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PHYSICAL PARAMETERS OF SYNTHESIZED HETEROMETALLIC COMPLEX COMPOUND

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ФІЗИЧНІ ПАРАМЕТРИ СИНТЕЗОВАНОЇ ГЕТЕРОМЕТАЛІЧНОЇ КОМПЛЕКСНОЇ СПОЛУКИ

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Abstract. *A new synthesized semiconductor material has been used as a material sensitive to the effects of temperature or magnetic field. The synthesis technique of heterometallic μ-isopropoxy-(copper(II), bismuth(III)) acetylacetonate (I) is presented in the paper. Using element analysis as well as IR-spectroscopy, magneto-chemical and thermo gravimetric researches the composition of the synthesized heterometallic μ-isopropoxy (copper(II), bismuth(III)) acetylacetonate have been examined. It corresponds to the chemical formula: $[Cu_3Bi(C_5H_7O_2)_4(OC_2H_5)_5]$, where $C_5H_7O_2 = H_3C–C(O)–CH–C(O^-)–CH_3$. The practical output is 82 % of the theoretical calculated one. The synthesized complex compound (I) is a fine crystalline powder, which has good solubility in a mixture of DMFA with chloroform (1:1) and worse solubility in alcohols, ether, better solubility in DMFA, and can be destroyed in water. An analysis of the experimental data from physical and chemical studies for compound (I) allowed to propose a chemical bonding scheme. The molecule of heterometallic μ-izopropoxy- (cuprum (II), bismuth (III)) acetylacetonate probably is a cube, and at the top of which there are three copper atoms (II) and one atom bismuth (III) linked to the atoms of oxygen of isopropoxy- groups, which acts as the tridentate ligand. For the isolated complex compound $[Cu_3Bi(C_5H_7O_2)_4(OC_3H_7\text{-}i)_5]$, a molar mass equal to 1090.5 g/mol and a calculated number of valence electrons in one molecule is 289. A cylindrical sample of mass 0.14 g and a volume of $17.67\cdot10^{-9}$ m^3 made of complex compound (I) by pressing was used for experimental studies. Experimental studies of the conductive properties of μ-isopropoxy- copper (II), bismuth(III)) acetylacetonate in the temperature range 313 K÷413 K, in compressed form, showed that at increased temperature its resistivity sharply decreases from 7·1010 to $4\cdot10^2$ Ohm·cm. The operating temperature range is from +273 K to +493 K, with the decomposition of the chemical compound from 523 K. The concentration of charge carriers increases from $1.3\cdot10^{19}$ m^{-3} at 273 K to $3.395\cdot10^{36}$ m^{-3} at 493 K, while at the quantum Hall constant with increasing temperature from 273 K to 493 K decreases from 0.566 m^3·Kl^{-1} to $2.167\cdot10^{-18}$m^3·Kl^{-1}. The Hall voltage in the magnetic field range from 0 to 1000 mT varies from $8.32\cdot10^{-14}$ to $8.32\cdot10^{-12}$ V.*

Key words*: magnetic field, induction, concentration, semiconductor, heterometallic complex compounds.*

