

Comparative Analysis of the Electrical Properties of Nanocrystalline NiMoO₄ Hydrate and α -NiMoO₄ Obtained by Hydrothermal Method

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We have investigated the impedance behavior and electrical conductivity of nanocrystalline hydrate and α -phase of nickel molybdates obtained by hydrothermal method. Frequency behavior of the real impedance part of obtained nickel molybdates points at space charge polarization under the impact of an applied electric field. The imaginary impedance component of α -NiMoO₄ substance proves the absence of relaxation in it, meaning that the transport of charge carriers between grains is possible in the whole frequency range. At the same time, we observe a temperature-dependent relaxation process for NiMoO₄ hydrate in the temperature range 175-200 °C caused by defects, namely vacancies. It has been shown that the conductivity of NiMoO₄ hydrate at a direct current is equal to $4 \cdot 10^{-5}$ S/m, whereas for NiMoO₄ α -phase it is $1.5 \cdot 10^{-4}$ S/m at room temperature due to the conditions for obtaining materials. The temperature dependencies of the frequency exponent s that we obtained make it possible to assert that the ac conductivity of NiMoO₄ hydrate can be explained on the basis of the correlated barrier hopping model, whereas of α -NiMoO₄ – by small polaron tunneling model.

Keywords: Nickel molybdate, Hydrothermal synthesis, Impedance analysis, Electrical conductivity.

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1. INTRODUCTION

At present times, a great deal of attention is being paid to multifunctional nanocrystalline materials with varied physical-chemical properties, which makes them promising for applications in electronics, environmental studies, pharmacology, medicine and many other fields of science. Nanocrystalline materials are polycrystalline materials with grain sizes up to 100 nm [1]. Due to their extremely small size, the biggest part of atoms is located at the grain boundaries. In addition, these boundaries have a very high density of defects such as vacancies, uncompensated chemical bonds, etc., which mainly determine the conductivity properties of these materials.

Nanosized mixed metal oxides, specifically molybdates, should be given more attention due to their wide applications in energy storage devices. Among molybdate combinations with the general formula MeMoO₄ (Me = Mg, Pb, Mn, Fe, Co, Ni, Zn), nickel molybdate has interesting magnetic, optical, photoluminescent, catalytic and electrochemical properties [2]. At ambient pressure, the α and β phases of nickel molybdates are present, which differ from each other in the coordination of molybdenum ions. Thus, the structural unit of α -NiMoO₄ is the octahedral group created by six oxygen atoms that surround a molybdenum atom, and of β -NiMoO₄ – the tetrahedral group created by four oxygen atoms. Ions of Ni²⁺ are in octahedral coordination in both phases [3]. There is also NiMoO₄ hydrate which is often used as the precursor for obtaining α and β phases. However, we have established in our research [4, 5] that NiMoO₄ hydrate, due to the presence of coordinated water molecules in the crystal structure, has better electrochemical activity and consequently higher capacitance features compared to the α -phase of NiMoO₄. In NiMoO₄ hydrates, the Ni²⁺ cations are also octahedral coordinated, while the Mo⁶⁺ ions are in tet-

rahedral coordination. The pure β -NiMoO₄ phase is obtained by calcination of the hydrate at 550 °C and cooling down to the temperature necessary for further work, which is always higher than 250 °C, and is a practically inefficient process [6].

A few publications in the literature are devoted to the conductive properties of nickel molybdates. Thus, it was shown in [7] that α -NiMoO₄ has two conductivity modes: in the metastable temperature range of 450-650 °C it acts as a p -type semiconductor ($E_a = 1.3$ eV), and at temperatures above 650 °C it has n -type semiconductor properties ($E_a = 1.89$ eV). It was also established in [6] that β -NiMoO₄ reaches a maximum conductivity of $4.4 \cdot 10^{-6}$ S/cm at 250 °C. NiMoO₄ hydrate conductivity features were investigated in a research work [5], where it was established that the electrical conductivity of NiMoO₄ hydrate is two sequences higher than the conductivity of nickel hydroxide.

