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CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Thermodynamic and Electrophysical Properties of $La_2SrNiTeO_7$

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Abstract—The isobaric heat capacity of nickelite-tellurite $La_2SrNiTeO_7$ was studied by calorimetry at 298.15–673 K. λ-Shaped effects related to the second-order phase transition were revealed for the compound in the given temperature range. The equations of the temperature dependence of the heat capacity were derived taking into account the transition temperatures. The temperature dependences of the heat capacity, entropy, enthalpy, and reduced thermodynamic potential were calculated from the experimental heat capacities and calculated standard entropies of nickelite-tellurite. The temperature dependences of the dielectric constant and electric resistance of nickelite-tellurite at 293–483 K were studied. The curves of the dependences $\log \varepsilon = f(T)$ and $\log R = f(T)$ have maxima and minima, which confirm the λ-shaped effects related to the second-order phase transition on the curve of $C_p^\circ = f(T)$ for the compound.

Keywords: nickelite-tellurite, heat capacity, thermodynamic functions, dielectric constant, electric resistance
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Among the most important classes of inorganic compounds employed in development of novel materials, selenium and tellurium compounds are of special interest. They are characterized by high chemical activity, which makes them promising for synthetic transformations aimed at obtaining new semiconductors, ferroelectrics, and radioluminescent materials with wide applications. This is especially true for complex oxocompounds, which were poorly studied, in particular, for binary and ternary tellurites of *d* and *f*-elements, while these compounds are of theoretical and practical interest as materials with valuable physicochemical properties [1, 2]. Recently, compounds based on rare-earth, alkaline-earth, and transition metal oxides have attracted the attention of researchers due to their promising properties for use in microelectronics [3–5].

In this context, it was of interest to study a combination of rare-earth, transition metal, and tellurium oxides in one compound. This paper presents the results of our study of the thermodynamic and electrophysical properties of lanthanum-strontium nickelite-tellurite $La_2SrNiTeO_7$.

EXPERIMENTAL

A new phase—nickelite-tellurite $La_2SrNiTeO_7$—was synthesized by ceramic technology from the oxides La_2O_3 ("os.ch." (extrapure)), NiO (extrapure), and TeO_2 ("ch.d.a." (analytical grade)) and strontium carbonate $SrCO_3$ (analytical grade) at 800–1200°C. Our previous paper [6] described the synthetic procedure and X-ray diffraction properties of this compound. It was found by X-ray diffractometry that the synthesized nickelite-tellurite $La_2SrNiTeO_7$ crystallizes in the cubic crystal system. The hypothetical structure of the synthesized nickelite-tellurite is of perovskite type with space group *Pm*3*m*.

The specific heat capacities were measured on an IT-S-400 calorimeter at 298.15–673 K and then used to calculate the molar heat capacities of $La_2SrNiTeO_7$. The operation principle of the device, its calibration, and data processing were described in detail in [2, 7–10].

The electrophysical properties of ceramic ferroelectrics generally depend on the temperature. We studied the temperature dependences of the dielectric constant and electric resistance of tellurite $La_2SrNiTeO_7$ at 293–483 K using the methods described in [11, 12].

The electrophysical properties (dielectric constant and electric resistance) of the compound were studied by measuring the electric capacity on an LCR-800 instrument (Taiwan) at a working frequency of 1 kHz continuously in dry air in a thermostatic mode, while keeping the compound at each fixed temperature.

The dielectric constant was determined from the electric capacity of the sample at the known sample thickness and surface area of electrodes. The relationship between the electric induction (*D*) and electric field strength (*E*) was determined using the Sawyer–

Table 1. Experimental heat capacities of $La_2SrNiTeO_7$

T, K	$C_p \pm \bar{\delta}$, J/(g K)	$C_p^\circ \pm \mathring{\Delta}$, J/(mol K)	T, K	$C_p \pm \bar{\delta}$, K/(g K)	$C_p^\circ \pm \mathring{\Delta}$, J/(mol K)
298.15	0.6841 ± 0.0099	281 ± 11	498	0.3821 ± 0.0102	157 ± 12
323	0.7513 ± 0.0099	309 ± 11	523	0.3378 ± 0.0114	139 ± 13
348	0.3513 ± 0.0059	144 ± 7	548	0.3730 ± 0.0064	153 ± 7
373	0.4706 ± 0.0115	193 ± 13	573	0.4075 ± 0.0089	168 ± 10
398	0.5452 ± 0.0083	224 ± 10	598	0.4470 ± 0.0076	184 ± 9
423	0.5795 ± 0.0123	238 ± 14	623	0.4642 ± 0.0054	191 ± 6
448	0.6029 ± 0.0114	248 ± 13	648	0.4935 ± 0.0100	203 ± 11
473	0.4613 ± 0.0081	190 ± 9	673	0.5207 ± 0.0087	214 ± 10