Анотація. Розглянуто можливість використання нового синтезованого напівпровідникового матеріалу, як матеріалу чутливого до впливу температури або магнітного поля. Показано методику синтезу гетерометалічного μ-ізопропоксо (купрум(ІІ), бісмут(ІІІ)) ацетилацетонату (І). На основі даних елементного аналізу, ІЧ-спектроскопічних, магнетохімічних та термогравіметричних досліджень встановлено склад синтезованого гетерометалічного μ-ізопропоксо(купрум(ІІ), бісмут(ІІІ)) ацетилацетонату, який відповідає такій хімічній формулі: $[Cu_3Bi(C_5H_7O_2)_4(OC_2H_5)_5]$, де $C_5H_7O_2 = H_3C–C(O)–CH–C(O^-)–CH_3$. Практичний вихід складає 82% від теоретично розрахованого. Виділена комплексна сполука (І), являє собою дрібнокристалічний порошок, який розчинний в суміші диметилформаміду з хлороформом (1:1), важко розчинний в спиртах, етері, краще розчиняється в диметилсульфоксиді, диметилформаміді, у воді руйнується. Аналіз отриманих експериментальних даних фізико-хімічних досліджень для сполуки (І) дозволив запропонувати схему розміщення хімічних зв'язків. Молекула гетерометалічного μ-ізопропоксо(купрум(ІІ), бісмут(ІІІ)) ацетилацетонату, вірогідно, являє собою куб, у вершинах якого розташовані три атоми купруму(ІІ) та один атом бісмуту(ІІІ), що з'єднані атомами оксигену ізопропоксо-груп, кожна з яких виконує роль тридентатного ліганда. Для виділеної комплексної сполуки $[Cu_3Bi(C_5H_7O_2)_4(OC_3H_7\text{-}i)_5]$, розраховано молярну масу, яка дорівнює 1090,5 г/моль та кількість валентних електронів в одній молекулі – 289. Для проведення експериментальних досліджень використовували циліндричний зразок масою 0,14 г та об'ємом $17{,}67 \cdot 10^{-9}$ $м^3$, який виготовляли з комплексної сполуки (I) методом пресування. Експериментальні дослідження електропровідних властивостей μ-ізопропоксо (купрум (II), бісмут (III)) ацетилацетонату в інтервалі температур 313 К – 413 К, в спресованому вигляді, показало, що при збільшені температури його питомий опір різко зменшується від $7 \cdot 10^{10}$ до $4 \cdot 10^{2}$Ом·см. Інтервал робочих температур складає від +273 до +493 К, причому розкладання хімічної сполуки відбувається з 523 К, концентрація носіїв заряду зростає від $1{,}3 \cdot 10^{19}$ $м^{-3}$ при 273 К до $3{,}395 \cdot 10^{36}$ $м^{-3}$ при 493 К., при цьому квантова константа Холла при збільшенні температури від 273 К до 493 К зменшується від 0,566 $м^3 \cdot Кл^{-1}$до $2{,}167 \cdot 10^{-18}$ $м^3 \cdot Кл^{-1}$, напруга Холла в діапазоні магнітного поля від 0 до 1000 мТ змінюється від $8{,}32 \cdot 10^{-14}$ до $8{,}32 \cdot 10^{-12}$ В.

Ключові слова: *магнітне поле, індукція, концентрація, напівпровідник, гетерометалічні комплексні сполуки.*

INTRODUCTION

The use of semiconductor sensors in production, engineering, and agriculture is an integral component of the present. Consequently, measuring the parameters of electrical and non-electrical quantities is a rather relevant scientific and technical problem [1]. Sensors are categorized into two groups: primary ones, which are affected by the measured value, i.e. the physical parameters of the sensitive material, and secondary ones, which can measure the change in these physical parameters and amplify it, if necessary. The converted signal is applied to the microcontroller and displayed. The materials used for production of primary sensors are rather important in obtaining greater sensitivity of the device. In most cases, these elements are based on a semiconductor material. Nowadays, the synthesis of new semiconductor complex compounds with the physical parameters that can change under the influence of temperature and magnetic field, is quite an urgent task [2–3]. The developed primary sensors based on such materials make it possible to develop new, more sensitive thermo- and magneto sensitive secondary sensors [4–5].

The aim of the work is to study the dependence of the physical parameters of the synthesized semiconductor material on the influence of temperature and magnetic field.

The objective of scientific research is to develop methods for the synthesis of a new heterometallic complex compound, which has semiconductor properties and to study the effect of magnetic field and temperature on its physical properties.

