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Heat Capacities and Thermodynamic Functions of New Nanosized Ferro-chromo-manganites $LaM^{II}_{0.5}FeCrMnO_{6.5}$ (M^{II}–Mg, Ca, Sr, Ba)

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Abstract—The heat capacities of nanosized ferro-chromo-manganites $LaM^{II}_{0.5}FeCrMnO_{6.5}$ (M^{II}–Mg, Ca, Sr, Ba) are measured via dynamic calorimetry in the temperature range of 298.15–673 K using an IT-S-400 instrument. It is established that the $C_p^\circ \sim f(T)$ function of $LaM^{II}_{0.5}FeCrMnO_{6.5}$ (M^{II}–Mg, Ca, Sr, Ba) has λ-type effects, due probably to phase transitions of the second order. Considering the temperatures of the phase transitions, equations of the heat capacity of ferro-chromo-manganites $LaM^{II}_{0.5}FeCrMnO_{6.5}$ (M^{II}–Mg, Ca, Sr, Ba) as a function of temperature are derived on the basis of experimental data. Thermodynamic functions $H^\circ(T) - H^\circ(298.15)$, $S^\circ(T)$, and $\Phi^{xx}(T)$ are calculated in the temperature range of 298.15–675 K.

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INTRODUCTION

The interest of many researchers in nanoobjects is due to the discovery of unusual physical and chemical properties of these objects. Magnetic ferrites of transient metals are increasingly used in modern nanotechnologies. They find wide application in electronics, material science, and medicine. This wide scope of application is based on the capability of magnetic nanoparticles to respond to the impact of external magnetic fields [1, 2]. It should be noted that manganites as materials with colossal magnetic resistance can be used as sensors of magnetic fields, reading heads for magnetic high density recording, and sensors of motion and temperature [3].

There is also interest in combining manganites, chromites and ferrites into single compounds in the form of ferro-chromo-manganites, and especially in the synthesis of nanoparticles of such new materials. The aim of this work was thus to study the thermodynamic properties of new nanosized ferro-chromo-manganites $LaM^{II}_{0.5}FeCrMnO_{6.5}$ (M^{II}–Mg, Ca, Sr, Ba).

EXPERIMENTAL

Specimens were synthesized using the ceramics technique with stoichiometric amounts of La_2O_3 (extra pure grade), Fe_2O_3, Cr_2O_3, Mn_2O_3 and carbonates of alkaline earth metals (all of analytical grade). The reagents were thoroughly mixed, ground in an agate mortar at ambient temperature, and then calcined in alundum crucibles in a SNOL furnace at 800–1200°C for 20 h. After each temperature increase of 200°C from 800 to 1200°C, the mixtures were cooled to ambient temperature and subjected to re-grinding. Low temperature annealing to obtain stable modifications at low temperatures was performed at 400°C for 10 h. Nanosized particles of synthesized ferro-chromo-manganites were obtained by grinding in a MM301 vibration mill (Retsch, Germany).

The sizes of milled particles were measured using a JSPM-5400 scanning probe microscope (JEOL). Nanoparticles (nanoclusters) with sizes of 40–100 nm were obtained (Fig. 1). X-ray phase analysis of the prepared nanosized ferro-chromo-manganites was performed using a DRON-2.0 diffractometer. X-ray patterns of nanosized particles of the considered com-

