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Properties of a new nanosized tin sulphide phase obtained by mechanochemical route

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Abstract

The paper deals with the properties of a new 4H-SnS_2 phase (N-phase) synthesized together with berndtite 4H-SnS_2 by a mechanochemical route from elemental tin and sulphur. The surface and bulk properties of SnS_2 phases were verified by surface area measurements, particle size analysis, electron microscopy, XRD, Mössbauer spectroscopy and chemical dissolution methods. The particles of synthesized product are 12–18 nm in size and during milling, secondary particles (aggregates) are formed that are 20–60 μm in size. The particle size and a high developed surface area (7–21 $m^2\ g^{-1}$) greatly influence the solid–liquid reaction and solid transformations of mechanosynthesized tin sulphide products. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nanostructures; Mechanical alloying; X-ray diffraction; Magnetic measurements

1. Introduction

Metal sulphides may be applied as advanced materials for many applications, e.g. intercalation precursors (TiS_2, TaS_2, NbS_2), precursors for synthesis of high temperature superconductors (La_2S_3), luminescence materials (CdS: Mn, Cu, Pb), diagnostic materials (Ag_2S), solar energy materials (ZnS, $CuInS_2$), materials for photoelectrolysis (FeS_2), high-energy density batteries (TiS_2) and further materials for opto-electric and magnetic applications [1].

Tin sulphides belong to materials which exhibit variable physico-chemical properties, such as polytypism, polymorphism and non-stoichiometry [2]. Some of them, e.g. SnS_2 consists of two layers of closely packed sulphur anions with sandwiched tin cations in octahedral coordination. The sulfides of this type have a number of empty sites in their structure and hence they are interesting host lattices for intercalation [3–8].

In recent years, a number of papers have been published on developing methods to synthesize inorganic materials via mechanochemical processes [9–12]. The application of intensive milling is one of the promising routes for the preparation of advanced materials of nanosized dimensions with unusual properties. Some sulphides, including tin sulphides were synthesized by this procedure [13–35].

The aim of the present work is to evaluate the bulk and surface properties as well as the reactivity of a new tin sulphide prepared by ball milling.

2. Experimental

2.1. Synthesis

For the mechanochemical synthesis of the new tin sulphide phase the following chemicals were used: tin (powder, −100 mesh, Alfa Ventron, Germany) and elemental sulphur (powder, Lachema, Czech Republic). The starting mixture was prepared from the elements according to the weight ratio Sn:S=1:1.85. The mixture was homogenized by mixing in methanol for 60 min. After drying, 4 g of powder was milled in a planetary mill URF-AGO 2 (Russia) using 110 steel balls with 5 mm diameter. The rotational speed of the planet carrier was

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700 min^{-1}, 1000 ms^{-2} providing a centrifugal acceleration on the thimble axes. Milling was performed in argon atmosphere for 30–120 min.

2.2. Characterization techniques

The powder X-ray diffraction measurements were performed on Rigaku Rad-B using Cu Kα radiation at (0.3 kW power, 0.5°/min scanning speed). The ZDS software product was used for crystalline size determination based on the analysis of selected X-ray diffraction profiles using the variance method.

Tin Mössbauer spectra were recorded in transmission geometry using a conventional microcomputer-controlled spectrometer in constant acceleration mode. A ^{119}Sn γ-ray source was used. The velocity scale was calibrated relative to $BaSnO_3$. A proportional counter was used to detect the transmitted γ-rays. Mössbauer spectral analysis software Recoil [36] was used for the quantitative evaluation of the spectra. The Voigt-based fitting method provided the distribution of the hyperfine parameters for multiple sites.

The specific surface area was determined by the low temperature nitrogen adsorption method in a Gemini 2360 sorption apparatus (Micromeritics, USA).

The particle size distribution was measured by a laser diffraction system using a Helos and Rodos granulometer (Sympatec, Germany).

Scanning electron micrographs were obtained on a BS 300 scanning electron microscope (Tesla, Czech Republic).

