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Rietveld refinement study of pyrite crystals

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Abstract

Rietveld refinement was performed for two samples prepared from natural pyrite (a polymorph of iron disulphide or iron persulphide, FeS_2) single crystals originating from Navajun (Spain) and from Ural Mts. (Russia). The present refinements provide the following crystallographic data: $a = 5.41784(2)$ and 5.41819(2) Å, $x = 0.3848(1)$ and 0.3840(1) for the above-mentioned crystals, respectively. They are comparable with those of several crystals from other geological deposits, reported in literature. The obtained diffraction results indicate an off-stoichiometry with a higher sulphur content in the sample from Ural. The last observation is qualitatively supported by the results of X-ray photoelectron spectroscopy. The crystallographic data are discussed on the basis of earlier literature information on composition and structure reported for synthetic bulk and thin-layered pyrite.

Keywords: Electrode materials; Crystal structure and symmetry; X-ray diffraction; Pyrite; FeS_2; Powder diffraction; Lattice parameter; Structure refinement; Rietveld method; Iron; Sulphur; Stoichiometry

1. Introduction

The pyrite (a cubic polymorph of iron disulphide or iron persulphide, FeS_2), is the most abundant sulphur-containing mineral in the earths crust [1]. Moreover, it is a second source of sulphur after that of native sulphur. Pyrite is also known as a natural component of sediments [1,2]. The name of pyrite comes from a Greek expression pyrites lithos—“a stone which strikes the fire”. It crystallises in space group $Pa\bar{3}$ with Fe atoms at (0, 0, 0) and S atoms at (u, u, u), with $u = \sim 0.385$. [Bayliss has attributed a (pseudocubic) triclinic structure to some pyrite samples exhibiting a weak anisotropy [3]; for discussion of other pseudocubic structures in pyrite family see Ref. [4]]. The electronic structure of pyrite has been studied or discussed in Refs. [5–12]. There are numerous indications that pyrite is or can be nonstoichiometric (see e.g. [5,13–16] and references therein). The deviation from stoichiometry is found to have a weak but well determined influence on the lattice parameter of bulk FeS_2 crystals [5].

It is worth noting that the analysis of geochemical processes involving pyrite at high pressure–high temperature conditions is thought to be important for understanding of geochemical synthesis of organic molecules 4 gigayears ago [17]. Moreover, models exist connecting pyrite and iron sulphides with emergence of life on the earth (see [18,19] and references therein). Just this last compound is present also in space, in protoplanetary disks and cometary dust [20], and detected in meteorites [21].

Photoelectrochemical energy conversion has been reported for ultrathin FeS_2 organo-metallic chemical-vapour-deposited layer on TiO_2 [22], so pyrite is a potentially photovoltaic material. The opportunity of its use in lithium batteries has been studied, e.g. in Refs. [23,24]. Some pyrite ores include impurities (inclusions) of noble metals (gold, silver) [1,25–28] and can be used for gold recovery; pyrite itself is a frequent (harmful) impurity phase in coal [1]. One of studied applications is the soil improvement/amendment [29–31]. On the other hand, the degree of pyritisation can be treated as an indicator helping in studies of geological sediments [32]. Pyrite is a basic component used in production of the sulphuric acid [1]. It is known to interact with

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the natural environment: the sulphuric acid together with iron hydroxides may form on the surface of stored crystals in contact with water or humid air; (this reaction is highly exothermic) [1]; for discussion of mechanisms, including chemical or microbial oxidation, see Refs [9,31,33–38]. On the other hand, pyrite is a largely 'destructive' mineral: as a major waste phase from mines it is a significant cause increasing the acidity of waters and thus a big menace for the environment (cf. remarks in Refs. [33,39]).

Very recently, pyrite has been proposed as a fine-tuning component of a tunable source of highly spin-polarised electrons, (Co, Fe)S_2 [40]. Moreover, (Co, Fe)S_2 is considered as a system offering insights into the design of half-metallic ferromagnets [41].

