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Surface and bulk properties of mechanically activated zinc sulphide

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BET, scanning electron microscopy, X-ray photoelectron, infrared, X-ray diffraction and Mössbauer spectroscopy methods were used to identify changes in surface, structural and spectroscopic properties of sphalerite produced by mechanical activation. Activated samples exhibit amorphization of crystallographic structure of the mineral, as well as of hyperfine structure of the accessory manganese. The presence of a new magnetic phase was disclosed in the samples activated for longer periods of time. Changes in structure are accompanied by mechanochemical oxidation of the surface layer of sphalerite.

1. Introduction

Zinc sulphide, ZnS, belongs to the group of substances exhibiting great sensitivity to mechanical stress [1–9]. The predisposition to this sensitivity is a consequence of crystallographic structure of zinc sulphides which are typical representatives of minerals with laminated lattices. In nature ZnS occurs in two forms, cubical sphalerite and hexagonal wurtzite. These two minerals are terminal members of the series comprising the so-called polytypes, the structure of which differ from each other only by the sequence of layers showing different periodicity of individual modifications [10]. It is known that only these structures contain the so-called stacking faults, the occurrence probability of which frequently depends on the energy necessary for a displacement of one layer with respect to the other [11]. The peculiarities of crystallographic structure are augmented by the presence of impurities of which iron and manganese isomorphically replace zinc in the lattice. The presence of these elements can be used for investigating the hyperfine structure of the mineral.

The aim of this study was to obtain information on the changes in surface and volume properties of the sphalerite which was subjected to mechanical activation by intensive grinding.

2. Experimental procedure

2.1. Materials

The investigations were carried out with sphalerite originating from the Soviet Union with the following composition: 44.60% Zn, 33.58% S, 15.53% Fe, 2.48% insoluble balance.

2.2. Mechanical activation

The mechanical activation of samples was performed in a vibration mill under the following conditions: revolutions of the mill 18.5 s^{-1}, amplitude 6.6 mm, ball charge 80 balls of 15 mm diameter, weighed amount of the sample 20 g, time of activation $t_G = 0.125, 0.25, 1, 2.5$ and 4 h.

2.3. Particle morphology

The particle morphology was monitored using a scanning electron microscope BS 300.

2.4. Surface area

The specific surface area, S_A, was determined from the adsorption isotherms of benzene vapour by the BET method [12].

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2.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCA 3 MK II apparatus in 10^{-6} Pa vacuum. The electrons were excited by AlK_α emission of $h\nu = 1486.6$ eV. The transmission energy of the electron analyser was 20 eV, and the width of the entrance slit of the analyser was 4 mm.

The surface concentrations were determined from the photoionization cross-sections [13] and attenuation electron lengths calculated from the equations suggested by Seah and Dench [14].

2.6. Infrared spectroscopy

The infrared spectra were obtained with Specord 75 IR using the KBr disc technique.

2.7. Crystallinity

The change in content of the crystalline phase, X, was estimated by diffraction phase analysis using the internal standard method. The diffraction data were obtained with a diffractometer DRON 2.0 working with CuK_α radiation, 30 kV, 20 mA, time constant 1 s, limit of measurement 10^3 impulses/s, rate of detector $2° \text{ min}^{-1}$, paper drive 2400 mm h^{-1}.

2.8. Electron paramagnetic resonance spectroscopy

Electron paramagnetic resonance (EPR) spectra of mechanically activated sphalerite were obtained using an ERS-XQ instrument.

2.9. Mössbauer spectroscopy

Mössbauer spectra were measured by the transmission method at room temperature and evaluated by computer. ^{57}Co in a rhenium matrix as a source of γ-radiation was used.

