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CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Heat Capacities and Thermodynamic Functions of New Cobalt Manganites $LaM_2^{II}CoMnO_6$ (M^{II}—Mg, Ca, Sr, Ba) in the 298.15–673 K Temperature Range

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Abstract—Temperature dependences of the heat capacities of cobalt manganites $LaM_2^{II}CoMnO_6$ (M^{II} = Mg, Ca, Sr, Ba) are investigated by means of dynamic calorimetry in the temperature range of 298.15–673 K. It is established that cobalt manganites display λ-like effects on the $C_p^\circ \sim f(T)$ curve, which are likely to be related to the type II phase transitions. Equations for the temperature dependence of the heat capacity of cobalt manganites are derived from the experimental data with allowance for phase transition temperatures. The values of $C_p^\circ(T)$ and 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

The complex oxides of transition metals are a broad spectrum of compounds prepared on the basis of a *d*-metal (Mn, Cu, Co, ...) with addition of one or more cations. Such compounds have evoked interest due to the discovery of colossal magnetoresistance (CMR) in complex manganese oxides (manganites) at the beginning of the 1990s [1].

Cobalt oxides are currently used in solid oxide fuel cells, oxygen membranes, catalysts, and membrane reactors for the oxidation of hydrocarbons, gas sensors, and thermoelectric devices [2].

The synthesis and investigation of the physical and chemical properties of cobalt- and manganese-based compounds has evoked particular interest. Due to this, the aim of this work was to investigate the thermodynamic properties of new cobalt manganites with the composition $LaM_2^{II}CoMnO_6$ (M^{II} = Mg, Ca, Sr, Ba).

EXPERIMENTAL

Cobalt manganites with $LaM_2^{II}CoMnO_6$ (M^{II} = Mg, Ca, Sr, Ba) composition were synthesized by ceramic technology from oxides of lanthanum, cobalt (II) and manganese (III) and carbonates of alkaline earth metals. Ultrapure La_2O_3 and chemically pure CoO, Mn_2O_3, $MgCO_3$, $CaCO_3$, $SrCO_3$, $BaCO_3$ were used. The above substances were mixed in stoichiometric quantities according to the $LaM_2^{II}CoMnO_6$ (M^{II} = Mg, Ca, Sr, Ba) composition of the resulting product and were annealed in a SNOL muffle furnace in the 600–1200°C temperature range for more than 40 h. Low-temperature annealing was performed at 400°C. Weight loss occurred only due to CO_2 formation. Since ultrapure and chemically pure compounds were used (>99% purity), we can confidently state that the resulting cobalt manganites had equal purity.

Table 1. Experimental values of the heat capacities of $LaM^{II}_2CoMnO_6$ (M^{II}—Mg, Ca, Sr, Ba) cobalt manganites