Tower diagram. The dielectric constant was determined at each temperature by the equation

$$\varepsilon = C/C_0, \quad (1)$$

where $C_0 = \varepsilon_0 S/d$ is the capacity of the capacitor without the (air) sample under study.

As ceramic materials have a certain response delay, the change in the electrophysical properties, as well as the integral electric resistance and electric capacity, were determined only after preliminary exposure for ~0.5 h at a fixed temperature. This is especially important in the range of anomalous changes in the above characteristics. To compare the electric conductivities, the measurements were also performed by the direct deflection method using an E6-13A teraohmmeter.

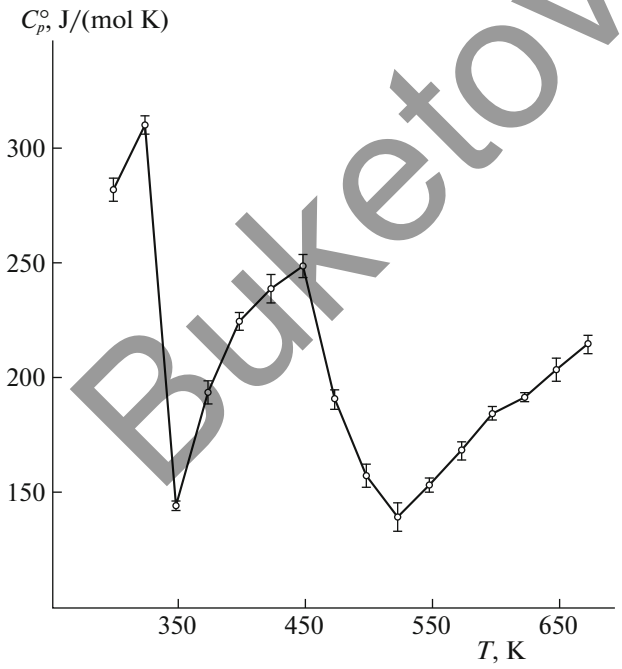

Fig. 1. Temperature dependence of the heat capacity of $La_2SrNiTeO_7$.

RESULTS AND DISCUSSION

Table 1 and Fig. 1 show the results of the calorimetric study of the heat capacity of the compound.

According to Table 1 and Fig. 1, the curves of the $C_p^\circ(T)$ dependences for $La_2SrNiTeO_7$ at 323 and 448 K show λ-shaped effects, apparently related to the second-order phase transitions. These transitions may be associated with cation redistributions, or with changes in the thermal expansion coefficients, magnetic moments, dielectric constant, electric resistance of the synthesized nickelite-tellurite, etc.

The equations of the temperature dependence of the heat capacity of $La_2SrNiTeO_7$ were derived by mathematical processing of the experimental data, taking into account the phase transition temperatures. According to Table 1 and Fig. 1, nickelite-tellurite exhibits phase transitions; therefore, the $C_p^\circ(T)$ dependence of the compound was described by several equations, whose coefficients are given in Table 2.

The technical characteristics of the IT-S-400 calorimeter do not allow us to calculate the standard entropy of the compound from the experimental heat capacities. Therefore, the standard entropy was evaluated using the system of ionic entropy increments [13]. Then the temperature dependences $C_p^\circ(T)$, entropies $S^\circ(T)$, enthalpies $H^\circ(T) - H^\circ(298.15)$, and reduced thermodynamic potential $\Phi^{xx}(T)$ at 298.15–673 K were calculated using the known relations [14] following [2] (Table 3). When evaluating the errors of the functions $S^\circ(T)$ and $\Phi^{xx}(T)$, the errors of $S^\circ(298.15)$ (±3%) were taken into account.

