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Electrical properties of the nanocomposite (copper, samarium)-containing complex compound

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Abstract. A new semiconductor material tetrakis-μ3-(methoxo)(methanol)-pentakis (acetylacetonate)(tricopper(II), samarium(III)) (I) with composition $[Cu_3Sm(AA)_5(OCH_3)_4CH_3OH]$, where HAA = $H_3C–C(O)–CH_2–C(O)–CH_3$ has been synthesized. By the data of elemental analysis and physicochemical research methods, it was established that the obtained complex compound (I) contained atoms of copper (II) and samarium (III) in ratio Cu:Sm = 3:1, and its composition corresponded to the gross formula $Cu_3SmO_{15}C_{30}H_{51}$. Electrical conductivity of the obtained material in pressed form was measured. For the complex compound (I) such parameters were calculated: the number of valence electrons in one molecule – 272; mass of one molecule – $164.867 \cdot 10^{-20}$ kg; the total number of molecules in the cylindrical sample of a 0.131 g mass and a $18.24 \cdot 10^{-9}$ m^3 volume – $7.946 \cdot 10^{13}$moleculas; the total number of valence electrons – 272. In the 303~413 K temperature range, the resistivity of the pressed sample decreases from $4 \cdot 10^{11}$ to $7 \cdot 10^4$Ohm·cm, which confirms that the isolated compound is a semiconductor with a bandgap ΔE = 1.526 eV. Electrical conductivity properties of the complex compound as thermo- and magnetically sensitive element were studied, for this purpose a test sample of compressed material with 0.5×0.5×1.0 mm geometric dimensions was utilized.

1. Introduction

Automation of technological processes in various fields of industry, research and everyday life requires the development of devices for controlling and regulating various parameters. Such devices are sensors located directly in the control area and designed to measure various physical quantities [1-2]. One of the most common parameters in both industry and research is temperature and magnetic field, their measurement having the largest part among all types of measurements [3-4]. Among other semiconductor devices, thermistors are most often used to measure temperature, they have a nonlinear, noticable temperature dependence of resistance and a negative or positive temperature coefficient of resistance. Thermistors are the simplest semiconductor devices, they are used in automatics and telemechanics, thermometry, electronics, electrical engineering, telephony to solve various technical problems [1-4]. They have a number of advantages over other devices suitable for similar purposes,

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these advantages are high temperature sensitivity, small size, stability of characteristics over time and almost no need for special care of thermistors during their operation. However, such factors as possible impurities in semiconductor materials, modes of their heat treatment, methods of contacting and others affect electrical parameters that complicates practical application of thermistors. Therefore, despite the fact that many semiconductors have a noticeble temperature dependence of resistivity, not all of them can be used for producing thermistors in large scale. So, the nature of conductivity, the effect of impurities and heat treatment on the electrical conductivity of semiconductor materials should be examined to develop a technology for producing thermistors that would meet requirements of technology.

Therefore, the synthesis of new semiconductor materials with significant conductivity and high values of the temperature coefficient of resistance is relevant, this will provide developing thermistors with high sensitivity to temperature changes.

It is known from [5-10] that heterometallic complex compounds containing atoms of transition metals and lanthanides are widely utilized due to their unique magnetic, electrical, optical, luminescent and other properties. Introducing different complexing metals and chelating ligands into a molecule of complex compound one can obtain compounds of different composition, i.e. to conduct a directed synthesis of compounds with a given range of operating properties. Heterometallicβ-diketonates, which have semiconductor properties, are of particular interest among this class of complex compounds [11-12].

2. Theoretical and experimental research

The aim of this work is studying thermoresistive and magnetic features of a semiconductor material based on heterometallic (copper, samarium)-containing acetylacetonate.

