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THE STRUCTURAL AND VIBRATIONAL PROPERTIES OF Ni-DOPED CHALCOPYRITE $CuFeS_2$

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The structural and vibrational properties of $CuFeS_2$ and $CuFe_{0.99}Ni_{0.01}S_2$ have been studied by X-ray powder diffraction and Raman spectroscopy methods. It has been found that, at normal conditions, the samples are characterized by space group I-42d. The relationship between the Raman spectra of $CuFeS_2$ and $CuFe_{0.99}Ni_{0.01}S_2$ of the vibrational modes were analyzed. Has been determined that, during the partial replacement of Fe^{3+} ions with Ni^{3+} ions in $CuFeS_2$ crystals, there changes occur in the dynamics of atomic.

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1. Introduction

$AB^{III}C_2^{VI}$ (A – one-valent cations, B − three-valent cations, C – chalcogen) triple chalcogenide compounds is a less studied compounds providing various physical properties [1-4]. There existence of many cation vacancies and anti-structure defects, causes formation of radiation centers. One of the most studied compounds in these compounds is a chalcopyrite $CuFeS_2$ compound. It has an extensive forbidden zone of the semiconductor properties, converts it to signifcant material for spintronica [5,6].

The crystalline structure of chalcopyrite $CuFeS_2$ compound having tetragonal symmetry of I-42d spatial group and lattice parameters: a = 5.24 Å və b = 10.3 Å having points [7]. The Cu atoms stand on the faces and nodes of elementary lattice. The S atoms creates FS_4 tetraedr around the Fe atoms symmetrical standing with Cu atoms on the faces and along the c axis [8]. The study of $TlFeS_2$ crystals having FeS_4 tetraedr indicating that, these crystals maintaining its own crystalline structure at wide temprature and presseure intervals [9-11].

There existence of Cu atoms in composition of compunds, causes not only changes of crystalline structure, also various physical properties. It has been determined that, in case the widht of the forbidden band of cubic symmetry FeS_2 compounds having Pa-3 spatial group [12,13], being the widht of forbidden band of tetragonal symmetry having I-42d spatial group is 0.5-0.7 eV [14]. The studies conducted on nano-structures of these compounds showed that, the widht of forbidden band in compounds having 70 nm sizes compatible with these points [15].

The theoretical calculations of atom dynamics shows that, there can be observed 15 optical and 2 acoustic mode in $CuFeS_2$ crystals: $\Gamma_{\mathrm{opt}} = 1A_1 + 2A_2 + 3B_1 + 3B_2 + 6E$ and $\Gamma_{\mathrm{ac}} = 1B_2 + E$ [16]. During the practices conducted with Raman spectroscopy there were observed maximum 4 of these modes [16]. The observance of vibration mode of $CuFeS_2$ compounds, depends on the size of powder grains.

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In submitted case, there were conducted partial replacements of Fe^{3+} ions with Ni^{3+} ions in chalcopyrite $CuFeS_2$ crystals. The crystalline structure and atomic dyanmics of obtained $CuFeS_2$ and $CuFe_{0.99}Ni_{0.01}S_2$ compounds were studied.

2. Experimental

$CuFeS_2$ and $CuFe_{0.99}Ni_{0.01}S_2$ compounds were synthesized by alloying elements of specific purity: carbonyl Fe and Ni, electrolytic copper – M0, OSCh 19-5 grade sulfur. The alloying was performed in evacuated (~ 0.1 Pa) quartz ampoules in divariant conditions. The partial pressure of volatile component was regulated by changing the temperature in the cold part of the ampoule. At the beginning of the process, the temperature of the high-temperature part of the ampoule was gradually raised up to 1100°C, while a part of the unreacted sulfur condensed in the cold part of the ampoule and was consumed as the synthesis proceeded. At the end of synthesis temperature of the cold part of ampoule was 450 °C; partial pressure of sulfur was over than 1 atm. After 6 hours of synthesis, the rate of cooling ampoule was 10grad/min.

Obtained samples were ground into powder and pressed at 200 atm, after that they were roasted at 700 °C during 200 hours.

