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Thermodynamic properties of titanium-manganite $LaCaTiMnO_6$

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By the method of dynamic calorimetry in the range of 298.15-673 K, the heat capacity of titanium-manganite LaCaTiMnO6, obtained by solid-phase interaction at 800-1200ºC from lanthanum, titanium (II), manganese (III) and calcium carbonate oxides was studied. On the dependence curve $Cp°\sim f(T)$ in the specified temperature range, a λ-shaped effect was detected at 598 K, probably related to the phase transition of the second kind. A fundamental constant is determined — the standard heat capacity of LaCaTiMnO6, equal to 221±14 J /(mol·K). Its standard entropy, equal to 206±6 J/(mol·K), was estimated by the approximate method of ion increments. Based on experimental data, taking into account the temperature of the phase transition, the equations describing the temperature dependences of $C_p°\sim f(T)$ and the thermodynamic functions $S^o(T)$, $H^o(T)$ — $H^o(298.15)$ and $\Phi^{xx}(T)$ of the investigated titanium-manganite lanthanum and calcium are calculated. The standard heat capacity of LaCaTiMnO6 is also calculated using the Debye method, the value of which is in good agreement with experimental data. According to the developed methodology, the standard enthalpy of titanium-manganite formation was calculated, equal to — 3867.5 kJ/mol.

Keywords: Titanium-manganite, lanthanum, calcium, heat capacity, phase transition, enthalpy of formation, thermodynamic properties.

Introduction

Manganites with an effect of colossal magneto resistance (CMR) have the significant innovative perspectives such as the functional materials for sensors in the consumer and industrial electronics and development of the information technologies [1-3]. Lanthanum manganites doped in B-sublattice with titanium have the high electrical conductivity. They can be applied as cathodes of the high-temperature solid oxide fuel cells, the ceramic membranes of the thermo-resistors and magneto-resistors. Titanium oxides with transition metal impurities fix attention as the advancing materials to use in the spin electronics and catalysis [4]. Many investigations described that the doping with TiO_2 can increase the sensitivity and capacity of devices [5]. Titanates of alkaline earth metals are semiconductors with a large band gap (3.0-3.2 eV). They can also be the potential photocatalysts under UV-irradiation [6]. The intensive studies of perovskite-like manganites of the rare earth metals are a basis of materials for various devices, and however, many fundamental problems of the chemistry of these oxides have not been studied well. Based on the above, the purpose of this investigation is to study the thermodynamic properties of titanium-manganite of $LaCaTiMnO_6$.

This titanium-manganite of $LaCaTiMnO_6$ was synthesized by a method of solid-phase synthesis from oxides of lanthanum (III) (puriss. spec.), titanium (IV), manganese (III) and calcium carbonate (p.a.) in the SNOL furnace in four stages: 1) annealing at 800 °C for 5 h, cooling to 25 °Cand grinding; 2) annealing at 1000 °C for 10 h; 3) annealing at 1200 °C for 4 h and 4) low-temperature annealing at 400 °C for 10 h.

The identification of an equilibrium composition formation was determined through X-ray phase analysis conducted on the DRON-2.0 diffractometer. The indexing of the X-ray photogram was performed by the analytical method. A type of syngony and crystal lattice parameters was determined: $LaCaTiMnO_6$ (cube) — a= 13.35 ± 0.02 Å; V^0 = 2376.3 ± 5.00 Å^3; Z = 4; $V°_{elec.cell}$= 594.08 ± 1.25 Å^3; $\rho_{roent.}$ = 3.96 g/cm^3; $\rho_{pick.}$ = 3.95 ± 0.02 g/cm^3 [7].

1. Experimental technique

The investigation of the isobaric heat capacity of LaCaTiMnO6 titanium-manganite was conducted using an IT-C-400 calorimeter over the temperature range of 298.15 K to 673 K. The calorimeter operates based on the comparative method, using a dynamic calorimeter with a heat meter. Temperature measurements were taken at fixed intervals of 25 °C. The device offers a precision of ±10 %. To ensure

accurate measurements, the device was calibrated based on the determination of the thermal conductivity of the KT heat meter [8, 9].

A standard deviation ($\overline{\delta}$) was computed for the averaged values of the specific heat capacity at each temperature, as explained in [9]:

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

where n represents the number of experiments, C_i denotes a measured value of specific heat capacity, and $\bar{C}$ represents the arithmetic average of the measured values of specific heat capacity.