The reactivity of mechanochemically synthesized tin sulphide was tested for dissolution within sodium sulphide and sodium hydroxide solution. During the sulphidic tin solubilization in this environment soluble thiostannates and sodiumtinhydroxide compounds of the $Na_2(SnS_3)$, $Na_4(SnS_4)$ and $Na_2Sn(OH)_6$ type can be formed [37]. Reaction conditions: 300 ml solution of 25 g l^{-1} Na_2S+ 12.5 g l^{-1} NaOH, weight of sample 400 mg, dissolution time 30 min, temperature 30–60°C.

The experimental results on tin dissolution were fitted to the kinetic equation

$$-\ln(1-\varepsilon_{Sn}) = kt_L \quad (1)$$

where the ε_{Sn}, k (s^{-1}) and t_L (s) stand for the conversion fraction, rate constant, and dissolution time, respectively.

The temperature dependence of the dissolution rate was fitted to the Arrhenius equation in order to determine the apparent activation energy.

Thermal characterization was carried out on a DTA-50 differential thermal analyser (Shimadzu, Japan). The typical sample mass was 35 mg. Al_2O_3 was used as reference material. The sensor of the DTA was a Pt–PtRh differential thermocouple with 0.1 μV sensitivity. The measurements were carried out at a heating rate of 40°C min^{-1} in 70 ml min^{-1} argon flow.

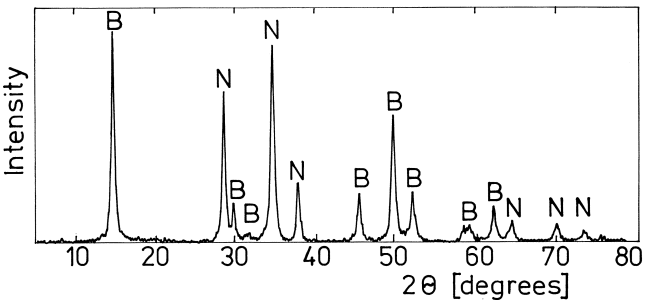

Fig. 1. XRD pattern of the mechanochemically synthesized tin sulphide phase, milling time 60 min; B, berndite 4H-SnS_2; N, new 4H-SnS_2 phase (N-phase).

3. Results and discussion

3.1. XRD and surface properties

The X-ray diffraction pattern of the mechanochemically prepared tin sulphide sample is given in Fig. 1. About half of the peaks were identified based on JCPDS card 21-1231. This structure corresponds to the pattern of the 4H polytype of tin sulphide: berndtite SnS_2. The other strong and sharp peaks at $d = 0.3114$, 0.2583 and 0.2369 nm, with relative intensities of $I/I_0 = 0.72$, 0.94 and 0.28, respectively, do not originate from that phase. Whitehouse and Balchin [38] reported that the milling process used to prepare powder specimens made the identification of SnS_2 polytypes difficult, except for the 2H modification. None of the X-ray patterns reported in Ref. [38] corresponds to the lines indicated by N in Fig. 1. It was concluded in our previous paper [26] that a new SnS_2 phase was created during high energy milling of the starting mixture of elemental tin and sulphur. The lines marked with 'N' originate from this phase.

In Table 1 the data on the crystallite size of the samples milled for different times are given. For the calculation of crystallite size of a new 4H-SnS_2 phase (N-phase) the peak at $d = 0.2583$ nm was selected. The crystallite size values of the 4H-SnS_2 and N-phases are similar.

