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STRUCTURAL AND VIBRATIONAL PROPERTIES OF $Bi_2(Sb_2)Se_3(Te_3)$ BINARY SEMICONDUCTORS

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Abstract. The crystal structures of the Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 compounds were investigated. The experiments were carried out using X-ray diffraction method at room temperature. It was found that the crystal structures of these compounds corresponds to rhombohedral symmetry with space group R-3m. Vibrational properties and atomic dynamics of Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 compounds were studied by Raman spectroscopy at room temperature. The differences in the crystal structure and atomic dynamics of these compounds are explained by the difference in the ionic radii of the Bi → Sb and Se → Te atoms.

Keywords: *binary semiconductor, atomic dynamic, ionic radii, XRD analysis, Raman spectroscopy.*

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1. Introduction

Binary and ternary semiconductors are among the most studied compounds due to their simple crystal structure and chemical composition (Haziyeva *et al*., 2018; Mamedov *et al*., 2019; Jabarov *et al*., 2018; Asadullayeva *et al*., 2019; Aliyev *et al*., 2019). The various physical properties of these compounds are studied under the influence of pressure, temperature and radiation (Azimova *et al*., 2020; Aliyev *et al*., 2020; Jabarov *et al*., 2015; Aliyev *et al*., 2019; Asgerov *et al*., 2018). The main reason for the interest in these materials (which retain their properties under high radiation conditions) is associated with the use of these materials in space and nuclear technology. It has been found that the effects of gamma rays, heavy ions and electron beams on these materials are different (Alekperov *et al*., 2019; Mirzayev *et al*., 2019; Mirzayev *et al*., 2019; Abdullayev *et al*., 2020; Mirzayev *et al*., 2020).

Structural studies have shown that the crystal structures of Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 have rhombohedral symmetry (Semiletov & Pinsker, 1955; Peacock & Berry, 1940; Semiletov, 1956). Differential thermal analysis shown that this crystal structure is retained up to a temperature of $T \approx 800$ K (Azimova *et al*., 2020). The thermodynamic properties of the Sb_2Te_3 compound irradiated with 167 MeV Xe ions have been investigated. At different irradiation doses, the Wigner entolpy in the Sb_2Te_3 compound decreased from 14.52 J/g to 6.08 J/g. The energy of the phase transition region decreased to 30.4 μJ in radiation to $\Phi = 3.83 \times 1014$ ion/cm2 fluence. It was found that there is a decrease in the value of the phase transition temperature, which occurs in the temperature range $510 \leq T \leq 657$ ºC (Azimova *et al*., 2020).

As one can see, the changes in various parameters of these compounds occurs as a result of external influences, but the general character remains unchanged. Therefore, the study of the crystal structure of these compounds will play an important role in

explaining various physical processes. In this work, the compounds Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 were synthesized and the crystal structures (by X-ray diffraction) and atomic dynamics (by Raman spectroscopy) were investigated of these compounds at room temperature.

2. Experiments

Single crystals of Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 compounds were synthesized by the Bridgman method (Azimova *et al*., 2020).

The structural phase analysis of the obtained samples was carried out by X-ray diffraction method using D8 Advance X-ray diffractometer (Bruker). Diffractometer parameters 40 kV, 40 mA, CuK_α - radiation (λ = 1.5406 Å). The experiments were carried out at room temperature. Synthesized single crystals were powdered for x-ray diffraction analysis.

Atomic dynamics of the samples were studied by Raman spectroscopy method. The experiments were carried out on the Nanofinder 30 Raman spectrometer at room temperature. Nd:YAG laser with a wavelength λ = 532 nm and a maximum power of 10 mW was used as an excitation source. The obtained spectra were analyzed by the Gaussian function in the Origin 9 software.

3. Results and discussion

3.1. Structural properties

Room temperature X-ray diffraction spectrum of the Bi_2Se_3 compound under normal conditions is shown in Fig 1. As can be seen from the fig 5. main diffraction maxima are observed in the range of 2θ = 5-70°. It was found that the crystal structure of the Bi_2Se_3 compound corresponds to the rhombohedral symmetry with the space group R-3mat room temperature. As a result of the analysis, it was determined that the diffraction maxima correspond to the planes (0 0 3), (0 0 6), (0 0 15), (0 0 18) and (0 0 21). For the distances between the planes d_{hkl}, the values of the cell parameters are determined by the following formula:

$$\frac{1}{d} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)(\cos^2\alpha - \cos\alpha)}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)} \quad (1)$$

The values of the lattice parameters are: $a = b = c$ = 9.4185 Å, $\alpha = \beta = \gamma$ = 24.065°.

