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Thermodynamic Properties of Zincate-Manganites of $LaM^{II}_2ZnMnO_6$ (M^{II} = Mg, Ca, Sr, Ba) Composition

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Abstract—Temperature dependences of the heat capacity of new zincate-manganites of $LaM^{II}_2ZnMnO_6$ (M^{II} = Mg, Ca, Sr, Ba) composition are studied via experimental calorimetry in the interval of 298.15–673 K. It is found that all compounds have λ-shape effects on the curve of dependence $C_p^\circ \sim f(T)$ with respect to phase transitions of the second kind. Equations for the temperature dependence of the heat capacity are derived with allowance for phase transition temperatures, and thermodynamic functions $H^\circ(T) - H^\circ(298.15)$, $S^\circ(T)$ and $\Phi^{xx}(T)$ are calculated on the basis of experimental data on $C_p^\circ(T)$ and the calculated $S^\circ(298.15)$ value.

Keywords: zincate-manganite, calorimetry, heat capacity, thermodynamic functions.

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INTRODUCTION

Due to the discovery of the colossal magnetic resistance effect in rare-earth manganites doped with alkali-earth metal oxides, interest in compounds of this type has grown dramatically. It was noted in [1] that the colossal magnetic resistance effect can be observed at temperatures close to room temperature after optimizing a sample's composition.

The aim of this work was to study the thermodynamic properties (the heat capacity in particular) of lanthanum zincate-manganites and alkali-earth metals of $LaM^{II}_2ZnMnO_6$ composition, where M^{II} denotes alkali-earth metals that we synthesized for the first time. Using ceramic technology, we synthesized zincate-manganites from La_2O_3, ZnO, Mn_2O_3 oxides and alkali-earth metal carbonates. All of the prepared zincate-manganites crystallized in the cubic syngony.

EXPERIMENTAL

The heat capacity of zincate-manganites was studied in the interval of 298.15–673 K on an IT-C-400 calorimeter. The specified limit of acceptable error was ±10.0%. Calibration of the device and a test of its performance were described in detail in [2–5]. Five parallel experiments were performed at each temperature within the technical capabilities of the device with steps of 25 K, and the results were averaged. Mean square deviations ($\bar{\delta}$) were calculated for the specific heat capacities; random error components ($\mathring{\Delta}$) were calculated for molar heat capacities [3, 6].

