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Calorimetric research of a heat capacity of a triple lanthanum tellurite in the range of 298.15–673 K

This paper presents detailed results of new lanthanum tellurite synthesis and its heat capacity calorimetric research. For the first time, a triple lanthanum tellurite was synthesized by the solid-phase method from oxides of lanthanum, nickel (II), tellurium (IV) and calcium carbonate. The generation of the equilibrium composition of the synthesized compound was controlled by the method of X-ray diffraction analysis (XDA) on the diffractometer DRON-2.0. By the results of the XDA it was established that there was synthesized a triple lanthanum tellurite $La_2CaNiTeO_7$. Heat capacity at constant pressure of the synthesized tellurite was researched by the method of dynamic calorimetry at the range of 298.15–673 K. Based on the experimental data, the equations, describing dependencies of heat capacity of the compound on temperature were calculated. When studying the temperature dependences of the heat capacity of $La_2CaNiTeO_7$, abnormally sharp λ-like peaks probably associated with second-order phase transitions, were observed at 423 K. Temperature dependencies of thermodynamic functions of $La_2CaNiTeO_7$ $S^o(T)$, $H^o(T)–H^o(298,15)$, $\Phi^{xx}(T)$ were calculated based on the experimental data $C_p^o(T)$ and the calculated value S^o (298.15).

Keywords: calorimetry, heat capacity, lanthanum tellurite, second-order phase transitions, thermodynamic functions.

The discovery of high-temperature superconductivity in 1986 has served as a powerful incentive in the development of chemistry of solids. A heightened interest in metal-oxide systems with the perovskite structure [1] is, primarily, connected to that. It is known, that lack of the symmetry center in its crystal structure is a strictly necessary condition of generation in solids of non-linear–optical and piezoelectric properties. Contrariwise, the increase in probability of generation of acentric structures is postulated at the introduction into the composition of ions' compound with an unshared electron pair, such as Bi^{3+}, Te^{4+}, Se^{4+} and so on [2]. One more factor, favoring the generation of an acentric crystal structure is the presence in the composition of compounds of *d*-metals, causing the distortion of the structure due to the Jahn-Teller effect.

The scientific interest to rare earth elements and compounds of lower oxides transition metals was primarily driven by their applicable properties such as optical, conducting, magnetic, etc. Based on these ideas we conduct a systematic search of different tellurite derivatives of rare earth, alkaline earth (alkaline) and *d*-metals.

This paper presents detailed results of new tellurite lanthanum synthesis and its heat capacity calorimetric research. Oxide of lanthanum, oxide of nickel (II), oxide of tellurium (IV) and calcium carbonate of «chemically pure» qualification were used for the synthesis of the triple tellurite of lanthanum. Stoichiometric amounts of basic substances were thoroughly grinded in an agate mortar and then were poured, in amounts, into alundum crucibles and treated with heat for solid phase interaction in the air in the Silicon Carbide Electric furnace. The following mode of thermal treatment were used: I^{st} stage — annealing during 70 hours at the temperature of 600–800–1000 ºC, II^{nd} stage — at 1100–1200–1300 ºC during 66 hours with

periodic grinding and mixing of basic substances. Annealing at 400–500 ºC during 22 hours was conducted to obtain cryotolerant equilibrium phases. The generation of the equilibrium composition of the synthesized compound was controlled by the method of X-ray diffraction analysis (XDA) on the diffractometer DRON-2.0. Indexing of X-ray photographs was conducted by the method of homology. A structural type of perovskite was selected as a homologue. By the results of the XDA it was established that was synthesized a triple lanthanum telluriteLa$_2$CaNiTeO$_7$.

Heat capacities at constant pressure La$_2$CaNiTeO$_7$ were researched by the method of dynamic calorimetry on the commercially produced instrument IT-S-400 at the temperature range of 298,15–673 K. Errors in measurement of heat capacity in the temperature range under test are within the limits of the instrument accuracy (±10 %) [3, 4]. Calibration of the instrument was carried out on a copper sample [3, 4]. At each temperature, five experiments were conducted, the results of which were averaged and processed by methods of mathematical statistics.

At each temperature the estimate of the root-mean-square deviation $\bar{\delta}$ was conducted for average values of specific heat [5]:

$$\bar{\delta} = \sqrt{\frac{\sum_{i=1}^{n} (C_i - \bar{C})^2}{n-1}},$$

where n is the number of tests; C_i is the measured value of specific heat; and $\bar{C}$ is the arithmetical average from measured values of specific heat. A random error component was calculated for the average values of molar heat capacity [6]:

$$\overset{\circ}{\Delta} = \frac{\delta \cdot t_p}{\bar{C}} \cdot 100,$$

where $\overset{\circ}{\Delta}$ is a random error component in %; t_p — Student's coefficient (for n = 5, t_p = 2.78 at p = 0.95 confidence interval).