T, K	$C_p \pm \bar{\delta}$, J/(g K)	$C_p^\circ \pm \mathring{\Delta}$, J/(mol K)	T, K	$C_p \pm \bar{\delta}$, J/(g K)	$C_p^\circ \pm \mathring{\Delta}$, J/(mol K)
$LaMg_2CoMnO_6$			$LaSr_2CoMnO_6$		
298.15	0.5774 ± 0.0198	229 ± 22	298.15	0.4722 ± 0.0107	231 ± 19
323	0.6262 ± 0.0134	249 ± 15	323	0.5107 ± 0.0075	268 ± 11
348	0.7050 ± 0.0114	280 ± 13	348	0.5399 ± 0.0113	283 ± 17
373	0.5040 ± 0.0131	200 ± 15	373	0.5807 ± 0.0164	304 ± 24
398	0.4793 ± 0.01174	191 ± 13	398	0.4142 ± 0.0141	217 ± 21
423	0.4328 ± 0.0099	172 ± 11	423	0.2954 ± 0.0097	155 ± 14
448	0.4898 ± 0.0094	195 ± 10	448	0.4004 ± 0.0076	210 ± 11
473	0.5353 ± 0.0103	213 ± 11	473	0.4360 ± 0.0084	229 ± 12
498	0.5164 ± 0.0101	205 ± 11	498	0.4694 ± 0.0086	246 ± 13
523	0.4546 ± 0.0140	181 ± 15	523	0.5124 ± 0.0145	269 ± 21
548	0.3767 ± 0.0074	150 ± 8	548	0.4448 ± 0.0120	233 ± 18
573	0.3302 ± 0.0067	131 ± 7	573	0.4147 ± 0.0077	217 ± 11
598	0.3640 ± 0.0054	145 ± 6	598	0.3376 ± 0.0081	177 ± 12
623	0.4188 ± 0.0073	166 ± 8	623	0.5197 ± 0.0084	272 ± 12
648	0.5230 ± 0.0110	208 ± 12	648	0.5614 ± 0.0115	294 ± 17
673	0.6298 ± 0.0080	250 ± 9	673	0.5826 ± 0.0078	305 ± 11
$LaCa_2CoMnO_6$			$LaBa_2CoMnO_6$		
298.15	0.5571 ± 0.0177	239 ± 21	298.15	0.3892 ± 0.0119	243 ± 21
323	0.6488 ± 0.0087	278 ± 10	323	0.4106 ± 0.0076	256 ± 13
348	0.6725 ± 0.0137	288 ± 16	348	0.4265 ± 0.0049	266 ± 8
373	0.6980 ± 0.0085	299 ± 10	373	0.4560 ± 0.0074	284 ± 13
398	0.5442 ± 0.0091	233 ± 11	398	0.5158 ± 0.0094	322 ± 16
423	0.4771 ± 0.0085	205 ± 10	423	0.3863 ± 0.0044	241 ± 8
448	0.4500 ± 0.0104	193 ± 12	448	0.3456 ± 0.0103	215 ± 18
473	0.5099 ± 0.0132	219 ± 16	473	0.3182 ± 0.0076	198 ± 13
498	0.6292 ± 0.0113	227 ± 7	498	0.2772 ± 0.0078	173 ± 14
523	0.7314 ± 0.0146	314 ± 17	523	0.2943 ± 0.0082	184 ± 14
548	0.5846 ± 0.0145	251 ± 17	548	0.3110 ± 0.0091	194 ± 16
573	0.4893 ± 0.0136	210 ± 16	573	0.3451 ± 0.0070	215 ± 12
598	0.5310 ± 0.0153	228 ± 18	598	0.3664 ± 0.0073	228 ± 13
623	0.5645 ± 0.0087	242 ± 10	623	0.3943 ± 0.0068	246 ± 12
648	0.5846 ± 0.0154	251 ± 18	648	0.4577 ± 0.0087	285 ± 15
673	0.6125 ± 0.0127	263 ± 15	673	0.5014 ± 0.0071	313 ± 12

Table 2. Equation coefficients of the heat capacity temperature dependeces for cobalt manganites $C_p^\circ = a + bT + cT^{-2}$, J/(mol K)

a	$b \times 10^{-3}$	$c \times 10^5$	ΔT, K
$LaMg_2CoMnO_6$			
−(73 ± 4)	1014 ± 60	–	298–348
−(4235 ± 250)	7207 ± 425	2431 ± 143	348–423
−(173 ± 10)	814 ± 48	–	423–473
1553 ± 92	−(2028 ± 120)	−(852 ± 50)	473–573
−(4346 ± 256)	5243 ± 309	4836 ± 285	573–673
$LaCa_2CoMnO_6$			
1657 ± 99	−(2474 ± 148)	−(604 ± 36)	298–373
−(2530 ± 151)	4020 ± 240	1850 ± 110	373–448
−(528 ± 32)	1610 ± 100	–	448–523
1400 ± 83	−(2080 ± 124)	–	523–573
820 ± 49	−(446 ± 27)	−(1163 ± 69)	573–673
$LaSr_2CoMnO_6$			
128 ± 8	548 ± 34	−(39 ± 2)	298–373
1420 ± 90	−(2991 ± 190)	–	373–423
1190 ± 76	−(991 ± 63)	−(1101 ± 70)	423–523
908 ± 58	−(1222 ± 78)	–	523–598
15760 ± 1000	−(15690 ± 995)	−(22176 ± 1407)	573–673
$LaBa_2CoMnO_6$			
−(372 ± 22)	1512 ± 88	146 ± 9	298–398
−(1655 ± 97)	2319 ± 135	1669 ± 97	398–498
−(1018 ± 59)	1695 ± 99	860 ± 50	498–623

