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CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

X-ray Diffraction and Thermodynamic Characteristics for Tellurite of the Composition Li_2CeTeO_5

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Abstract—Tellurite of the composition Li_2CeTeO_5 is synthesized by solid-phase method from cerium(IV) and tellurium(IV) oxides and lithium carbonate. The type of syngony, the unit cell parameters, and the compound's X-ray and pycnometry densities are determined via X-ray diffraction analysis. The isobaric heat capacity of lithium–cerium tellurite is studied by means of dynamic calorimetry in the temperature range of 298.15–673 K; the results serve as the basis for deriving $C_p^\circ \sim f(T)$ dependency equations and determining the compound's thermodynamic functions. λ-shaped anomalous effects, due probably to Type II phase transitions, are found on the $C_p^\circ \sim f(T)$ dependence.

Keywords: lithium–cerium tellurite, X-ray diffraction analysis, heat capacity, thermodynamic functions
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INTRODUCTION

Rare-earth elements (REE) form numerous compounds of various types with other elements. With respect to electric properties, some of these compounds are magnetic semiconductors, since the presence of REE ions with vacant 4*f*-electron shells in them results in uncompensated for spin and orbital moments and the emergence of ordering at a specific temperature [1]. Studies of the chemical and physicochemical properties of compounds based on oxides of rare-earth, alkali (alkali-earth) metals, and tellurium are thus of interest from both theoretical and practical viewpoints [2].

The aim of this work was to study the X-ray diffraction and thermodynamic properties of tellurite of the composition Li_2CeTeO_5.

EXPERIMENTAL

The compound was synthesized in accordance with ceramic technology using cerium(IV) and tellurium(IV) oxides, and lithium carbonate of chemically pure grade. Stoichiometric quantities of the initial compounds were thoroughly ground in an agate mortar and transferred quantitatively to alundum crucibles. The mixtures were subjected to thermal treatment for solid-phase interaction in air in an SNOL furnace at 400–800 and 1000°C for 25 and 15 h. Prior to any temperature increase at 400–800 and 1000°C, the mixtures were cooled, thoroughly homogenized, and ground. To obtain equilibrium phases that were stable at low temperatures, low-temperature annealing at 400°C was conducted for 20 h.

The formation of the equilibrium compound's composition was controlled via X-ray diffraction analysis using a DRON-2.0 difractometer (CuK_α radiation; U = 30 kV; I = 10 mA; pulse counter scale, 1000 pulses/s; counter rotation speed, 2 deg/min; time constant τ = 5 s; angle range (2θ), 10°–90°). The intensities of the diffraction maxima were determined using a 100-point scale. The XRD patterns were indexed by means of homology [3]. The pycnometry density was determined as described in [4]. Tetrabromoethane was used as an indifferent liquid.

The tellurite heat capacity was studied by means of dynamic calorimetry using an IT-S-400 device in the temperature range of 298.15–673 K [5]. The device was calibrated by determining its heat conductivity K_h [5, 6]. Several experiments with a copper sample and an empty ampoule were performed for this purpose. The calorimeter's heat conductivity was determined according to the formula

$$K_h = C_{\mathrm{Cu\ sam}}/(\bar{\tau}_{\mathrm{hm}} - \bar{\tau}_{\mathrm{h}}^0), \qquad (1)$$

where $C_{\mathrm{Cu\ sam}}$ is the total heat capacity of the copper sample, J/K; $\bar{\tau}_{hm}$ is the average value of the calorimeter's time delay in experiments with the copper sample, s; and $\bar{\tau}_{\mathrm{h}}^0$ is the calorimeter's average time delay in experiments with the empty ampoule, s.

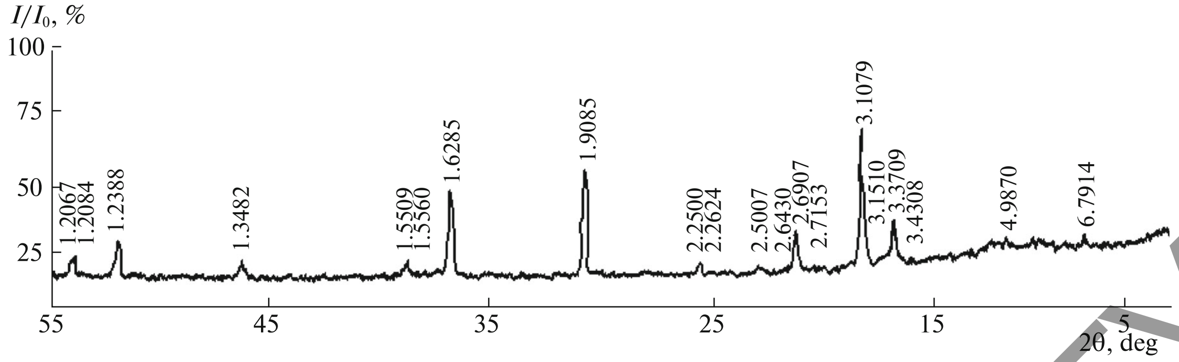

Fig. 1. X-ray diffraction image of the synthesized tellurite (Li_2CeTeO_5).

