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# ЭЛЕКТРОФИЗИЧЕСКИЕ СВОЙСТВА ОКСИДНОЙ БРОНЗЫ $NA_XWO_3$

*Экспериментально определены закономерности формирования электрофизических свойств наночастиц путем измерения удельной проводимости образцов при нагреве и термостимулированной деинтеркаляцией ионов щелочных металлов. Разработан и собран экспериментальный стенд программно-управляемого нагрева и термоциклирования со специальной измерительной ячейкой для порошковых материалов. С его помощью была проведена сравнительная оценка эффективной энергии активации процессов деинтеркаляции ионов щелочных металлов в синтезированных образцах оксидных бронз и порошках, подвергавшихся дроблению в условиях интенсивного механического помола.*

*Ключевые слова: наночастицы, энергия активации, оксидные бронзы.*

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# ELECTROPHYSICAL PROPERTIES OF OXIDE BRONZE $NA_XWO_3$

*Experimentally determined regularities of the formation of the electrophysical properties of nanoparticles of oxide bronzes. Samples of oxide bronzes were obtained by self-propagating high-temperature synthesis. Then the samples were subjected to mechanical crushing. Measured conductivity of the samples during heating. Created a special measurement cell for powder materials. Created automated experimental stand. On the experimental test bench conducted a comparative assessment of effective energy of activation of processes of deintercalation of alkali metal ions in the powders.*

*Key words: nanoparticles, activation energy, oxide bronzes.*

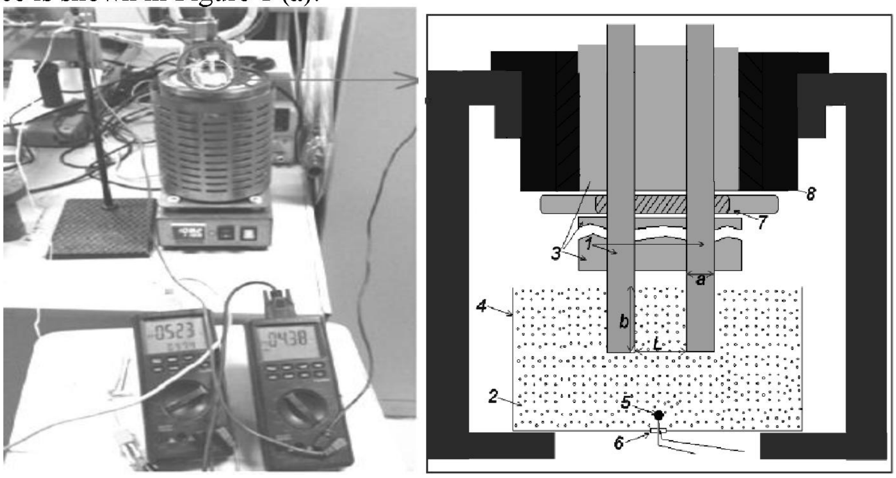
## Introduction

A large number of publications today dedicated to the materials after grinding to the nano range has acquired new optical and electrical properties [1, 2]. They can therefore be used as functional materials [3]. Nanoparticles of noble metals have found wide application in Biomedicine [4]. Open questions remain of conductivity [5] nanoscale layered and tunnel structures by their doping with alkali and alkaline earth metals. The paper presents first results of determination of the electrophysical properties of synthesized oxide bronzes.

***The aim*** of this study was comparative examination of electrical conductivity of oxide bronzes for determine the activation energy in the processes of deintercalation.

