron.

## 148 **2.6 Computational details**

### 149 **2.6.1 DFT band structure calculations**

150 Density Functional Theory (DFT) calculations were carried out on diamagnetic  $\text{CrSi}_2$  using  
151 the *Quantum Espresso* package<sup>57,58</sup>. The cell parameters and atomic positions were fixed  
152 at their experimental values ( $\text{CrSi}_{2-r}$  in Table 1). The generalized gradient approxima-  
153 tion Burke, Perdew and Ernzerhof (PBE) functional<sup>59</sup> and the projector augmented-wave  
154 (PAW) method<sup>60</sup> were used. A kinetic energy cutoff of 200 Ry and a ten-times higher  
155 charge density cutoff were used for the calculations as a result of the convergence tests.  
156 Convergence threshold energy for self consistent calculations was  $1 \times 10^{-10}$  Ry per cell.  
157 The Brillouin zone (BZ) integration was performed using a  $11 \times 11 \times 7$  Monkhorst-pack  
158 grid<sup>61,62</sup> generating 847  $k$ -points in the irreducible part of the BZ.



## 159 2.6.2 Density of states and transport properties calculations

160 A Wannier function method was used for the extrapolation of electronic structure in the  
161 reciprocal space, as implemented in the *Wannier90* code and its *Boltzmann* module<sup>63,64</sup>.  
162 The initial Wannier projection were chosen to be Cr 3*d* and Si 3*s* and 3*p* orbitals. The  
163 Wannierized wavefunctions from the Cr 3*d* orbitals have ignorable difference from their  
164 atomic orbital counterparts, thus the Wannier functions can still be indexed by the 3*d*  
165 atomic orbital index. The density of states (DOS) was calculated by summing up the  
166 contribution from all bands and *k*-points from the Wannier extrapolation on a grid 50 ×  
167 50 × 30. The temperature dependent chemical potential  $\mu(T)$  estimated from experiments  
168 (see section 4.6.3), the calculated band structure and a constant carrier lifetime  $\tau = 5.5$   
169 × 10<sup>-15</sup>s were used for the calculation of the transport properties using the linearized  
170 semi-classical Boltzmann equation<sup>65</sup>. The anisotropic values were obtained by using the  
171 following expressions:

$$\{\alpha, \rho\}_{\parallel c} = \{\alpha, \rho\}_{zz} \quad (2)$$

172 and

$$\{\alpha, \rho\}_{\perp c} = (\{\alpha, \rho\}_{xx} + \{\alpha, \rho\}_{yy})/2 \quad (3)$$

173 for both Seebeck coefficients and electrical resistivity along and perpendicular to the  
174 *c*-axis, the index *x,y* and *z* correspond the Cartesian axes. The anisotropic properties cal-  
175 culated in such way correspond to the case of an ideal single crystal, but due to the high  
176 texturation, they should also be comparable to our experimental measurements. COHP  
177 (Crystal Orbital Hamilton Population) curves which indicate energetic contributions of  
178 crystal orbitals between atoms, were calculated using the LOBSTER code<sup>66-69</sup>.

179

### 180 2.6.3 Carrier concentration determination

181 As an important input for the transport calculation, the temperature dependent chemical  
182 potential  $\mu(T)$  was determined from the carrier concentration  $n$  experimentally obtained  
183 from Hall measurements at room temperature, using the charge neutrality requirement  
184  $n_h(\mu, T) - n_e(\mu, T) = n$  with  $n_h$  and  $n_e$  the concentration of holes and electrons, respec-  
185 tively, which depend on the temperature  $T$  and the chemical potential  $\mu$  according to the  
186 expression<sup>70</sup>:

$$n_h = \frac{1}{V} \int_{-\infty}^{\varepsilon_v} D(\varepsilon) (1 - f(\mu, \varepsilon, T)) d\varepsilon \quad (4)$$

$$n_e = \frac{1}{V} \int_{\varepsilon_c}^{\infty} D(\varepsilon) f(\mu, \varepsilon, T) d\varepsilon \quad (5)$$

187 with  $\varepsilon_v$  and  $\varepsilon_c$  the energies of the valence band maximum (VBM) and the conduction  
188 band minimum (CBM),  $V$  the volume of the unit cell,  $D(\varepsilon)$  the density of states obtained  
189 from the electronic structure calculation, and  $f(\mu, \varepsilon, T)$  the Fermi-Dirac distribution func-  
190 tion. The carrier concentration  $n = 1 \times 10^{20} \text{ cm}^{-3}$  was assumed to remain constant all over  
191 the temperature range.  $\mu(T)$  was determined numerically using the equations (4) and (5).  
192 Since  $n$  is high, the calculated chemical potential was found below the valence band maxi-  
193 mum at room temperature. It was shifted upward with increasing temperature but always  
194 found below VBM in the current assumption. A temperature dependent  $\mu(T)$  was used  
195 for the calculations of the electrical resistivity and Seebeck coefficient. The above calcu-  
196 lated carrier concentrations  $n_h$  and  $n_e$  with respect to temperature are shown in Figure SI 1.

197

## 3 Results and discussion

### 3.1 Synthesis of textured CrSi<sub>2</sub>

A crucial step to obtain materials with high texturation using the magnetic slip casting process is the careful preparation of a stable slurry composed of single crystalline and mono-dispersed particles. Formation of aggregates would reduce the rotation movement of the particles in the dispersion and prevent the good alignment of their easy magnetization axis with the magnetic field. In addition, important aggregation of the particles may result in fast sedimentation of the slurry and the formation of a low-density green body with weak mechanical resistance. The particle size distribution is an important parameter that dictates the stability of the dispersion. Dispersions composed of particles with size less than 1  $\mu\text{m}$  are expected to show higher stability as the effect of the Brownian force acting on the individual particles becomes preponderant over the gravitational attraction which tends to promote their settlement. However, the random nature of the Brownian motion may also interfere with the proper alignment of small particles. Indeed, the magnitude of the magnetic torque  $T_m$  that rotates the individual particles upon application of a magnetic field  $B$  is given by the relation<sup>42</sup>:

$$T_m = -\frac{\Delta\chi VB^2}{2\mu_0} \times \sin(2\theta) \quad (6)$$

where  $\Delta\chi$  is the difference of diamagnetic susceptibilities between the hard and the easy magnetization axes,  $V$  is the volume of the particle,  $\theta$  is the angle between the imposed magnetic field direction and the easy magnetization axis and  $\mu_0$  is the vacuum permeability. Relation (6) clearly shows that the magnitude of the magnetic torque is proportional to the particle volume. In practice, a good alignment of particles with size inferior to about 200 nm becomes challenging even with a magnetic field as high as 12 T due to

221 both lower  $T_m$  and increasing effect of the Brownian motion. Thus, a compromise on the  
222 particle size needs to be reached in order to allow both a good stability of the dispersion  
223 and a strong alignment of the particles. Considering the average diamagnetic constant  
224  $\chi_{dia} \approx -10^{-5}$  for  $\text{CrSi}_2$ <sup>71</sup>, powders with a medium value of the particle size distribution  $d_{50}$   
225 between 1  $\mu\text{m}$  and 200 nm are expected to give the best results.

226

227 The bulk  $\text{CrSi}_2$  ingot used for the powder preparation was synthesized conventionally  
228 by arc-melting process. The XRD pattern of the as-cast ingot is shown in Figure 1a. All  
229 peaks could be indexed with the  $\text{CrSi}_2$  structure which adopts the hexagonal  $C40$  structure-  
230 type (space group  $P6_222$ , No. 180) shown in Figure 2a. Le Bail refinement gave lattice  
231 parameters  $a = 4.42724(6)$  Å and  $c = 6.36194(9)$  Å in agreement with literature data<sup>72</sup>.  
232 As shown in Figure 1b, the ingot was mostly composed of macroscopic crystals with size  
233 superior to 100  $\mu\text{m}$  that were pulverized into powder using wet ball-milling. Figures 1c  
234 and d show a SEM image and the size distribution determined by DLS of the ball-milled  
235  $\text{CrSi}_2$  powder, respectively. The particle size distribution follows a log-normal law charac-  
236 terized by an average size and a standard deviation of 444 nm and 132 nm, respectively.  
237 A  $d_{50}$  value of 405 nm was determined from the cumulative frequency curve. The pow-  
238 der particles are fragments of large macroscopic crystals constituting the as-cast ingot and  
239 are thus considered as single crystalline. The present powder fulfills all the requirements  
240 stated above for the preparation of high-quality slurry for magnetic slip casting.

