

# Properties and Reactivity of Mechanochemically Synthesized Tin Sulfides

P. Baláž,\* T. Ohtani,† Z. Bastl,‡ and E. Boldižárová

\**Institute of Geotechnics of the Slovak Academy of Sciences, 043 53 Košice, Slovakia;* †*Laboratory for Solid State Chemistry, Okayama University of Science, Okayama 700, Japan;* ‡*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague, Czech Republic*

Received September 4, 1997; in revised form June 8, 1998; accepted June 24 1998

The paper deals with the study of SnS, Sn<sub>3</sub>S<sub>4</sub> (SnS+Sn<sub>2</sub>S<sub>3</sub>), Sn<sub>2</sub>S<sub>3</sub> and SnS<sub>2</sub>. The sulfides were prepared by mechanochemical synthesis in a planetary mill. The surface and bulk composition of the sulfides were verified by XPS and XRD methods. The particles of synthesized sulfides are formed by crystallites that are 11–27 nm in size. These crystallites form secondary particles (agglomerates) with 30–50 μm size due to intensive milling. The samples have great reactivity during their dissolution in an alkaline solution of Na<sub>2</sub>S. The apparent activation energy of SnS dissolution is 27 kJ mol<sup>-1</sup>. © 1999 Academic Press

## INTRODUCTION

Sulfides are currently recognized as advanced inorganic materials with nonconventional applications. Research activities for new methods of sulfide synthesis are focused on solid state chemistry and mechanosynthesis. The application of mechanosynthesis using for high-energy grinding enables the mixing of components on the atomic level, a shift of the reaction regime from diffusion to kinetic or close to kinetic and a preparation of products with maximum interfacial area/total volume ratio (1–3). Since it is possible to study the progress of mechanosynthesis using various identification and/or analytical methods, it is also possible to prepare partially or totally synthesized tin sulfides with controlled structures (4–11).

Tin sulfides represent a complex system with a wide compositional range. They frequently show the features of low dimensional chalcogenides: polytypism, polymorphism, nonstoichiometry and the possibility of exfoliation (12–14). Some of them, e.g. SnS<sub>2</sub> consists of two layers of closely packed sulfur anions with sandwiched tin cations in octahedral coordination. The sulfides of this type have a large number of empty sites in their structure and hence they are interesting host lattices for intercalation (15–16).

The aim of the presented work is to evaluate the bulk and surface composition as well as the reactivity of some tin sulfides prepared by mechanochemical synthesis.

## EXPERIMENTAL

### Material

For the mechanochemical synthesis of tin sulfides the following chemicals were used: tin (powder, 100 mesh, Alfa Ventron, Germany) and elemental sulfur (powder, Lachema, Czech Republic). The starting mixtures were prepared from the individual elements with the following S:Sn weight ratios: 1:3.70 (sample Sn-S/1), 1:2.78 (sample Sn-S/2) and 1:2.47 (sample Sn-S/3). After weighing the individual components the mixture was homogenized by mixing in methanol for 60 min. After drying, 4 g of the mixture was milled in a planetary activator URF-AGO 2 (Russia) under the following conditions: charge, 110 steel balls with 5 mm diameter, 60 min milling time in argon atmosphere, 70 min<sup>-1</sup> rotational speed of the planet carrier, 1000 ms<sup>-2</sup> centrifugal acceleration on thimble axes.

### Methods

Powder X-ray diffraction measurements were performed on RIGAKU RAD-B using CuK $\alpha$  radiation (0.3 kW, 0.5°/min). Lattice parameters were determined by the least-squares methods.

The ZDS software product was used for crystallite size determination based on the analysis of selected X-ray diffraction profiles using the variance method.

Scanning electron micrographs of the investigated samples were obtained on a BS 300 (Tesla, Czech Republic) scanning electron microscope (SEM).

The photoelectron spectra (XPS) were recorded on a VG ESCA 3 Mk II electron spectrometer (VG Scientific, Great

Britain). The pressure of residual gases during spectra acquisition was in the  $10^{-6}$  Pa range. The XPS measurements were performed using an AlK $\alpha$  (1486.6 eV) source at 220 V power. The spectrometer was operated in the fixed analyzer transmission mode with a pass energy of 20 eV, giving a resolution of 1.1 eV on Au ( $4f_{7/2}$ ) line. The Fermi level of the spectrometer served as an energy reference. The photoelectron spectra were calibrated using the C 1s binding energy of adventitious carbon at 284.8 eV. The specimens were prepared by pressing the powder samples onto indium foil attached to the sample probe. The probe was cooled by liquid nitrogen to eliminate sublimation of elemental sulfur that may be present in sample. The spectra of S 2p, Sn 3d, O 1s, and C 1s photoelectrons were measured. All samples were measured using the same protocol. For the binding energy data, was estimated an error limit of 0.2 eV. The estimated accuracy of the calculated ratios of atomic concentrations amounts to 10%.