Accurate structural data of the bulk pyrite can be helpful in understanding its physical properties and designing its applications. In particular, full understanding of structural features connected with nonstoichiometric composition and with cationic or anionic substitution in pyrite are, still, at their infancy. The reported experimental data concerning FeS_2 include results of structural studies by single crystal diffraction and powder diffraction. Moreover, a number of papers are devoted to structure calculation from first principles [11,39,42–44]. The experimental structural data concern natural crystals [13,23,45,46], synthetic bulk crystals [5,23,47–52], and pure and doped polycrystalline [15,16,53] and monocrystalline [54] thin layers (see Table 1). Systematic, combined or comparative studies involve, e.g. XPS and theoretical investigation of pyrite surface [36], X-ray diffraction (XRD) and XPS study of high-quality thin FeS_2 films [54], the variation of structural properties with Fe:S ratio [5,15,16] and a study of synthetic and natural crystals [23]. The (minor) discrepancies between the reported a and x values are due to both, the sample properties (nonstoichiometry, impurities in mineral samples) as well as to instrumental factors. Influence of some impurities on the lattice constant is known, e.g. a raising tendency in a is observed when substituting Fe by Ni (see Ref. [53]), while for Zn substitution at Fe sites no such influence has been detected [47].

In the present study, Rietveld refinements for FeS_2 powdered natural single crystals were performed on sample A originating from Navajun (Spain) and sample B from Ural Mts. (Russia). The mentioned calculation method has already been found to be useful in studies of bulk FeS_2 crystals [23], arsenopyrite formation [55], in crystallographic/mineralogical studies including the pyrite phase (Rietveld refinement study of pyrite in coals [14]) and in mixture with marcasite [48] as well as in investigation of synthetic pyrite thin films [15,16].

2. Experimental

The purity was checked by X-ray photoelectron spectroscopy (XPS) (for experimental conditions see Ref. [56]). The amount of impurity elements in the studied samples is below the detectability level of this method. The X-ray diffraction data were collected in the 2θ range 5–160° using a Bragg–Brentano diffractometer. The instrument is equipped with a computerised GUR4 goniometer and a graphite monochromator cutting off the white radiation and fluorescence as well as Kβ spectral components. This kind of monochromator is especially important for the present specimens because of the Fe fluorescence emitted with the Cu radiation. External silicon standard was used for calibration. The experimental data-collection conditions at both instruments (datasets for samples A and B, respectively) are summarised in Table 2.

The samples for diffraction experiments were prepared by dusting the powder on a thin vaseline layer covering the surface of (5 1 0) oriented silicon single crystal, in order to reduce the background and minimise the possible preferred-orientation effects. Rietveld refinement was performed using the DBWS98.07 program (upgraded version of the program described in [57,58]) supported by DMPLOT3.48 graphical interface [59]. The pseudo-Voigt profile shape was assumed, as it gave markedly better fits than the Pearson VII function. Nineteen parameters were refined: scale factor, six background parameters, one lattice parameter, the free positional parameter, x, overall atomic displacement parameters, sulphur site occupancy factor, peak shape parameters, sample displacement, and profile asymmetry (the zero position was fixed at a value calibrated before this study). Two asymmetry models, those by Rietveld and by Riello et al. [60], were considered. The latter was used in final refinements due to better fitting results obtained. The preferred-orientation correction according to the Rietveld model was included assuming various possible orientations. This correction did not cause any improvement of the fitting results (showing that the sample preparation has eliminated the preferred orientation effects), therefore it is not included into the final refinements.

3. Results and discussion

Diffraction patterns of samples A and B exhibited the peak-to-background ratio (P/B), at the strongest 002 reflection, evaluated to be ∼95 and ∼115 for crystals A and B, respectively. Phase analysis indicated that there is no secondary phase in the studied specimens at the detectability limit of the applied measurement conditions (this limit is evaluated to be about 1% in the given case). Therefore, the initial structural model was built according to the single-phase pyrite structure (space group $Pa\bar{3}$). The result of the final Rietveld refinement is shown in Figs. 1 and 2. The final values of structural parameters and of the agreement factors R_{wp} and goodness of fit (GOF) are listed in Table 3. In general, the refined data are consistent with experimental and theoretical ones reported in the literature (cf. Table 3).

The refined lattice constants for the samples A from Navajun and B from Ural Mts. are $a = 5.41784(2)$ and 5.41819(2) Å, and the free positional parameter for sulphur