THEORETICAL AND EXPERIMENTAL RESEARCHES

From the papers [6–9] it is known that heterometallic complex compounds have various physical and chemical properties and are used in divers branches of technology. In compressed form, such compounds have a wide range of electrically conductive properties, which depend on the kind of metals and ligands and vary from dielectric to low resistance semiconductor. The kind of the central metal atom, heteroatom, and chelating and bridge ligands effect on the semiconductor properties and the operating temperature range of heterometallic complex compounds. In practice, these compounds can be used as a semiconductor material for the producing of thermistors.

In order to search for new heterometallic complex compounds having semiconductor properties, a method was developed for the synthesis of heterometallic *μ-isopropoxy* -(copper (II), bismuth (III)) acetylacetonate (I), with the following stages: $[Cu_3Bi(C_5H_7O_2)_4(OC_3H_7\text{-}i)_5]$, where $C_5H_7O_2 = H_3C–C(O)–CH–C(O^-)–CH_3$.

The heterometallic complex compound (I) was synthesized in a conical flask with a reversible water refrigerator according to the following procedure: batch of the 1.62 g (12 mmol) of anhydrous copper(II) chloride salts and 1.27 g (4 mmol) of bismuth (III) chloride were dissolved in 120 ml of isopropyl alcohol on the electric magnetic stirrer with continuous stirring and heating (~ 50 ° C. After complete dissolution of the salts, 1.70 ml (16 mmol) of acetylacetone were added to the resulting solution. Further, piperidine was added to the reaction mixture in small portions to pH = 8 and continued to stir and heat (~ 50 ° C) for 1.5 hours. This formed a homogeneous fine crystalline precipitate of blue color, the amount of which increased with cooling of the reaction mass. After cooling, the precipitate was filtered on a glass filter, washed with a small amount of anhydrous ethyl alcohol, diethyl ether and dried in a vacuum desiccator above silica gel. The practical yield is 3.58 g, which is 82% of the theoretical calculated. Isolated complex compound (I), is a fine crystalline powder, which is soluble in a mixture of dimethylformamide with chloroform (1:1), hardly soluble in alcohols, ether, better soluble in dimethyl sulfoxide, dimethylformamide, in water is destroyed.

An elemental analysis was committed for the synthesized heterometallic *µ-isopropy-(*copper(II), bismuth (III)), acetylacetonate, as well as magneto chemical, IR spectroscopic and thermo gravimetric studies were performed on the basis of which determined the composition of compound (I) corresponding to the following chemical formula: $[Cu_3Bi(C_5H_7O_2)_4(OC_3H_7\text{-i})_5]$, where $C_5H_7O_2 = H_3C–C(O)–CH–C(O^-)–CH_3$.

A detailed analysis of the obtained experimental physical and chemical data for the detection of compounds (I) allowed to suggest a scheme of placing of the chemicals links. The molecule of heterometallic *µ-isopropoxy-* (cuprum (II), bismuth (III)) acetylacetonate probably is a cube, and at the top of which there are three copper atoms (II) and one atom bismuth (III) linked to the atoms of oxygen of *isopropoxy-* groups, which acts as the tridentate ligand (Fig. 1) [10].

The molar mass for $[Cu_3Bi(C_5H_7O_2)_4(OC_3H_7\text{-i})_5]$ was calculated. It equals to 1090.5 g / mol, and the number of valence electrons in one molecule - 289 for the selected complex compounds.

A cylindrical sample with a mass of 0.14 g and a volume of $17.67 \cdot 10^{-9}$ m^3 made of complex compound (I) by pressing was used for performing experimental studies. Based on these data, according to the formula (1), the density of the substance was calculated:

$$\rho = m/v = 7{,}923 \cdot 10^3 \text{ kg/m}^3, \quad (1)$$

where ρ – the density of the substance; m – the mass of the experimental sample, V – the volume of the experimental sample.

