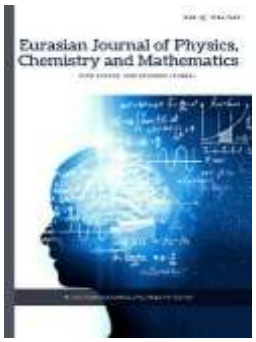

Investigation of the Nanostructure of Crystals by the Method of X-Ray Structural Analysis

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ABSTRACT

The significance and role of using the method of X-ray diffraction analysis in the study of the nanostructure of crystals are incomparable. By analyzing X-ray images obtained with an X-ray diffractometer, one can obtain sufficient information about the nanostructure of a crystal. Crystal symmetry, crystal lattice parameter, crystallite size, density of dislocations, microstrains, etc. are determined by X-ray diffraction analysis. This article discusses the determination of these structural parameters by X-ray diffraction analysis.

Keywords: XRD, nanostructure, crystallite size, dislocation density, microstrain, FullProf.

1. Introduction

X-ray diffraction analysis is one of the diffraction methods for studying the structure of a substance. This method is based on the phenomenon of X-ray diffraction on a three-dimensional crystal lattice. X-ray diffraction (abbr., XRD) - X-ray scattering by crystals (or molecules of liquids and gases) as a result of the interaction of X-rays with electrons of a substance, in which secondary deflected beams of the same wavelength arise from the initial beam of rays [1].

The direction and intensity of the secondary beams depend on the structure of the object on which the x-rays are scattered. A crystal is a natural three-dimensional diffraction grating for X-rays, since the wavelength of X-rays is of the same order as the distance between scattering centers (atoms) in a crystal (~1Å).

X-ray diffraction is the basis for such research methods as X-ray diffraction analysis and X-ray powder diffraction. X-ray diffraction analysis is based on the phenomenon of X-ray diffraction on the three-dimensional crystal lattice of an individual single crystal. The method makes it possible to determine the atomic structure of a substance, which includes the space group of an elementary cell, its size and shape, and also to determine the crystal symmetry group. Powder X-ray diffraction is a method for studying the structural characteristics of a material using X-ray diffraction on a powder or polycrystalline sample of the material under study. The result of the study is the dependence of the scattered radiation intensity on the scattering angle. The method makes it possible to determine the qualitative and semi-quantitative composition of the sample, the unit cell parameters of the sample, the texture of the material, and the sizes of crystallites (regions of coherent scattering) of a polycrystalline sample.

Diffraction determination of the average size of crystallites is an indirect method for determining the average size of small particles

(more correctly, coherent scattering regions) by broadening diffraction reflections (X-ray or electron diffraction) with a decrease in the size of crystallites of compact and powdery nanostructured substances and materials.

The diffraction method makes it possible to estimate the size of crystallites, averaged over the volume of the substance under study and somewhat underestimated in comparison with the results of electron microscopy. The small particle size is not the only possible reason for the broadening of diffraction reflections. Microdeformations and chemical inhomogeneity, i.e., inhomogeneity of the composition of the compound under study over the volume of the sample, are also responsible for the broadening of reflections.

The characteristic of the form of diffraction reflection is the full width at half-maximum (FWHM). The form of reflection is best described by the pseudo-Voigt function, which is a superposition of the Lorentz and Gauss functions.

The crystallite size is determined by the Debye–Scherrer formula [2]:

$$D = \frac{k\lambda}{\beta cos\theta} \quad (1)$$

where D – average crystallite size, k – geometric coefficient (=0.9), λ – X-ray wavelength (=1.5406 Å), β – diffraction reflection width at half maximum (FWHM), θ – diffraction angle.

In practice, the sizes of crystallites can be determined by formula (1) in the range from ~1500–2000 Å to 15–20 Å, and in different crystallographic directions (using lines with different indices). In addition, the broadening of the diffraction peaks can be due to microstrain in the crystals.

