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CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Heat Capacity and Thermodynamic Functions of Cerium Tellurites in the Range of 298.15–673 K

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Abstract—The isobaric heat capacity of cerium tellurites is studied in the range of 298.15–673 K and used as a basis for deriving dependences $C_p^\circ \sim f(T)$ and determining their thermodynamic functions. Dependences $C_p^\circ \sim f(T)$ are found to have abnormally sharp λ-like peaks, due probably to second-order phase transitions.

Keywords: calorimetry, heat capacity, calcium–cerium tellurites, strontium–cerium tellurites, second-order phase transitions, thermodynamic functions.

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INTRODUCTION

Compounds based on rare-earth metal oxides have a unique combination of electrical, magnetic, thermal, optical, and other properties, due to the specificity of the electron structure of lanthanides. They are widely used in modern microelectronics and many other fields of new techniques for creating multifunctional systems [1].

Nonsymmetric cationic coordination environments in oxide materials are critical for such technologically important physical properties as ferroelectricity, piezoelectricity, pyroelectricity, dielectric behavior, and the second optical harmonic [2]. It is known that a strict condition for a solid to have nonlinear optical and piezoelectrical properties is that it contain no center of symmetry in its crystal structure. On the other hand, it was postulated in [3] that the probability of the formation of acentric structures rises when we introduce ions with unshared electron pairs (e.g., Bi^{3+}, Te^{4+}, Se^{4+}, etc.) into the composition of a compound. As a result, tellurites are now being actively studied [4–6] as possible new piezoelectrics and crystals suitable for generating the second optical harmonic. From this viewpoint, double tellurites of *s–d* and *s–f* elements remain poorly studied.

The aim of this work was to study the heat capacities and thermodynamic properties of double cerium tellurites in the temperature range of 298.15–673 K.

EXPERIMENTAL

Cerium tellurites $Me^{II}CeTe_3O_9$ (Me^{II} – Ca, Sr) were synthesized by ceramic technology from cerium(IV) oxide, tellurium(IV) oxide, and calcium (strontium) carbonate of chemically pure grade. The synthesis and X-ray and electrophysical properties of these compounds were described in [7]. The formation of the equilibrium composition of a compound was monitored by X-ray diffraction. The X-ray powder diffraction pattern of each compound was indexed by means of homology in [8]. The data from X-ray diffraction studies show that the synthesized compounds crystallize in the structure of distorted perovskite P_m3_m. The correctness of indexing was confirmed by the good reproducibility of experimental $10^4/d^2$ values and the agreement between the X-ray and pycnometric densities.

The heat capacities of tellurites were studied via dynamic calorimetry on an commercial IT-S-400 calorimeter in the temperature range of 298.15–673 K (Table 1). The operating principle of the calorimeter is based on the comparative method of a dynamic *c*-calorimeter equipped with a heat gauge.

Experiments were performed with the monotonical (nearly linear) heating of each sample at an average rate of ~0.1 K/s. The temperature dependence of the studied parameter was determined for each experiment. The calorimeter circuit allowed temperature measurements at fixed points every 25 K. This was achieved using the constant-current potentiometer built into the calorimeter and a switcher. The volumetric range was no less than 1×10^7 J/(K m^3). The time required to perform measurements over the range of temperatures with the processing of experimental data was no more than 2.5 h. The error in measuring heat capacity on the IT-S-400 calorimeter does not exceed ±10% [9, 10].

Each sample placed into the metallic ampoule of the measurement cell was continuously heated with a

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Table 1. Experimental specific and molar heat capacities of the studied compounds

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)
		$CaCeTe_3O_9$			
298.15	0.4025 ± 0.0142	283 ± 10	498	0.4976 ± 0.0153	350 ± 9
323	0.9134 ± 0.0129	646 ± 4	523	0.5016 ± 0.0154	354 ± 9
348	0.4413 ± 0.0095	311 ± 6	548	0.5661 ± 0.0123	400 ± 6
373	0.6135 ± 0.0181	435 ± 8	573	0.5933 ± 0.0121	421 ± 6
398	0.6025 ± 0.0164	424 ± 8	598	0.6099 ± 0.0104	433 ± 4
423	0.7085 ± 0.0185	500 ± 7	623	0.6711 ± 0.0239	474 ± 10
448	0.7354 ± 0.0213	517 ± 8	648	0.6773 ± 0.0158	480 ± 6
473	0.4248 ± 0.0129	300 ± 8	673	0.7046 ± 0.0144	500 ± 6
		$SrCeTe_3O_9$			
298.15	0.2869 ± 0.0102	216 ± 10	498	0.6232 ± 0.0186	470 ± 8
323	0.3297 ± 0.0107	249 ± 9	523	0.4160 ± 0.0136	314 ± 9
348	0.4185 ± 0.0103	316 ± 7	548	0.4513 ± 0.0142	341 ± 9
373	0.4742 ± 0.0119	358 ± 7	573	0.5247 ± 0.0183	396 ± 10
398	0.5619 ± 0.0177	424 ± 9	598	0.6012 ± 0.0180	454 ± 8
423	0.4609 ± 0.0131	348 ± 8	623	0.6241 ± 0.0135	471 ± 6
448	0.4294 ± 0.0137	324 ± 9	648	0.6647 ± 0.0199	502 ± 8
473	0.5156 ± 0.0177	389 ± 10	673	0.7139 ± 0.0213	539 ± 8

heat flow through a heat gauge. The time delay of the ampoule's temperature with respect to the base's temperature was measured every 25 K of heating using an F-136 microvoltammeter and a commercial SETs-100 second meter. The calorimeter was calibrated by determining the heat conductivity of the heat gauge, K_{hg}. To accomplish this, several experiments were performed with copper samples and empty ampoules.