The random error was determined for the averaged values of the molar heat capacity, as outlined in [9]:

$$\overset{\circ}{\Delta} = \frac{\delta \cdot t_p}{\overline{C}} \cdot 100, \quad (2)$$

where, $\overset{\circ}{\Delta}$ - a random error in %, t_p– Student coefficient (for n = 5, t_p= 2.75 at p = 0.95 of the confidence range).

2. Results and discussion

The operation of the device was confirmed by determining of the heat capacity of α-Al_2O_3 (p.a.) (TU 6.09-426-75)). In order to prove measurements of the heat capacity of α-Al_2O_3, we compare our results with new literature data [10] (Table 1).

Table 1

Comparison of the heat capacity of α-Al_2O_3 used to verify a calorimeter operation with the literature data in [10]

T, K	C_p (T), J/(mol·K)		T, K	C_p (T), J/(mol·K)	
	Our data	Data in [10]		Our data	Data in [10]
180	44,50	43,83	400	94,12	95,21
230	64,86	61,18	450	100,26	101,8
250	70,37	67,08	500	105,47	106,1
280	77,07	74,82	550	110,09	109,7
300	76,31	79,41	600	114,29	112,5
350	86,49	88,86	650	118,20	114,9

The data shows that our scientific results of α-Al_2O_3 heat capacity between of 173-673 K satisfactorily conform to results described in [10] within the operating accuracy of IT-C-400 calorimeter. Liquid nitrogen was as a cooling agent in our experiments.

Results of the calorimetric studies are illustrated in Figure and Table 2.

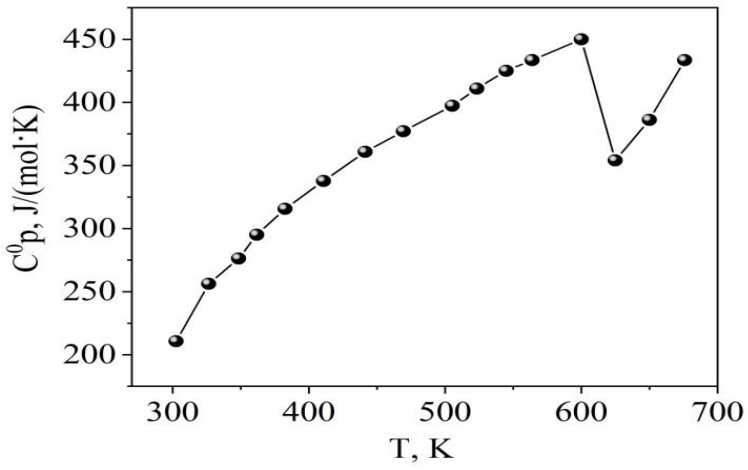

Figure. Diagram of dependence of heat capacity on temperature $LaCaTiMnO_6$

Table 2

Experimental data of the heat capacity of $LaCaTiMnO_6$

T, K	$C_p \pm \overline{\delta}$, J/(g·K)	$C_p \pm \overset{o}{\Delta}$, J/(mol·K)	T, K	$C_p \pm \overline{\delta}$, J/(g·K)	$C_p \pm \overset{o}{\Delta}$, J/(mol·K)
298,15	0,5861 ± 0,0136	221 ± 14	498	1,0018 ± 0,0152	378 ± 16
323	0,7050 ± 0,0188	266 ± 20	523	1,0622 ± 0,0223	401 ± 23
348	0,7805 ± 0,0145	295 ± 15	548	1,0954 ± 0,0211	414 ± 22
373	0,8128 ± 0,0177	307 ± 19	573	1,1096 ± 0,0135	419 ± 14
398	0,8397 ± 0,0149	317 ± 16	598	1,1794 ± 0,0289	446 ± 30
423	0,8835 ± 0,0133	334 ± 14	623	0,9457 ± 0,0190	357 ± 20
448	0,9195 ± 0,0162	347 ± 17	648	1,0880 ± 0,0177	411 ± 19
473	0,9476 ± 0,0216	358 ± 23	673	1,1530 ± 0,0153	436 ± 16

By analyzing the values presented in Figure and Table 2, a distinct and abrupt discontinuity was observed in the temperature-dependent heat capacity of $LaCaTiMnO_6$. The dependence curve, $C_p^0 \sim f(T)$, exhibited a λ-shaped maximum. This remarkable behavior is likely associated with a second-order phase transition occurring at a temperature of 598 K. The transition could be attributed to various factors such as Schottky effects, the Curie and Neel points, alterations in magnetic resistance [12], modifications in electrical conductivity, and changes in dielectric permittivity, and other.

