

NANOSTRUCTURED NICKEL SULFIDES WITH DIFFERENT STOICHIOMETRIES PREPARED BY MECHANOCHEMICAL SYNTHESIS

M. KRISTL^{a*}, S. GYERGYEK^{b,a}, J. KRISTL^c

^a*University of Maribor, Faculty of Chemistry and Chemical Engineering, 2000 Maribor, Slovenia*

^b*Jožef Stefan Institute, Department of Materials Synthesis, 1000 Ljubljana, Slovenia*

^c*University of Maribor, Faculty of Agriculture and Life Sciences, 2311 Hoče, Slovenia*

By reactions between nickel and sulfur, products with different stoichiometries can be obtained, from the nickel - rich compounds like Ni_3S_2 , over NiS to sulfur - rich compounds like Ni_3S_4 and NiS_2 . Nickel sulfides have been recently used in many applications, like solar cell materials, catalysts and cathode material for lithium batteries. In this paper, we present the synthesis of different nanosized nickel sulfides by high – energy milling of nickel powder with elemental sulfur in different molar ratios, using milling times between 1h and 8h. The products were characterized by X-ray powder diffraction, TEM including EDX analysis, elemental analysis and UV – Vis spectroscopy. Following products have been obtained in good yield: by milling a Ni : S mixture in molar ratio 1 : 1, $\text{NiS}_{1.03}$ was obtained after 8h milling time. Using a Ni : S mixture in molar ratio 1 : 2, NiS_2 was obtained after 8h. Finally, from a Ni : S = 3 : 2 mixture, nanosized Ni_3S_2 can be obtained after 2h.

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1. Introduction

As a subgroup of transition metal chalcogenides, nickel sulfides with the general formula Ni_xS_y have attracted considerable attention due to their various phases and stoichiometries as well as promising properties allowing a wide variety of applications [1]. Different compositions and phases of nickel sulfides include Ni_3S_2 , Ni_6S_5 , Ni_7S_6 , Ni_9S_8 , Ni_{1+x}S , NiS , Ni_3S_4 and NiS_2 [2, 3]. NiS exists in two phases, the hexagonal α - NiS , which is only stable at elevated temperatures, and the rhomboedral β - NiS , stable at low temperatures [4]. Many applications of nickel sulfides have been reported recently, for instance as electrode materials for highly effective counter electrodes for solar cells [5-7]. NiS has also been reported to be a suitable material for supercapacitors [8] and an ideal candidate for cathode material used in lithium batteries [9, 10].

Among many reported methods for the preparation of nickel sulfides, the direct high-temperature synthesis from elemental precursors is most traditional one. However, as for most of high-temperature reactions, the reaction is difficult to control and usually yields bulk materials instead of nanosized products. Additionally, the combination of long reaction times and high temperatures may cause contamination of the products with impurities from reactor walls [11]. Other methods have been proposed for the preparation of nanosized nickel sulfides. One possible method is the reaction of sulfide ions to an aqueous solution of nickel(II) ions [12], while many other techniques have been reported later. Among the most important are hydrothermal/solvothermal methods [13,14], microwave synthesis [15] and decomposition of single-source precursors [3, 16]. Another promising method for the synthesis of nanosized nickel sulfides is the sonochemical approach, where reactions take place inside the collapsing bubbles under intense ultrasonic irradiation [17, 18]. The sonochemical preparation of various transition

* Corresponding author: matjaz.kristl@um.si

metal and main group chalcogenides has been reported by our group during the last decade, like copper selenides [19], silver chalcogenides [20], indium sulfide [21] as well as NiS and Ni₃S₄ nanoparticles reported recently [1].

The mechanochemical synthesis, sometimes also referred to as mechanical alloying, is a simple solid-state method where the reactions take place by cold welding of powder particles in a high-energy ball mill. The method was originally developed in the 1970s for the production of ‘superalloys’ for aerospace industry and later used for production of advanced ceramics [22]. The first mechanochemical syntheses of transition metal chalcogenides were reported in the 1990s [23, 24] and were focused mainly on copper chalcogenides. In the 2000s, mechanochemical preparations of cadmium chalcogenides and further mechanochemical syntheses of copper sulfide by metathesis were reported [25, 26]. Recently, mechanochemical syntheses of aluminum and gallium sulfides and selenides [27] were reported by our group. The present study aimed at successful preparation of different nickel sulfides from elemental precursors by using the simple and low – cost mechanochemical method.