Investigation of the electrical properties of nanocrystalline nickel molybdates is an integral part of their further use in energy storage devices. Impedance spectroscopy is a non-destructive and informative method of investigating electrical properties of nanocrystalline materials in a broad frequency range [8]. The method makes it possible to separate the contribution from electroactive grains and grain boundaries. The article investigates the electrical properties of the hydrate and α -phase of NiMoO₄ depending on the frequency and temperature by impedance spectroscopy, and also studies the conductivity mechanisms of the given materials.

2. EXPERIMENTAL

NiMoO₄ hydrate was obtained by hydrothermal method using Ni(NO₃)₂·6H₂O and Na₂MoO₄·2H₂O as precursors in equal molar ratio; α -phase was prepared

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by calcination of the hydrate material at a temperature of 400 °C within 2 h. A detailed synthesis procedure was described in [9]. It was also confirmed by Raman spectroscopy that, as a result of hydrothermal synthesis, we obtained NiMoO₄ hydrate with a triclinic system and space group $P\bar{1}$, and when it was calcined – a monoclinic α -phase with a crystal structure belonging to space group C2/m. The electrical properties were studied using an AUTOLAB PGSTAT12 measuring complex in the frequency range 10^{-2} - 10^5 Hz at a voltage of 0 V and a temperature range of 25-200 °C. The temperature range was limited to 200 °C in order to prevent the phase transition of nickel molybdates. The samples were pressed in a cylindrical mold with 14 mm in diameter and 1 mm in thickness of the material. The real part of the electrical conductivity was determined according to the formula: $\sigma = h/Z'S$, where h is the sample thickness, Z' is the real part of the resistance, S is the surface area of the sample under investigation.

3. RESULTS AND DISCUSSION

Fig. 1 shows frequency dependencies of the real and imaginary parts of the complex impedance of NiMoO₄ hydrate and α -NiMoO₄ materials within the temperature range 25-200 °C. For both samples, the value of Z' at all temperatures decreases monotonically with increasing frequency and becomes frequency-independent at a frequency greater than 10^3 Hz (Fig. 1a, c). Such behavior of the real component of the impedance is explained by the polarization of the space charge under the action of an applied electric field and, as a consequence, a decrease in the barrier properties of semiconductor materials [10].

In the spectrum of the imaginary component of the impedance of NiMoO₄ hydrate, there are peaks at temperatures of 175 and 200 °C, which shift to higher frequencies with increasing temperature (Fig. 1b). The shift and broadening of the peak suggest the existence of electrical relaxation processes. The relaxation time was defined as $\tau = \omega^{-1}$ and was 2.27 and 0.66 s at temperatures of 175 and 200 °C, respectively. The temperature-dependent relaxation process is related to the presence of immobile particles at low temperatures and defects, in particular, vacancies at higher temperatures [11], which is typical of our case. The temperature-dependent relaxation process is related to the presence of immobile particles at low temperatures and defects, in particular, vacancies at higher temperatures [11], which is typical of our case. The imaginary component of the impedance (Z'') (Fig. 1d) of α -NiMoO₄ demonstrates behavior similar to the real component. The absence of maxima indicates the absence of a relaxation phenomenon in the material, i.e., the transfer of charge carriers between grains is possible in the entire frequency range.

In general, impedance characteristics indicate the effect of grains and grain boundaries in the material. Accordingly, each component of a polycrystalline material, namely grains and grain boundaries, can be modeled by RC circuits connected in series. In the impedance spectra of this model, two semicircles correspond, indicating the existence of two different electrical conduction mechanisms in the polycrystalline material. It is known that the high-frequency region is associated with grains, while the low-frequency region is associated with grain boundaries [12].

