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THERMOPHYSICAL PROPERTIES OF MATERIALS

Heat Capacity and Thermodynamic Functions of New Cobaltic Manganites $NdM^{II}_2CoMnO_6$ (M^{II} is Mg, Ca, Sr, or Ba) Within the Temperature Range of 298.15–673 K

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Abstract—The results of thermodynamic studies of the cobaltic manganites $NdM^{II}_2CoMnO_6$ (M^{II} is Mg, Ca, Sr, or Ba) are presented. In the calorimetric studies of the heat capacity within the range of 298.15–673 K, a second kind λ-shaped phase transitions in the $C_p(T)$ dependences was discovered: at the temperatures of 373 and 523 K for $NdMg_2CoMnO_6$; at 348 and 498 K for $NdCa_2CoMnO_6$; at 423 and 548 K for $NdSr_2CoMnO_6$; and at 323 and 498 K for $NdBa_2CoMnO_6$. We derive the equations for the temperature dependence of the heat capacity with account for these phase transitions. We calculate the temperature dependences of the thermodynamic functions: entropy, $S^0(T)$, enthalpy, $H^0(T) - H^0(298.15)$, and the reduced thermodynamic potential, $\Phi^{xx}(T)$, of the studied manganites.

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INTRODUCTION

Recently, interest has increased in study of the physicochemical properties of the cobaltites of lanthanum and other rare-earth elements due to the presence of the particular magnetic and electrical properties and high electrochemical and catalytic activity of these compounds. Thus, these compounds are widely applied as electrode materials for galvanic elements with a solid electrolyte, in ceramic membrane production to obtain pure oxygen from air, and also in spintronics [1–3].

Replacement of the lanthanum ion by a rare-earth ion results in ferromagnetism and metal-type conductivity in both types of oxide. The rare earth ion manganites and cobaltites show great magnetoresistance in the metamorphic phase transitions [4].

Synthesis of new compounds on the basis of cobaltite and manganite and study of their properties are an important task in both fundamental investigations and practical application.

In this work, we present the results of the calorimetric investigation of the heat capacity of new compounds with the composition $NdM^{II}_2CoMnO_6$ (M^{II} is Mg, Ca, Sr, or Ba). Then, we obtain the variations of the entropy, $S^0(T)$, the enthalpy, $H^0(T) - H^0(298.15)$, and the reduced thermodynamic potential, $\Phi^{xx}(T)$, necessary for the directed synthesis of similar phase compounds with the given composition, to reveal the second kind phase transitions in the curves of the temperature dependence of the heat capacity and to obtain the fundamental thermodynamic constants.

EXPERIMENT

We measured the specific heat capacities of the $NdM^{II}_2CoMnO_6$ (M^{II} is Mg, Ca, Sr, or Ba) compounds by means of the IT-S-400 calorimeter within the temperature range 298.15–673 K and then calculated the molar heat capacities. The duration of the measurement within the whole temperature range, with the experimental data processing, was within 2.5 h. The tolerated error limit was equal to ±10% [5, 6].

The cobaltic manganites of the composition described above are synthesized by means of the ceramic technology from chemically pure neodymium oxide (III), manganese oxide, and "pure for analysis" quality carbonates of magnesium, calcium, strontium, and barium.

Before the experiment, we calibrated the device: the calorimeter heat capacity, K_T, was determined experimentally. Here, we performed parallel experiments: five with the copper specimen and five with the empty ampoule. We tested the device operation by measuring the α-Al_2O_3 standard heat capacity; the measured value, 76.0 J/(mol K) is in satisfactory agreement with that recommended, 79.0 J/(mol K) [7].

Table 1. Experimental values of the $NdM^{II}_2CoMnO_6$ (M^{II} is Mg, Ca, Sr, or Ba) cobaltic manganite heat capacities: $C_{p(sp)} \pm \overline{\delta}$, J/(g K); $C^0_{p(m)} \pm \overset{0}{\Delta}$, J/(mol K)