241 The electrostatic interactions between the particles in a dispersion is an other important  
242 parameter to take into account to prevent their aggregation and settlement. Increasing  
243 the repulsive electrostatic interactions between the particles was realized by adsorbing PEI  
244 at their surface. The zeta-potential, approximately corresponding to the surface electric  
245 charge of the particles, was increased from about -10 mV to -50 mV by adjusting the acid-  
246 ity of the solution with acetic acid. The viscosity of the slurry with a solid load of 20 wt.%  
247 was monitored for more than 2 hours and remained stable around 1.42 mPa s, confirming

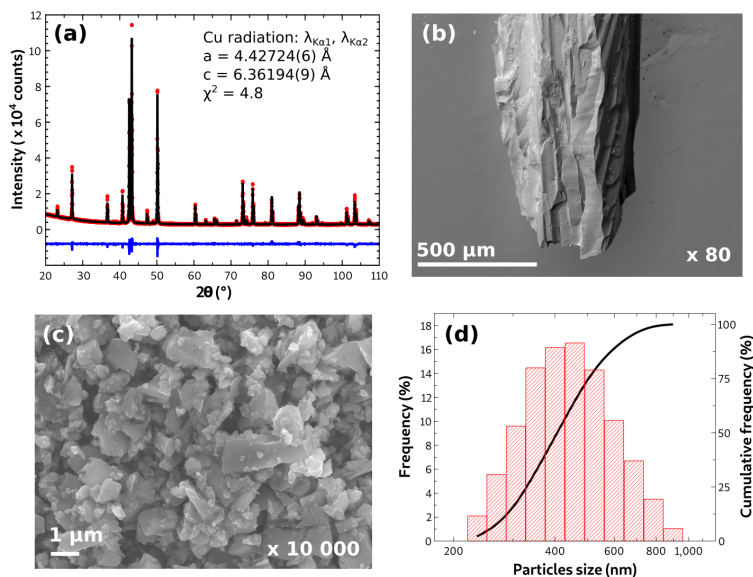


Figure 1: (a) Le Bail refined pattern and (b) SEM image of the as-casted  $\text{CrSi}_2$  ingot showing that it is mostly composed of well-faceted macroscopic crystals, (c) SEM secondary electron images and (d) particle size distribution of the ball-milled  $\text{CrSi}_2$  powder determined by DLS

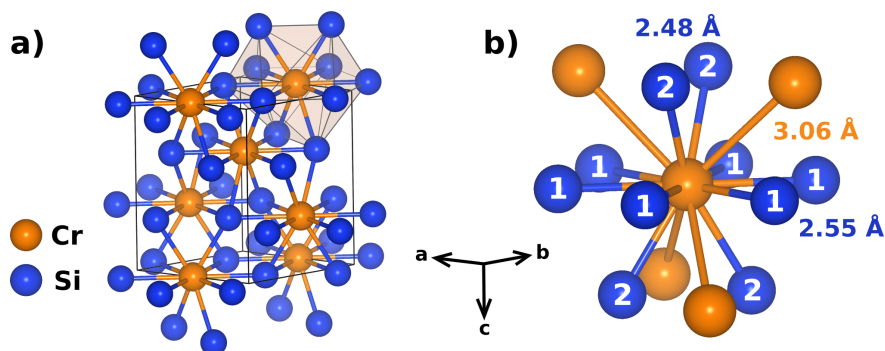


Figure 2: (a) Crystal structure of  $\text{CrSi}_2$  and (b) coordination sphere around Cr composed of 10 Si and 4 Cr atoms

248 its good stability over time.

249

250 The slip-casting set-up is shown in Figure 3. After the slurry was poured, the mold was  
 251 placed inside a superconducting magnet applying a 12 T static magnetic field. Depend-  
 252 ing on the desired texture direction, the magnetic field was applied either perpendicular  
 253 or parallel to the slip casting direction. Indeed, the full characterization of TE materials  
 254 requires samples shaped as thin pellets for thermal conductivity measurements with the

255 LFA method and bars for electric resistivity and Seebeck coefficient measurements using  
256 the 4-probe method. In the case of textured materials, the texture orientation needs to be  
257 the same, perpendicular to the pellet surface and parallel to the bar length. In the case of  
258 anisotropic materials, measurements of the TE properties along different texture directions  
259 may result in a highly overestimated  $ZT$ . Proper characterizations are usually achieved by  
260 cutting a thick densified pellet into smaller samples with shapes and dimensions well-  
261 adapted for the measurements. Instead, two different oriented samples with thickness  
262 of about 2 mm and complementary texture orientations were synthesized by setting the  
263 magnetic field direction vertically (sample CrSi<sub>2</sub>-v) or horizontally (sample CrSi<sub>2</sub>-h). A  
264 reference sample with random orientation (CrSi<sub>2</sub>-r) was also prepared using the same pro-  
265 cess but without magnetic field. Within 8 hours, the solvent of the dispersion went entirely  
266 through the membrane into the porous support leaving green bodies with relative densities  
267 of about 55 %. In those conditions, the green bodies did not show enough mechanically  
268 stability to withstand the uniaxial pressure applied during sintering. Therefore, they were  
269 first consolidated via CIP technique to a relative density  $\approx$  65 % while preventing degra-  
270 dation of the texturation (see Figure SI 2). Finally, the green bodies were sintered via SPS  
271 technique into pellets with relative density of 98 % and 96 % for random and oriented  
272 samples, respectively. Despite identical sintering conditions for all the samples, crystallo-  
273 graphic orientations of the grains in the green bodies may affect significantly the surface  
274 energy and therefore the densification mechanisms resulting in slightly different densities.

275

276 The powder XRD patterns of the sintered random and oriented pellets shown in Figure 4a  
277 were well indexed with the CrSi<sub>2</sub> structure. SEM back-scattered electron image and EDS  
278 analyses of the CrSi<sub>2</sub>-v sample surface are shown in Figure 4b and Figure SI 3, confirming  
279 that CrSi<sub>2</sub> is the main phase. However, SEM analyses also revealed some CrSi impurity  
280 visible as light gray spots of about 1  $\mu$ m for all the samples. These impurities representing  
281 a negligible phase fraction of the samples were not detected on the XRD patterns. One

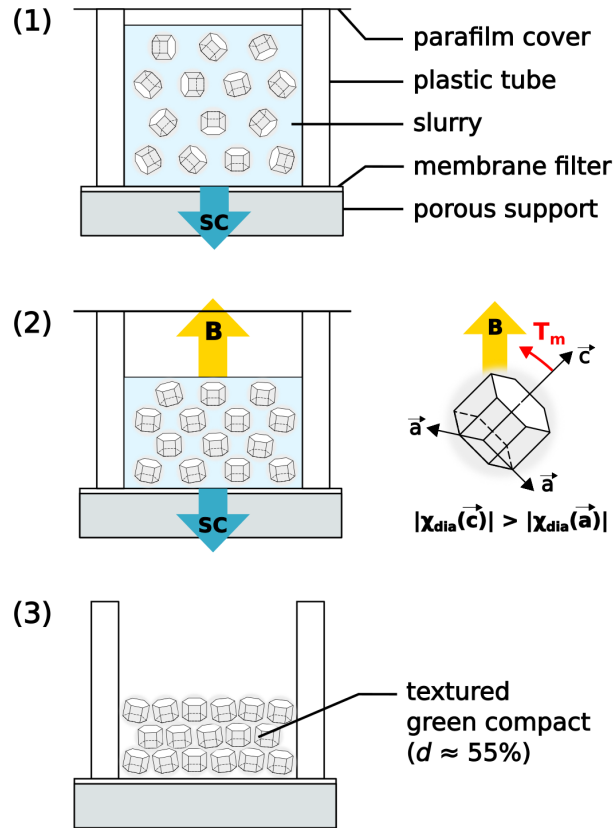


Figure 3: Description of the texturation process in 3 steps: (1) the slurry is poured in the slip casting (blue arrow) set-up and the solvent starts to be slowly drained through the membrane inside the porous support (2) the particles in the slurry are being aligned along their easy magnetization axis by application of a vertical 12 T magnetic field (yellow arrow) inducing a magnetic torque (3) a textured green body is obtained after all the solvent had been removed

282 possible explanation to the presence of CrSi is probably the reaction of residual dispersant  
 283 at the surface of the particles with the CrSi<sub>2</sub> matrix during sintering. However, such a  
 284 small amount of impurity was not expected to be detrimental to the TE properties and  
 285 these samples were used for TE measurements. The XRD patterns of CrSi<sub>2</sub>-v and CrSi<sub>2</sub>-h  
 286 shown in Figure 4a indicate large discrepancies of the peak intensities compared to CrSi<sub>2</sub>-  
 287 r. This is attributed to large crystallographic texturations. In the case of CrSi<sub>2</sub>-v, which  
 288 was synthesized with the magnetic field direction perpendicular to the pellet surface, only  
 289 the diffraction peaks 0003 and 0006, using the 4-index *hkil* Miller-Bravais notation, are  
 290 visible at  $2\theta \sim 42^\circ$  and  $\sim 96^\circ$ , respectively. This indicates that the *c*-axis of CrSi<sub>2</sub> is the

291 easy magnetization axis and thus the diamagnetic constant  $|\chi_c|$  is inferior to  $|\chi_{a,b}|$ . On the  
 292 contrary, the pattern of CrSi<sub>2</sub>-h shows largely reduced 000*l* peaks compared for example  
 293 to 11 $\bar{2}$ 0 at  $2\theta \sim 40^\circ$  for CrSi<sub>2</sub>-r. These results clearly indicate that the present process is  
 294 an efficient route to synthesize highly textured CrSi<sub>2</sub> samples with good purity.