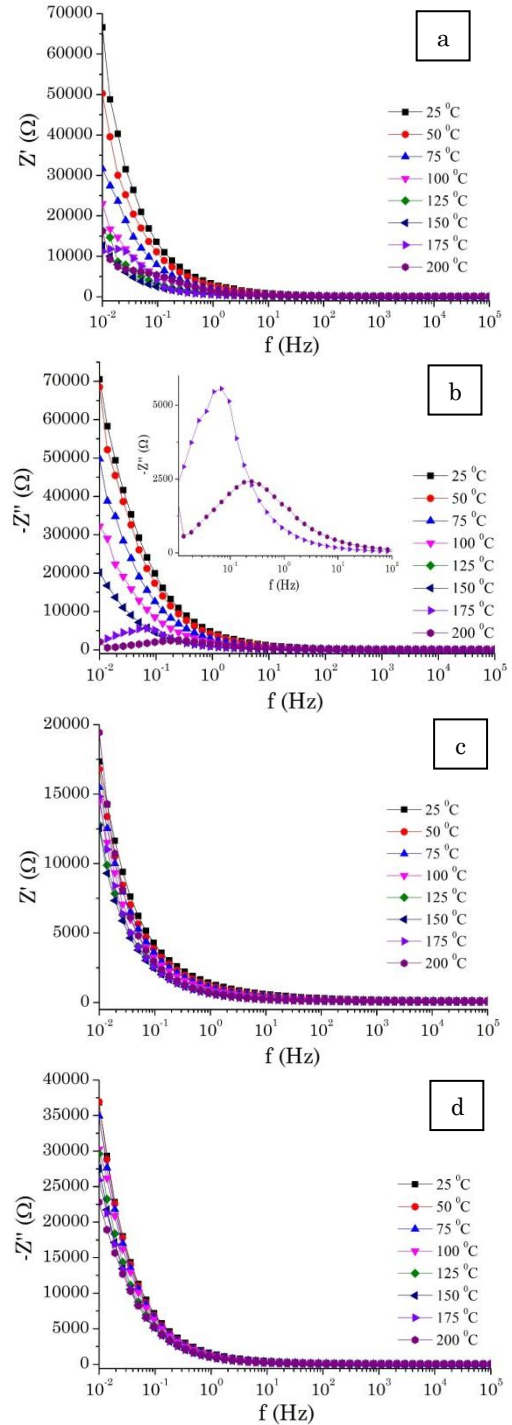


Fig. 1 – Frequency dependencies of the real (Z') and imaginary (Z'') parts of the impedance in a temperature range of 25-200 °C for NiMoO₄ hydrate (a, b) and α -NiMoO₄ (c, d)

The impedance curves of hydrothermally derived nickel molybdates form arcs of semicircles (Fig. 2) in a temperature range of 25-200 °C, which are often observed in impedance analysis of structurally disordered materials at low temperatures [13]. Accordingly, in this case it is impossible to separate the contribution of semiconducting grains in the high-frequency region and non-conducting grain boundaries in the low-frequency region to the total resistivity of the materials under study. The arc radius of semicircles decreases

with increasing temperature of both materials, which indicates the presence of an activation mechanism of conductivity and an increase in the mobility of charge carriers. When the temperature rises to 175-200 °C, the impedance curves of NiMoO₄ hydrate form a semicircle.

Temperature dependencies of the real part of the conductivity taken in the temperature range 25-200 °C and the frequency range 10⁻²-10⁵ Hz are shown in Fig. 3.

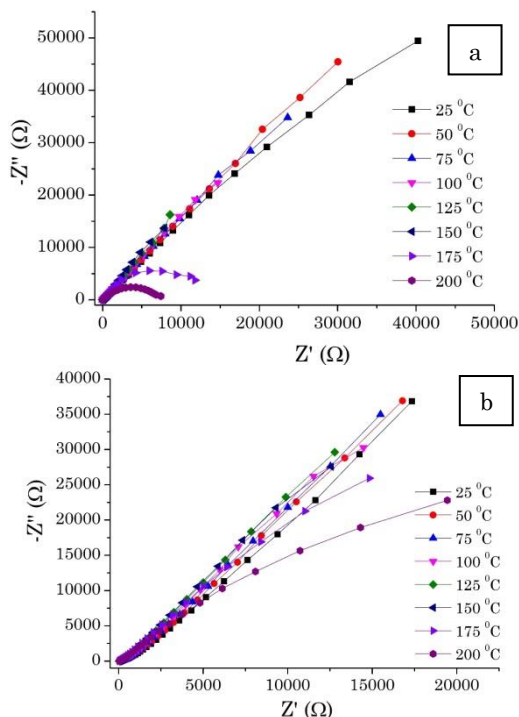


Fig. 2 – Nyquist plots of NiMoO₄ hydrate (a) and α -NiMoO₄ (b) in a temperature range of 25-200 °C