2. Experimental

Nickel powder (99.7%, ≈3 μm, Aldrich) and elemental sulfur (99+ %, < 40 μm, Merck) were used for the preparation of nickel sulfides as purchased, without further purification. The powders were mixed using a SPEX 8000M mill inside a Model 8007 stainless steel vial (approx. 6.35 cm diameter x 7.62 cm height) with two 1.27 cm stainless steel milling balls. The mass of the milling balls was approximately 15 g and the mass of the mixture during all syntheses was kept at 1.5 g to maintain the constant ball - to - powder mass ratio of 10 : 1. In a typical procedure using a Ni : S = 1 : 1 molar ratio, 0.9732 g (= 16.6 mmol) Ni and 0.5328 g (= 16.6 mmol) S were milled together using different milling times ranging from 1 h to 8 h. During subsequent experiments, the molar ratio was changed from Ni : S = 1 : 2 to Ni : S = 2 : 1.

All products were characterized by X-ray powder diffraction (XRPD) using an AXS-Bruker/Siemens model D5005 X-ray powder diffractometer. The samples were attached to a Si holder and measured in the range $10^\circ \leq 2\theta \leq 70^\circ$ using CuK α radiation and a graphite monochromator ($\lambda = 1.54178 \text{ \AA}$) with a step size of 0.0358° and time/step = 1s. The crystallite size was estimated from the average of two strongest diffraction peaks, using the *Scherrer* formula:

$$d_{hkl} = \frac{0.94\lambda}{\beta_{hkl} \cos\theta_{hkl}}$$

Here, λ is the wavelength of the X – ray radiation (nm), β_{hkl} the full – width at half – maximum (FWHM) of the corresponding peak ($^\circ$) and θ_{hkl} is the Bragg diffraction angle ($^\circ$). The effects of instrumental broadening were subtracted by measuring an external macrocrystalline standard under the same instrumental conditions.

A JEOL 2100 TEM microscope operating at 200 kV was used for transmission electron microscopy (TEM) measurements. The nanoparticles were dispersed in ethanol using an ultrasonic bath and placed on a carbon - coated Cu grid. The nickel content of the samples was determined using a Varian SpectrAA-10 flame atomic spectrometer equipped with a deuterium background corrector. Nickel calibration standard solutions were prepared by diluting the standard stock solutions containing 1000 mg/L (Certipur, Merck) using high-purity water. The samples were placed in PTFE vessels and heated with concentrated nitric acid in a microwave oven CEM (MDS 2000). The digested solutions were allowed to cooled to room temperature and diluted to a total volume of 50 mL. UV- Vis absorption spectra of NiS_{1.03} dispersed in ethanol were measured using a Varian Cary 50 UV/Vis spectrophotometer.

3. Results and discussion

XRPD patterns of products, obtained by high - energy milling of nickel powder with sulfur in molar ratio 1 : 1 for different time periods between 1h and 8h, are shown in Fig. 1. Due to the known tendency of Ni and S to form various phases with different stoichiometries, as well as nonstoichiometric products, a complex system is observed after short milling times. In detail, after 1h and 2h milling time, at least 3 nickel sulfides could be identified: hexagonal $\text{NiS}_{1.03}$ (JCPDS No. 00-002-1273), rhombohedral NiS (JCPDS No. 00-012-0041) and Ni_7S_6 (JCPDS No. 00-014-0275) together with traces of unreacted nickel and sulfur. By prolonging milling times, peaks of unreacted Ni and S as well as those of NiS and Ni_7S_6 become weaker and finally after 8h of milling, all observable peaks can be identified as belonging to $\text{NiS}_{1.03}$.

