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The Influence of Physical Quantities on Electrical Parameters of Heterometallic μ-Methoxy (Copper (II), Bismuth (III)) Acetylacetonate

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The paper presents a technique for obtaining the complex *μ-methoxy* (copper (II), bismuth (III)) acetylacetonate, $Cu_3Bi(AA)_4(OCH_3)_5$, where HAA = $H_3C–C(O)–CH_2–C(O)–CH_3$, and results of studying the electrical parameters of this substance. The studied material has been established to be a semiconductor. The composition, structure, and physicochemical properties of the synthesized heterometallic *μ-methoxy* (copper (II), bismuth (III)) acetylacetonate were verified by elemental, X-ray phase, magnetochemical, IR spectroscopy and thermogravimetric examination. A molar mass and a number of valence electrons in one molecule were calculated for a selected complex compound $(AA)_4(OCH_3)_5$ (I). The molar mass was equal to 950.5 g/mol, and the number of valence electrons was 229. For experimental studies, a cylindrical sample with a mass of 0.1 g and a volume of $17.67\ 10^{-9}$ m^3 made of the complex compound (I) by a pressing method was utilized. Investigation of conductive properties of *μ-methoxy* (copper (II), bismuth (III)) acetylacetonate in compressed form within the temperature range 50-120 °C showed that the electrical resistivity sharply decreases from $8\cdot10^9$ to $7\cdot10^3$ Ohm·cm with increasing temperature, which is typical for semiconductor materials. Conductivities of the material were calculated considering the experimental measurements: σ_1 was equal to $1.25\cdot10^{-8}$ 1/(Ohm·m) for 50 °C and σ_2 was equal to $1.4\cdot10^{-2}$ 1/(Ohm·m) for 120 °C. The influence of a magnetic field on the electric field strength inside the test sample of the substance was investigated. The magnetic field induction dependence of the Hall voltage for the sample substance was obtained as well. The operating temperature range is from 50 to 220 °C, with chemical compound decomposing at 260 °C. The charge carrier concentration increases from $7.8\cdot10^{17}$ m^{-3} at 50 °C to $4.14\cdot10^{29}$ m^{-3} at 220 °C, while the Hall constant decreases from 9.43 m$^3\cdot$C^{-1} to $1.8\cdot10^{-11}$ m$^3\cdot$C^{-1}, when the temperature increases from 50 to 220 °C. The Hall voltage varies from $1.97\cdot10^{-5}$ to $1.97\cdot10^{-3}$ V in the magnetic field range from 0 to 1000 mT. The new magnetically sensitive element based on a synthesized semiconductor material will be used to develop magnetic field sensors.

Keywords: Temperature properties, Magnetic field, Charge carrier concentration, Semiconductor material.

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1. INTRODUCTION

The measurement of magnetic field parameters is now a relevant scientific and technical problem. At present, a large variety of primary magnetic field transducers (sensors) are mass-produced by industry. They differ both in their principle of operation and in the operating parameters [1, 2].

In recent years, much attention has been paid to the problem of designing new materials with specific electro-physical properties, for the manufacturing of magnetic field sensors [3, 4]. From this point of view, materials created on the basis of complex compounds are causing considerable interest [5, 6]. It can be explained as follows: they, on the one hand, have a much greater variety of structural and physicochemical properties compared with traditional inorganic semiconductors and metals, and on the other hand, have the possibility of their chemical modification. It is worth mentioning the important method of modifying complex compounds associated with the production of composite materials based on them, which allows changing the mechanical and electrophysical characteristics of these substances smoothly and in the right direction.

The development of new electrically conductive materials enables to implementation of new physical principles, which, in turn, are supposed to improve the quality, reliability, and efficiency of many products as well as significantly to reduce the consumption of materials for them [7, 8].

The aim of the study is to develop a new magnetic field-sensitive element based on a synthesized semiconductor material.

2. DESCRIPTION OF OBJECTS AND INVESTIGATION METHODS

It is known that heterometallic and complex compounds have semiconductor conductivity [3, 4, 7] and their operating temperature range depends on the nature of central atoms, bridge ligands, and metal-ligand environment stereochemistry. They can be used as a semiconductor material for making thermistors [9, 10].