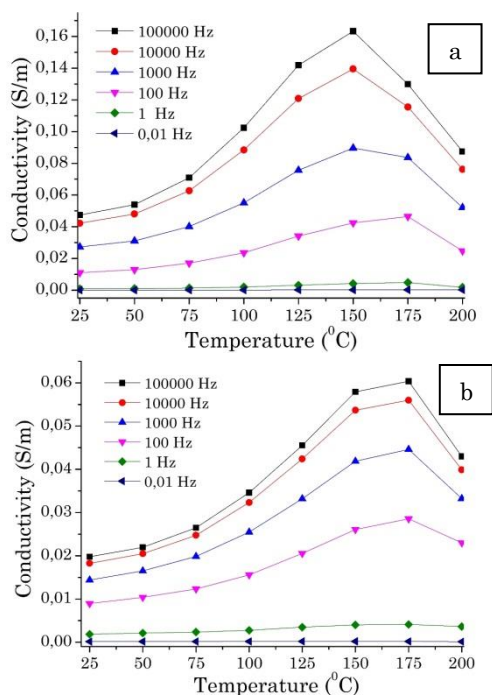


Fig. 3 – Temperature dependencies of conductivity of NiMoO₄ hydrate (a) and α -NiMoO₄ (b)

As the temperature increases, the electrical conductivity increases, which is characteristic of disordered oxide systems and their nanocomposites. However, the conductivity reaches a maximum at a certain temperature and this maximum shifts to the low-temperature region with increasing frequency. Thus, for hydrate in the frequency range 10³-10⁵ Hz, the critical temperature is 150 °C, while for α -NiMoO₄ it is 175 °C in the same frequency range. Since nickel molybdate is a mixed oxide, the presence of higher oxidation states of Ni and Mo as point defects that can occupy internode positions or replace other atoms and vacancies is quite likely. At temperatures of 175-200 °C, complete ionization of defects in the crystal structure is achieved and the density of charge carriers becomes temperature independent. The decrease in the electrical conductivity in this temperature range is probably due to the activation of the scattering mechanism of charge carriers by the atoms of the crystal lattice, resulting in a decrease in their mobility and, consequently, electrical conductivity.

Conductivity of both materials increases with frequency (Fig. 4); such behavior can be explained on the basis of Koop's model. According to this model, in the low-frequency region, the grain boundaries of nickel molybdates with high resistivity are responsible for the dc conductivity, while in the high-frequency region, the ac conductivity increase is associated with grains that are more conductive than their boundaries [14]. The conductivity plots we obtained can be divided into three regions: a low-frequency (dc conductivity (σ_{dc})) plateau, a medium-frequency dispersion mode and a high-frequency plateau (above 10³ Hz).

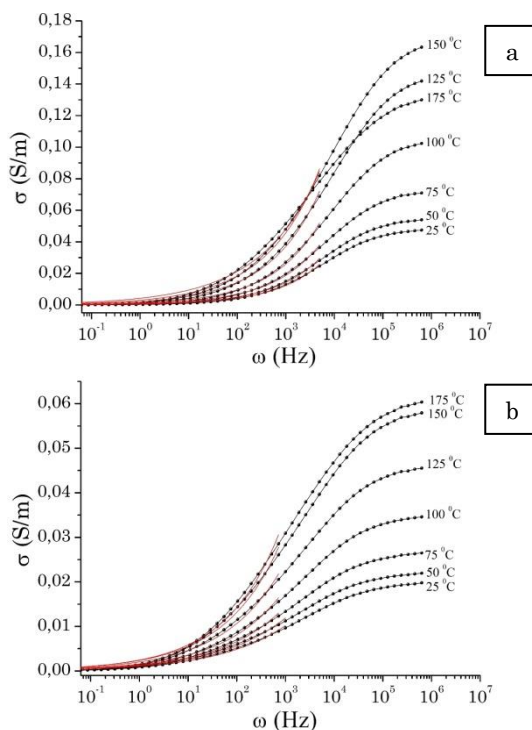


Fig. 4 – Frequency dependencies of conductivity of NiMoO₄ hydrate (a) and α -NiMoO₄ (b) at different temperatures