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

The reactivity of mechanochemically synthesized tin sulfides was tested for dissolution reaction with sodium sulfide and sodium hydroxide solution. During the sulfidic tin solubilization in this environment tinsulfates and sodium–tin hydroxide compounds of the  $\text{Na}_2(\text{SnS}_3)$ ,  $\text{Na}_4(\text{SnS}_4)$  and  $\text{Na}_2(\text{Sn}(\text{OH})_6)$  type can be formed (17). Reaction conditions: 300 mL solution of  $25 \text{ gL}^{-1} \text{ Na}_2\text{S} + 12.5 \text{ gL}^{-1} \text{ NaOH}$ , weight of tin sulfide: 400 mg, dissolution time: 30 min, temperature 30–60°C.

The experimental results were fitted to the kinetic equation

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

where the  $\varepsilon_{\text{Sn}}$ ,  $k$  ( $\text{s}^{-1}$ ) and  $t_L$  (s) stand for the conversion degree, rate constant, and dissolution time respectively.

The temperature dependence of the dissolution was fitted to the Arrhenius equation from which the apparent activation energy  $E$  was calculated.

## RESULTS AND DISCUSSION

### *The Structure and Properties of Mechanochemically Synthesized Tin Sulfides*

The results of the qualitative diffraction phase analysis show that the main product of mechanochemical synthesis are SnS,  $\text{Sn}_3\text{S}_4$  (or  $\text{SnS} + \text{Sn}_2\text{S}_3$ ), and  $\text{Sn}_2\text{S}_3$ .

In case of specimen Sn–S/1 the X-ray diffraction pattern (Fig. 1C) is similar to that of the SnS of JCPDS card No. 39-0354. Almost all the peaks were indexed on the basis of an orthorhombic structure with the spacegroup  $Pbnm$ . The calculated lattice parameters ( $a = 0.4318 \text{ nm}$ ,  $b = 1.1200 \text{ nm}$ ,

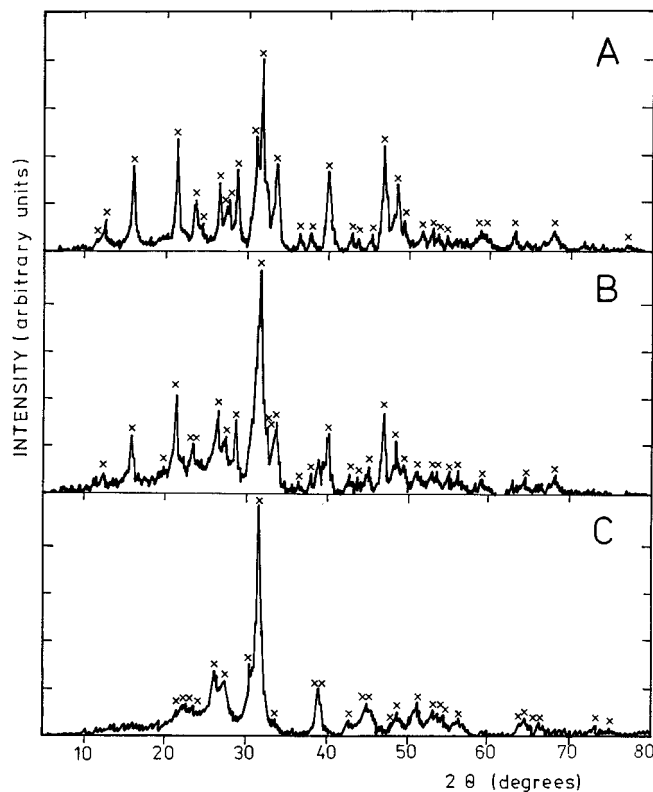


FIG. 1. XRD pattern of Sn–S samples: (A) Sn–S/1 sample, (x) SnS (JCPDS 39-0354); (B) Sn–S/2 sample, (x)  $\text{Sn}_3\text{S}_4$  (JCPDS 27-0900), (o) SnS (JCPDS 39-0354); (C) Sn–S/3 sample, (x)  $\text{Sn}_2\text{S}_3$  (JCPDS 14-0619).

