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# Preparation, thermal stability and electrical transport properties of vaesite, NiS<sub>2</sub>

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Vaesite, a nickel chalcogenide with NiS<sub>2</sub> formula, has been synthesized and studied by theoretical and experimental methods. NiS<sub>2</sub> was prepared by solid-state reaction under vacuum and densified by hot-pressing, at different consolidation conditions. Dense single-phase pellets (relative densities >94%) were obtained, without significant lattice distortions for different hot-pressing conditions. The thermal stability of NiS<sub>2</sub> was studied by thermogravimetric analysis. Both as-synthesized and hot-pressed NiS<sub>2</sub> have a single phase nature, although some hot-pressed samples had traces of the sulfur deficient phase, Ni<sub>1-x</sub>S (<1%vol), due to the strong desulfurization at T > 340°C. The electronic band structure and density of states were calculated by Density Functional Theory (DFT), indicating a metallic behavior. However, the electronic transport measurements showed p-type semiconductivity for bulk NiS<sub>2</sub>, verifying its characteristic behavior has a Mott insulator. The consolidation conditions strongly influence the electronic properties, with the best room-temperature Seebeck coefficient, electrical resistivity and power factor being 182µVK<sup>-1</sup>, 2257µΩm and 14.1µWK<sup>-2</sup>m<sup>-1</sup>, respectively, pointing this compound as a good starting point for a new family of thermoelectric materials.

1 **Preparation, thermal stability and electrical transport**  
2 **properties of vaesite, NiS<sub>2</sub>**

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**39 Abstract**

40 Vaesite, a nickel chalcogenide with  $\text{NiS}_2$  formula, has been synthesized and studied by  
41 theoretical and experimental methods.  $\text{NiS}_2$  was prepared by solid-state reaction under vacuum  
42 and densified by hot-pressing, at different consolidation conditions. Dense single-phase pellets  
43 (relative densities >94%) were obtained, without significant lattice distortions for different hot-  
44 pressing conditions. The thermal stability of  $\text{NiS}_2$  was studied by thermogravimetric analysis.  
45 Both as-synthesized and hot-pressed  $\text{NiS}_2$  have a single phase nature, although some hot-pressed  
46 samples had traces of the sulfur deficient phase,  $\text{Ni}_{1-x}\text{S}$  (<1%vol), due to the strong  
47 desulfurization at  $T > 340$  °C. The electronic band structure and density of states were calculated  
48 by Density Functional Theory (DFT), indicating a metallic behavior. However, the electronic  
49 transport measurements showed p-type semiconductivity for bulk  $\text{NiS}_2$ , pointing to the presence  
50 of important electron correlation effects that lead to a Mott insulator behavior. The consolidation  
51 conditions strongly influence the electronic properties, with the best room-temperature Seebeck  
52 coefficient, electrical resistivity and power factor being  $182 \mu\text{VK}^{-1}$ ,  $2257 \mu\Omega\text{m}$  and  $14.1 \mu\text{WK}^{-1}$   
53  $\text{m}^{-1}$ , respectively, pointing this compound as a good starting point for a new family of  
54 thermoelectric materials.

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**57 Introduction**

58 The search for new, clean, energy sources, as well as the optimization of their use, has become a  
59 major issue in contemporary societies. According to the European Environment Agency, current  
60 conventional thermal power plants have an energy efficiency around 35-45%, most of the energy  
61 being lost as wasted heat [EEA 2013]. Thermoelectric (TE) materials, which convert thermal  
62 energy into electric energy (Seebeck effect) and vice-versa (Peltier effect), are a promising  
63 solution to increase the efficiency of many devices and equipment. The potential of a material for  
64 thermoelectrics can be evaluated by its figure of merit,  $zT = \alpha^2 T / \rho \lambda$ , where  $\alpha$ ,  $T$ ,  $\rho$  and  $\lambda$  are the  
65 Seebeck coefficient, absolute temperature, electrical resistivity and thermal conductivity,  
66 respectively [Gonçalves & Godart, 2014].

67 Current commercially available TE materials contain rare, expensive and toxic elements, being  
68 necessary to develop new, cheap, abundant and environment-friendly alternatives. Metal sulfides  
69 are interesting candidates, as they fulfill these requirements [Ge et al., 2016]. Tetrahedrites are  
70 cheap and easily available mineral sulfosalts that present large figures of merit and are seen as  
71 having good potential for thermoelectric applications [Lu et al., 2016]. Pyrite ( $\text{FeS}_2$ ) is low cost  
72 sulfide with simple synthesis and moderate thermoelectric properties [Harada, 1998; Zuñiga-  
73 Puelles et al., 2019]. In this compound, the large electrical resistivity and thermal conductivity  
74 observed in the pristine material are the major constraints to their practical use. These properties  
75 can be tuned to much lower values by changing both the composition and microstructure [Uhlig,  
76 2014]. Vaesite ( $\text{NiS}_2$ ), another transition mineral sulfide with pyrite structure [Krill et al., 1976],  
77 was reported, but its thermoelectric properties were only poorly explored. At equilibrium

78 conditions, NiS<sub>2</sub> is a stoichiometric compound, stable up to 1020 °C [Waldner & Pelton, 2004].  
79 However, previous studies also suggested that vaesite is an intrinsic non-stoichiometric  
80 compound, with a variable metal concentration and a stable anion content. These deviations from  
81 stoichiometry, corroborated by a change of the cell parameters, have important consequences in  
82 the electrical and magnetic properties [Gautier et al., 1972; Krill et al., 1976]. Measurements on  
83 single crystals, natural materials and samples prepared by high-pressure synthesis indicated a  
84 semiconducting behavior for this compound [Bither et al., 1968; Kautz et al., 1972; Gautier et  
85 al., 1972; Krill et al., 1976], which pointed to the possibility of using it as thermoelectric  
86 material. Nevertheless, thermoelectric measurements made on thin films showed a p-type  
87 semiconducting behavior, but small room temperature Seebeck coefficients, which contrasts with  
88 the large values obtained on single crystals prepared by halogen transport [Bither et al., 1968].  
89 Moreover, albeit the preparation of synthetic bulk NiS<sub>2</sub> by solid state route has been previously  
90 described [Krill et al., 1976; Matsuura et al., 2000], it resulted in highly porous pellets, easily  
91 disaggregated, not suitable for the electrical transport properties study. In this work, we explored  
92 the solid-state route followed by hot-press to prepare dense vaesite samples, suitable for their  
93 characterization, including the electrical transport properties (electrical resistivity and Seebeck  
94 coefficient) investigation. Density functional theory calculations were also performed and their  
95 results compared with the experimental data.