The *dc* conductivity (σ_{dc}) is identical to the value that can be defined as the point of intersection of the complex impedance arc in the low-frequency region

with the real axis. For NiMoO₄ hydrate, the dc conductivity is 4 · 10⁻⁵ S/m, whereas for NiMoO₄ α-phase it is 1.5 · 10⁻⁴ S/m at room temperature (Fig. 5a). With increasing temperature, there is a slight increase in the dc conductivity up to 1.6 · 10⁻⁴ S/m of NiMoO₄ hydrate, while the dc conductivity of α-NiMoO₄ (2.1 · 10⁻⁴ S/m) remains almost unchanged at 150 °C. The lower conductivity of NiMoO₄ hydrate is explained by a decrease in the mobility of charge carriers, which leads to an increase in the resistance of grain boundaries and reduces the probability of electron transfer through them.

The activation energy can be calculated using the Arrhenius equation: $\sigma = \sigma_0 \exp(-E/kT)$, where E is the activation energy, k is the Boltzmann constant, σ_0 is a constant, T is the temperature. Solid lines in Fig. 5b correspond to the linear approximation of the data. The activation energy was: $E_{dc} = 0.13$ eV for NiMoO₄ hydrate and $E_{dc} = 0.03$ eV for α-NiMoO₄. The higher activation energy of nickel molybdate hydrate as compared to the α-phase can be explained by the conditions of production. Nanocrystalline NiMoO₄ hydrate has a large number of smaller grains and, correspondingly, grain boundaries, while calcination of the hydrate to produce α-NiMoO₄ leads to agglomeration of particles and an increase in grain size. Accordingly, the surface barrier is larger for smaller crystals and, therefore, the activation energy is larger.

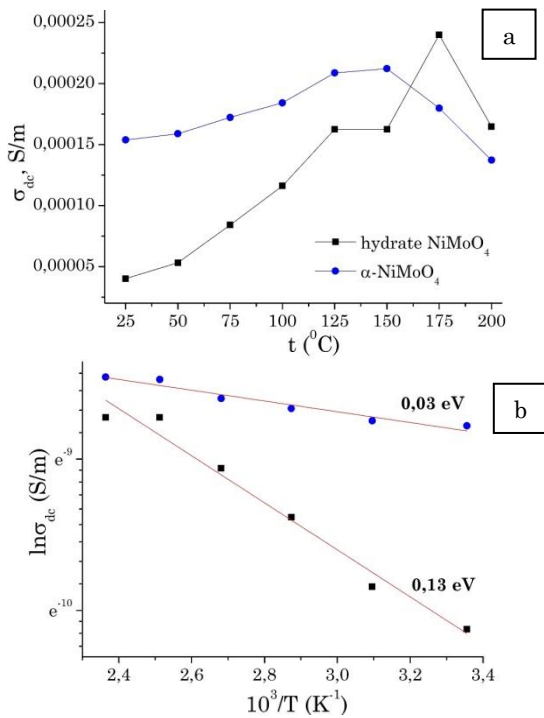


Fig. 5 – DC conductivity of NiMoO₄ hydrate and α-NiMoO₄ (a). Plots $\ln \sigma_{dc}$ versus $10^3/T$ of NiMoO₄ hydrate (black squares) and α-NiMoO₄ (blue circles) at a frequency of 0.01 Hz (b)

Conductivity plots in a frequency range of 0.01-1000 Hz (Fig. 4) are described by a power law [15]:

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^s,$$

where σ_{dc} is the frequency-independent conductivity, A is a magnitude constant that depends on temperature and determines the degree of polarization, s is the fre-

quency exponent representing the degree of interaction between mobile ions and the surrounding crystal lattice, if $s < 1$, the motion is sequential jumps over short distances, and if $s > 1$, the motion is localized [16]. Also, if the value of $s < 1$, the material is characterized by a non-Debye type of behavior.