A technique was developed for synthesizing the heterometallic complex compound – tetrakis-μ3-(methoxo)(methanol)-pentakis(acetylacetonate)(tricopper (II), samarium(III)) (I) with such composition:

$$[Cu_3Sm(AA)_5(OCH_3)_4CH_3OH], \text{ where HAA} = H_3C–C(O)–CH_2–C(O)–CH_3.$$

The authors obtained the heterometallic complex compound (I) by the following procedure: salts of 7.23 g (30 mmol) copper(II) nitrate trihydrate and 4.44 g (10 mmol) samarium(III) nitrate hexahydrate were dissolved in 160 ml of absolute methyl alcohol, which contained 70 ml of orthomut ether. The obtained mixture was kept for 2 hours in a hermetically sealed conical flaskat room temperature. Further, 5.4 ml (50 mmol) of acetylacetone was added to the mixture. Then, the conical flask was closed with a reversible water refrigerator and placed on a heated magnetic stirrer. After that, piperidine was introduced in batchesto the mixture to pH = 8bypermanent stirring and heating (~323.15 K). Moreover, it was heated and stirred for an hour more. A color of the derived solution changed and a sediment appeared. Next, the reaction mass was heated (~323.15 K) with continuous stirring for an hour. A homogeneous blue fine crystalline sediment was formedafter cooling. The sedimentwas filtered on a glass filter. Later, it waswashed with a small quantity of absolute methanol, diethyl ether. Then, it was driedover silica gel in a vacuum desiccator. The practical yield was 8.13 g, which was 82% of the theoretically calculated one. So, the isolated complex compound (I) is a fine crystalline powder of blue color, it is soluble in a mixture of dimethylformamide with chloroform (1:1), poorly soluble in alcohols, diethyl ether, better soluble in dimethyl sulfoxide, dimethylformamide, it ruins in water.

Elemental chemical analysis of the isolated complex compound (I) was performed which showed that it contained in dry powder state:

$$Cu – 19.19\%; Sm – 15.11\%; C – 36.27\%; H – 5.14\%.$$

The above-mentioned data substantiate that the isolated complex compound contains atoms of metals of different nature, and their ratio inside the heterometallic compound (I) Cu is Sm = 3:1.We performed an X-ray phase analysis, magnetochemical and thermogravimetric studies, IR spectroscopic

investigations to establish a plausible scheme of chemical bond arrangement in this compound and its structure. On the basis of the performed studies, we established the composition of the selected complex compound (I), which corresponded to a gross formula $Cu_3SmO_{15}C_{30}H_{51}$ and proposed the scheme of chemical bonds arrangement (Figure 1).

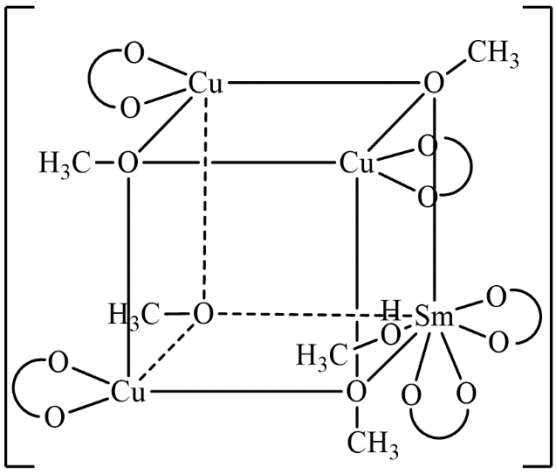


Figure 1. Scheme of chemical bond arrangement in [Cu3Sm(AA)5(OCH3)4CH3OH], where HAA = H3C – C (O)–CH2 – C (O) –CH3.

To conduct measurements of electrical conductivity, the microcrystalline powder of the isolated complex compound $[Cu_3Sm(AA)_5(OCH_3)_4CH_3OH]$ was pressed with a specially designed pressing device. A cylindrical sample of a 0.131 g mass and a $18.24 \cdot 10^{-9}$ m^3 volume was made and used in experimental studies.

Taking into account these data, the density of the cylindrical sample pressed material was calculated by formula (1):

$$\rho = m / v = 7.182 \cdot 10^3 kg / m^3, \quad (1)$$

where m is the experimentalsample mass; V is the experimentalsample volume.

The molar mass of the complex compound $[Cu_3Sm(AA)_5(OCH_3)_4CH_3OH]$ was calculated as being 992.5 g/mol, and the number of valence electrons in one molecule was calculated as being 272.

The mass of one molecule of the compound (I) is

$$m_0 = M / N_A = 164.867 \cdot 10^{-20} kg, \quad (2)$$

where M is the molar mass of the compound (I); N_A is the Avogadro number.