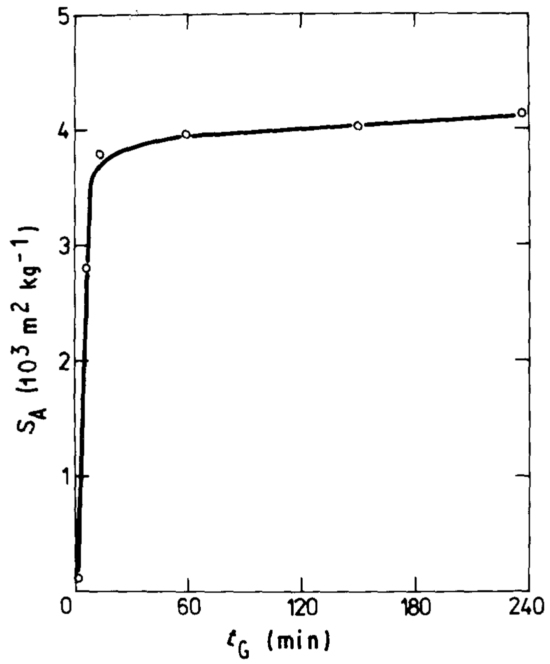

Figure 1 The influence of grinding time, t_G, of sphalerite on the specific area, S_A.

3. Results and discussion

3.1. Surface area

The course of new surface formation of sphalerite as a function of grinding time, t_G, is represented in Fig. 1. The value of specific surface, S_A, rapidly increases up to $t_G = 7.5$ min. For $t_G \geqslant 15$ min the rate of new surface formation is practically constant, and only a small increase in S_A is obtained.

3.2. Scanning electron micrographs

The morphology of the ground particles is characterized by the scanning electron micrographs given in Fig. 2. At $t_G = 7.5$ min, not only the disintegration but

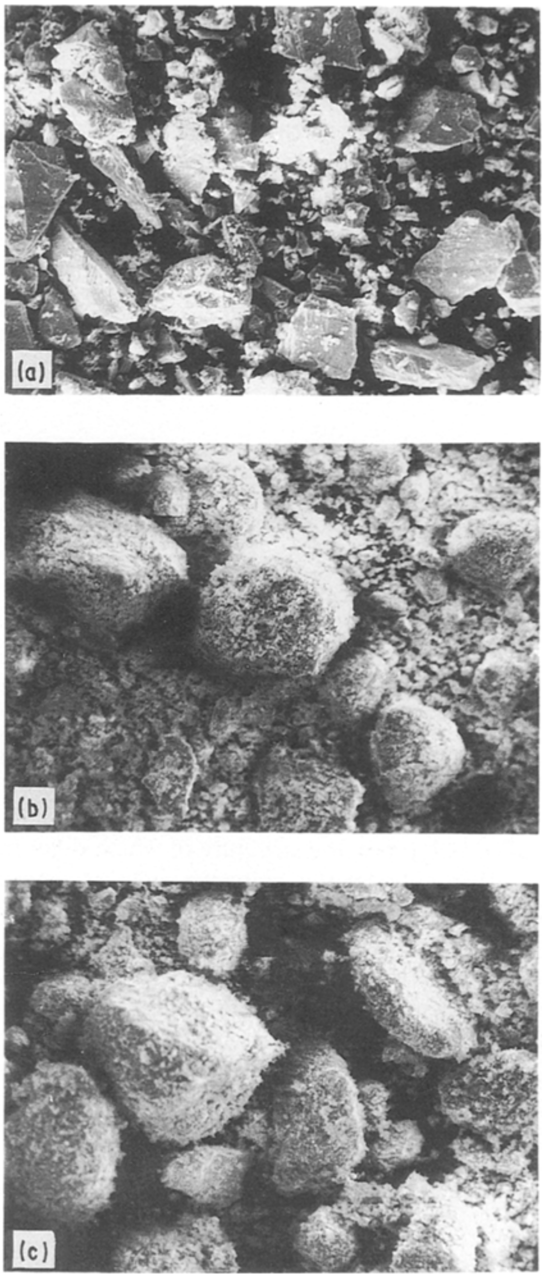

Figure 2 Scanning electron micrographs of sphalerite: (a) standard (non-activated) sample, (b) mechanical activation, $t_G = 7.5$ min, (c) mechanical activation, $t_G = 240$ min. × 200

also the accumulation of ground particles and the formation of aggregates begins (Fig. 2b). The aggregation becomes a dominant process at $t_G = 240$ min (Fig. 2c).

