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Thermal capacity of new nanodimensional cobalt-cuprate-manganite $LaLi_2CoCuMnO_6$ and nickelite-cuprate-manganite $LaLi_2NiCuMnO_6$ in the interval of 298.15–673 K and their thermodynamic properties

The specific thermal capacities of our new obtained nanodimensional cobalt-cuprate-manganite and nickelite-cuprate-manganite of lanthanum and lithium of structures $LaLi_2CoCuMnO_6$ and $LaLi_2NiCuMnO_6$ were first studied with the method of a dynamic calorimetry in the interval of temperatures of 298.15–673 K. Their mole thermal capacities were calculated from specific thermal capacities. It was established that $LaLi_2CoCuMnO_6$ at 398 K and $LaLi_2NiCuMnO_6$ at 373 K and 573 K were subjected to II-type phase transitions. Based on temperature of phase transitions the equations of temperature dependence of thermal capacity were set up. All obtained experimental and calculated data were processed strictly with methods of mathematical statistics. The mean square deviations were measured for average values of specific thermal capacities, as well as random components of an error for mole thermal capacities. The standard entropies of the studied compounds were calculated with method of ionic increments. Referring to the experimental data on thermal capacities and calculated values of standard entropies in the interval of 298.15–675 with step through 50 K the temperature dependences of an enthalpy of $H^o(T)–H^o(298.15)$, entropy of $S^o(T)$ and the specified thermodynamic potential $\Phi^{xx}(T)$ were calculated.

Keywords: thermodynamics, cobalt, nickelite, cuprate, manganite, thermal capacity, calorimetry, lanthanum, lithium.

Introduction

It has been known that cuprates, cobaltites, nickelites and manganites of the rare-earth elements doped with oxides of alkaline and alkaline-earth metals have the unique physical and chemical properties as semiconductor, magnetic, superconducting and they represent as materials of operative memory [1–9]. For several years we have been conducting the systematic and purposeful researches on synthesis and studying the thermodynamic and electrophysical properties of double and threefold manganites, chromites, ferrites, cuprate-manganites, manganite-ferrites, chromite-manganites, cobalt-manganites, nickelite-manganites, ferro-chrome manganites, etc. [10–15].

The certain theoretical and practical interest includes the research of thermodynamic properties of new phases consisting of cobaltites, nickelites, cuprates and manganites. Thus, this paper demonstrates the research results of the thermodynamic properties of new nanodimensional cobalt-cuprate-manganite and nickelite-cuprate-manganite of lanthanum and lithium of structures $LaLi_2CoCuMnO_6$ and $LaLi_2NiCuMnO_6$.

Experimental

$LaLi_2CoCuMnO_6$ and $LaLi_2NiCuMnO_6$ were synthesized with method of the ceramic technology in the interval of 800–1200 ºC by interaction of La_2O_3 (especially pure), CoO (analytically pure), NiO (analytically pure), CuO (analytically pure), Mn_2O_3 (analytically pure) and Li_2CO_3 (analytically pure) with intermediate milling and stirring every 100 ºC for 20 h. Low-temperature annealing for obtaining a stable phase at a low temperature was made at 400 ºC for 10 h. By grinding of polycrystalline samples in a vibration mill of the Retsch (Germany) company of the MM301 brand there have been obtained their nanodimensional (nanocluster) particles, the sizes (40–90 nm) of which were determined on an atomic-force microscope JSPM-5400 Scanning Probe Microscope «JEOL» (Japan). The radiographic research of nanodimensional $LaLi_2CoCuMnO_6$ and $LaLi_2NiCuMnO_6$ was performed on the DRON-2.0 diffractometer at FeK_α — radiation, with Ni-filter. It was established with the indexing of roentgenograms of compounds that they were crystallized in an isometric system with the following parameters of grid: $LaLi_2CoCuMnO_6$ — $a = 11.33\pm0.02$Å; $V^o = 2563.20\pm0.06$Å^3; $Z = 4$; $V^o_{elec.cell} = 640.80\pm0.02$Å^3; $\rho_{roent.} = 4.0$ g/cm^3; $\rho_{pick.} = 3.90\pm0.02$ g/cm^3; $LaLi_2NiCuMnO_6$ — $a = 13.83\pm0.02$Å; $V^o = 2644.16\pm0.06$Å^3; $Z = 4$; $V^o_{elec.cell} = 661.04\pm0.02$Å^3; $\rho_{roent.} = 4.03$ g/cm^3; $\rho_{pick} = 3.99\pm0.01$ g/cm^3 [16, 17].