In order to search for new heterometallic complex compounds having semiconductor properties, a method

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for the synthesis of heterometallic *μ-methoxy* (copper (II), bismuth (III)) acetylacetonate (I) having the composition: $Cu_3Bi(AA)_4(OCH_3)_5$, where HAA = $H_3C–C(O)–CH_2–C(O)–CH_3$, has been developed. The heterometallic complex compound (I) was obtained in a conical flask with a circulating water cooler according to the following process: 120 ml of absolute methyl alcohol containing 2.04 ml (40 mmol) of acetylacetone was added to a mixture of 4.05 g (30 mmol) of anhydrous copper (II) chloride and 3.16 g (10 mmol) of bismuth (III) chloride. With permanent stirring, the mixture was heated in a water bath (~50 °C) until the starting materials dissolved, and then piperidine was added to the reaction mixture in small portions till pH = 8. Then, the reaction mass was heated in a water bath (~50 °C) with permanent stirring for two hours. After cooling, a homogeneous blue crystalline residue was formed. It was filtered on a glass filter, washed with a small amount of absolute methanol, diethyl ether and dried in a vacuum desiccator above silica gel. The practical yield is 7.79 g, which is 82 % of the theoretical one. The separated complex compound (I) is a crystalline powder, well dissoluble in a mixture of dimethylformamide and chloroform (1:1), difficultly soluble in alcohols, ether, better dissoluble in dimethyl sulfoxide, dimethylformamide, and degradable in water. The composition, structure, and physicochemical properties of the synthesized heterometallic *μ-methoxy* (copper (II), bismuth (III)) acetylacetonate were verified on the basis of elemental, X-ray phase, magnetochemical, IR spectroscopic, and thermogravimetric studies [11, 12]. The composition was determined, and the following chemical bond placement scheme was proposed as a result of performing research (Fig. 1) in order to extract the complex compound (I).

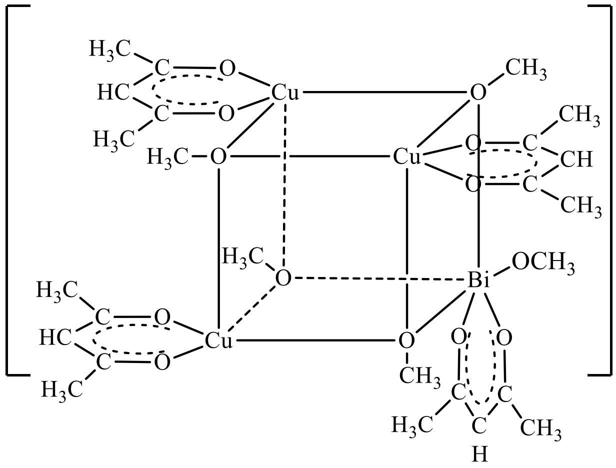


Fig. 1 – Model of chemical bonding in *μ-methoxy* (copper (II), bismuth (III)) acetylacetonate

A molar mass and a number of valence electrons in one molecule were calculated for the selected complex compound $(AA)_4(OCH_3)_5$ (I). The molar mass is equal to 950.5 g/mol, and the number of valence electrons is 229.

For experimental studies, a cylindrical sample with a mass of 0.1 g and a volume of $17.67 \cdot 10^{-9}$ m^3 made of complex compound (I) by pressing, was used. Using these data, the density of the material was calculated by means of the formula (1):

$$\rho = m / v = 5.659 \cdot 10^3\, kg / m^3 , \qquad (1)$$

where ρ is the density of the material, v is the experimental sample volume, and m is the mass of the experimental sample.

The mass of one molecule of the studied compound (I) was calculated by the formula (2):

$$m_0 = M / N_A = 157.837 \cdot 10^{-26}\, kg , \qquad (2)$$

where m_0 is the mass of one molecule of the compound (I), M is the molar mass of the compound (I), N_a is the Avogadro constant.