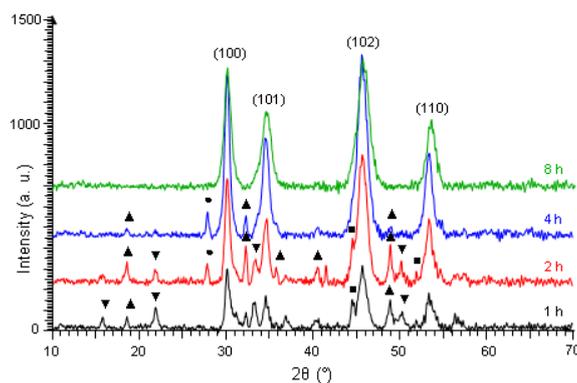


Fig. 1: X-ray powder diffraction patterns of nickel sulfides prepared by high - energy milling of the $\text{Ni} : \text{S} = 1 : 1$ mixture after 1 h, 2 h, 4 h and 8 h milling time. The indexed peaks belong to $\text{NiS}_{1.03}$. $\bullet = \text{S}$, $\blacksquare = \text{Ni}$, $\blacktriangledown = \text{Ni}_7\text{S}_6$, $\blacktriangle = \text{Millerite, NiS}$

Due to the great variety of possible products in the $\text{Ni} : \text{S}$ system, it is not always possible to clearly distinguish between different Ni_xS_y phases using only XRPD patterns. Most notably, $\text{NiS}_{1.03}$ has a pattern very similar to that of $\text{NiS}_{1.19}$ (JCPDS No. 00-002-1277). Thus, in addition to the chemical analysis, which confirmed the formation of the $\text{NiS}_{1.03}$ product (meas. 64.2% Ni, 35.7% S) we performed another experiment with a $\text{Ni} : \text{S} = 1 : 1.2$ molar ratio. The pattern (Fig. 2) shows a mixture of $\text{NiS}_{1.03}$ and NiS_2 , further confirming that the product obtained from the 1 : 1 mixture is indeed $\text{NiS}_{1.03}$, since the increase of the sulfur amount above 1 : 1 leads to the beginning of the formation of the new phase, NiS_2 . If $\text{NiS}_{1.19}$ had been synthesized by the mechanochemical reaction, the formation of a pure phase would be expected when using 1 : 1.2 molar ratio.

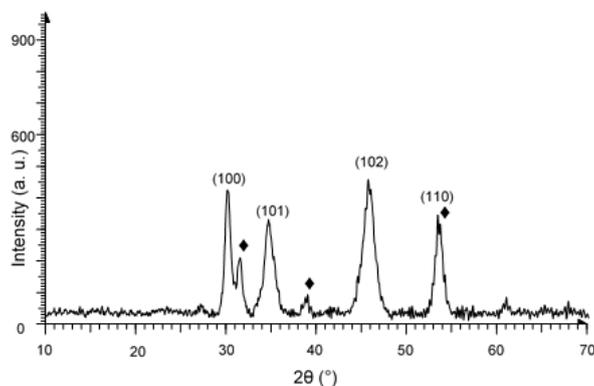


Fig. 2: X-ray powder diffraction patterns of the products prepared by high - energy milling of the $\text{Ni} : \text{S} = 1 : 1.2$ mixture after 4 h milling time. The indexed peaks belong to $\text{NiS}_{1.03}$. $\blacklozenge = \text{NiS}_2$

Fig. 3 presents XRPD patterns of products, obtained by high - energy milling of nickel powder with sulfur in molar ratio 1 : 2 for different time periods between 1h and 8h. The 1 : 2 system is less complicated than the 1 : 1 system, yielding cubic NiS_2 (JCPDS No. 00-011-0099) after 8 h of milling, while peaks of unreacted S can be observed next to NiS_2 after shorter reaction times. Peaks belonging to $\text{NiS}_{1.03}$ at 30.1° , 34.5° and 45.6° which are clearly visible after 1 h - 4 h, almost completely disappear after 8 h milling time, indicating a complete reaction of both precursors into NiS_2 .

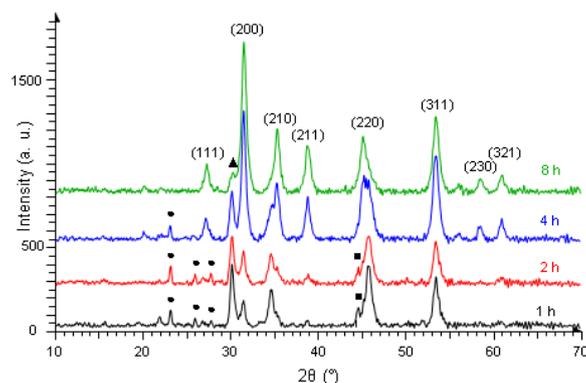


Fig. 3: X-ray powder diffraction patterns of nickel sulfides prepared by high - energy milling of the Ni : S = 1 : 2 mixture after 1 h, 2 h, 4 h and 8 h milling time. The indexed peaks belong to NiS_2 . ● = S, ■ = Ni, ▲ = $\text{NiS}_{1.03}$

