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Heat Capacity and Thermodynamic Functions of New Cobalt Manganites $NdM^I_2CoMnO_5$ (M^I = Li, Na, and K) in the Range of 298.15–673 K

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Abstract—Temperature dependences of the heat capacity of cobalt manganites $NdM^I_2CoMnO_5$ (M^I = Li, Na, and K) are studied by means of dynamic calorimetry in the range of 298.15–673 K. It is found that λ-shaped effects are observed on the $C_p^\circ \sim f(T)$ curve of cobalt manganites, due probably to second order phase transitions. Based on the experimental data, equations for the temperature dependences of the heat capacity of cobalt manganite are derived with allowance for the temperatures of phase transitions. The values of thermodynamic functions $H^\circ(T)–H^\circ(298.15)$, $S^\circ(T)$, and $\Phi^{xx}(T)$ are calculated.

Keywords: cobalt manganite, dynamic calorimetry, heat capacity, thermodynamic functions

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INTRODUCTION

Compounds with perovskite structure are of growing interest, due to their unique physical and physicochemical properties: high-temperature superconductivity, giant magnetoresistance, mixed electronic–ionic conductivity, and so on [1].

The aim of this work was to study the thermodynamic properties of new cobalt manganites $NdM^I_2CoMnO_5$ (M^I = Li, Na, K).

EXPERIMENTAL

Using ceramic technology, cobalt manganites $NdM^I_2CoMnO_5$ (M^I = Li, Na, and K) were synthesized from oxides of neodymium, cobalt(II), manganese(III), and carbonates of lithium, sodium, and potassium. High purity Nd_2O_3 and chemically pure oxides CoO and Mn_2O_3 were used as the initial materials, along with carbonates Li_2CO_3, Na_2CO_3, and K_2CO_3. Mixtures of these compounds based on their stoichiometric amounts in recalculating final formula $NdM^I_2CoMnO_5$ were thoroughly mixed and calcined at 600–1200°C for more than 40 h. Low-temperature annealing was performed at 400°C. Mass loss was observed only for CO_2. Since substances of more than 99% purity were used in the synthesis, we can claim with certainty that the resulting cobalt manganites were at least 99% pure.

X-ray powder diffraction studies of cobalt manganites were performed on a DRON-2.0 diffractometer. The X-ray powder diffraction patterns were indexed analytically [2]. The pycnometric density was determined as in [3]. By indexing the X-ray diffraction patterns, we established that the studied compounds crystallized in a cubic crystal system with lattice parameters a = 15.80, 15.34, and 16.70 Å; V^0 = 3942.68, 3610.31, and 4660.82 Å^3; V^0_{cell} = 657.11, 601.72, and 766.80 Å^3; Z = 6; $\rho_{X\text{-ray}}$ = 5.59, 5.40, and 5.14 g/cm^3; and ρ_{picn} = 5.61 ± 0.05, 5.43 ± 0.05, and 5.11 ± 0.03 g/cm^3 for M^I = Li, Na, and K, respectively. The isobaric specific heat of cobalt manganites $NdM^I_2CoMnO_5$ (M^I = Li, Na, and K) was studied at 298.15–673 K on an IT-S-400 calorimeter. The time of measuring over the temperature range of data processing was ~2.5 h. According to the unit's manufacturer, its maximum permissible error was ±10%. The unit was calibrated by determining thermal conductivity K_h of the heat meter [4–6]. This required experiments with a copper sample and an empty ampoule. The unit's operation was confirmed by determining

Table 1. Experimental values of the heat capacities of cobalt manganites $NdM^{I}_2CoMnO_5$ (M^I = Li, Na, and K) [$C_p \pm \bar{\delta}$, J/(g K); $C_p^\circ \pm \mathring{\Delta}$, J/(mol K)]