The thermal capacity of compounds was investigated on IT-S-400 calorimeter in the interval of 298.15–673 K. Calibration of the device was performed using copper standard, and checking operation — measurement of thermal capacity of α-Al_2O_3. The specific thermal capacity ($C_{p(specific)}$) was measured at each temperature every 25 K from which the mole thermal capacity ($C^o_{p\ (m)}$) was calculated. The procedure of experiments is in detail described in [18]. Our similar researches on this calorimeter were performed in [10–15, 19]. Table 1 demonstrates below the results of calorimetric researches.

Table 1

Experimental values of thermal capacities of $LaLi_2CoCuMnO_6$ and $LaLi_2NiCuMnO_6$

[$C_{p(specific)} \pm \bar{\delta}$, J/(g·K); $C^o_{p(m)} \pm \overset{0}{\Delta}$, J/(mol·K)]

T, K	$LaLi_2CoCuMnO_6$		$LaLi_2NiCuMnO_6$	
	$C_{p(specific)} \pm \bar{\delta}$	$C^o_{p(m)} \pm \overset{0}{\Delta}$	$C_{p(specific)} \pm \bar{\delta}$	$C^o_{p(m)} \pm \overset{0}{\Delta}$
298.15	0.6022±0.0056	257±7	0.5962±0.0183	254±22
323	0.7895±0.0077	336±9	0.7704±0.0130	328±15
348	0.8035±0.0081	342±10	0.8730±0.0058	372±7
373	0.8384±0.0077	357±9	0.9014±0.0099	384±12
398	0.8736±0.0072	372±9	0.8199±0.0139	349±16
423	0.8233±0.0204	351±24	0.9554±0.0138	407±16
448	0.9887±0.0084	421±10	0.9975±0.0098	425±12
473	1.0365±0.0107	442±13	1.0553±0.0154	450±18
498	1.0468±0.0108	446±13	1.0689±0.0187	455±22
523	1.0678±0.0141	455±17	1.1006±0.0208	469±25
548	1.0917±0.0130	465±15	1.1132±0.0120	474±14
573	1.1136±0.0082	475±10	1.1465±0.0186	488±22
598	1.1293±0.0112	481±13	1.0405±0.0168	443±20
623	1.1428±0.0078	487±9	1.1089±0.0261	472±31
648	1.1588±0.0127	494±15	1.1314±0.0152	482±18
673	1.1751±0.0052	501±6	1.1691±0.0185	498±22

Results and Discussion

Results of the calorimetric researches in Figure 1 and Table 1 show that there were defined the anomalies changes of thermal capacity probably connected with II-type phase transitions on the curve of dependence $C^o_p \sim f(T)$ for $LaLi_2CoCuMnO_6$ at 398 K, and $LaLi_2NiCuMnO_6$ at 373 K and 573 K. These transitions might be caused with Schottky effects, changes of magnetic resistance, conductivity, dielectric permeability, existence of Curie and Neel points, etc. Including temperatures of phase transitions the equations of temperature dependence of thermal capacity were set up for $LaLi_2CoCuMnO_6$ [J/(mol·K)]:

$$C^o_{p(1)} = (1284\pm37) - (1454.1\pm41.9)\cdot10^{-3}T - (527.7\pm15.2)\cdot10^{5}T^{-2}, \ (298.15\text{–}398\ \text{K}); \quad (1)$$