3.3. X-ray photoelectron spectroscopy

The XPS spectrum of the sphalerite ground for 240 min (Curve 1) as well as the XPS spectrum of the unground sample (standard, Curve 2) is represented in Fig. 3. The measurements performed at high resolution have shown that the spectra of the ground samples differ from those of the standard in distribution of sulphur, zinc, iron, and oxygen.

In the surface of the standard, sulphur is present merely as S^{2-}, while not only the sulphidic form but also the sulphate form occurs in the ground samples (Fig. 4). The ground sample differs from the standard also by the presence of iron, the content of which in the samples ground for a longer time rapidly increases. Oxygen is present in all samples, but its relative content in the ground samples is higher. The spectra show the presence of carbon which is a common contaminant of natural materials. Its concentration is independent of the grinding time. A quantitative evaluation of the content of individual elements expressed in atomic ratio is given in Table I. The ratio of atomic concentrations $(O/Zn)_r$ or S^{6+}/S^{2-}, is plotted against grinding time, t_G, in Fig. 5. (The value of $(O/Zn)_r$ was obtained by subtracting the value $O/Zn = 1.50$ obtained for the standard from the values of O/Zn obtained for the corresponding ground samples.)

3.4. Infrared spectroscopy

The general information about infrared spectra of the mechanically activated sphalerite is given in Fig. 6. The standard (Curve 0) exhibits a poor spectrum with an information content (as with other sulphides) within the range $\bar{\nu} < 400\ \text{cm}^{-1}$ [15]. In comparison with the standard, the spectra comprise new bands at 460,

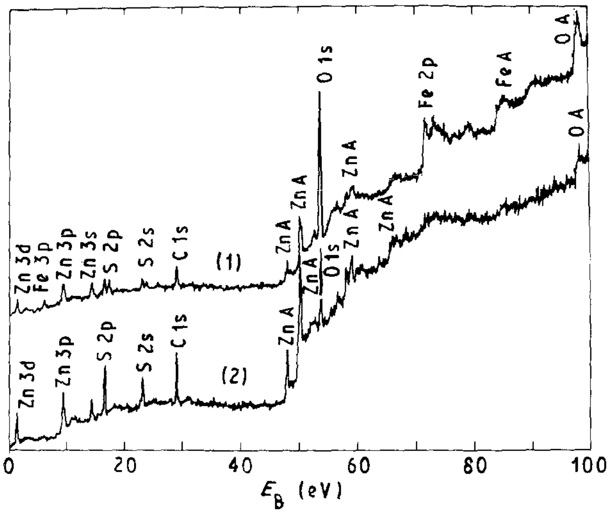

Figure 3 XPS review spectra of sphalerite. 1, Mechanical activation, $t_G = 240$ min; 2, standard (non-activated) sample.

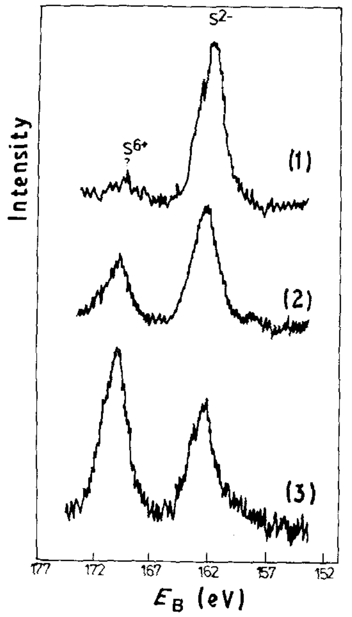

Figure 4 XPS spectra of sulphur forms in sphalerite. 1, Standard (non-activated) sample; 2, mechanical activation, $t_G = 7.5$ min, 3, mechanical activation, $t_G = 60$ min.