T, K	$C_p \pm \overline{\delta}$	$C^0_p \pm \overset{0}{\Delta}$	T, K	$C_p \pm \overline{\delta}$,	$C^0_p \pm \overset{0}{\Delta}$
		$NdMg_2CoMnO_6$			
298.15	0.57 ± 0.01	230 ± 16	498	0.62 ± 0.01	249 ± 10
323	0.59 ± 0.01	239 ± 12	523*	0.72 ± 0.01	291 ± 13
348	0.64 ± 0.01	257 ± 10	548	0.68 ± 0.01	272 ± 12
373*	0.72 ± 0.01	292 ± 12	573	0.60 ± 0.01	243 ± 14
398	0.51 ± 0.01	207 ± 8	598	0.47 ± 0.01	188 ± 11
423	0.48 ± 0.01	191 ± 10	623	0.60 ± 0.01	240 ± 10
448	0.45 ± 0.01	182 ± 15	648	0.76 ± 0.01	307 ± 8
473	0.43 ± 0.01	172 ± 9	673	0.86 ± 0.01	345 ± 16
		$NdCa_2CoMnO_6$			
298.15	0.55 ± 0.01	240 ± 16	498*	0.78 ± 0.01	338 ± 15
323	0.69 ± 0.01	301 ± 9	523	0.73 ± 0.02	317 ± 24
348*	0.82 ± 0.01	357 ± 14	548	0.69 ± 0.01	299 ± 11
373	0.70 ± 0.01	306 ± 12	573	0.68 ± 0.01	293 ± 15
398	0.67 ± 0.01	290 ± 13	598	0.65 ± 0.01	283 ± 13
423	0.61 ± 0.01	266 ± 12	623	0.70 ± 0.01	305 ± 12
448	0.56 ± 0.01	244 ± 11	648	0.76 ± 0.01	330 ± 15
473	0.53 ± 0.01	232 ± 16	673	0.86 ± 0.01	375 ± 16
		$NdSr_2CoMnO_6$			
298.15	0.47 ± 0.01	248 ± 21	498	0.49 ± 0.01	262 ± 13
323	0.50 ± 0.01	266 ± 13	523	0.55 ± 0.01	290 ± 17
348	0.52 ± 0.01	277 ± 17	548*	0.57 ± 0.01	304 ± 10
373	0.56 ± 0.01	298 ± 10	573	0.47 ± 0.01	251 ± 15
398	0.59 ± 0.01	313 ± 15	598	0.52 ± 0.01	276 ± 17
423*	0.72 ± 0.01	380 ± 13	623	0.57 ± 0.01	303 ± 10
448	0.58 ± 0.01	309 ± 17	648	0.59 ± 0.01	312 ± 13
473	0.42 ± 0.01	222 ± 10	673	0.61 ± 0.01	325 ± 10
		$NdBa_2CoMnO_6$			
298.15	0.39 ± 0.01	248 ± 20	498*	0.33 ± 0.01	210 ± 8
323*	0.44 ± 0.01	278 ± 13	523	0.18 ± 0.01	116 ± 9
348	0.32 ± 0.01	203 ± 15	548	0.21 ± 0.01	130 ± 8
373	0.27 ± 0.01	171 ± 11	573	0.23 ± 0.01	145 ± 11
398	0.24 ± 0.01	152 ± 9	598	0.26 ± 0.01	161 ± 12
423	0.23 ± 0.01	144 ± 9	623	0.29 ± 0.01	184 ± 8
448	0.26 ± 0.01	162 ± 12	648	0.33 ± 0.01	207 ± 10
473	0.29 ± 0.01	184 ± 13	673	0.37 ± 0.01	234 ± 8

At each temperature (the step being equal to 25 K) for each compound, we performed five parallel experiments; then we averaged the results obtained and processed them by the methods of mathematical statistics. To average the specific and the molar heat capacity values, we calculated the mean square deviation, $\overline{\delta}$,

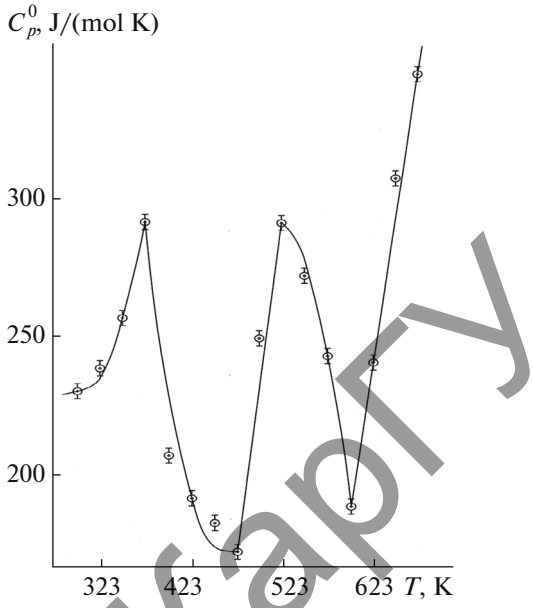
and the random constituents of the error, $\overset{0}{\Delta}$, for each temperature [8].