The total heat capacity of the copper sample was calculated according to the formula

$$C_{\mathrm{Cu\ sam}} = C_{\mathrm{Cu}} m_{\mathrm{sam}}, \tag{2}$$

where C_{Cu} is the reference value of the copper's specific heat capacity, J/(kg K); and m_{sam} is the mass of the copper sample, kg.

The value of the specific heat capacity of the investigated substance was calculated according to the formula

$$C_{\mathrm{spec}} = K_{\mathrm{h}}(\tau_{\mathrm{h}} - \tau_{\mathrm{h}}^0)/m_0, \tag{3}$$

where K_{h} is the calorimeter's heat conductivity; m_0 is the mass of the investigated substance, kg; τ_{h} is the calorimeter's time delay, s; and τ_{h}^0 is the calorimeter's time delay in experiments with the empty ampoule, s. The values of the molar heat capacity were then calculated from those of the specific heat capacity according to the formula

$$C_M = C_{\mathrm{spec}} M, \tag{4}$$

where C_{spec} is the substance's specific heat capacity, J/(kg K); and M is the substance's molar mass, kg/mol.

Table 1. Results from indexing the X-ray diffraction image of double tellurite (Li_2CeTeO_5)

I/I_0, %	d, Å	$10^4/d^2_{\mathrm{exp}}$	*hkl*	$10^4/d^2_{\mathrm{calc}}$
10	6.7914	217	101	217
8	4.9870	402	003	406
9	3.4308	850	210	859
32	3.3709	880	202	868
100	3.1079	1035	212	1040
30	2.6641	1409	204	1409
5	2.6430	1432	221	1420
7	2.5007	1599	301	1592
10	2.2624	1954	303	1953
10	2.2500	1975	116	1968
75	1.9085	2745	400	2750
63	1.6285	3771	307	3757
7	1.5509	4158	424	4160
26	1.2388	6516	507	6508
15	1.2084	6848	1.1.12	6840
12	1.2067	6868	620	6876

At each fixed temperature of every 25 K, five parallel experiments were performed and their results were averaged and processed by means of mathematical statistics. At each temperature, the mean-square deviation ($\bar{\delta}$, J/(g K)) was estimated for averaged values of the specific heat capacity and a random error component ($\overset{\circ}{\Delta}$ (J/(mol K)) was calculated for averaged values of the molar heat capacity [7].

The calorimeter's operation was tested by determining the heat capacity of α-Al_2O_3. Experimental value $C_p^\circ(298.15)$ of α-Al_2O_3 equal to 76.0 J/(mol K) was in agreement with its recommended value of 79.0 J/(mol K) [8]. The reliability of the experimental values of heat capacity was also corroborated by the experimental value of the heat capacity of sodium arsenate (Na_3AsO_4) determined earlier using the same IT-S-400 calorimeter [9] and equal to 169.1 J/(mol K), being in agreement with the recommended value (170.3 J/(mol K)) given in [10].

RESULTS AND DISCUSSION

Figure 1 shows an X-ray image of the synthesized tellurite (Li_2CeTeO_5). Table 1 shows the results from indexing the X-ray image of double lithium–cerium tellurite of the composition Li_2CeTeO_5.

As seen from Table 1, the values of experimental and calculated values of $10^4/d^2$ and X-ray and pycnometry densities (Table 2) are in satisfactory agreement with one another, as is corroborated by the reliability and accuracy of indexing results. We may state

Table 2. Type of syngony and unit cell parameters of the synthesized tellurite

Compound	Type of syngony	Lattice parameters, Å		V^0_{cell}, Å^3	$V^0_{\text{un.cell}}$, Å^3	Z	Density, g/cm^3	
		a	c				$\rho_{\text{X-ray}}$	ρ_{pycn}
Li_2CeTeO_5	Tetragonal	6.72	13.11	1154.98	144.37	8	4.16	4.08 ± 0.10

Table 3. Experimental values of specific and molar heat capacities of tellurite (Li_2CeTeO_5)

