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Structural investigations on iron containing natural Zincblende using EBSD

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ABSTRACT

A sample of natural zinc sulfide containing iron (from Portugal, Albergaria, Velha) was systematically investigated with respect to its microstructure using XRD (X-ray diffraction) and EBSD (electron back scatter diffraction). The habitus of the black sample suggests a hexagonal crystal structure, i.e. the occurrence of the Wurtzite phase. Nevertheless, using XRD and EBSD allowed only detecting and localizing the cubic Zincblende structure within the sample with the fibrous habitus while the expected hexagonal Wurtzite structure and possibly a hexagonal FeS structure were missed. The macroscopic fibrous structures consist of non-uniform and elongated grain structures which possess a preferred orientation with the $<224>$-direction parallel to the fiber direction. Inside the grains, twinning occurs ($\Sigma 3$-Twinning) as well as grain fragmentation. Iron is not distributed homogeneously; instead areas with unique iron concentrations occurred. They were arranged like twins with iron concentrations from 4.1 up to 5.1 at% as detected and localized using energy dispersive x-ray spectroscopy (EDS). Fe^{2+} is incorporated in lattice sites of Zn^{2+}. Although the phase diagram FeS-Zn-S is not yet completely determined in all composition ranges of interest, coexisting phases (zincblende and FeS) should be expected at room temperatures. The results may contribute to further insights into the growth mechanisms of natural zinc sulfide, respectively to the discussion about. Furthermore, it was shown, that the crystal habitus not always allows concluding on the crystals symmetry with certainty.

1. Introduction

Zinc sulfide is a well investigated mineral. It often occurs in the shape of Schalenblende as component in several ores and is the major ore used for zinc extraction in metallurgy. Major deposits of zinc sulfide in minerals are located in Portugal as described by several authors [1–4]. ZnS occurs in nature as cubic Zincblende, also denoted Sphalerite, as well as hexagonal Wurtzite [5–7]. The lattice structures, Zincblende and Wurtzite are well investigated and described and they are used as model structures for other phases and semiconductor materials of the same crystal symmetry but different chemistry, for example SiC, GaN, AlN, ZnSe, CdS and CdTe etc.[8]. Besides, numerous hexagonal polytypes of larger unit cells have been synthesized and described in the literature [5,9–11]. That is in analogy to similar phases such as silicon carbide [12,13].

Minerals from natural deposits are usually not pure but contain impurities, i.e. other metal component which might form solid solutions or additional phases, yielding in varying physical properties [14,15]. The formation of natural samples underlies different complex growth mechanisms (see ref. [14]) and it is good to understand them in the geological context. Investigation on the microstructure, phase composition, element distribution, textures and crystal orientation characteristics allow to obtain further insights into growth mechanisms and may allow to conclude on the geological conditions during formation.

In former times, especially in the last two centuries and up to day the habitus, the cleavability as well as the macroscopic shape and morphology have been used in mineralogy to distinguish Zincblende and Wurtzite and also to identify other occurring phases. That procedure has also been used for natural ZnS minerals, which were taken from the Velha mine in Albergaria, Portugal [1,2]. Several authors described the samples as fibrous, with a hexagonal habitus, and identified Wurtzite [1,3]. However, a few authors noticed, that a columnar and fibrous structure not always allows it to conclude on the occurrence of Wurtzite [1,3]. In the meantime, several new techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), electron backscatter diffraction (EBSD) and

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transmission electron microscopy became applicable and can be used for more detailed investigations.

2. Experimental methods

Natural ZnS samples were studied by X-ray diffraction (XRD) using a SIEMENS D5000 diffractometer and CuKα radiation. In order to refine the lattice parameter at a given crystal symmetry, corundum powder was added to the powdered sample for a more precise peak adjustment. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and electron backscatter diffraction (EBSD) were performed using a Jeol JSM-7001F equipped with a TSL Digiview 3 EBSD-camera. Surface charging in the SEM sample was avoided by contacting the samples with Ag-paste and applying a thin layer of carbon at a pressure of about 10^{-3} Pa.

EBSD-scans were captured and evaluated using the programs TSL OIM Data Collection 5.31 and TSL OIM Analysis 5.31. The EBSD-scans were performed using a voltage of 20 kV. For the calculation of pole figures (PF) with stereographic projection only reliably indexed data points with a confidence index (CI) ≥ 0.1 were used. Cleanups of the scan data were performed by CI-standardization and grain dilation. Pol figures of textures are presented in multiples of a random distribution (MRD).

3. Results

3.1. Shape of the sample

Fig. 1 shows an image of the studied sample of natural ZnS with a size of 10.5 cm x 8.5 cm x 3.4 cm. It shows a macroscopically columnar structure, as expected from a hexagonal Wurtzite sample. The color of the specimen is black.

