DOI 10.31489/2019Ch2/69-75

UDC 546.244:65:46:74:541.11+537.226

K.T. Rustembekov, M.S. Kasymova, Ye.V. Minayeva, A.Zh. Bekturganova

Ye.A. Buketov Karaganda State University, Kazakhstan
(E-mail: rustembekov_kt@mail.ru)

Lanthanum-magnesium-nickel tellurite: thermodynamic and electrophysical characteristics

Lanthanum-magnesium-nickel tellurite with composition of $La_2MgNiTeO_7$ was synthesized from La_2O_3, NiO, TeO_2 oxides and $MgCO_3$ with the help of the ceramic technology. The temperature dependences of the isobaric heat capacity of tellurite $La_2MgNiTeO_7$ were studied on an IT-S-400 calorimeter using an experimental method of dynamic calorimetry in the range of 298.15–673 K. The operation of the calorimeter was checked by measuring the standard heat capacity of α-Al_2O_3. The specific heat capacities were measured, and then the molar heat capacities of the synthesized tellurite were calculated using them. In the study of the dependence of the heat capacity of tellurite $La_2MgNiTeO_7$ on temperature at 423 K, a sharp anomalous λ-shaped jump was found, probably related to a second-order phase transition. This transition can be associated with cationic redistribution, changes in the coefficient of thermal expansion and magnetic moment, as well as changes in dielectric constant and electrical resistivity. The equation of the temperature dependence of the heat capacity of the compound is derived on the basis of the experimental data, taking into account the phase transition temperature of the second kind. The temperature dependences of the heat capacity C_p^0(T) and thermodynamic functions, namely, the entropy $S^0(T)$, the enthalpy $H^0(T) - H^0(298.15)$ and the reduced thermodynamic potential $\Phi^{xx}(T)$ were calculated based on the experimental data on heat capacities and the calculated standard entropy value $S^0(298.15)$ in the interval 298.15–673 K. For the first time, the temperature dependences of the dielectric constant and electrical resistance of tellurite $La_2MgNiTeO_7$ in the temperature range of 293–483 K were studied on the LCR-800 instrument. There are maxima and minima on the curves of lgƐ~*f*(*T*) and lgR~*f*(*T*), which confirm the λ-shaped effect on the C_p^0~*f*(*T*) curve of a successful compound, related to the second-order phase transition. The data obtained show that the tellurite studied has semiconductor properties.

Keywords: lanthanum-magnesium-nickel tellurite, heat capacity, thermodynamic functions, dielectric constant, electrical resistance.

The study of complex oxides of 3*d*- and 4*f*-elements with a perovskite structure is important for inorganic materials science [1]. In this regard, the purpose of this work is to study the thermodynamic and electrophysical characteristics of new lanthanum-magnesium-nickel tellurite $La_2MgNiTeO_7$. Ceramic technology was used to synthesize lanthanum-magnesium-nickel $La_2MgNiTeO_7$ tellurite from oxides La_2O_3, NiO («high pure»), TeO_2 («reagent grade») and carbonate $MgCO_3$ («reagent grade»). The method of synthesis and X-ray study of this compound are described in detail in our previous work [2]. The proposed structure of the synthesized tellurite is perovskite with the space group P_m3_m.

The isobaric heat capacity of $La_2MgNiTeO_7$ was studied by dynamic calorimetry on an IT-C-400 instrument in the temperature range 298.15–673 K. The operation of the calorimeter was checked by measuring the standard heat capacity of α-Al_2O_3. The value of C_p(298.15) α-Al_2O_3 found experimentally was 76.0 J/(mol K), which fully satisfies the reference value (79 J/(mol K)) [3]. At each temperature, the estimation of standard deviation ($\bar{\delta}$) was carried out for the averaged values of specific heat capacity, and the random error component ($\bar{\delta}$) [4] was calculated for the molar heat capacity. The measurement errors of the heat capacity at all temperatures are within the accuracy of the instrument (± 10 %) [5]. The specific heat capacities of tellurite were studied, then its molar heat capacities were calculated from the experimental values obtained [6]. The experimental values of the heat capacity of the tellurite under study are listed in Table 1.