The XRD patterns of the prepared cobalt manganites were measured on a DRON 2 diffractometer. The XRD data were indexed using analytical method in [3]. Pycnometric density was determined as described in [4].

RESULTS AND DISCUSSION

From the indexing of the X-ray diffraction patterns, it was determined that the obtained materials crystallize in a monoclinic lattice with the following parameters: $LaMg_2CoMnO_6$: $a = 16.761 \pm 0.062$ Å, $V^\circ = 4708.69 \pm 0.019$ Å^3, $Z = 6$, $V^\circ_{u.c} = 787.78 \pm 0.03$ Å^3, $\rho_{X\text{-ray}} = 5.78$, $\rho_{pycnom} = 5.84 \pm 0.10$ g/cm^3; $LaCa_2CoMnO_6$: $a = 16.650 \pm 0.026$ Å, $V^\circ = 4609.11 \pm 0.06$ Å^3, $Z = 6$, $V^\circ_{u.c} = 768.19 \pm 0.01$ Å^3, $\rho_{X\text{-ray}} = 5.63$, $\rho_{pycnom} = 5.56 \pm 0.10$ g/cm^3; $LaSr_2CoMnO_6$: $a = 16.711 \pm 0.034$ Å, $V^\circ = 4666.59 \pm 0.09$Å^3, $Z = 6$, $V^\circ_{u.c} = 777.77 \pm 0.02$ Å^3, $\rho_{X\text{-ray}} = 6.44$, $\rho_{pycnom} = 6.37 \pm 0.11$ g/cm^3; $LaBa_2CoMnO_6$: $a = 16.840 \pm 0.030$ Å^3, $V^\circ = 4775.58 \pm 0.09$ Å^3, $Z = 6$, $V^\circ_{u.c} = 795.3 \pm 0.02$ Å^3, $\rho_{X\text{-ray}} = 7.09$, $\rho_{pycnom} = 6.95 \pm 0.09$ g/cm^3.