Table 1 and the figure show the results of the calorimetric study of the cobaltic manganite heat capacities for the example of $NdMg_2CoMnO_6$.

DISCUSSION

The measurement results show that the studied compounds undergo the lambda-shaped phase transitions of the second kind at the temperatures marked with an asterisk in Table 1. This might indicate the presence of a specific property. The phase transitions discovered might be related to the Schottky effect, to the Curie and the Néel points, to the permittivity and/or electrical resistance change, or to other peculiarities characteristic for such transitions.

With account for the phase transition temperatures obtained in the experiment (Table 1), we derive the equations of the temperature dependence of the cobaltic manganite heat capacities (Table 2).



Temperature dependence of the $NdMg_2CoMnO_6$ heat capacity.

Table 2. Equations for the temperature dependence of the heat capacity of cobaltic manganite, $NdM_2^{II}CoMnO_6$ (M^{II} is Mg, Ca, Sr, or Ba)

Compound	Coefficients of the equation $C_p^0 = a + bT + CT^{-2}$, J/(mol K)			ΔT, K
	a	b, 10^{-3}	$-c$, 10^5	
$NdMg_2CoMnO_6$	−(1378.6 ± 67.1)	3518.4 ± 172.1	497.7 ± 24.2	298–373
	−(2184 ± 106.3)	3387 ± 165.0	1685.9 ± 82.1	373–473
	−(952.6 ± 46.4)	2377.7 ± 115.6	–	473–523
	6257 ± 305	−(7605 ± 370)	−(5439.9 ± 264.9)	523–598
	−(1060.7 ± 51.6)	2088.4 ± 101.7	–	598–673
$NdCa_2CoMnO_6$	−(455.3 ± 21.6)	2332.9 ± 110.5	–	298–348
	−(51.7 ± 2.5)	220 ± 10.4	401.76 ± 19.022	348–473
	−(1778. ± 84)	4249.4 ± 201.2	–	473–498
	2.361 ± 0.11	189 ± 9	598.9 ± 28.36	498–598
	−(4999 ± 237)	5990.4 ± 283.6	6078.6 ± 287.8	598–673
$NdSr_2CoMnO_6$	−(1130 ± 55)	3002.4 ± 145.7	429.1 ± 20.8	298–423
	1041.7 ± 50.5	−(1732 ± 84)	–	423–473
	2177.7 ± 105.6	−(2134.1 ± 103.5)	−(2116.2 ± 102.7)	473–548
	1458.4 ± 70.7	−(2107.5 ± 102.2)	–	548–573
	2146.3 ± 104.1	−(1736.8 ± 84.3)	−(956 ± 143.4)	573–673
$NdBa_2CoMnO_6$	−(111 ± 7)	1205.5 ± 73.8	–	298–323
	−(1531.1 ± 93.7)	2642.6 ± 161.7	997.3 ± 61.1	323–423
	−(904 ± 55)	1858.2 ± 113.7	468.6 ± 28.7	423–498
	2090.4 ± 127.9	−(3775 ± 231)	–	498–523
	−(1217.9 ± 74.6)	1809 ± 111	1060.6 ± 64.9	523–673

Table 3. Calculated values of the thermodynamic functions of the cobaltic manganites

