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SHORT COMMUNICATIONS

Calorimetric Studies of LaM_2NiMnO_5 (M—Li, Na, K) Nickelite-Manganite Heat Capacity within the Temperature Range of 298.15–673 K

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Abstract—By means of the calorimetric method, we investigate the LaM_2NiMnO_5 (M—Li, Na, K) nickelite-manganite heat capacities within the range of 298.15–673 K. For the studied compounds, within the stated temperature range, we reveal the λ-like effects respective to the second kind phase transition at 323 and 498 K for compounds containing Li, 323 K and 523 K for compounds containing Na, and 448 K for those containing K. Taking into consideration the phase transition temperatures, we derive the equations of the temperature dependence of the compound heat capacity. On the basis of the experimental values of the heat capacities as well as of the calculation data on the nickelite-manganite standard entropy, we calculate the temperature dependences of the heat capacity, the entropy, the enthalpy, and the reduced thermodynamic potential.

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INTRODUCTION

Increased attention to rare-earth manganites is due to their use in current sensors, magnetic field, pressure, and temperature. Of particular interest is the substitution of manganese by ions of other transition metals (Cr, Fe, Co, Ni, Cu). Substitution of the Mn^{3+} ions by the Ni^{3+} ions results in a reduction of the lattice parameter, *a*, and the phase transition temperatures due to infringement of the super-exchange interactions between the different valency manganese ions, Mn^{3+} and Mn^{4+} [1].

The present work is aimed at a calorimetric study of the heat capacity and at the calculation of thermodynamic functions of the LaM_2NiMnO_5 (M—Li, Na, K) nickelite-manganites.

EXPERIMENTAL

We performed synthesis by applying ceramic technology from the following initial substances: La_2O_3 (extra pure), NiO (extra pure), carbonates of the respective alkali metals (pure for analysis), and Mn_2O_3 (pure for analysis). We thoroughly mixed the stoichiometric quantities of the nickelite-manganites, grinded them, and annealed in a SNOL oven at 800–1200°C for 20 h. The low-temperature annealing at 400°C lasted 10 h. Through the X-ray technique, we ascertained that the synthesized nickelite-manganites, LaM_2NiMnO_5 (M—Li, Na, K), crystallize in the cubic system.

By means of the IT-C-400 calorimeter, within the range of 298.15–673 K, we measured the unit then calculated the molar heat capacities of LaM_2NiMnO_5 (M—Li, Na, K). Device operation, calibration, and the data processing technique are presented in detail in [2–6].

Table 1 and the figure present, through $LaLi_2NiMnO_5$, the results of the calorimetric investigation of heat capacity of the compounds.

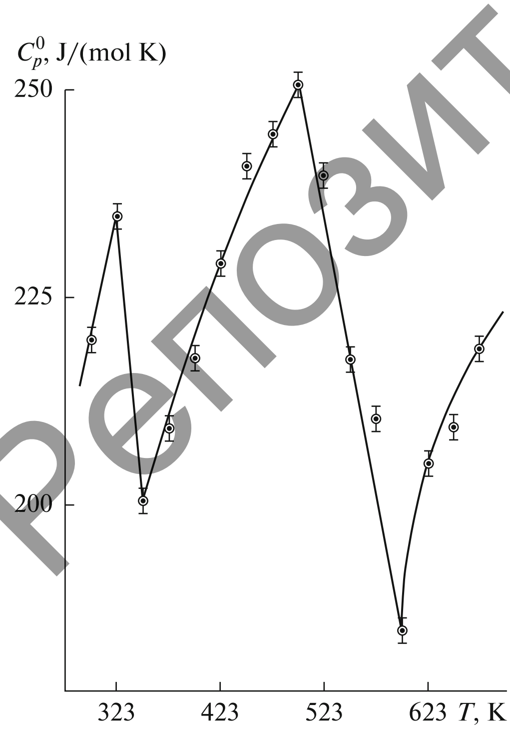
RESULTS AND DISCUSSION

From the data in Table 1 and the figure, we see that, in the curve of the $C_p^\circ \sim f(T)$ dependences, at 323 K and 498 K for $LaLi_2NiMnO_5$, at 323 K and 523 K for $LaNa_2NiMnO_5$, and at 448 K for LaK_2NiMnO_5, the λ-like effects are observed as possibly related to the second kind phase transitions. These transitions might be related to the cation redistributions, with variations of the thermal expansion coefficients, of magnetic moments of the synthesized nickelite-manganites, of inductive capacity, electrical resistivity, etc.