The values of specific surface areas for the synthesized tin–sulphur compounds are of 1–2 orders of magnitude larger than in the case of the reaction precursors, i.e. elementary tin and sulphur: the values of 0.11 and 0.16 m^2

Table 1
Crystalline size, D and specific surface area, S_A of SnS_2 phases after milling for different time, t

t min	D, nm		S_A m^2 g^{-1}
	4H-SnS_2	N-phase	
30	18	17	7.2
45	14	13	16.7
60	17	13	16.0
90	15	12	21.0
120	16	15	14.1

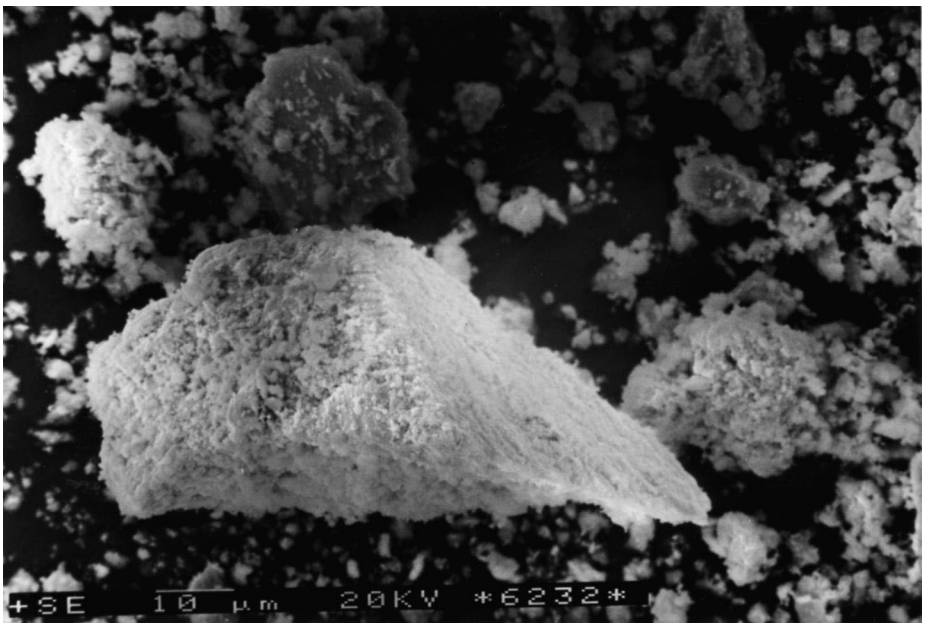

Fig. 2. Photomicrograph of tin sulphide phase, milling time 30 min.

g^{-1} were determined for Sn and S, respectively. The specific surface of the sample milled for 30 min is 7.2 m^2 g^{-1} while the same value for the sample milled for 120 min is equal to 21.0 m^2 g^{-1}.

There is a close correlation between the crystallite size D of the N-phase and the S_A values of synthesized samples (Fig. 2).

The microphotographs of both samples are given in Figs. 3 and 4. Careful inspection of the microphotographs reveals that the mechanosynthesized samples are in fact aggregates composed of sub-micron particles formed by small crystallite grains. The particle size distribution in Figs. 5 and 6 show that a rather inhomogenous, trimodal distribution of aggregates is present with the maxima at 1.2, 6.8 and 16.5 μm for samples synthesized by milling for both 30 and 120 min.

Fig. 3. Photomicrograph of tin sulphide phase, milling time 120 min.