XRPD patterns of products, prepared from Ni : S mixtures with excess amounts of nickel (molar ratio Ni : S = 3 : 2) are presented in Fig. 4. By milling of the 3 : 2 mixture, pure rhombohedral Ni_3S_2 (JCPDS No. 00-030-0863) can be observed after 2 h of milling time, while some unreacted Ni can be detected after 1 h milling time. Note that the apparently broader peak at $\approx 50^\circ$ is in fact due to the overlapping of the (113) peak at 49.72° and the (211) peak at 50.12° . Milling of the 2 : 1 mixture also yields predominantly Ni_3S_2 , however with peaks of unreacted Ni which slowly turns into NiO by prolonging milling times above 4 h (patterns not shown). By performing further experiments with an Ni : S ratio higher than 2 : 1, we could only obtain Ni_3S_2 with increasing amounts of Ni and/or NiO in all cases.

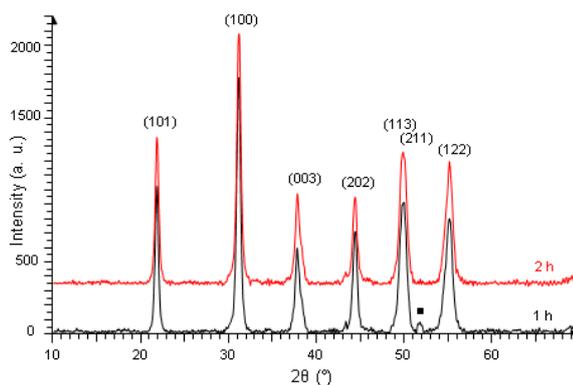


Fig. 4. X-ray powder diffraction patterns of Ni_3S_2 prepared by high - energy milling of the Ni : S = 3 : 2 mixture after 1 h and 2 h milling time. ■ = Ni

The morphology of $\text{NiS}_{1.03}$ particles, prepared by mechanochemical synthesis from the 1 : 1 mixture after 8 h milling time, is presented in Figs. 5 (a) and 5 (b). It can be seen that the product consists of primary spherical nanoparticles with diameters between 10 and 15 nm. Due to strong mechanical forces during the prolonged milling, these particles are strongly agglomerated into

clusters with dimensions of several hundred nm. The EDX analysis performed on several spots revealed an Ni : S ratio of approximately 1 : 1, with no evidence of nickel oxides in the products.

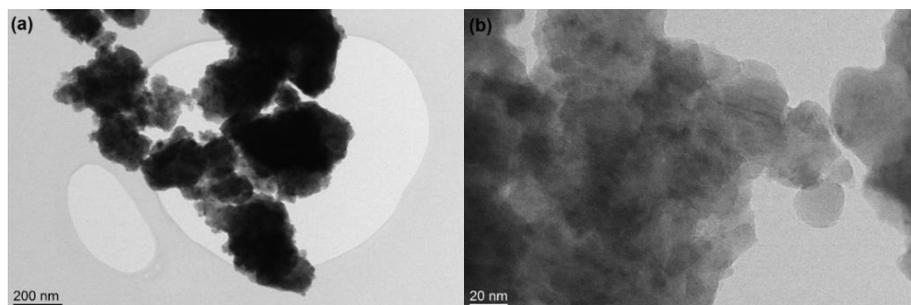


Fig. 5. TEM images of $\text{NiS}_{1.03}$ nanoparticles obtained from elemental Ni and S (molar ratio 1 : 1) after 8 h milling time

TEM images of NiS_2 , prepared by mechanochemical synthesis from a 1 : 2 mixture after 8 h milling time, are shown in Figs. 6 (a) and f (b). The particle size distribution analysis is difficult due to the strong agglomeration, however individual nanoparticles, roughly 15 – 20 nm in diameter, can be observed at higher magnification. The EDX measurements confirm the Ni : S ratio of 1 : 2, already observed by powder X-ray measurements. Despite the difficulties due to the strong agglomeration, there is a fairly good agreement between particle sizes observed by TEM and those estimated by Scherrer equation. A summary of experimental conditions, obtained products and calculated crystallite sizes is provided in Table 1.