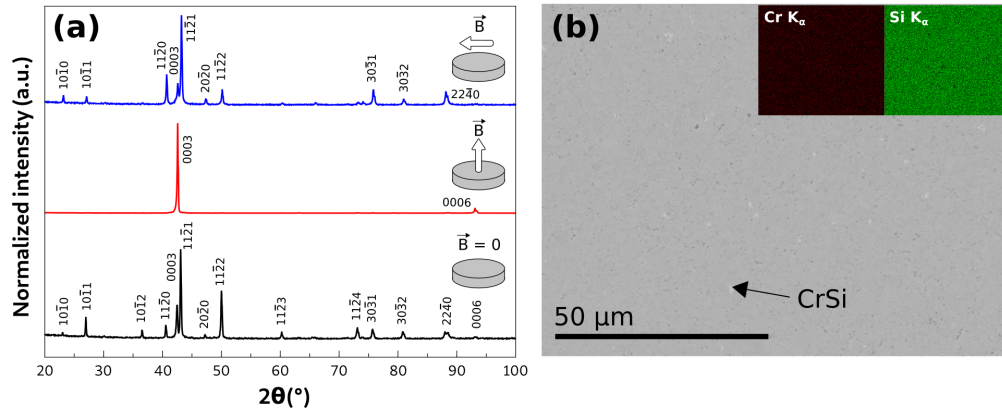


Figure 4: (a) XRD patterns of CrSi<sub>2</sub>-r (black), CrSi<sub>2</sub>-v (red) and CrSi<sub>2</sub>-h (blue) sintered samples (b) SEM back-scattered electron image of the sample's surface of CrSi<sub>2</sub>-v with corresponding EDS elementary maps

### 295 3.2 Quantitative texture analyses

296 In order to unambiguously study the effect of texturation on the TE properties and to  
 297 make meaningful comparisons between different synthesis methods of texturation, it is es-  
 298 sential to determine quantitatively the orientation and the strength of the main alignment  
 299 components of the textures. In the present case, this was realized using both complemen-  
 300 tary EBSD and XRD techniques. EBSD maps of the CrSi<sub>2</sub> samples are shown in Figure  
 301 5. The black areas correspond to unindexed zones which are mostly attributed to surface  
 302 imperfections consecutive to polishing and, to a lesser extent, residual porosities and CrSi  
 303 secondary phase. The crystallite orientation map and inverse pole figure (IPF) with homo-  
 304 geneous orientation density of 1 mrd (multiple random distribution) confirm the absence  
 305 of texturation for CrSi<sub>2</sub>-r. In the case of the oriented samples, visual inspection of the  
 306 maps clearly reveals the presence of textures with the majority of the crystallites showing  
 307 a {000*l*} and a {*hki*0} orientations for CrSi<sub>2</sub>-v and CrSi<sub>2</sub>-h, respectively. The IPF of CrSi<sub>2</sub>-v



308 shows an important *c*-axis texturation of about 20 mrd along the X direction of the sample  
309 surface. A similar *c*-axis texture of about 20 mrd is also found for CrSi<sub>2</sub>-h but along the Y  
310 direction that is parallel to the sample surface. In both cases, the main alignment compo-  
311 nent is aligned with the magnetic field direction applied during slip casting. The IPF along  
312 the Y and Z directions of CrSi<sub>2</sub>-v and the X and Z directions of CrSi<sub>2</sub>-h reveals that the  
313 *a*-axis of the crystallites is randomly oriented in the plane perpendicular to the easy-axis  
314 direction resulting in a fiber texture symmetry. This suggests that the dispersed particles in  
315 the slurry remain free to rotate around the *c*-axis when the magnetic field is applied. Such  
316 a fiber texture symmetry is common for materials synthesized by this process and can be  
317 found, for example, in hexagonal Al<sub>2</sub>O<sub>3</sub><sup>73</sup> and LiCoO<sub>2</sub><sup>74</sup>.

318

319 XRD measurements were performed as a complementary texture characterization present-  
320 ing the advantage to analyze a larger volume fraction of the sample. The analyses con-  
321 sisted in measuring several  $\theta$ - $2\theta$  scans at different tilting angles  $\chi$  and azimuthal rotation  
322  $\phi$  using a X-ray diffractometer equipped with  $\chi$ - $\phi$  attachment as schematized in Figure 6a.  
323 Figures 6b and 6c show the square root of the diffracted intensities for CrSi<sub>2</sub>-r and CrSi<sub>2</sub>-v,  
324 respectively, at different  $\chi$  angles. Measurements with different  $\phi$  rotation were unneces-  
325 sary because of the texture symmetry of these samples evidenced by EBSD analyses. In  
326 the opposite case of CrSi<sub>2</sub>-h, the texture axis is parallel to the sample surface and the rel-  
327 ative diffracted intensities are thus expected to vary with  $\phi$  rotation. Because of the large  
328 number of measured patterns for CrSi<sub>2</sub>-h (162 in total) the square root of the diffracted  
329 intensities is only shown in Figure 6d for fixed  $\chi = 25^\circ$ . Diffraction data for  $\chi \leq 40^\circ$  were  
330 not taken into account in the analysis because of the defocusing effect which provokes a  
331 large broadening of the peaks at higher angles. The analyses of the crystal structure and  
332 texturation of the samples were performed simultaneously by fitting the whole collection  
333 of diffraction patterns using conventional Rietveld method combined with a refinement of  
334 the orientation distribution (OD) with the algorithm E-WIMV<sup>75,76</sup> as implemented in the

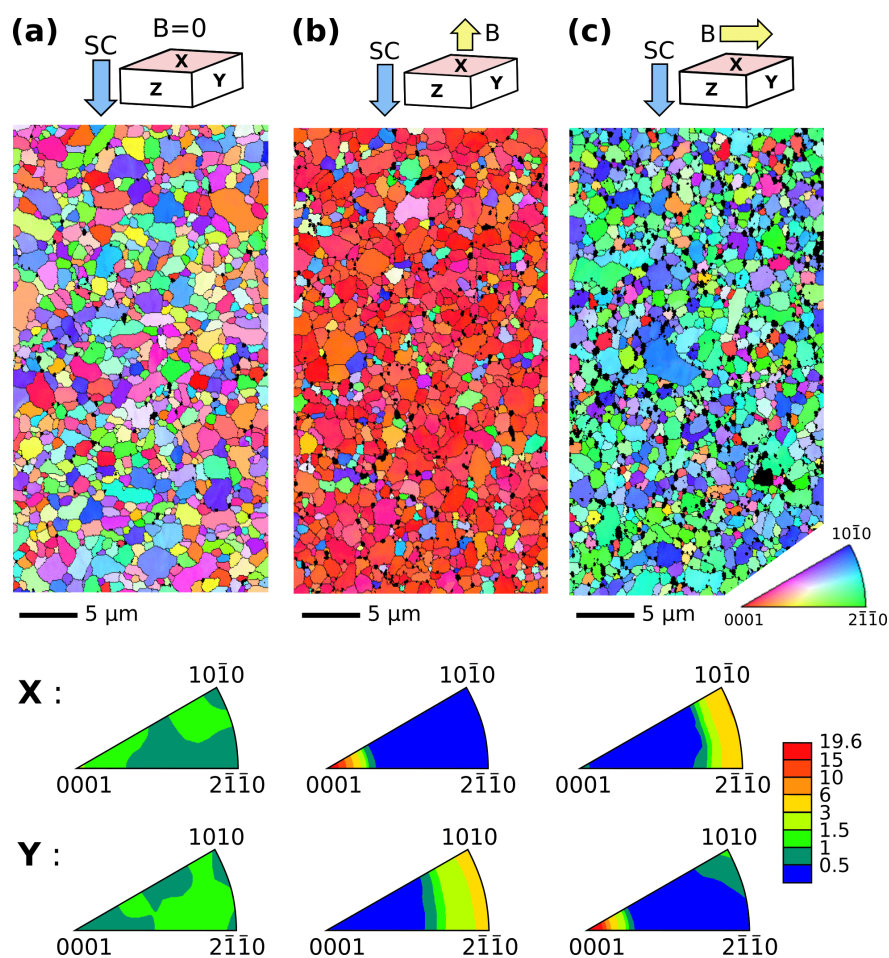


Figure 5: EBSD maps of the surface of (a) CrSi<sub>2</sub>-r, (b) CrSi<sub>2</sub>-v and (c) CrSi<sub>2</sub>-h. with the corresponding IPF

