

SHORT
COMMUNICATIONS

Heat Capacity and Thermodynamic Functions of New Nanostructured Cuprate–Manganite $\text{NdCa}_2\text{CuMnO}_6$

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Abstract—Heat capacities of nanostructured $\text{NdCa}_2\text{CuMnO}_6$ cuprate–manganite are measured by means of dynamic calorimetry on an IT-C-400 unit in the temperature interval of 298.15–673 K. It is established that a λ -shaped phase transition of the second kind is revealed at 348 K on the curve of the dependence $C_p^\circ \sim f(T)$ of $\text{NdCa}_2\text{CuMnO}_6$. Equations for the temperature dependence of the heat capacity of $\text{NdCa}_2\text{CuMnO}_6$ cuprate–manganite are derived from experimental data including the temperature of phase transition. Thermodynamic functions $H^\circ(T) - H^\circ(298.15)$, $S^\circ(T)$, and $\Phi^{**}(T)$ are calculated in the interval of 298.15–675 K.

Keywords: cuprate–manganite, heat capacity, thermodynamic functions.

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INTRODUCTION

Compounds based on cuprates and manganites of rare-earth elements doped with oxides of alkali-earth metals have unique properties that include superconductivity and colossal magnetoresistance [1–3].

It should be noted that to date, cuprates and manganites have mainly been studied separately, but the preparation and study of the physicochemical properties of nanostructured particles of compounds containing both cuprates and manganites of the above-mentioned elements are of theoretical and practical interest.

The aim of this work was therefore to study the thermodynamic properties of a new nanostructured cuprate–manganite, $\text{NdCa}_2\text{CuMnO}_6$.

EXPERIMENTAL

Cuprate–manganite was synthesized using ceramic technology with stoichiometric amounts of neodymium (ultra pure grade), copper (II), manganese (III) oxides, and barium carbonate (analytical grade), carefully mixed in a SNOL oven at 800–1200°C for 20 h. Before each increase at 800–1000 and 1200°C, the mixtures were cooled, carefully

mixed, and ground. Low-temperature annealing at 400°C for 20 h was performed to obtain phases that were in equilibrium and stable at low temperatures.

Nanoparticles of cuprate–manganite $\text{NdCa}_2\text{CuMnO}_6$ were obtained by grinding on an MM301 vibration mill (Retsch, Germany) as in [4]. The nanoparticle sizes were determined on a TESCAN electron microscope: 105, 66, 74, 146, 36, 77, 35, 26, 73, 128, 63, 58, 51, 30, 210, 64, 42, 51 nm (Fig. 1).

X-ray phase analysis of the nanosized cuprate–manganite particles was performed on a DRON-2.0 diffractometer. The X-ray patterns of the nanosized particles of the studied compound were indexed analytically [5], on the basis of which it was established that $\text{NdCa}_2\text{CuMnO}_6$ crystallizes in cubic syngony with the following lattice parameters: $a = 15.516 \pm 0.04 \text{ \AA}$, $V^0 = 3735.42 \pm 0.12 \text{ \AA}^3$, $Z = 4$, $V_{\text{unit cell}}^0 = 935.86 \text{ \AA}^3$, $\rho_{\text{X-ray}} = 3.81$, $\rho_{\text{pinc}} = 3.77 \pm 0.05 \text{ g/cm}^3$.

The temperature dependence of the heat capacity was then studied and the thermodynamic functions of $\text{NdCa}_2\text{CuMnO}_6$ cuprate–manganite were calculated. In the temperature interval of 298.15–673 K, the specific heat capacity was measured on an IT-C-400 calorimeter, and the molar heat capacity of $\text{NdCa}_2\text{CuMnO}_6$ was calculated. The duration of the measurements over the temperature interval com-



Fig. 1. Electron photomicrograph of $\text{NdCa}_2\text{CuMnO}_6$.

bined with the processing of experimental data was no more than 2.5 h. The limit of the allowable error was $\pm 10\%$ [6, 7].

The device was calibrated before performing each experiment via experimental determination of

the calorimeter's heat conductivity, K_T . To accomplish this, we performed five parallel experiments each on a copper sample and on an empty ampoule. The functioning of the device was checked by determining the standard heat capacity of $\alpha\text{-Al}_2\text{O}_3$, the

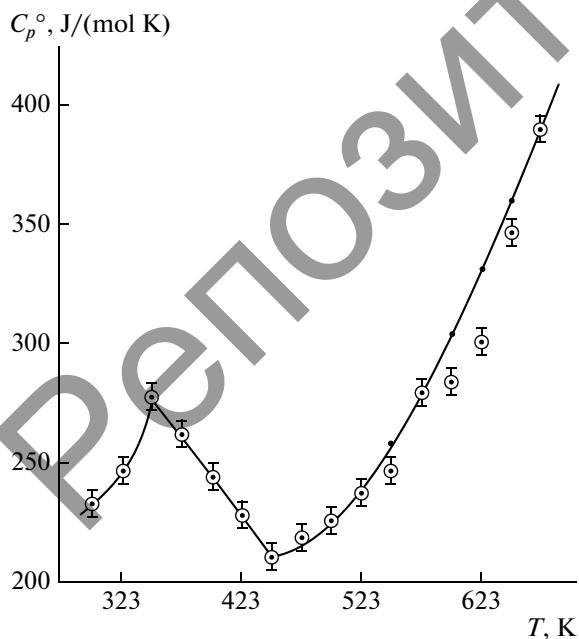
Table 1. Experimental values of heat capacities of $\text{NdCa}_2\text{CuMnO}_6$