When studying the dependence of the heat capacity of $La_2MgNiTeO_7$ tellurite on temperature at 423 K, a sharp anomalous λ-shaped jump (Fig. 1) was found, probably related to a second-order phase transition. This transition can be associated with cationic redistribution, changes in the coefficient of thermal expansion and magnetic moment, as well as changes in dielectric constant and electrical resistivity.

Table 1

Experimental values of the heat capacities of $La_2MgNiTeO_7$

T, K	$C_p \pm \bar{\delta}$, J/(g K)	$C_p^0 \pm \overset{0}{\Delta}$, J/(mol K)
298.15	0.5337±0.0124	332±21
323	0.5562±0.0173	334±29
348	0.6225±0.0155	374±26
373	0.7365±0.0201	442±34
398	0.8892±0.2277	534±38
423	1.0677±0.0100	641±17
448	1.0231±0.0119	614±20
473	0.9651±0.0266	580±44
498	0.8953±0.0248	538±41
523	0.8070±0.0134	485±22
548	0.7252±0.0189	435±32
573	0.7813±0.0177	469±30
598	0.8532±0.0145	512±24
623	0.9263±0.0191	556±32
648	1.0213±0.0111	613±19
673	1.1270±0.0291	677±49

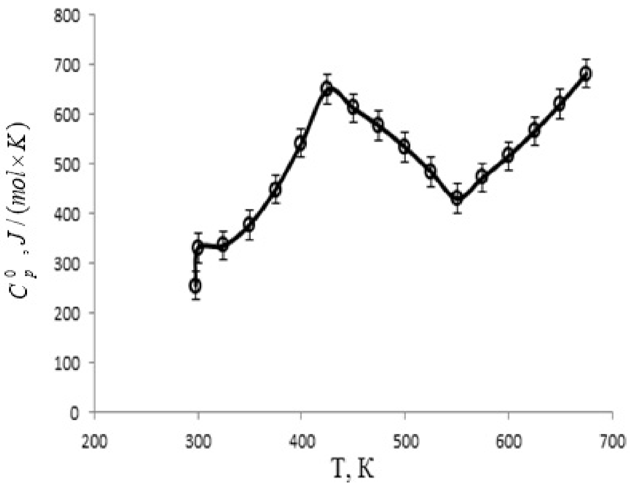

Figure 1. Temperature dependence of the heat capacity of $La_2MgNiTeO_7$

The equation of the temperature dependence of the heat capacity of the compound is derived On the basis of experimental data (Table 1), taking into account the temperature of a phase transition of the second kind,

$$C_p^0, \text{J/(mol×K)} = a + bT + cT^{-2}, \quad (1)$$

coefficients are given in Table 2.

Table 2

The coefficients of equation (1) in the range of 298.15 — 673 K

ΔT, K	a	$b\times10^3$	$c\times10^{-5}$
298–423	–(3174±191)	7542.7±454.8	1118.15±67.43
423–548	2643±159	–(3428.5±206.7)	–(986.92±59.51)
548–673	–(2534±153)	4010.5±241.8	2317.69±139.76

We used the mean random error values for the temperature ranges under consideration to determine the error of the coefficients in the $C_p^0 \sim f(T)$ dependency equations.

The temperature dependences of the functions $S^0(T)$, $H^0(T) - H^0(298.15)$ and $\Phi^{xx}(T)$ have been calculated based on the known relations [6], using the experimental data on $C_p^0 \sim f(T)$ and the calculated value

S^0(298.15). The results are shown in Table 3. Due to the fact that the technical characteristics of the device do not directly calculate the standard entropy of S^0(298.15) tellurite from experimental data on $C_p^0(T)$, it was estimated using the ion increment method [7].