$c = 0.3984 \text{ nm}$ ) were consistent with the data of the JCPDS card.

The X-ray pattern of sample Sn–S/2 (Fig. 1B) is similar to that of  $\text{Sn}_3\text{S}_4$  of JCPDS card No. 27-0900. Still the JCPDS card is questionable because there is no report about the existence of the  $\text{Sn}_3\text{S}_4$  phase in the binary phase diagrams of the tin–sulfur system (18). The X-ray pattern seems to correspond to a mixed SnS and  $\text{Sn}_2\text{S}_3$  phase.

TABLE 1  
Qualitative XRD Analysis, Iron Wear by Grinding, Crystallite Size, and Specific Surface Area of Mechanochemically Synthesized Products in Tin–Sulfur System

Sample	XRD analysis (major component)	Iron wear by grinding (%)	Crystallite size, $D$ (nm)	Specific surface area, $S \times 10^3$ ( $\text{m}^2 \text{ kg}^{-1}$ )
Sn–S/1	SnS	0.49	11	3.32
Sn–S/2	$\text{Sn}_3\text{S}_4$ (SnS + $\text{Sn}_2\text{S}_3$ )	0.19	13	5.36
Sn–S/3	$\text{Sn}_2\text{S}_3$	0.25	27	7.28

The X-ray pattern of sample Sn-S/3 (Fig. 1A) was consistent with that of JCPDS card No. 14-0619. The calculated lattice parameters ( $a = 0.8889$  nm,  $b = 1.4020$  nm,  $c = 0.3744$  nm) were also in accordance with the data for  $\text{Sn}_2\text{S}_3$ .

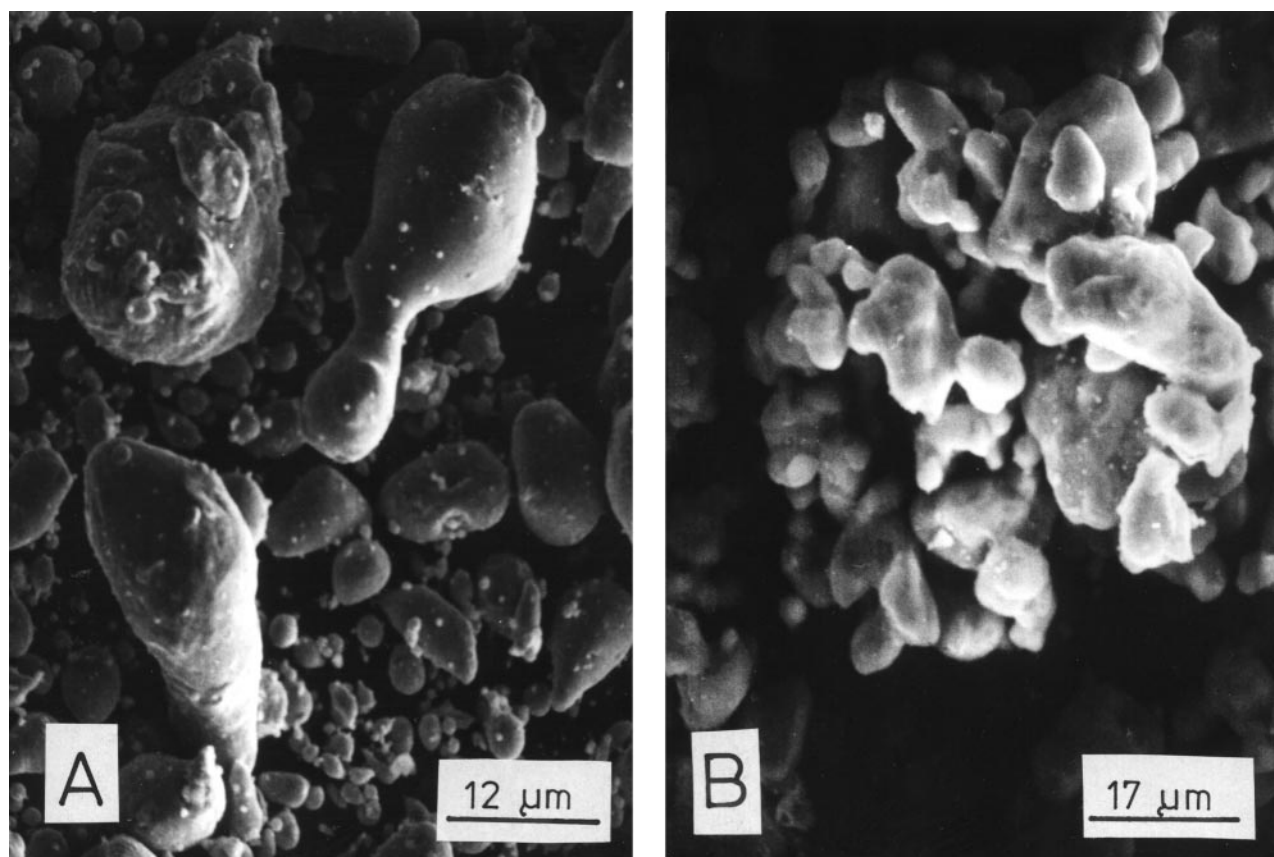
In Table 1 the data on the crystal size and specific surface area of the mechanochemically synthesized sulfides are given together with data on the quantity of Fe that was abraded from the mill. The crystal size was calculated from the X-ray analysis data. Their size varies from 11 to 27 nm and increasing with the increasing proportion of sulfur. A similar situation prevails also in case of specific surface. The specific surface of sulfides is by one order of magnitude greater than in case of the precursors of the synthesis, i.e. metallic tin and elementary sulfur. The specific surface value is in the range that is achieved by intensive milling of sulfides (19).