Applying formula (3), we calculated the total number of molecules in the cylindrical sample of a 0.121 g mass and a $18.24 \cdot 10^{-9}$ m^3 volume:

$$N_{mol} = m / m_0 = 7.946 \cdot 10^{13} molecules, \quad (3)$$

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

Total number of valence electrons:

$$N = 272 \cdot N_{mol} = 21.6131 \cdot 10^{15}. \quad (4)$$

The experiment showed that in the 303~413 K temperature range the resistivity of the pressed sample of compound (I) decreases from $4 \cdot 10^{11}$ to $7 \cdot 10^4$Ohm·cm, i.e. the isolated compound is a semiconductor.

This experimental investigation contributes to calculations of material'sspecific conductivity at these temperatures and to determination of the bandgap width:

$$\Delta E = \frac{k \ln \frac{\sigma_1}{\sigma_2}}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = 2,4416 \cdot 10^{-19}\ J = 1,526 eV\ , \quad (5)$$

where σ is material's specific conductivity; T is the absolute temperature; k is the Boltzmann constant.

The calculations confirmed that this material is a semiconductor.

To use this nanocomposite material as a sensor of non-electric quantities, such as magnetic field induction and temperature, the compound was pressed into an element with geometric sizes of 0.5×0.5×1.0 mm.

Knowing the bandgap width of the studied material and applying the experimental results, we obtained the temperature dependence of specific conductivity. Figure 2 illustrates a received graph of the temperature dependence of specific conductivity.

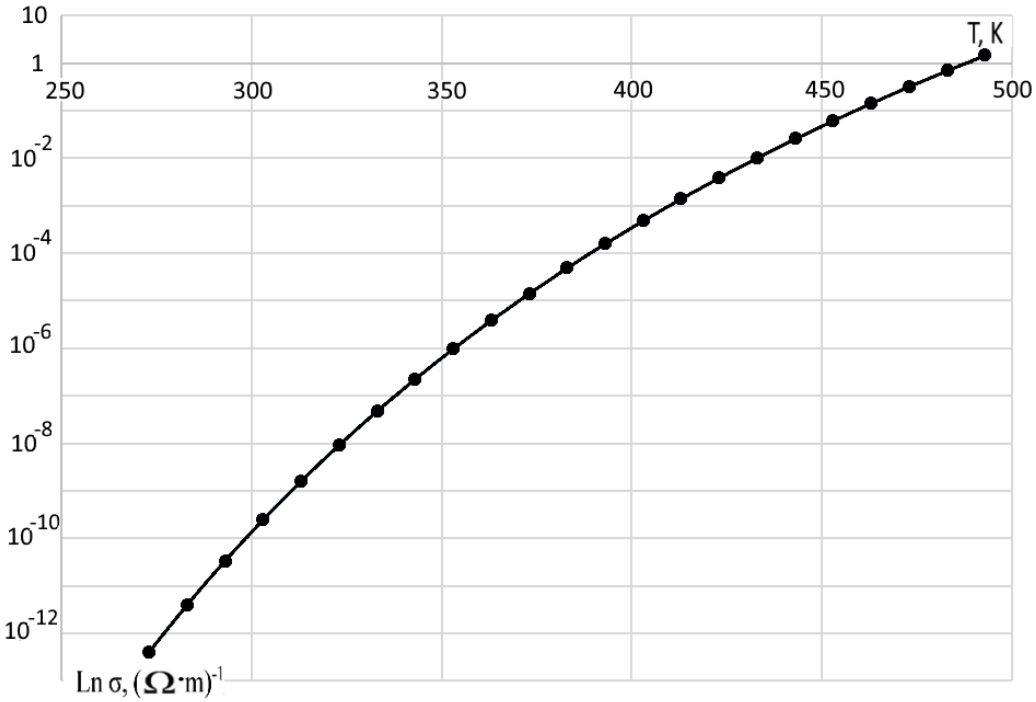


Figure 2. Temperature dependence of specific conductivity of complex compound.

The graph in Figure 2 indicates that the specific conductivity of the studied structure grows from $4.084 \cdot 10^{-13}$ $(Ohm \cdot m)^{-1}$ to 1.4838 $(Ohm \cdot m)^{-1}$ when the temperature rises from 273 K to the value of 493 K.