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## 101 **Materials & Methods**

102 NiS<sub>2</sub> samples, with an average mass of ~1.5 g, were prepared by high-temperature reacting the  
103 elements inside quartz ampoules. The desired quantities of Ni and S were put inside the quartz  
104 ampoules (8 mm inner diameter, 1 mm wall thickness), which were evacuated down to  
105  $6 \times 10^{-5}$  mbar and sealed. An excess of 5wt% of the chalcogenide element was considered in  
106 order to compensate eventual evaporation losses. The ampoules were placed in a horizontal tube  
107 furnace pre-heated at 150 °C, and heated at 800 °C for 12 h, with a heating speed of 0.3 °Cmin<sup>-1</sup>  
108 and two intermediate dwells at 400 °C and 650 °C for 8 h. Afterwards, they were slowly cooled  
109 inside the furnace. The samples were then manually ground, cold-pressed, sealed in evacuated  
110 quartz ampoules and heated again in the same conditions. Finally, the samples were once more  
111 manually powdered, a ~30wt% excess of S was added, and ~0.6 g of the resulting powder was  
112 charged in a high-density graphite mould that was used in the hot-pressing procedure. The hot-  
113 press was made under inert atmosphere (Ar), increasing the pressure at 3 MPa•min<sup>-1</sup> up to  
114 56 MPa and the temperature at 25 °Cmin<sup>-1</sup> up to three different dwell temperatures, 700 °C,  
115 720 °C and 750 °C, staying there for 1h30 min. Temperature was then decreased to <100 °C at  
116 25 °Cmin<sup>-1</sup> and the pressure removed at 3 MPa•min<sup>-1</sup>.

117 Part of each pellet was manually ground and characterized by powder X-ray diffraction (XRD).  
118 A PANalytical X'Pert PRO diffractometer (Bragg-Brentano geometry, Cu K $\alpha$  radiation) was  
119 used. The powders were placed in a low-noise Si single crystal XRD holder and  $2\theta$  was scanned  
120 from  $20^\circ$  to  $90^\circ$ , with a step size of  $0.033^\circ$  and a time per step of 50 s. Phase identification was  
121 made through comparison of the collected diffractograms with reference patterns taken from the  
122 literature. Cell parameters and theoretical density were calculated and refined from the powder  
123 diffraction data, using the Unit-Cell software [Holland & Redfern, 1997]. Experimental values of  
124 density were determined by the Archimedes method. Porosity was estimated by image analysis,  
125 using the ImageJ software.

126 Optical microscopy, scanning electron microscopy (SEM) and energy-dispersive spectroscopy  
127 (EDS) were used for microstructure characterization and chemical composition analysis. It was  
128 used an optical microscope ZEISS SteREO Discovery V20 and a JEOL JSM-7001F field  
129 emission gun scanning electron microscope (accelerating voltage of 25kV), with an Oxford  
130 Instruments EDS spectroscopy system attached.

131 Thermal stability was evaluated with thermogravimetric analysis (TGA). A Dupont 951 Thermo-  
132 gravimetric Analyzer was used. Samples were manually grounded, placed in platinum pans, and  
133 heated from  $25^\circ\text{C}$  to  $950^\circ\text{C}$ , at a heating rate of  $10^\circ\text{Cmin}^{-1}$  in an inert atmosphere ( $\text{N}_2$ ) flowing  
134 at a rate of  $60\text{ mL}\cdot\text{min}^{-1}$ .

135 The nature of chemical bonding was analysed by Raman spectroscopy, using a Horiba LabRam  
136 HR Evolution Raman microspectrometer (laser with  $\lambda=532\text{ nm}$  and  $10\text{ mW}$  power). Raman  
137 spectra were collected from  $150$  to  $1800\text{ cm}^{-1}$ , the laser light being focused with a  $100\times$   
138 objective. 4 scans, with 30 seconds each, were made for each spectrum. Lower laser powers (25-  
139 50% of maximum) were required in some measurements to avoid the surface damage.

140 Electrical transport properties were measured between  $20$ - $300\text{ K}$ , at a rate of  $0.3\text{ Kmin}^{-1}$  for the  
141 Seebeck coefficient and  $0.5\text{ Kmin}^{-1}$  for electrical resistivity, using a closed-cycle cryostat. A  
142 system based on the Chaikin's device to measure organic single crystals [Chaikin & Kwak,  
143 1975] was used to measure the Seebeck coefficient. The samples were first shaped to a plate-like  
144 geometry ( $\sim 0.5\times 0.5\times 3.5\text{ mm}^3$ ) and glued with GE varnish to two gold foils (located in two single  
145 crystal quartz blocks heated independently), and the foils are glued with GE varnish to the quartz  
146 blocks, so that each side of the sample is thermally anchored to one of the blocks. Two gold  
147 wires connected to the sample, then establishing the electrical contacts. The voltage was  
148 measured with a low frequency AC technique, with a maximum temperature gradient in the  
149 sample of  $1\text{ K}$ , controlled by two Au-Fe-Chromel thermocouples connected to the quartz blocks.  
150 The electrical resistivity was measured in the same bar-shaped samples through the four-point  
151 technique, using an AC resistance bridge and a current of  $1\text{ mA}$ . Activation energies were  
152 obtained from the electrical resistivity data.