Table 3

Thermodynamic functions of tellurite $La_2MgNiTeO_7$ in the range of 298.15 — 673 K

T, K	$C_p^0(T)\pm\mathring{\Delta}$, J/(mol × K)	$S^0(T)\pm\mathring{\Delta}$, J/(mol×K)	$H^\circ(T)-H^\circ(298.15)\pm\mathring{\Delta}$, J/mol	$\Phi^{xx}(T)\pm\overset{0}{\Delta}$, J/(mol×K)
298.15	255±15	251±8	–	251±8
300	331±20	253±23	660±40	251±23
325	336±20	279±25	8900±540	252±23
350	378±23	306±28	17760±1070	255±23
375	449±27	334±30	28050±1690	259±23
400	542±33	366±33	40390±2440	265±24
425	650±39	402±36	55260±3330	272±25
450	613±37	438±40	70930±4280	280±25
475	577±35	470±42	85820±5180	289±26
500	534±32	498±45	99720±6010	299±27
525	485±29	523±47	112460±6780	309±28
550	431±26	545±49	123920±7470	319±29
575	473±29	565±51	135290±8160	330±30
600	516±31	586±53	147630±8900	340±31
625	566±34	608±55	161140±9720	350±32
650	621±38	631±57	175970±10610	360±33
675	682±41	656±59	192240±11590	371±34

The average random components and errors were estimated for all values of heat capacity and enthalpy over the entire temperature range, and the accuracy of entropy calculation (± 3 %) was included in the error estimate for the values of entropy and reduced thermodynamic potential. The presence of a phase transition of the second kind on the plot of $C_p^0\sim f(T)$ for the tellurite under study suggests that this compound may have unique electrophysical properties.

In this connection, the temperature dependences of the dielectric constant and electrical resistance of tellurium $La_2MgNiTeO_7$ in the temperature range 293–483 K were investigated. The study of electrophysical properties was carried out by measuring the electrical capacitance of samples on an LCR-800 instrument (Taiwan) at a working frequency of 1 kHz continuously in dry air in a thermostat mode with an exposure time at each fixed temperature.

Previously, plane-parallel samples were made in the form of discs with a diameter of 10 mm and a thickness of 1–5 mm with a binding additive (~1.5 %). Pressing was carried out under a pressure of 20 kg/cm^2. The resulting discs were fired in a silica oven at 1000 for 6 hours.

The samples were kept for 8 hours at a temperature of 600 ºC in order to impart sufficient strength for the experiment they were thoroughly double-sided polished. The two-electrode system is applied; the electrodes are applied by firing silver paste.

The dielectric constant was determined from the electrical capacity of the sample for known values of the sample thickness and the surface area of the electrodes. The Sawyer-Tower circuit was used to obtain the relationship between the electric induction D and the electric field strength E. A visual observation of D (E hysteresis loop) was carried out on a C1–83 oscilloscope with a voltage divider consisting of a resistance of 6 MΩ and 700 kΩ and a reference capacitor of 0.15 μF. The frequency of the generator is 300 Hz. In all temperature studies, the samples were placed in a furnace, the temperature was measured with a chromel-alumel thermocouple connected to a B2–34 voltmeter with an error of ± 0.1 mV. The rate of temperature change is ~5 K/min. The value of the dielectric constant at each temperature was determined by the formula:

$$\varepsilon=\frac{C}{C_0}, \tag{2}$$

where $C_0=\frac{\varepsilon_0\cdot S}{d}$ is the capacitance of the capacitor without the test substance (air).

Since ceramic materials have certain inertia, the change in electrical properties, the data on the integral electrical resistance and electrical capacity were determined only after preliminary exposure for ~0.5 hours at a fixed temperature. This is especially important in the area of abnormal changes in the above characteristics., measurements are also carried out by the method of direct deflection using an E6–13A thermometer to compare the data on the electrical conductivity.

Experimental data on the study of the electrophysical properties of $La_2MgNiTeO_7$ ternary tellurite are given in Table 4 and in Figures 2, 3.