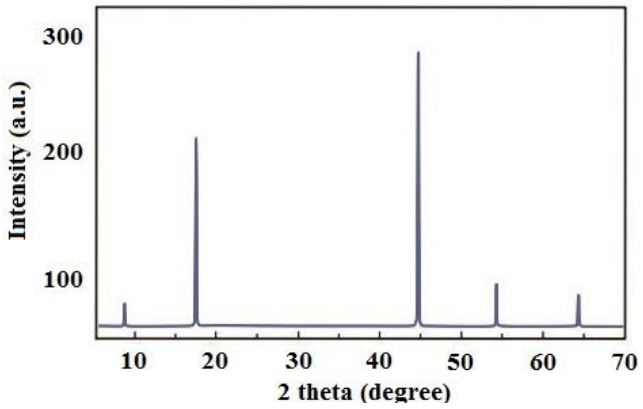

Fig 1. X-ray diffraction spectra of the Bi_2Se_3

X-ray diffraction spectrum of the Bi_2Te_3 compound at room temperature and under normal conditions is shown in Fig.2. As can be seen from the spectrum, 5 main diffraction maxima are observed in the range 2θ = 5-70°. It was found that the crystal structure of the Bi_2Te_3 compound also corresponds to the rhombohedral symmetry with the space group R-3mat room temperature.As a result of the analysis, it was determined that the diffraction maxima correspond to the planes (0 0 3), (0 0 6), (116), (0 2 10) and (1115). The values of the cell parameters were determined by formula (1). The values of the lattice parameters are: $a = b = c$ = 10.1386 Å, $\alpha = \beta = \gamma$ = 24.178°.

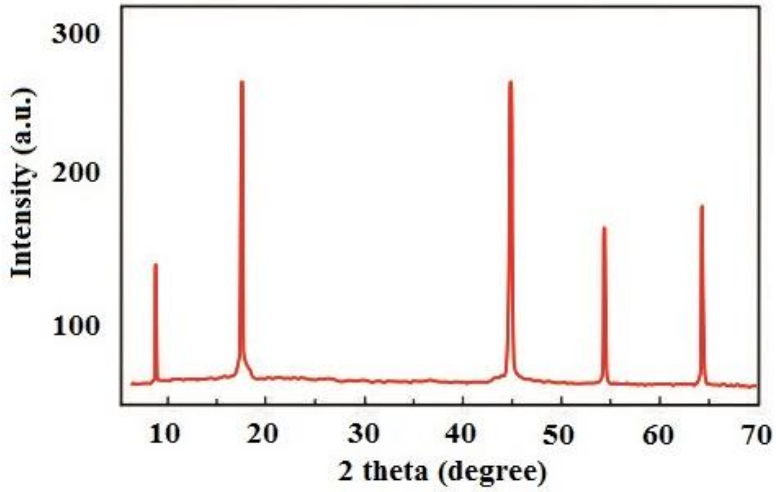

Fig. 2. X-ray diffraction spectra of the Bi_2Te_3

The difference in the lattice parameters of the Bi_2Se_3 and Bi_2Te_3 compounds ($\Delta a = \Delta b = \Delta c$ = 0.7201 Å) is explained by the difference in the ionic radii of the selenium and tellurium atoms. The ionic radii of these chemical elements also differ depending on the valence (Bugaenko *et al.*, 2008). Se atoms have an ionic radius of R_{Se2} = 0.69 Å in the two valent state, R_{Se4} = 0.54 Å in the four valent state, and R_{Se6} = 0.38 Å in the six valent state. Te atoms have an ionic radius of: R_{Te2} = 0.89 Å in the two valent state, R_{Te4} = 0.75 Å in the four valent state, and R_{Te6} = 0.56 Å in the six valent state.

X-ray diffraction spectrum of the Sb_2Te_3 compound at room temperature and under normal conditions is shown in Fig 3. As can be seen from the spectrum, 6 main diffraction maxima are observed in the range 2θ = 5-70°. As a result of the analysis, it was determined that the diffraction maxima correspond to the planes (0 0 3), (0 0 6), (0015), (0 0 18), (0 0 19) and (0121). It was found that the crystal structure of the Sb_2Te_3 compound corresponds to the rhombohedral symmetry with the space group R-3mat room temperature.In contrast to the crystal structures of the Bi_2Se_3 and Bi_2Te_3 compounds, the crystal structure of the Sb_2Te_3 compound is better interpreted by the hexagonal crystal structure. For the distances between the planes d_{hkl}, the values of the cell parameters are determined by the following formula:

$$\frac{1}{d^2} = \frac{4}{3} \cdot \frac{(h^2+kh+k^2)}{a^2} + \frac{l^2}{c^2} \ . \qquad (2)$$

The values of the lattice parameters are: $a = b = c$ = 10.1386 Å, $\alpha = \beta = \gamma$ = 24.178°.

