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Synthesis and electrophysical study of cobaltites of composition $LnM^{II}CoO_{3.5}$ (M^{II} — Mg, Ca, Sr, Ba)

This work is devoted to study of electrical properties, phases of $LnM^{II}CoO_{3.5}$ (M^{II} – Mg, Ca, Sr, Ba) which structure resembles to the structure of perovskite. The phases were obtained by solid-phase synthesis in accordance with the ceramic technology. The phase composition was determined by X-ray phase analysis. The diffractograms of the powders were indexed, the lattice parameters and its symmetry class were determined. It was found that the new compounds had a tetragonal symmetry, in the unit cell of which 16 structural units were located. Since complex oxides have high melting temperatures of about 1500–2000 ºC, it is impossible to obtain good quality single crystals suitable for measurements. For this reason, the study of their thermodynamic and electrophysical properties was carried out on samples in the form of sintered powders. In this study, the conductivity isotherms were measured by impedance spectroscopy at different temperatures. Resistance hodographs on the complex plane were constructed. Using the method of equivalent circuits, the grain boundaries and the bulk resistances of the sample grains were determined. The results showed that the new compounds had a small grain-boundary resistance. Using the temperature dependences, the activation energies of the conductivity of new cobaltites were calculated. The activation energy of conductivity for these compounds was 0.113–0.184 eV. The character of the dependence of the conductivity at moderate temperatures showed their thermal activation. In the Arrhenius coordinates, these sections of the graph were described by a straight line. An increase in the activation energy of the conductivity in the series of Mg^{2+}–Ca^{2+}–Sr^{2+}–Ba^{2+}cations was observed. The introduction of an alkaline earth ion with a large ionic radius led to a local distortion of the crystal lattice. This changed the value of the splitting of the d-levels of the transition metal-cobalt. This change in the activation energy as the alkaline earth metal cation changes can be explained by the change in the width of the forbidden band. Also, the replacement of rare-earth elements ions with alkaline-earth metal ions led to a structural disorder, to an increase in the formation of equilibrium charged point defects in the crystal structure, in which the strength of the bond with trapped charge carriers by electrons or holes in point defects in the crystal lattice with different alkaline-earth ions was different.

Keywords: solid-phase synthesis, rare-earth and alkali metals cobaltites, thermal dependence of electrical conductivity, complex oxides, impedance spectroscopy, Bode plots, conduction activation energy, conductivity isotherms.

Introduction

At present, electrochemical devices operating at elevated (> 30 ºC) and high (> 100 ºC) temperatures are beginning to be used in industry: solid electrolyte fuel cells, oxygen sensors, electrolyzers for oxygen production, oxygen pumps, etc. However, good materials for oxygen electrodes and switching elements capable of replacing metals, which are now used in these devices. These materials must be stable in highly oxidative and in some cases reducing media should have sufficient electrical conductivity. The latter should provide small ohmic losses at the electrodes and electrode-solid electrolyte contact, which should not change during long time operation. One of the promising materials for electrochemical elements operating at high temperatures is complex oxides of transition and rare-earth elements of the type ABO_3 with a perovskite structure or close to it [1–3].

The purpose of this work is the synthesis, radiographic and electrophysical study of complex cobaltites of alkaline earth and rare earth metals of composition $LnM^{II}CoO_{3.5}$, where M^{II} are alkaline earth metals (M^{II} — Mg, Ca, Sr, Ba), which have promising electrophysical properties (semiconductor, ferroelectric, magnetic, superconducting, etc.).

Synthesis of compounds was carried out by solid-phase annealing in three stages at different temperatures. The initial components for the synthesis were lanthanum oxide of«puriss. spec.» grade, cobalt oxide (II) of «puriss.» grade and carbonates of alkaline earth metals of «puriss.» grade. The weights of the initial substances were weighed to the fourth decimal place. Their calculation was carried out in terms of specific final compositions of complex cobaltites. The mixtures of reagents were thoroughly rubbed in an agate mortar, and then they were quantitated into alundum crucibles for annealing in a selitic furnace. The synthesis was carried out as follows: the 1st stage — 10 hours, at 800 ºC, the 2nd stage at 1300 ºC — 10 hours with periodic grinding in a mortar; An annealing was carried out at 400 ºC for 20 hours in order to obtain stable compounds under normal conditions.