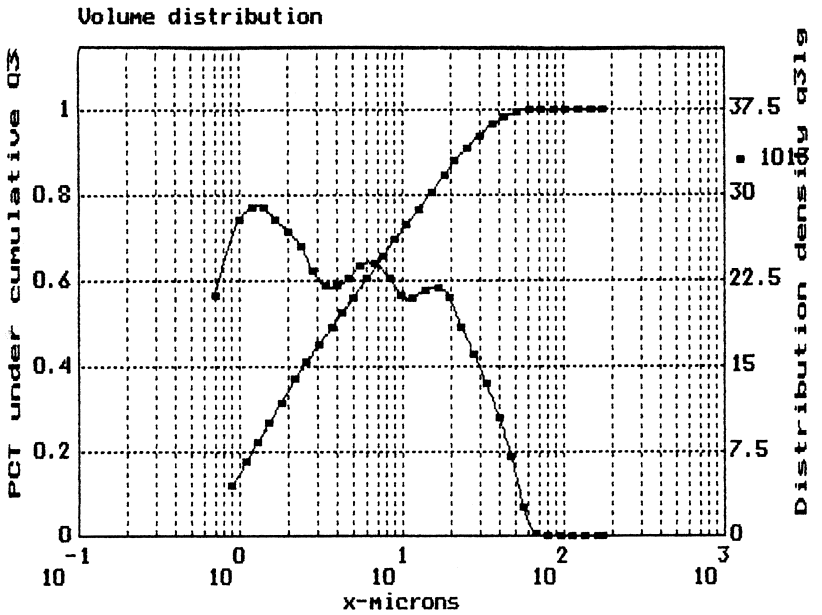

Fig. 4. Particle size distribution of the mechanochemically synthesized tin sulphide phase, milling time 30 min.

3.2. Mössbauer properties of the N-phase

Mössbauer spectra of the mechanosynthesized products milled for 30, 60 and 120 min, respectively, are given in Fig. 7 together with the Mössbauer pattern of elemental tin.

The main component of the spectrum of elemental tin is a singlet with isomer shift IS = 2.5 mm s^{-1}. A minor singlet corresponding to Sn^{2+} in SnO_2 is also visible, its relative intensity is 6.1% (Table 2).

Mössbauer spectra after mechanochemical synthesis for 30–120 min are characterized by a dominant singlet with IS = 1.02 mm s^{-1}. The singlet is slightly deformed as it is the superposition of two compounds with parameters corresponding to different forms of SnS_2. The value of the isomer shift indicates the presence of polar covalent bonds [39]. The representation of the minor phase is in the amount of 6–10% (Table 3). By confrontation with the results of XRD measurements one can conclude that the minor SnS_2 phase identified by Mössbauer spectroscopy is

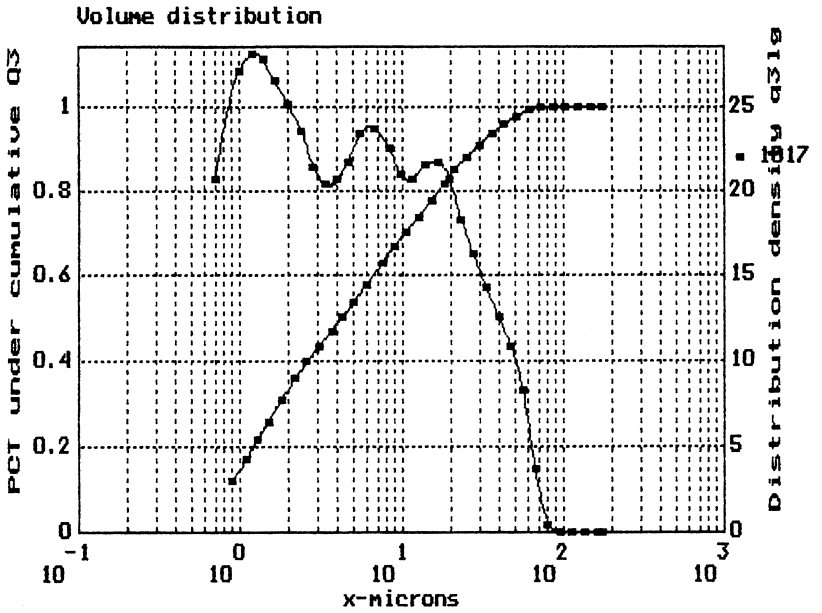

Fig. 5. Particle size distribution of the mechanochemically synthesized tin sulphide phase, milling time 120 min.