$$C^o_{p(2)} = (714\pm21) - (857.7\pm24.7)\cdot10^{-3}T, \ (398\text{–}423\ \text{K}); \quad (2)$$

$$C^{\circ}_{p(3)} = (959\pm28) - (430.6\pm12.4)\cdot10^{-3}T - (761.8\pm21.9)\cdot10^{5}T^{-2}, (423\text{–}673\ \text{K}) \quad (3)$$

and for $LaLi_2NiCuMnO_6$ [J/(mol·K)]:

$$C^{\circ}_{p(1)} = (2402.31\pm105.7) - (3540.0\pm155.76)\cdot10^{-3}T - (971.0\pm42.72)\cdot10^{5}T^{-2}, (298.15\text{–}373\ \text{K}); \quad (4)$$

$$C^{\circ}_{p(2)} = (902.0\pm39.69) - (1388.80\pm61.11)\cdot10^{-3}T, (373\text{–}398\ \text{K}); \quad (5)$$

$$C^{\circ}_{p(3)} = (915.07\pm40.26) - (403.53\pm17.76)\cdot10^{-3}T - (641.86\pm28.24)\cdot10^{5}T^{-2}, (398\text{–}573\ \text{K}); \quad (6)$$

$$C^{\circ}_{p(4)} = (1522.45\pm66.99) - (1804.72\pm79.41)\cdot10^{-3}T, (573\text{–}598\ \text{K}); \quad (7)$$

$$C^{\circ}_{p(5)} = (635.83\pm27.98) + (70.76\pm3.11)\cdot10^{-3}T - (840.05\pm36.96)\cdot10^{5}T^{-2}. (598\text{–}673\ \text{K}). \quad (8)$$

The standard entropy of $LaLi_2CoCuMnO_6$ and $LaLi_2NiCuMnO_6$ was calculated with system of ionic entropy increments according to [20].