335 software MAUD<sup>56</sup>. In the initial step of this procedure, a first refinement of the OD was  
 336 made from the integrated intensities determined by Le Bail refinement. The obtained OD  
 337 was then introduced in the Rietveld algorithm and the initial structural model was refined.  
 338 The refined set of structural parameters was then used for OD refinement and so on until  
 339 the refinement procedure converged. Conventional  $R_{wp}$ ,  $R_{exp}$  and  $\chi^2$  profile reliability val-  
 340 ues were used to assess the conformity of the Rietveld refinement of the whole data set.  
 341 Similarly, the Rietveld-like  $R_b$  and  $R_w$  reliability values were used to assess the quality of  
 342 the OD refinement<sup>76</sup>. A selection of refined diffraction patterns for CrSi<sub>2</sub>-h and the refined  
 343 structural parameters for all the samples are shown in Figure 7a and **Table 1**, respectively.  
 344 A selection of refined diffraction patterns for CrSi<sub>2</sub>-r and CrSi<sub>2</sub>-v can be found in Figures

345 SI 4 and SI 5. The refined OD were used to calculate the IPF for all the samples shown in  
 346 Figure 7b. In addition to give precious texture information, this method has the advantage  
 347 to enable crystal structure refinement of the samples used for TE measurements despite  
 348 the strong effect of the texture on the diffracted intensities.

349

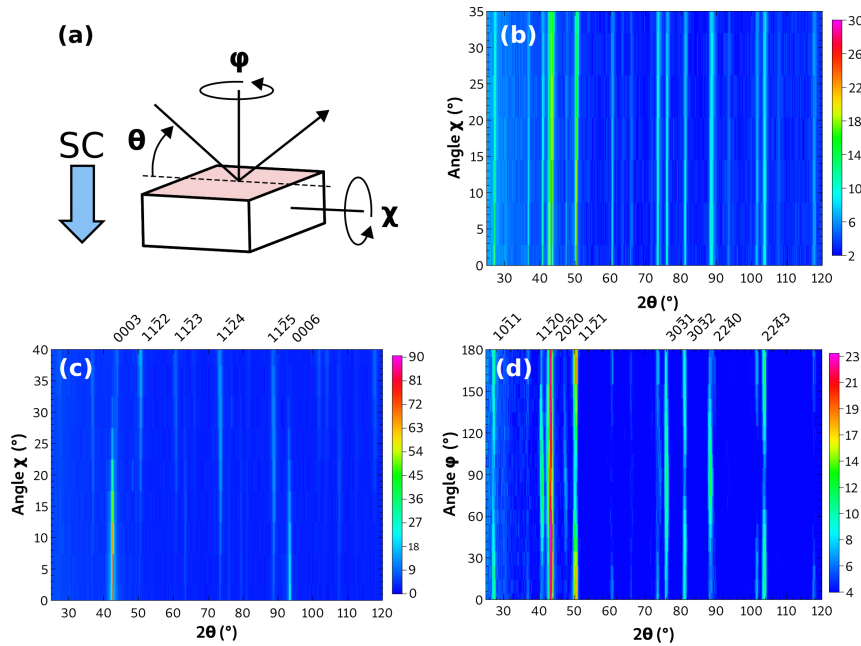


Figure 6: (a) Schematic representation of the XRD geometry used for texture analyses. 2D maps showing the square root of the diffracted intensities for (b)  $\text{CrSi}_2\text{-r}$  with  $0^\circ \leq \chi \leq 35^\circ$ , (c)  $\text{CrSi}_2\text{-v}$  with  $0^\circ \leq \chi \leq 40^\circ$  and (d)  $\text{CrSi}_2\text{-h}$  with  $0^\circ \leq \phi \leq 180^\circ$  and  $\chi = 25^\circ$

350 The refined lattice and structural parameters are similar for all the samples with  $a \approx$   
 351  $4.43 \text{ \AA}$ ,  $c \approx 6.36 \text{ \AA}$  and  $x \approx 0.166$  for the position coordinate of Si on the 6j Wickoff site.  
 352 These values correspond well to those determined above for the as-cast ingot and those  
 353 reported in the literature<sup>72</sup>. High profile reliability values were obtained due to the large  
 354 number of data patterns used for the refinement but also to the difficulty to take into  
 355 account the asymmetry of the very intense 0003 peak at low  $\chi$  angles in the patterns of  
 356  $\text{CrSi}_2\text{-v}$ . However, the OD  $R$ -factors show acceptable values especially in the case of the  
 357 present sample showing strong texturation strength. In the case of randomly oriented

358 CrSi<sub>2</sub>-r shown in Figure 6b, no visible variation of the relative peak intensities was noticed  
359 upon increasing of  $\chi$  angle. In agreement with EBSD analysis, the calculated IPF show no  
360 significant texturation. The XRD patterns of CrSi<sub>2</sub>-v and CrSi<sub>2</sub>-h reveal clear variation of  
361 the relative intensity of the peaks with  $\chi$  and  $\phi$  angles, respectively. In the case of CrSi<sub>2</sub>-v  
362 (Figure 6c), the intense 0003 reflection at  $\chi = 0^\circ$  rapidly decreases to become weak at  $\chi$   
363  $= 25^\circ$ . The  $11\bar{2}4$  reflection at  $2\theta \sim 74^\circ$ , with weak intensity at  $\chi = 0^\circ$ , becomes relatively  
364 intense at  $\chi = 30^\circ$ . It corresponds well to the angle of  $27.6^\circ$  that forms between the nor-  
365 mal of the families of Miller planes  $11\bar{2}4$  and 0003 and thus where they are expected to  
366 be in diffraction condition in the case of a perfectly oriented sample. In the case of CrSi<sub>2</sub>-  
367 h (Figure 6d), were the crystallites are predominantly oriented with their *c*-axis along *Y*  
368 direction, the Bragg intensities are strongly varying with the  $\phi$  rotation. For example, the  
369  $11\bar{2}0$  reflection at  $2\theta \sim 40^\circ$  is the most intense reflection when the sample *c*-axis texture  
370 direction is parallel with the diffraction plane (at  $\phi = 90^\circ$ ) than perpendicular (at  $\phi = 0^\circ$   
371 or  $180^\circ$ ). In the opposite, other Bragg reflections such as  $30\bar{3}2$  at  $2\theta \sim 81^\circ$  or  $22\bar{4}3$  at  $2\theta$   
372  $\sim 104^\circ$  have their maximum intensities at  $\phi = 0^\circ \equiv 180^\circ$ . Calculated IPF for CrSi<sub>2</sub>-v and  
373 CrSi<sub>2</sub>-h show high *c*-axis texture along the *X* and *Y* directions, respectively, in agreement  
374 with EBSD results. The maximum orientation densities of about 10 mrd in both cases are  
375 about twice smaller than those determined by EBSD. The discrepancy between the two  
376 techniques can be attributed to the limited number of analyzed grains by EBSD but also  
377 because of the imperfect fitting of the XRD diffraction patterns. However, both techniques  
378 agreed that the easy axis texture has a high and comparable orientation strength regard-  
379 less of the magnetic field direction. This is of uttermost importance in order to properly  
380 compare the directional TE properties and obtain reliable estimation of *ZT*.