T, K	$C_p \pm \bar{\delta}$	$C_p^\circ \pm \mathring{\Delta}$	T, K	$C_p \pm \bar{\delta}$	$C_p^\circ \pm \mathring{\Delta}$
$NdLi_2CoMnO_5$ (sample weight, 1.2911 g; molar mass, 351.9902)			$NdNa_2CoMnO_5$ (sample weight, 1.944 g; molar mass, 384.0877)		
298.15	0.6061 ± 0.0072	213 ± 7	498	0.8305 ± 0.0152	319 ± 16
323	0.6138 ± 0.0111	216 ± 10	523	0.7684 ± 0.0167	295 ± 18
348	0.6465 ± 0.1186	228 ± 12	548	0.6403 ± 0.0192	246 ± 21
373	0.6927 ± 0.0015	244 ± 15	573	0.6866 ± 0.0195	264 ± 21
398	0.7518 ± 0.0091	265 ± 9	598	0.7304 ± 0.0150	281 ± 16
423	0.8125 ± 0.0122	286 ± 12	623	0.7603 ± 0.0091	292 ± 10
448	0.9139 ± 0.0141	322 ± 14	648	0.7786 ± 0.0126	299 ± 13
473	0.6944 ± 0.0146	244 ± 14	673	0.7987 ± 0.0096	307 ± 10
498	0.5856 ± 0.0140	206 ± 14	NdK_2CoMnO_5 (sample weight, 1.6392 g; molar mass, 416.3048)		
523	0.5383 ± 0.0175	190 ± 17	298.15	0.5469 ± 0.0123	228 ± 14
548	0.5792 ± 0.0148	204 ± 14	323	0.5676 ± 0.0085	236 ± 10
573	0.6165 ± 0.0151	217 ± 15	348	0.6213 ± 0.0080	259 ± 9
598	0.6369 ± 0.0017	224 ± 16	373	0.6422 ± 0.0134	267 ± 16
623	0.6819 ± 0.0168	240 ± 16	398	0.6859 ± 0.0171	286 ± 20
648	0.7018 ± 0.0202	247 ± 20	423	0.7436 ± 0.0138	310 ± 16
673	0.7243 ± 0.0209	255 ± 20	448	0.9256 ± 0.0161	385 ± 19
$NdNa_2CoMnO_5$ (sample weight, 1.944 g; molar mass, 384.0877)			473	0.7866 ± 0.0157	328 ± 18
298.15	0.5823 ± 0.0100	223 ± 11	498	0.6826 ± 0.0207	284 ± 24
323	0.5925 ± 0.0069	228 ± 7	523	0.6328 ± 0.0218	264 ± 25
348	0.64403 ± 0.0096	247 ± 10	548	0.5853 ± 0.0088	244 ± 10
373	0.6756 ± 0.0113	260 ± 12	573	0.5610 ± 0.0193	234 ± 22
398	0.7761 ± 0.0148	298 ± 16	598	0.5889 ± 0.0163	245 ± 19
423	0.9354 ± 0.0135	359 ± 14	623	0.6152 ± 0.0136	256 ± 16
448	0.9028 ± 0.0139	347 ± 15	648	0.6796 ± 0.0166	283 ± 19
473	0.8602 ± 0.0131	330 ± 14	673	0.7858 ± 0.0105	327 ± 12

the heat capacity of α-Al_2O_3. The resulting value of C_p°(298.15) for Al_2O_3 (76 ± 4 J/(mol K)) is in satisfactory agreement with the reference data (79 ± 2 J/(mol K) [7, 8]). Five parallel experiments were performed for each temperature (25 K step); the results were averaged and treated using mathematical statistics [9]. Standard deviations ($\bar{\delta}$) were calculated for specific heat values, while random error components ($\mathring{\Delta}$) were calculated for the molar heat capacities. Systematic error and errors in measuring temperature were not considered in our experiments, since they were negligible compared to the random components of error. The atomic weights of the elements were taken from [10] to calculate the molar masses.