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)
298.15	0.5274 ± 0.0111	191 ± 5	498	0.8409 ± 0.0056	304 ± 8
323	0.6972 ± 0.0055	252 ± 6	523	0.7986 ± 0.0059	289 ± 7
348	0.5696 ± 0.0055	206 ± 5	548	0.6776 ± 0.0055	245 ± 6
373	0.4524 ± 0.0054	164 ± 4	573	0.5954 ± 0.0050	215 ± 5
398	0.5611 ± 0.0057	203 ± 5	598	0.6270 ± 0.0053	227 ± 6
423	0.6417 ± 0.0050	232 ± 6	623	0.6560 ± 0.0055	237 ± 6
448	0.7379 ± 0.0057	267 ± 7	648	0.6712 ± 0.0053	243 ± 6
473	0.8044 ± 0.0055	291 ± 7	673	0.6925 ± 0.0051	250 ± 6

that lithium–cerium tellurite (Li_2CeTeO_5) crystallizes in tetragonal syngony and has the unit cell parameters presented in Table 2.

The experimental values of the specific heat capacity and the calculated values of the molar capacity for Li_2CeTeO_5 tellurite are shown in Table 3.

As seen from the data of Table 3 and Fig. 2, the $C_p^\circ \sim f(T)$ dependence for Li_2CeTeO_5 at 323 and 498 K contains anomalous λ-shaped peaks, due probably to Type II phase transitions. These peaks are likely related to cationic redistributions, changes in the coefficients of thermal expansion, electroconductivity, and dielectric permittivity, the Schottky capacity and effects, the Curie point, ferroelectric and antiferroelectric transitions, and so on [11].

Our experimental data on C_p° for tellurite can be approximated using the equation

$$C_p^\circ = a + bT + cT^{-2}, \tag{5}$$

the coefficients of which are shown in Table 4. Errors in the coefficients of the tellurite heat capacity equation were estimated from the average random values for the investigated temperature ranges.

The calorimeter's technical limitations did not allow calculations of the tellurite standard entropy directly from the experimental data. It was therefore estimated using ionic entropy increments according to [12]. Based on the experimental data on $C_p^\circ \sim f(T)$ and the calculated value of $S^\circ(298.15)$, we calculated the temperature dependences of the following thermodynamic functions: $C_p^\circ(T)$, $S^\circ(T)$, $H^\circ(T) - H^\circ(298.15)$, and $\Phi^{xx}(T)$ (Table 5).

Thermodynamic functions $H^\circ(T) - H^\circ(298.15)$, $S^\circ(T)$, and $\Phi^{xx}(T)$ were calculated according to the formulas

$$H^\circ(T) - H^\circ(298.15) = \int_{298.15}^{T} C_p^\circ dT, \tag{6}$$

$$S^\circ(T) = S^\circ(298.15) + \int_{298.15}^{T} \frac{C_p}{T} dT, \tag{7}$$

$$\Phi^{xx}(T) = S^\circ(T) - \left[H^\circ(T) - H^\circ(298.15)\right]/T. \tag{8}$$

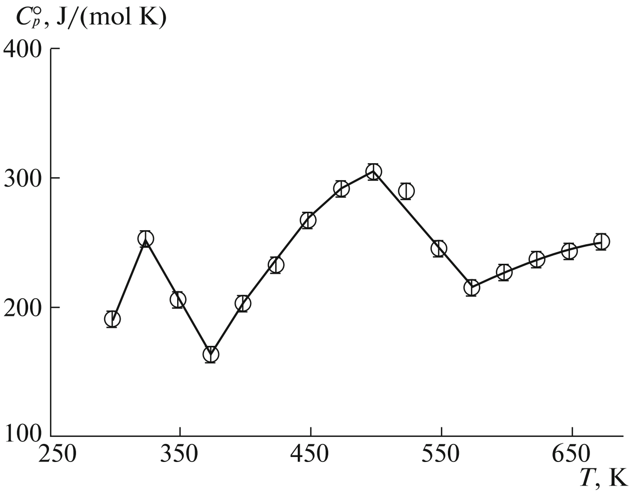

Fig. 2. Temperature dependence of the heat capacity of Li_2CeTeO_5.

Table 4. Coefficients of Eq. (5) in the range 298.15–673 K for Li_2CeTeO_5

T, K	a	$b \times 10^{-3}$	$c \times 10^5$
298–323	−541.5 ± 13.7	2456.9 ± 62.2	–
323–373	824.1 ± 20.9	−1770.8 ± 44.8	–
373–498	752.6 ± 19.0	−409.0 ± 10.4	−607.3 ± 15.4
498–573	893.7 ± 22.6	−1184.0 ± 30.0	–
573–673	693.7 ± 17.6	−374.1 ± 9.5	−866.0 ± 21.9

Errors in the temperature dependences of thermodynamic functions were calculated with allowance for the average errors of determining heat capacity and the accuracy of our entropy calculations (±3%).