381

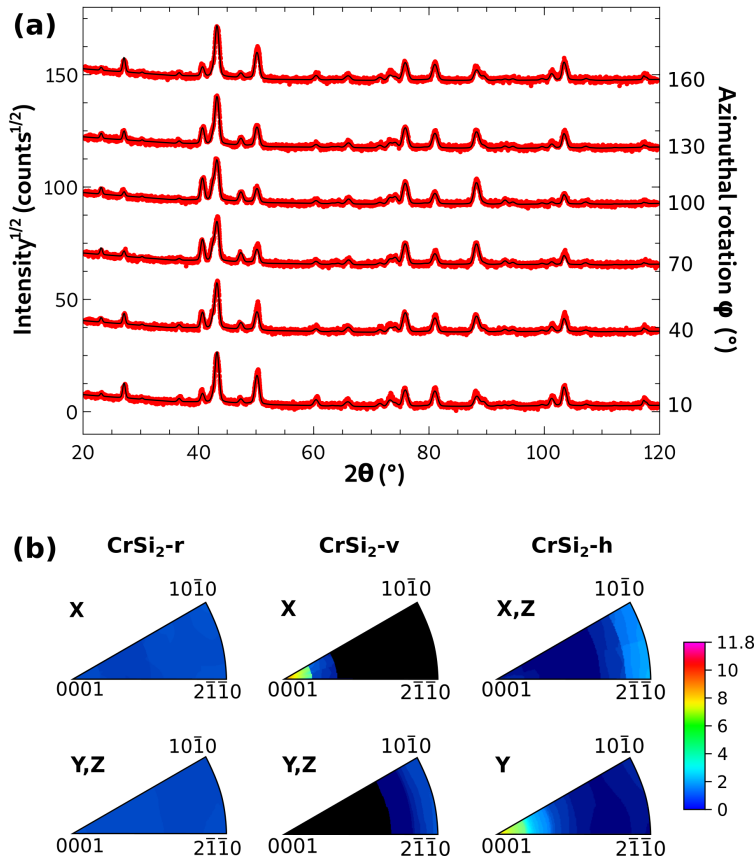


Figure 7: (a) Selection of Rietveld refined XRD patterns of CrSi<sub>2</sub>-h measured at different  $\phi$  rotations and at  $\chi = 20^\circ$  (b) IPF calculated from the combined Rietveld and OD refinements of the XRD patterns

### 3.3 Thermoelectric property measurements

The Seebeck coefficient, electrical resistivity and thermal conductivity of the magnetically oriented bulk CrSi<sub>2</sub> samples were measured over the 300-800 K temperature range, in order to evaluate their anisotropy. As shown in Figure 8, the thermal conductivity parallel ( $\kappa_{\parallel c}$ ) and perpendicular ( $\kappa_{\perp c}$ ) to the *c*-axis texture were measured on the pellet-shaped CrSi<sub>2</sub>-v and CrSi<sub>2</sub>-h samples, respectively. The measured thermal conductivities shown in Figure 9a reveal a moderate anisotropy. At 323 K for instance,  $\kappa_{\parallel c}$  is higher than  $\kappa_{\perp c}$  with values of 13.5 and 10.9 W m<sup>-1</sup> K<sup>-1</sup>, respectively. It corresponds to a  $\kappa_{\parallel c}/\kappa_{\perp c}$  ratio of 1.25 that remains constant up to the highest measured temperature of 773 K. This ratio is lower than for single crystals with reported value of 1.5<sup>34</sup>. This must be due the lower

Table 1: Structural parameters and R-values obtained by the combined structural and OD refinement of CrSi<sub>2</sub>-r, CrSi<sub>2</sub>-v and CrSi<sub>2</sub>-h XRD patterns

	CrSi <sub>2</sub> -r	CrSi <sub>2</sub> -v	CrSi <sub>2</sub> -h
Number patterns	8	9	162
<i>a</i> (Å)	4.43015(5)	4.42850(8)	4.42996(5)
<i>c</i> (Å)	6.36161(8)	6.36234(4)	6.36117(7)
Volume (Å <sup>3</sup> )	108.12	107.67	108.11
	Cr at 1/2, 0, 0 (Wickoff pos. 3d)		
<i>B</i> <sub>iso</sub> (Å <sup>2</sup> )	0.25(2)	0.15(1)	0.31(2)
	Si at <i>x</i> , - <i>x</i> , 1/3 (Wickoff pos. 6j)		
<i>x</i>	0.1662(4)	0.1669(5)	0.1661(5)
<i>B</i> <sub>iso</sub> (Å <sup>2</sup> )	0.29(2)	0.48(2)	0.37(2)
	Profil R-factors		
<i>R</i> <sub>wp</sub> (%)	23.3	31.0	29.85
<i>R</i> <sub>exp</sub> (%)	19.6	17.9	20.0
$\chi^2$	1.4	3.0	2.3
	OD R-factors		
<i>R</i> <sub>w</sub> (%)	4.6	13.4	14.5
<i>R</i> <sub>b</sub> (%)	7.6	15.4	16.3

orientation strength in the textured polycrystalline sample as well as the presence of grain boundaries participating in the diffusion of heat-carrying phonons. Randomly textured CrSi<sub>2</sub>-r logically shows intermediate values with  $\kappa$  of 11.9 W m<sup>-1</sup> K<sup>-1</sup> at 323 K.

The electronic contribution to the thermal conductivity was estimated using the Wiedemann-Franz law to be around 0.60±0.15 W m<sup>-1</sup> K<sup>-1</sup> for all the samples. This means that the difference of total thermal conductivities along the different crystallographic directions is mostly due to different lattice thermal conductivities, *i.e.*, propagation of heat-carrying phonons by the lattice. The present thermal conductivities are slightly higher than some reported  $\kappa$  values for polycrystalline CrSi<sub>2</sub> which are generally close to 10 W m<sup>-1</sup> K<sup>-1</sup> at the same temperature<sup>77</sup>. This is attributed to the higher relative density of our samples

402 ( $> 96\%$ ) compared to samples from the literature which usually show relative densities in  
 403 the range of 90 - 92 %. In the present case, higher densities could be achieved by increas-  
 404 ing significantly the sintering temperature to 1573 K using a pyrometer for temperature  
 405 control instead of a conventional K-type thermocouple limited to a maximum temperature  
 406 of 1273 K. Note that it has been shown both experimentally<sup>78,79</sup> and theoretically<sup>80</sup> that  
 407  $\kappa$  for  $\text{CrSi}_2$  is relatively high mainly owing to the high lattice thermal conductivity part,  
 408 which is responsible for over 90 % of  $\kappa$ .

409

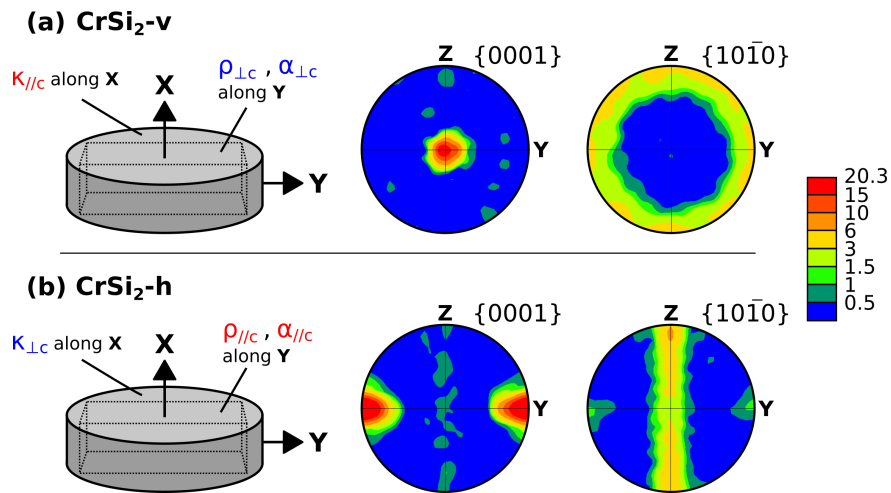


Figure 8: Scheme showing how the pellets of (a)  $\text{CrSi}_2\text{-v}$  and (b)  $\text{CrSi}_2\text{-h}$  were cut and measured for directional TE measurements and the corresponding  $\{0001\}$  and  $\{10\bar{1}0\}$  EBSD pole figures

410 For the measurement of electrical transport properties  $\parallel c$  and  $\perp c$ , the pellets were cut  
 411 into bars along the directions shown in Figure 8. The Seebeck coefficients and electrical  
 412 resistivities parallel ( $\alpha_{\parallel c}$  and  $\rho_{\parallel c}$ ) and perpendicular ( $\alpha_{\perp c}$  and  $\rho_{\perp c}$ ) to the  $c$ -axis texture  
 413 direction were measured on the samples  $\text{CrSi}_2\text{-h}$  and  $\text{CrSi}_2\text{-v}$ , respectively. The temper-  
 414 ature dependence of  $\alpha$  for all samples follows the same general tendency, *i.e.* increases  
 415 from 327 K to their maximum values around 625 - 650 K and then decreases up to the  
 416 highest measured temperature (Figure 9b). However, the magnitude of  $\alpha$  strongly varies  
 417 with regards to the crystallographic orientation. Indeed,  $\alpha_{\parallel c}$  reaches  $198 \mu\text{V K}^{-1}$  at 627

418 K while  $\alpha_{\perp c}$  is only  $134 \mu\text{V K}^{-1}$  at the same temperature which results in a  $\alpha_{\parallel c}/\alpha_{\perp c}$  ratio  
419 of 1.5. All these values compare very well with corresponding single crystal data from the  
420 literature reporting  $\alpha_{\parallel c}$  and  $\alpha_{\perp c}$  of about 200 and  $135 \mu\text{V K}^{-1}$ , respectively<sup>34</sup>.