The total number of molecules in the volume of the studied cylindrical sample filled with compound (I) is given by:

$$N_{mol} = m / m_0 = 6.335 \cdot 10^{19} \text{ molecules} , \qquad (3)$$

where N_{mol} is the total number of molecules in the volume of the cylindrical studied sample, m is the mass of the experimental sample, m_0 is the mass of one molecule of the compound (I).

The total number of valence electrons is:

$$N = 229 \cdot N_{mol} = 1450.715 \cdot 10^{19} . \qquad (4)$$

It allowed us to calculate the concentration of charge carriers at the temperature of 120 °C:

$$n = N / V = 8.89 \cdot 10^{23} \text{ m}^{-3} . \qquad (5)$$

3. RESULTS AND DISCUSSION

The study of the conductive properties of *μ-methoxy* (copper (II), bismuth (III)) acetylacetonate in compressed form within the temperature range 50-120 °C showed a sharply decreasing its electrical resistivity from $8 \cdot 10^9$ to $7 \cdot 10^3$ Ohm·cm with increasing temperature, which is typical of semiconductor materials.

Conductivities of the material were calculated on the base of the experimental measurements: σ_1 is equal to $1.25 \cdot 10^{-8}$ 1/(Ohm·m) for 50 °C (T_1 = 323 K) and σ_2 is equal to $1.4 \cdot 10^{-2}$ 1/(Ohm·m) for 120 °C (T_2 = 393 K). In terms of the aforementioned data, the band gap is determined as

$$\Delta E = \frac{k \ln \dfrac{\sigma_1}{\sigma_2}}{\left(\dfrac{1}{T_2} - \dfrac{1}{T_2} \right)} = 3.49 \cdot 10^{-19} J = 2.18\ eV , \qquad (6)$$

where k is the Boltzmann constant, σ is the material conductivity at various temperatures, T is absolute zero.

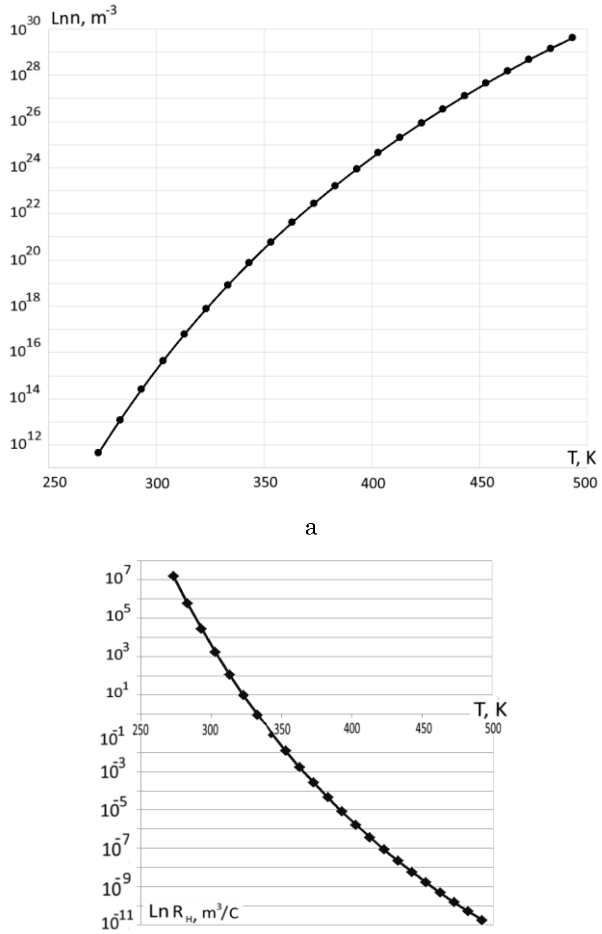
Calculations confirm that this material is indeed a semiconductor, and has current carriers of both signs.

Taking into account the band gap of a semiconductor and using the formula for the dependence of charge carrier concentration on temperature, the logarithmic graph was obtained. It is presented in Fig. 2a.