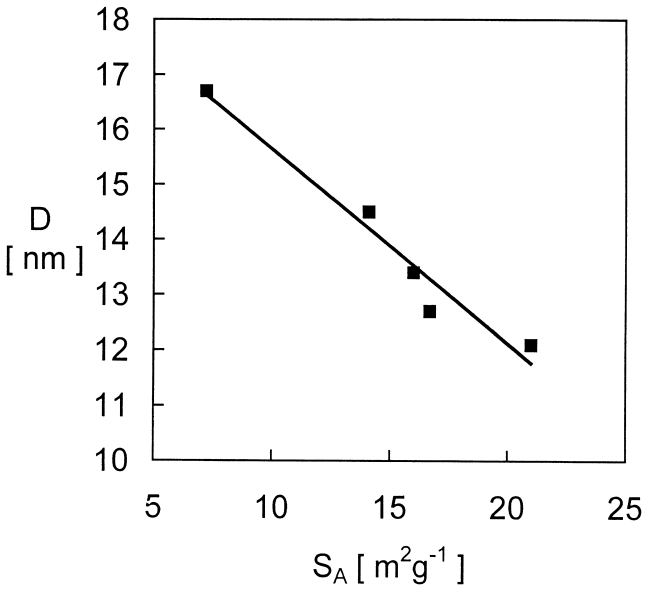

Fig. 6. Relationship between the crystallite size of N-phase, D and the specific surface area, S_A.

with great probability the N-phase identified by the XRD method.

It follows from the site populations analysis given in Table 2 that besides sulphidic products, also an oxidic phase can be identified among the products of mechanosynthesis. For milling times of 30–90 min the amount of SnO_2 is equal to ~6% (in addition to the fraction of oxide present in starting β-Sn).

The applied experimental techniques are not able to explain why a limiting fraction of the N-phase exists in the mechanosynthesized products. There is possibly a mechanochemical equilibrium between 4H-berndtite SnS_2 and the new SnS_2 phase (N-phase), which may be the consequence of several factors. External conditions such as the applied energy of milling and internal factors such as the decrease of crystallite size and steric limitations among SnS_2 phases may be of importance and play a crucial role.

3.3. Reactivity of mechanosynthesized phases

3.3.1. Dissolution reaction

The mechanosynthesized samples were subjected to dissolution in alkaline sodium sulphide solution. Fig. 8 shows the relationship between the degree of tin solubilization ε_{Sn} and dissolution time t_L. The reaction propagation is very fast: depending on the history of the sample, 50% or more of tin was dissolved after only 5 min or more of reaction.

The dissolution kinetics was fitted to Eq. (1) in order to calculate the rate constant k. The k values are shown as a function of milling time in Fig. 9. An attempt to eliminate the influence of surface area by introducing the specific rate constant k_S (the rate constant divided by the specific surface area) is also given in this figure. However, the influence of surface area is not decisive in this case and the structural imperfections must also play an important role [40].