The photomicrographs of the mechanochemically synthesized sulfides as well as of the reactants entering the process are shown in Figs. 2 and 3. In one direction the particles show a 30 to 50  $\mu\text{m}$  size and their structure resembles clusters of secondary sulfide particles (agglomerates) that were subjected to intensive milling (19).

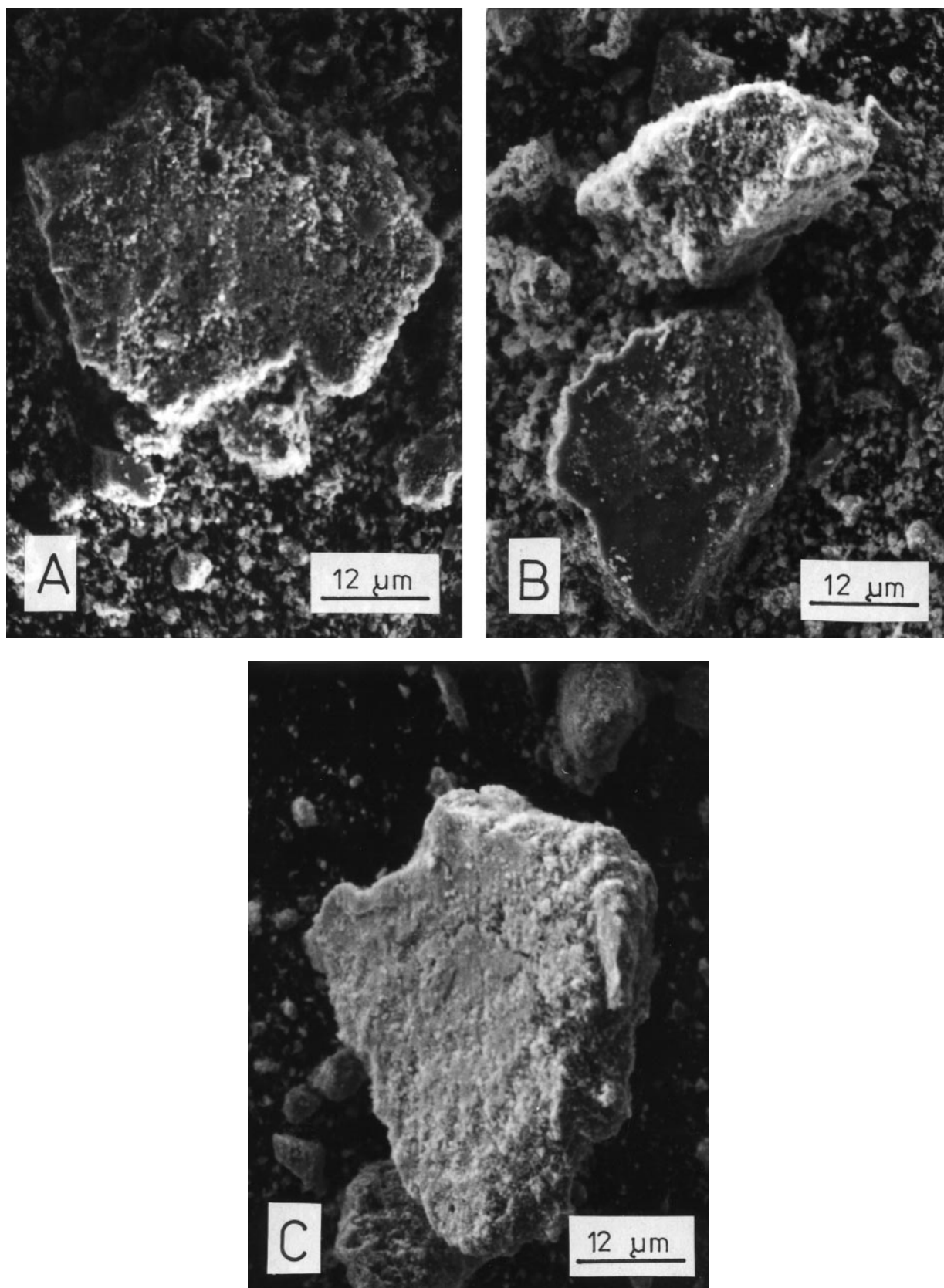
**TABLE 2**  
Core Level Binding Energies and Widths of the Photoemission Lines (in Parenthesis)