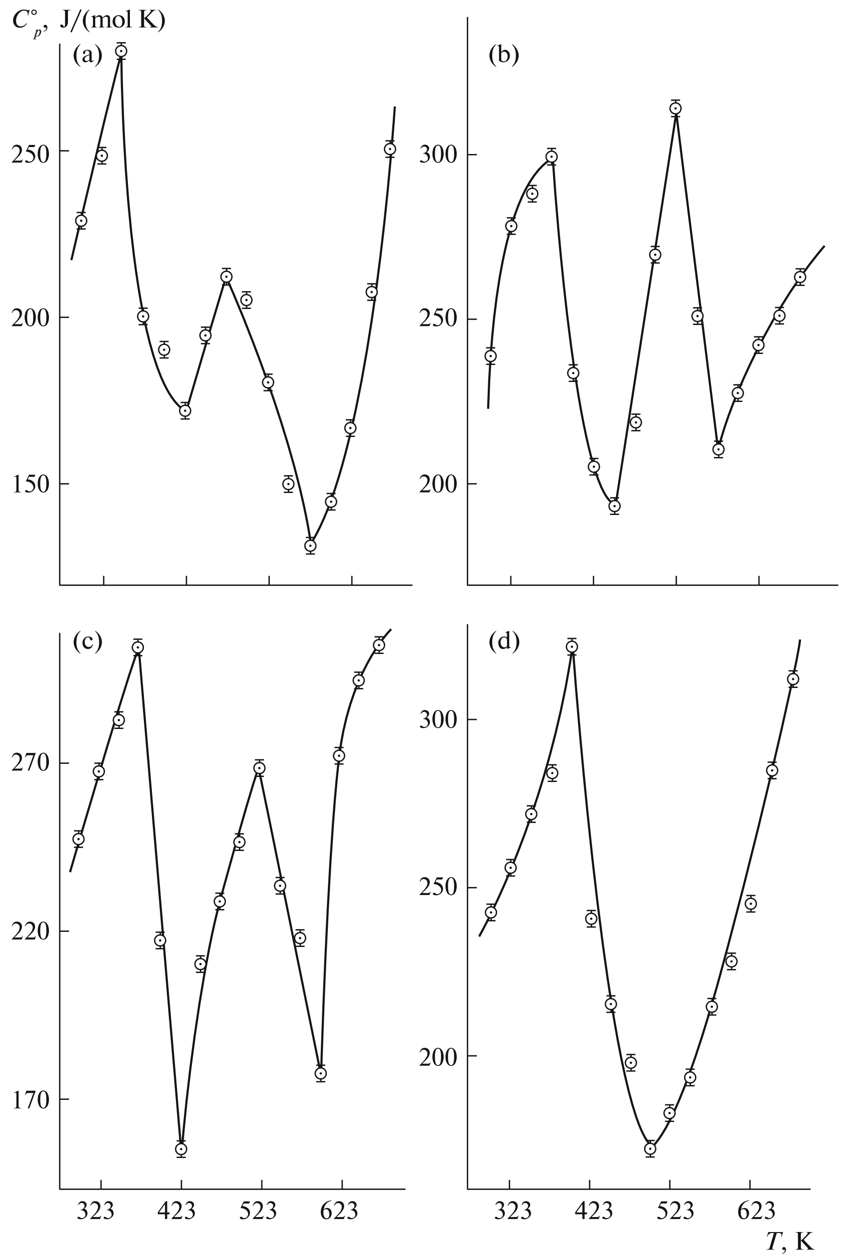
The isobaric heat capacity of $LaM^{II}_2CoMnO_6$ (M^{II} = Mg, Ca, Sr, Ba) cobalt manganites was determined in the 298.15–673 K temperature range on an IT-S-400 calorimeter. Measurement duration over the whole temperature range was ~2.5 h. The stated maximum error of the device was ±10%. The device was calibrated by determining heat conductance K_h of the heat meter [5, 6]. Experiments with a copper sample and an empty ampoule were performed for this purpose. The performance of the apparatus was evaluated by determining the heat capacity of α-Al_2O_3. The resulting value of C_p° (298.15) for Al_2O_3 [76.0 ± 1.5 J/(mol K)] satisfactorily matched with the reference value [79.0 ± 0.17 J/(mol K)] [7, 8]. Five parallel experiments were performed at each temperature point with 25 K step. The results were averaged and analyzed using mathematical statistics [9]. Mean-square deviations ($\bar{\delta}$) were calculated for specific heat capacities, and random error components were calculated for molar heat capacities ($\mathring{\Delta}$). Systematic error and errors in measurements were not considered in our experiments, since they were negligible compared to the error random components.

The results from our calorimetric experiments are presented in Table 1 and in the figure.

According to the experimental data presented in Table 1 and in the figure, it was determined that the $C_p^\circ \sim f(T)$ curve contained anomalous λ-like peaks at 348 and 473 K for $LaMg_2CoMnO_6$, at 373 and 523 K for $LaCa_2CoMnO_6$ and $LaSr_2CoMnO_6$ and at 398 K for $LaBa_2CoMnO_6$, due likely to type II phase transitions. These phase transitions were probably conditional on Schottky effects; the transition from semiconductivity to metallic conductivity; and on variations in capacity, dielectric permittivity, the occurrence of Curie or Néel points, and so forth.