TABLE I Ratio of atomic concentrations of sulphur, iron, zinc and oxygen in surface layer of sphalerite

Grinding time, t_G (min)	S^{6+}/S^{2-}	Fe/Zn	O/Zn
0 (standard)	0	0	1.55
7.5	0.49	0.2	3.37
15	0.63	0.2	3.89
60	1.30	0.2	4.80
150	1.12	0.4	5.79
240	0.77	0.5	5.16

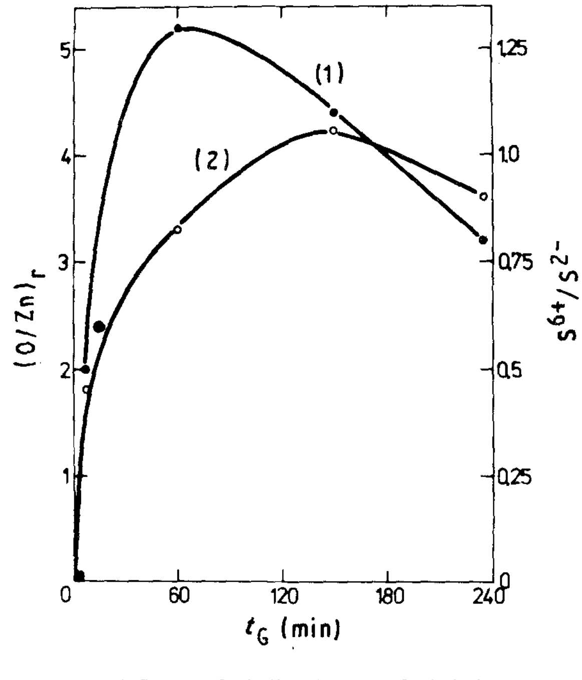

Figure 5 The influence of grinding time, t_G, of sphalerite on (1) ratio of atomic concentrations $(O/Zn)_r$ and (2) oxidation forms of sulphur S^{6+}/S^{2-}.

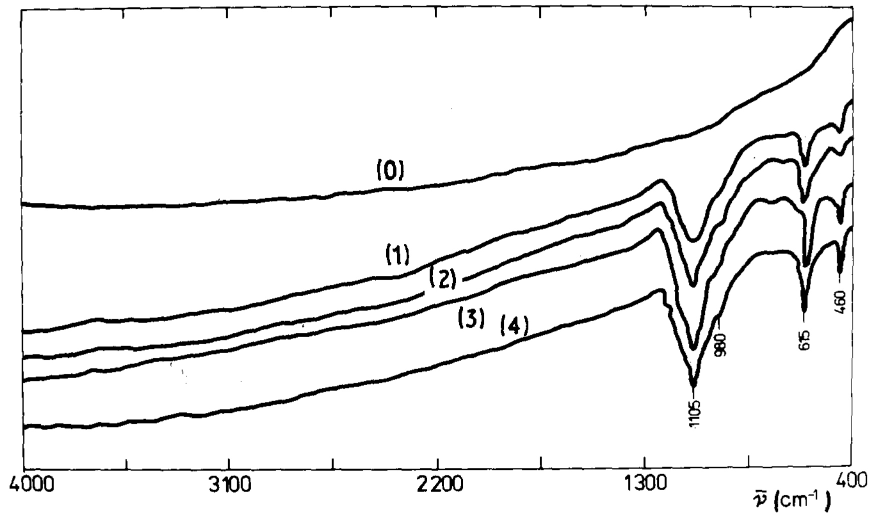

Figure 6 Infrared spectra of sphalerite: (0) standard sample (− 74 μm), (1–4) mechanically activated samples for t_G = 7.5, 15, 60, and 240 min.