Sample	Line	
	Sn $3d_{5/2}$	S $2p_{3/2}$
Sn-S/1	486.6 (2.5)	161.6 (2/3)
Sn-S/2	486.6 (2.4)	161.7 (2.2)
Sn-S/3	486.8 (3.4)	161.9 (3.1)

The analysis of XPS spectra of the mechanochemically synthesized sulfides is shown on Figs. 4–6. From a qualitative standpoint the spectra are very similar. Figure 5 shows the spectrum of the S  $2p$  electron doublet. It can be seen that sulfur is present in a single chemical state. From the comparison of the measured values of the binding energy of S  $2p$  electrons (Table 2) with the published values (20) it follows, that it is a sulfidic sulfur. Figure 6 shows the spectra of Sn  $3d$  electrons. The values of the binding energy of the Sn  $3d$  electrons for the analyzed samples are given in Table 2 and



**FIG. 2.** Photomicrographs of tin sulfides synthesis precursors: (A) elemental Sn; (B) elemental S.



**FIG. 3.** Photomicrographs of mechanochemically synthesized tin sulfides: (A) SnS; (B)  $\text{Sn}_3\text{S}_4(\text{SnS} + \text{Sn}_2\text{S}_3)$ ; (C)  $\text{Sn}_2\text{S}_3$ .

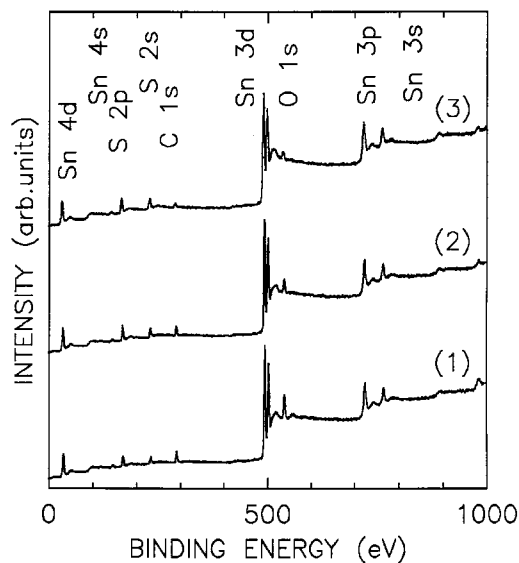


FIG. 4. The XPS survey spectrum of mechanically synthesized product in the tin-sulfur samples: (1) Sn-S/1; (2) Sn-S/2; (3) Sn-S/3.