T, K	$C_p^0(T) \pm \overset{0}{\Delta}$, J/(mol K)	$S°(T) \pm \overset{0}{\Delta}$, J/(mol K)	$H°(T) - H°(298.15) \pm \overset{0}{\Delta}$, J/mol	$\Phi^{xx}(T) \pm \overset{0}{\Delta}$, J/(mol K)
		$NdMg_2CoMnO_6$		
298.15	229 ± 11	223 ± 7	–	223 ± 7
300	230 ± 11	225 ± 11	460 ± 20	224 ± 11
350	259 ± 13	262 ± 13	12400 ± 600	227 ± 11
400	225 ± 11	297 ± 15	25620 ± 1250	233 ± 11
450	173 ± 8	320 ± 16	35250 ± 1720	242 ± 12
500	236 ± 12	340 ± 17	44700 ± 2180	251 ± 12
550	276 ± 13	366 ± 18	58490 ± 2850	260 ± 13
600	183 ± 9	387 ± 19	70290 ± 3420	270 ± 13
650	297 ± 15	406 ± 20	82510 ± 4020	279 ± 14
675	349 ± 17	419 ± 20	90590 ± 4410	284 ± 14
		$NdCa_2CoMnO_6$		
298.15	239 ± 11	254.7 ± 8	–	254.7 ± 8
300	245 ± 12	256 ± 20	490 ± 20	255 ± 20
350	361 ± 17	303 ± 23	15630 ± 740	258 ± 20
400	287 ± 14	345 ± 27	31520 ± 1490	267 ± 21
450	246 ± 12	377 ± 29	44770 ± 2120	277 ± 21
500	347 ± 16	402 ± 31	56790 ± 2690	288 ± 22
550	305 ± 14	432 ± 33	72771 ± 3450	300 ± 23
600	284 ± 13	458 ± 35	87290 ± 4130	312 ± 24
650	334 ± 16	482 ± 37	102470 ± 4850	324 ± 25
675	379 ± 18	495 ± 38	111350 ± 5270	330 ± 26
		$NdSr_2CoMnO_6$		
298.15	244 ± 12	277 ± 13	–	277 ± 13
300	248 ± 12	278 ± 22	500 ± 20	277 ± 22
350	271 ± 13	318 ± 25	13210 ± 640	280 ± 22
400	339 ± 17	358 ± 28	28330 ± 1370	287 ± 23
450	262 ± 13	396 ± 31	44450 ± 2160	297 ± 23
500	264 ± 13	422 ± 33	56620 ± 2750	308 ± 24
550	299 ± 15	450 ± 35	71710 ± 2480	320 ± 25
600	283 ± 14	474 ± 37	85260 ± 4140	332 ± 26
650	318 ± 15	498 ± 39	100400 ± 4870	344 ± 27
675	325 ± 16	510 ± 40	108460 ± 5260	350 ± 27
		$NdBa_2CoMnO_6$		
298.15	243 ± 14	278 ± 8	–	278 ± 8
300	251 ± 15	280 ± 26	500 ± 30	278 ± 25
350	208 ± 13	319 ± 29	13070 ± 800	281 ± 26
400	149 ± 9	342 ± 31	21680 ± 1330	287 ± 26
450	164 ± 10	359 ± 33	28980 ± 1770	294 ± 27
500	203 ± 12	381 ± 35	39600 ± 2420	302 ± 28
550	128 ± 8	394 ± 36	46540 ± 2850	310 ± 28
600	162 ± 10	407 ± 37	53720 ± 3290	317 ± 29
650	209 ± 13	422 ± 38	62960 ± 3850	325 ± 30
675	236 ± 14	430 ± 39	68510 ± 4200	329 ± 30

By the ion increment method [9], we calculated the standard entropies of the investigated compounds.

Then, on the basis of the experimental data on the $C_p^0(T)$ and the calculated values of $S^0(298.15)$, according to the known expressions [10], we calculated the temperature dependences of the heat capacity, $C_p^0(T)$, and the thermodynamic functions: entropy, $S^0(T)$, enthalpy, $H^0(T) - H^0(298.15)$, and the reduced thermodynamic potential, $\Phi^{xx}(T)$, of the $NdM_2^{II}CoMnO_6$ (M^{II} is Mg, Ca, Sr, or Ba) cobaltic manganites (Table 3). Note that the $\Phi^{xx}(T)$ function is a very handy, correct, and reliable thermodynamic potential to calculate the chemical equilibrium according to the third law of thermodynamics. When estimating the errors of $S^0(T)$ and $\Phi^{xx}(T)$, we took into account the errors of the $S^0(298.15)$ estimation (±3.0).

CONCLUSIONS

(1) We investigated the temperature dependences of the $NdM_2^{II}CoMnO_6$ (M^{II} is Mg, Ca, Sr, or Ba) heat capacity by the calorimetric method and determined their standard values.

(2) In the curves of the temperature dependences of the heat capacity, we revealed the λ-shaped variations referred to as the phase transitions of the II kind. With account for the phase transition temperatures, we obtained the equations of the $C_p^0(T)$ dependences for the investigated compounds.

(3) We calculated the standard entropies of the studied manganites. With application of the experimental data on the heat capacities and the calculated $S^0(298.15)$ values, we calculated the temperature dependences of the thermodynamic functions of the compounds studied.

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