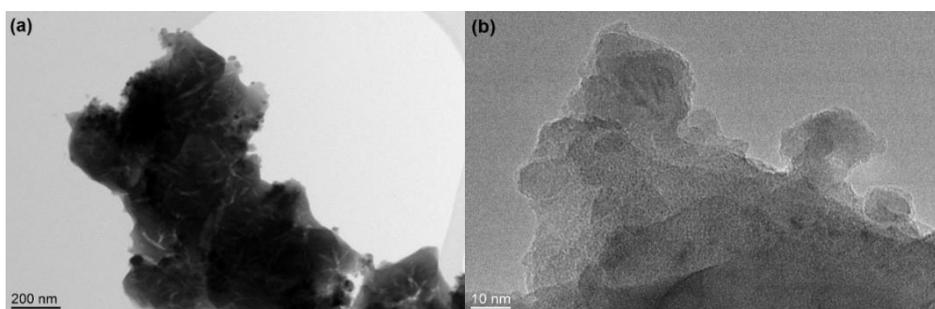


Fig. 6. TEM images of NiS_2 nanoparticles obtained from elemental Ni and S (molar ratio 1 : 2) after 8 h milling time

The UV – Vis absorption spectrum of $\text{NiS}_{1.03}$, prepared from a 1 : 1 mixture of Ni and S after 8 h milling time, is presented in Fig. 7. The transmission edge was observed at 330 nm. By using Tauc plots and the extrapolation method, the E_g value of 3.7 eV was calculated, showing a significant blue shift when compared to the values reported for bulk NiS (~ 2.1 eV). The results are in close agreement with values reported recently for NiS nanoparticles prepared by other methods [1, 28].

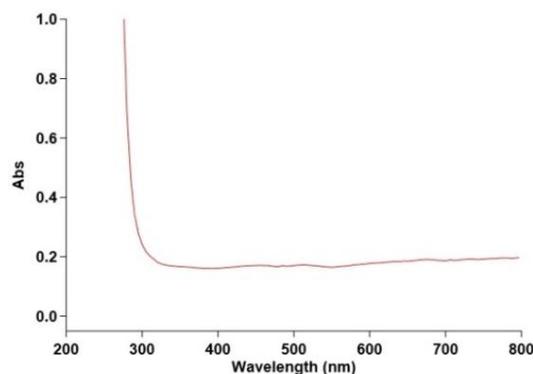


Fig. 7. UV – Vis spectrum of $\text{NiS}_{1.03}$ mechanochemically synthesized from a 1 : 1 mixture of Ni and S after 8 h milling time

Table 1. Precursors, milling times, and products of the mechanochemical preparation of nickel sulfides. The crystallite size was calculated only in cases where pure nickel chalcogenides without detectable impurities were obtained.

Ni : S molar ratio	Milling time	Product(s)	Crystallite size (nm)
1 : 1	1 h	Ni_7S_6 , NiS, $\text{NiS}_{1.03}$, Ni	-
	2 h	Ni_7S_6 , NiS, $\text{NiS}_{1.03}$, Ni, S	-
	4 h	NiS, $\text{NiS}_{1.03}$, S	-
	8 h	$\text{NiS}_{1.03}$	11
1 : 1.2	4 h	$\text{NiS}_{1.03}$, NiS_2	-
1 : 2	1 h	$\text{NiS}_{1.03}$, NiS_2 , S	-
	2 h	$\text{NiS}_{1.03}$, NiS_2 , S	-
	4 h	$\text{NiS}_{1.03}$, NiS_2 , S	-
	8 h	NiS_2	17
3 : 2	1 h	Ni_3S_2 , Ni	-
	2 h	Ni_3S_2	21
2 : 1	1 h	Ni_3S_2 , Ni, NiO	-
	2 h	Ni_3S_2 , Ni, NiO	-

4. Conclusions

Several nickel sulfides with different compositions have been successfully prepared from elemental precursor using mechanochemical synthesis: $\text{NiS}_{1.03}$, NiS_2 and Ni_3S_2 . Primary nanoparticles with crystallite sizes between approx. 10 and 20 nm, strongly agglomerated into secondary clusters, have been obtained.

The mechanochemical method is simple and economical when compared to most of the reported preparation procedures, and environmental friendly due to the total absence of organic solvents and toxic precursors. Further research might be focused on the possibility of application of surfactants during syntheses, which are supposed to prevent the agglomeration during milling.

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