153

## 154 **Band structure calculations**

155 The band structure and density of states of  $\text{NiS}_2$  were calculated with the help of the WIEN2k  
156 package [Blaha et al., 2018]. Calculations were performed within the density functional theory

157 (DFT), using linear augmented plane wave (LAPW) method to solve the Kohn-Sham equations.  
158 Lattice parameters and atomic positions were taken from experimental data [Villars & Calvert,  
159 1986]. Both local spin density approximation (LSDA) and generalized gradient approximation  
160 with a modified Becke-Johnson potential (GGA+mBJ) were used to approach the exchange-  
161 correlation energy [Koller, Trans & Blaha, 2012]. The parametrization developed by Perdew-  
162 Burke-Ernzerhof was applied for the generalized gradient approximation (PBE-GGA) [Perdew,  
163 Burke & Ernzerhof, 1996]. A cut-off energy of 6 Ry and 1000 k-points in the irreducible part of  
164 the Brillouin zone were used for the self-consistent calculations. The criteria of convergence was  
165 set at 0.0001 Ry.

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## 168 Results and discussion

169 The powder X-ray diffraction results always point to single phase samples, both after solid-state  
170 reaction and hot-pressing (**Figure 1**). All peaks are indexed to the NiS<sub>2</sub> crystal structure, of cubic  
171 Pa3 space group. The lattice parameter after solid-state reaction is  $a=5.685(2)$  Å. Lattice  
172 constants were also calculated for the pellets densified at different consolidation conditions  
173 (**Table 1**), remaining unchanged.

174 The pellets obtained after the initial heating cycle were highly porous and easily disaggregated,  
175 in agreement with the previous results [Krill et al., 1976; Matsuura et al., 2000]. Representative  
176 microstructures of NiS<sub>2</sub>, as-synthesized and hot-pressed, were captured by SEM (**Figure 2**). As-  
177 synthesized samples have several pores at the surface, visible to the naked eye, and poorly  
178 agglomerated grains. On the other hand, after hot-pressing there is no distinguishable grain  
179 boundaries and the porosity decreased substantially (only small closed pores are present)  
180 indicating a successful sintering of the grains. The measured compositions, analyzed by EDS, as  
181 well as secondary phases detected, are summarized in **Table 2**. The microstructure of all samples  
182 is homogeneous, being mainly composed of NiS<sub>2</sub>. In samples consolidated at 700 °C/56 MPa and  
183 750 °C/56 MPa there is the presence of a sulfur deficient phase, Ni<sub>1-x</sub>S, but in minor amounts (<  
184 1vol%). A small deviation from the nominal composition was observed in all samples.

185 The relative density of the consolidated samples increased with increasing hot-pressing  
186 temperature, achieving 97% of the theoretical density when processed at 750 °C and 56 MPa.  
187 The high relative densities, >94%, and low estimated porosity, <6% (obtained by image  
188 analysis), indicate a successful consolidation of the pellets.

189 Raman spectroscopy was used to characterize the vibrational frequencies specific of the chemical  
190 bonds on the hot-pressed samples. Due to their similarity, only one spectrum is shown (**Figure**  
191 **3**). The spectra are in qualitative agreement with literature reports [Marini et al., 2011]. Vaesite  
192 has five Raman active modes: A<sub>g</sub>, E<sub>g</sub> and three T<sub>g</sub> modes. Since Ni atoms are located at the  
193 center of inversion, all Raman active modes correspond to displacements of the sulfur atoms.  
194 Two T<sub>g</sub> and E<sub>g</sub> modes correspond to S-S pairs libration. A<sub>g</sub> and a T<sub>g</sub> modes correspond,  
195 respectively, to in-phase and out-of-phase stretching of the S-S dimers [Marini et al., 2011]. In  
196 the collected spectra only four peaks were detected: two peaks at 268 and 278 cm<sup>-1</sup>,



197 corresponding to  $T_g(1)$  and  $E_g$  symmetries (S-S libration); a peak at  $474\text{ cm}^{-1}$  and a shoulder at  
198  $485\text{ cm}^{-1}$ , corresponding to  $A_g$  and  $T_g(2)$  vibrational modes (stretching vibrations). The fifth  
199 Raman active mode,  $T_g(3)$ , is not visible in the spectra and has never been reported before in  
200 previous Raman data available in the literature [Marini et al., 2011]. In all the consolidation  
201 conditions, the peaks are located at the same shift values and have similar widths, suggesting that  
202 the different sintering temperatures do not introduce distortions or strains in the crystal lattice  
203 and that the type and number of bonds are similar.

204 The thermal stability of  $\text{NiS}_2$  was evaluated by thermogravimetric analysis under  $\text{N}_2$  atmosphere,  
205 before and after hot-pressing. The results are shown in **Figure 4**. There is a small mass loss at  
206  $\sim 80^\circ\text{C}$  for both non-consolidated and consolidated samples, of 4wt% and  $<1\text{wt}\%$ , respectively,  
207 due to dehydration and desorption of chemical species formed during storage under air (the non-  
208 consolidated materials was stored for  $\sim 6$  months, while the consolidated was characterized just  
209 after the preparation). At higher temperatures, a significant mass drop ( $\sim 35\%$ ) is observed for  
210 both samples, due to desulfurization of  $\text{NiS}_2$ . The desulfurization starts at  $\sim 340^\circ\text{C}$  in the hot-  
211 pressed sample and at  $\sim 440^\circ\text{C}$  in non-consolidated powders. This difference of almost  $100^\circ\text{C}$  is  
212 most likely related with the excess of 30% of sulfur added to the samples prior hot-pressing. The  
213 real amount of lost sulfur during the hot consolidation was not controlled and therefore, it is  
214 possible that not all the sulfur in excess has been evaporated from the pellet, originating a sulfur-  
215 saturated vaesite structure. If that happened, then the early sulfur loss can be caused by the  
216 excess of sulfur. Previously reported thermogravimetric analysis of elemental sulfur indicate that  
217 sulfur starts to evaporate at  $200^\circ\text{C}$  and by  $320^\circ\text{C}$  the analyzed mass is lost in its total [Takahashi  
218 et al., 2015]. If there is excess of sulfur in vaesite structure, then sulfur might start being released  
219 at lower temperatures. In order to avoid thermal degradation of  $\text{NiS}_2$  and formation of S-deficient  
220 phases, the service temperature of these materials should not surpass  $\sim 340^\circ\text{C}$ . There are no  
221 previous studies on the mechanisms of decomposition of vaesite but the similarity with pyrite  
222 TGA results [Lambert, Simkovich & Walker, 1998] suggests that  $\text{NiS}_2$  might decompose by  
223 similar mechanisms of sulfur direct escape from vaesite lattice, followed by a decomposition of  
224  $\text{NiS}_2$  into  $\text{Ni}_{1-x}\text{S}$  and subsequently, into  $\text{NiS}$ .