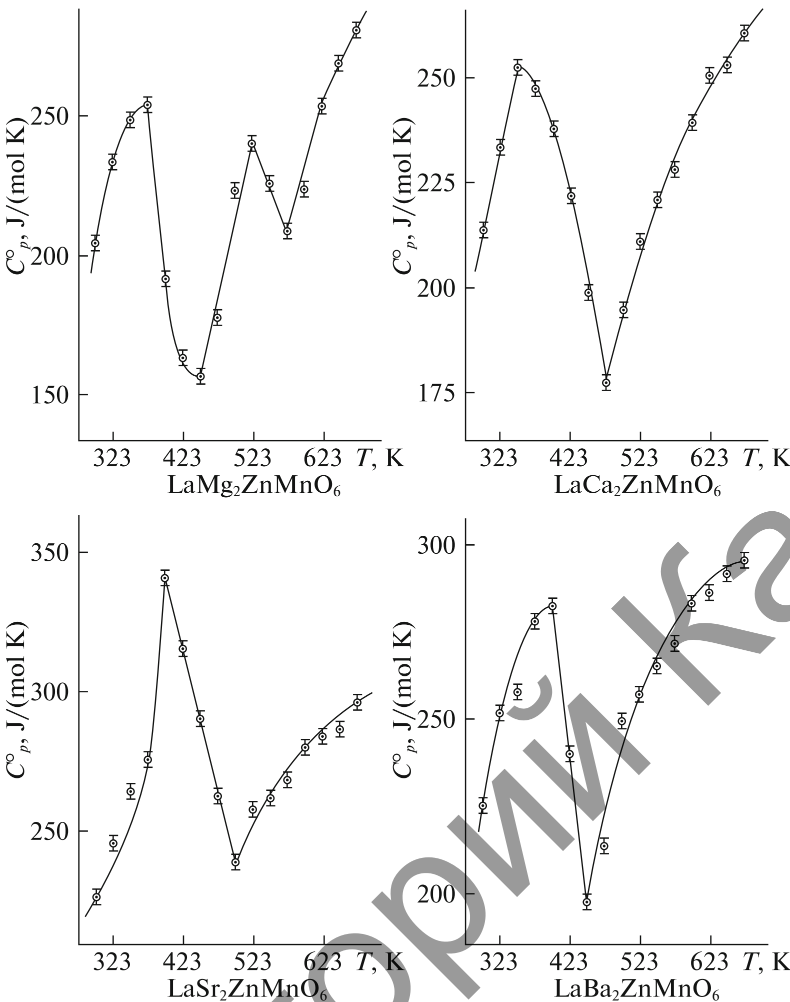
RESULTS AND DISCUSSION

Table 1 and the figure below present the results from our calorimetric studies.

The data of Table 1 and the figure show that all of the studied zincate-manganites experienced anomalous λ-shape effects, due probably to K phase transitions of the second kind: $LaMg_2ZnMnO_6$ at 373 and 573 K, $LaCa_2ZnMnO_6$ at 373 K, $LaSr_2ZnMnO_6$ at 398 K, and $LaBa_2ZnMnO_6$ at 398 K. These phase transitions were likely due to Schottky effects with changes in capacity, dielectric permittivity, the transition from the semiconductor to metal conductivity, the emergence of Curie and Néel points, and so on.

Table 1. Experimental values of the heat capacities of zincate-manganites $LaM^{II}_2ZnMnO_6$ (M^{II} = Mg, Ca, Sr, Ba) [$C_p \pm \bar{\delta}$, J/(g K); $C^\circ_p \pm \mathring{\Delta}$, J/(mol K)]

T, K	$C_p \pm \bar{\delta}$	$C^\circ_p \pm \mathring{\Delta}$	T, K	$C_p \pm \bar{\delta}$,	$C^\circ_p \pm \mathring{\Delta}$
		$LaMg_2ZnMnO_6$			
298.15	0.506 ± 0.017	204 ± 19	498	0.553 ± 0.012	223 ± 14
323	0.578 ± 0.018	234 ± 21	523	0.594 ± 0.014	240 ± 15
348	0.616 ± 0.017	249 ± 19	548	0.559 ± 0.016	226 ± 18
373	0.629 ± 0.015	254 ± 17	573	0.517 ± 0.014	209 ± 16
398	0.474 ± 0.016	191 ± 18	598	0.554 ± 0.016	224 ± 18
423	0.404 ± 0.014	163 ± 16	623	0.627 ± 0.013	253 ± 15
448	0.388 ± 0.012	157 ± 13	648	0.665 ± 0.014	269 ± 15
473	0.440 ± 0.010	176 ± 11	673	0.695 ± 0.012	281 ± 14
		$LaCa_2ZnMnO_6$			
298.15	0.491 ± 0.011	214 ± 14	498	0.447 ± 0.012	195 ± 14
323	0.537 ± 0.018	236 ± 22	523	0.485 ± 0.017	211 ± 20
348	0.580 ± 0.014	253 ± 17	548	0.508 ± 0.014	221 ± 17
373	0.568 ± 0.018	248 ± 21	573	0.525 ± 0.014	228 ± 17
398	0.547 ± 0.017	238 ± 21	598	0.550 ± 0.014	239 ± 17
423	0.510 ± 0.016	222 ± 19	623	0.576 ± 0.014	251 ± 17
448	0.457 ± 0.014	199 ± 17	648	0.581 ± 0.012	253 ± 14
473	0.408 ± 0.014	177 ± 18	673	0.599 ± 0.012	261 ± 15
		$LaSr_2ZnMnO_6$			
298.15	0.427 ± 0.011	226 ± 17	498	0.450 ± 0.014	239 ± 20
323	0.463 ± 0.007	246 ± 10	523	0.486 ± 0.013	258 ± 19
348	0.498 ± 0.013	264 ± 18	548	0.493 ± 0.011	262 ± 16
373	0.520 ± 0.011	276 ± 15	573	0.506 ± 0.012	268 ± 18
398	0.642 ± 0.009	341 ± 14	598	0.527 ± 0.014	280 ± 21
423	0.594 ± 0.012	315 ± 18	623	0.535 ± 0.012	284 ± 18
448	0.547 ± 0.012	290 ± 17	648	0.540 ± 0.013	286 ± 19
473	0.495 ± 0.014	262 ± 20	673	0.558 ± 0.013	296 ± 20
		$LaBa_2ZnMnO_6$			
298.15	0.358 ± 0.010	226 ± 18	498	0.396 ± 0.012	250 ± 22
323	0.400 ± 0.009	252 ± 16	523	0.409 ± 0.008	258 ± 15
348	0.410 ± 0.009	258 ± 16	548	0.422 ± 0.006	266 ± 11
373	0.442 ± 0.013	279 ± 22	573	0.432 ± 0.008	272 ± 14
398	0.449 ± 0.009	283 ± 16	598	0.450 ± 0.011	284 ± 19
423	0.382 ± 0.007	240 ± 13	623	0.455 ± 0.009	287 ± 16
448	0.314 ± 0.010	198 ± 17	648	0.463 ± 0.012	292 ± 21
473	0.340 ± 0.010	214 ± 18	673	0.470 ± 0.010	296 ± 18



