Band Structure And Optical Functions Of *SnS* Compound

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Abstract—**In the present work, on the basis of calculations from the first principles within the framework of the pseudopotential theory, the band structure of the** SnS **binary compound was calculated. It is revealed that the band structure can be divided into three subgroups: the lowest group, which is distant from the main group of the valence band by a wide energy gap of about 6 eV, is derived from the s-states of the anion. The next group, consisting of four bands and located about -7 eV, is associated with the s-states of Sn. The calculated values of the band gap with the available theoretical data for the monoclinic structure of the crystal lattice were compared. The calculation of the band structure of the compound shows a satisfactory agreement with the experimental data.**
In the paper, based on the electronic structure of the compound, the calculation results from first principles, using the LAPW - Linearized Augmented Plane Wave method by WIEN2k software package, atomic coordinates in the unit cell and the parameters of the Murnaghan and Birch-Murnaghan equation of state are presented. The fluorescence spectra of SnS were studied in the wavelength range 200-600 nm, and it was found that this material can be widely used in multifunctional electronic devices and used as new types of composites with unique properties.

Keywords—Compound SnS *; Pseudopotential; Band structure; Optical functions.*

INTRODUCTION

Tin sulfide (SnS) belongs to the class of $A^{IV}B^{VI}$ semiconductors with p- and n-type conductivity depending on the elemental composition and is characterized by the orthorhombic crystal structure of B16 (structural type GeS, orthorhombic (*Pbnm*) symmetry). Tin sulphide is characterized by a layered crystalline structure, whose atomic layers are bound only by van der Waals forces [1]. In this connection, there are no unfilled electron levels on the surface of SnS crystals, due to which the surface of the material is characterized by high chemical stability. These features of the electronic structure make it possible to use SnS to create heterojunctions with a high degree of heterogeneity without intermediate electronic levels at

the contact surface of the layers [2]. The width of the band gap is 1.5 eV, the absorption coefficient is about 105 см$^{-1}$, so this material is used in various optoelectronic devices [3–6]. At present, interest is noted in the use of SnS as an absorbing layer in thin-film solar radiation converters [5, 6], due to the low cost of the material, which is caused by the wide spread of tin and sulfur in nature. The purpose of this work is to obtain thin SnS films by technologically simple and do not require subsequent hot wall annealing, and also to study their physical properties, depending on the conditions of production.

EXPERIMENTAL PROCEDURE

For the synthesis, a stoichiometric mixture (accurate to $5 \cdot 10^{-4}$g) of Sn and S materials (purity 99.999%) was prepared, which was placed in a quartz ampoule and sealed at a pressure of 0.0133Pa. The ampoule was placed in electric oven. It was heated at a rate of 25^0C/h to 450^0C and kept at this temperature for 24 hours, and then at 700^0C for another 20 hours. After this, the ampoule was cooled to room temperature at a rate of 20^0C/h.

A Cary Eclipse spectrofluorimeter was used to study the fluorescence spectrum. The source of excitation is a pulsed xenon lamp, with technical characteristics of 80 flashes per second, equivalent power 75 kW under the peak. Focusing optics is the Schwarzschild collector. Monochromators and a horizontal slit are controlled using the Czerny-Turner construction. There are six selectable slits: 1.5; 2.5; 5; 10; 20; 10mm. Eclipse includes 2 monochromators and can be independently scanned by each of the monochromators. If an excitation monochromator is fixed and scanned by an emission monochromator, an emission spectrum, often called the fluorescence spectrum, is obtained. The emission spectrum has information about the molecular structure and the nature of the material.

The shape of the fluorescent spectrum does not depend on the wavelength of the exciting light, since the emission is generated by the lowest of the excited states.

RESULTS AND DISCUSSION

To calculate the energy spectrum of the compound, the pseudopotential method was used. The pseudopotential method is one of the main methods for calculating the energy spectrum of charge carriers of semiconductors. This method discussed in [7-12].

The pseudopotential theory is based on three fundamental physical approximations.

1. The first approximation is the self-consistent field approximation. In this approximation, the interaction between electrons is described by some average potential, which itself depends on the states in which the electrons are located, and the electronic states in turn are determined by the average potential.

2. In the second approximation, all electronic states are divided into internal shells ("core") and conduction band states, and assume that the wave functions of the inner shells are strongly localized.

3. The third fundamental approximation is the use of perturbation theory for electrons in the conduction band.

Nonlocal ion pseudopotentials in the configuration space were constructed according to the scheme proposed in Refs. [10,12].

In [13], symmetry elements of the $D_{2h}^{16}(P_{cmn})$ space group, the Brillouin zone, tables of irreducible representations of the groups of wave vectors of symmetric points and lines of the Brillouin zone, and the rules for selecting dipole transitions for some symmetric points and lines are obtained.

We calculated the band structure of the SnS compound by the pseudopotential method. Nonlocal ion pseudopotentials in the configuration space were constructed according to the scheme proposed in [11].

When calculating the band structure of a given compound, the shielding of the ion charge, as well as the exchange-correlation effects were taken into account in the framework of the dielectric formalism according to the Hubbard-Shem model with some selective charge distribution around each ion (Table 1).