225 The band structure and density of states of  $\text{NiS}_2$  calculated using GGA+mBJ (the LSDA give  
226 similar results) are shown in **Figure 5**. From the DFT calculations, one could expect  $\text{NiS}_2$  to be  
227 metallic due to the partly filled  $e_g$  band. The temperature dependence of Seebeck coefficient and  
228 electrical resistivity, for the different consolidation conditions, are indicated in **Figures 6 and 7**.  
229 Seebeck coefficient, electrical resistivity and power factors at room temperature are shown in  
230 **Table 3**. In all samples, the Seebeck coefficient is positive, indicating that the major charge  
231 carriers are holes (p-type semiconductor). The incoherence between the theoretical and  
232 experimental results can be related to the electron-electron interactions that lead to a Mott  
233 insulator, i.e., an insulator material due to strong correlation effects originated by electrostatic  
234 repulsion between electrons, which are not accounted for by conventional band theories. The  
235 bandgap of vaesite has been reported to be  $0.27\text{ eV}$  [Kautz et al., 1972].



236 The highest Seebeck coefficient and power factor were obtained for the pellet hot-pressed at  
237 720 °C and 56 MPa. Unlike the other samples, this pellet did not show evidences of secondary  
238 sulfur-deficient NiS. No experimental work regarding NiS electrical properties was found, but  
239 DFT calculations predict a metallic character [Persson, 2014]. The presence of a metallic phase,  
240 even if in small amounts, is expected to be detrimental to the vaesite thermoelectric properties  
241 and can be the reason for the lower power factors on the pellets hot-pressed at 700 °C and  
242 750 °C. Conversely, the non-presence of NiS in the pellet hot-pressed at 720 °C points to a lower  
243 sulfur content on it (that due to the small difference to the 1:2 stoichiometry could not be  
244 detected), which is able to affect the Seebeck coefficient. Therefore, a higher Seebeck coefficient  
245 does not seem to be related with the aggregation of the samples, but with the sensitivity of the  
246 electronic properties (carrier concentration and type, conductivity and mobility) to stoichiometric  
247 variations and crystal defects (grain boundaries and impurities).

248 The values of  $\rho$  correspond to the values reported in the literature for polycrystalline samples  
249 [Gautier et al., 1972; Krill et al., 1976]. A decrease of resistivity is verified with the increase of  
250 the hot-pressing temperature. A higher hot-pressing temperature led to a higher aggregation of  
251 the grains, translated into a higher relative density and less grain boundary area, resulting in a  
252 decrease of the resistivity. The activation energy of these materials is slightly smaller than the  
253 one observed in Bi<sub>2</sub>Te<sub>3</sub> (**Table 3**) pointing to a possible use as thermoelectric materials close to  
254 room temperature. To the best of our knowledge, there are no reported measurements of the  
255 Seebeck coefficient of bulk samples. Reported values of  $\alpha$  and  $\rho$  for single crystals and thin films  
256 tend to be higher than the obtained in this work, probably due to the isotropic character of bulk  
257 polycrystalline samples. The drop in electrical resistivity curves at 50 K, signaled by an arrow,  
258 indicate a magnetic phase transition of NiS<sub>2</sub> from antiferromagnetic to weak ferromagnetic.  
259 The electrical resistivity increases with decreasing temperature, indicating a semiconducting  
260 behavior. On the other hand, the decrease of the Seebeck coefficient with decreasing temperature  
261 contrasts with the resistivity results and could point to multiple bands, with two types of charge  
262 carriers.

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## 265 **Conclusions**

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267 The preparation of NiS<sub>2</sub> by solid-state route, followed by hot-pressing resulted in single phase  
268 pellets. Relative densities superior to 94% were achieved. No significant changes in chemical  
269 bonds and lattice distortions were verified for the different hot-pressing conditions.

270 Thermogravimetric analysis of these compounds indicates a strong desulfurization above 340 °C,  
271 which limits their service temperature. As opposite to the band structure calculations that  
272 suggested a metallic behavior, bulk NiS<sub>2</sub> is a p-type semiconductor. The maximum power factor  
273 obtained for vaesite (14.1  $\mu\text{WK}^{-2}\text{m}^{-1}$ ), which is significantly higher than the pristine pyrite  
274 [Zuñiga-Puelles et al., 2019], is a good starting point for further improvements. This work  
275 indicates that the consolidation conditions had a notable influence on the resistivity, with denser

276 pellets showing a higher electrical conduction, pointing to an intimate relation between the  
277 electronic transport properties and the processing conditions, defects (stoichiometric deviations,  
278 grain boundaries) and changes in the chemical composition. Therefore, we can expect that, with  
279 a proper optimization of the chemical composition and microstructure, these sulfides could  
280 become viable thermoelectric materials.

281 Several aspects were left unexplored in this work. Since the potential of a material for  
282 thermoelectricity is also related with its thermal transport properties, a further study of the  
283 thermal conductivity is required. The selection of the optimal chemical composition of vaesite,  
284 through elemental substitutions, is also necessary. The coupling of these materials in a  
285 thermoelectric module also demands good mechanical properties, which so far were never  
286 studied. In this project, the thermal stability of vaesite under inert atmosphere was studied but it  
287 would be interesting to also evaluate its stability in air (oxidation testing).

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**Table 1** (on next page)

Comparison of physical properties of NiS<sub>2</sub>, at different consolidation conditions.