The instrument operation was checked by determining the standard heat capacity α-Al$_2$O$_3$. The obtained result for Al$_2$O$_3$ at temperature of 298.15 K value C_p^0 = 76.0 J/(mol·K) is satisfactorily consistent with its recommending [7] value79.0 J/ (mol·K) within the limits of the instrument error. The experimental values of heat capacity of the triple tellurite are shown in Table 1.

Table 1

Experimental values of the specific and molar heat capacities La$_2$CaNiTeO$_7$

T, K	$C_p \pm \bar{\delta}$, J/ (g·K)	$C_p^0 \pm \overset{\circ}{\Delta}$, J/ (mol·K)	T, K	$C_p \pm \bar{\delta}$, J/ (g·K)	$C_p^0 \pm \overset{\circ}{\Delta}$, J/ (mol·K)
298.15	0.4768±0.0136	294±23	498	0.3618±0.0086	223±15
323	0.5031±0.0104	310±18	523	0.3395±0.0093	209±16
348	0.5345±0.0083	329±14	548	0.3749±0.0113	231±19
373	0.5681±0.0121	350±21	573	0.4033±0.0083	249±14
398	0.6591±0.0086	406±15	598	0.4442±0.0098	274±17
423	0.7435±0.0187	458±32	623	0.4831±0.0131	298±22
448	0.5512±0.0186	340±32	648	0.5352±0.0101	330±17
473	0.4290±0.0132	264±23	673	0.5906±0.0149	364±26

When studying the temperature dependences of the heat capacity of La$_2$CaNiTeO$_7$, abnormally sharp λ-like peaks probably associated with second-order phase transition, were observed at 423 K. This transition may be related to the cationic redistribution, modification of the thermal-expansion coefficient and modification of the magnetic moment of the synthesized tellurite (see Fig.).

Based on the experimental data, the equations, describing dependencies of heat capacity of the compound on temperature were calculated. Due to the fact that tellurite had the phase transition of the IInd type at 423 K, the dependency $C_p^0 \sim f(T)$ La$_2$CaNiTeO$_7$ was described by three equations, which coefficients are shown in Table 2. An average random error component for all considered temperature intervals was used to determine coefficient errors in the equations of the temperature dependence of heat capacity La$_2$CaNiTeO$_7$.

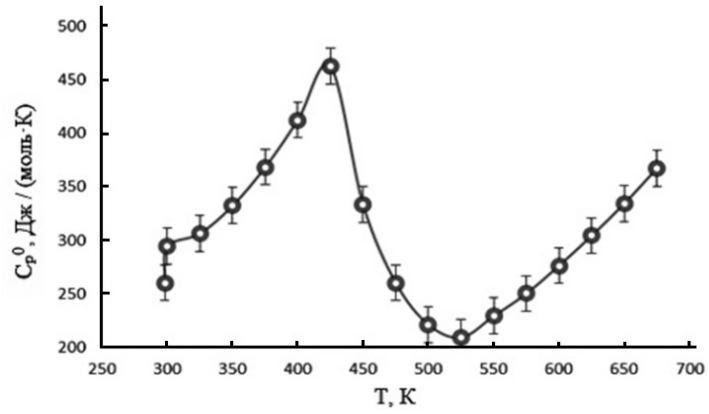

Figure. Temperature dependence of heat capacity $La_2CaNiTeO_7$

Table 2

Coefficients of the equation of the temperature dependence of heat capacity $C_p^0 = a + bT + cT^{-2}$, J/(mol·K) $La_2CaNiTeO_7$

Coefficients			ΔT, K
a	$b \cdot 10^{-3}$	$-c \cdot 10^5$	
–(1115.28±74.33)	3177.27±211.76	410.48±27.35	298–423
–(4737.36±315.53)	6284.80±418.86	4539.43±302.54	423–523
–(1164.69±77.62)	1956.86±130.42	958.52±63.99	523–673

Since technical characteristics of the calorimeter IT-S-400 don't allow to calculate the value of the standard entropy $S^0(298.15)$ of the studied phases directly from the experimental data, it was valued by the method of ionic entropy increments of Cumok [8].

The temperature dependences of the thermodynamic functions of $La_2CaNiTeO_7$ $S^0(T)$, $H^0(T)$ — $H^0(298{,}15)$, $\Phi^{xx}(T)$ based on the experimental data $C_p^0(T)$ and the calculated value S^0 (298.15) were calculated (Table 3).