Table 1-Parameters of the optimized *SnS* lattice

Lattice parameters(Å)	SnS	
	Theory	Exp.
a	4.246	4.334
b	10.943	11.200
c	3.922	3.987
x (cation)	0.1155	0.1198
y (cation)	0.1175	0.1194
x (anion)	0.4745	0.4793
y (anion)	0.8535	0.8508

Approximately 2500 plane waves are used in the expansion of the wave function. The maximum kinetic energy of the being plane waves taken into account was 20 Ry. As can be seen from Fig.1 valence band consists of three groups of zones.
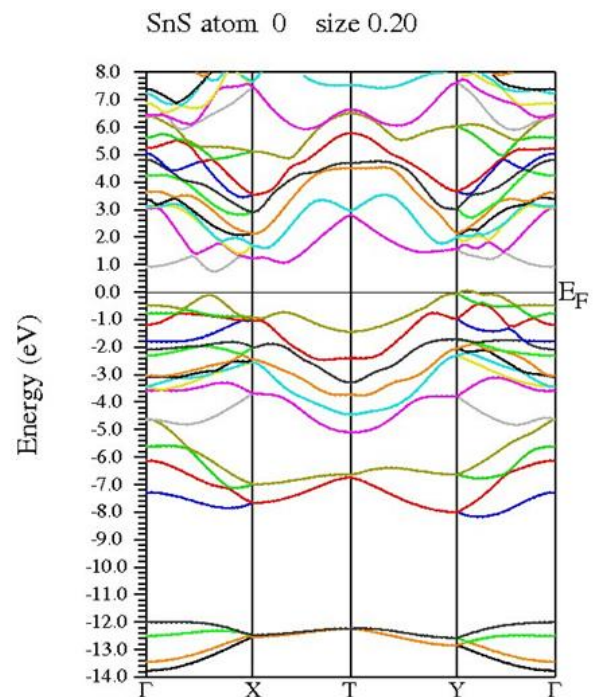

Fig.1. Zone structure of *SnS* compound

The characteristic pairwise arrangement of the valence bands is a consequence of layered structure of the crystal. An analysis of wave functions of valence states shows that the lowest group remote from the main group of valence band by a wide energy gap of

about 6eV occurs from the s-states of the anion. The next group, consisting of four zones and located about -7eV, is connected with the s-states of Sn. The highest group of twelve zones, located in the range from 0 to -5eV, owes its origin to the p-states of the cation and anion. The analysis of the origin of the valence states agrees well with the data of photoelectron emission. The width of the band gap, calculated from the band structure, agrees well with its experimentally determined value. Based on the electronic structure of the compound the calculation results from first principles, using the LAPW - Linearized Augmented Plane Wave method by WIEN2k software package [15], atomic coordinates in the unit cell and the parameters of the Murnaghan and Birch-Murnaghan equation of state [16] are presented.

It is known that when an external exposed to crystal, it undergoes deformation. In this case, both the lattice parameters and the parameters determining the position of the atoms (their coordinates) change.Therefore, the calculation of these parameters for a given strain value is an important task. It is assumed that the pressure is determined by the derivative of the total energy from volume at constant entropy S

$$P = -\left(\frac{\partial E}{\partial V}\right)_S ,$$

and the modulus of all-round compression is the pressure derivative from the volume at a constant temperature

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T .$$

In the experiment, the derivative of the all-round compression modulus is determined at small changes in pressure

$$B' = \left(\frac{\partial B}{\partial P}\right)_T .$$

If we accept that $B' = B_0'$,

then

$$B = B_0 + B_0' P .$$

Then,

$$\frac{dV}{V} = -\frac{dP}{B_0 + B_0' P} \qquad (1)$$

Integrating this expression, we obtain

$$P(V) = \frac{B_0}{B_0'}\left(\left(\frac{V_0}{V}\right)^{B_0'} - 1\right) \qquad (2)$$

Where have

$$V(P) = V_0\left(1 + B_0' \frac{P}{B_0}\right)^{-1/B_0'} . \qquad (3)$$

As is known, solids have a certain volume of equilibrium of the unit cell, and with a change in this volume by a small amount, the total energy of the crystal increases. Murnaghan state equation [16] describes the dependence of total energy (E) by changing the volume (V) of the unit cell.

$$E(V) = E_o + \left[\frac{B_o V}{B_0'}\left(\frac{(V_o/V)^{B_0'}}{B_0' - 1} + 1\right) - \frac{B_o V}{B_0' - 1}\right]\frac{1}{14703.6} \qquad (4)$$