The high-frequency region (Fig. 4) is probably associated with localized or reoriented jump motion, but these phenomena occur in the GHz frequency range [17], which cannot be investigated in our frequency range – MHz.

The behavior of the frequency exponent s on temperature can be used to determine the type of conduction mechanism. The value of the exponent s at temperatures of 25-175 °C was determined by approximating the dependencies with the Jonscher equation. The change in the exponent s for both materials with a change in temperature is presented in Fig. 6.

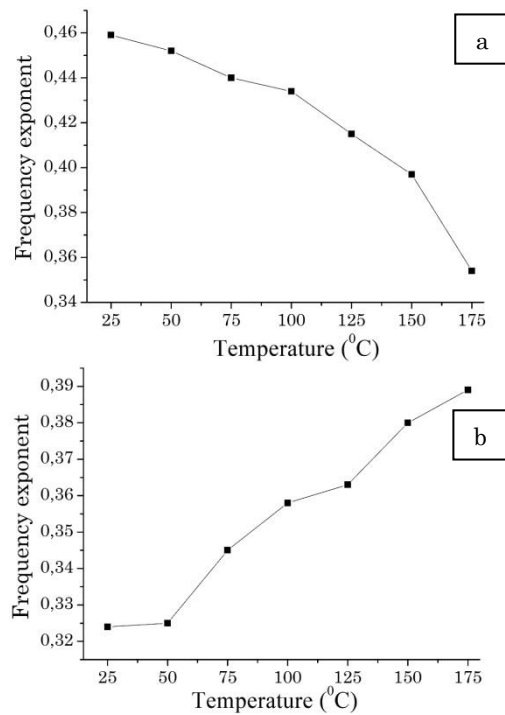


Fig. 6 – Dependencies of the frequency exponent on temperature of NiMoO₄ hydrate (a) and α-NiMoO₄ (b)

There are several theoretical models explaining conduction mechanisms [18]. For the quantum mechanical tunneling model, the frequency exponent s is equal or close to 0.8 and slightly increases with increasing temperature or is independent of temperature. The model of correlated barrier hopping involves unipolar or bipolar jumps of carriers from a series through a potential barrier separating two defect centers. According to this model, the value of s decreases with increasing temperature. This agrees well with the results obtained for NiMoO₄ hydrate. For the small polaron tunneling model, the s value increases with increasing temperature. Thus, the s value for α-NiMoO₄ corresponds to this model. In the large polaron tunneling model, the s value depends on both temperature and frequency. In addition, s decreases as the temperature rises to a minimum value at a certain temperature, and then continues to increase as the temperature rises.

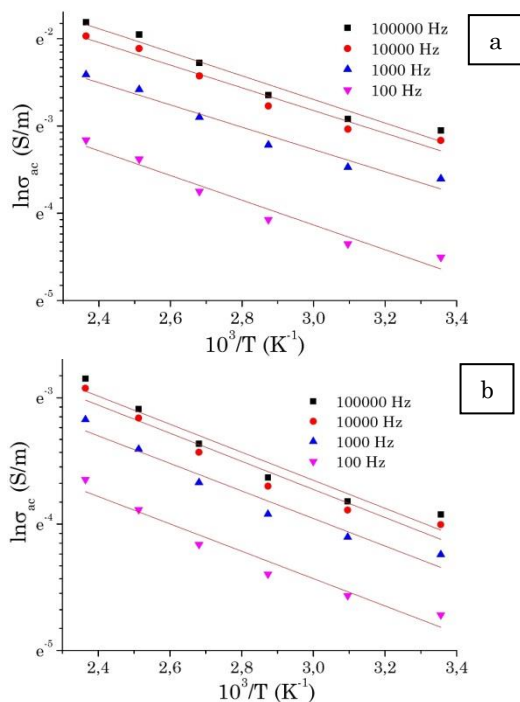


Fig. 7 – Temperature dependencies of $\ln \sigma_{ac}$ of NiMoO₄ hydrate (a) and α -NiMoO₄ (b) at different frequencies

The activation energy E_{ac} was calculated from the slope of the Arrhenius plots (Fig. 7) by approximating the experimental data with the Arrhenius relation.