By means of mathematical processing of the experimental data with consideration to the phase transi-

Table 1. Experimental values of heat capacities of the nickelite-manganites, LaM_2NiMnO_5 (M—Li, Na, K)

T, K	$C_p \pm \bar{\delta}$, (J/g K)	$C_p^\circ \pm \overset{0}{\Delta}$, J/(mol K)]	T, K	$C_p \pm \bar{\delta}$, (J/g K)	$C_p^\circ \pm \overset{0}{\Delta}$, J/(mol K)]
1	2	3	4	5	6
		$LaLi_2NiMnO_5$			
298.15	0.63 ± 0.01	219 ± 11	498	0.72 ± 0.01	250 ± 11
323	0.68 ± 0.01	235 ± 9	523	0.69 ± 0.01	240 ± 11
348	0.58 ± 0.02	200 ± 15	548	0.63 ± 0.01	217 ± 7
373	0.60 ± 0.01	209 ± 7	573	0.61 ± 0.01	210 ± 13
398	0.63 ± 0.01	218 ± 7	598	0.53 ± 0.01	185 ± 10
423	0.66 ± 0.01	229 ± 14	623	0.59 ± 0.01	205 ± 7
448	0.70 ± 0.01	241 ± 11	648	0.60 ± 0.01	209 ± 7
473	0.71 ± 0.01	244 ± 14	673	0.63 ± 0.01	219 ± 7
		$LaNa_2NiMnO_5$			
298.15	0.60 ± 0.01	229 ± 11	498	0.82 ± 0.02	309 ± 17
323	0.70 ± 0.01	266 ± 7	523	0.83 ± 0.01	314 ± 11
348	0.65 ± 0.01	245 ± 7	548	0.78 ± 0.01	295 ± 9
373	0.57 ± 0.01	215 ± 7	573	0.72 ± 0.01	270 ± 11
398	0.52 ± 0.01	197 ± 7	598	0.64 ± 0.01	242 ± 10
423	0.72 ± 0.01	271 ± 8	623	0.78 ± 0.01	294 ± 11
448	0.79 ± 0.01	299 ± 11	648	0.81 ± 0.01	307 ± 8
473	0.80 ± 0.01	303 ± 7	673	0.83 ± 0.01	315 ± 11
		LaK_2NiMnO_5			
298.15	0.58 ± 0.01	240 ± 17	498	0.76 ± 0.01	313 ± 14
323	0.56 ± 0.01	229 ± 8	523	0.72 ± 0.01	295 ± 15
348	0.54 ± 0.01	223 ± 8	548	0.66 ± 0.01	272 ± 8
373	0.58 ± 0.02	239 ± 20	573	0.55 ± 0.01	224 ± 12
398	0.65 ± 0.01	267 ± 11	598	0.33 ± 0.01	135 ± 12
423	0.77 ± 0.01	318 ± 8	623	0.48 ± 0.01	199 ± 17
448	0.86 ± 0.01	355 ± 8	648	0.53 ± 0.02	216 ± 18
473	0.81 ± 0.0134	332 ± 15	673	0.57 ± 0.01	235 ± 9



Temperature dependence of the $LaLi_2NiMnO_5$ heat capacity.

tion temperatures, we derive the equations of the temperature dependence of the heat capacity of the nickelite-manganites, LaM_2NiMnO_5 (M—Li, Na, K). According to the data in Table 1 and the figure, the phase transitions are observed for all the nickelite-manganites; thus, the $C_p^\circ \sim f(T)$ dependence for the compounds is described by several equations with coefficients presented in Table 2.

Technical characteristics of the IT-C-400 calorimeter make it impossible to calculate the values of the standard entropies of the compounds from the experimental data on the heat capacities. Thus, we estimate them using the system of ion entropy increments [7]. Then, from known relations [8], within the range of 298.15–673 K, similarly to [9, 10], we calculate the temperature dependences of $C_p^\circ(T)$ and of entropy, $S^\circ(T)$; enthalpy, $H^\circ(T) - H^\circ(298.15)$; and the reduced thermodynamic potential, $\Phi^{xx}(T)$. The results are presented in Table 3. At the estimates of the $S^\circ(T)$ and $\Phi^{xx}(T)$ function errors, we took into consideration the errors of the $S^\circ(298.15)$ estimate (±3.0%).