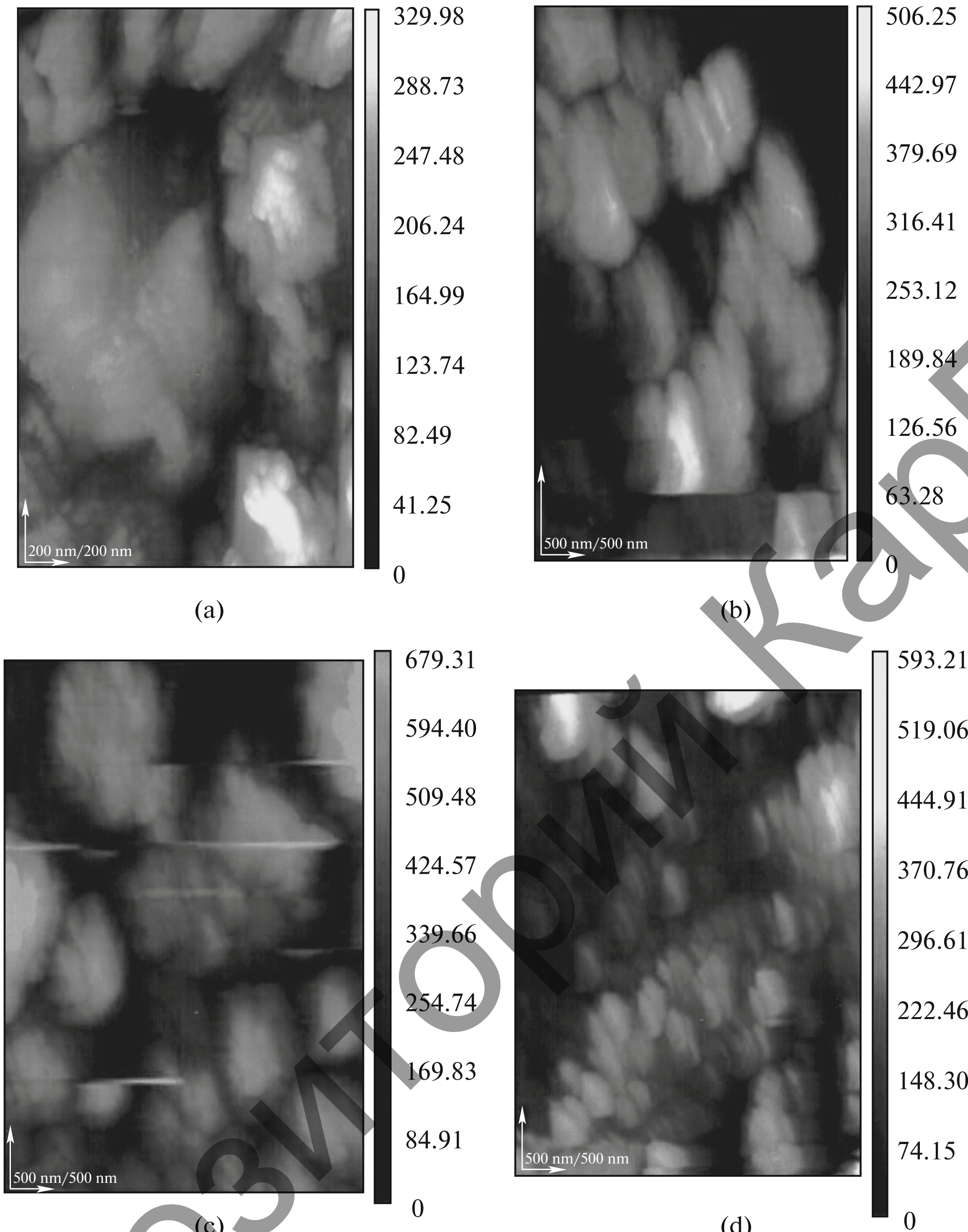

Fig. 1. Electronic microimages of nanosized (nanocluster) ferro-chromo-manganites $LaM_{0.5}FeCrMnO_{6.5}$; (a) M^{II}–Mg, (b) Ca, (c) Sr, and (d) Ba.

pounds were indexed using the analytical approach [4]. The XRD results show that the synthesized nanosized (nanoclustered) particles of ferro-chromo-manganites of lanthanum and alkaline earth metals crystalize in a cubic system: $LaMg_{0.5}FeCrMnO_{6.5}$—a = 20.160 ± 0.034 Å, V° = 8193.54 ± 0.10 Å^3, Z = 8, $V^{\circ}_{\mathrm{el.cell}}$ = 1024.19 ± 0.01 Å^3, $\rho_{\text{X-ray}}$ = 5.15, ρ_{pycn} = 5.12 ± 0.06 g/cm^3; $LaCa_{0.5}FeCrMnO_{6.5}$—a = 20.143 ± 0.036 Å, Z = 8, V° = 8172.83 ± 0.11 Å^3, $V^{\circ}_{\mathrm{el.cell}}$ = 021.60 ± 0.01 Å^3, $\rho_{\text{X-ray}}$ = 5.16, ρ_{pycn} = 5.18 ± 0.02 g/cm^3; $LaSr_{0.5}FeCrMnO_{6.5}$—a = 20.103 ± 0.025 Å, Z = 8, V° = 8124.24 ± 0.08 Å^3, $V^{\circ}_{\mathrm{el.cell}}$ = 1015.53 ± 0.01 Å^3, $\rho_{\text{X-ray}}$ = 5.38, ρ_{pycn} = 5.37 ± 0.02 g/cm^3; $LaBa_{0.5}FeCrMnO_{6.5}$—a = 20.335 ± 0.038 Å, Z = 8, V° = 8408.77 ± 0.11 Å^3, $V^{\circ}_{\mathrm{el.cell}}$ = 1051.10 ± 0.01 Å^3, $\rho_{\text{X-ray}}$ = 5.60, ρ_{pycn} = 5.66 ± 0.06 g/cm^3.