1  
2

Consolidation conditions	Porosity (%)	Lattice constant (Å)	Theoretical density (g/cm <sup>3</sup> )	Apparent density (g/cm <sup>3</sup> )	Relative density (%)
HP at 700°C/56MPa	6±1	5.687(6)	4.435	4.18±0.01	94
HP at 720°C/56MPa	6±1	5.686(4)	4.437	4.20±0.07	95
HP at 750°C/56MPa	4±1	5.687(8)	4.434	4.31±0.02	97

3  
4



**Table 2** (on next page)

Measured composition and secondary phases detected by EDS.

1

Consolidation conditions	Measured composition	Secondary phases
HP at 700°C/56MPa	$\text{NiS}_{2\pm 0.06}$	$\text{Ni}_{1-x}\text{S}$ ( $x=0.11$ )
HP at 720°C/56MPa	$\text{NiS}_{2.05\pm 0.02}$	Not detected
HP at 750°C/56MPa	$\text{NiS}_{2\pm 0.05}$	$\text{Ni}_{1-x}\text{S}$ ( $x=0.12$ )

2

3

**Table 3** (on next page)

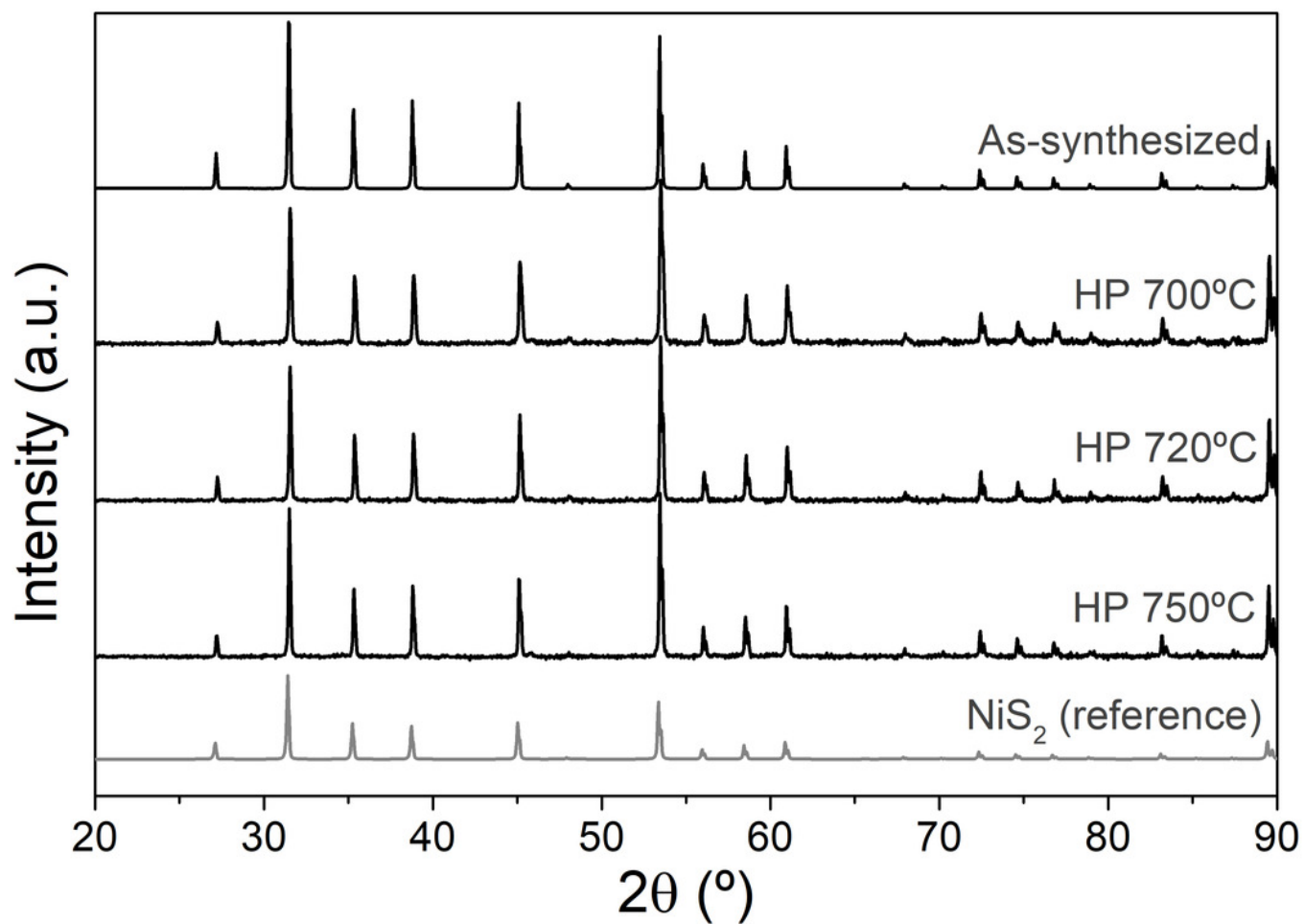
Activation energy ( $E_a$ ), room temperature Seebeck coefficient ( $\alpha$ ), electrical resistivity ( $\rho$ ) and power factor (PF) of NiS<sub>2</sub> hot-pressed at different temperatures.

1  
2

Consolidation conditions	$E_a$ (meV)	$\alpha_{300K}$ ( $\mu\text{V/K}$ )	$\rho_{300K}$ ( $\mu\Omega\text{m}$ )	$\text{PF}_{300K}$ ( $\mu\text{WK}^{-2}\text{m}^{-1}$ )
HP at 700°C/56MPa	43	128	3230	5.1
HP at 720°C/56MPa	64	182	2350	14.1
HP at 750°C/56MPa	68	119	2257	6.3

# Figure 1

XRD diffractograms of as-synthesized  $\text{NiS}_2$  and hot-pressed at different temperature conditions. Reference pattern of  $\text{NiS}_2$  in gray [Villars & Calvert, 1986].



