*Conference Proceedings*

# 16th International Conference on Advanced Trends in Radioelectronics, Telecommunications and Computer Engineering (TCSET)

in partnership with

**Lviv-Slavske, Ukraine**
**February 22-26, 2022**

Proceedings of 16th International Conference on Advanced Trends in Radioelectronics, Telecommunications and Computer Engineering (TCSET), Lviv-Slavske, Ukraine, February 22 – 26, 2022, 866 p.

These proceedings depict new areas of development of information and communication systems, networks and technology, principles of optical transport networks construction, signals processing methods and methods of data protection in telecommunication networks, radio electronic devices and systems, and computer engineering.

**IEEE Catalogue Number: CFP2238R-USB**

**ISBN (IEEE): 978-1-6654-6860-2**

**Papers are presented in authors' edition.**

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# Physical Parameters of the Synthesized Semiconductor Material Based on a Heterometallic Complex Compound of Copper (II) with N, N'-Bis(Salicylidene)Semicarbazide

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***Abstract*—A new stuff, heterometallic barium di[N,N'-bis(salicylidene)thiosemicarbazidatocuprate (II)] monohydrate (I) with such composition $Ba[CuL']\cdot H_2O$, where $H_3L$ = N, N'-bis (salicylidene)thiosemicarbazide, has been synthesized. Investigations of electrical conductive properties for the compound I as compressed cylindrical specimen showed that its specific resistance was $6\cdot 10^{12}$ Ohm·cm at 313 K temperature, and there was a rectilinear relationship between the specific resistance and the temperature at the temperature rising from 313 K to 413 K, which was typical for semiconductor materials. Calculated at 333 K values of a temperature coefficient of resistance (TCR) for compound I (-11.39% $K^{-1}$) and sensitivity (B) of the semiconductor stuff (12630 K) confirm that this compound is a semiconductor of medium sensitivity in the 313~413 K operating temperature range.**

***Keywords—semiconductor, magnetic field, induction, concentration, temperature, heterometallic complex compounds***

## I. Introduction

At present, measuring parameters of non-electric quantities is a relevant scientific and practical task [1]. Contemporary physics meets the necessity to investigate properties of new composite compounds for creating primary sensors of such quantities [2]. Magnetic field, temperature and humidity sensors are no exception [3]. Utilization of nanocomposite materials will not only expand horizons of using such sensors, but also allow finding new opportunities for their application in micro- and nanoelectronic circuitry [4, 5].

The objective of the study is to design a modern sensor of barium di [N,N'-bis (salicylidene)thiosemicarba-zidatocuprate(II)] based on the synthesized semiconductor material.

Nowadays, modern synthetic coordination chemistry is a promising area, because it provides synthesizing a variety of complex compounds with a wide range of physicochemical properties and their practical application in various fields [6, 7]. In this regard, heterometallic complexes with Schiff bases are quite promising. Presently, Schiff bases are of great interest because they contain O, N, S heteroatoms that are able to coordinate with metals [8, 9]. Moreover, heterocomplexes obtained on their base by combining two metals of different nature often have an effective biological activity and various conductive properties [10, 11]. In practical applications, such compounds can be employed for manufacture of thermistors as semiconductor stuff [12, 13]. Therefore, synthesizing and studying properties of coordination compounds of transition metals with azomethine are relevant both from a scientific and practical point of view [14, 15].

To find some novel heterometallic complex compounds having certain semiconductor properties, a technique was devised and applied for the synthesis of heterometallic barium di[N, N'-bis(salicylidene)thiosemicarbasedatocuprate (II)] monohydrate (I) of the following composition $Ba[CuL']\cdot H_2O$, here $H_3L$ = N, N'-bis (salicylidene)thiosemicarbazide.