The temperature dependence of heat capacity was studied and the thermodynamic functions of nanosized ferro-chromo-manganites $LaM^{II}_{0.5}FeCrMnO_{6.5}$ (M^{II}–Mg, Ca, Sr, Ba) were derived.

Table 1. Experimental values of the heat capacities of ferro-chromo-manganites $LaM^{II}_{0.5}FeCrMnO_{6.5}$ (M^{II}–Mg, Ca, Sr, Ba), [$C_p \pm \bar{\delta}$, 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	$C_p \pm \bar{\delta}$	$C_p^\circ \pm \mathring{\Delta}$	T, K	$C_p \pm \bar{\delta}$	$C_p^\circ \pm \mathring{\Delta}$
$LaMg_{0.5}FeCrMnO_{6.5}$			$LaCa_{0.5}FeCrMnO_{6.5}$			$LaSr_{0.5}FeCrMnO_{6.5}$		
298.15	0.5527 ± 0.0139	231 ± 16	448	0.7437 ± 0.0139	317 ± 17	573	0.5319 ± 0.0119	239 ± 15
323	0.5588 ± 0.0102	234 ± 12	473	0.6930 ± 0.0179	295 ± 21	598	0.4431 ± 0.0086	199 ± 11
348	0.5827 ± 0.0132	244 ± 15	498	0.6448 ± 0.0130	275 ± 15	623	0.5899 ± 0.0135	265 ± 17
373	0.6346 ± 0.0093	265 ± 11	523	0.6197 ± 0.0170	264 ± 20	648	0.6500 ± 0.0144	292 ± 18
398	0.6810 ± 0.0130	285 ± 15	548	0.5878 ± 0.0074	250 ± 9	673	0.7115 ± 0.0085	320 ± 11
423	0.8020 ± 0.0097	335 ± 11	573	0.5728 ± 0.0114	244 ± 14	$LaBa_{0.5}FeCrMnO_{6.5}$		
448	0.7027 ± 0.0110	294 ± 13	598	0.5812 ± 0.0154	247 ± 18	298.15	0.5145 ± 0.0114	244 ± 15
473	0.6255 ± 0.0098	261 ± 11	623	0.6320 ± 0.0135	269 ± 16	323	0.5228 ± 0.0064	248 ± 9
498	0.5639 ± 0.0124	236 ± 14	648	0.7030 ± 0.0187	299 ± 22	348	0.5633 ± 0.0130	267 ± 17
523	0.5107 ± 0.0132	213 ± 15	673	0.8153 ± 0.0124	347 ± 15	373	0.6161 ± 0.0105	292 ± 14
548	0.4813 ± 0.0136	201 ± 16	$LaSr_{0.5}FeCrMnO_{6.5}$			398	0.7050 ± 0.0088	334 ± 12
573	0.4465 ± 0.0135	187 ± 16	298.15	0.5122 ± 0.0103	230 ± 13	423	0.8176 ± 0.0163	388 ± 22
598	0.5606 ± 0.0122	234 ± 14	323	0.5149 ± 0.0157	232 ± 20	448	0.6944 ± 0.0139	329 ± 18
623	0.6090 ± 0.0103	255 ± 12	348	0.5345 ± 0.0109	240 ± 14	473	0.6202 ± 0.0140	294 ± 19
648	0.6318 ± 0.0085	264 ± 10	373	0.5726 ± 0.0103	257 ± 13	498	0.5609 ± 0.0076	266 ± 10
673	0.6492 ± 0.0094	271 ± 11	398	0.6122 ± 0.0116	275 ± 14	523	0.5269 ± 0.0129	250 ± 17
$LaCa_{0.5}FeCrMnO_{6.5}$			423	0.6638 ± 0.0094	298 ± 12	548	0.5048 ± 0.0074	240 ± 10
298.15	0.5462 ± 0.0139	233 ± 16	448	0.7423 ± 0.0127	334 ± 16	573	0.4921 ± 0.0134	233 ± 18
323	0.5627 ± 0.0074	240 ± 9	473	0.7242 ± 0.0151	326 ± 19	598	0.5031 ± 0.0137	239 ± 18
348	0.6116 ± 0.0096	260 ± 11	498	0.6940 ± 0.0127	312 ± 16	623	0.5256 ± 0.0115	249 ± 15
373	0.6714 ± 0.0077	286 ± 9	523	0.6455 ± 0.0121	290 ± 15	648	0.5660 ± 0.0140	269 ± 18
398	0.7481 ± 0.0113	319 ± 13	548	0.5903 ± 0.0116	265 ± 15	673	0.6276 ± 0.0111	298 ± 15
423	0.8268 ± 0.0137	352 ± 16						