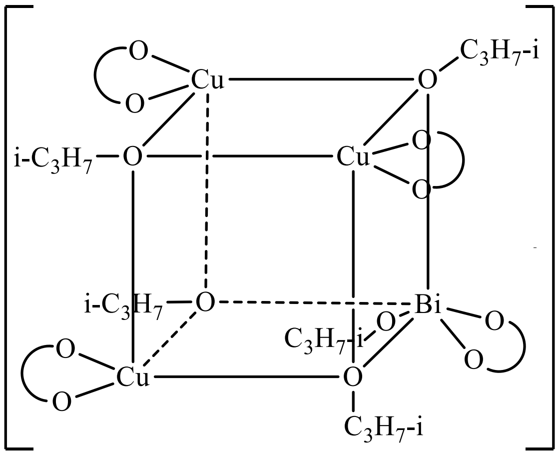

Figure 1 – The layout of chemical bonds in *µ-isopropoxo-*(copper (1), bismuth (2)) acetylacetonate

To find the mass of one molecule of the compound (I) in question, formula (2) was used:

$$m_0 = M/N_A = 181.086 \cdot 10^{-20} \text{ kg}, \quad (2)$$

where m_0 – the mass of an one molecule of the compound (I); N_A – the Avogadro constant; M – the molar mass of the compound (I).

Using the formula (3), we were able to calculate the total number of molecules in the volume of the studied cylindrical sample filled with compound (I).

$$N_{mol} = m/m_0 = 7.73 \cdot 10^{13} \text{ molecules}, \quad (3)$$

where N_{mol} – the total number of molecules ; m_0 – the mass of one molecule of the compound (I); m – the mass of the experimental sample.

An amount of valence electrons was found by using formula (4):

$$N = 259 \cdot N_{mol} = 2233.72 \cdot 10^{15}. \quad (4)$$

The concentration of charge carriers was calculated at the temperature of 313 K:

$$n = N / V = 126.427 \cdot 10^{22} \text{ m}^{-3}. \quad (5)$$

The studies of the electrically conductive properties of *μ-isopropoxy*-(copper (II), bismuth (III)) acetylacetonate in compressed form within the temperature range 313–413 K showed that its resistivity sharply decreases from $7 \cdot 10^{10}$ Ohm·cm to $4 \cdot 10^{2}$ Ohm·cm, while temperature is increasing, which is typical for semiconductor materials.

Experimental measurements made it possible to calculate the specific conductivity of the material for these temperatures. The conductivity $\sigma_1 = 1,43 \cdot 10^{-9}$ (Ohm·cm)$^{-1}$ at the temperature $T_1 = 313$ K, and at the temperature $T_2 = 413$ K the conductivity $\sigma_2 = 25 \cdot 10^{-2}$ (Ohm·cm)$^{-1}$. These experimental studies allowed us to determine the band gap:

$$\Delta E = \frac{k \ln \frac{\sigma_1}{\sigma_2}}{\left(1/T_2 - 1/T_2\right)} = 3.38574 \cdot 10^{-19} \text{ J} = 2.116 \text{ eV}, \quad (6)$$

where T – absolute temperature; σ – the material conductivity; k – Boltzmann constant.

Based on the calculations, we received confirmation that this material is a semiconductor with current carriers of both signs.

The band gap and the formula for the temperature dependence of the concentration of charge carriers of a semiconductor make it possible to obtain a graph of the dependence of the concentration of charge carriers on temperature, which is presented in the logarithmic form in Figure 2.