615, 980 and 1105 cm^{-1} which correspond to the SO_4^{2-} group. A similar effect was also observed by Gock [4].

3.5. Crystallinity

The crystalline phase content of the ground samples, X, and the corresponding amorphization of their structure, A, calculated from X $(A = 1 - X)$ is represented in Fig. 7 as a function of grinding.

3.6. EPR spectroscopy

The EPR properties of sphalerite demonstrate the intricacy of its ultrafine structure [16]. The presence of manganese as a paramagnetic marker is used for investigating these properties. In a standard sample of sphalerite we can identify the main spectrum of manganese, Mn^{2+}, the centre of which is characterized by the value $g = 2.001$. The spectrum shows hyperfine splitting at 6.7 mT. On the basis of the shape of the spectrum we can assume that the Mn^{2+} ions occupy positions corresponding to cations in the lattice of sphalerite [17]. In the course of mechanical activation the amplitude of the manganese lines rapidly decreases and their widths simultaneously increase (Fig. 8). The changes in parameters A and ΔH of the EPR spectrum of manganese are a consequence of different local electric fields produced by mechanical activation. For a sample activated at $t_G = 180$ min, a new spectrum of manganese, indicating the presence of a new phase, appears. The centre of the spectrum exhibiting hyperfine splitting at 9.5 mT corresponds to the value $g = 2.020$. The new likely amorphous phase is characterized by the Mn^{2+} ions built in interstitial positions of the lattice of sphalerite [9].

3.7. Mössbauer spectroscopy

The Mössbauer spectrum of a ground sample (Fig. 9) like that of the standard originates from paramagnetic

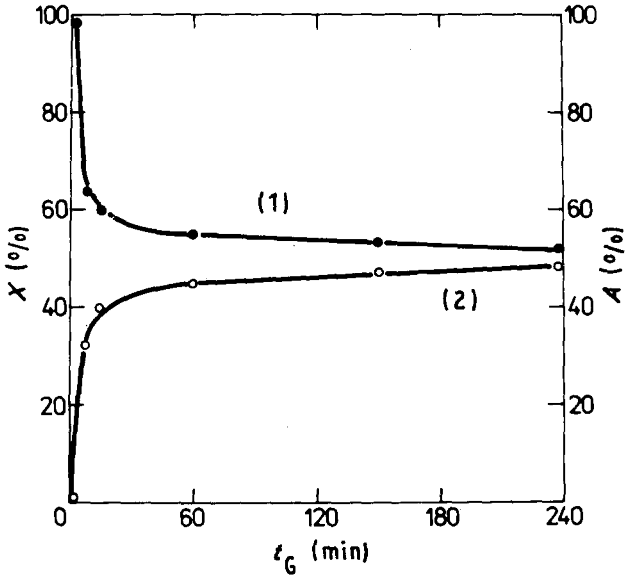

Figure 7 The influence of grinding time, t_G, on changes in content of (1) crystalline phase, X, and (2) amorphization, A, of sphalerite.

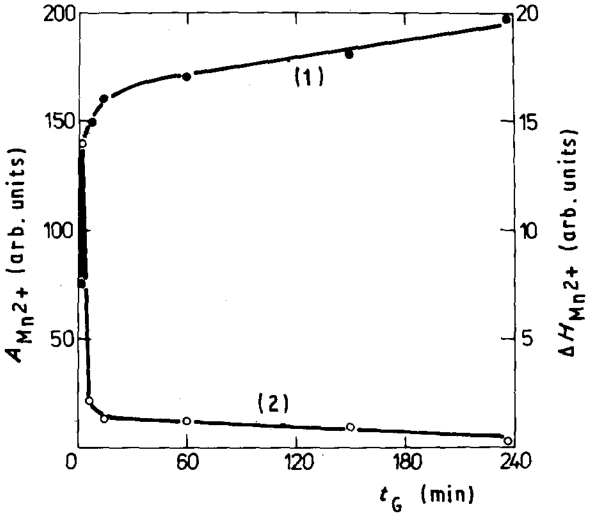

Figure 8 The influence of grinding time, t_G, on (1) amplitude $A_{Mn^{2+}}$ and (2) width $\Delta H_{Mn^{2+}}$ of the resonance line of manganese.