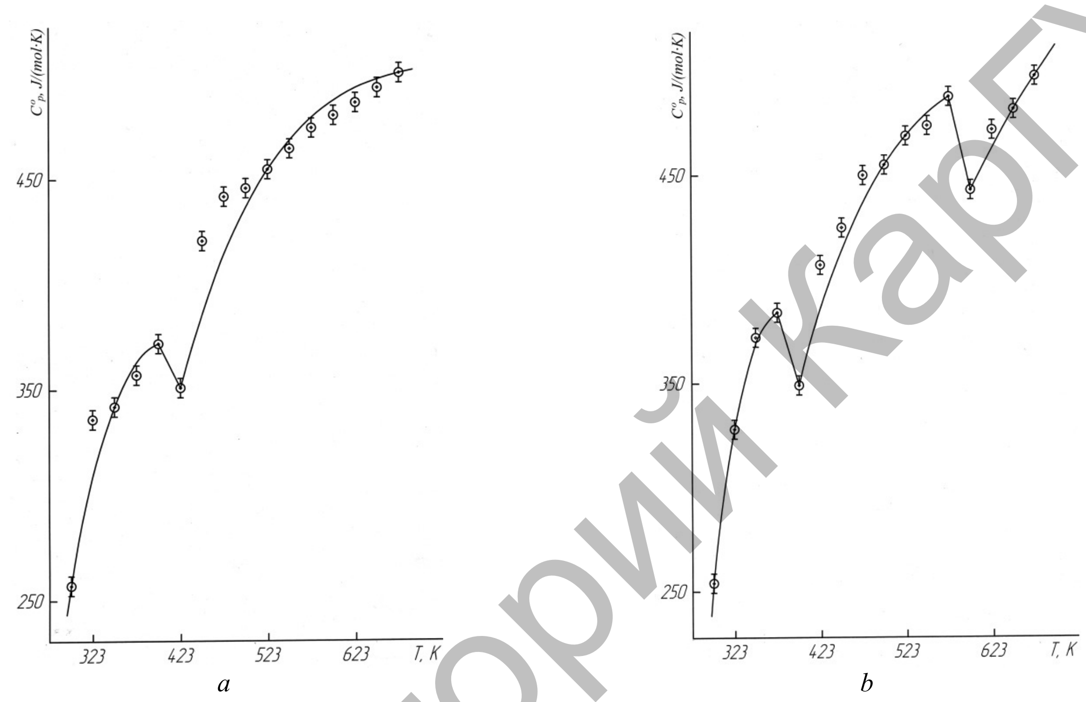

Figure. Dependence of thermal capacity of $LaLi_2CoCuMnO_6$ (*a*) and $LaLi_2NiCuMnO_6$ (*b*) on temperature in the interval of 298.15–673 K

Referring to the experimental data on $C^{\circ}_p(T)$ and calculated values of standard entropies of $S^{\circ}(298.15)$ the temperature dependences of the thermodynamic functions of $H^{\circ}(T)$–$H^{\circ}(298.15)$, $S^{\circ}(T)$ and $\Phi^{xx}(T)$ were calculated. Their values are presented in Table 2. Errors of thermodynamic functions were calculated using errors of the experimental data on $C^{\circ}_p(T)$ and calculated values of $S^{\circ}(298.15)$.

Table 2

Thermodynamic functions of $LaLi_2CoCuMnO_6$ and $LaLi_2NiCuMnO_6$

T, K	$LaLi_2CoCuMnO_6$				$LaLi_2NiCuMnO_6$			
	$C^{\circ}_p(T)$, J/(mol·K)	$S^{\circ}(T)$, J/(mol·K)	$H^{\circ}(T)$–H°(298.15), kJ/mol	$\Phi^{xx}(T)$, J/(mol·K)	$C^{\circ}_p(T)$, J/(mol·K)	$S^{\circ}(T)$, J/(mol·K)	$H^{\circ}(T)$–$H^{\circ}(298.15)$, kJ/mol	$\Phi^{xx}(T)$, J/(mol·K)
298	257±7	248±7	–	248±15	254±11	239±7	–	239±18
300	262±8	250±15	520±15	248±15	261±11	241±18	515±20	239±18
350	345±10	298±18	15970±460	252±15	371±16	291±21	16870±740	243±18
400	373±11	345±20	34070±980	261±15	346±15	341±25	35450±1560	252±19
450	389±11	389±23	52370±1510	273±16	417±18	386±29	54790±2410	265±20
500	439±13	433±25	73160±2107	286±17	457±20	433±32	76700±3370	279±21
550	470±13	476±28	95940±2760	302±18	481±21	477±35	100190±4410	295±22
600	489±14	518±30	107840±3100	318±19	440±19	519±38	123870±5450	312±23
650	499±14	557±33	131160±3780	335±20	483±21	556±41	147100±6470	329±24
675	501±14	576±34	157180±4520	343±20	499±22	574±42	159390±7010	338±25

The standard enthalpies of formation $\Delta_f H^o(298.15)$ of $LaLi_2CoCuMnO_6$ and $LaLi_2CoCuMnO_6$ calculated by the method developed by us are equal to 2934.3 and 2935.3 to kJ/mol, respectively [21].

Conclusions

The isobaric thermal capacity of new nanodimensional (nanocluster) cobalt-cuprate-manganite and nickelite-cuprate-manganite of lanthanum and lithium of structures $LaLi_2CoCuMnO_6$ and $LaLi_2NiCuMnO_6$ was investigated in the interval of 298.15–673 K. Temperatures of II-type phase transitions were determined. The equations describing temperature dependences of thermal capacity compounds were set up with the help of temperatures of phase transitions.

The temperature dependences of the thermodynamic functions $S^o(T)$, $H^o(T)$–$H^o(298,15)$ and $\Phi^{xx}(T)$ of cobalt-cuprate-manganite and nickelite-cuprate-manganite were calculated on the basis of the experimental data on $C^o_p(T)$ and calculated values of $S^o(298.15)$ in the interval of 298.15–675 K.