RESULTS AND DISCUSSION

Table 1 and the Fig. 1 present the results from our calorimetric studies. On the basis of these data, it was established that abnormal X-shaped peaks are observed on the $C_p^\circ \sim f(T)$ dependences for $NdLi_2CoMnO_5$ in the ranges of 323–523, 323–548, and 298.15–573 K for M^I = Li, Na, and K, respectively, due probably to second order phase transitions. These transitions could result from, among other things, cation redistribution or changes in the thermal expansion coefficients, the magnetic moments of the synthesized cobalt manganite, the dielectric constant, and the electrical resistance.

Using the identified phase transition temperatures, we calculated the equations for the dependences of

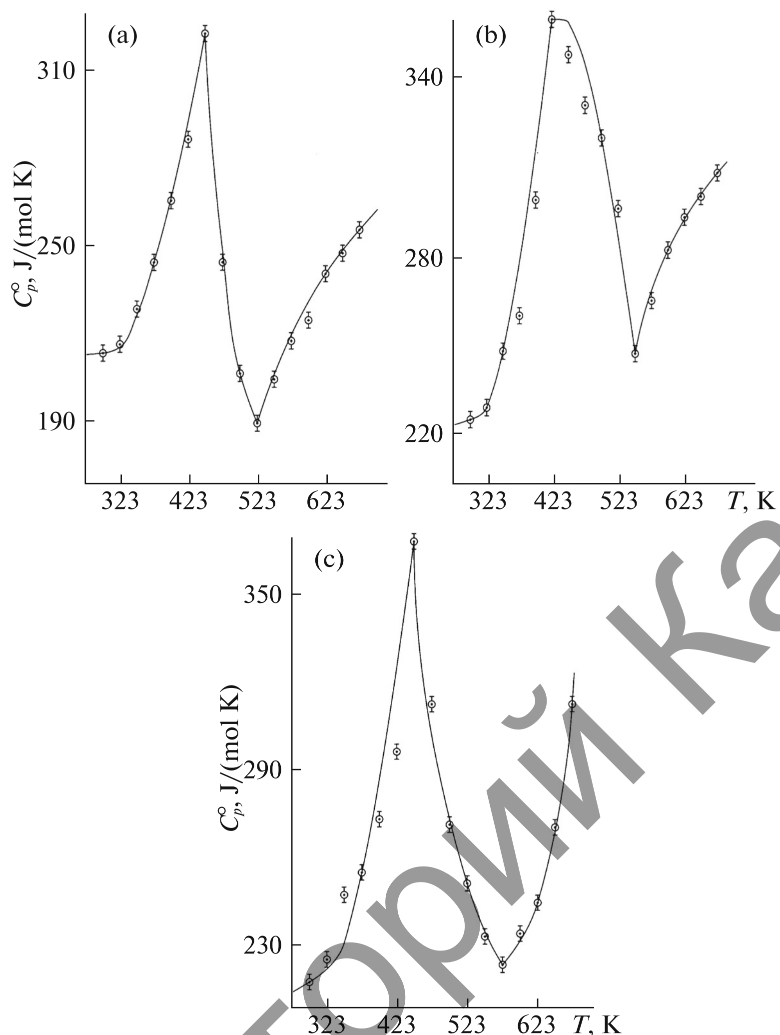

Fig. 1. Temperature dependences of the heat capacity of cobalt manganites: (a) $NdLi_2CoMnO_5$, (b) $NdNa_2CoMnO_5$, and (c) NdK_2CoMnO_5.

cobalt manganite: $C_p^\circ \sim f(T)$ (see Table 2). Due to the technical limitations of the IT-S-400 calorimeter, which prevented us from calculating S° (298.15) from the experimental data on $C_p^\circ(T)$ of the investigated compounds, we estimated them using the ion entropy increment system in [11].