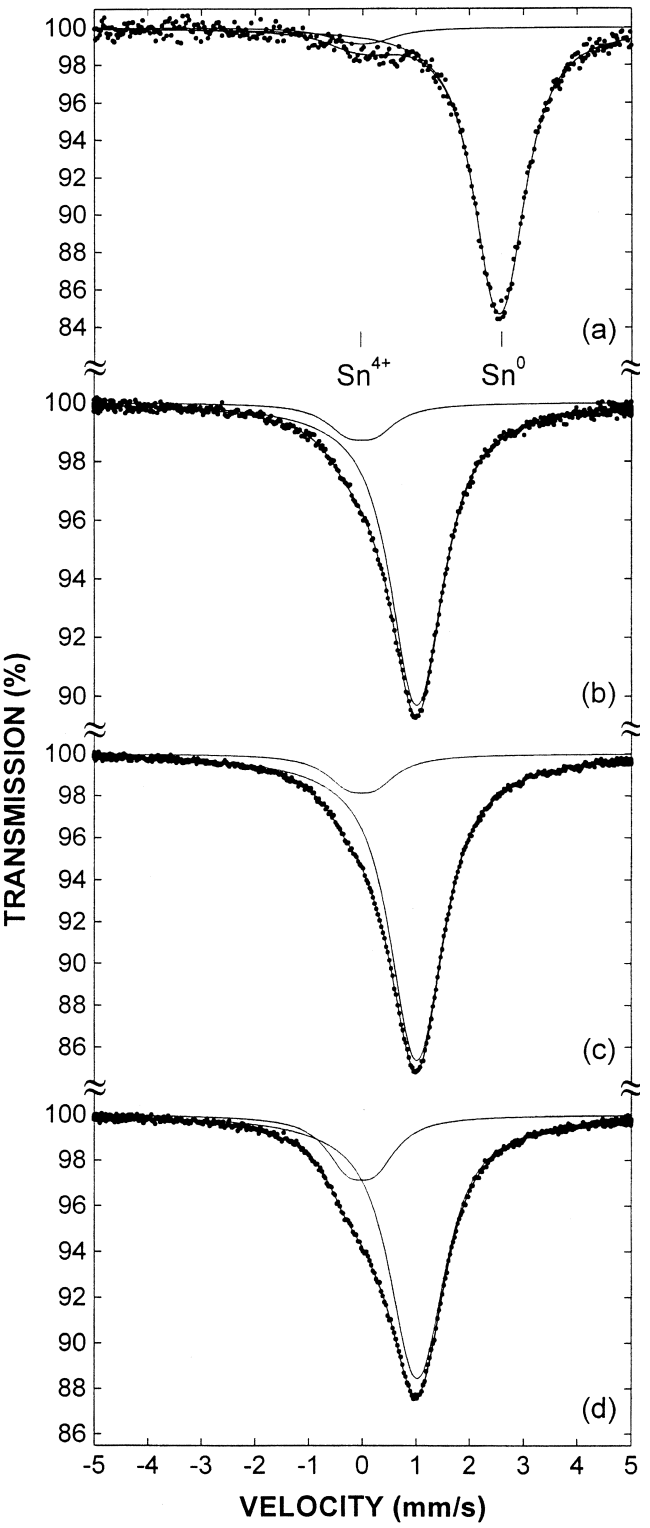

Fig. 7. Mössbauer spectra of tin compounds: elemental tin standard (a), mechanosynthesized tin sulphide phase milled for (b) 30 min, (c) 60 min, (d) 120 min.

Table 2
Mössbauer distribution analysis of tin compounds calculated from site populations

Milling time (min)	Site populations (%)		
	β-Sn	SnS_2 [a]	SnO_2
–	93.87	–	6.1
30	–	88.1	11.9
45	–	87.8	12.2
60	–	88.1	11.9
90	–	87.6	12.4
120	–	79.3	20.7

[a] 4H-berndtite SnS_2 plus N-phase.

Table 3
Mössbauer analysis of tin sulphide phases calculated from distribution parameters

Milling time (min)	%	
	Major phase (4H-SnS_2)	Minor phase (N-phase)
30	93.6	6.4
45	89.6	10.4
60	90.5	9.5
90	89.5	10.5
120	91.3	8.7

The temperature sensitivity of tin solubilization of the mechanochemically synthesized samples was characterized by calculations of the apparent activation energy E. The