The X-ray diffraction measurement was performed using a Bruker D8 Advance powder diffractometer with the following parameters: 40 kV, 40 mA, Cu $K\alpha$ radiation ($\lambda = 1.5406$ A). The X-ray diffraction data were treated using the FullProf program [17].

The Raman spectra were measured using a LabRam spectrometer (NeHe laser with wavelength 633 nm, confocal slit 110 μm, ×50 lens).

3. Results and discussion

The specters of $CuFeS_2$ and $CuFe_{0.99}Ni_{0.01}S_2$ compounds obtained through X-ray diffraction method at room temperature showed in fig. 1. According to the obtained spectr the crystalline structure was determined through the Ritveld method [18]. It was determined that, $CuFeS_2$ having tetragonal structure I-42d spatial groups in normal condition, lattice parameters: corresponds to $a = 5.2904(5)$ Å, $c = 10.4266(1)$ Å points and this compatible to the previous results [11]. The atomic coodinates of $CuFeS_2$ compounds provided in the table 1.

Table 1. Coordinate atoms of CuFe(Ni)S_2 compounds.

Atom	***x***	***y***	***z***
Cu	0.5	0	0.25
Fe1(Ni1)	0.00000	0.00000	0.00000
Fe2(Ni2)	0.00000	0.00000	0.2573(1)
S	0.2406(6)	0.2406(6)	0.1166(8)

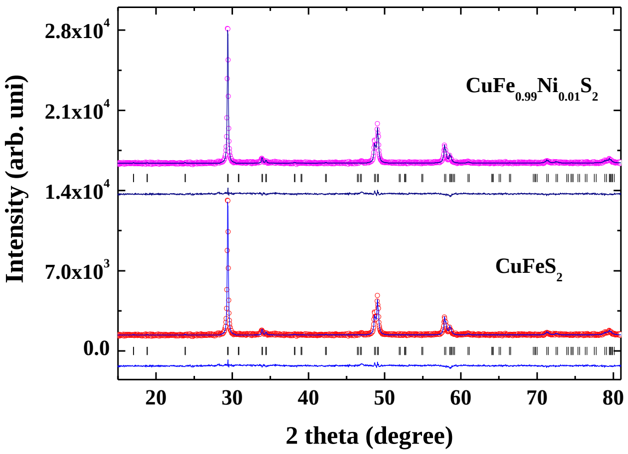

Fig. 1. X-ray diffraction spectra of $CuFeS_2$ and $CuFe_{0.99}Ni_{0.01}S_2$ measured at room temperatures. Experimental points, calculated profile, difference curve, and calculated positions of diffraction peaks are shown.

It was found that, the obtained $CuFe_{0.99}Ni_{0.01}S_2$ compounds in normal condition having I-42d spatial group of partial replacement of Fe atoms of $CuFeS_2$ with Ni atoms almost there is no difference in points of lattice parameters and atom coordination. This compliance, occurs regarding to having ion radius familiar to Fe^{3+} ions (r_{Fe} = 0.623 Å) Ni^{3+} ions (r_{Ni} = 0.623 Å) [19]. There were provided crystalline structure of $CuFeS_2$ and $CuFe_{0.99}Ni_{0.01}S_2$ compounds obtained in DIAMOND program [20] with the assistance of atom coordination (table) determined by X-ray diffraction in fig. 2. It seems from crystalline structure, these compounds creates $Fe(Ni)S_4$ tetraedr (fig. 2). During the partial replacement of Fe atoms with Ni atoms, there are no difference in tetraedr sizes because of having adjacent atomic numbers.

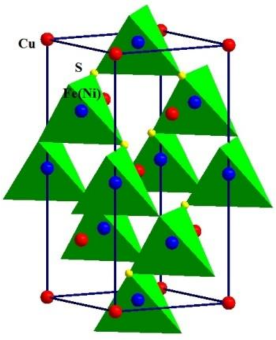

Fig. 2. Crystal structure of chalcopyrite $CuFeS_2$ ($CuFe_{0.99}Ni_{0.01}S_2$).