Based on the revealed temperature of the phase transition, the equations of dependencies of $C^0_p \sim f(T)$, [J/(mol·K)] were calculated:

$$C^0_p = (172 \pm 9) + (498.1 \pm 26.4)\ 10^{-3}T - (88.3 \pm 4.7)\ 10^{5}T^{-2}\ (298\text{-}598\ K), \quad (3)$$

$$C^0_p = (2558 \pm 136) - (3532.4 \pm 187.6)\ 10^{-3}T\ (598\text{-}623\ K), \quad (4)$$

$$C^0_p = -(619 \pm 3\ 3) + (1567.0 \pm 83.2)\ 10^{-3}T\ (623\text{-}673\ K). \quad (5)$$

The graph depicted in Figure was generated using the KOMPAS-3D LT program, using experimental data and equations 3-5 as the basis for plotting.

Direct calculation of $S^0(298.15)$ for LaCaTiMnO6 from the experimental data is not feasible with the computational capabilities of the IT-C-400 calorimeter. Therefore, it was estimated using a system of the ionic entropy increments [11]. Then, based on the experimental values on $C^0_p(T)$ and a calculated parameters of $S^0(298.15)$, functions of $S^0(T)$, $H^0(T)-H^0(298.15)$ and $\Phi^{xx}(T)$ were also calculated (Table 3).

Table 3

Thermodynamic parameters of $LaCaTiMnO_6$ in the temperature range of 298.15-675 K

T, K	$C_p°(T) \pm \overset{\circ}{\Delta}$, J/(mol·K)	$S°(T) \pm \overset{\circ}{\Delta}$, J/(mol·K)	$H°(T)-H°(298.15) \pm \overset{\circ}{\Delta}$, J/mol	$\Phi^{xx}(T) \pm \overset{\circ}{\Delta}$, J/(mol·K)
298.15	221 ± 12	206 ± 6	–	206 ± 17
300	224 ± 12	208 ± 17	445 ± 20	206 ± 17
325	251 ± 13	227 ± 19	6380 ± 340	207 ± 17
350	275 ± 15	246 ± 20	12960 ± 700	209 ± 17
375	296 ± 16	266 ± 22	20100 ± 1070	212 ± 18
400	316 ± 17	286 ± 24	27760 ± 1470	216 ± 18
425	335 ± 18	305 ± 25	35910 ± 1910	221 ± 18
450	353 ± 19	325 ± 27	44520 ± 2360	226 ± 19
475	370 ± 20	345 ± 29	53550 ± 2840	232 ± 19
500	386 ± 20	364 ± 30	63000 ± 3340	238 ± 20
525	402 ± 21	383 ± 32	72860 ± 3870	245 ± 20
550	417 ± 22	402 ± 33	83090 ± 4410	251 ± 21
575	432 ± 23	421 ± 35	93710 ± 4980	258 ± 21
600	447 ± 24	440 ± 37	104700 ± 5560	265 ± 22
625	350 ± 19	456 ± 38	114560 ± 6080	273 ± 23
650	400 ± 21	471 ± 39	124060 ± 6590	280 ± 23
675	439 ± 23	487 ± 40	134540 ± 7140	288 ± 24

For comparison with experimental values, the standard heat capacity of LaCaTiMnO6 was also calculated using the Debye method [13]. For this calculation, the Debye characteristic temperatures (Q_D, K) of the constituent elements in the compound and the melting points of the elements in the compound (T_{mp}, K) were utilized. The melting point of $LaCaTiMnO_6$ was determined to be 1273 K. The characteristic temperatures (Q_D) of the elements in $LaCaTiMnO_6$ were computed using the Koref equation [13]:

$$Q'_D = Q_D \cdot \sqrt{T'_{melt.} \div T_{melt.}}, \quad (6)$$

where, $T'_{mp.}$ and $T_{mp.}$ are melting points of the compound and element, respectively. Then the isochoric heat capacities of the elements were calculated using Debye functions. They were summarized together to calculate the isochoric heat capacity of $LaCaTiMnO_6$. Isochoric-isobaric heat capacity transition of $LaCaTiMnO_6$ was made using the Nernst-Lindemann equation:

$$C_p = C_v + 0.0051 \cdot T \cdot C_p^2 / T_{melt}. \quad (7)$$

Based on the above, the following data was used to calculate $C^0_p(298.15)$ of $LaCaTiMnO_6$: $T_{melt.}$, K for La = 1193, Ca — 1112, Ti = 1941, Mn = 1517, O_2 = 54.7; the characteristic temperatures: Q_D, K for La = 135, Ca — 230, Ti = 380, Mn = 303, O_2 = 89 [13]. By equation (9) we calculated Q'_D, K for La = 144.05; Ca — 263.30; Ti = 307.74; Mn = 277.56; O_2 = 429.35. Then, the arguments of the Debye function (Q'_D/T) were calculated using tabular data: (T=298.15) — La = 0.48; Ca — 0.88; Ti = 1.03; Mn = 0.93; and O_2 = 1.44.

The relevant isochoric heat capacities to Q'_D/T on the basis of tabular data are equal to La = 24.64; Ca, 24.02; Ti = 23.76; Mn = 24.02; O_2 = 22.68 J/(mol·K). Then we used the scheme for calculation:

$$C_v\ LaCaTiMnO_6 = C_vLa + C_vCa + C_vTi + C_vMn + 3C_vO_2. \quad (8)$$

We calculated the isochoric heat capacity of $LaCaTiMnO_6$ equal to 164.48 J/(mol·K).

The standard isobaric heat capacity of $C_p^0(298.15)$ of $LaCaTiMnO_6$ equal to 224.9 J/(mol·K) was calculated using the Nernst-Lindemann equation (10). Its value was consistent with the experimental data of 221.0 J/(mol·K) with 1.73 % accuracy.

Based on our developed method [14] and similarly [15], we calculated the standard enthalpy of formation of $LaCaTiMnO_6$ equal to 3867.5 J/(mol·K). The initial data for calculation were applied as described in [13, 16-19].

Conclusions

1. The heat capacity of titanium-manganite of $LaCaTiMnO_6$ was first investigated by the dynamic calorimetry in the interval of 298.15-673 K.

2. Using the experimental data, a fundamental thermochemical constant for the standard heat capacity of $LaCaTiMnO_6$ was determined.

3. The anomalous discontinuity in heat capacity was determined on the dependence curve of $C^o_p \sim f(T)$ at 598 K. This feature is likely attributed to a second-order phase transition. Based on a temperature of the phase transition, the equations of the temperature dependence of the studied titanium-manganite were derived.

4. Using the experimental data obtained for $C^0_p(T)$ and the calculated value of $S^0(298.15)$ with a 25 K step within the temperature range of 298.15 K to 673 K, the temperature dependencies of $C^0_p(T)$, as well as the thermodynamic functions $S^0(T)$, $H^0(T)-H^0(298.15)$, and $\Phi^{xx}(T)$, were calculated for LaCaTiMnO6.

5. The standard heat capacity of $LaCaTiMnO_6$ was calculated by an independent Debye method. It corresponded satisfactorily with the experimental data.

6. According to a method developed by the authors, the standard enthalpy of formation of $LaCaTiMnO_6$ was calculated.

7. The obtained results carry both theoretical and practical significance, enabling the prediction of directed synthesis for similar compounds possessing valuable physical and chemical properties. Furthermore, these results facilitate the analysis of heterogeneous equilibria involving this specific compound and other

similar phases. The new thermochemical constants are initial data to load into the fundamental guides and databanks of the thermodynamic constants of substances.

Acknowledgments

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$LaCaTiMnO_6$ титан манганитінің термодинамикалық қасиеттері