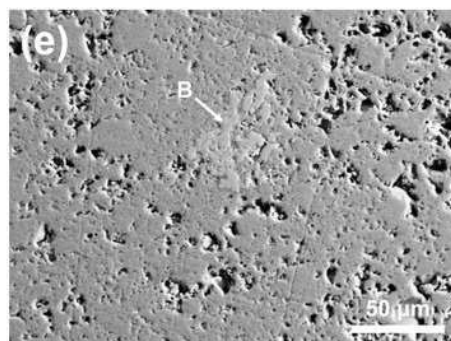
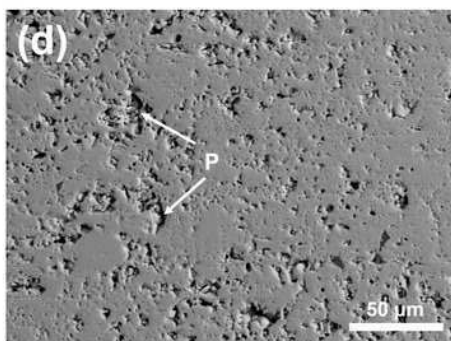
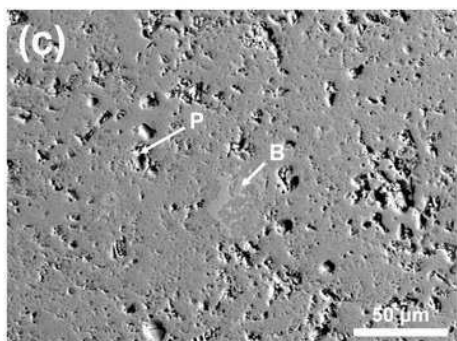
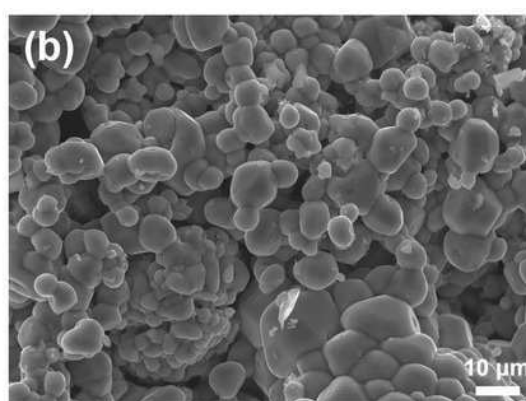
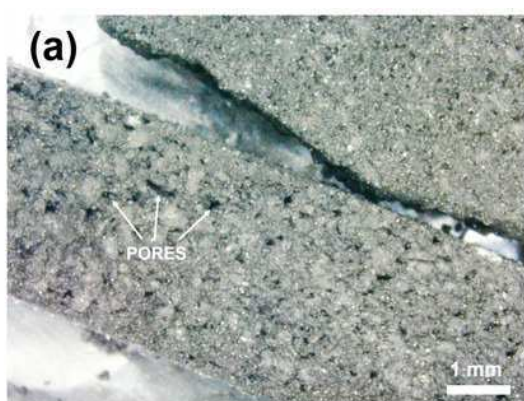
## Figure 2

Optical and SEM images of as-synthesized  $\text{NiS}_2$ ,

captured by (a) optical microscope (20x) and (b) SE-SEM (1000x magnification). BS-SEM

(500x) images of  $\text{NiS}_2$  hot-pressed at 56MPa for 1,5h, at different temperatures: (c)700°C, (b)

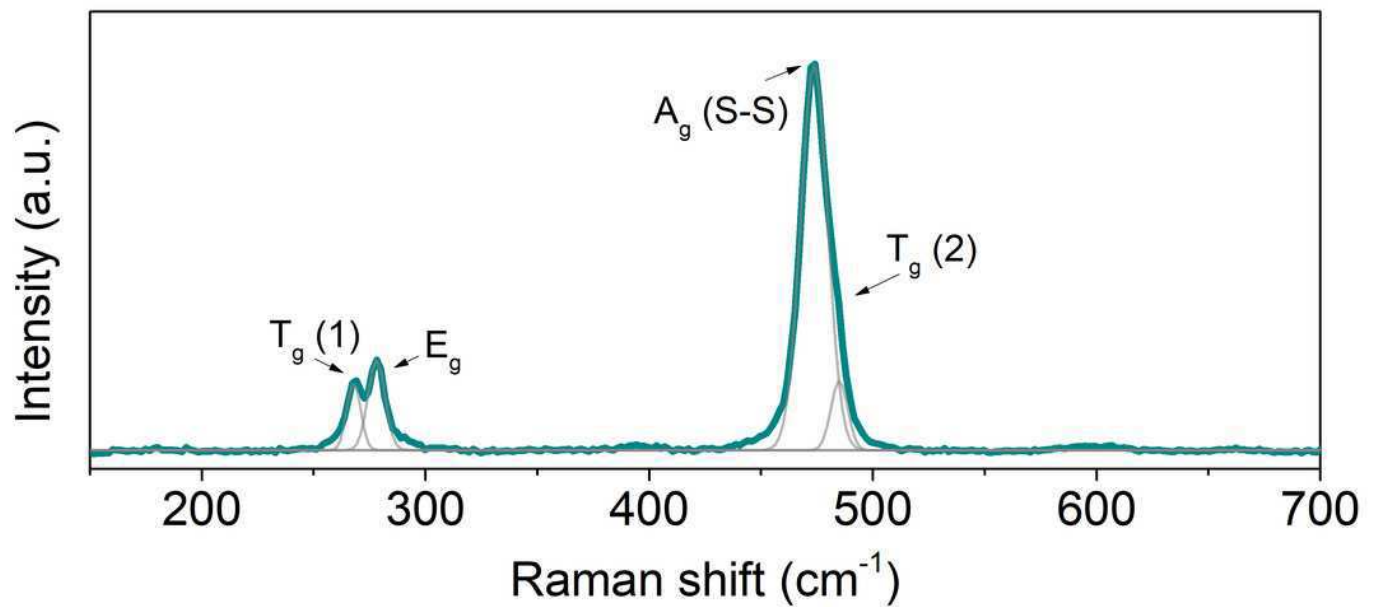
720°C, (c) 750°C. P - Pores, B - Sulfur-deficient phase  $\text{Ni}_{1-x}\text{S}$ .