Table 4

Dependence of electric capacitance (C), dielectric constant (ε) and electrical resistance (R) of tellurite $La_2MgNiTeO_7$ on temperature

T, K	*C*, μF	ε	lg ε	*R*, Ohm	lg *R*
293	9.24	52	1.71	366300	5.56
303	9.23	52	1.71	230100	5.36
313	9.17	51	1.71	114100	5.06
323	9.49	53	1.73	30340	4.48
333	9.87	55	1.74	395300	5.60
343	10.17	57	1.76	647600	5.81
353	10.60	60	1.77	1043000	6.02
363	10.07	57	1.75	2389000	6.38
373	10.63	60	1.78	2905000	6.46
383	11.07	62	1.79	3115000	6.49
393	11.27	63	1.80	3210000	6.51
403	10.52	59	1.77	2508000	6.40
413	8.85	50	1.70	612800	5.79
423	8.70	49	1.69	436500	5.64
433	8.89	49	1.69	562200	5.75
443	8.89	50	1.70	760500	5.88
453	9.08	51	1.71	1021000	6.01
463	9.29	52	1.72	1179000	6.07
473	9.40	53	1.72	1241000	6.09
483	9.57	54	1.73	1397000	6.15

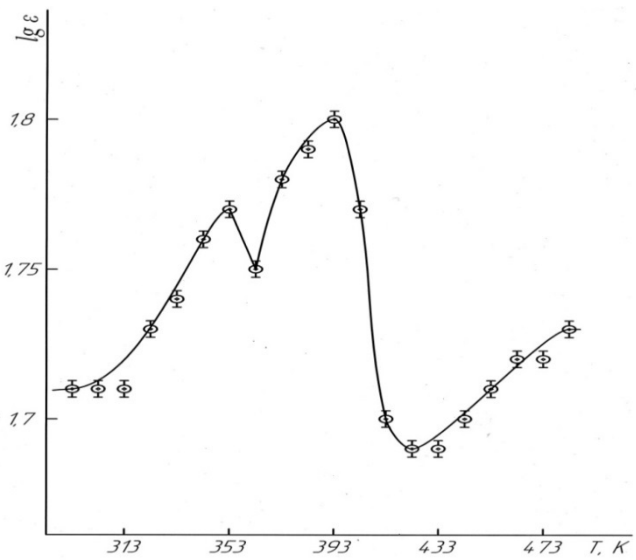

Figure 2. Temperature dependence of dielectric constant of $La_2MgNiTeO_7$

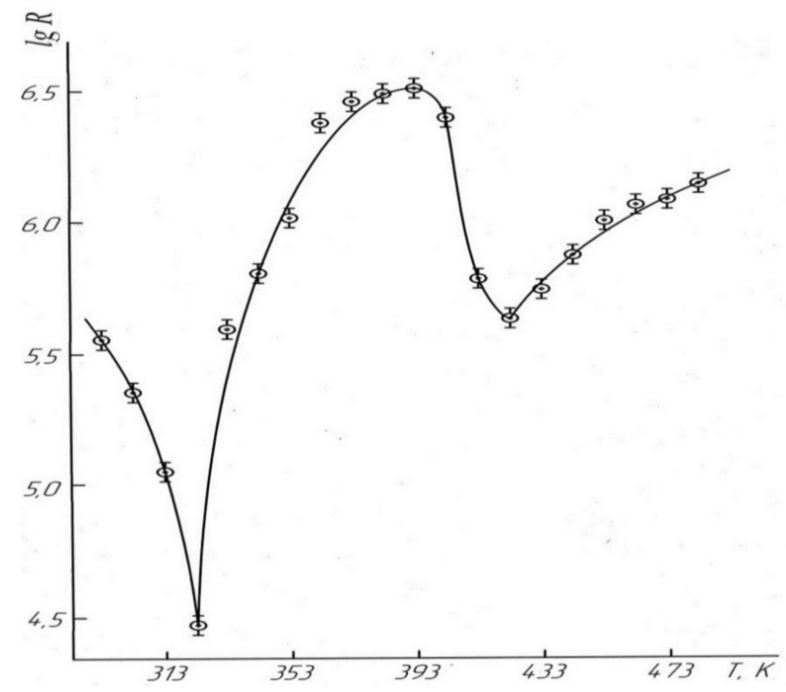

Figure 3. Temperature dependence of the electrical resistance of $La_2MgNiTeO_7$

Analysis of the data in Table 4 and Figures 2 and 3 shows that $La_2MgNiTeO_7$ compound in the range of 293–323 K exhibits semiconductor, at 323–393 K — metallic, at 393–423 K — semiconductor and at 433–483 K — metallic conductivity.