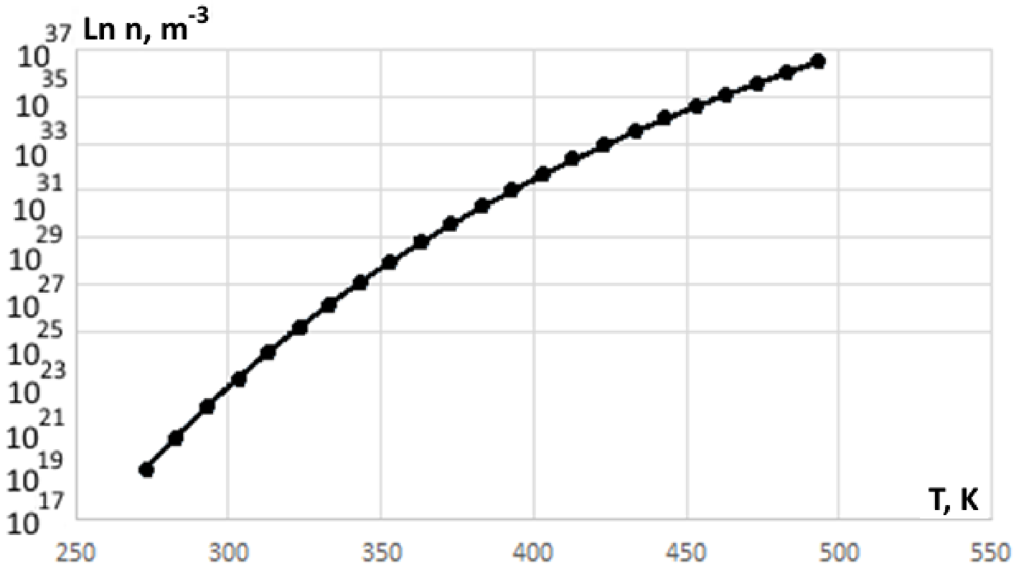

Figure 2 – The logarithmic dependence of charge carrier concentration on temperature

As can be seen from Fig. 2, the concentration of charge carriers in the temperature range from 273 °C to 493 °C increases from $1.3 \cdot 10^{19}$ m^{3} to $3.4 \cdot 10^{36}$ m^{-3}.

The Hall constant, calculated for the temperature 313 K, is

$$R_H = 1 / nq = 4.943 \cdot 10^{-6} \text{ m}^3 \cdot \text{C}^{-1}, \quad (7)$$

where q – the electron charge; n – the charge carriers concentration.

Formula (8) makes it possible to calculate the quantum Hall constant:

$$R_{qH} = -3\pi / 8nq = -5.8179 \cdot 10^{-6} \text{ m}^3 \cdot \text{C}^{-1}. \quad (8)$$

Having combined the equations of the dependence of the concentration of charge carriers on temperature and formula (8), we obtained the formula for the dependence of the Hall constant on temperature (9):

$$R_{qH} = -\frac{3\pi}{8qn_0} \cdot e\frac{\Delta E}{kT}. \tag{9}$$

On the basis of formula (9), a logarithmic dependence of the quantum Hall constant on temperature was calculated (Fig. 3).

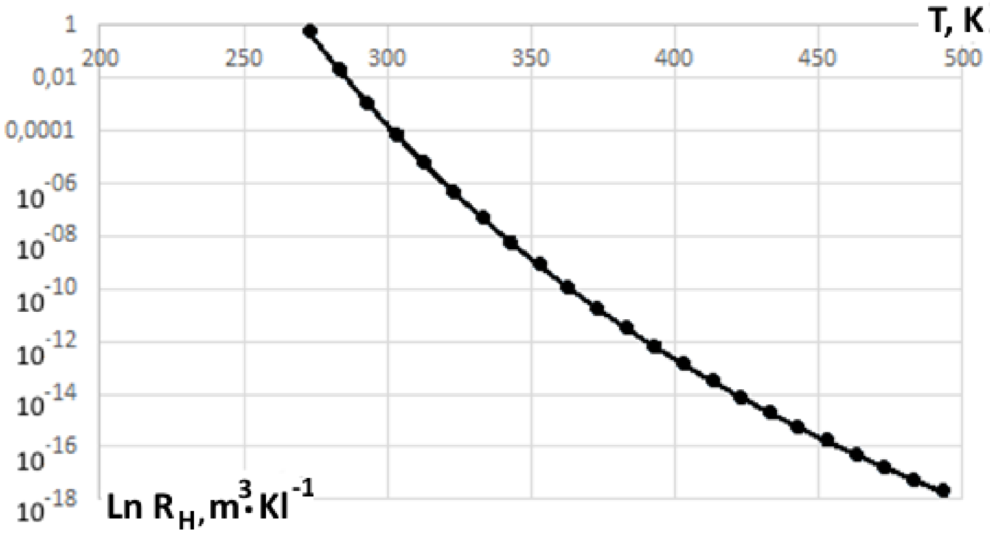

Figure 3 – Logarithmic dependence of the quantum Hall constant on the temperature