## Experimental techniques

The basis of measuring stand for measuring the conductivity of oxide bronze powders when heated inside a tube furnace is shown in Figure 1 (a).



a) b)

**Fig. 1** – a) Experimental setup; b) Measuring cell: 1-tungsten electrodes inserted into the cylindrical channels; 2-the studied material; 3-a tube of dielectric material with cylindrical hollow channels; 4 – capacity of the dielectric; 5 – thermocouple; 6 – hole for thermocouple; 7-ceramic washer; 8-a hollow bolt

The measuring cell is an iron U – shaped steel frame with curved inside edges. Inside the bolt is a tube of dielectric material (porcelain) with a cylindrical hollow channels. In the tube channels are inserted two tungsten electrodes. In a small thin-walled ceramic container is filled and compacted the investigated powder (or placed a small solid sample of the test material). Between the tube with electrodes and the hollow bolt is placed a thin dielectric washer. She has a hole diameter smaller than the diameter of the tube. The design is fixed hollow bolt. A chromel – alumel thermocouple is placed in a volume of powder through an additional hole in a ceramic container. Measuring cell with powder mounted on a tripod and placed in a high temperature furnace «UDIAN». Tungsten electrodes and a thermocouple connected to a digital multimeter «True RMS» via RS-232 output. Connecting to a computer using environment «MatLab» allows you to record the resistance and temperature of the test material at specified intervals of time. Measurement of temperature and resistance were conducted simultaneously, which allowed to analyze the temperature dependence of the electrical conductivity of oxide bronzes.

## Mathematical model

As is well known [6, 7], at low temperatures the concentration of electrons in the conduction band of one type of impurity is determined from the equation:

$$\sigma = AT^{3/2}\exp\left(-\frac{E_a}{kT}\right), \tag{1}$$

where $E_a$ is the activation energy of the impurity semiconductor, $k$=1,38·$10^{-23}$ J/K=8,625·$10^{-5}$ eV is the Boltzmann's constant. As the mobility μ and the factor $T^{3/2}$ change slowly compared to the exponential member in the region of low temperatures the conductivity of doped semiconductor is changed by the exponential law:

$$\sigma = \sigma_0\exp\left(-\frac{E_a}{kT}\right), \tag{2}$$

where the coefficient $\sigma_0$ depends on the kind of semiconductor.

One of the main characteristics of a semiconductor is its energy of activation. By measuring the resistance R at different temperatures T and build a graph of 1/T in a semilog scale, it is possible to find the activation energy. This is a straight line, i.e., the model: $y=a+bx$, $y=ln\sigma$, $x=T^{-1}$, $a=ln\sigma_0$, $b=-Ea\cdot k^{-1}$. The angular coefficient of this straight line we find the activation energy of impurity semiconductor.

## Experimental results and discussion

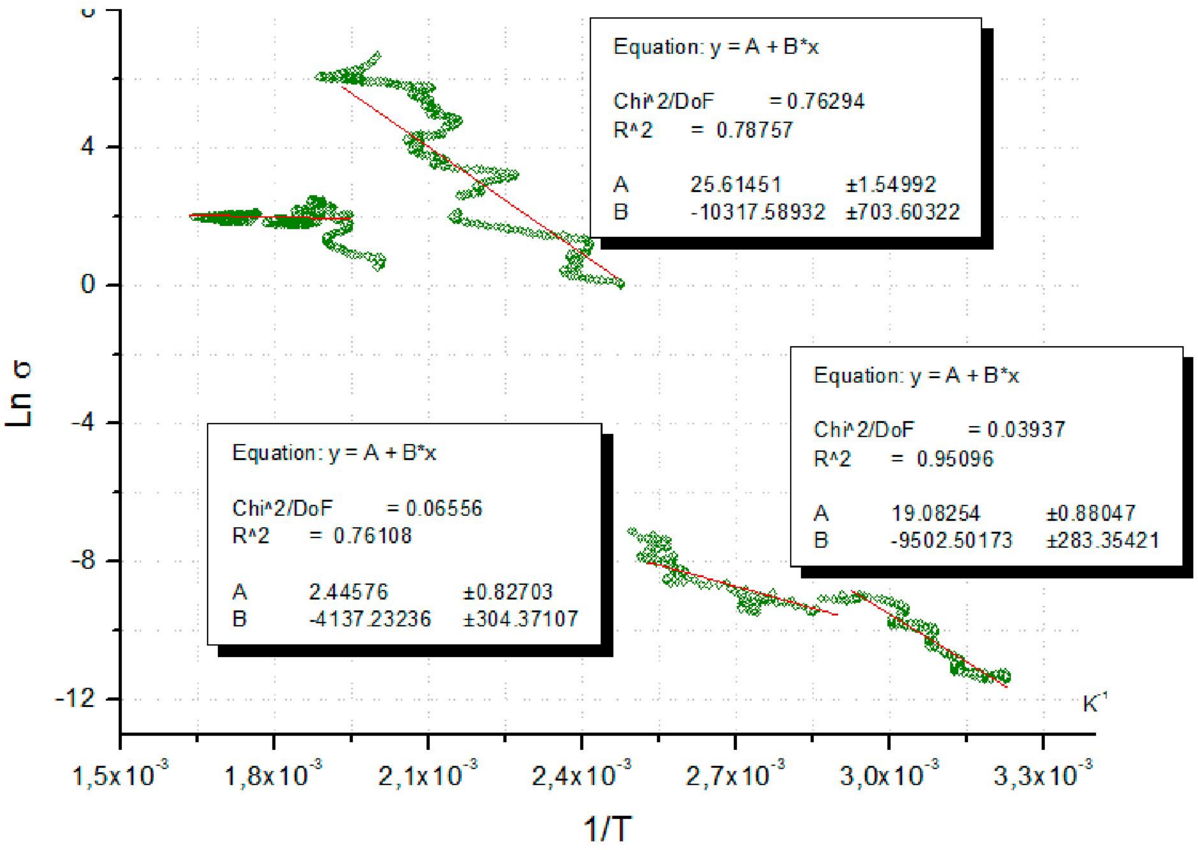
Taking into account the methods of temperature analysis of SHS materials [8] and the introduction of corrections [9], with a limited number of distinguishable signal gradations against a noise background [10], activation energies were determined from the temperature dependence of the specific electric conductivity, as shown in Fig. 2.