## II. Synthesizing

The authors have synthesized barium di[N, N'-bis (salicylidene)thiosemicar-bazidatocuprate(II)] monohydrate (I) by applying the next technique: a 1.95 g (10 mmol) portion of thiosemicarbazone salicylic aldehyde should be dissolved in a 20 ml mixture of water and ethanol (1:1) in a heated bath at temperature $t \approx 343$ K. An aqueous solution of $Ba(OH)_2$ was introduced in portions into the mixture up to pH = 8, and then another 1.22 g of salicylic aldehyde (10 mmol) was supplemented to it. Next, this reaction mixture was warmed up to 343 K, then 1.71 g of $CuCl_2\cdot 2H_2O$ (10 mmol) previously dissolved in 20 ml of ethanol was added to it. After formation of the crystal solution, an aqueous solution of barium hydroxide was added and warmed up to pH = 9 – 10 being stirred constantly. The fine-crystalline sediment of greenish color appeared, later it became brown. Further, the reaction mixture was sustained in the heated bath for 1 h, then it was

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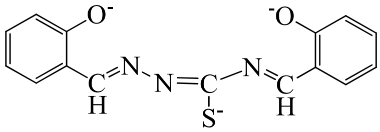
cooled. Next, the sediment was placed under mother liquor overnight, then it was filtered using Schott's filter. After that, the brown-colored sediment was washed with some cold ethanol and a certain amount of ether, then it was dried in a desiccator over $CaCl_2$ until its mass became constant. So, the yield is 2.93 g, this is about 67% of the theoretically counted. This isolated heterometallic compound (I) turned to be a fine-crystalline powder. It is quite well soluble in DMSO and DMFA, but worse soluble in acetone and ethanol, moreover it is almost dissoluble in water, acetonitrile, chloroform, tetrachlormetan.

The authors have determined a composition of the obtained compound (I) considering the data obtained from the performed element analysis, infrared spectroscopy, as well as magneto-chemical and thermogravimetric examinations, also by the data on molecular conductivity. The composition consists of two chemically different metals (s-, d-) and may be written by the chemical formula:

$Ba[CuL']_2 \cdot H_2O$, where $L' = C_{15}H_{10}N_3O_2S$ or



## III. MATERIAL CHARACTERISTICS

Considering the fact that the obtained heterometallic coordination compound of copper (II) and barium with N,N'-bis(salicylidene)thiosemicarbazide contains a crystallization molecule of water, the authors measured its electrical conductivity after having kept it in a desiccator at a 378 K temperature until its mass became constant.

For the extracted and dehydrated compound $Ba[Cu(C_{15}H_{10}N_3O_2S)]_2$ the molar mass calculated as being 857.08 g/mol. Moreover, we calculated the number of valence electrons in a molecule, it equaled 210.

Investigations of electrical conductive properties performed for the compound I as compressed cylindrical specimen showed that its specific resistance was $6 \cdot 10^{12}$ Ohm·cm at 313 K temperature, while when the temperature rose from 40 ºC up to 313 K, some rectilinear relationship between two parameters – the specific resistance (ρ) and the temperature (T) was observed, which was typical for semiconductor materials.

The value of temperature coefficient of resistance (TCR) for compound I (-11.39% $K^{-1}$) and the value of sensitivity (B) of the semiconductor stuff (12630 K) counted at 333 K confirm that this compound is a semiconductor with medium sensitivity in a 313~413 K operating temperature range in comparison with other similar materials [16].

A cylindrical specimen with 0.11 g mass and $17.67 \cdot 10^{-9}$ $m^3$ volume created from the studied compound (I) by compression method was utilized in experimental inquiry. Considering these data, its density was calculated by formula (1):

$$\rho = m / v = 6.225 \cdot 10^3 \, kg / \mathrm{m}^3 , \qquad (1)$$

where $\rho$ is the density of the material; $V$ is the volume of the tested specimen; $m$ is the mass of the tested specimen.

The mass of a molecule in the compound (I) was determined by the following formula

$$m_0 = M / N_A = 142.32 \cdot 10^{-26} kg , \qquad (2)$$

where $m_0$ is the mass of the compound molecule; $M$ is the molar mass, $N_A$ is the Avogadro number.

The total number of molecules in the $17.67 \cdot 10^{-9}$ $m^3$ volume was calculated by the following formula

$$N_{mol} = m / m_0 = 7.729 \cdot 10^{19} , \qquad (3)$$

where $N_{mol}$ is the total number of molecules; $m$ is the mass of the test specimen; $m_0$ is the mass of one molecule of the compound (I).