Table 3

Temperature dependencies of thermodynamic functions $La_2CaNiTeO_7$ at the interval of 298.15–675 K

T, K	$C_p^0(T) \pm \Delta$, J/(mol·K)	$S^0(T) \pm \Delta$, J/(mol·K)	$H^0(T)-H^0(298.15) \pm \Delta$ J/(mol·K)	$\Phi^{xx}(T) \pm \Delta$ J/(mol·K)
298.15	260±17	266±8	–	266±8
300	294±20	279±27	600±40	277±27
325	306±20	303±29	8050±540	278±27
350	332±22	327±32	16000±1070	281±27
375	368±25	351±34	24730±1650	285±28
400	412±28	376±36	34470±2300	290±28
425	462±31	402±39	45390±3000	300±29
450	333±22	424±41	55040±3670	302±29
475	260±17	440±43	62360±4160	309±30
500	221±15	452±44	68310±4550	316±31
525	209±14	463±45	73630±4910	323±31
550	229±15	473±46	79100±5270	329±32
575	250±17	484±47	85090±5670	336±32
600	276±18	495±48	91660±6110	342±33
625	304±20	507±49	98890±6590	348±34
650	334±22	519±50	106860±7120	355±34
675	367±24	532±52	115620±7710	361±35

Errors of the temperature dependence of the thermodynamic functions, with account for the average random heat capacity error and accuracy of calculation of the standard entropy (~3 %), were determined.

Therefore, the new triple tellurite of the compound $La_2CaNiTeO_7$ was synthesized for the first time by the method of ceramic technology from oxides La, Ni (II), Te (IV) and calcium carbonate. The temperature dependence of heat capacity $La_2CaNiTeO_7$ was studied by the calorimetric method in the range of 298.15–673 K, the standard heat capacity is equal to 260±17 J/(mol·K). The dependence equations $C_p^0 \sim f(T)$ were established and thermodynamic functions were determined. The phased transition of the IInd type was found the dependence curve $C_p^0 \sim f(T)$ at 423 K which indicates of the presence of valuable physical-chemical properties [9, 10]. Thermodynamic characteristics of the new tellurite can be the initial information arrays of basic reference books and data banks and are of interest for the chemical informatics.

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298,15–673 К аралығында лантан үштік теллуриттінің жылу сыйымдылығын калориметрлік зерттеу

Мақалада лантанның жаңа теллуриттінің синтезі және жылу сыйымдылығын калориметрлік зерттеудің нәтижелері келтірілген. Қатты фазалық әдіспен алғаш рет лантан, никель (II), теллур (IV) оксидтері және кальций карбонатынан лантан үштік теллуриті синтезделді. Синтезделген қосылыстың тепетеңдік құрамының түзілуі ДРОН-2,0 дифрактометрінде рентгенфазалық әдіспен бақыланды. РФА нәтижелері бойынша лантантың үштік теллуриті $La_2CaNiTeO_7$ синтезделгені айқындалды. 298,15–673 К аралығында динамикалық калориметрия әдісімен синтезделген теллуриттің изобаралық жылу сыйымдылығы зерттелді. Тәжірибе мәліметтері негізінде қосылыс жылу сыйымдылығының температурадан тәуелділік теңдеулері шығарылды. $La_2CaNiTeO_7$ жылу сыйымдылығының температурадан тәуелділігін зерттеу барысында 423 К температурада II-текті фазалық ауысуға жатуы мүмкін λ-тәрізді аномальді секіріс байқалды. $C_p^0(T)$ тәжірибелік мәндері және $S^0(298.15)$ есептелген мәні негізінде $La_2CaNiTeO_7$ термодинамикалық функцияларының $S^0(T)$, $H^0(T)–H^0(298,15)$, $\Phi^{xx}(T)$ температуралық тәуелділіктері есептелді.

Кілт сөздер: калориметрия, жылу сыйымдылық, лантан теллуриті, екінші текті фазалық ауысу, термодинамикалық функциялар.

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Калориметрическое исследование теплоемкости тройного теллурита лантана в интервале 298,15–673 К

В статье приведены результаты синтеза и калориметрического исследования теплоемкости нового теллурита лантана. Впервые твердофазным способом из оксидов лантана, никеля (II), теллура (IV) и карбоната кальция синтезирован тройной теллурит лантана. Образование равновесного состава синтезируемого соединения контролировалось методом рентгенофазового анализа на дифрактометре ДРОН-2.0. По результатам РФА установлено, что был синтезирован тройной теллурит лантана $La_2CaNiTeO_7$. Методом динамической калориметрии в интервале 298,15–673 К исследована изобарная теплоемкость синтезированного теллурита. На основе экспериментальных данных рассчитаны уравнения, описывающие зависимости теплоемкости соединения от температуры. При исследовании зависимости теплоемкости $La_2CaNiTeO_7$ от температуры при 423 К обнаружен резкий аномальный λ-образный скачок, связанный, вероятно, с фазовым переходом II рода. На основании опытных данных $C_p^0(T)$ и расчетного значения $S^0(298{,}15)$ вычислили температурные зависимости термодинамических функций $La_2CaNiTeO_7$ $S^0(T)$, $H^0(T)–H^0(298{,}15)$, $\Phi^{xx}(T)$.

Ключевые слова: калориметрия, теплоемкость, теллурит лантана, фазовый переход второго рода, термодинамические функции.

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