Knowing the behavior of specific conductivity with temperature, we can calculate the inverse value – specific resistivity. The temperature dependence of the specific resistivity of this material is shown in Figure 3.

The graph in Figure 3 shows that the specific resistivity decreases from $2.44 \cdot 10^{12}$ Ohm·m to 0.674 Ohm·m.

Figure 4 presents the temperature dependence of the resistance of heterometallic β-diketonate with sizes 0.5×0.5×1.0 mm.

The dependence in Figure 4 shows that the resistance decreases from $9.79 \cdot 10^{15}$ Ohms, at a 273 K temperature to 2695.75 Ohms at a 493 K temperature.

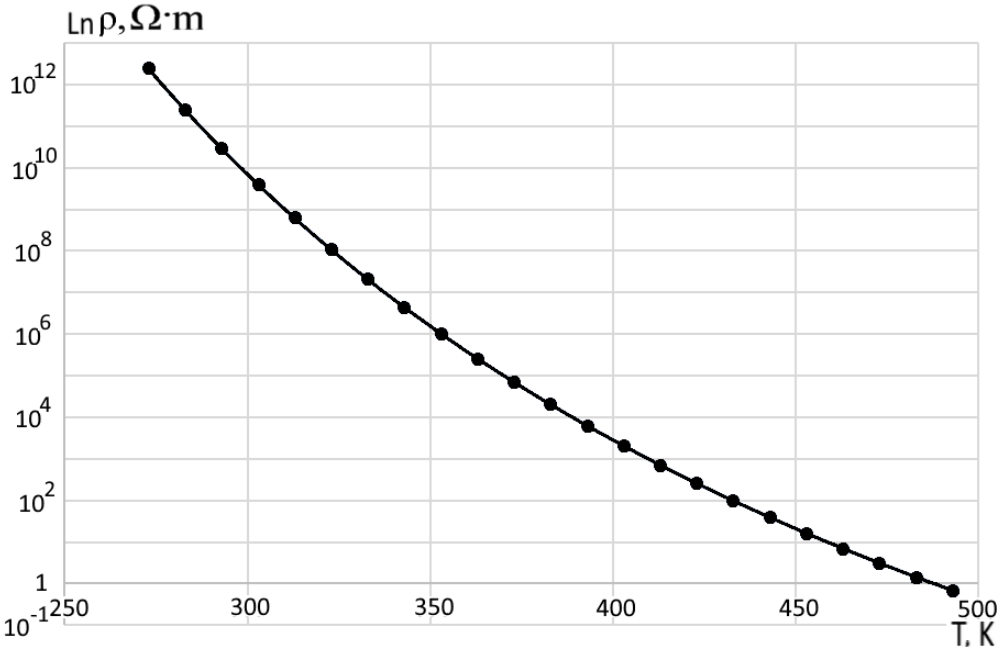


Figure 3. Temperature dependence of the specific resistivity of the material.