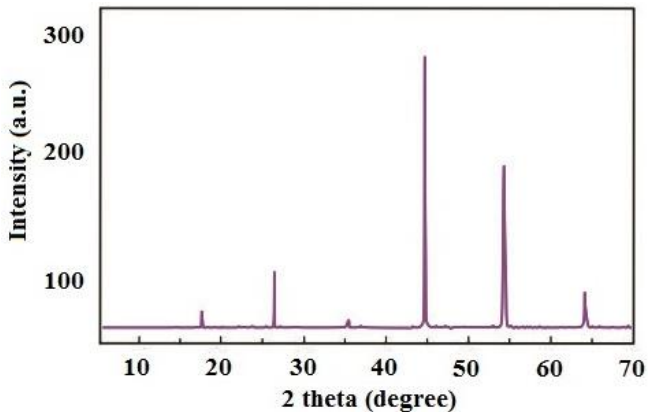

Fig. 3. X-ray diffraction spectra of the Sb_2Te_3

The difference in the ionic radii of the Bi and Sb is also reflected in the crystal structure of the Bi_2Te_3 and Sb_2Te_3 compounds. These elements have three valence in binary semiconductors: Bi_2Se_3 Bi_2Te_3 and Sb_2Te_3. In this case, the ionic radii are: R_{Bi3} = 1.02 Å, R_{Sb3} = 0.82 Å (Bugaenko *et al.*, 2008). $\Delta R_{(Bi\text{-}Sb)3}$ = 0.2 Å, which leads to significant differences in the crystal structure of Bi_2Te_3 and Sb_2Te_3 compounds.

3.2. Vibrational properties

Atomic dynamics were studied to determine the structural properties of the compounds Bi_2Se_3 Bi_2Te_3 and Sb_2Te_3.Raman spectra of Bi_2Se_3 Bi_2Te_3 and Sb_2Te_3, obtained at room temperature and under normal conditions are shown in Fig 4.

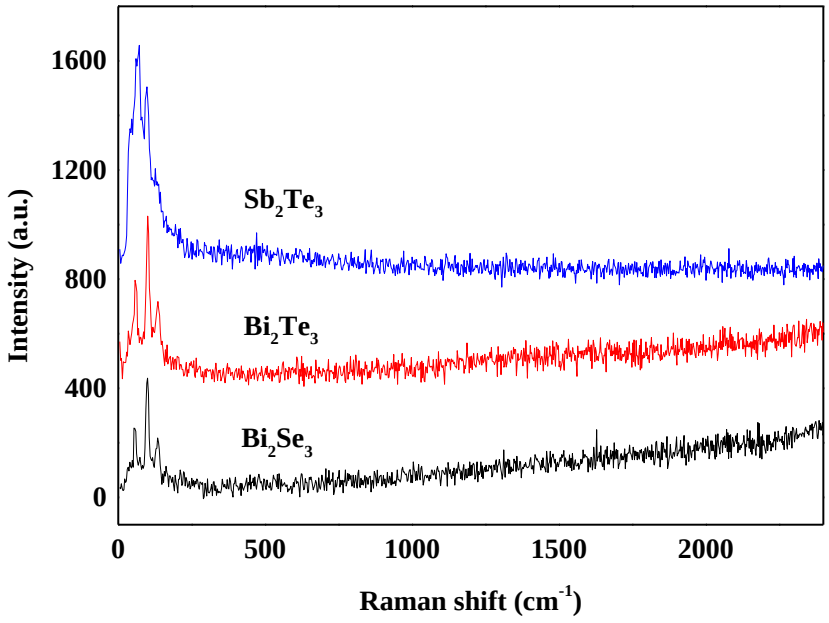

Fig. 4. Raman spectra of the Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3

It has been determined that the vibrational modes corresponding to these crystals are mainly observed in the frequency range ν = 50-200 sm^{-1}. This is due to the fact that the compounds do not contain atoms of light elements such as oxygen, carbon and hydrogen.

Vibrational modes: ν_1 = 56.22 sm^{-1}, ν_2 =98.73 sm^{-1} və ν_3 = 133.84 sm^{-1} were observed in the Raman spectrum of the Bi_2Se_3 combination. This is in line with previous research (Humlíček *et al*., 2014). The Raman spectrum of the Bi_2Te_3 compound also corresponds to the vibrational modes observed in the Raman spectrum of the Bi_2Se_3 compound: ν_1 = 59.19 sm^{-1}, ν_2 =100.52 $sm^{-1}$and ν_3 = 135.34 sm^{-1}.A more complex character is observed in the atomic dynamics of the Sb_2Te_3 compound.In the Raman spectrum: ν_1 = 43.31 cm^{-1}, ν_2 =66.32 cm^{-1} , ν_3 = 97.27 $cm^{-1}$and ν_4 = 131.08 cm^{-1} vibrational modes were observed. This is in line with previous research (Zybala *et al*., 2017).

4. Conclusion

The structural properties of Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 crystals have been studied at room temperature and normal conditions. It was found that a small difference in ionic radii (~ 2 Å) of Bi → Sb and Se → Te atoms causes significant differences both in the crystal structure and in the atomic dynamics of crystals. This difference is more pronounced with cationic substitution. The crystal structure and atomic dynamics of the Bi_2Se_3 and Bi_2Te_3 compounds are more similar. Compounds Bi_2Te_3 and Sb_2Te_3 differs in both number of combination modes and interpretation of the crystal structure.

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