In order to control the phase composition of the synthesis products, X-ray studies were carried out on a MiniFlex-400 diffractometer in Cu $K_{\alpha 1}$ radiation at a voltage of 40 kV and a current of 40 mA. The survey was conducted in the interval $2\theta = 20^\circ–80^\circ$ in steps of 0.05º and exposure of 1 sec. to the point. To determine the phase composition at the synthesis stage, a set of specialized programs applied to the instrument for preliminary processing of experimental data was used. Performed phase analysis reveals the absence of initial reagents in the sample and the crystallinity of the reaction product. The diffraction patterns were detected and the unit cell parameters were determined by means of programs and checked by good agreement between the experimental and calculated values of $10^4/d^2$. Further, according to XRF data, types of syngony were determined, and parameters of the elementary cells of the cobaltites were studied. Their values are given in Table 1 below.

Table 1

Crystallochemical characteristics of synthesized compounds

Compound	Type of the system	Lattice parameters, Å		V^o, $Å^3$	$V^o_{unit\ cell}$, $Å^3$	Z
		A	c			
$LaMgCoO_{3.5}$	Tetragon.	10.77	16.25	1884.88	117.80	16
$LaCaCoO_{3.5}$	Tetragon.	10.86	16.75	1975.49	123.47	16
$LaBaCoO_{3.5}$	Tetragon.	10.89	17.10	2027.93	126.75	16
$LaSrCoO_{3.5}$	Tetragon.	10.81	16.92	1977.21	123.58	16

Experimental part

Tablets were obtained from the previously obtained solid-phase synthesis of powders on a hand press at a pressure of 20 kg/cm^2. As a plasticizer, a solution of natural rubber in toluene was used. The resulting disks were annealed in a muffle furnace at 1100 ºC for 6 hours. In order to make it sufficient for the experiment, the samples were held for 8 hours at a temperature of 600 ºC. Further, a thorough two-sided grinding was carried out. Platinum electrodes were applied to the ground surface of the sintered samples. For the preparation of platinum electrodes, finely dispersed platinum paste was used, mixed with an alcohol solution of rosin. The roasting of the electrodes was carried out in air at a temperature of 1100 for 1–1.5 hours.

Using the method of electrochemical impedance in the frequency range from 10 Hz to 1 MHz in a 2-contact cell, the temperature dependence of the electrical conductivity of the samples was investigated. The relative error in measuring the components of the impedance is in the range 0.3–0.5 %. Conductivity measurements were carried out in the temperature range 40–800 ºC. The shooting was carried out in the cooling mode. To measure the polytherm of the total conductivity, a dynamic mode with a cooling rate of 1.5 ºC/min was used. The study of the isotherms was carried out in a static mode with a step of 10–20 ºC and shutter speeds at each point before the onset of equilibrium. In the course of the experiment, the furnace temperature was set by the Varta TP403 temperature regulator. The temperature control near the sample was carried out using a platinum-rhodium-platinum thermocouple TPP-10. Figure 1 shows the hodographs of $LaMgCoO_{3.5}$ samples taken at different temperatures.