After determining the crystallite size, the dislocation density is determined by the equation:

$$\delta = \frac{1}{D^2} \quad (2)$$

The magnitude of the microstrain in the crystal was calculated using the Stokes-Wilson equation [3]:

$$\varepsilon = \frac{\beta}{4\tan\theta} \quad (3)$$

In this work, the nanostructure of a ZnS crystal is studied by X-ray diffraction, which explains the importance of X-ray diffraction analysis in studying the nanostructure of crystals.

2. Experimental methods

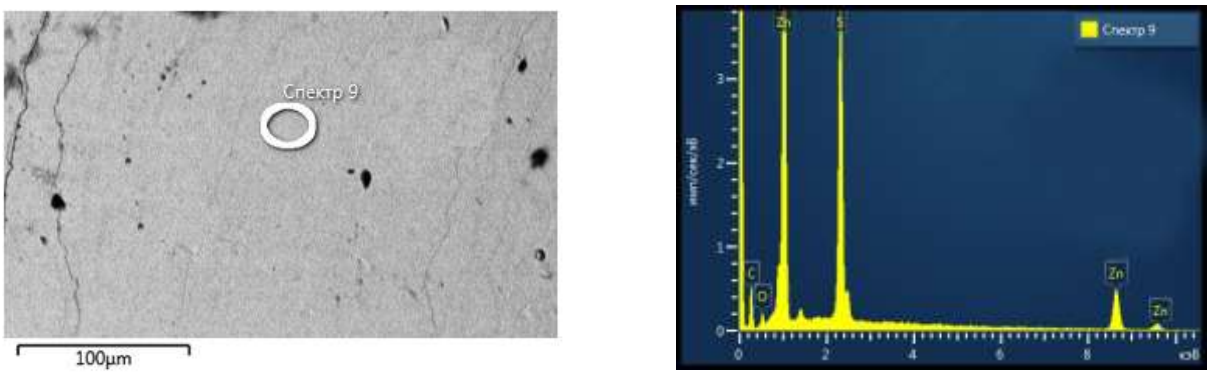
The studied ZnS crystal was grown by the CVD method [4, 5]. This method is one of the most convenient and reliable methods and is useful for large area industrial applications. The thickness of the ZnS sample studied in this work is 1.5 mm, and the base surface is 1 × 0.5 cm^2.

The elemental composition of the sample was determined using a SEM EVO MA10 scanning electron microscope (Oxford Instruments) by energy dispersive spectroscopy (Carl Zeiss).

X-ray diffraction studies of the ZnS structure were carried out on an Empyrean PAnalytical Series 3 diffractometer with CuKα (radiation wavelength λ=1.5406 Å). X-ray diffraction analysis data were processed by the Rietveld method using the Fullprof program. [6].

3. Results and discussion

The EDS spectrum of a ZnS crystal is shown in Fig.1. The result of measuring the elemental composition of the ZnS crystal was as follows: the weight of Zn atoms is 47.58%, and the weight of S atoms is 45.15%. This indicates that the sample is a pristine ZnS crystal.



(a) (b)

Fig.1. EDS spectrum of a ZnS crystal.
a) scanning electron microscopy (SEM) ZnS crystal;
b) the elemental composition of the depicted particles given in (a), measured by energy dispersive analysis, revealed Zn and S.

The X-ray diffraction pattern of the ZnS crystal is shown in Fig.2. To determine the structure and structural parameters of the ZnS crystal, its X-ray diffraction pattern was processed by the Rietveld method using the Fullprof program and calculations were performed. As a result of calculations (Bragg R-factor: 2.82; RF-factor: 2.43; χ^2= 3.11) it was found that the structure of this ZnS crystal belongs to the space group F-43m with a cubic structure (a=5.41695 Å) modified by α-ZnS. On the X-ray diffraction pattern of the ZnS crystal, (111), (220), (311), (331), (422), (511), (440), and (531) are clearly visible. The X-ray diffraction pattern showed a dominant peak belonging to the (220) plane of the cubic phase.