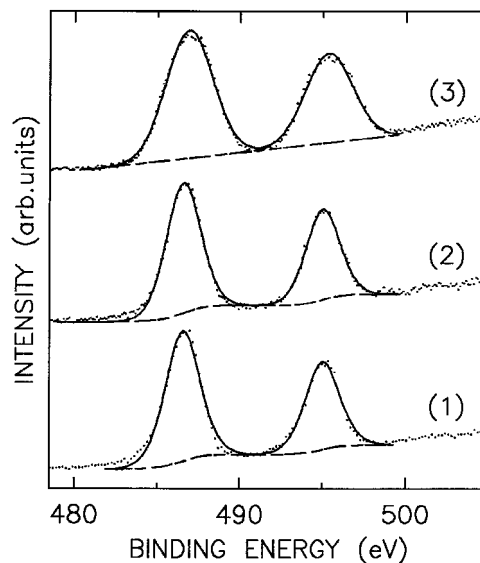


FIG. 6. The Sn3d XPS spectrum of mechanochemically synthesized product in the tin-sulfur samples: (1) Sn-S/1; (2) Sn-S/2; (3) Sn-S/3.

have a spread that is within the range of experimental error. It is also consistent with the presence of tin sulfides. Figure 7 shows the relation between the ratios  $(S/Sn)_{XPS}$  calculated from XPS analysis of the atomic concentrations of sulfur and tin and the ratios  $(S/Sn)_{MS}$  calculated from the atomic concentrations of sulfur and tin and the ratios  $(S/Sn)_{MS}$

calculated from the atomic concentrations of the same elements mixed for the mechano-synthesis (MS). For the analyzed specimens, the values that characterize the  $(S/Sn)_{XPS}$  surface composition of the sulfides are lower than the values that characterize the bulk composition  $(S/Sn)_{MS}$ . There is, however a linear relationship between these two ratios.

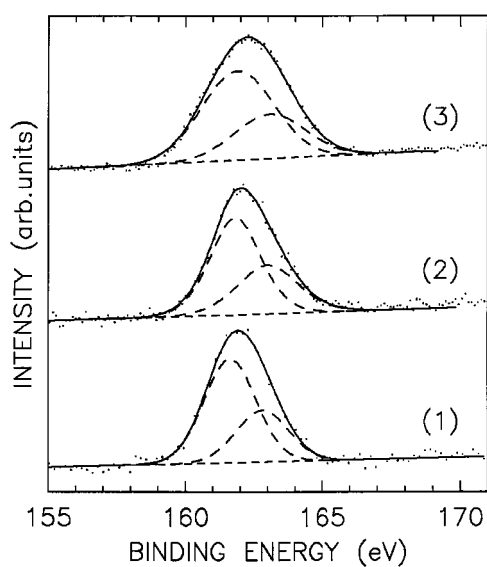


FIG. 5. The S2p XPS spectrum of mechanochemically synthesized product in the tin-sulfur samples: (1) Sn-S/1; (2) Sn-S/2; (3) Sn-S/3.

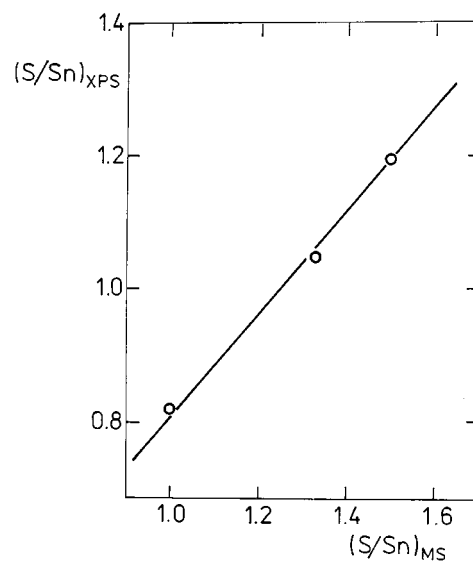


FIG. 7. Ratio of sulfur and tin XPS atomic concentrations,  $(S/Sn)_{XPS}$  vs ratio of sulfur and tin calculated from the atomic concentrations of the same elements mixed for the mechano-synthesis (MS).