The specific heat capacities of ferro-chromo-manganites in the temperature range of 298.15–673 K were measured using an IT-S-400 calorimeter, and the molar heat capacities were calculated. The allowable accuracy was ±10% [5, 6]. The procedures for testing, calibrating, and verifying calorimeter operation were similar to those used in [7, 8].

RESULTS AND DISCUSSION

Table 1 summarizes the results from calorimetry. From the data in Table 1 and Fig. 2, we can see that $LaMg_{0.5}FeCrMnO_{6.5}$, $LaCa_{0.5}FeCrMnO_{6.5}$, and $LaBa_{0.5}FeCrMnO_{6.5}$ at 423 K, and $LaSr_{0.5}FeCrMnO_{6.5}$ at 448 K undergo λ-type second order phase transitions, due possibly to the Schottky effect; the Curie and Neel points; and variations in dielectric permeability, electric conductivity, and other features. The equations $C_p^\circ \sim f(\mathrm{T})$ summarized in Table 2 were derived by allowing for the obtained temperatures of phase transitions.

Since the calorimeter's capabilities did not allow us to calculate the standard entropies of the considered compounds on the basis of the measured heat capaci-

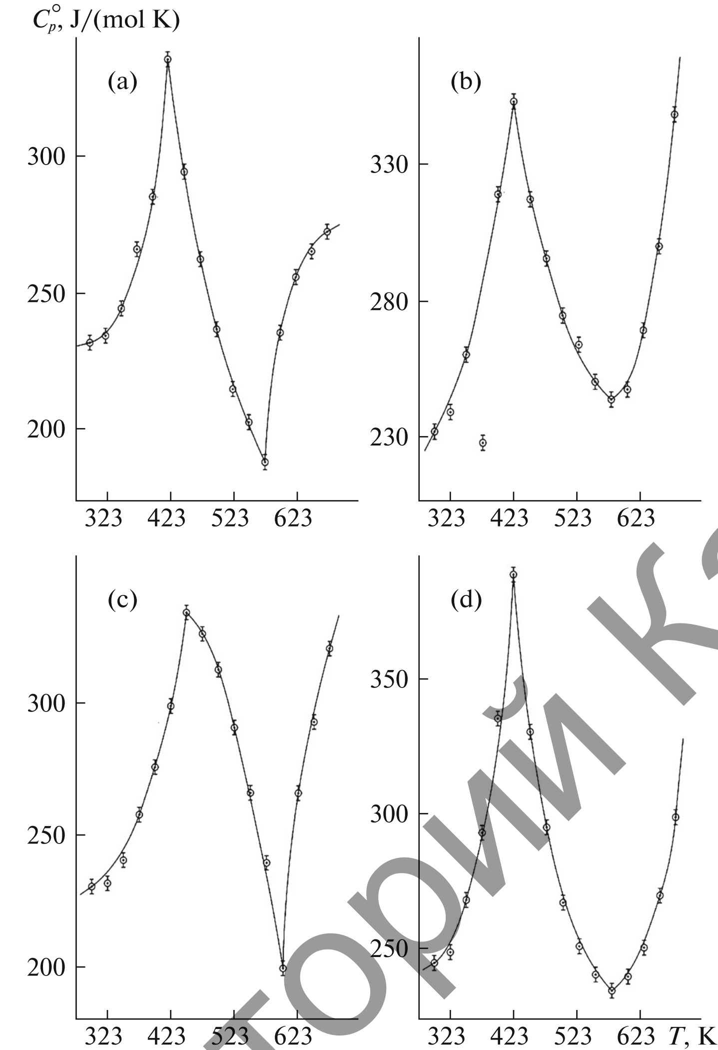

Fig. 2. Temperature dependences of the heat capacity of ferro-chromo-manganites (a–d); see Fig. 1.

Table 2. Coefficients of the temperature dependences of the heat capacities of ferro-chromo-manganites (C_p°, J/(mol K) = $a + bT + cT^{-2}$)

M^{II}	a	$b \times 10^{-3}$	$c \times 10^5$	ΔT, K
Mg	−(1001 ± 55)	2634 ± 145	397 ± 22	298–423
	−(375 ± 21)	509 ± 28	884 ± 49	423–573
	−(3688 ± 203)	−(3410 ± 187)	−(5081 ± 280)	573–673
Ca	−(725 ± 39)	2188 ± 118	271.5 ± 14.7	298–423
	−(392 ± 21)	672 ± 36	822 ± 45	423–573
	−(4466 ± 242)	5430 ± 294	5248 ± 284	573–673
Sr	−(598 ± 33)	1791 ± 98	263.1 ± 14.0	298–448
	1904 ± 104	−(2376 ± 130)	−(1015 ± 56)	448–598
	7363 ± 403	−(6906 ± 378)	−(10850 ± 594)	598–673
Ba	−(1254 ± 70)	3272 ± 182	468 ± 26	298–423
	−(1160 ± 65)	1604 ± 89	1553 ± 87	423–573
	−(3013 ± 168)	3717 ± 207	3668 ± 205	573–673