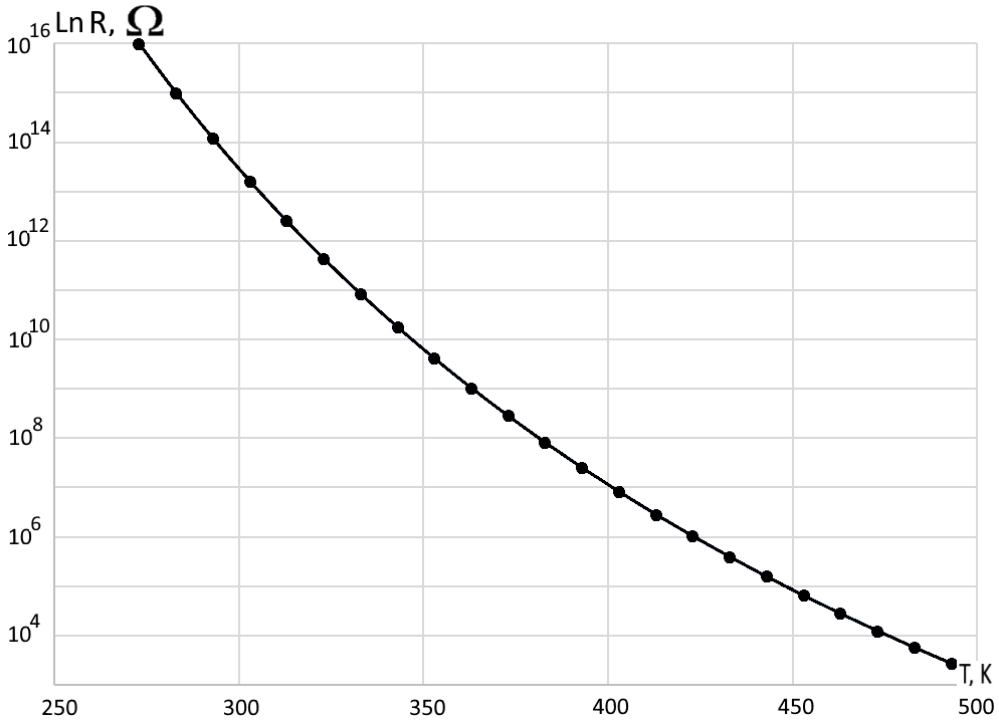


Figure 4. Temperature dependence of resistance of the heterometallic complex compound.

Figure 5 demonstrates the temperature dependence of current density at a supply voltage of 10 volts.

The graph in Figure 5 demonstrates that when the temperature changed by 220 degrees, the current density increased from $4.084 \cdot 10^{-9}$ A/m^2 to $1.48 \cdot 10^{4}$ A/m^2.

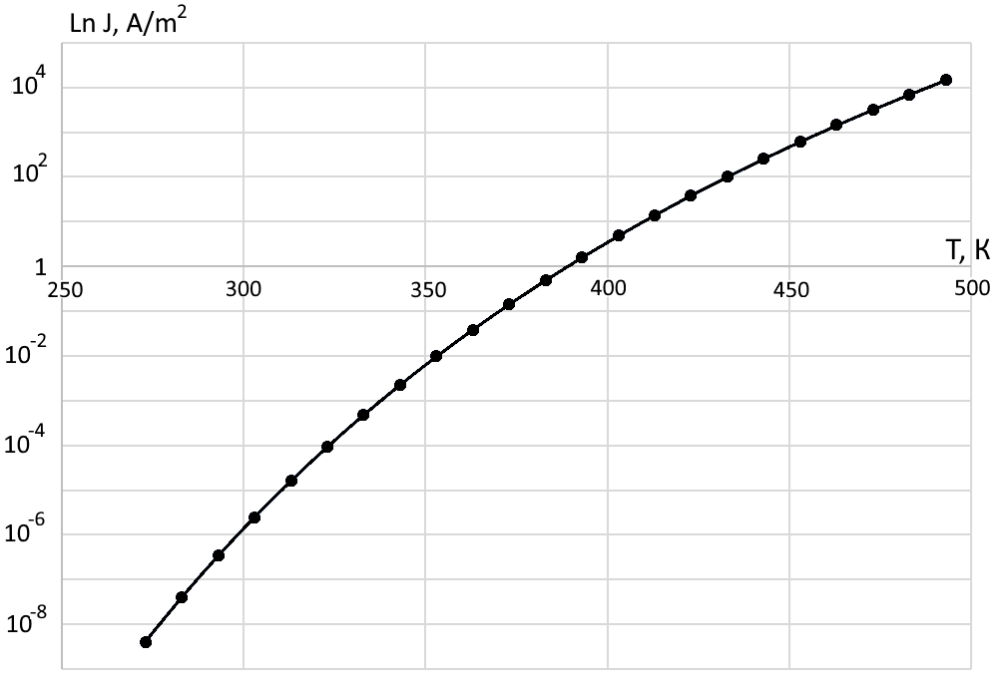


Figure 5. Temperature dependence of current density.

The temperature dependence of concentration can be found from the bandgap width of this material. A graph of the charge carrier concentration change due to the temperature change is shown in Figure 6.

The graph in Figure 6 demonstrates that the charge carrier concentration rises from $2.55 \cdot 10^{13}$ m^{-3} to $9.272 \cdot 10^{25}$ m^{-3} when the temperature grows from 273 K to the value of 493 K.