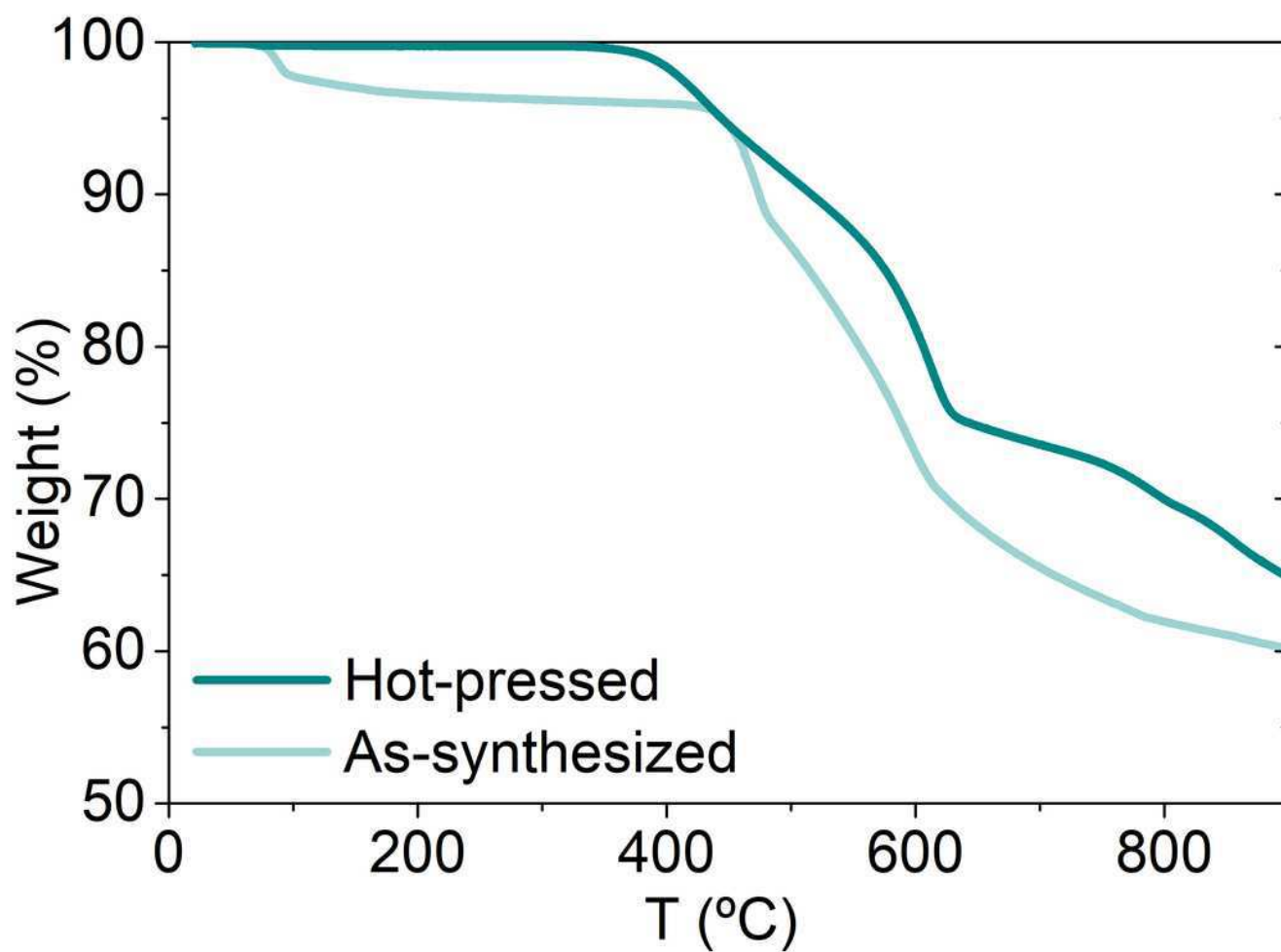
## Figure 3

Raman spectrum of hot-pressed NiS<sub>2</sub>.