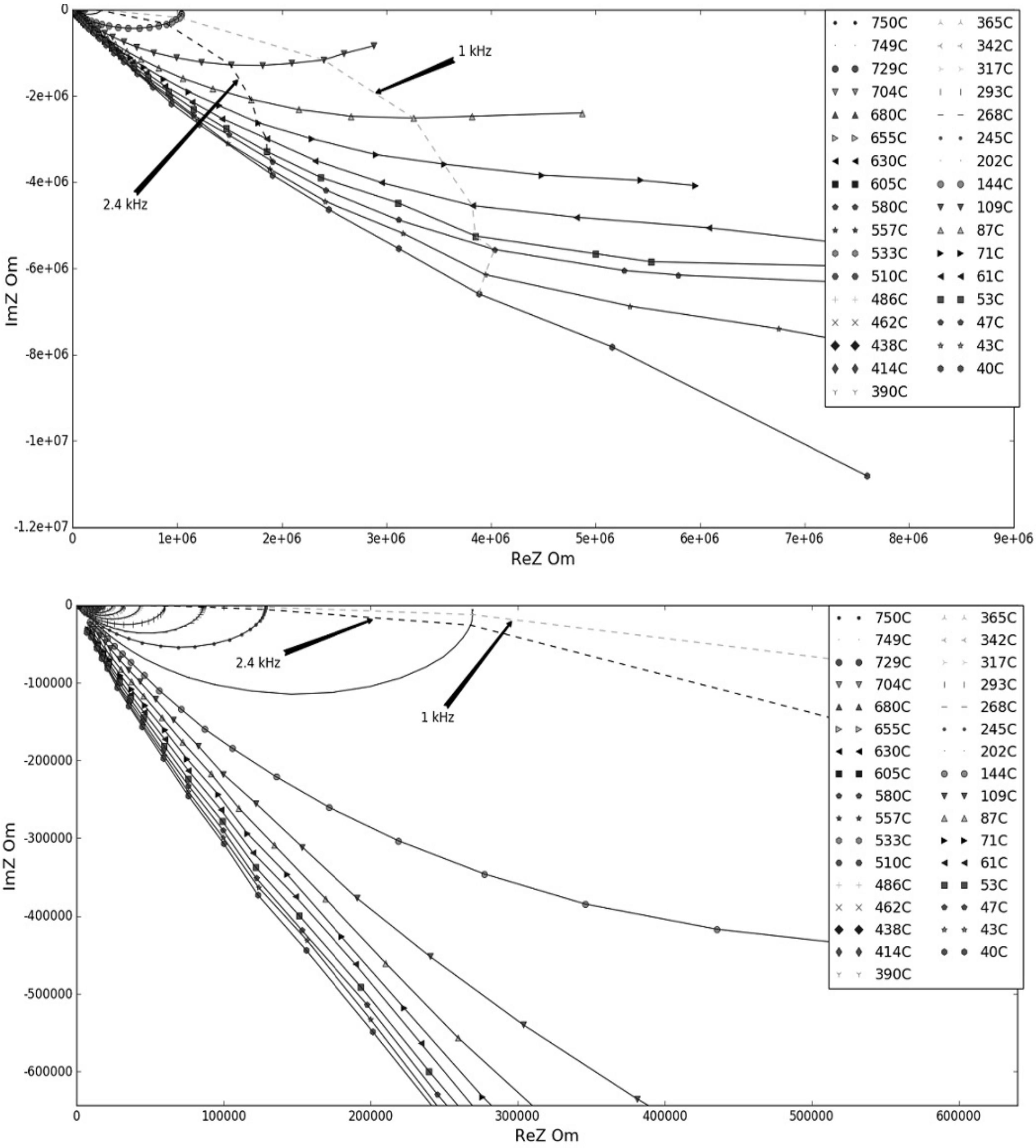

Figure 1. Hodographs sample $LaMgCoO_{3.5}$ obtained at different temperatures 40–750 ºC in different scales

The processing of data obtained in alternating current experiments is performed by representing them in the complex plane (the hodograph method) in coordinates. The imaginary part (for example, Im Z) is the real part (ReZ). The dotted line connects the points that correspond to measurements at a frequency of 1 kHz, 2.4 kHz.

To refine the study of the electrical characteristics of the samples, another installation has been assembled to study the temperature dependence of the electrical complex conductivity in a two-electrode method.