The activation energy in the temperature range 25-150 °C of NiMoO₄ hydrate was 0.12 eV, whereas that of α -NiMoO₄ was 0.10 eV in the frequency range 10²-10⁵ Hz. The low activation energy of nickel molybdates is associated with defects present in the materials. In a research work [19], it was shown that for transition metal molybdates, the conductivity below the phase transition temperature (in our case, 400 °C) can

be caused by the conductivity of ionized defect centers. The activation energy of donors or acceptors is usually ~ 0.1 eV, which coincides with the values of activation energies we calculated for the hydrate and α -phase of nickel molybdate.

4. CONCLUSIONS

The real part of the impedance of NiMoO₄ hydrate and α -NiMoO₄ in the temperature range of 25-200 °C monotonically decreases with increasing frequency and becomes frequency-independent at frequencies above than 10³ Hz, which is explained by the polarization of the space charge and a decrease in the barriers between the particles of the materials studied. An analysis of the dependencies of the imaginary components of the impedance showed that in NiMoO₄ hydrate there are temperature-dependent relaxation processes. Nyquist diagrams of hydrothermally produced nickel molybdates form arcs of semicircles, which is characteristic of structurally disordered materials at low temperatures. The decrease in the electrical conductivity of NiMoO₄ hydrate and α -NiMoO₄ at temperatures above 175 °C is associated with the activation of the mechanism of scattering of charge carriers by atoms of the crystal lattice. It was found that the dc activation energy of NiMoO₄ hydrate (0.13 eV) is higher than that of α -NiMoO₄ (0.03 eV), which can be explained by the smaller grain size of the hydrate and, consequently, a larger number of grain boundaries. The temperature behavior of the frequency exponent of NiMoO₄ hydrate indicates a conduction mechanism described by the correlated barrier hopping model, while for α -NiMoO₄, the small polaron tunneling mechanism is typical.

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Порівняльний аналіз електричних властивостей нанокристалічних гідрату NiMoO_4 та $\alpha\text{-NiMoO}_4$, отриманих гідротермальним методом

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Досліджено імпедансу поведінку та електропровідність нанокристалічних гідрату та α -фази молібдатів нікелю, отриманих гідротермальним способом. Частотна поведінка дійсних складових імпедансу отриманих молібдатів нікелю вказує на поляризацію просторового заряду під дією прикладеного електричного поля. Уявна складова імпедансу матеріалу $\alpha\text{-NiMoO}_4$ свідчить про відсутність явища релаксації у ньому, тобто можливий транспорт носіїв заряду між зернами у всьому частотному діапазоні. Водночас для гідрату NiMoO_4 спостерігається температурно-залежний процес релаксації в температурному діапазоні 175-200 °С, пов'язаний з наявністю дефектів, зокрема вакансій. Показано, що електропровідність гідрату NiMoO_4 при постійному струмі становить $4 \cdot 10^{-5}$ См/м, тоді як α -фази NiMoO_4 – $1,5 \cdot 10^{-4}$ См/м при кімнатній температурі, що пов'язано з умовами отримання матеріалів. Отримані температурні залежності показника частоти дають підстави стверджувати, що провідність при змінному струмі гідрату NiMoO_4 можна пояснити на основі моделі корельованих бар'єрних перешкодок, тоді як $\alpha\text{-NiMoO}_4$ – моделлю тунелювання малих поляронів.

Ключові слова: Молібдат нікелю, Гідротермальний синтез, Імпедансний аналіз, Електропровідність.