The calculation of the width of the forbidden zone was calculated by the formula

$$\Delta E = \frac{2kT_1T_2}{T_2 - T_1} \ln \frac{R_1}{R_2}, \qquad (3)$$

where k is the Boltzmann constant; R_1 and R_2 are resistances at temperatures T_1 and T_2, respectively.

The width of the forbidden zone (ΔE), calculated by the formula (3), in the interval 293–323 K is 1.57 eV, and it is 2.56 eV in the interval 393–423 K. The research results given in Table 4 and in Figures 2 and 3 shows that the new tellurite $La_2MgNiTeO_7$ exhibits semiconductor properties.

Thus, for the first time, the isobaric heat capacity of lanthanum-magnesium-nickel tellurite $La_2MgNiTeO_7$ was experimentally investigated by dynamic calorimetry in the temperature range 298.15–673 K. The temperature dependences of the heat capacity for the compound under study are derived based on the experimental values. The standard heat capacity of ternary tellurite was determined experimentally. The temperature dependences of the thermodynamic functions $S^0(T)$, $H^0(T) - H^0(298.15)$ and $\Phi^{xx}(T)$ are calculated in the range of 298.15–673 K. There is a λ-shaped peak related to a second-order phase transition on the $C_p^0 \sim f(T)$ dependence curve of lanthanum-magnesium-nickel tellurite $La_2MgNiTeO_7$ at a temperature of 423 K.

For the first time, the temperature dependences of the dielectric constant and electrical resistance of tellurite $La_2MgNiTeO_7$ have been studied on the LCR instrument. The curves $\lg\varepsilon \sim f(T)$ and $\lg R \sim f(T)$ have maxima and minima, which confirm the λ-like effect on the $C_p^0 \sim f(T)$ dependence curve of the indicated compound, related to the phase transition of the second kind.

The obtained data showed that the $La_2MgNiTeO_7$ tellurite had semiconductor properties and was of interest for electronic technology.

The obtained new thermochemical and thermodynamic data serve as initial information files for fundamental data banks and reference books; they are of theoretical and practical interest for inorganic materials science in the field of directional synthesis of compounds with multifunctional properties.

References

1 Третьяков Ю.Д. Новые поколения неорганических функциональных материалов / Ю.Д. Третьяков, О.А. Брылев // Журнал Российского химического общества им. Д.И. Менделеева. — 2000. — Т. 45, № 4. — С. 10.

2 Бектурганова А.Ж. Синтез и рентгенографическое исследование новых никелито-теллуритов $La_2MNiTeO_7$ (M — Mg, Ca, Sr, Ba) / А.Ж. Бектурганова, Ж.И. Сагинтаева, К.Т. Рустембеков и др. // Известия НАН РК. Серия химии и технологии. — 2017. — № 2(422). — С. 99.

3 Robie R.A. Thermodynamic Properties of Minerals and Related Substances at 298.15 and (10^5 Paskals) Pressure and at Higher Temperatures / R.A. Robie, B.S. Hewingway, I.R. Fisher // Washington: United States Government Printing Office, 1978. — 456 p.

4 Спиридонов В.П. Математическая обработка экспериментальных данных / В.П. Спиридонов, Л.В. Лопаткин. — М.: Изд-во МГУ, 1970. — 221 с.

5 Техническое описание и инструкции по эксплуатации ИТ-С-400. — Актюбинск: Актюбинский завод «Эталон», 1986. — 48 с.

6 Rustembekov K.T. X-ray Diffraction and Thermodynamic Characteristics for Tellurite of the Composition Li_2CeTeO_5 / K.T. Rustembekov, A.Zh. Bekturganova // Russian Journal of Physical Chemistry A. — 2017. — Vol. 91, № 4. — P. 622–626.