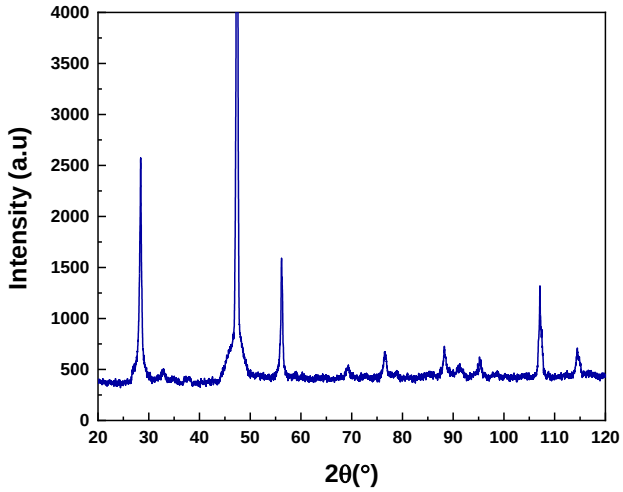


Fig.2. X-ray diffraction pattern of a ZnS crystal.

When calculating the structural parameters (lattice constant, crystallite size, microstresses, and dislocation density), peaks (111), (220), (311), (331), (422), (511), (440), and (531) were used. The Origin software was used to calculate the full half-widths of all peaks. The determined and calculated structural parameters are presented in Table 1.

Table 1.

№	hkl	2θ (°)	β FWHM (°)	D (nm)	δ (10^{15} m^{-2})	ε, (10^{-3})	a, (nm)
1	111	28.39	0.407	20.14	2.47	7.02	0.5441
2	220	47.39	0.285	30.41	1.08	2.84	0.5421

3	311	56.20	0.396	22.76	1.93	3.23	0.5424
4	331	76.57	0.687	14.74	4.60	3.79	0.5420
5	422	88.34	0.653	16.95	3.48	2.93	0.5416
6	511	95.25	0.591	19.95	2.51	2.35	0.5418
7	440	107.17	0.699	19.15	2.73	2.25	0.5415
8	531	114.58	0.896	16.40	3.75	2.51	0.5416

Therefore, by analyzing the Bragg angles and half-widths of each peak with high accuracy, it is possible to calculate the sizes of crystallites using the Debye-Scherrer formula. Knowing the size of crystallites, it is possible to calculate the density of dislocations and microstrain. The crystallite size of the studied ZnS crystal is from 15 to 30 nm. The dislocation density ranged from $1.1 \cdot 10^{15}$ m^{-2} to $4.6 \cdot 10^{15}$ m^{-2}, while microstrain ranged from $2.3 \cdot 10^{-3}$ to $7 \cdot 10^{-3}$.

When a crystal is exposed to external influences (for example, mechanical, thermal, radiation), changes occur in its nanostructure. For example, in the scientific work [7], when a ZnS crystal was irradiated with high-energy (8 MeV) accelerated electrons, the size of its crystallites increased. The increase in the crystallite size was analyzed by X-ray diffraction. In addition, a decrease in the density of dislocations and microstrain was observed, which was explained by an increase in the size of crystallites. It is assumed that such changes in the nanostructure affected the optical properties of the crystal. Therefore, the possibility of studying changes in the nanostructure of crystals by X-ray diffraction analysis is considered the most effective.

4. Conclusions

This paper shows how to use the method of X-ray diffraction analysis in the study of the nanostructure of crystals. Here, using the example of a ZnS sample, the issues of determining structural parameters, such as crystal symmetry, crystal lattice parameter, crystallite size, dislocation density, microstresses, are solved. It has been shown that sufficient information about the nanostructure of a crystal can be obtained by analyzing X-ray images obtained with an X-ray diffractometer. The results of this experimental work will serve as a database for further research.

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