The furnace consists of a working chamber formed by a lining of a layer of refractory bricks, heaters and a thermal insulation layer insulated from the metal casing. The parts operating in the furnace chamber were made of heat-resistant materials. To measure the temperature, a chromel-alumel thermocouple was used with a TPM202 measuring regulator, which was connected to the computer by dint of interface converter (RS485 –> RS232) of the AC-3-M24. To exchange data and control signals between the regulator and the computer was carried out according to the protocol of the firm «Owen». The limit of the basic permissible reduced error of TPM202 during the temperature measurement by the chromel-alumel thermocouple according to the converter meter documentation was 0.5 %.

The complex resistance was measured with the help of the RLC meter E7–21 by the voltmeter-ammeter method with an alternating current at a frequency of 1 kHz, in which the operating frequency voltage from the generator is applied to the measured object connected to the converter Y (conductivity) –> UT, UH. The converter generates two voltages, one of which (UT) is proportional to the current flowing through the measured object, the other (UH) is the voltage on it. The ratio of these voltages is equal to the complex conductivity (Y) or complex resistance (Z) of the object. The measurements were averaged over 10 measuring cycles. The heating rate of the sample is 5°/min.

Figure 2 shows the temperature dependence of the conductivity of cobaltite samples.

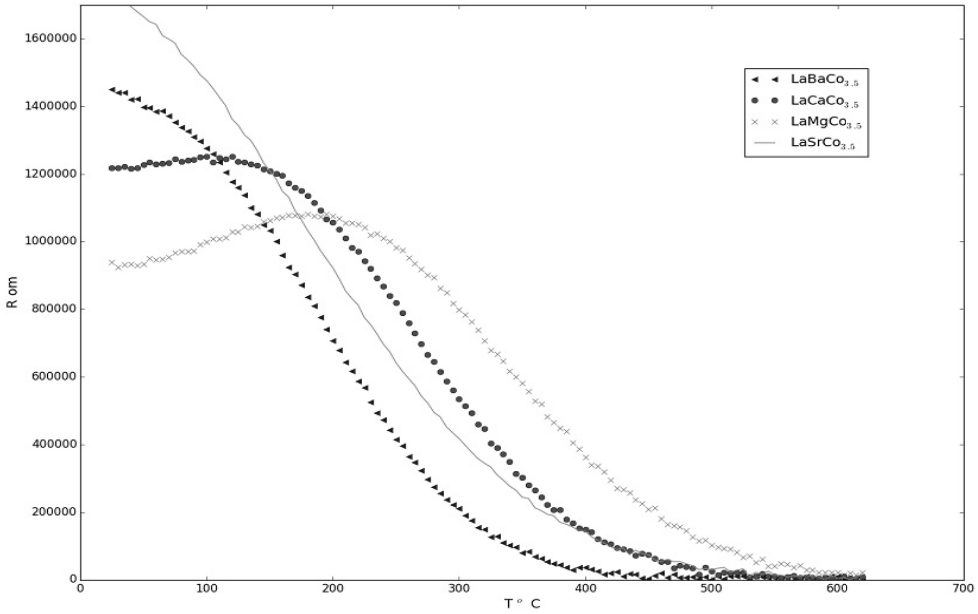

Figure 2. The dependence of the electrical resistance of $LaM^{II}CoO_{3.5}$ samples, where (M^{II} — Mg, Ca, Sr, Ba) on the temperature

Specific resistance of the sample was determined by the formula (1):

$$\rho = \frac{R \cdot S}{l}, \tag{1}$$

where R — is the resistance of the sample; S — is the cross-sectional area of the sample; l — is the length of the sample.

The specific conductivity of the sample δwas determined from formula:

$$\delta = \frac{1}{\rho}. \tag{2}$$

Results and Discussion

It can be seen from the graphs that at low frequencies at room temperatures the travel time curves represent inclined straight lines or arcs of circles of large radius, at high frequencies at high temperatures of the semicircle. The curves of the resistance versus temperature at 1 kHz show a sharp decrease in resistance. In the experiments we used electrochemical cells with blocking platinum electrodes. The equivalent circuitry of the cell corresponding to high temperatures can be represented by a series connection of resistances and the presence of a capacitance. Also the kind of impedance shows a significant contribution of electronic conductivity at high temperatures. At low temperatures, the effect of the capacitance of the double electrode/sample layer and the weak electronic conductivity is manifested. The activation energy of electrical conductivity was calculated from the slope of the dependence of lnσ on the reciprocal temperature. The activation energies of conductivity for new compounds are determined using the obtained data and the values of activation energies are given in Table 2.