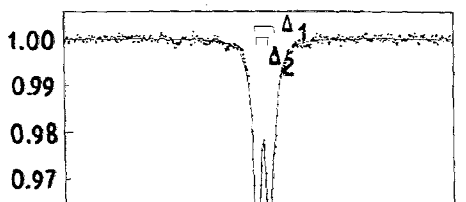

Figure 9 Mössbauer spectrum of mechanically activated sphalerite ($t_G = 15$ min).

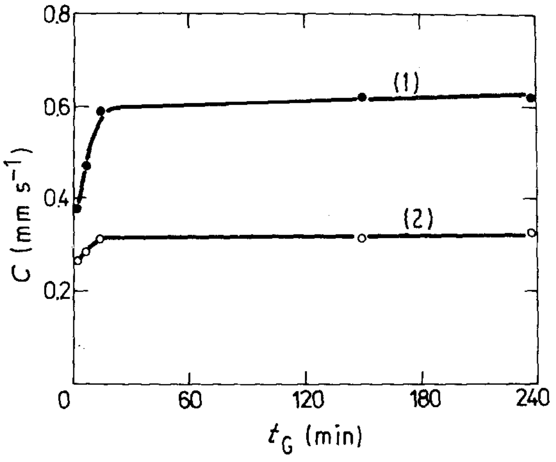

Figure 10 The influence of grinding time, t_G, on width C of doublets Δ_1 and Δ_2 for (1) sphalerite and (2) pyrite.

components. We performed an approximation by using two doublets, Δ_1 and Δ_2. Doublet Δ_1 corresponds to bivalent iron substituted in cationic positions of the lattice of sphalerite, while the parameters of doublet Δ_2 are identical to those of pyrite the presence of which was also evinced by XRD. The width of the corresponding doublet, C, which is a measure of violation of magnetic arrangement of the structure of the investigated mineral as a function of grinding time, t_G, is shown in Fig. 10.

4. Conclusions

The changes in morphology (SEM) and surface properties (S_A) as well as in crystallographic order (X, A) of sphalerite are consistent with published data and confirm its sensitivity to mechanical stress. A multiple increase in the quantities mentioned, compared with the standard (unground sample), occurs with grinding time. We can observe two regions in the relationships between these quantities and the time of mechanical activation (Figs 1, 7, 8, 10). These quantities increase rapidly at $t = 0$–15 min, while the increase slows down at higher values of t_G. We assume that this retardation is due to the formation of agglomerates (Fig. 2). In most cases, this agglomeration is incidental to grinding in the gaseous phase. The agglomeration of fine particles has an attenuating effect on propagation of defects in the solid phase. A similar effect was also observed in the course of dry grinding of the chalcopyrite–pyrite mixture [18].

In spite of the retardation effect of agglomeration, the surface layers of sphalerite are subjected to changes which indicate mechanochemical oxidation. We have ascertained by the methods of XPS and infrared spectroscopy that owing to mechanical stress the sulphidic sulphur in the surface of sphalerite is oxidized and transformed into the hexavalent sulphate form.

In addition to surface changes, there are also changes in hyperfine structure (Fig. 8). Their character is analogous to the changes in crystallographic order (Fig. 7). However, at extreme stress ($t_G \geqslant 150$ min), a new phase arises and it is characteristic of this phase that the manganese ions pass from the cationic positions in the lattice of sphalerite into its interstitial positions. This abrupt change in structure may be due to increased occurrence of the iron atoms in the surface of the mineral which was also recorded by XPS (Table I). We also observed a similar threshold effect when studying the hyperfine structure of mechanically activated chalcopyrite. That observation has been described in our previous paper [19].

Acknowledgement

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