The experimental data on the electrophysical properties of $La_2SrNiTeO_7$ are given in Table 4 and Figs. 2 and 3.

Table 2. Coefficients of the equation $C_p^\circ = a + bT + cT^{-2}$ for the temperature dependence of the heat capacity of $La_2SrNiTeO_7$ (J/(mol K))

a	$b \times 10^3$	$c \times 10^{-5}$	ΔT, K
150 ± 8	440.0 ± 23.45	–	298–323
2203 ± 117	–(5916.0 ± 315.25)	–	323–348
1598 ± 85	–(1988.2 ± 105.95)	–(922.76 ± 49.17)	348–448
–(1810 ± 96)	2259.5 ± 120.40	2098.81 ± 111.84	448–523
122 ± 6	229.6 ± 12.24	–(281.17 ± 14.98)	523–673

Table 3. Thermodynamic functions of $La_2SrNiTeO_7$

T, K	$C_p^\circ \pm \mathring{\Delta}$, 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)
298.15	262 ± 14	277 ± 8	–	277 ± 8
300	282 ± 15	279 ± 23	560 ± 30	277 ± 23
325	293 ± 16	302 ± 25	7760 ± 410	278 ± 23
350	133 ± 7	318 ± 27	12920 ± 690	281 ± 24
375	197 ± 11	330 ± 28	17280 ± 920	284 ± 24
400	226 ± 12	344 ± 29	22600 ± 1200	288 ± 24
425	242 ± 13	358 ± 30	28480 ± 1520	291 ± 24
450	248 ± 13	373 ± 31	34630 ± 1850	295 ± 25
475	193 ± 10	384 ± 32	40050 ± 2130	300 ± 25
500	159 ± 9	393 ± 33	44420 ± 2400	304 ± 25
525	138 ± 7	400 ± 33	48100 ± 2560	309 ± 26
550	155 ± 8	407 ± 34	51790 ± 2760	313 ± 26
575	169 ± 9	414 ± 35	55840 ± 2980	317 ± 26
600	181 ± 10	422 ± 35	60210 ± 3210	321 ± 27
625	193 ± 10	429 ± 36	64890 ± 3460	326 ± 27
650	204 ± 11	437 ± 36	69860 ± 3720	330 ± 28
675	215 ± 12	445 ± 37	75100 ± 4000	334 ± 28

An analysis of the data of Table 4 and Figs. 2 and 3 shows that $La_2SrNiTeO_7$ is metallic conductor at 313–343 K, semiconductor at 353–373 K, metallic conductor at 393–403 K, semiconductor at 403–423 K, and metallic conductor at 453–483 K.

The band gap was calculated by the equation

$$\Delta E = \frac{2kT_1T_2}{T_2 - T_1} \ln \frac{R_1}{R_2}, \quad (2)$$

where k is the Boltzmann constant; R_1 and R_2 are the resistances at the temperatures T_1 and T_2, respectively.

The band gap (ΔE) calculated by Eq. (2) for $La_2SrNiTeO_7$ is 2.75 eV at 353–373 K and 3.57 eV at 403–423 K.

Thus, the temperature dependences of the isobaric heat capacity of $La_2SrNiTeO_7$ were studied for the first time by experimental dynamic calorimetry at 298.15–673 K, and its fundamental constant—the standard heat capacity—was established. For nickelite-tellurite at temperatures in the ranges under study, the curves of $C_p^\circ(T)$ show the λ-shaped temperature dependences of the heat capacity related to the second-order phase transition.

The equations for the temperature dependence of the heat capacity of nickelite-tellurite were derived taking into account the transition temperatures. The standard entropy of the tellurite was calculated by the ionic increments method. The temperature dependences of the heat capacity and thermodynamic func-