As can be seen from the graph (Fig. 3), the value of the quantum Hall constant for such a complex compound decreases from $0.566\ \text{m}^3{\cdot}\text{C}^{-1}$ to $2.167{\cdot}10^{-18}\,\text{m}^3{\cdot}\text{C}^{-1}$ with increasing temperature from 273 to 493 K.

From the experimental data of the resistivity, at 313 K, $\rho = 7{\cdot}108\ \text{Ohm}{\cdot}\text{m}$, to find the carriers mobility, the specific conductivity $\sigma = 1.43{\cdot}10^{-9}\ \text{mS/cm}$ was calculated.

$$\mu_n = R_H \cdot \sigma. \tag{10}$$

In the quantum case, we can determine the charge carriers mobility

$$\mu_n = R_{кв\ H} \cdot \sigma = 8{,}323 \cdot 10^{-15}\ \text{м}^3 \times (\text{В} \times \text{с})^{-1}. \tag{11}$$

Substituting in (11) the dependence of the specific conductivity on temperature and the Hall constant on temperature, the charge carriers mobility is found not to depend on temperature and to be equal to $\mu = 8{,}323 \times 10^{-15}\ \text{m}^3/(\text{V}{\cdot}\text{s})$.

The calculation of the dependences of the Hall electric field inside a semiconductor with dimensions of $0.5 \times 0.5 \times 0.15\ \text{mm}$ arising under the influence of a magnetic field inside the semiconductor is shown in Figure 4.

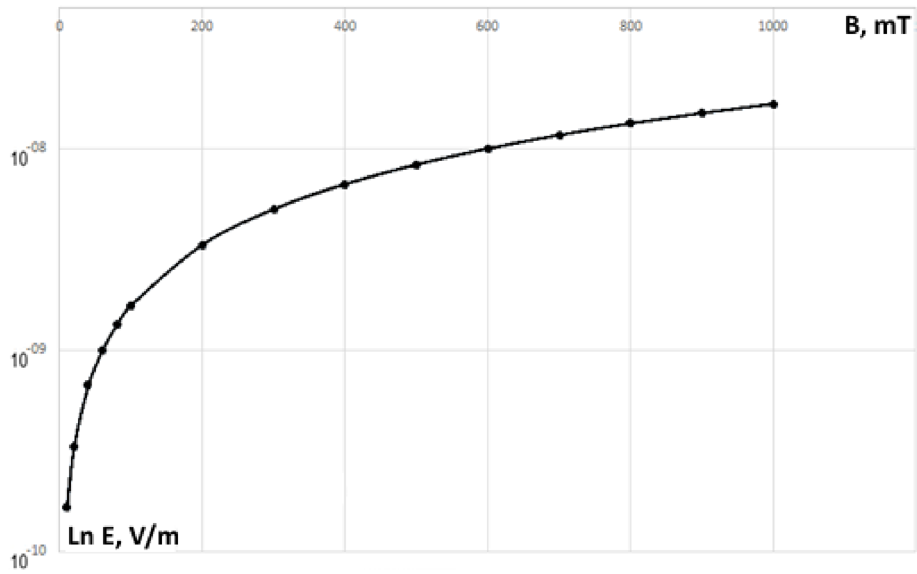

Figure 4 – Logarithmic dependence of the electric field strength inside a semiconductor on the magnetic induction

The graph in the Figure 4 shows that within the range from 10 to 100 mT, the tension increases from $1.66\cdot10^{-10}$ V/m to $1.66\cdot10^{-9}$ V/m, and within the range from 100 to 1000 mT, the graph acquires a linear character and the tension changes from $1.66\cdot10^{-9}$ V/m to $1.66\cdot10^{-8}$ V/m.