Table 2

Energy of activation of high-temperature electrical conductivity of cobaltites

Compound	The activation energy of conductivity, eV
$LaMgCoO_{3.5}$	0.113
$LaCaCoO_{3.5}$	0.147
$LaSrCoO_{3.5}$	0.169
$LaBaCoO_{3.5}$	0.184

The character of the dependence of the conductivity at moderate temperatures shows their thermal activation, in the Arrhenius coordinates these sections of the graph are described by a straight line. An increase in the activation energy of the conductivity in the series of Mg^{2+}–Ca^{2+}–Sr^{2+}–Ba^{2+} cations was observed. The introduction of an alkaline earth ion with a large ionic radius led to a local distortion of the crystal lattice. This changed the value of the splitting of the *d*-levels of the transition metal-cobalt. This change in the activation energy as the alkaline earth metal cation changes can be explained by the change in the width of the forbidden band. Also, the replacement of rare-earth elements ions with alkaline-earth metal ions led to a structural disorder, to an increase in the formation of equilibrium charged point defects in the crystal structure, in which the strength of the bond with trapped charge carriers by electrons or holes in point defects in the crystal lattice with different alkaline-earth ions was different.

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$LnM^{II}CoO_{3.5}$ (M^{II} — Mg, Ca, Sr, Ba) құрамды кобальтиттерін синтездеу және электрфизикалық зерттеу

Мақала құрылысы перовскиттің құрылысына ұқсас $LnM^{II}CoO_{3.5}$ (M^{II} — Mg, Ca, Sr, Ba) қосылыстары фазаларының электрлік қасиеттерін зерттеуге арналған. Фазалар керамикалық технологиялар бойынша қатты фазалық синтездеу әдісімен алынды. Фазалық құрам рентгенфазалық талдау әдісімен анықталды, ұнтақтардың дифрактограммаларын индицирлеу жүргізілді, кристалдық тордың параметрлері және симметрия класы анықталды. Жаңа қосылыстар тетрагоналды симметрияға ие, элементарлы ұяшықтарында 16 құрылымдық бірліктер орналасқандығы анықталды. Күрделі оксидтер шамамен 1500–2000 ºС жоғары балқу температурасына ие болғандықтан, өлшеулер жүргізуге болатын сапасы жақсы монокристалдар алу мүмкін емес. Сондықтан олардың термодинамикалық және электрфизикалық қасиеттерін зерттеу күйдірілген ұнтақтар түріндегі үлгілермен жүргізіледі. Берілген жұмыста өткізгіштіктің изотермалары әртүрлі температураларда импедансты спектроскопия әдісімен өлшенді. Кешенді жазықтықта кедергінің годографтары салынды. Эквивалентті нұсқалар әдісін пайдаланып, үлгі дәндерінің дәндішекаралық және көлемдік кедергілері анықталды. Нәтижелер жаңа қосылыстар төмен дәндішекаралық кедергіге ие екендігін көрсетті. Температуралық тәуелділік нәтижелерін пайдалана отырып, жаңа кобальтиттердің өткізгіштіктерінің активтену энергиялары есептелінді. Берілген қосылыстар үшін өткізгіштіктің активтену энергиялары 0,113–0,184 eV тең. Орта температураларда өткізгіштіктің тәуелділік сипаттамалары олардың термиялық активтенуін көрсетті, Аррениус координаттарында графиктің бұл аймақтары тік сызықпен сипатталды. Mg^{2+}–Ca^{2+}–Sr^{2+}–Ba^{2+} катиондары қатарында өткізгіштіктің активтену энергиясының жоғарылауы байқалады. Иондық радиусы үлкен сілтілікжер ионын енгізу кристалдық тордың жергілікті қисаюына себеп болды. Бұл ауыспалы металл — кобальттің *d*-деңгейінің ыдырау мәнін өзгертеді. Сілтілікжер металл катионы өзгерген сайын активтену энергиясының байқалған өзгерістерін тыйым салынған аймақтың жалпақтығымен түсіндіруге болады. СЖЭ иондарын сілтілікжер металдарының иондарымен ауыстыру құрылымдық ретсіздікке әкеледі, кристалдық құрылыста тепе-теңдіктегі нүктелік бұзылымның пайда болуының артуына себеп болады, олардағы кристалдық тордағы нүктелік бұзылымдарда электрондар мен тесіктердің зарядты тасымалдаушыларды ұстап алу байланыстардың беріктігі әртүрлі сілтілікжер иондары үшін әртүрлі.