421

422 The electrical resistivity (Figure 9c) exhibits less anisotropic behavior compared to the  
423 Seebeck coefficient. At about 650 K where the lowest electrical resistivities are measured,  
424 a  $\rho_{\parallel c}/\rho_{\perp c}$  anisotropy of about 0.75 is observed with  $\rho_{\parallel c} = 15 \mu\Omega \text{ m}$  and  $\rho_{\perp c} = 20 \mu\Omega$   
425 m. Measurements previously reported on single crystal confirms the lower  $\rho$  along [0001]  
426 than [10 $\bar{1}$ 0] but with a significantly larger anisotropy with a  $\rho_{[0001]}/\rho_{[10\bar{1}0]}$  ratio of 0.5 at  
427 650 K<sup>34,81</sup>. Note that a quantitative comparison of electronic resistivities between poly-  
428 crystalline samples and single crystals is in turn difficult to establish due to the presence of  
429 grain boundaries in the former. Surprisingly, electrical resistivity of CrSi<sub>2-r</sub> is consistently  
430 lower on the whole temperature range than for both textured samples whereas intermedi-  
431 ate values would be expected. Hall measurement performed on the non-textured sample  
432 CrSi<sub>2-r</sub> gives a charge carrier concentration  $n = 9 \times 10^{20} \text{ cm}^{-3}$  and an electron mobility  $\mu$   
433  $= 7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at 298 K which are consistent with literature data<sup>21</sup>. The lower resistivity  
434 of CrSi<sub>2-r</sub> is not attributed to different charge carrier concentrations among the sample as  
435 they were synthesized from the same powder batch and using the same process conditions.  
436 Unfortunately, this could not be verified experimentally since Hall measurements of non-  
437 isotropic materials require the determination of the galvanomagnetic tensor entering the  
438 Hall equation<sup>82</sup> which cannot be accurately determined on textured samples due to the  
439 imperfect crystallographic orientations<sup>83</sup>. The lower electrical resistivity of CrSi<sub>2-r</sub> is more  
440 likely due to its higher density (98 %) compared to that of the textured samples (96 %).

441

442 It is well known that  $\alpha$  and  $\rho$  are interdependent in TE materials which makes large  
443 improvement of the power factor ( $PF$ ) challenging. Interestingly, in the case of CrSi<sub>2</sub>, both  
444  $\alpha$  and  $\rho$  show the best TE properties along the  $c$ -axis. As a result, the magnetically oriented



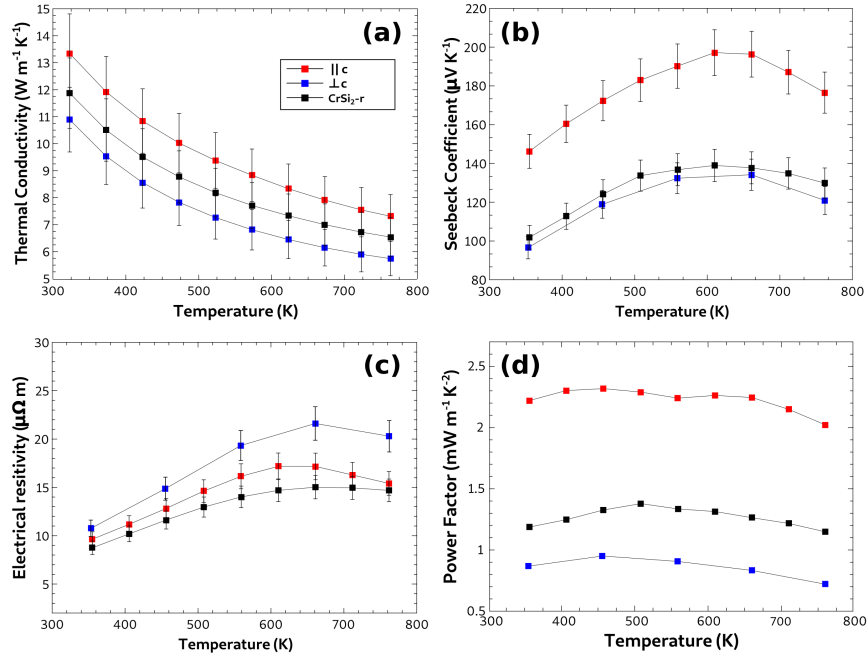


Figure 9: High temperature thermoelectric properties of  $\text{CrSi}_2$  parallel to the  $c$ -axis orientation (red), perpendicular to the  $c$ -axis orientation (blue), for random orientation (black) and for the reference sample (white): (a) thermal conductivity, (b) Seebeck coefficient, (c) electrical conductivity and (d) power factor. The estimated relative uncertainty is 11 %, 8 % and 6 % for the thermal conductivity, electrical resistivity and Seebeck coefficient, respectively<sup>84</sup>.

445 samples show that  $PF_{\parallel c}$  is much higher than  $PF_{\perp c}$  with values superior to  $2 \text{ mW m}^{-1} \text{ K}^{-2}$   
 446 over the whole temperature range measured as shown in Figure 9d. From the TE prop-  
 447 erties measured along the different texture direction on the samples  $\text{CrSi}_2\text{-v}$  and  $\text{CrSi}_2\text{-h}$ ,  
 448 it is possible to calculate an estimated directional  $ZT$  (Figure 10). It is worth to notice  
 449 that because the thermal conductivity and electronic properties measured  $\parallel c$  and  $\perp c$  were  
 450 not performed on the same samples, the  $ZT$  values presented here can only be taken as an  
 451 estimation. Nevertheless,  $\text{CrSi}_2\text{-r}$  have a maximum  $ZT$  of 0.13 at 773 K which is in good  
 452 agreement with literature data for polycrystalline  $\text{CrSi}_2$ <sup>20</sup>. Thanks to the larger  $PF$  and  
 453 despite a higher thermal conductivity,  $ZT_{\parallel c}$  is much higher than  $ZT_{\perp c}$  on the whole temper-  
 454 ature range reaching a maximum of 0.20 at 773 K. This represents a 50 % improvement of  
 455  $ZT$  compared to the randomly oriented sample. A prove of the high quality of the textura-  
 456 tion is that the present estimated  $ZT_{\parallel c}$  is very similar to the  $ZT$  along the  $c$ -axis reported for

457 single crystals (Figure 10)<sup>34</sup>. This demonstrates that slip casting under a magnetic field  
 458 is promising as a texturation processing route to fully take advantage of thermoelectric  
 459 materials with anisotropically decoupled electrical transport properties.

460

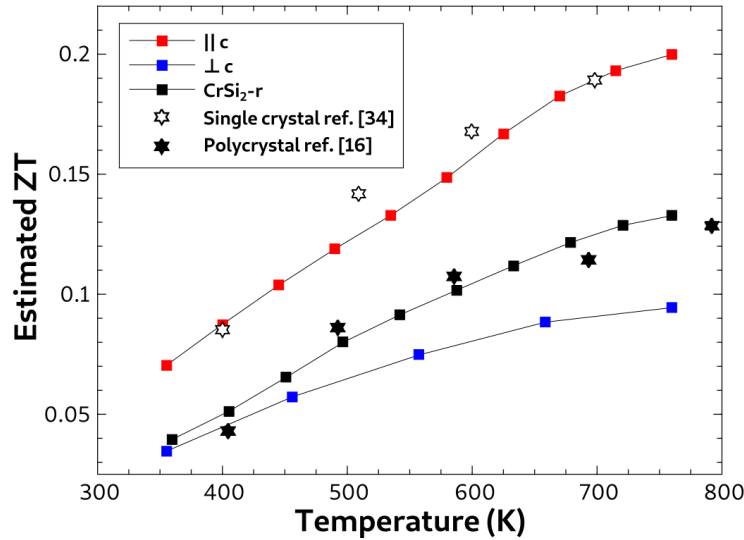


Figure 10: Estimated  $ZT$  of  $\text{CrSi}_2$  parallel to the  $c$ -axis orientation (red), perpendicular to the  $c$ -axis orientation (blue), for random orientation (black) and for the reference sample (white). Literature  $ZT$  values measured on single crystalline<sup>34</sup> and polycrystalline<sup>16</sup> samples are shown with empty and filled star symbols, respectively.