T , K	$C_p \pm \bar{\delta}$, J/(g K)	$C_p^\circ \pm \bar{\Delta}$, J/(mol K)	T , K	$C_p \pm \bar{\delta}$, J/(g K)	$C_p^\circ \pm \bar{\Delta}$, J/(mol K)
298.15	0.530 ± 0.018	233 ± 23	498	0.514 ± 0.015	226 ± 18
323	0.561 ± 0.011	246 ± 13	523	0.540 ± 0.014	237 ± 17
348	0.632 ± 0.012	277 ± 14	548	0.561 ± 0.017	246 ± 21
373	0.596 ± 0.011	262 ± 13	573	0.637 ± 0.012	280 ± 15
398	0.556 ± 0.016	244 ± 20	598	0.648 ± 0.011	284 ± 14
423	0.519 ± 0.009	228 ± 11	623	0.686 ± 0.020	301 ± 21
448	0.480 ± 0.014	211 ± 17	648	0.790 ± 0.015	347 ± 18
473	0.498 ± 0.011	218 ± 13	673	0.889 ± 0.016	390 ± 20

Table 2. Thermodynamic functions of cuprate–manganite $\text{NdCa}_2\text{CuMnO}_6$

T, K	$C_p^\circ(T) \pm \Delta,$ $\text{J}/(\text{mol K})$	$S^\circ(T) \pm \Delta,$ $\text{J}/(\text{mol K})$	$H^\circ(T) - H^\circ(298.15) \pm \Delta,$ J/mol	$\Phi^{\text{xx}}(T) \pm \Delta,$ $\text{J}/(\text{mol K})$
298.15	233 ± 15	254 ± 8	–	254 ± 8
300	233 ± 15	255 ± 24	460 ± 30	254 ± 24
350	281 ± 18	294 ± 28	13020 ± 850	257 ± 28
400	243 ± 16	328 ± 31	25990 ± 1700	263 ± 31
450	209 ± 14	355 ± 34	37280 ± 2440	272 ± 34
500	226 ± 15	378 ± 36	48100 ± 3150	282 ± 36
550	260 ± 17	401 ± 38	60160 ± 3930	291 ± 38
600	306 ± 20	425 ± 41	74260 ± 4860	302 ± 41
650	362 ± 24	452 ± 43	90940 ± 5950	312 ± 43
675	393 ± 26	466 ± 44	100370 ± 6570	318 ± 44

value of which ($76.0 \text{ J}/(\text{mol K})$) was in satisfactory agreement with the recommended value ($79.0 \text{ J}/(\text{mol K})$) [8]. Five parallel experiments were performed at each temperature (with steps of 25 K), the results were averaged and processed by means of mathematical statistics [7, 9] (Table 1). The heat capacities of analogous manganite–ferrites were studied in a similar manner in [10].

**Fig. 2.** Temperature dependence of the heat capacity of $\text{NdCa}_2\text{CuMnO}_6$.

RESULTS AND DISCUSSION

It can be seen from data of Table 1 and Fig. 2 that $\text{NdCa}_2\text{CuMnO}_6$ undergoes a λ -shaped phase transition of the second kind at 348 K, due possibly to Schottky effects, Curie and Néel points, changes in dielectric permittivity and conduction, and other features. Considering the temperature of the phase transition from the experimental data, we derived equations for the temperature dependence of the heat capacity of cuprate–manganite, $\text{J}/(\text{mol K})$:

$$C_p^0 = -(1502.6 \pm 98.3) + (3920.7 \pm 256.4) \times 10^{-3} T - (503.4 \pm 32.9) \times 10^5 T^{-2} (298-348 \text{ K}), \quad (1)$$

$$C_p^0 = (510.5 \pm 33.4) - (669.7 \pm 43.8) \times 10^{-3} T (348-448 \text{ K}), \quad (2)$$

$$C_p^0 = -(959.8 \pm 62.8) + (1752.0 \pm 114.6) \times 10^{-3} T - (773.6 \pm 50.6) \times 10^5 T^{-2} (448-673 \text{ K}). \quad (3)$$

The value of the compound's standard entropy was estimated by ion entropy increments [11].

The thermodynamic functions $H^\circ(T) - H^\circ(298.15)$, $S^\circ(T)$, and $\Phi^{**}(T)$ were calculated from the experimental data on heat capacities of cuprate–manganite and its standard entropy. The obtained results are given in Table 2.

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