Research results are of interest to the physical and chemical modeling of the directed synthesis of obtained and similar compounds, used as basic data for the fundamental reference books and databanks and have an importance for physical chemistry of oxide materials and prediction of valuable physical and chemical properties of cobalt (nickelite)-cuprate-manganites.

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298,15–673 К аралығында жаңа наномөлшерлі кобальт-купрат-манганиті $LaLi_2CoCuMnO_6$ мен $LaLi_2NiCuMnO_6$ никелит-купрат-манганитінің жылусыйымдылығы және олардың термодинамикалық қасиеттері

298,15–673 К аралығында динамикалық калориметрия әдісімен алғаш рет синтездеп алған жаңа наномөлшерлі $LaLi_2CoCuMnO_6$ мен $LaLi_2NiCuMnO_6$ құрамды кобальт-купрат-манганит пен никелит-купрат-манганитінің меншікті жылусыйымдылықтары зерттелді. Меншікті жылусыйымдылықтардан олардың мольдік жылусыйымдылықтары есептелінді. $LaLi_2CoCuMnO_6$ 398 К және $LaLi_2NiCuMnO_6$ 373 К мен 573 К температурасында II-ші реттегі фазалық өзгерістер анықталды. Фазалық өзгерістердің температураларын ескере отырып, жылусыйымдылықтардың теңдеулері қорытылып шығарылды. Барлық алынған тәжірибелік және есептеу нәтижелері математикалық статистика әдістерімен нақты түрде өңделді, меншікті жылусыйымдылықтарының орташа мәндері орташі квадраттық ауытқушылықтармен, ал мольдік жылу сыйымдылықтары ауытқушылықтың кездейсоқтық құрамымен анықталды. Иондық инкрементер әдісімен зерттеліп отырған қосылыстардың стандарттық энтропиялары есептелді. Жылусыйымдылықтарының тәжірибелік және стандарттық энтропиялардың есептеу мәндерінің негізінде 298,15–673 К аралығында 50 К сайын энтальпияның $H^o(T)–H^o(298,15)$, энтропияның $S^o(T)$ және келтірілген термодинамикалық потенциалдық $\Phi^{xx}(T)$-тің температураға тәуелділіктері есептелді.

Кілт сөздері: термодинамика, кобальт, никелит, купрат, манганит, жылусыйымдылық, калориметрия, лантан, сілтілік металдар.

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Теплоемкость новых наноразмерных кобальто-купрато-манганита $LaLi_2CoCuMnO_6$ и никелито-купрато-манганита $LaLi_2NiCuMnO_6$ в интервале 298,15–673 К и их термодинамические свойства

Методом динамической калориметрии в интервале температур 298,15–673 К впервые исследованы удельные теплоемкости полученных нами новых наноразмерных кобальто-купрато-манганита и никелито-купрато-манганита лантана и лития составов $LaLi_2CoCuMnO_6$ и $LaLi_2NiCuMnO_6$. Из удельных теплоемкостей рассчитаны их мольные теплоемкости. Установлено, что $LaLi_2CoCuMnO_6$ при 398 К и $LaLi_2NiCuMnO_6$ при 373 К и 573 К претерпевают фазовые переходы II-рода. С учетом температур фазовых переходов выведены уравнения температурной зависимости теплоемкости. Все полученные экспериментальные и расчетные данные обработаны строго методами математической статистики, для усредненных значений удельных теплоемкостей рассчитаны среднеквадратичные отклонения, а для мольных теплоемкостей — случайные составляющие погрешности. Методом ионных инкрементов вычислены стандартные энтропии исследуемых соединений. На основе опытных данных по теплоемкостям и расчетных значений стандартных энтропий в интервале 298,15–675 К шагом через 50 К вычислены температурные зависимости энтальпии $H^o(T)$–$H^o(298,15)$, энтропии $S^o(T)$ и приведенного термодинамического потенциала $\Phi^{xx}(T)$.

Ключевые слова: термодинамика, кобальт, никелит, купрат, манганит, теплоемкость, калориметрия, лантан, литий.

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