Table 3. Thermodynamic functions of ferro-chromo-manganites in the range of 298.15–675 K

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)
		$LaMg_{0.5}FeCrMnO_{6.5}$		
298.15	229 ± 13	212 ± 6	–	212 ± 10
300	230 ± 13	214 ± 18	460 ± 30	212 ± 18
325	231 ± 13	232 ± 20	6190 ± 30	213 ± 18
350	245 ± 14	250 ± 21	12120 ± 670	215 ± 18
375	269 ± 15	267 ± 23	18530 ± 1020	218 ± 19
400	301 ± 17	286 ± 24	25640 ± 1410	222 ± 19
425	338 ± 19	305 ± 26	33610 ± 1850	226 ± 19
450	291 ± 16	323 ± 27	41380 ± 2250	231 ± 20
475	259 ± 14	338 ± 29	48250 ± 2650	236 ± 20
500	234 ± 13	350 ± 30	54400 ± 2990	242 ± 21
525	214 ± 12	361 ± 31	59980 ± 3300	247 ± 21
550	198 ± 11	371 ± 32	65120 ± 3580	252 ± 21
575	186 ± 10	379 ± 32	69900 ± 3840	258 ± 22
600	231 ± 13	388 ± 33	75200 ± 4130	263 ± 22
625	256 ± 14	398 ± 34	81310 ± 4470	268 ± 23
650	269 ± 15	409 ± 35	87900 ± 4830	273 ± 23
675	271 ± 15	419 ± 36	94670 ± 5200	279 ± 24
		$LaCa_{0.5}FeCrMnO_{6.5}$		
298.15	232 ± 13	220 ± 7	–	220 ± 7
300	233 ± 13	222 ± 19	470 ± 30	220 ± 19
325	243 ± 13	241 ± 20	6390 ± 350	221 ± 19
350	262 ± 14	259 ± 22	12690 ± 690	223 ± 19
375	288 ± 16	278 ± 23	19600 ± 1060	226 ± 19
400	320 ± 17	298 ± 25	27150 ± 1470	230 ± 19
425	355 ± 19	318 ± 27	35570 ± 1930	234 ± 20
450	317 ± 17	337 ± 28	43870 ± 2380	240 ± 20
475	292 ± 16	354 ± 30	51470 ± 2790	245 ± 21
500	273 ± 15	368 ± 31	58520 ± 3170	251 ± 21
525	259 ± 14	381 ± 32	65170 ± 3530	257 ± 22
550	250 ± 14	393 ± 33	71530 ± 3870	263 ± 22
575	244 ± 13	404 ± 34	77680 ± 4210	269 ± 23
600	250 ± 14	414 ± 35	83820 ± 4540	275 ± 23
625	271 ± 15	425 ± 36	90300 ± 4900	280 ± 24
650	300 ± 17	436 ± 37	97490 ± 5280	286 ± 24
675	351 ± 19	448 ± 38	105680 ± 5720	291 ± 25
		$LaSr_{0.5}FeCrMnO_{6.5}$		
298.15	229 ± 13	226 ± 7	–	226 ± 7
300	230 ± 13	227 ± 19	460 ± 30	226 ± 19
325	231 ± 13	245 ± 21	6200 ± 340	226 ± 19
350	242 ± 13	263 ± 22	12100 ± 660	228 ± 19
375	259 ± 14	280 ± 24	18350 ± 1000	231 ± 20
400	281 ± 15	298 ± 25	25090 ± 1370	235 ± 20
425	307 ± 17	315 ± 27	32440 ± 1780	239 ± 20