Кілт сөздер: қатты фазалық синтез, сирекжер және сілтілік металдардың кобальтиттері, электрөткізгіштіктің термиялық тәуелділігі, күрделі оксидтер, импедансты спектроскопия, Боде диаграммалары, өткізгіштіктің активтену энергиясы, өткізгіштік изотермалары.

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Синтез и электрофизические исследования кобальтитов состава $LnM^{II}CoO_{3.5}$ (M^{II} — Mg, Ca, Sr, Ba)

Статья посвящена изучению электрических свойств фаз $LnM^{II}CoO_{3.5}$ (M^{II} — Mg, Ca, Sr, Ba), имеющих структуру, близкую к структуре перовскита. Фазы были получены методом твердофазного синтеза в соответствии с керамической технологией. Фазовый состав был определен методом рентгенофазового анализа, проведено индицирование дифрактограммы порошков, определены параметры решетки и ее класс симметрии. Обнаружено, что новые соединения имеют тетрагональную симметрию, в элементарной ячейке которой расположены 16 структурных единиц. Так как сложные оксиды обладают высокими температурами плавления порядка 1500–2000 ºС, монокристаллы хорошего качества, пригодные для проведения измерений, получить невозможно. Поэтому изучение их термодинамических и электрофизических свойств проводят на образцах в виде спеченных порошков. В данной работе проведены измерения изотерм проводимости методом импедансной спектроскопии при разных температурах. Построены годографы сопротивлений на комплексной плоскости. Используя метод эквивалентных схем, определены зернограничные и объемные сопротивления зерен образца. Результаты показали, что новые соединения имеют малое зернограничное сопротивление. Используя температурные зависимости, вычислены энергии активации проводимости новых кобальтитов. Энергия активации проводимости для данных соединений составляет 0,113–0,184 eV. Характер зависимости проводимости при средних температурах показывает их термическую активацию, в координатах Аррениуса эти участки графика описываются прямой линией. Наблюдается увеличение энергии активации проводимости в ряду катионов Mg^{2+}–Ca^{2+}–Sr^{2+}–Ba^{2+}. Введение щелочноземельного иона с большим ионным радиусом приводит к локальному искажению кристаллической решетки. Это меняет величину расщепления *d*-уровней переходного металла — кобальта. Наблюдаемое изменение энергии активации по мере изменения катиона щелочноземельного металла можно объяснить изменением ширины запрещенной зоны. Также замещение ионов РЗЭ ионами щелочноземельных металлов приводит к структурной неупорядоченности, к увеличению образования в кристаллической структуре равновесных заряженных точечных дефектов, в которых прочность связи с захваченными носителями заряда электронами или дырками у точечных дефектов в кристаллической решетке с разными щелочноземельными ионами различна.

Ключевые слова: твердофазный синтез, кобальтиты редкоземельных и щелочных металлов, термическая зависимость электрической проводимости, сложные оксиды, импедансная спектроскопия, диаграммы Боде, энергия активации проводимости, изотермы проводимости.

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