The number of valence electrons can be founded as:

$$N = 210 \cdot N_{mol} = 1623.103 \cdot 10^{19} . \qquad (4)$$

Studying the properties of the compressed barium d [N,N'-bis(salicylidene) thiosemicarbazidatocuprate (II)] monohydrate (I) in the 313~413 K temperature span showed that when the temperature rises, the specific resistance decreases sharply from $6.0 \cdot 10^{10}$ Ohm·m to $3.4 \cdot 10^6$ Ohm·m. Calculation of the specific conductivity of the stuff at regarded temperatures enabled to determine the bandgap width:

$$\Delta E = \frac{k \ln \dfrac{\sigma_1}{\sigma_2}}{\left( \dfrac{1}{T_2} - \dfrac{1}{T_1} \right)} = 1,745 \cdot 10^{-19} \, J = 1,09 \, eV , \qquad (5)$$

where σ is the specific conductivity of the stuff; $T$ is the absolute temperature; $k$ is the Boltzmann constant.

The performed calculations substantiate that this stuff is a semiconductor. To utilize this nanocomposite material as sensor of non-electric quantities, such as temperature or magnetic field induction, the compound was pressed into an element with dimensions of 0.5 × 0.5 × 1.0 mm.

Taking into account the bandgap of the stuff and empirical evidence, a temperature dependence of the specific conductivity can be calculated. Fig. 1 illustrates the plot of temperature dependence of the specific conductivity. According to Fig. 1, as the temperature rises from 273 K to 493 K, the specific conductivity of this structure increases from $4.45 \cdot 10^{-14}$ $(\mathrm{Ohm \cdot m})^{-1}$ up to $4.22 \cdot 10^{-5}$ $(\mathrm{Ohm \cdot m})^{-1}$.

The dependence of resistance of the semiconductor with 0.5×0.5×1.0 mm dimensions on temperature is shown in Fig. 2. The Figure 2 shows that the resistance decreases from $8.97 \cdot 10^{16}$ Ohms at 273 K temperature to $9.47 \cdot 10^7$ Ohms at 493 K temperature.

Fig. 3 presents the graph of changes which take place in the charge carrier concentration through temperature.

According to Fig. 3, when the temperature rises steadily in a 273 K ~ 493 K span, the charge carrier concentration grows from $2.78 \cdot 10^{12}$ $m^{-3}$ to $2.63 \cdot 10^{21}$ $m^{-3}$.

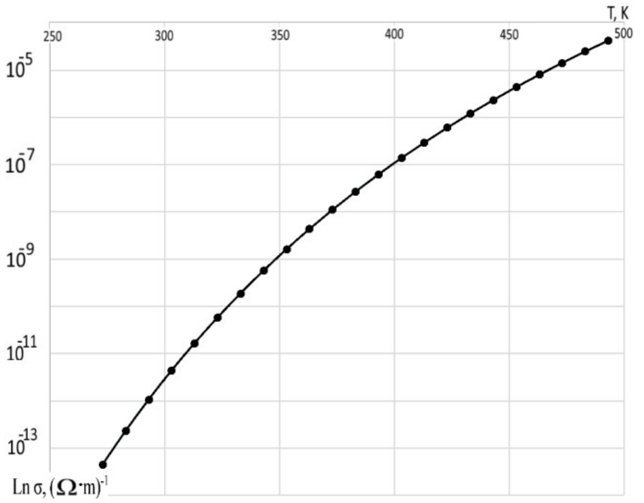



Fig. 1. Temperature dependence of the specific conductivity of the material.