7 Кумок В.Н. Прямые и обратные задачи химической термодинамики / В.Н. Кумок. — Новосибирск: Наука, 1987. — С. 108.

К.Т. Рүстембеков, М.С. Қасымова, Е.В. Минаева, А.Ж. Бектұрғанова

Лантан-магний-никель теллуриті: термодинамикалық және электрфизикалық сипаттамалары

Керамикалық технология әдісімен La_2O_3, NiO, TeO_2 оксидтері мен $MgCO_3$ карбонатынан $La_2MgNiTeO_7$ құрамды лантан-магний-никель теллуриті синтезделді. ИТ-С-400 калориметрінде динамикалық калометрияның тәжірибелік әдісімен 298,15–673 К аралығында $La_2MgNiTeO_7$ теллуритінің изобаралық жылусыйымдылығы зерттелді. Калориметрдің жұмысы α-Al_2O_3 стандартты жылусыйымдылығын өлшеумен тексерілді. Меншікті жылусыйымдылық өлшенді, кейін олар бойынша синтезделген теллуриттің мольдік жылусыйымдылығы есептелді. $La_2MgNiTeO_7$ теллуриті жылусыйымдылығының температурадан тәуелділігін зерттеу барысында 423 К күрт аномальді λ-тәрізді секіріс байқалды, оның ІІ-ші текті фазалық ауысуға сәйкес келуі мүмкін. Бұл ауысу катиондардың қайта бөлінулерімен, термиялық ұлғаю коэффициенттерінің және магниттік моментінің өзгерістерімен, сол сияқты диэлектрлік өткізгіштігі және электрлік кедергісінің өзгерістерімен байланысты болуы мүмкін. Тәжірибелік мәліметтерінің негізінде, ІІ-ші текті фазалық ауысу температурасын ескере отырып, қосылыстың жылусыйымдылығының температуралық тәуелділік теңдеулері шығарылды. Жылусыйымдылықтарының тәжірибелік мәліметтерінің және стандартты энтропияның S^0(298,15) есептелген мәнінің негізінде 298,15–673 К аралығында жылусыйымдылықтың $C_p^0(T)$ және термодинамикалық функциялардың: энтропияның $S^0(T)$, энтальпияның $H^0(T) - H^0(298{,}15)$ және келтірілген термодинамикалық потенциалдың Φ^{xx}(Т) температуралық тәуелділіктері есептелді. LCR-800 құрылғысында алғаш рет 293–483 К температура аралығында $La_2MgNiTeO_7$ теллуритінің диэлектрлік өткізгіштігі мен электрлік кедергісінің температуралық тәуелділігі зерттелді. $\lg\varepsilon \sim f(T)$ және $\lg R \sim f(T)$ тәуелділік қисықтарында максимумдар мен минимумдардың болуы, бұл қосылыстың $C_p^0 \sim f(T)$ тәуелділік қисығындағы, ІІ-ші фазалық ауысуға тиесілі λ-тәрізді эффектіні дәлелдеді. Алынған мәліметтер зерттеліп отырған теллуриттің жартылайөткізгіштік қасиеттерге ие болатындығын көрсетті.

Кілт сөздер: лантан-магний-никель теллуриті, жылусыйымдылық, термодинамикалық функциялар, диэлектрлік өткізгіштік, электркедергісі.

К.Т. Рустембеков, М.С. Касымова, Е.В. Минаева, А.Ж. Бектурганова

Теллурит лантана-магния-никеля: термодинамические и электрофизические характеристики