As can be seen in Fig. 2a, the charge carriers concentration increases from $7.8 \cdot 10^{17}$ m^{-3} to $4.14 \cdot 10^{29}$ m^{-3}

within a temperature range from 50 °C to 220 °C.

The calculation of the Hall constant at 50 °C gives the following results:



a

b

Fig. 2 – Logarithmic dependence of charge carrier concentration on temperature (a), and logarithmic dependence of the quantum Hall constant on the temperature (b)

$$R_H = 1/nq = 8.012 \ m^3 \cdot C^{-1}, \tag{7}$$

where n is the concentration of charge carriers, q is the electron charge.

Estimation of the quantum Hall constant was committed by means of the formula (8):

$$R_{qH} = -3\pi/8nq = -9{,}43 \ m^3 \cdot C^{-1}. \tag{8}$$

The expression (9) was obtained using formula (8) and the equation for the dependence of carrier concentration on temperature. It defines the dependence of the Hall constant on temperature:

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

Using the formula (9), the logarithmic dependence of the quantum Hall constant on temperature was calculated, which is shown in Fig. 2b. As can be seen in Fig. 2,b, the value of the quantum Hall constant of the studied material decreases from 9.432 $m^3 \cdot C^{-1}$ to $1.8 \cdot 10^{-11}$ $m^3 \cdot C^{-1}$ while the temperature increases from 50 °C to 220 °C.

In order to find epy charge carrier mobility using experimental resistivity data at 50 °C, the conductivity $\sigma = 1.25 \cdot 10^{-8}$ S/m was calculated as

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

The carrier mobility for the quantum case can be defined as

$$\mu_n = R_{qH} \cdot \sigma = 1.18 \cdot 10^{-7} \ m^3 \cdot (V \cdot s)^{-1}. \tag{11}$$

When substituting the dependencies of the Hall constant and conductivity on temperature, it was determined that the charge carrier mobility μ is invariable and equals to $1.18 \cdot 10^{-7}$ $m^3/(V \cdot s)$ and does not depend on temperature.

A test sample with dimensions of 0.5 × 0.5 × 1.0 mm was made to carry out experimental measurements with the synthesized material of the complex compound (I). The dependence of the resistance of the test sample on temperature has been studied.

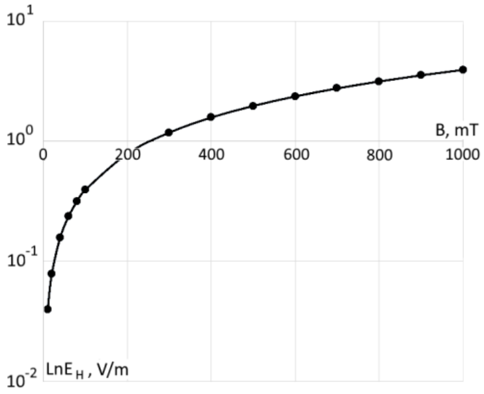
The studied sample's resistance declines rapidly: for instance, at a temperature of 273 K, it is equal to $5.41 \cdot 10^{17}$ Ohm, at 323 K it is equal to $3.2 \cdot 10^{11}$ Ohm, whereas at 493 K resistance is equal to 0,6 Ohm. It means that heterometallic *μ-methoxy* (copper (II), bismuth (III)) acetylacetonate can be used to form temperature-sensitive resistors or more complex instruments that can operate in a wide temperature range with a sensitivity of $2.46 \cdot 10^{15}$ Ohm/K.

On the base of the law of charge carrier concentration dependence and material resistance on temperature, the change in the magnitude of the current passing through the studied test sample at the temperature was determined for voltage 10 V.