298.15-673 К аралығындағы динамикалық калориметрия әдісімен лантан, титан (II), марганец (III) тотықтары және кальций карбонаты 800-1200°С кезінде қатты фазалық өзара әрекеттесу нәтижесінде алынған $LaCaTiMnO_6$ титан-манганитінің жылу сыйымдылығы зерттелді. Рентгенографиялық әдістермен бұл қосылыс тор параметрлерімен келесідей кубтық сингонияда кристалданатыны анықталды: a = 13,35 ± 0,02 Å; V^0 = 2376,3 ± 5,00 Å^3; Z = 4; $V°_{эл.ұяш}$ = 594,08 ± 1,25 Å^3; $\rho_{рент.}$ = 3,96 г/см^3; $\rho_{пикн.}$ = 3,95 ± 0,02 г/см^3. Көрсетілген температуралық аралықта $C_p°{\sim}f(T)$ тәуелділік қисығында 598 К — де λ-тәрізді әсер айқындалды, бұл II-текті фазалық ауысуға қатысты болуы мүмкін. Осы фазалық ауысу Шоттки эффектілерімен, Кюри, Нель нүктелерінің болуымен, магниттік кедергінің өзгеруімен, электр өткізгіштікпен, диэлектрлік өтімділікпен және т.б. байланысты болуы мүмкін. $LaCaTiMnO_6$ қосылысының 221±14 Дж/(моль·К)-ге тең болатын, іргелілік тұрақтысы — стандартты жылу сыйымдылығы анықталды. Иондық инкременттерінің жуықталған әдісімен оның 206±6 Дж/(моль·К) –ге тең болатын стандартты энтропиясы бағаланды. Фазалық ауысу температурасын ескере және тәжірибелік мәліметтерге сүйене отырып, зетртеліп отырған лантан және кальций титан манганитінің $C_p°{\sim}f(T)$ температураға тәуелділікті сипаттайтын теңдеулері мен қадамы 25 К болатын $S^o(T)$, $H^o(T)$ — $H^O(298.15)$ және $Ф^{xx}(T)$ термодинамикалық функциялар есептелді. $LaCaTiMnO_6$ стандартты жылу сыйымдылығы дебай әдісімен де есептелді, оның мәні тәжірибелік деректермен жақсы үйлеседі. Әзірленген әдістеме бойынша титан-манганиттің стандартты түзілу энтальпиясы есептелді, ол — 3867,5 кДж/моль тең.

Кілт сөздер: титан-манганит, лантан, кальций, жылу сыйымдылығы, фазалық ауысу, түзілу энтальпиясы, термодинамикалық қасиеттері.

Б.К. Касенов, Ш.Б. Касенова, Ж.И. Сагинтаева, С.О. Байсанов, Н.Ю. Лу, Ж.С. Бектурганов,
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Термодинамические свойства титано-манганита $LaCaTiMnO_6$

Методом динамической калориметрии в интервале 298,15–673 К исследована теплоемкость титано-манганита $LaCaTiMnO_6$, полученного твердофазным взаимодействием при 800–1200°С из оксидов лантана, титана (II), марганца (III) и карбоната кальция. Рентгенографическими методами установлено, что данное соединение кристаллизуется в кубической сингонии со следующими параметрами решетки: a = 13,35 ± 0,02 Å; V^0 = 2376,3 ± 5,00 Å^3; Z = 4; $V°_{эл.яч}$ = 594,08 ± 1,25 Å^3; $\rho_{рент.}$ = 3,96 г/см^3; $\rho_{пикн.}$ = 3,95 ± 0,02 г/см^3. На кривой зависимости $C_p°{\sim}f(T)$ в указанном интервале температур обнаружен λ-образный эффект при 598 К, относящийся, вероятно, к фазовому переходу II рода. Данный фазовый переход, возможно, связан с эффектами Шоттки, наличием точек Кюри, Нееля, изменениями магнитного сопротивления, электропроводности, диэлектрической проницаемости и др. Определена фундаментальная константа — стандартная теплоемкость $LaCaTiMnO_6$, равная 221±14 Дж/(моль·К). Приближенным методом ионных инкрементов оценена его стандартная энтропия, равная 206±6 Дж/(моль·К). На основании опытных данных с учетом температуры фазового перехода вычислены уравнения, описывающие температурные зависимости $C_p°{\sim}f(T)$ и шагом через 25 К термодинамические функции $S^o(T)$, $H^o(T)$ — $H^O(298,15)$ и $Ф^{xx}(T)$ исследуемого титано-манганита лантана и кальция. Стандартная теплоемкость $LaCaTiMnO_6$ рассчитана также по методу Дебая, значение которой хорошо согласуется с опытными данными. По разработанной методике вычислена стандартная энтальпия образования титано-манганита, равная 3867,5 кДж/моль.

Ключевые слова: титано-манганит, лантан, кальций, теплоемкость, фазовый переход, энтальпия образования, термодинамические свойства.

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