Temperature dependences of the heat capacity of $LaM^{II}_2ZnMnO_6$ (M^{II} = Mg, Ca, Sr, Ba) in the interval of 298.15–673 K.

Table 2. Coefficients of equation $C^\circ_p = a + bT + cT^{-2}$, J/(mol K) for the temperature dependence of the heat capacities of zincate-manganites $LaM^{II}_2ZnMnO_6$ (M^{II} = Mg, Ca, Sr, Ba)

A	$b \times 10^{-3}$	$-c \times 10^5$	ΔT, K
	$LaMg_2ZnMnO_6$		
1093 ± 81	–(1486 ± 110)	396 ± 29	298–373
–(3199 ± 237)	5078 ± 376	–(2170 ± 160)	373–448
–(341 ± 25)	1111 ± 82	–	448–523
568 ± 42	–(626 ± 46)	–	523–573
703 ± 52	–(249 ± 18)	1155 ± 85	573–673
	$LaCa_2ZnMnO_6$		
–(17 ± 1)	776 ± 60	–	298–348
1157 ± 90	–(1722 ± 133)	369 ± 29	348–473
395 ± 31	–(61 ± 5)	422 ± 33	473–673
	$LaSr_2ZnMnO_6$		
–(2717 ± 174)	6096 ± 391	–(1001 ± 64)	298–398
746 ± 48	–(1019 ± 65)	–	398–498
474 ± 30	–(123 ± 8)	432 ± 28	498–673
	$LaBa_2ZnMnO_6$		
770 ± 51	–(788 ± 52)	–275 ± 18	298–373
958 ± 63	–(1698 ± 112)	–	448–523
701 ± 46	–(383 ± 25)	665 ± 43	373–448

Table 3. Thermodynamic characteristics of zincate-manganites of the composition $LaM^{II}_2ZnMnO_6$ (M^{II} = Mg, Ca, Sr, Ba), [$C^{\circ}_p(T)$, $S^{\circ}(T)$, $\Phi^{xx}(T)$, J/(mol K); $H^{\circ}(T) - H^{\circ}(298.15)$, J/mol]