The obtained values of effective activation energy for the processes of intercalation in oxide bronzes:

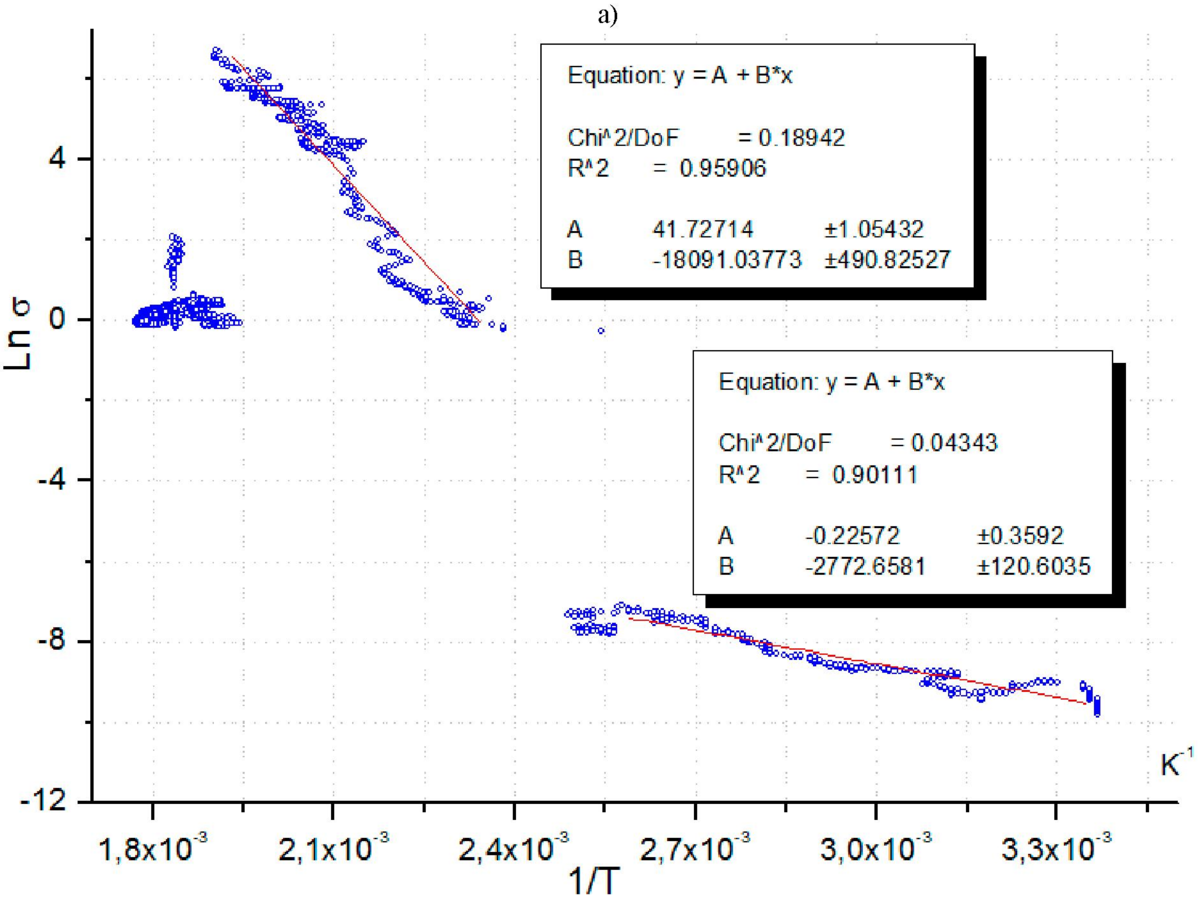
$$E_a=8,625\cdot10^{-5}eV\cdot10317=88984\cdot10^{-5}eV=0,898eV\ (Na_{0,1}WO_3); \tag{3}$$