3.2. Phase identification

Due to the fact, that it is not known how the studied fragment sample laid in the earth or how it was oriented relatively to the layers it originates from, the sample was cut in two different ways: the first was parallel and the second was perpendicular to the macroscopic columnar structures. The occurring phases were characterized by XRD. The XRD-patterns shown in Fig. 2 were obtained from a powdered sample (a), and from bulk samples (b) and (c). Pattern (b) was recorded from a sample cut perpendicular to the columnar structures and pattern (c) from a sample cut parallel, i.e. along to the columnar structures. The graphs (d) and (e) show theoretical patterns according to the JCPDS files for the cubic Zincblende and the hexagonal Wurtzite structure, respectively. Normalizing the patterns to the 111-peak respectively the 0002-peak allows a better evaluation of possibly occurring preferred orientations.

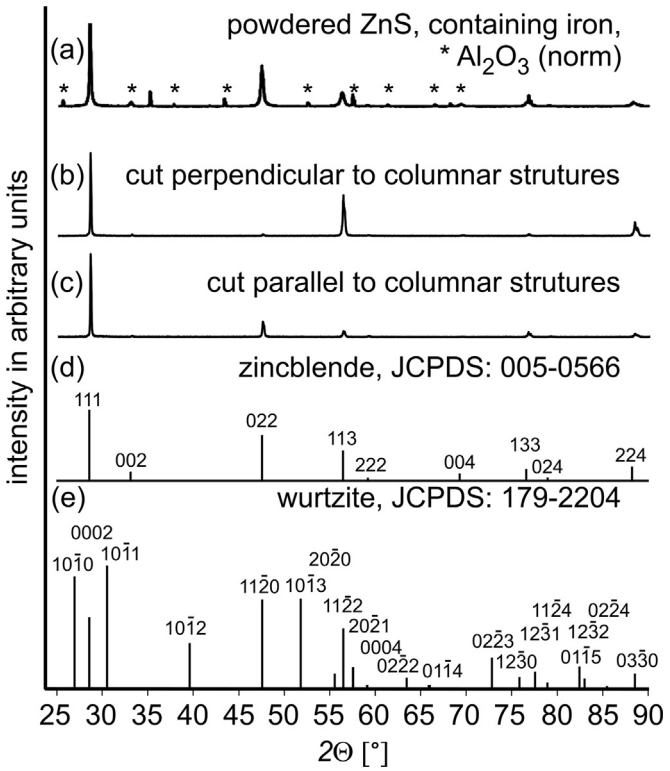

Fig. 2. XRD-patterns: (a) obtained from a powdered sample, (b) from a compact sample, cut perpendicular to the columnar structures, (c) from a compact sample, cut parallel to the columnar structures and for comparison (d) and (e) the patterns of statistically oriented Zincblende (JCPDS No. 005–0566) and Wurtzite (JCPDS No. 179–2204), respectively.

Pattern (a) presents the raw data of the powdered sample with corundum, which was added for normalization and a more accurate determination of the 2θ-values. The pattern fits very well in the intensities with the theoretical JCPDS file of Zincblende (d) after refining the lattice parameter to a = 5.41(36) Å, which will be discussed later on. The high intensity peaks at 2θ = 26.9 ° and 30.5° as well as 51.7° of Wurtzite are not observed within the error limits of XRD. In the XRD pattern obtained from the cut

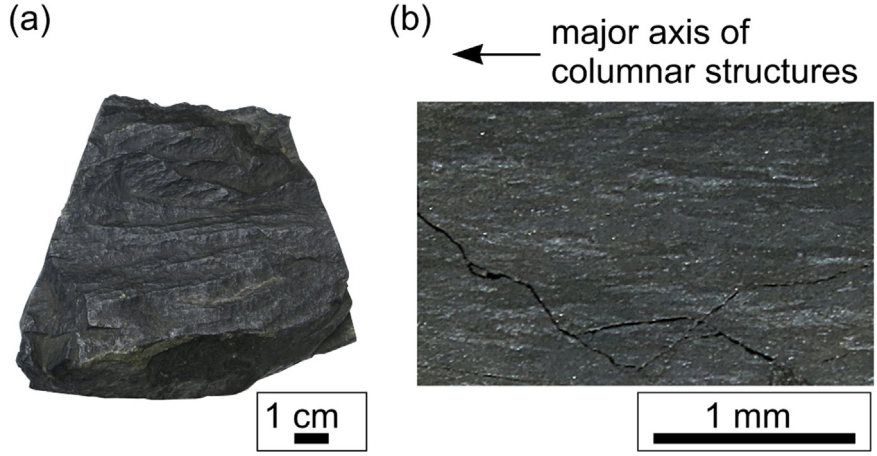

Fig. 1. Images of natural Zincblende: (a) whole bulk sample, (b) cut through the sample showing a macroscopic columnar structure.