Методом керамической технологии из оксидов La_2O_3, NiO, TeO_2 и карбоната $MgCO_3$ синтезирован теллурит лантана-магния-никеля состава $La_2MgNiTeO_7$. На калориметре ИТ-С-400 экспериментальным методом динамической калориметрии в интервале 298,15–673 К исследованы температурные зависимости изобарной теплоемкости теллурита $La_2MgNiTeO_7$. Проверку работы калориметра проводили измерением стандартной теплоемкости α-Al_2O_3. Измерены удельные, а затем по ним рассчитаны мольные теплоемкости синтезированного теллурита. При исследовании зависимости теплоемкости теллурита $La_2MgNiTeO_7$ от температуры при 423 К обнаружен резкий аномальный λ-образный скачок, связанный, вероятно, с фазовым переходом II рода. Этот переход может быть связан с катионным перераспределением, с изменениями коэффициента термического расширения и магнитного момента, а также с изменениями диэлектрической проницаемости и электросопротивления. На основании экпериментальных данных, с учетом температуры фазового перехода II рода выведено уравнение температурной зависимости теплоемкости соединения. На основании опытных данных по теплоемкостям и расчетного значения стандартной энтропии $S^0(298,15)$ в интервале 298,15–673 К вычислены температурные зависимости теплоемкости $C_p^0(T)$ и термодинамических функций: энтропии $S^0(T)$, энтальпии $H^0(T) - H^0(298,15)$ и приведенного термодинамического потенциала $\Phi^{xx}(T)$. Впервые на приборе LCR-800 исследованы температурные зависимости диэлектрической проницаемости и электросопротивления теллурита $La_2MgNiTeO_7$ в диапозоне температуры 293–483 К. На кривых зависимостях $\lg\varepsilon{\sim}f(T)$ и $\lg R{\sim}f(T)$ имеются максимумы и минимумы, которые подтверждают λ-образный эффект на кривой зависимости $C_p^0{\sim}f(T)$ удачного соединения, отнесенный к фазовому переходу II рода. Полученные данные показали, что исследуемый теллурит обладает полупроводниковыми свойствами.

Ключевые слова: теллурит лантана-магния-никеля, теплоемкость, термодинамические функции, диэлектрическая проницаемость, электросопротивление.

References

1 Tretyakov, Yu.D., & Brylev, O.A. (2000). Novye pokoleniia neorhanicheskikh funktsionalnykh materialov [New generations of inorganic functional materials]. *Zhurnal Rossiiskoho khimicheskoho obshchestva im. D.I. Mendeleeva — Journal of the Russian Chemical Society, named after D.I. Mendeleev*, *Vol. 45, 4,* 10 [in Russian].

2 Bekturganova, A.Zh., Sagintaeva Zh.I., & Rustembekov K.T. et al. (2017). Sintez i renthenohraficheskoe issledovanie novykh nikelito-telluritov $La_2MNiTeO_7$ (M — Mg, Ca, Sr, Ba) [Synthesis and X-ray study of new nickelite-tellurites $La_2MNiTeO_7$ (M — Mg, Ca, Sr, Ba). *Izvestiia NAN RK. Seriia Khimiia i tekhnolohii — News of the National Academy of Sciences of Kazakhstan. A series of chemistry and technology, 422, 2*, 99 [in Russian].

3 Robie, R.A., Hewingway, B.S., & Fisher, I.R. (1978). *Thermodynamic Properties of Minerals and Related Substances at 298.15 and (105 Paskals) Pressure and at Higher Temperatures.* Washington: United States Government Printing Office.

4 Spiridonov, V.P., & Lopatkin, L.V. (1970). *Matematicheskaia obrabotka eksperimentalnykh dannykh [Mathematical processing of experimental data]*. Moscow: Izd-vo MHU [in Russian].

5 *Tekhnicheskoe opisanie i instruktsii po ekspluatatsii IT-S-400 [Technical description and operating instructions for IT-C-400]*. Aktiubinsk: Aktiubinskii zavod «Etalon». (1986) [in Russian].

6 Rustembekov, K.T., & Bekturganova, A.Zh. (2017). Diffraction and Thermodynamic Characteristics for Tellurite of the Composition Li_2CeTeO_5. *Russian Journal of Physical Chemistry A*, *91*(4), 622–626.

7 Kumok, V.N. (1987). *Priamye i obratnye zadachi khimicheskoi termodinamiki [Direct and inverse problems of chemical thermodynamics]*. Novosibirsk: Nauka [in Russian].