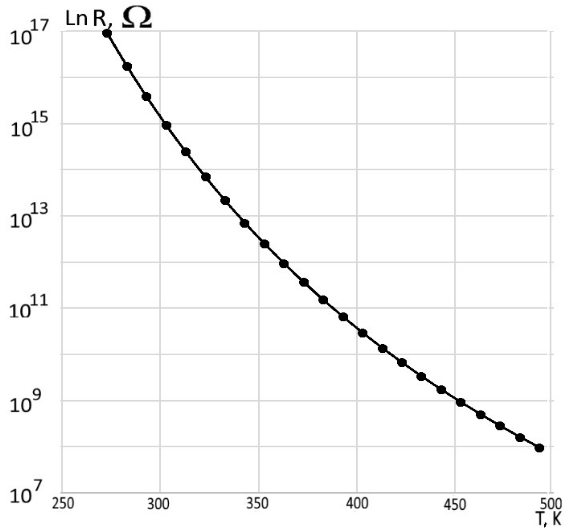



Fig. 2. Temperature dependence of resistance of the nanocomposite material.

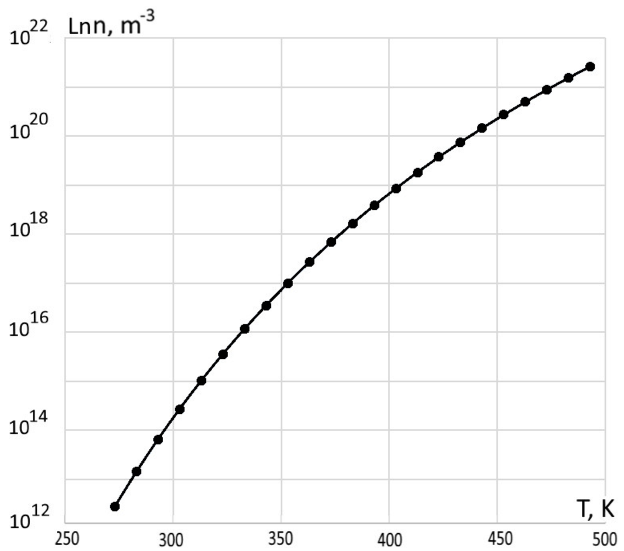



Fig. 3. Temperature dependence of the charge carrier concentration.

Calculating the quantum Hall constant at 373 K yielded the following results:

$$R_{qu\ H} = -3\pi / 8nq = 10,69 m^3 \cdot K^{-1}, \qquad (6)$$

where $q$ is the electron charge; n is the concentration of charge carriers.

Having combined the equation of the temperature dependence of the charge carrier concentration and expression (7), the authors acquired the temperature dependence of the Hall constant (7):

$$R_{qu\ H} = -\frac{3\pi}{8qn_0} \cdot e^{\frac{\Delta E}{kT}}. \qquad (7)$$

By this formula (7), the graph of temperature dependence of the quantum Hall constant was obtained (Fig. 4).

According the graph in Fig. 4, when the temperature rises steadily in the 273 K ~ 493 K span, the quantity of the quantum Hall constant for the explored compound diminishes from $2.6 \cdot 10^6 m^3 \cdot K^{-1}$ to $2.7 \cdot 10^{-3} m^3 \cdot K^{-1}$.

Having determined the charge carrier mobility, we obtained for the quantum case:

$$\mu_n = R_{qu\ H} \cdot \sigma = 1.178 \cdot 10^{-7} m^3 \cdot (V \cdot s)^{-1}. \qquad (8)$$

According to the calculations, the charge carrier mobility is a constant value and does not depend on temperature.

Fig. 5 shows the dependence of the Hall electric field inside the 0.5×0.5×1.0 mm semiconductor, which arises when a magnetic field is present. Fig. 5 depict that the voltage grows from $3.9 \cdot 10^{-2}$ to 3.9 V/m in the 10 to 1000 mT span.

Fig. 6 demonstrates dependence of the Hall voltage on magnetic field induction, which was obtained for the explored compound. The obtained graph demonstrates that the Hall voltage rises from $1.96 \cdot 10^{-5}$ V to $1.96 \cdot 10^{-4}$ V in the 10–100 mT span. Moreover, it rises from $1.96 \cdot 10^{-4}$ V to $7.84 \cdot 10^{-4}$ V in the 100~400 mT span. Furthermore, is rises from $7.84 \cdot 10^{-4}$ to $1.96 \cdot 10^{-3}$ V in the 400 mT – 1000 mT span.

