Promising oxide nanomaterials with regulated electrical conductivity

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Abstract. The dependence of electrical conductivity of crystals of oxide titanium bronzes from their degree of dispersion has been studied in the work. It has been shown that the structure defect of crystalline samples increases with increasing degree of dispersion. Certain emerging defect (particularly edge dislocation) has been identified. The temperature dependence of the electrical conductivity of the nanocrystalline samples of titanium oxide of bronze has been obtained and discussed. A sharp discontinuity in conductivity at temperatures above 125 °C indicates a change in the nature of conductivity. The obtained data can be used to obtain samples of oxide bronzes with the given electrical conductivity.

1. Introduction
The so-called oxide bronzes, which are solid solutions of trapping of alkali metals in the structure of the oxide of the transition metal, are “exemplary” examples of crystals that meet the requirements of ion conductivity [1-3]. On the one hand, this connection with nonstoichiometry through atoms of alkali metal and oxygen atoms, on the other hand, are substances in the crystal structure of which there is a grid of channels providing ions with high mobility. Last years, authors are increasingly paying attention to the oxide bronze as materials for alternative energy sources [4-6]. This work is devoted to study of the effect of the degree of dispersion of samples of oxide titanium bronzes on their conductivity.

2. Experimental procedure
Synthesis of \( K_xTiO_2 \) \( (0,06<x<0,12) \) was performed according to the method [7] under the control of the XFA - X-ray fluorescence analysis, figure 1 shows x-ray diffraction of the obtained sample. Crushing of SV-synthesis products was carried out in the mill AGO-2.

![Figure 1. X-ray diffraction of the synthesis products.](image-url)
The separation of the nanoparticles was carried out by means of hydrodynamic method. For this purpose a portion of the sample weighing 2 g was placed in a vertical vessel (measuring cylinder) filled with distilled water, shaken and left for 72 hours. 100 ml of suspension was taken at the top of the vessel. Portion of the solution was subjected to analysis to determine the size of the particles, the remaining suspension was evaporated at a temperature of 100 °C and then it was dried in a drying oven at a temperature of 60 °C until complete removal of water. Control of the degree of dispersion of the particles dimensions of which exceeded 100 nm, was performed through of laser diffractograph with the apparatus LA-300 (Horiba, Japan). Figure 2 presents the diagram of particles distribution of KxTiO2.

Fused beads were prepared of individual fractions of the powders by compression at a pressure of 20 MPa, measurement for conductivity was carried out by the four-probe method for samples of each fraction. The product of synthesis was placed in a ceramic tube with titanium electrodes and a
chromel-alumel thermocouple, which was sealed at both ends to study the temperature dependence. The tube was placed in an oven and heated to a temperature of 300 ºС. Conductivity measurement was performed at a constant current (0.05-0.5 мА).

Analysis of the microstructure of the crystals was performed using high-resolution TEM (electron microscope JEM-2500SE). Both HRTEM images and digital electron diffractions obtained after data processing using the program «IMAGE» (algorithm FFT) were subjected to the analysis.

3. Results and discussion

The average sizes of the selected fractions are 100, 0.5 and 0.05 microns. The results of determining the electrical conductivity of the samples K₅TiO₃ at 25 ºC are presented in table 1.

| Sizes of particles, microns | Electrical conductivity, Ohm⁻¹sm⁻¹ |
|-----------------------------|-----------------------------------|
| 100                         | 0.012                             |
| 0.5                         | 0.046                             |
| 0.05                        | 0.069                             |

It is obvious that electrical conductivity increases with increasing degree of dispersion. Crystallographic defects greatly influence the conductivity of any oxides: cationic and anionic vacancies, grain and blocks boundaries. Due to the high degree of order of defect-free crystal, its thermodynamic probability (entropy) will tend to zero, and the free energy - to its maximum value. The authors of works [8, 9] indicate the electronic n-type of semiconductor conductivity of a large number of oxide bronzes.