T, K	$C^{\circ}_p(T) \pm \mathring{\Delta}$	$S^{\circ}(T) \pm \mathring{\Delta}$	$H^{\circ}(T) - H^{\circ}(298.15) \pm \mathring{\Delta}$	$\Phi^{xx}(T) \pm \mathring{\Delta}$
		$LaMg_2ZnMnO_6$		
298.15	204 ± 19	213 ± 6	–	213 ± 6
300	208 ± 15	214 ± 22	410 ± 30	213 ± 22
350	250 ± 18	250 ± 26	12060 ± 890	215 ± 22
400	190 ± 14	281 ± 29	23750 ± 1760	222 ± 23
450	157 ± 12	300 ± 31	31960 ± 2360	229 ± 24
500	214 ± 16	320 ± 33	41300 ± 3060	237 ± 25
550	223 ± 17	342 ± 36	52780 ± 3900	246 ± 26
600	233 ± 17	361 ± 38	63710 ± 4710	255 ± 26
650	268 ± 20	381 ± 40	76280 ± 5640	264 ± 27
675	282 ± 21	391 ± 41	83160 ± 6150	268 ± 28
		$LaCa_2ZnMnO_6$		
298.15	214 ± 17	244 ± 7	–	244 ± 7
300	215 ± 17	245 ± 26	430 ± 30	244 ± 26
350	254 ± 20	281 ± 30	12170 ± 950	246 ± 27
400	237 ± 18	314 ± 34	24540 ± 1900	253 ± 27
450	200 ± 16	340 ± 37	35530 ± 2760	261 ± 28
500	196 ± 15	360 ± 39	44910 ± 3490	270 ± 29
550	222 ± 17	380 ± 41	55390 ± 4300	279 ± 30
600	241 ± 19	400 ± 43	66990 ± 5200	288 ± 31
650	256 ± 20	420 ± 45	79420 ± 6160	298 ± 32
675	261 ± 20	430 ± 46	85880 ± 6660	302 ± 33
		$LaSr_2ZnMnO_6$		
298.15	226 ± 17	239 ± 7	–	239 ± 7
300	224 ± 14	240 ± 23	450 ± 30	239 ± 22
350	233 ± 15	274 ± 26	11310 ± 720	241 ± 23
400	347 ± 22	311 ± 29	25480 ± 1640	248 ± 23
450	288 ± 18	348 ± 33	41140 ± 2640	257 ± 24
500	237 ± 15	376 ± 35	54240 ± 3480	267 ± 25
550	264 ± 17	400 ± 38	66870 ± 4290	278 ± 26
600	280 ± 18	424 ± 40	80490 ± 5170	289 ± 27
650	292 ± 19	447 ± 42	94820 ± 6070	301 ± 28
675	296 ± 19	458 ± 43	102170 ± 6560	306 ± 29
		$LaBa_2ZnMnO_6$		
298.15	226 ± 15	287 ± 9	–	287 ± 9
300	228 ± 15	288 ± 28	453.57 ± 30	287 ± 27
350	270 ± 18	327 ± 31	13054 ± 860	290 ± 28
400	283 ± 19	364 ± 35	26959 ± 1780	297 ± 28
450	195 ± 13	392 ± 38	38808 ± 2560	306 ± 29
500	243 ± 16	416 ± 40	49977 ± 3300	316 ± 30
550	270 ± 18	440 ± 42	62879 ± 4140	326 ± 31
600	286 ± 19	464 ± 45	76841 ± 5060	336 ± 32
650	295 ± 19	488 ± 47	91398 ± 6023	347 ± 33
675	297 ± 20	499 ± 48	98791 ± 6510	353 ± 34

Table 2 presents equations for the temperature dependence of the heat capacity of zincate-manganites, derived from experimental data with allowance for phase transition temperatures.

Since the capabilities of our calorimeter did not allow us to calculate the standard entropies of zincate-manganites directly from the experimental data, they were calculated using a system of ion entropy increments [7]. Using the experimental data on $C_p^\circ(T)$ and the calculated values of $S^\circ(298.15)$, temperature dependences of thermodynamic functions $S^\circ(T)$, $H^\circ(T) - H^\circ(298.15)$, $\Phi^{xx}(T)$ were calculated in the interval of 298.15–673 K (Table 3). Errors in the entropy increments of ions (~3.0) were taken into account, along with errors in heat capacities in estimating the errors of $S^\circ(T)$ and $\Phi^{xx}(T)$ [7].

CONCLUSIONS

(1) The heat capacities of zincate-manganites $LaM_2^{II}ZnMnO_6$ (M^{II} = Mg, Ca, Sr, Ba) were studied for the first time in the interval of 298.15–673 K.

(2) Some λ-shape effects associated with phase transitions of the second kind were observed on the curves of dependences $C_p^\circ \sim f(T)$ for zincate-manganites.

(3) Equations for the temperature dependences of the heat capacities of zincate-manganites were derived with allowance for phase transition temperatures.

(4) The temperature dependences of thermodynamic functions were calculated using experimental data on heat capacities and calculated values for standard entropies.

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