The equations derived for the $C_p^\circ \sim f(T)$ dependences are presented in Table 2.

Due to the technical limitations of the IT-S-400 calorimeter, which do not permit calculation of $S^\circ(298.15)$ from the experimental data on $C_p^\circ(T)$ of the investigated compounds, they were evaluated using the ionic entropy increment system [10]. The entropy



Temperature dependences of the heat capacities for cobalt manganites $LaMg_2CoMnO_6$ (a), $LaCa_2CoMnO_6$ (b), $LaSr_2CoMnO_6$ (c), $LaBa_2CoMnO_6$ (d).

increments [$S^i(298.15)$] of the following ions were used to calculate the standard entropies of cobalt manganites: La^{3+}, 29.3; Mg^{2+}, 22.2; Ca^{2+}, 27.3; Sr^{2+}, 29.3; Ba^{2+}, 28.4; Co^{2+}, 31.3; Mn^{3+}, 25.0; O^{2-}, 16.7 J/(mol K) [10].

The entropies of the cobalt manganites were subsequently determined by summing the ions' $S^i(298.15)$ according to the stoichiometric composition of the compounds. The calculation error was ~3.0% [10]. The temperature dependences of thermodynamic functions (Table 3) were then calculated on the basis of the experimental data on heat capacities and the calculated values of the cobalt manganite standard entropies.

CONCLUSIONS

The isobaric heat capacities of $LaM^{II}_2CoMnO_6$ (M^{II} = Mg, Ca, Sr, Ba) cobalt manganites were exper-

Table 3. Thermodynamic functions for the cobalt manganites in the 298.15–675 K temperature range

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)
		$LaMg_2CoMnO_6$		
298.15	230 ± 14	216 ± 7	–	216 ± 7
300	232 ± 14	218 ± 19	460 ± 30	216 ± 19
325	257 ± 15	237 ± 21	6600 ± 400	217 ± 19
350	282 ± 17	257 ± 23	13300 ± 800	219 ± 20
375	196 ± 12	273 ± 24	19000 ± 1100	222 ± 20
400	167 ± 10	284 ± 25	23500 ± 1400	226 ± 20
425	174 ± 10	295 ± 26	27700 ± 1600	229 ± 20
450	194 ± 11	305 ± 27	32300 ± 1900	233 ± 21
475	214 ± 13	316 ± 28	37400 ± 2200	237 ± 21
500	198 ± 12	327 ± 29	42500 ± 2500	242 ± 22
525	179 ± 11	336 ± 30	47200 ± 2800	246 ± 22
550	156 ± 9	344 ± 31	51400 ± 3000	250 ± 22
575	129 ± 8	350 ± 31	55000 ± 3300	254 ± 23
600	143 ± 9	356 ± 32	58400 ± 3400	258 ± 23
625	169 ± 10	362 ± 32	62300 ± 3700	262 ± 23
650	207 ± 12	369 ± 33	66900 ± 3900	266 ± 24
675	255 ± 15	378 ± 34	72700 ± 4300	270 ± 24
		$LaCa_2CoMnO_6$		
298.15	240 ± 14	247 ± 7	–	247 ± 7
300	243 ± 15	249 ± 22	500 ± 30	247 ± 22
325	281 ± 17	270 ± 24	7100 ± 400	248 ± 22
350	297 ± 18	291 ± 26	14300 ± 900	250 ± 22
375	299 ± 18	312 ± 28	21800 ± 1300	254 ± 23
400	235 ± 14	329 ± 30	28400 ± 1700	258 ± 23
425	203 ± 12	342 ± 31	33800 ± 2000	262 ± 24
450	193 ± 12	353 ± 32	38700 ± 2300	267 ± 24
475	236 ± 14	365 ± 33	44100 ± 2600	272 ± 24
500	277 ± 17	378 ± 34	50500 ± 3000	277 ± 25
525	317 ± 19	392 ± 35	57900 ± 3400	282 ± 25
550	258 ± 15	406 ± 36	65000 ± 3900	287 ± 26
575	205 ± 12	416 ± 37	70800 ± 4200	293 ± 26
600	229 ± 14	425 ± 38	76300 ± 4500	298 ± 27
625	243 ± 15	435 ± 39	82200 ± 4900	303 ± 27
650	255 ± 15	445 ± 40	88500 ± 5300	309 ± 28
675	263 ± 16	454 ± 41	94900 ± 5700	314 ± 28
		$LaSr_2CoMnO_6$		
298.15	245 ± 15	269 ± 8	–	269 ± 8
300	249 ± 16	271 ± 25	500 ± 30	269 ± 25
325	269 ± 17	291 ± 27	7000 ± 400	270 ± 25
350	288 ± 18	312 ± 29	13900 ± 900	272 ± 25
375	306 ± 19	332 ± 31	21400 ± 1300	275 ± 25
400	224 ± 14	349 ± 32	27900 ± 1700	280 ± 26
425	149 ± 9	361 ± 33	32500 ± 2000	284 ± 26
450	200 ± 12	371 ± 34	37100 ± 2300	289 ± 27