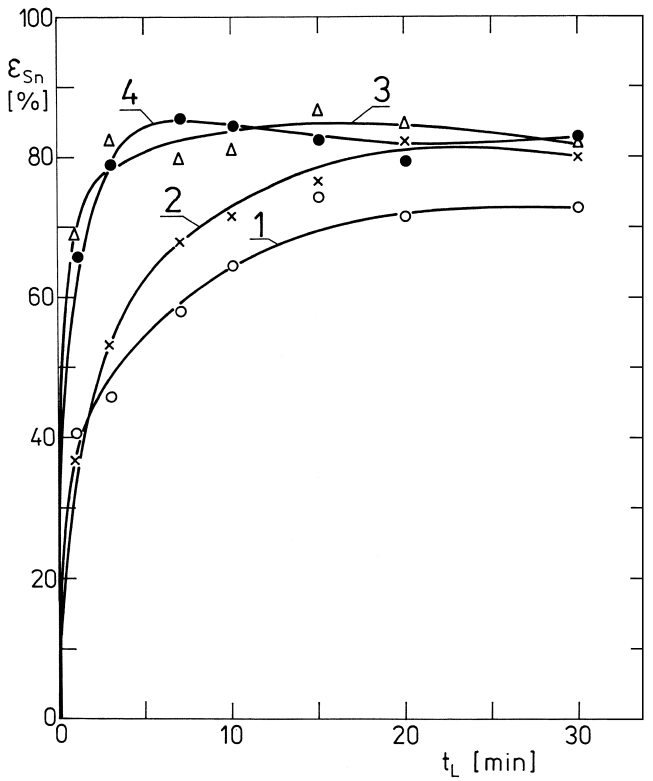

Fig. 8. Influence of dissolution time, t_L on the recovery of tin, ε_{Sn} from the mechanochemically synthesized tin sulphide phase, milling time: 1, 45 min; 2, 60 min; 3, 90 min; 4, 120 min.

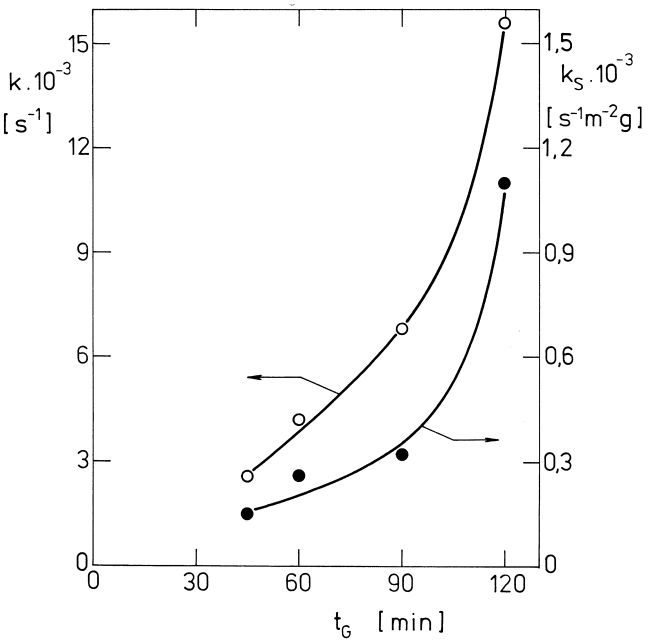

Fig. 9. Influence of milling time, t_G on the rate constant, k and the specific rate constant, k_S of tin dissolution from the mechanochemically synthesized tin sulphide phase.

values $E = 65$ and 45 kJ/mol were found for samples milled for 45 and 90 min, respectively. According to the literature [41,42] these values correspond to values typical for heterogeneous reactions where the rate of chemical reaction is the rate determining step.

3.3.2. Thermal transformation

The XRD characterization was performed for the sample mechanosynthesized for 45 min and annealed in argon in the DTA regime. After heating to 700°C the phase identified as SnS_2 loses much sulphur and it consists of large-grain SnS and Sn_2S_3 identified by X-ray diffraction measurements. The chemical transformation of tin sulphide phase may be described by the equation

$$4SnS_2 \rightarrow Sn_2S_3 + 2SnS + 3S \quad (2)$$

4. Conclusions

1. New 4H-SnS_2 and berndtite 4H-SnS_2 phases were prepared from elemental tin and sulphur by mechanochemical processing. The new phase has relatively strong and sharp peaks in the XRD pattern and its occurrence is supported by Mössbauer spectroscopy.
2. The grains of the synthesized sulphides are 12–18 nm in size. During milling secondary particles (aggregates) are formed that are 20–60 μm in size.
3. The particle size and the related large specific surface area (7–21 $m^2\ g^{-1}$) strongly influence the chemical

dissolution of tin from mechanochemically synthesized sulphides.

4. The thermal decomposition of SnS_2 phases is characterized by the loss of elemental sulphur and the formation of large grained SnS and Sn_2S_3 compounds.

Acknowledgements

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