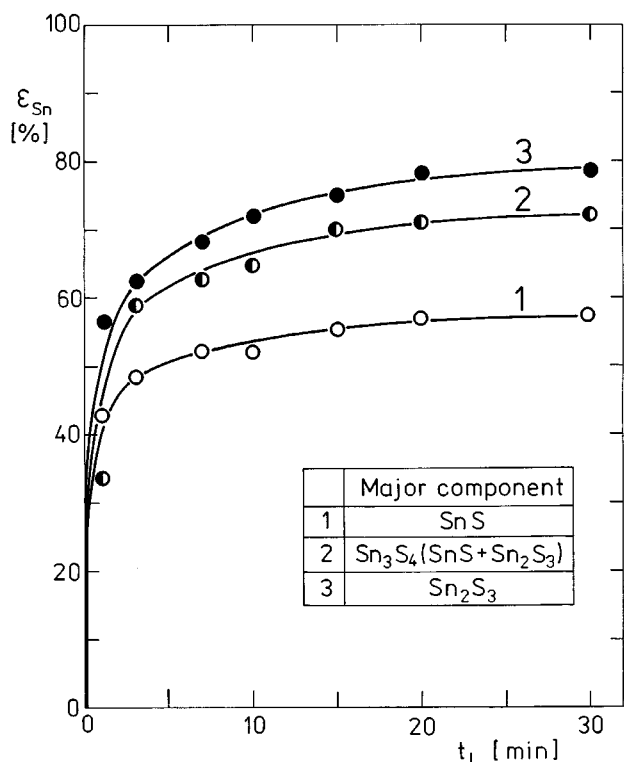


FIG. 8. Influence of dissolution time,  $t_L$  on the recovery of tin,  $\epsilon_{Sn}$  from the mechanochemically synthesized product in the tin-sulfur samples: (1) Sn-S/1; (2) Sn-S/2; (3) Sn-S/3.

### Reactivity of the Mechanochemically Synthesized Tin Sulfides

The samples of mechanochemically synthesized sulfides were subjected to dissolution reaction in the alkaline environment of Na<sub>2</sub>S. For the reaction temperature  $T = 30^\circ\text{C}$ , Figure 8 shows the relationship between the degree of conversion  $\epsilon_{Sn}$  and dissolution time  $t_L$ . The process of dissolution is characterized by great initial speed. After 5 min of reaction, more than 50% of the tin bound to a sulfidic form was dissolved.

The temperature sensitivity ( $T = 30\text{--}60^\circ\text{C}$ ) of the mechanochemically synthesized SnS is given in Fig. 9. Its assessment in Arrhenius coordinates (Fig. 10) shows that the apparent activation energy is  $E = 27 \text{ kJ mol}^{-1}$ . This value suggests that the factor determining the speed of the dissolution is probably the chemical reaction on phase boundaries (21).

### CONCLUSIONS

1. SnS, Sn<sub>3</sub>S<sub>4</sub> (SnS + Sn<sub>2</sub>S<sub>3</sub>), Sn<sub>2</sub>S<sub>3</sub>, and SnS<sub>2</sub> were prepared by mechanochemical synthesis in a planetary mill. Their surface and bulk composition were determined by XPS and XRD methods.

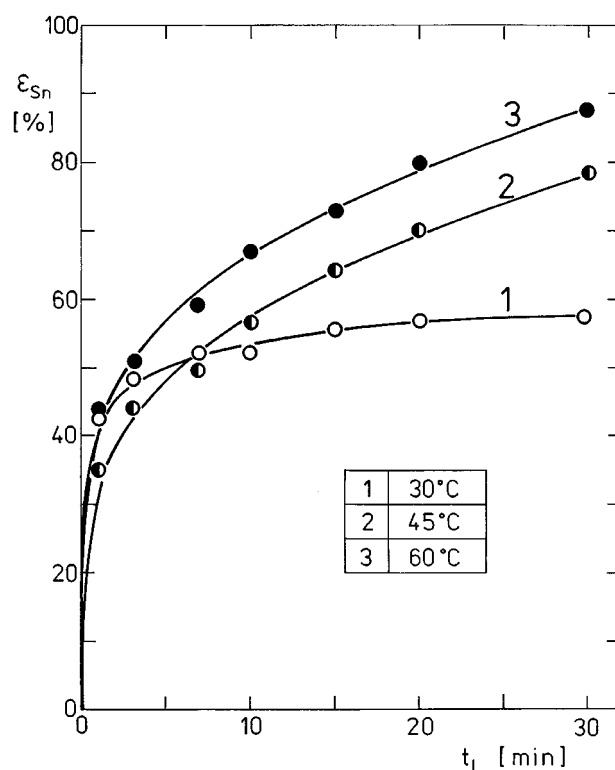


FIG. 9. Influence of dissolution time,  $t_L$  on the recovery of tin,  $\epsilon_{Sn}$  from mechanochemically synthesized product in the Sn-S/1 sample. Temperature of reaction: (1) 30°C; (2) 45°C; (3) 60°C.

2. The particles of synthesized sulfides are 11–27 nm in size. During milling, secondary particles (aggregates) are formed that have 30–50  $\mu\text{m}$  size.