The quantum Hall constant at 373 K is:

$$R_{qH} = -3\pi / 8nq = 8.2 \cdot 10^{-3} m^3 \cdot C^{-1}, \quad (6)$$

where q is the charge of electron; n is the charge carrier concentration.

Formula (6) yields $R_H < 0$ for the case of electronic conductivity. While, if the current is carried mainly by holes, which are attributed to positive charges, then the Hall voltage changes its sign and $R_H > 0$.

Let us investigate the change in the Hall constant with temperature. For that purpose, we combine the equation of the temperature dependence of the charge carrier concentration and formula (6):

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

The temperature dependence of the quantum Hall constant shown in Figure 7was obtained by applying this equation.

The graph in Figure 7 demonstrates that the value of the quantum Hall constant for the compound drops from $2.88 \cdot 10^{5}$ m$^3 \cdot$C^{-1} to $7.93 \cdot 10^{-8}$m$^3 \cdot$C^{-1} when the temperature grows from 273 K to the value of 493 K.

The charge carrier mobility does not depend on temperature and is a constant value:

$$\mu_n = R_{q\,H} \cdot \sigma \;=\; 1.177 \cdot 10^{-7}\, m^3 \cdot (V \cdot s)^{-1}. \tag{8}$$

Figure 8 illustrates a dependence of the Hall electric field strength that appears under the action of a magnetic field inside the 0.5×0.5×1.0 mm semiconductor

Figure 8 illustrates the voltage rising from $1.17 \cdot 10^{-2}$ to 1.17 V/m in the 10–1000 mTrange.

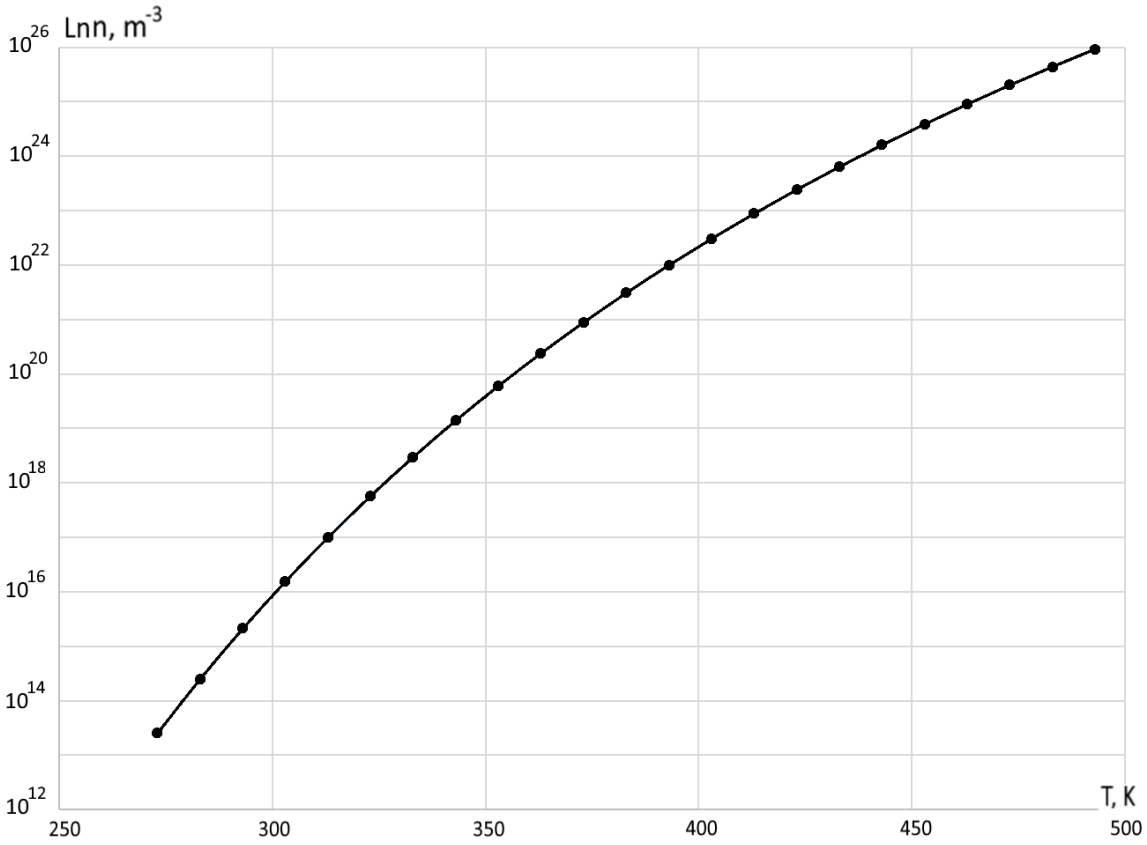


Figure 6. Temperature dependence of charge carrier concentration.