Table 3. (Contd.)

T, K	$C_p^\circ(T) \pm \overset{\circ}{\Delta}$, J/(mol K)	$S^\circ(T) \pm \overset{\circ}{\Delta}$, J/(mol K)	$H^\circ(T) - H^\circ(298.15) \pm \overset{\circ}{\Delta}$, J/mol	$\Phi^{xx}(T) \pm \overset{\circ}{\Delta}$, J/(mol K)
475	231 ± 14	383 ± 35	42400 ± 2600	293 ± 27
500	253 ± 16	395 ± 36	48500 ± 3000	298 ± 28
525	270 ± 17	408 ± 38	55100 ± 3400	303 ± 28
550	236 ± 15	419 ± 39	61300 ± 3800	308 ± 28
575	205 ± 13	429 ± 40	66800 ± 4200	313 ± 29
600	175 ± 11	437 ± 40	71600 ± 4500	318 ± 29
625	278 ± 17	447 ± 41	77500 ± 4800	323 ± 30
650	314 ± 20	459 ± 42	85000 ± 5300	328 ± 30
675	303 ± 19	471 ± 43	92800 ± 5800	333 ± 31
		$LaBa_2CoMnO_6$		
298.15	243 ± 14	290 ± 9	–	290 ± 9
300	244 ± 14	292 ± 26	500 ± 30	290 ± 26
325	257 ± 15	312 ± 28	6700 ± 400	291 ± 26
350	276 ± 16	332 ± 29	13400 ± 800	293 ± 26
375	298 ± 17	351 ± 31	20600 ± 1200	296 ± 26
400	324 ± 19	371 ± 33	28300 ± 1700	301 ± 27
425	255 ± 15	389 ± 34	35400 ± 2100	305 ± 27
450	213 ± 12	402 ± 36	41200 ± 2400	310 ± 27
475	186 ± 11	413 ± 36	46200 ± 2700	315 ± 28
500	172 ± 10	422 ± 37	50600 ± 3000	320 ± 28
525	184 ± 11	430 ± 38	55100 ± 3200	325 ± 29
550	199 ± 12	439 ± 39	59900 ± 3500	330 ± 29
575	217 ± 13	448 ± 40	65100 ± 3800	335 ± 30
600	238 ± 14	458 ± 41	70700 ± 4100	340 ± 30
625	262 ± 15	468 ± 41	77000 ± 4500	345 ± 31
650	287 ± 17	479 ± 42	83800 ± 4900	350 ± 31
675	315 ± 18	490 ± 43	91300 ± 5400	355 ± 31

imentally investigated in the 298.15–673 K temperature range for the first time.

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