A corresponding dependence is observed for the Hall voltage as well. The logarithmic dependence of the Hall voltage on the induction of the magnetic field is shown in Figure 5.

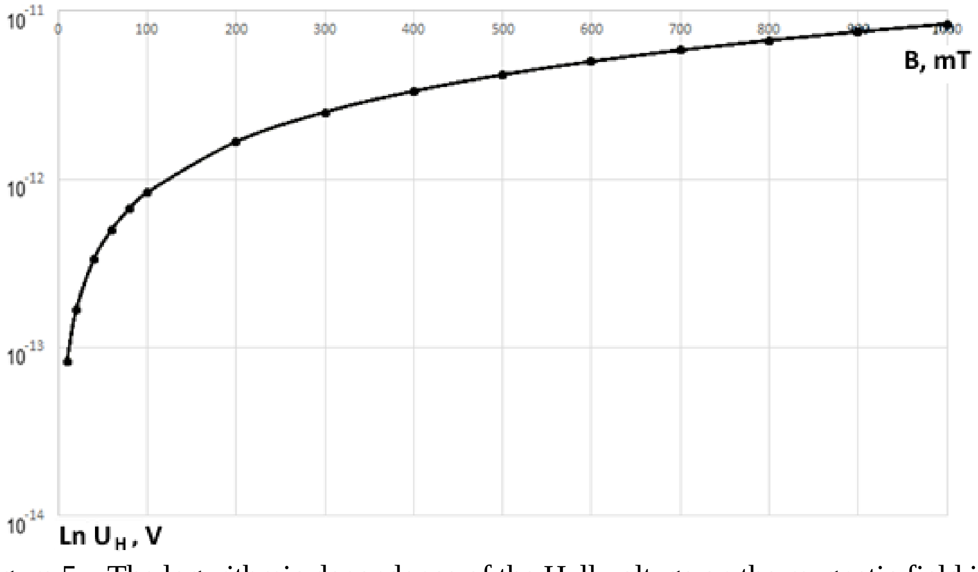

Figure 5 – The logarithmic dependence of the Hall voltage on the magnetic field induction

The graph shows that in the range from 10 to 100 mT, the Hall voltage increases from $8.3\cdot10^{-14}$ V to $8.3\cdot10^{-13}$ V, and from 100 to 1000 mT the Hall voltage increases from $18.3\cdot10^{-13}$ V to $8.3\cdot10^{-12}$ V.

CONCLUSIONS

The properties of a new synthesized semiconductor material are considered, and a method for synthesizing such a material is presented. The effect of temperature and magnetic field on its physical properties is studied.

Experimental studies of the electrically conductive properties of *μ-isopropoxy-* copper (II), bismuth (III)) acetylacetonate in the temperature range 313 K – 413 K, in compressed form, showed that, with increasing temperature, its resistivity sharply decreases from $7{\cdot}10^{10}\,\text{Ohm}\cdot\text{cm}$ to $4{\cdot}10^{2}\,\text{Ohm}\cdot\text{cm}$, that is typical for semiconductor materials.

The range of operating temperatures is +273 ÷ +493 K, and the decomposition of the chemical compound takes place at 523 K. The charge carriers concentration increases from $1.3{\cdot}10^{19}\ \text{m}^{-3}$ at 273 K to $3.395{\cdot}10^{36}\ \text{m}^{-3}$ at 493 K, while the Hall constant decreases from $0.566\ \text{m}^{3}{\cdot}\text{C}^{-1}$ to $2.167{\cdot}10^{-18}\ \text{m}^{3}{\cdot}\text{C}^{-1}$ as the temperature increases from 273 K to 493 K. The Hall voltage in the magnetic field range from 0 to 1000 mT varies from $8.32{\cdot}10^{-14}\ \text{V}$ up to $8.32{\cdot}10^{-12}\ \text{V}$.

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