Table 2. Equations for the temperature dependence of the nickelite-manganite heat capacities

Compound	Coefficients in equation $C_p^\circ = a + bT + cT^{-2}$, J/(mol K)			ΔT, K
	a	$b \times 10^{-3}$	$-c \times 10^5$	
$LaLi_2NiMnO_5$	43 ± 2	595 ± 28	–	298.15–323
	674 ± 32	–(1369 ± 66)	–	323–348
	200 ± 10	153 ± 7	64.13 ± 3	348–498
	578 ± 28	–(657 ± 31)	–	498–598
	276 ± 13	73 ± 3	481.14 ± 23	598–673
$LaNa_2NiMnO_5$	–(213 ± 7)	1484 ± 52	–	298.15–323
	561 ± 19	–(914 ± 32)	–	323–398
	1935 ± 67	–(2101 ± 73)	1427.52 ± 49	398–523
	816 ± 28	–(959 ± 33)	–	523–598
	4979 ± 173	–(4600 ± 160)	7102.36 ± 247	598–673
LaK_2NiMnO_5	337 ± 17	–(327 ± 17)	–	298.15–348
	–(1641 ± 85)	3659 ± 190	–(716.34 ± 37)	348–448
	2634 ± 137	–(3519 ± 183)	1410.36 ± 73	448–598
	294 ± 15	328 ± 17	1268.60 ± 66	598–673

Table 3. Thermodynamic functions of the nickelite-manganite

T, K	$C_p^\circ(T) \pm \mathring{\Delta}$, J/(mol K)	$S^\circ(T) \pm \mathring{\Delta}$, J/(mol K)	$H^\circ(T) - H^\circ(298.15) \pm \mathring{\Delta}$, J/mol	$\Phi^{xx}(T) \pm \mathring{\Delta}$, J/(mol K)
		$LaLi_2NiMnO_5$		
298	220 ± 10	191 ± 9	–	191 ± 9
300	221 ± 11	193 ± 15	440 ± 20	191 ± 15
350	198 ± 9	227 ± 18	11520 ± 550	194 ± 15
400	221 ± 11	255 ± 20	22110 ± 1060	200 ± 16
450	237 ± 11	282 ± 22	33600 ± 1610	207 ± 16
500	251 ± 12	308 ± 24	45820 ± 2200	216 ± 17
550	216 ± 10	330 ± 26	57460 ± 2760	226 ± 18
600	183 ± 9	347 ± 27	67460 ± 3240	235 ± 18
650	209 ± 10	363 ± 28	77360 ± 3710	244 ± 19
675	219 ± 10	371 ± 29	82720 ± 3970	249 ± 19
		$LaNa_2NiMnO_5$		
298	229 ± 8	231 ± 8	–	231 ± 8
300	232 ± 8	233 ± 15	460 ± 20	231 ± 15
350	241 ± 8	272 ± 18	13040 ± 450	234 ± 15
400	196 ± 7	301 ± 19	23960 ± 830	241 ± 16
450	284 ± 10	330 ± 21	36410 ± 1270	249 ± 16
500	313 ± 11	362 ± 23	51530 ± 1800	259 ± 17
550	288 ± 10	391 ± 25	66890 ± 2330	270 ± 17
600	240 ± 8	414 ± 27	80100 ± 2790	281 ± 18
650	308 ± 11	437 ± 28	94250 ± 3290	292 ± 19
675	315 ± 11	449 ± 29	102080 ± 3560	297 ± 19
		LaK_2NiMnO_5		
298.15	239 ± 12	257 ± 13	–	257 ± 13
300	239 ± 12	258 ± 21	480 ± 20	257 ± 21
350	223 ± 11	294 ± 24	12030 ± 620	259 ± 21
400	270 ± 14	326 ± 27	24160 ± 1250	266 ± 22
450	359 ± 19	363 ± 30	39740 ± 2060	274 ± 22
500	310 ± 16	398 ± 32	56530 ± 2930	285 ± 23
550	232 ± 12	424 ± 35	70220 ± 3640	297 ± 24
600	131 ± 7	440 ± 36	79380 ± 4120	308 ± 25
650	207 ± 11	459 ± 37	91040 ± 4720	319 ± 26
675	237 ± 12	468 ± 38	96590 ± 5010	324 ± 27

CONCLUSIONS

1. By means of the experimental dynamic calorimetry method, within the range of 298.15–673 K, we investigated the temperature dependences of the isobaric heat capacity of $LaLi_2NiMnO_5$, $LaNa_2NiMnO_5$, and LaK_2NiMnO_5 and determined their fundamental thermodynamic constants—the standard heat capacities.

2. For all the studied nickelite-manganites, within the taken temperature ranges, in the $C_p^\circ \sim f(T)$ curve, we ascertained the λ-like temperature dependences of the heat capacities related to the second kind phase transition.

3. Taking into consideration the phase transition temperatures, we derived the equations of the temperature dependence of the nickelite-manganite heat capacity.

4. By means of the ion increment technique, we calculated the standard entropies of the studied nickelite-manganites. Within the range of 298.15–673 K, we calculated the temperature dependences of the heat capacities, $C_p^\circ(T)$, and of the thermodynamic functions: entropy, $S^\circ(T)$, enthalpy, $H^\circ(T) - H^\circ(298.15)$, and the reduced thermodynamic potential, $\Phi^{xx}(T)$.

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