3. Tin sulfides prepared by mechanochemical route have great dissolution reactivity in Na<sub>2</sub>S solution.

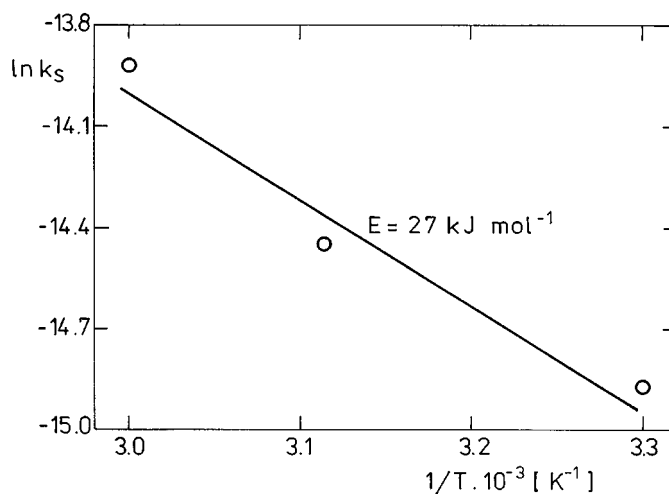


FIG. 10. Arrhenius plot of the specific rate constant,  $k_s$  ( $k_s = k/S$ ;  $k$  = rate constant from equation [1];  $S$  = specific surface area) of tin dissolution in the Sn-S/1 sample.

## ACKNOWLEDGMENT

This work was partly supported (P.B.) by Slovak Grant Agency for Science VEGA (grant 95/5305/561).

## REFERENCES

1. E. G. Avvakumov, *Sibir. Chim. Ž.* **5**, 62 (1991).
2. P. J. Butjagin, *Dokl. Akad. Nauk SSR* **319**, 384 (1991).
3. V. V. Boldyrev and E. Boldyreva, *Mater. Sci. Forum* **88–90**, 711 (1992).
4. Ch. Chakurov, G. G. Gospodinov, and Z. Bontschev, *J. Solid State Chem.* **41**, 244 (1982).
5. Ch. Chakurov, V. Rusanov, and G. Gospodinov, *J. Solid State Chem.* **59**, 265 (1985).
6. Ch. Chakurov, V. Rusanov, and J. Koichev, *J. Solid State Chem.* **71**, 522 (1987).
7. V. Rusanov and Ch. Chakurov, *J. Solid State Chem.* **79**, 181 (1989).
8. V. Rusanov and Ch. Chakurov, *J. Solid State Chem.* **89**, 1 (1990).
9. T. Havlík, P. Baláž, Z. Bastl, J. Briančin, and R. Kammel, *Kovové Mater. (Metallic Materials)* **34**, 376 (1996).
10. L. Takacs and M. A. Susol, *J. Solid State Chem.* **121**, 394 (1996).
11. P. Baláž, Z. Bastl, T. Havlík, J. Lipka, and I. Tóth, *Mater. Sci. Forum* **235–238**, 217 (1997).
12. M. Senna, *Crystal Res. Technol.* **20**, 209 (1985).
13. F. Jellinek, *Reac. Solids* **5**, 323 (1988).
14. J. Rouxel, A. Meerschaut, and G. A. Wiegers, *J. Alloys Comp.* **229**, 144 (1995).
15. J. Morales, C. Perez-Vicente, and J. L. Tirado, *Solid State Ionics* **51**, 133 (1992).
16. W. Müller-Warmuth and R. Schöllhorn (Eds.), "Progress in Intercalation Research," Kluwer Academic, Dordrecht, 1994.
17. H. Remy, "Anorganická chemie," SNTL, Praha, 1961. [in Czech]
18. R. C. Sharma and Y. A. Chang, in "Binary Alloy Phase Diagram" (T. B. Massalsky, H. Okamoto, P. R. Subramanian, and L. Kacprzak, Eds.), p. 3280, ASM International, 1990.
19. P. Baláž, "Mechanical Activation in the Processes of Extractive Metallurgy," Veda, Bratislava, 1997. [in Slovak]
20. The NIST X-ray Photoelectron Spectroscopy Database, U.S. Department of Commerce, Gaithersburg, MD, 1989.
21. Habashi, "Principles of Extractive Metallurgy, Vol. I—General Principles," Gordon & Breach, New York, 1974.