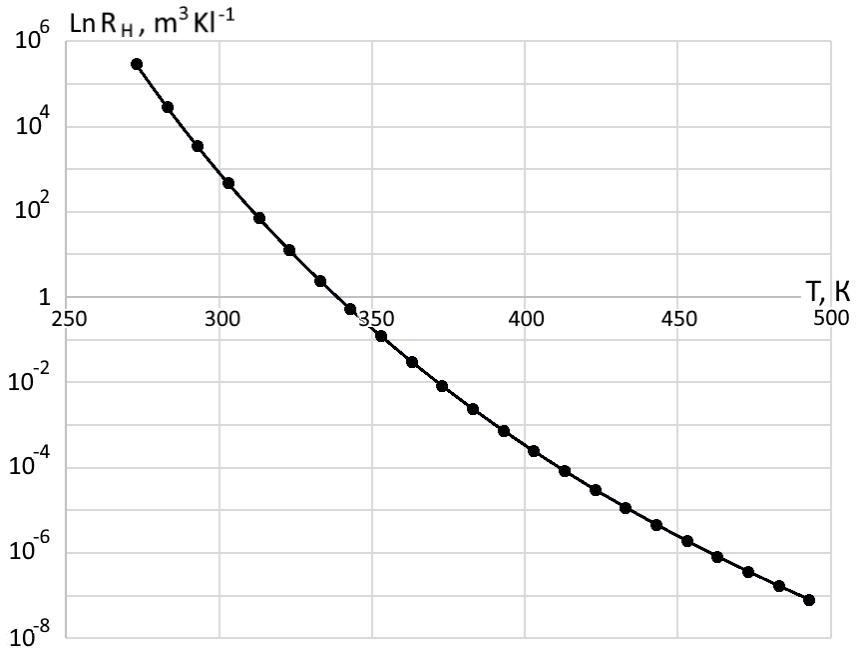


Figure 7. Temperature dependence of the quantum Hall constant of the semiconductor.

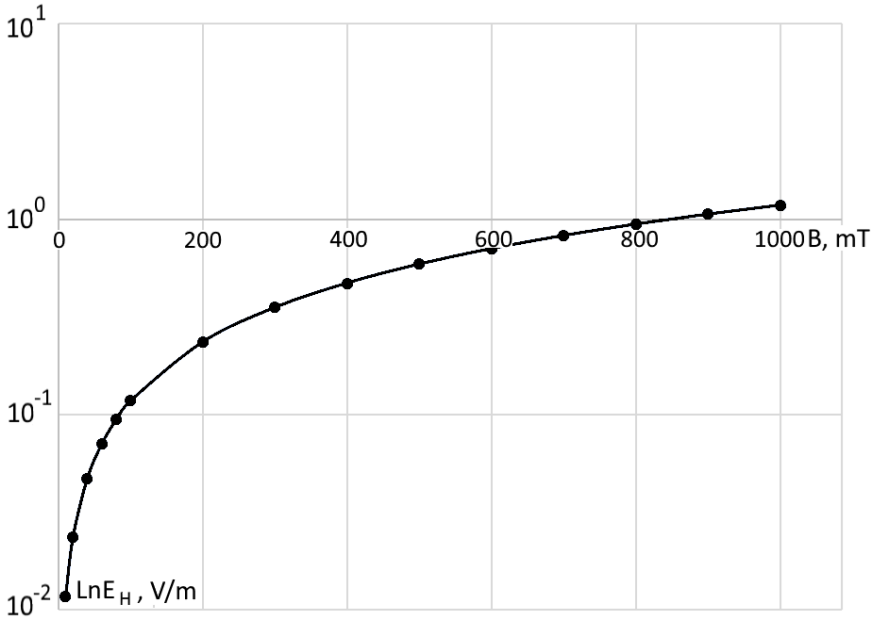


Figure 8. Magnetic field induction dependence of electric field strength in the semiconductor.