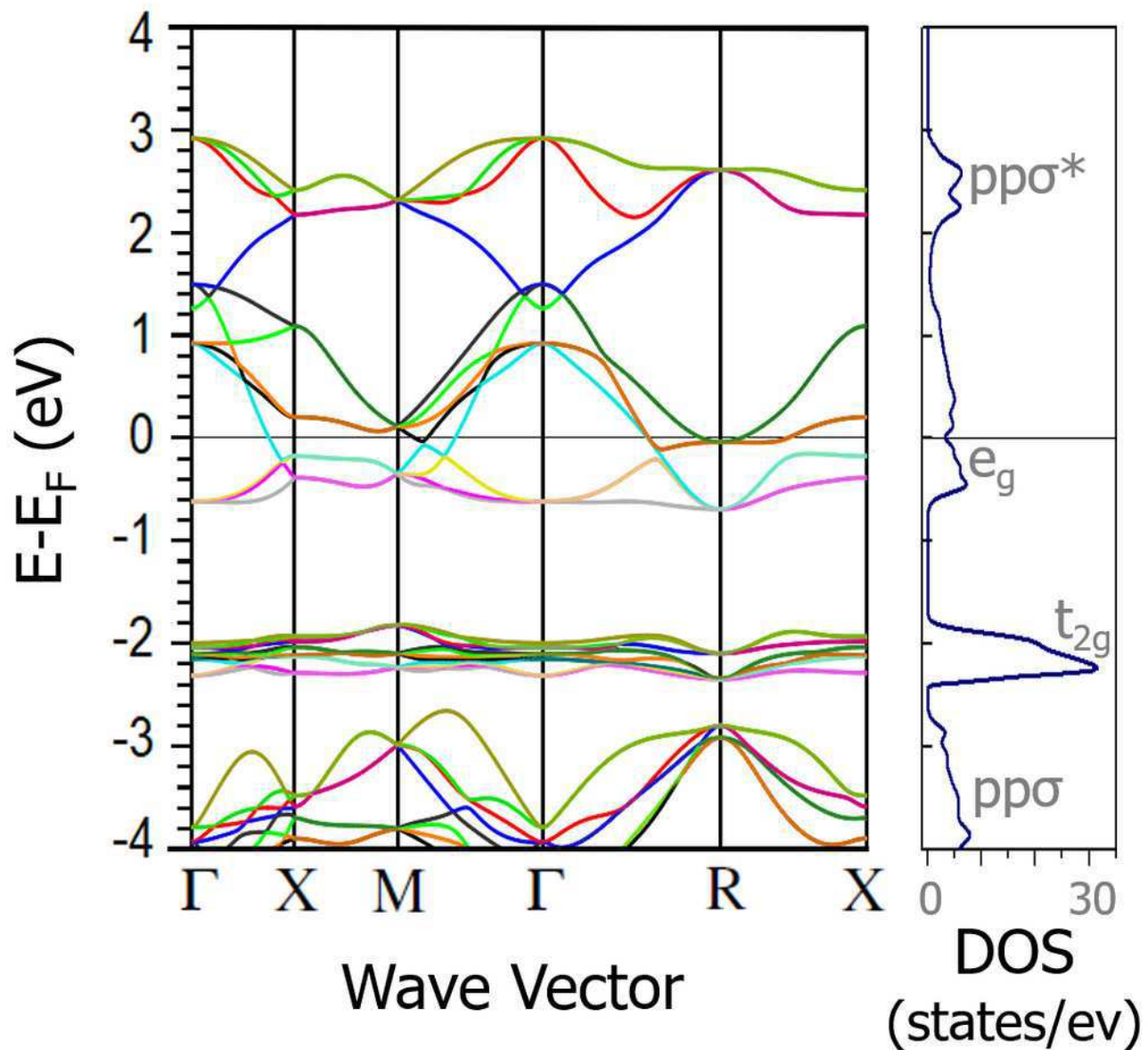
## Figure 4

Thermogravimetric analysis of as-synthesized and hot-pressed  $\text{NiS}_2$ .



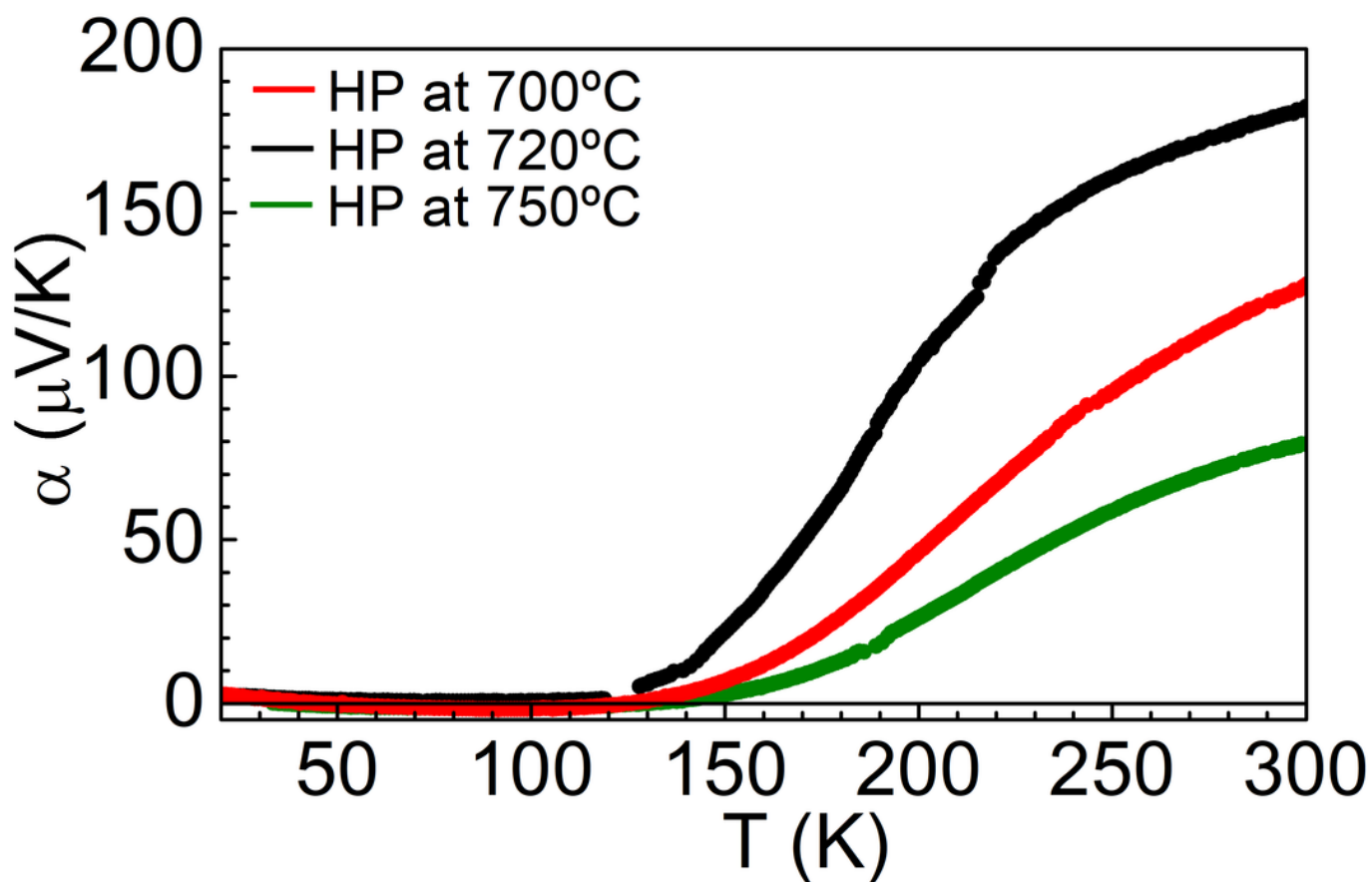
## Figure 5

Band structure and density of states DFT calculations of NiS<sub>2</sub>.



## Figure 6

Temperature dependence of Seebeck coefficient of  $\text{NiS}_2$ , at different consolidation conditions.



## Figure 7

Temperature dependence of electrical resistivity of  $\text{NiS}_2$ , at different consolidation conditions.