### 461 3.4 Theoretical calculations

462 DFT band structure calculations and electronic transport property computations were per-  
 463 formed on bulk  $\text{CrSi}_2$  in order to rationalize the anisotropy of the Seebeck coefficient and  
 464 the electrical resistivity experimentally observed for the magnetically  $c$ -axis oriented sam-  
 465 ples (see the experimental section for computational details). The calculated band struc-  
 466 ture and DOS are shown in Figures 11a and b, respectively. The band structure reveals  
 467 semiconducting properties with an indirect band gap of 0.35 eV between a valence-band  
 468 maximum at  $L$  and a conduction band minimum at  $M$ . The smallest value for a direct  
 469 band gap is 0.52 eV at  $L$  (see the first Brillouin zone (BZ) in Figure SI 6 for the label-  
 470 ing of the symmetry points and symmetry lines). These band gap values are in a good

471 agreement with those computed previously<sup>77,81,85</sup> and the experimentally measured opti-  
472 cal value<sup>86,87</sup>.

473

474 As previously noticed, the electronic structure of CrSi<sub>2</sub> is quite complicated due to its  
475 specific atomic arrangement<sup>77,81,85</sup> with both flat and dispersive bands computed in al-  
476 most all directions of the BZ (Figure 11a). Indeed, the crystal structure of CrSi<sub>2</sub> contains  
477 individual hexagonal CrSi<sub>2</sub> layers stacking along the *c*-axis which are interrelated via non-  
478 primitive translations ( $t = c/3$  and  $2c/3$ ) (Figure 2a). Such a stacking implies that each  
479 Si and Cr atom is surrounded by a well-defined polyhedron made of ten nearest neigh-  
480 bors with comparable Cr-Si and Si-Si bond distances. In addition to six planar neighbors  
481 (Si1) situated at 2.55 Å apart in the *a,b*-plane, each Cr is tetrahedrally coordinated along  
482 the *c*-axis with four interplanar neighbors (Si2) positioned at a shorter distance of 2.47 Å.  
483 Additionally, somewhat further apart from the central Cr atom, 4 Cr atoms form a dis-  
484 torted tetrahedron at a distance of about 3.06 Å which reflects some bonding interaction  
485 (see Figure 2b for the Cr atomic surrounding). Atom-projected DOS curves in the [-5,  
486 5] eV range (not shown here) indicate that the valence-band and conduction-band states  
487 originate from Cr states hybridized with Si states, whereas the states around the band  
488 gap show a predominantly Cr 3d character. This demonstrates strong covalent interac-  
489 tions in the structure. With shorter Cr-Si bonding distances and some Cr-Cr interaction  
490 along the *c*-axis, stronger covalency is expected than in the *a,b*-plane and consequently  
491 some anisotropy in the electronic transport properties should occur. This stronger cova-  
492 lency along the *c*-axis is demonstrated by the atomic orbital-projected DOS which indicate  
493 higher dispersion for the Cr  $d_{z^2}$  one (Figure 11b).

494

495 The electronic transport properties, namely the Seebeck coefficient and the electrical  
496 resistivity were computed as function of the temperature both parallel and perpendicular  
497 to the *c*-axis. There are compared to experiments in Figure 12. A good quantitative agree-

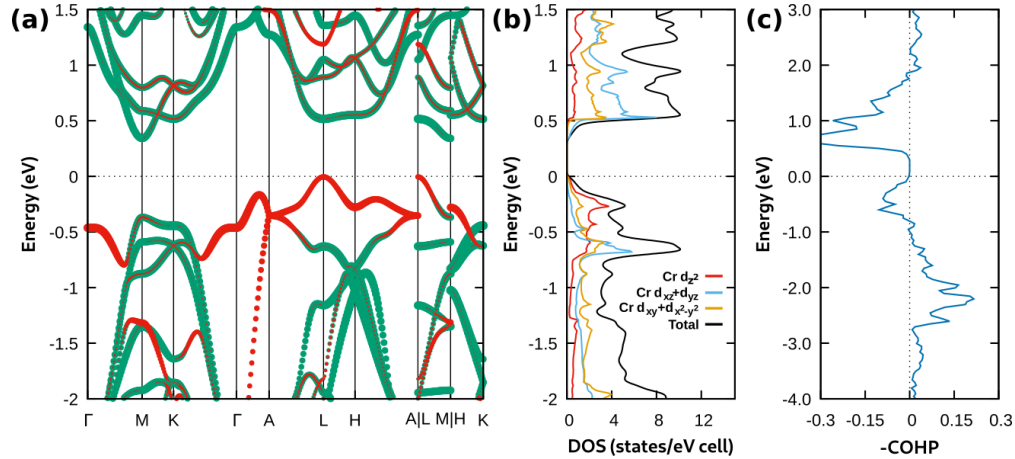


Figure 11: (a) calculated band-structure of  $\text{CrSi}_2$  with the contribution of the  $3d_{z^2}$  orbital in red and other 3d orbitals in green. (b) corresponding total and projected density of states (DOS). The cartesian axes  $z$ , and  $x$  and  $y$  are along the  $c$ -axis and in the  $a, b$ -plane, respectively. (c) Calculated COHP for Cr-Cr interactions in  $\text{CrSi}_2$ .

498 ment between theory and experiments is observed overall for the Seebeck coefficient. The  
 499 gradual increase with the temperature is well reproduced up to 600 K both for  $\alpha_{\parallel c}$  and  $\alpha_{\perp c}$ .  
 500 On the other hand, the rapid decrease of the Seebeck coefficient observed experimentally  
 501 above 600 K is not predicted by the calculations. Note that in our calculations, the number  
 502 of  $n$ -type carriers is always far less than the  $p$ -type holes due to the high extrinsic  $p$ -type  
 503 carrier concentration, and therefore the intrinsic bipolar excitation effect should be un-  
 504 significant. We think that a possible reason for the decrease of the thermopower beyond  
 505 600 K for both  $\alpha_{\parallel c}$  and  $\alpha_{\perp c}$  may be extrinsic excitations occurring at high temperature  
 506 rather than bipolar diffusion of carriers. Interestingly, the large anisotropy  $\alpha_{\parallel c}/\alpha_{\perp c}$  of the  
 507 Seebeck coefficient evidenced experimentally is theoretically confirmed. This anisotropy  
 508 needs to be rationalized. Indeed, in a single band model without competing scattering  
 509 events, the Seebeck coefficient is expected to be isotropic even if the electrons may have  
 510 a different effective mass along different crystallographic directions<sup>88,89</sup>. In the case of  
 511  $\text{CrSi}_2$ , the band structure shows a band along the  $\Gamma \rightarrow A$  symmetry line ( $\Delta$ ) (corresponding  
 512 to the  $c$ -direction in the real space) with the maximum in the vicinity of  $A$  that is only 0.15  
 513 eV below the maximum at  $L$  of the valence band along the  $A \rightarrow L$  symmetry direction ( $R$ )

514 (corresponding to the  $a,b$ -plane in the real space). The anisotropy of the Seebeck coeffi-  
 515 cient in  $\text{CrSi}_2$  may thus originate from a multi-band conduction with a different electron  
 516 mobility ratio along the  $c$ -axis and the  $a,b$ -plane. In a two-band model, the combined  
 517 Seebeck coefficient  $\alpha_{tot}$  is the electron mobility  $m^*$  weight average of the contributions  $\alpha_R$   
 518 and  $\alpha_\Delta$  of the bands  $R$  and  $\Delta$ , respectively, along a specific crystallographic direction in the  
 519 reciprocal space<sup>90,91</sup>:

$$\alpha_{tot} = \frac{N_R \beta \alpha_R + N_\Delta \alpha_\Delta}{N_R \beta + N_\Delta} \quad (7)$$

520 with  $N_R$  and  $N_\Delta$  the multiplicity of the bands and  $\beta$  the mobility ratio between the two  
 521 bands along this crystallographic direction:

$$\beta = \frac{m_R^*}{m_\Delta^*} \quad (8)$$

522 The effective masses and multiplicities of the two bands  $R$  and  $\Delta$  calculated from the  
 523 band structure calculations are given in Table 2.