The data from our X-ray diffraction studies show that the synthesized tellurite crystallizes in the structural type of distorted perovskite P_m3_m. We may therefore assume that this compound is characterized by valuable electrophysical properties [13]. Our earlier studies of the temperature dependence and electrophysical properties of a series of double selenates and tellurites of *s–d*- and *s–f*-elements showed that the graphs of these dependences probably contained Type II phase transitions related to anomalous changes in heat capacity or electrophysical properties, depending on temperature [2, 14–16]. The Type II phase transition characteristic of semiconductors was observed in studying the temperature dependence of the electric resistance of $CaCeTe_3O_9$ and $SrCeTe_3O_9$ tellurites in the temperature range 300–600 K [2]. The assumption that the Type II phase transition characteristic of semiconductors can be observed in the above temperature range agrees with the data from studies of the temperature dependences of these tellurites' heat capacities in the range of 298.15–673 K [16].

In [17], we studied the temperature dependence of the electric resistance of K_2CeTeO_5 tellurite in the temperature range of 300–600 K. As the temperature rose, major changes in this characteristic were revealed in a certain temperature range, as with ceramic materials. The electric resistance grew in the range of 300–340 K; afterwards (at 340–420 K), we observed a jump with a minimum at 420 K, and finally reversed changes, i.e., a rise in resistance (at 430–520 K). A positive temperature resistance coefficient at 430–520 K indicated a phase transition (possibly Type II) in this range. In the range of 340–420 K, the sample exhibited semiconductor properties; i.e., the electric resistance fell along with the temperature. The calculated width of the forbidden band (ΔE_0) for the studied compound was 1.12 eV. Simple explanations for such behavior are changes in the type, variety, and nature of the charge carriers. The possibility of structural changes was indicated by the probability of two phases coexisting in the above temperature ranges.

Table 5. Temperature dependences of the thermodynamic functions of tellurite (Li_2CeTeO_5) in the temperature range of 298.15–673 K

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)
298.15	191 ± 5	173 ± 5	–	173 ± 5
300	196 ± 5	174 ± 10	386 ± 10	173 ± 10
325	257 ± 7	192 ± 11	6044 ± 153	174 ± 10
350	204 ± 5	209 ± 12	11705 ± 296	176 ± 10
375	160 ± 4	222 ± 12	16260 ± 411	178 ± 10
400	209 ± 5	234 ± 13	20992 ± 531	181 ± 10
425	243 ± 6	248 ± 14	26659 ± 675	185 ± 10
450	269 ± 7	262 ± 15	33063 ± 837	189 ± 10
475	289 ± 7	277 ± 15	40046 ± 1013	193 ± 11
500	305 ± 8	293 ± 16	47485 ± 1202	198 ± 11
525	272 ± 7	307 ± 17	54658 ± 1383	202 ± 11
550	243 ± 6	319 ± 18	61091 ± 1546	207 ± 11
575	213 ± 5	329 ± 18	66784 ± 1690	213 ± 12
600	228 ± 6	338 ± 19	72349 ± 1831	218 ± 12
625	238 ± 6	348 ± 19	78181 ± 1978	223 ± 12
650	245 ± 6	357 ± 20	84224 ± 2131	228 ± 13
675	251 ± 6	367 ± 20	90428 ± 2288	233 ± 13

As a rule, a temperature dependence of electrophysical properties is observed in ceramic ferroelectrics.

Our data serve as the basis for attributing the phase transitions on the $C_p^\circ \sim f(T)$ curve of Li_2CeTeO_5 (an analog of K_2CeTeO_5) to possible Type II transitions caused by anomalous changes in the material's electrophysical properties.

CONCLUSIONS

Tellurite of the composition Li_2CeTeO_5 was synthesized from cerium(IV) and tellurium(IV) oxides and lithium carbonate by solid-phase means. The type of syngony, the unit cell parameters, and the X-ray and pycnometry densities of the synthesized lithium–cerium tellurite were determined for the first time. The isobaric heat capacity of Li_2CeTeO_5 tellurite was determined for the first time via dynamic calorimetry in the temperature range of 298.15–673 K. Equations describing its dependence on temperature were derived. The temperature dependences of the following thermodynamic functions were calculated: $C_p^\circ(T)$, $S^\circ(T)$, $H^\circ(T) - H^\circ(298.15)$, and $\Phi^{xx}(T)$. The anomalous λ-shaped effects observed on the temperature dependence of the synthesized compound's heat capacity probably indicate Type II phase transitions caused by valuable electrophysical properties of the new double cerium tellurite. Our results can be used in predicting, synthesizing, and studying of new compounds of tellurium and rare-earth elements characterized by important electrophysical properties.

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