Table 3. (Contd.)

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)
450	336 ± 18	334 ± 28	40470 ± 2220	244 ± 21
475	325 ± 18	352 ± 30	48730 ± 2670	249 ± 21
500	310 ± 17	368 ± 31	56680 ± 3100	255 ± 22
525	288 ± 16	383 ± 32	64170 ± 3510	260 ± 22
550	262 ± 14	395 ± 34	71050 ± 3900	266 ± 23
575	231 ± 13	406 ± 34	77210 ± 4230	272 ± 23
600	206 ± 11	413 ± 35	81230 ± 4450	278 ± 24
625	269 ± 15	423 ± 36	87220 ± 4780	283 ± 24
650	306 ± 17	434 ± 37	94470 ± 5170	289 ± 25
675	320 ± 18	446 ± 38	102340 ± 5600	295 ± 25
		$LaBa_{0.5}FeCrMnO_{6.5}$		
298.15	232 ± 13	231 ± 7	–	231 ± 7
300	244 ± 14	232 ± 20	490 ± 30	231 ± 20
325	249 ± 14	252 ± 22	6600 ± 370	232 ± 20
350	269 ± 15	271 ± 23	13050 ± 730	234 ± 20
375	302 ± 17	291 ± 25	20170 ± 1120	237 ± 20
400	344 ± 19	312 ± 27	28220 ± 1570	241 ± 21
425	392 ± 22	334 ± 29	37400 ± 2080	246 ± 21
450	330 ± 18	354 ± 30	46280 ± 2580	251 ± 22
475	292 ± 16	371 ± 32	54020 ± 3010	257 ± 22
500	265 ± 15	385 ± 33	60950 ± 3400	263 ± 23
525	247 ± 14	397 ± 34	67330 ± 3750	269 ± 23
550	237 ± 13	409 ± 35	73360 ± 4090	275 ± 24
575	233 ± 13	419 ± 36	79220 ± 4420	281 ± 24
600	236 ± 13	429 ± 37	85060 ± 4740	287 ± 25
625	249 ± 14	439 ± 38	91090 ± 5080	293 ± 25
650	271 ± 15	449 ± 39	97560 ± 5440	299 ± 26
675	300 ± 17	460 ± 39	104680 ± 5840	305 ± 26

ties, they were estimated using ionic entropy increments [9].

Based on the measured heat capacities and calculated standard entropies of ferro-chromo-manganites, the temperature dependences of their thermodynamic functions were then obtained. They are summarized in Table 3.

CONCLUSIONS

The isobaric heat capacities of ferro-chromo-manganites $LaM^{II}_{0.5}FeCrMnO_{6.5}$ (M^{II}–Mg, Ca, Sr, Ba) were experimentally studied for the first time in the temperature range of 298.15–673 K, and the temperature dependences of their thermodynamic functions were obtained.

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