The standard entropies of cobalt manganites was calculated using the equation

$$S^\circ(298.15)\mathrm{NdM}^{\mathrm{I}}_2\mathrm{CoMnO}_5 = S^{\mathrm{i}}(298.15)\mathrm{Nd}^{3+} + 2S^{\mathrm{i}}(298.15)\mathrm{M}^{+} + S^{\mathrm{i}}(298.15)\mathrm{Co}^{2+} + S^{\mathrm{i}}(298.15)\mathrm{Mn}^{3+} + 5S^{\mathrm{i}}(298.15)\mathrm{O}^{2-}, \quad (1)$$

where $S^{\mathrm{i}}(298.15)$ denotes the ion entropy increments; M^+ = Li, Na, and K. We used the following values of the ion entropy increments to calculate $S^\circ(298.15)$ of cobalt manganites [J/(mol K)]: $Li^+ = 14.5 \pm 4$, $Na^+ = 34.6 \pm 1.0$, $K^+ = 47.2 \pm 1.4$, $Nd^{3+} = 48.2 \pm 1.4$, $Co^{2+} = 37.6 \pm 1.1$, and $Mn^{3+} = 34.7 \pm 1.0$ [10].

Using the familiar relations of the experimental data on $C_p^\circ \sim f(T)$ and the estimated value of $S^\circ(298.15)$ with a 25 K step, we calculated the temperature dependences of $C_p^\circ(T)$ along with thermodynamic functions $H^\circ(T)$–$H^\circ(298.15)$, $S^\circ(T)$, and $\Phi^{xx}(T)$ (see Table 3). It should be noted that the reduced potential function $\Phi^{xx}(T)$ is very useful in calculating the standard heat effect of the chemical reactions according to the third law of thermodynamics, starting from 298.15 K [11].

CONCLUSIONS

The isobaric heat capacity of cobalt manganites $NdM^{\mathrm{I}}_2CoMnO_5$ (M^{I} = Li, Na, and K) were investi-

Table 2. Coefficients of the equations for the temperature dependence of specific heats C_p°, J/(mol K)= $a + bT + cT^{-2}$

Compound	A	$b \times 10^{-3}$	$c \times 10^5$	ΔT, K
$NdLi_2CoMnO_5$	$-(604 \pm 37)$	1784 ± 108	254 ± 15	298–448
	$-(4258 \pm 258)$	5595 ± 339	4160 ± 252	448–523
	487 ± 30	$-(147 \pm 9)$	$-(604 \pm 37)$	523–673
$NdNa_2CoMnO_5$	$-(1130 \pm 56)$	2971 ± 146	416 ± 21	298–423
	2564 ± 126	$-(3393 \pm 167)$	$-(1376 \pm 68)$	423–548
	978 ± 48	$-(601 \pm 30)$	$-(1211 \pm 60)$	548–673
NdK_2CoMnO_5	$-(1080 \pm 66)$	2804 ± 172.3	419 ± 26	298–448
	$-(1288 \pm 79)$	1670 ± 102	1859 ± 114	448–573
	$-(4079 \pm 251)$	4968 ± 305	4812 ± 296	573–673

Table 3. Thermodynamic functions of cobalt manganites in the range of 298.15–675 K [$C_p^\circ(T)$, $S^\circ(T)$, $\Phi^{xx}(T)$, J/(mol K); $H^\circ(T)-H^\circ(298.15)$, J/mol]