Figure 9 depicts the received magnetic field induction dependence of the Hall voltage for the examined compound.

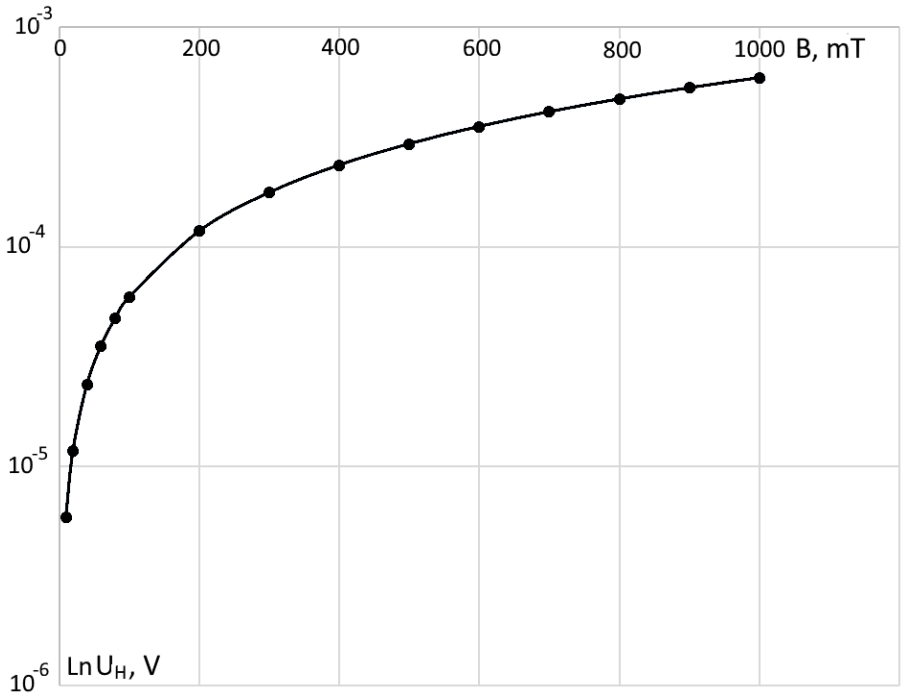


Figure 9. Magnetic field induction dependence of the Hall voltage.

The graph illustrates the Hall voltage growing from $5.88 \cdot 10^{-6}$ to $5.88 \cdot 10^{-5}$ V in the 10 to 100 mTrange, from $5.88 \cdot 10^{-5}$ V to $2.3 \cdot 10^{-4}$ V in the 100 to 400 mTrange, and from $2.3 \cdot 10^{-4}$ to $5.88 \cdot 10^{-4}$ V in the 400 mT to 1000 mTrange.

3. Conclusion

A new sensitive element based on the synthesized complex compound of tetrakis-μ3-(methoxo)(methanol)-pentakis(acetylacetonate)(tricopper (II), samarium(III)) (I) was derived. The technique to synthesize such material is given and the influence of temperature and magnetic field on electrophysical features of such semiconductor is examined.

The study of conductive features of the synthesized complex compound in compressed form in the 273 K ~ 493 K temperature range showed that when temperature increased, its resistivity decreased sharply from $2.44 \cdot 10^{12}$Ohm·m to 0.674 Ohm·m, and the bandgap was 1.526 eV, which was common for semiconductor materials. The chemical compound decomposes at 523 K, the charge carrier concentration grows from $2.55 \cdot 10^{13}$ m^{-3} at 273 K to $9.27 \cdot 10^{25}$ m^{-3} at 493 K, as the quantum Hall constant drops from $2.88 \cdot 10^{5}$ $m^3 \cdot C^{-1}$ to $7.93 \cdot 10^{-8} m^3 \cdot C^{-1}$ when temperature rises from 273 to 493 K, the Hall voltage grows from $5.88 \cdot 10^{-6}$ to $5.88 \cdot 10^{-4}$ B in the 0 to 1000 mT magnetic field range.

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