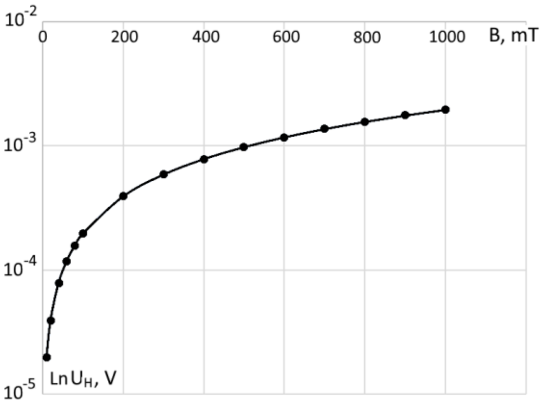
At the temperature 273 K and supply voltage value of $U_4 = 10$ V the current value is $1.85 \cdot 10^{-17}$ A. The maximum value of the current is reached at a temperature of 493 K: at the supply voltage value $U_4 = 10$ V the current value is 16.6 A.

The logarithmic dependence of the Hall electric field inside the semiconductor on the magnetic field induction at various temperatures is given in Fig. 3a.

The plot in Fig. 3a shows that within the range from 0 to 100 mT, the electric field strength increases by 10



a



b

Fig. 3 – Logarithmic dependence of the electric field strength inside a semiconductor on the magnetic induction (a), and the logarithmic dependence of the Hall voltage on the magnetic field induction (b)

times, and within the range from 400 to 1000 mT, the curve is getting linear i.e., the electric field strength nearly does not change.

A similar dependence is observed for the Hall voltage. The logarithmic dependence of the Hall voltage on the induction of the magnetic field is shown in Fig. 3b.

It can be seen in Fig. 3b that the Hall voltage increases from $1.97 \cdot 10^{-5}$ to $3.93 \cdot 10^{-4}$ V within the range from 0 to 200 mT, from $3.93 \cdot 10^{-4}$ V to $1.18 \cdot 10^{-3}$ within the range from 200 to 600 mT, and from $1.18 \cdot 10^{-3}$ V to $1.96 \cdot 10^{-3}$ V within the range from 600 mT to 1000 mT.

The dependencies of the intensity of the Hall field inside a semiconductor on the magnetic field induction at various temperatures (Fig. 3a) and the Hall voltages (Fig. 3b) show that these values are independent of temperature, and their curves are coincident.

4. CONCLUSIONS

A new magneto-sensitive element based on a synthesized semiconductor material has been developed. The study of the conductive properties of *μ-methoxy* (copper (II), bismuth (III)) acetylacetonate in compressed form within the temperature range 50-120 °C showed that while the temperature is increasing, its resistivity sharply decreases from $8 \cdot 10^{9}$ to $7 \cdot 10^{3}$ Ohm·cm, which is typical of semiconductor materials. The operating temperature range is from + 50 to + 220 °C, with the chemical compound decomposing at 260 °C. The charge carriers concentration increases from $7.8 \cdot 10^{17}$ m^{3} at 50 °C to $4.147 \cdot 10^{29}$ m^{3} at 220 °C, while Hall constant decreases from 9.43 m^{3}·C^{-1} to $1.8 \cdot 10^{-11}$ m^{3}·C^{-1}, when the temperature increases from 50 to 220 °C. The Hall voltage varies from $1.97 \cdot 10^{-5}$ to $1.97 \cdot 10^{-3}$ V in the magnetic field range from 0 to 1000 mT.

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REFERENCES

1. V. Ramdas, R. Sethunadh, *IEEE Access* **10**, 81846 (2022).
2. L. Yue, D. Cheng, Y. Qiao, J. Zhao, *IEEE Trans. Instrum. Meas.* **71**, 1005411 (2022).
3. W. N. Santi, M. Toifur, *Key Eng. Mater.* **885**, 141 (2021).
4. O. Pajuelo-Corral, S. Pérez-Yáñez, I. J Vitorica-Yrezabal, G. Beobide, A. Zabala-Lekuona, A. Rodríguez-Diéguez, J. M. Seco, J. Cepeda, *Mater. Today Chem.* **24**, 100794 (2022).
5. Q. Zhang, S. Wen, Q. Feng, Y. Miao, *Separation and Purification Technology* **2821**, 120109 (2022).
6. M. Enamullah, A.-C. Chamayou, K. S. Banu, A. C. Kautz, C. Janiak, *Inorg. Chimica Acta* **464**, 186 (2017).
7. J. Conradie, *Data Brief* **28**, 104833 (2020).
8. J. Devi, R. Kumar, *International Journal of Chemical Sciences* **11** No 2, 1075 (2013)
9. R. Candra, N. Flaminggo, A. Natalia, E. Yuliza, K. Khairurrijal, *J. Phys.: Conf. Series* **1204**, 012116 (2019).
10. N.J. Blasdel, C.N. Monty, *Smart Sensors, Measurement and Instrumentation* **15**, 193 (2015).
11. O. Osadchuk, V. Martyniuk, O. Semenova, I. Osadchuk, M. Evseeva, T. Yushchenko, *2020 IEEE 40th International Conference on Electronics and Nanotechnology (ELNANO)*, art. no. 19668871, 43 (2020).
12. O. Osadchuk, V. Martyniuk, O. Semenova, A. Semenov, H. Martyniuk, T. Sydoruk, *2022 IEEE 16th International Conference on Advanced Trends in Radioelectronics, Telecommunications and Computer Engineering (TCSET)*, art. no. 21757621, 432 (2022).