We have studied the microstructure of samples of oxide titanium bronzes with different degree of dispersion. Figure 4 shows the TEM image and electron-diffraction photograph of the surface of the nanocrystals K₅TiO₃ (the average particle size is 0.05 microns). Generally, TEM image of nanocrystals K₅TiO₃ revealed their highly defective structure, although there are quite absolute areas of order with layer organization in the body of the crystals. Areas of one-dimensional order are well differentiated.

![Figure 4. TEM image (a) and electron-diffraction photograph (b) of the surface of the nanocrystals K₅TiO₃ and schemes of dislocation (c).](image-url)
The formation of an edge dislocation in the direction 321 is clearly seen in the figure. It should be noted that TEM image of larger crystals of oxide bronzes of similar composition did not reveal such highly defective structure.

Obviously, the high density of surface and other defects (defects nonstoichiometry, interstitial atoms and vacancies, dislocations) determine the nature of conductivity in nanoscale samples.

Figure 5 shows the recorded temperature dependence of the electrical conductivity of nanopowders.

![Figure 5. The temperature dependence of the electrical conductivity of nanocrystals KₓTiO₂.](image)

The electrical conductivity weakly linearly increases with increasing temperature up to 125 °C and has low values of specific electrical conductivity of 0.08 Ohm⁻¹·cm⁻¹. There is a sharp increase with increasing temperature, the dependence has an exponential character. At 300 °C, the electrical conductivity increases by an order. A sharp discontinuity in conductivity at temperatures above 125 °C, in all probability, indicates a change in the conductivity mechanism. There are few and conflicting data on the measurement and interpretation of temperature dependence of conductivity in crystals of oxide bronzes in the literature. Thus, the authors [10] in the temperature range of 130-330 K watched the two jump of conductivity (in this case at T >300 K the conductivity was metallic in nature) that was explained by the presence of two phase transitions. The data on temperature dependence of conductivity in stoichiometric single crystals of WO₃ doped with impurities of alkali metals, obtained at direct and alternating currents in the frequency range 50-10 MHz in the temperature range 130-300 K were given in [11]. The authors have explained the obtained experimental curves in terms of the transfer model via localized states near the conduction band, linking them spatially with crystallographic shear planes (it should be said that, this is a prevalent defect of minor nonstoichiometry in oxides of transition metals). The authors [12] have interpreted the temperature dependence of conductivity in amorphous films of WO₃ based on the theory of hopping conduction, and the authors of [13] are based on the theory of an activation conduction, proceeding into thermally lighter tunneling. It is important to note that oxide bronzes belong to the so-called mixed-valence compounds (some atoms of titanium in the formation of bronze remain in the highest oxidation state of +4 at titanium bronzes, part of them – restored and have a lower degree of oxidation). The presence of aliovalent cations in the crystal structure of the oxide bronze provides the ability of overleaping mechanism of electrical conductivity due to exchange of electrons between these ions.
4. Conclusion
Synthesis of titanium oxide of bronze structure $K_xTiO_2$ (0.06<x<0.12) was conducted by SHS. Milling of the obtained samples was carried out in the mill AGO-2. Separation of fractions according to particle size was carried out by hydrodynamic method, subjecting an aqueous suspension of crystals to sedimentation in a vertical vessel. Various fractions of substances differing in the degree of dispersion have been received. The minimum average size of obtained crystals was 50 nm. The dependence of electrical conductivity of crystals of titanium oxide of bronze from their degree of dispersion: the defect of structure of the crystal samples increases with increasing degree of dispersion, which leads to increase of electrical conductivity. Certain types of emerging defects (particularly edge dislocation) were identified. The temperature dependence of the electrical conductivity of the nanocrystalline samples of oxide titanium bronze has been received and discussed. Sharp discontinuity in conductivity at temperatures above 125 °C indicates a change in the nature of conductivity.

5. References
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