Table 2: Multiplicities and calculated effective masses along  $c$  and in the  $a,b$  plane for the band  $R$  and  $\Delta$  of  $\text{CrSi}_2$

	Band $R$	Band $\Delta$
$m_c^*$	0.88	0.56
$m_{a,b}^*$	1.37	3.10
N	3	2

524 The Seebeck contribution of each band with respect to the temperature was calculated  
 525 using the parabolic band model and an estimated chemical potential  $\mu(T)$  (see the exper-  
 526 imental section for details) using the equation:

$$\alpha(T) = \frac{1}{eT} \frac{\int \epsilon^{3/2+\eta} (\epsilon - \mu) \left(-\frac{\partial f}{\partial \epsilon}\right) d\epsilon}{\int \epsilon^{3/2+\eta} \left(-\frac{\partial f}{\partial \epsilon}\right) d\epsilon} \quad (9)$$

527 with  $\eta = -1/2$  for acoustic phonon scattering. The Seebeck coefficient values obtained  
 528 from equation (7) by introducing  $\alpha(T)$  calculated from eq. (9) and the parameters given  
 529 in Table 2 for each band successfully predict qualitatively the large anisotropy measured  
 530 experimentally with a  $\alpha_{\parallel c}/\alpha_{\perp c}$  ratio of about 1.4 all over the 300 - 800 K temperature  
 531 range (Figure SI 7a). This result shows that the anisotropy in Seebeck must come from the  
 532 difference in mobility ratio between the hole pocket participating in the electrical conduc-  
 533 tion. The contribution from the pocket  $\Delta$  is large and leads to a much enhanced Seebeck  
 534 coefficient along the  $c$ -axis. Note that using a somewhat more sophisticated approach de-  
 535 rived from the microscopic electronic model for multi-valleyed materials with parabolic  
 536 bands proposed by Bies *et al.*<sup>89</sup> modified for non-degenerate bands, leads to a more quan-  
 537 titative agreement (compare Figure 12a and Figure SI 7b).

538

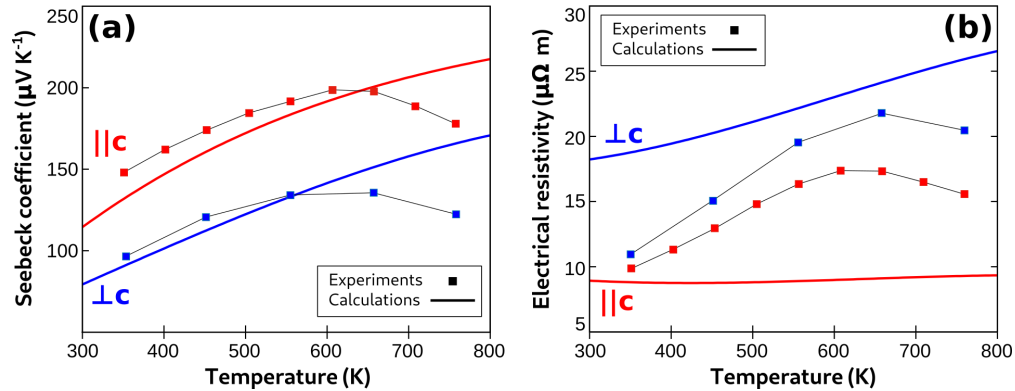


Figure 12: Calculated (solid line) and experimental (signs) Seebeck coefficient (a) and electrical resistivity (b) for CrSi<sub>2</sub>. Transport properties along the  $c$ -axis and in the  $a,b$ -plane are in blue and red, respectively.

539 The electrical resistivity behavior (especially  $\rho_{\perp c}$ ) shown in Figure 12b indicates a  
 540 degenerated-semiconductor character for CrSi<sub>2</sub> because of the high hole concentration  
 541 that remains stable over the whole 300 - 800 K temperature range (Figure SI 1). However,  
 542 it largely deviates quantitatively from the experimental data as a result of the constant  
 543 carrier lifetime approximation used for the calculations, within which the temperature de-  
 544 pendence of the scattering time as the result of lattice thermal vibration is not considered

545 at all. Nonetheless, the anisotropy is correctly reproduced by the calculations with the  
546 highest electrical resistivity computed along the  $c$ -axis. Note that both  $R$  and  $\Delta$  bands (Ta-  
547 ble 2) show small effective masses  $m_c^*$  with respect to  $m_{a,b}^*$ , and therefore high hole mobility  
548 along the  $c$ -axis. This is in agreement with the Si-Si, Si-Cr and Cr-Cr covalent character  
549 stronger along the  $c$ -axis than in the  $a,b$ -plane which leads to more dispersive bands favor-  
550 ing smaller effective masses. In particular, the strong Cr-Cr interaction along the  $c$ -axis is  
551 confirmed by an analysis of its corresponding COHP curve (Figure 11c) and its integrated-  
552 ICOHP value (0.364 Ry/cell) with respect to that of the very weak Cr-Cr interaction in  
553 the  $a,b$ -plane (-ICOHP = 0.036 Ry/cell). In agreement with a previous report<sup>77</sup>, the Cr-Cr  
554 COHP curve along the  $c$ -axis features quite substantially Cr antibonding states below the  
555 Fermi level. This indicates that (i) the bonding situation in CrSi<sub>2</sub> is not fully optimized,  
556 and (ii) these antibonding states play a major role in determining the electrical transport  
557 properties.

## 558 4 Conclusion

559 In this paper, an original synthesis method to obtained good quality and highly textured  
560 polycrystalline CrSi<sub>2</sub> material is presented. It consists in applying a strong magnetic field  
561 during the slip casting of a CrSi<sub>2</sub> suspension to orient the particles along their easy mag-  
562 netization. Both EBSD and XRD analyses indicated a strong fiber texture symmetry of the  
563 sintered pellets with maximum {0001} texture densities > 10 mrd parallel to the magnetic  
564 field direction. The TE properties were measured parallel and perpendicular to the texture  
565 direction. The thermal conductivity showed a moderate anisotropy with a  $\kappa_{\parallel c}/\kappa_{\perp c}$  ratio  
566 of 1.25 at 773 K. Surprisingly, the Seebeck coefficient showed a much larger anisotropy  
567 with  $\alpha_{\parallel c}/\alpha_{\perp c} \sim 1.5$  and  $\alpha_{\parallel c}$  reaching a maximum of 198  $\mu\text{V K}^{-1}$  at 650 K. The electrical  
568 resistivity was also lower  $\parallel c$  which results in largely improved  $PF_{\parallel c}$  of about 2  $\text{mW m}^{-1}$   
569  $\text{K}^{-2}$  on the whole temperature range. This is 100 % and 60 % higher than  $PF_{\perp c}$  and  $PF$  of  
570 a randomly oriented sample, respectively. DFT calculations revealed that the high  $\alpha_{\parallel c}$ , and

571 consequently  $PF_{\parallel c}$ , originate from a two-band conduction and the large presence of the Cr  
572  $d_{z^2}$  states near the valence band maximum in  $\text{CrSi}_2$ . The measurements of the TE proper-  
573 ties along the different texture directions of two oriented samples enable the estimation  
574 of the directional  $ZT$ . A maximum  $ZT_{\parallel c}$  of 0.2 at 773 K was estimated which is consistent  
575 with values reported for single crystal and represents a 50 % improvement compared to  
576 untextured polycrystalline  $\text{CrSi}_2$ . The present work clearly shows that texturation can be  
577 advantageously used to improved the TE properties of bulk polycrystalline thermoelectric  
578 silicides that are promising materials for industrial applications. Additional studies are  
579 currently being undertaken to increase even more the industrial potential of this process,  
580 for example, by increasing the dimension of the samples that can be synthesized (without  
581 inducing texture heterogeneity) but also by reducing the magnetic field strength required  
582 for the particles orientation (ideally using permanent magnets). Finally, the approach used  
583 here for silicides can certainly also be applied to other high performance materials showing  
584 large anisotropy of their TE properties such as higher manganese silicides or SnSe.

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## 588 **Supporting Information**

589 Supporting Information Available: Calculated carrier concentration as a function of tem-  
590 perature, XRD patterns of the samples  $\text{CrSi}_2$ -v,  $\text{CrSi}_2$ -h and  $\text{CrSi}_2$ -r after CIP treatment,  
591 SEM-EDS spectrum of the  $\text{CrSi}_2$  phase, Rietveld refined XRD patterns of  $\text{CrSi}_2$ -v measured  
592 at different  $\chi$  rotations and at  $\phi = 0^\circ$ , Rietveld refined XRD patterns of  $\text{CrSi}_2$ -r measured  
593 at different  $\chi$  rotations and at  $\phi = 0^\circ$ , First Brillouin zone of  $\text{CrSi}_2$  and Calculated thermal  
594 dependence of the Seebeck coefficient of  $\text{CrSi}_2$  using two different theoretical models.

595 This material is available free of charge via the Internet at <http://pubs.acs.org>



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859 **Graphical TOC Entry**

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