Вплив фізичних величин на електричні параметри гетерометалевого *μ*-метокси (міді (II), вісмуту (III)) ацетилацетонату

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У роботі представлений спосіб отримання комплексного *μ*-метокси (міді (II), вісмуту (III)) ацетилацетонату $Cu_3Bi(AA)_4(OCH3)_5$, де HAA = H_3C-C(O)-CH_2-C(O)-CH_3 і результати досліджень електричних параметрів цієї речовини. Встановлено, що досліджуваний матеріал є напівпровідником. Склад, структуру та фізико-хімічні властивості синтезованого гетерометалевого *μ*-метокси (міді (II), вісмуту (III)) ацетилацетонату перевірено елементним, рентгенофазовим, магнітохімічним, ІЧ-спектроскопічним та термогравіметричним дослідженнями. Для виділеної комплексної сполуки $(AA)_4(OCH_3)_5$ (I) розраховано молярну масу та кількість валентних електронів в одній молекулі. Молярна маса дорівнювала 950,5 г/моль, а число валентних електронів – 229. Для експериментальних досліджень було створено циліндричний зразок масою 0,1 г і об'ємом $17{,}67\cdot10^{-9}$ м^3 із комплексної сполуки (I) методом пресування. Дослідження електропровідних властивостей ацетилацетонату µ-метокси (міді (II), вісмуту (III)) у стиснутому вигляді в інтервалі температур 50~120 °C показало різке зниження питомого електричного опору від $8\cdot10^9$ до $7\cdot10^3$ Ом·см з підвищення температури, що є характерним для напівпровідникових матеріалів. Електричну провідність матеріалу розраховували з урахуванням експериментальних вимірювань: σ_1 дорівнює $1{,}25\cdot-10^{8}$ 1/(Ом·м) для 50 °C і σ_2 дорівнює $1{,}4\cdot10^{-2}$ 1/(Ом·м) для 120 °C. Досліджено вплив магнітного поля на напруженість електричного поля всередині досліджуваного зразка речовини. Також було отримано залежність напруги Холла від індукції магнітного поля для речовини зразка. Діапазон робочих температур від +50 до + 220 °C, хімічна сполука розкладається при 260 °C. Концентрація носіїв заряду зростає від $7{,}8\cdot10^{17}$ м$^{-3}$ при 50 °C до $4{,}14\cdot10^{29}$ м$^{-3}$ при 220 °C, а постійна Холла зменшується з 9,43 м$^3\cdot$C^{-1} до $1{,}8\cdot10^{-11}$ м$^3\cdot$C^{-1}, при підвищенні температури від 50 до 220 °C. Напруга Холла змінюється від $1{,}97\cdot10^{-5}$ В до $1{,}97\cdot10^{-3}$ В у діапазоні магнітного поля від 0 до 1000 мТл. Новий магніточутливий елемент на основі синтезованого напівпровідникового матеріалу буде використовуватися для створення датчиків магнітного поля.

Ключові слова: Температурні властивості, Магнітне поле, Концентрація носіїв заряду, Напівпровідниковий матеріал.