$$E_a=8,625\cdot10^{-5}eV\cdot2772=81954\cdot10^{-5}eV=0,820eV\ (Na_{0,2}TiO_2); \tag{4}$$

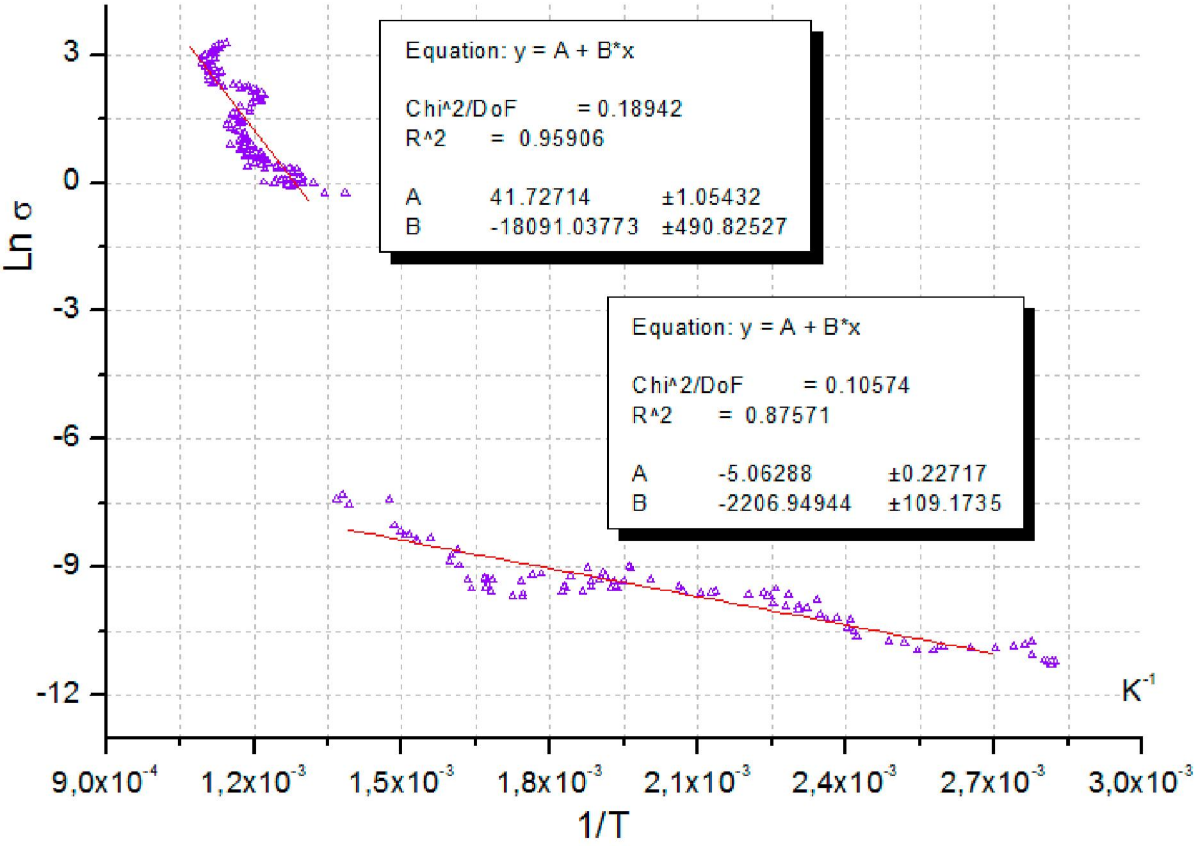
$$E_a=8,625\cdot10^{-5}eV\cdot18091=35681\cdot10^{-5}eV=0,357eV\ (K_{0,12}TiO_2). \tag{5}$$