There showed spectrs obtained through Raman spectroscopy in 100-700 cm^{-1} interval at room temprature of $CuFeS_2$ and $CuFe_{0.99}Ni_{0.01}S_2$ compounds in fig. 3. It seems from the figure that, there are observed 3 various maximum in Raman spectr of $CuFeS_2$ compounds: ν_1 = 210 cm^{-1}, ν_2 = 274 cm^{-1}, and ν_1 = 387 cm^{-1}. These modes corresponds to rejimes in theoretical calculation ν_1 = 189 cm^{-1}, ν_2 = 270 cm^{-1}, and ν_1 = 383 cm^{-1} [11]. When the Ni atoms entered into compounds, there observed fundamental changes in Raman spectrs.

It seems from fig. 3, observed two mode having ν_1 = 258 cm^{-1} və ν_1 = 283 cm^{-1} points. The morphology studies that sizes magnified ×50 times shows that, Ni atoms entering to these compounds, increases the brightness of the samples (fig. 4). Here we come to the conclusion that, upon replacement of Fe atoms partially with Ni atoms, observed optical activity and there can be observed only faint v_1 = 258 cm^{-1} mode in v_1 = 283 cm^{-1} mode background corresponds to NiS_4 tetraedr vibration.

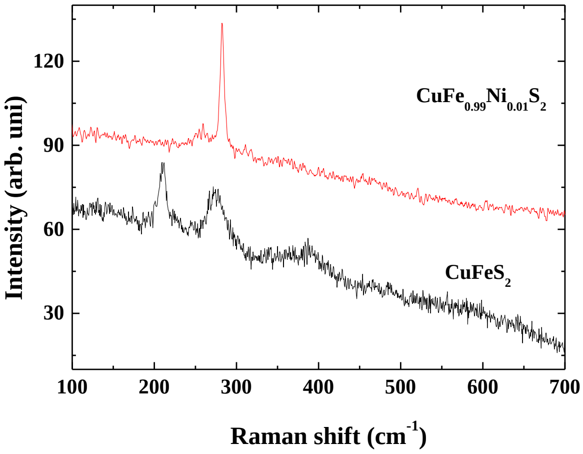

Fig. 3. Raman spectra of $CuFeS_2$ and $CuFe_{0.99}Ni_{0.01}S_2$ at room temperature.

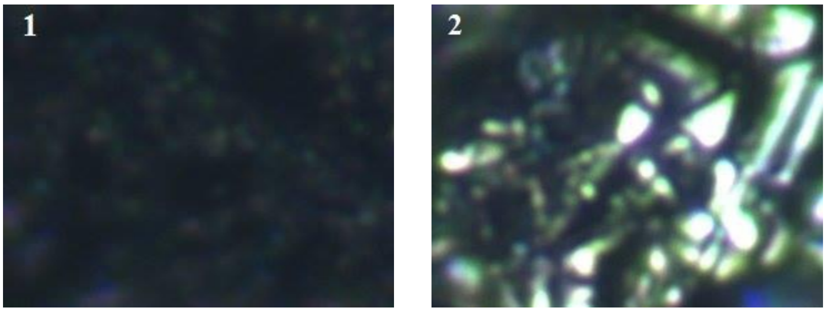

Fig. 4. 1) $CuFeS_2$ və 2) $CuFe_{0.99}Ni_{0.01}S_2$ surface of polycrystalline magnified in 50 times at optical microscope.

4. Conclusions

The crystalline structure of $CuFeS_2$ and $CuFe_{0.99}Ni_{0.01}S_2$ were studied by polycrystalline and X-ray diffraction of atomic dynamics and Raman spectroscopy methods. It was determined that, the crystalline structure and atomic coordination of these compounds are not differed. Thus, Fe and Ni atoms being in three-valent, their ions being the identical [14]. Therefore, in case being Ni atoms in compounds, there occurs fundamental changes in atom dynamics. There are observed active vibration of NiS_4 tetraedr, so it was explained by optical activity of compounds entered Ni atoms. It was approved once again with the surface brightness, being in optical active in relation with $CuFeS_2$ polycrystalline of $CuFe_{0.99}Ni_{0.01}S_2$ polycrystalline.

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