Here, $E_0 = E(V_0)$ - the energy corresponding to the V_0 equilibrium volume (i.e., the energy minimum), $B = -V(\delta P/\delta V)_T$ – the modulus of all-round compression, B_0 – is the same parameter in the equilibrium state corresponding to the pressure $P = 0$, $B' = (\delta B/\delta P)_T$ – its first derivative from pressure at a constant temperature. The multiplier $\frac{1}{14703.6}$ in equation (4) is introduced to obtain the total energy values in units of Rydberg (the volume is calculated in atomic units – a.u.). To determine the parameters of the crystal lattice we changed in the calculations the volume of the unit cell within $\pm 8\%$ and calculated the corresponding values of the total energy. The parameters entering into Murnaghan's equation state were chosen in such a way that the dependence of the total energy on the volume of the unit cell $E(V)$ (Fig.2), obtained from the equation (shown in the solid line), passed through the calculated points (shown in the figure with the notation +). According to the results of the calculations, the volume of the unit cell in the equilibrium state is V_o=1341,8693 a.u., the modulus of all-round compression is B=55,6175 GPa, its derivative from pressure is B'=4,1103. These results are in good agreement with the calculations carried out using the Birch-Murnaghan equation [16] (Table 2.).

$$E(V) = E_0 + \frac{9V_0 B_0}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^3 B_0' + \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^2\left[6 - 4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right]\right\}\frac{1}{14703.6}$$

$$(5)$$

The calculations of the parameters in the equilibrium state were carried out with allowance for the constancy of the ratio of the lattice parameters a, b, and c.

$$\frac{a'}{c'} = \frac{7.5401}{8.2015} = 0.9193$$

$$\frac{b'}{c'} = \frac{2116.52}{8.2015} = 2.5806$$

Due to the fact that the volume of the unit cell is equal to $V = abc$ and the obtained volume of the equilibrium state $V_0 = 1341.8693$ a.u., calculations allow one to find the lattice parameters.
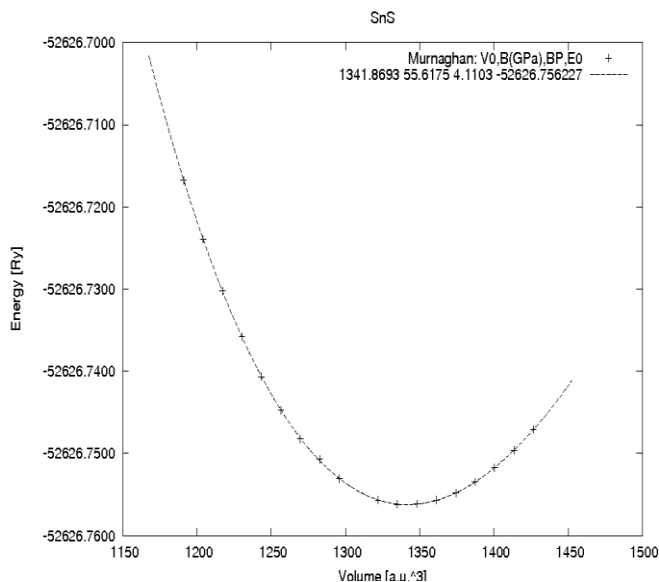
Fig.2. Dependence of the total energy on the volume of the unit cell (solid line-calculations for Murnaghan, detached + - calculated values)

A characteristic feature of the fluorescence spectrum (FS) is a high resolving power, accompanied by processes associated with the chemical composition of the sample, structural elements and other dynamic changes. The FS has a fairly short time range, since fluorescence begins after 10^{-8} sec after absorption of light. Over this period of time, all processes are performed at the molecular level. Non-radiative energy transfers, as well as the exchange of charges and energies between components, are reflected in the fluorescence spectra, the results of short-term dynamic processes, in the study of static properties and properties of processes that are detected with a light signal that detects narrow luminescence bands.
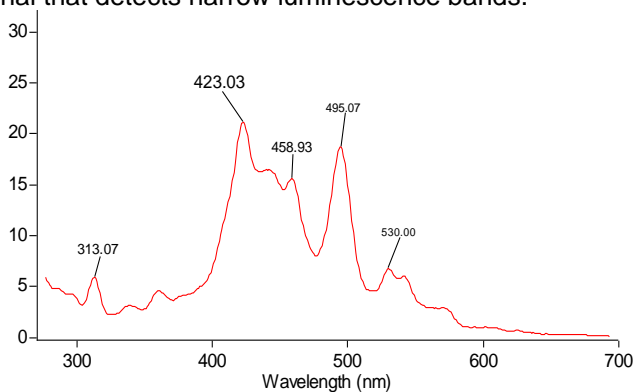

Fig.3. The overall excitation spectrum of SnS

The results of the investigation of the excitation spectra of SnS are shown in Fig.3. The obtained spectrum reflects the characteristic radiation, which is obtained upon excitation of SnS with light of length 230 nm. The spectrum includes different peaks, some of which correspond to fluorescence and are presented in Fig.3. As can be seen from Fig. 3, when the excitation signal is 388, 240.93, and 254.06 wavelengths, fluorescence effects are observed at wavelengths of

528.95, 491.94, and 421.96, respectively. The intensity of the detected fluorescence peaks is practically in all comparable with the intensity of the exciting signals. Comparing the intensity of the exciting signals with the observed intensities of the fluorescence peaks, one can come to the conclusion that the investigated material has pronounced fluorescence properties. Thus, the fluorescence spectra of SnS were studied in the wavelength interval 200-600 nm, and it was found that this material can be widely used in multifunctional electronic devices and used as new types of composites with unique properties.

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