Equation: y = A + B*x
Chi^2/DoF = 0.76294
R^2 = 0.78757
A 25.61451 ±1.54992
B -10317.58932 ±703.60322
Equation: y = A + B*x
Chi^2/DoF = 0.03937
R^2 = 0.95096
A 19.08254 ±0.88047
B -9502.50173 ±283.35421
Equation: y = A + B*x
Chi^2/DoF = 0.06556
R^2 = 0.76108
A 2.44576 ±0.82703
B -4137.23236 ±304.37107
Ln σ
4
0
-4
-8
-12
K-1
1,5x10-3
1,8x10-3
2,1x10-3
2,4x10-3
2,7x10-3
3,0x10-3
3,3x10-3
1/T

a)


Equation: y = A + B*x
Chi^2/DoF = 0.18942
R^2 = 0.95906
A 41.72714 ±1.05432
B -18091.03773 ±490.82527
Equation: y = A + B*x
Chi^2/DoF = 0.04343
R^2 = 0.90111
A -0.22572 ±0.3592
B -2772.6581 ±120.6035
Ln σ
4
0
-4
-8
-12
K-1
1,8x10-3
2,1x10-3
2,4x10-3
2,7x10-3
3,0x10-3
3,3x10-3
1/T

b)



c)

**Fig. 2** – The inverse temperature dependence of electrical conductivity:
a) $Na_{0,1}WO_3$; b) $Na_{0,2}TiO_2$; c) $K_{0,12}TiO_2$

Biofunctional material based $Na_{0.1}WO_3$ illuminated by Er-laser radiation with a wavelength of 1.3-1.5 μm [11], which corresponds to:

$$\lambda=hc/Ea;\ hc =4,1\cdot 10\text{-}15 \cdot 3\cdot 108=12,3\cdot 10\text{-}7\ eV\cdot m; \quad (6)$$

$$Ea(\lambda=1,5\mu m)=0,82eV;\ Ea(\lambda=1,3\mu m)=0,9eV. \quad (7)$$

Given the above, the thermal effect is observed due to the educated «intercalation» levels.

## Conclusions

Chemical methods, laser-chemical and SHS received a new biofunctional synthesis of nanoparticles of complex metal oxides and oxide bronzes. Nanoparticles of oxide bronzes of transition metals possess high photothermal effect of the absorption of quanta of light by nanocrystals [12]. Such nano-sized crystals of complex oxides and oxide bronzes having the properties of semiconductors with low activation energy of conductivity have a high absorption in the IR region of the spectrum. The special role of the surface in semiconductors is that it has a surface energy levels located in the bandgap (surface States); electrons and holes within those levels localized near the surface. Therefore, along with deep "intercalation" levels, should be formed near surface levels. The levels of both types detected in all samples. The energies corresponding to them can differ in 2 times.

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