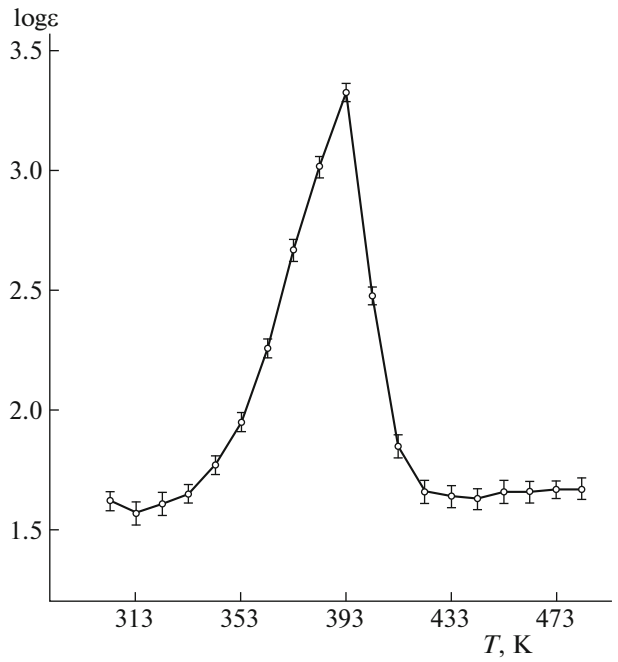

Fig. 2. Temperature dependence of the dielectric constant of $La_2SrNiTeO_7$.

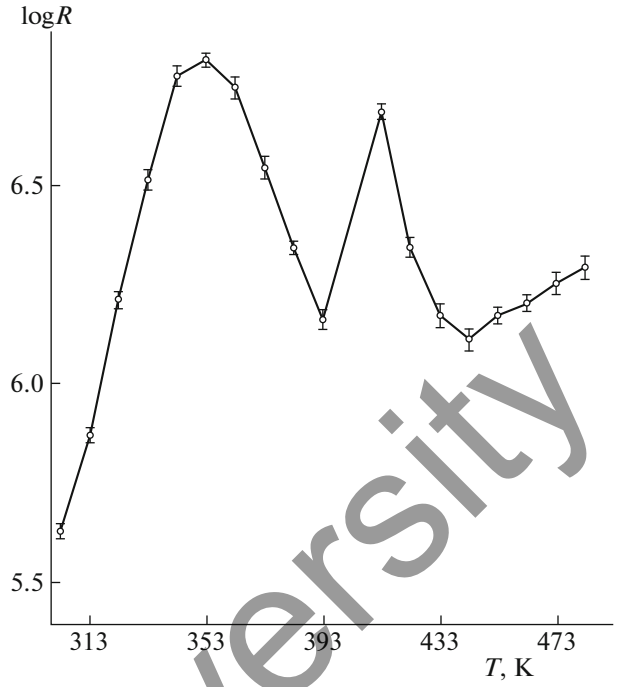

Fig. 3. Temperature dependence of the electric resistance of $La_2SrNiTeO_7$.

tions at 298.15–673 K: the entropy $S°(T)$, enthalpy $H°(T) - H°(298.15)$, and reduced thermodynamic potential $\Phi^{xx}(T)$ were calculated.

Table 4. Temperature dependence of the electric capacity (C), dielectric constant (ε), and electric resistance (R) of $La_2SrNiTeO_7$

T, K	C, μF	ε	logε	R, kΩ	log R
303	8.21	41	1.62	429.3	5.63
313	7.45	38	1.57	742.1	5.87
323	8.01	40	1.61	1640	6.21
333	8.88	45	1.65	3271	6.51
343	11.58	58	1.77	5849	6.77
353	17.65	89	1.95	6511	6.81
363	36.49	184	2.26	5452	6.74
373	92.86	468	2.67	3472	6.54
383	209.64	1056	3.02	2201	6.34
393	421.18	2122	3.33	1460	6.16
403	60.47	305	2.48	4190	6.62
413	13.91	70	1.85	4815	6.68
423	9.17	46	1.66	2184	6.34
433	8.57	43	1.64	1478	6.17
443	8.40	42	1.63	1295	6.11
453	8.97	45	1.66	1484	6.17
463	9.10	46	1.66	1603	6.20
473	9.24	47	1.67	1783	6.25
483	9.37	47	1.67	1946	6.29

The temperature dependences of the electrophysical properties (dielectric constant and electric resistance) of $La_2SrNiTeO_7$ were studied on an LCR instrument. The curves of the log ε(T) and log R(T) dependences have maxima and minima, which confirm the λ-like effects on the curve of the $C_p°(T)$ dependence of this compound, which were attributed to the second-order phase transition.

The data obtained showed that $La_2SrNiTeO_7$ has semiconductor properties and is of interest for electronic technology.

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