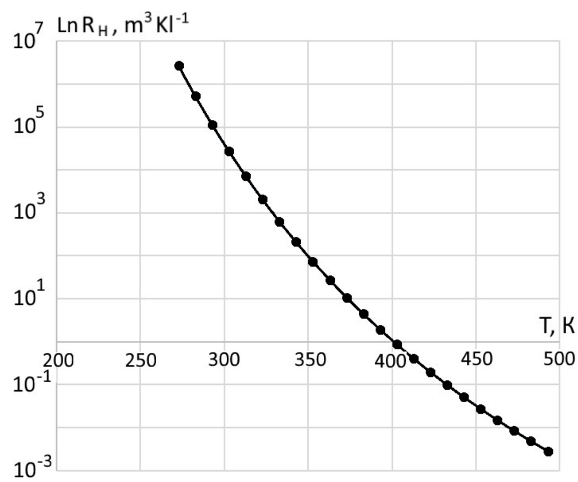



Fig. 4. Temperature dependence of the quantum Hall constant.

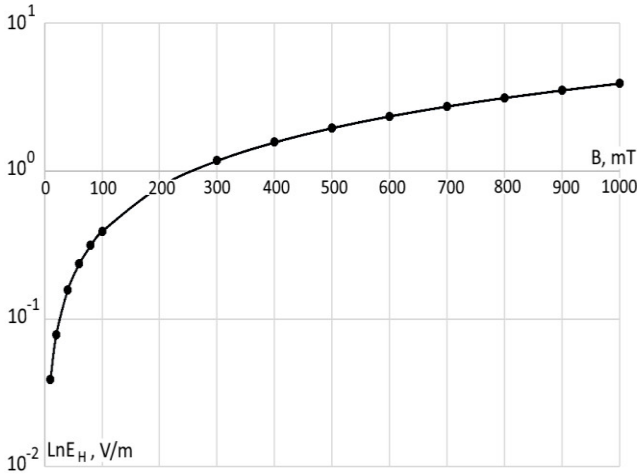



Fig. 5. Magnetic field induction dependence of the electric field in the semiconductor.

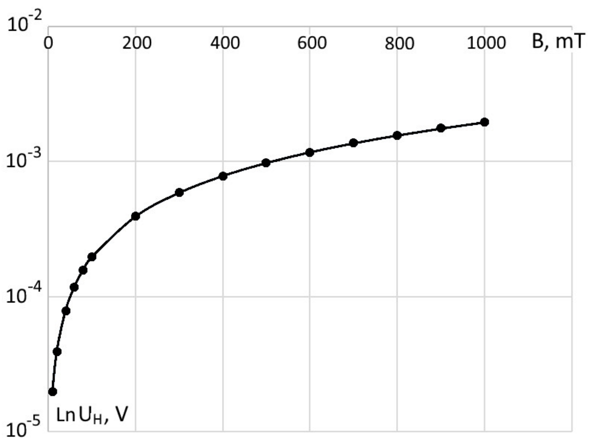



Fig. 6. Magnetic field induction dependence of the Hall voltage.

## IV. Conclusions

A novel sensitive element built on the obtained complex compound of barium di[N,N'-bis(salicylidene) thiosemicarbazidatocuprate(II)] was created. Examination of electrical conductive properties for the investigated complex compound in compressed form in 273 K ~ 493 K temperature span demonstrated that its specific resistance dropped dramatically from $2.24\cdot10^{13}$ Ohm·m to $2.36\cdot10^{4}$ Ohm·m with temperature growing, and its bandgap width was 1.09 eV, that was typical for a semiconductor stuff. The chemical compound begins to decompose at 523 K, the charge carrier concentration increases from $2.78\cdot10^{12}$ $m^{-3}$ at 273 K to $2.63\cdot10^{21}$ $m^{-3}$ at 493 K, whereas the quantum Hall coefficient drops from $2.64\cdot10^{6}$ $m^3\cdot K^{-1}$ to $2.7\cdot10^{-5}$ $m^3\cdot K^{-1}$ with temperature rising from 273 K to 493 K, the Hall voltage grows from $1.96\cdot10^{-5}$ to $1.96\cdot10^{-3}$ V in the magnetic field span of 0~1000 mT.

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