T, K	$C_p^\circ(T) \pm \mathring{\Delta}$	$S_p^\circ(T) \pm \mathring{\Delta}$	$H^\circ(T) - H^\circ(298.15) \pm \mathring{\Delta}$	$\Phi^{xx}(T) \pm \mathring{\Delta}$	T, K	$C_p^\circ(T) \pm \mathring{\Delta}$	$S_p^\circ(T) \pm \mathring{\Delta}$	$H^\circ(T) - H^\circ(298.15) \pm \mathring{\Delta}$	$\Phi^{xx}(T) \pm \mathring{\Delta}$
		$NdLi_2CoMnO_5$					$NdNa_2CoMnO_6$		
298.15	209 ± 13	208 ± 6	–	208 ± 6	500	317 ± 16	400 ± 32	60600 ± 3000	279 ± 22
300	213 ± 13	209 ± 19	400 ± 50	208 ± 19	525	283 ± 14	415 ± 33	68100 ± 4000	285 ± 23
325	216 ± 13	227 ± 21	5800 ± 300	209 ± 19	550	243 ± 12	427 ± 34	74700 ± 3700	291 ± 23
350	228 ± 14	243 ± 22	11300 ± 700	211 ± 19	575	267 ± 13	438 ± 35	81100 ± 4000	29 ± 24
375	245 ± 15	259 ± 24	17200 ± 1000	213 ± 19	600	282 ± 14	450 ± 36	88000 ± 4300	303 ± 24
400	268 ± 16	276 ± 25	23600 ± 1400	217 ± 20	625	293 ± 14	462 ± 37	95200 ± 4700	309 ± 25
425	295 ± 15	293 ± 27	30600 ± 1600	221 ± 20	650	301 ± 15	473 ± 38	102620 ± 5050	315 ± 25
450	324 ± 20	310 ± 28	38400 ± 2300	225 ± 20	675	307 ± 15	485±38	110200 ± 5400	322 ± 26
475	244 ± 15	325 ± 30	45300 ± 2700	230 ± 21			NdK_2CoMnO_5		
500	204 ± 12	337 ± 31	50800 ± 3100	235 ± 21	298.15	224 ± 14	273 ± 8	–	273 ± 8
525	189 ± 12	346 ± 31	55700 ± 3370	240 ± 22	300	227 ± 14	275 ± 25	450 ± 30	273 ± 25
550	207 ± 13	346 ± 31	60700 ± 3700	236 ± 21	325	228 ± 14	293 ± 27	6100 ± 400	274 ± 25
575	220 ± 13	356 ± 32	66000 ± 4000	241 ± 22	350	244 ± 15	310 ± 28	12000 ± 700	276 ± 25
600	231 ± 14	365 ± 33	71600 ± 4300	246 ± 22	375	270 ± 17	328 ± 30	18400 ± 1100	279 ± 26
625	241 ± 15	375 ± 34	77500 ± 4700	251 ± 23	400	304 ± 19	347 ± 32	25500 ± 1600	283 ± 26
650	249 ± 15	384 ± 35	83700 ± 5100	256 ± 23	425	344 ± 21	366 ± 34	33600 ± 2100	287 ± 26
675	255 ± 16	394 ± 36	90000 ± 5400	261 ± 24	450	389 ± 24	387 ± 35	42800 ± 2600	292 ± 27
		$NdNa_2CoMnO_6$			475	323 ± 20	406 ± 37	51600 ± 3200	298 ± 27
298.15	221 ± 11	248 ± 7	–	248 ± 7	500	289 ± 18	422 ± 39	59300 ± 3600	303 ± 28
300	223 ± 11	250 ± 20	450 ± 20	248 ± 20	525	262 ± 16	435 ± 40	66200 ± 4100	309 ± 28
325	229 ± 11	268 ± 21	6100 ± 300	249 ± 20	550	244 ± 15	447 ± 41	72500 ± 4460	315 ± 29
350	249 ± 12	286 ± 23	12000 ± 600	251 ± 20	575	233 ± 14	458 ± 42	78400 ± 4800	321 ± 29
375	280 ± 14	304 ± 24	18600 ± 900	254 ± 20	600	239 ± 15	468 ± 43	84300 ± 5200	327 ± 30
400	318 ± 16	323 ± 26	26100 ± 1300	258 ± 20	625	258 ± 16	478 ± 44	90500 ± 5600	333 ± 31
425	363 ± 18	343 ± 27	34600 ± 1700	260 ± 21	650	289 ± 18	488 ± 45	97300 ± 6000	339 ± 31
450	357 ± 18	364 ± 29	43600 ± 2100	267 ± 21	675	331 ± 20	500 ± 46	105000 ± 6400	345 ± 32
475	342 ± 17	383 ±30	52300 ±2600	273 ± 22					

gated experimentally for the first time in the 298.15–673 K temperature range.

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