The heat gauge's heat conductivity was calculated as

$$K_{hg} = C_{sCu}/(\bar{\tau}_{hgCu} - \bar{\tau}^0_{hg}), \tag{1}$$

where C_{sCu} is the total heat capacity of a copper sample, J/K; $\bar{\tau}_{hgCu}$ is the average delay for the heat gauge in experiments with copper samples, s; and $\bar{\tau}^0_{hg}$ is the average delay for the heat gauge in the experiment with an empty ampoule, s.

The total heat capacity of each copper sample was determined as

$$C_{sCu} = C_{Cu} m_s, \tag{2}$$

where C_{Cu} is the tabular specific heat capacity of copper, J/(kg K); m_s is the mass of the copper sample, kg.

Five parallel experiments were performed at each fixed temperature in steps of 25 K. The delays for the heat gauge were averaged and processed by means of mathematical statistics. The mean-square deviations ($\bar{\delta}$) of averaged specific heat capacities at each temperature were calculated as

$$\bar{\delta} = \left(\sum_{i=1}^{n} \frac{(C_i - \bar{C})^2}{n-1} \right)^{1/2}, \tag{3}$$

where n is the number of experiments, C_i is the measured specific heat capacity, and $\bar{C}$ is the arithmetic mean of specific heat capacities.

The random error component was calculated for the average molar heat capacity as [11, 12]

$$\mathring{\Delta}, \% = \frac{\delta t_p}{\bar{C}} 100, \tag{4}$$

where $\mathring{\Delta}$ is the random error component, %; t_p is Student's coefficient, equal to 2.78 for $n = 5$ at $p = 0.95$. Random error component ($\mathring{\Delta}$) is expressed in J/(mol K); mean-square deviation ($\bar{\delta}$) is measured in J/(g K).

Operation of the calorimeter was tested by measuring the heat capacity of α-Al_2O_3. The resulting $C_p^\circ(298.15) = 76.0$ J/(mol K) was in satisfactory agreement with the reference value (79.0 J/(mol K)) [13]. These characteristics of the calorimeter testify to the reliability of the obtained heat capacities of tellurites.

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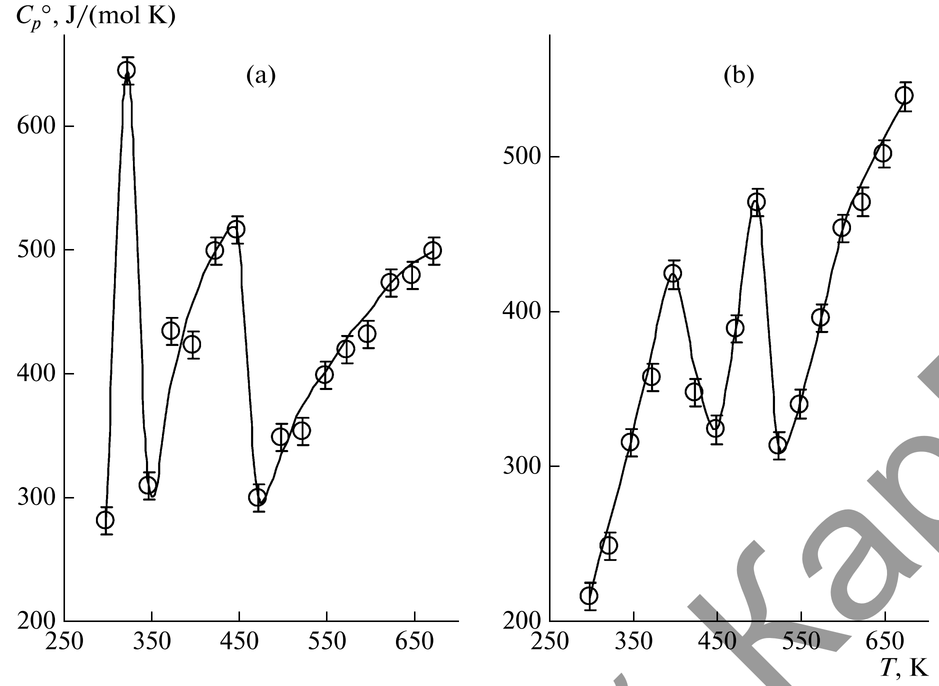

Fig. 1. Heat capacities versus temperature for (a) $CaCeTe_3O_9$ and (b) $SrCeTe_3O_9$ tellurites.

The specific heat capacity of each compound was calculated as

$$C_{sp} = \frac{K_{hg}}{m_0}(\tau_{hg} - \tau^0_{hg}), \qquad (5)$$

where K_{hg} is the heat conductivity of the heat gauge, m_0 is the mass of the studied compound, kg, τ_{hg} is the temperature delay for the heat gauge, and $\bar{\tau}^0_{hg}$ is the temperature delay for the heat gauge in experiments with an empty ampoule, s. The specific heat capacities were then used to calculate the molar heat capacity using the formula

$$C_m = C_{sp}M, \qquad (6)$$

where C_{sp} is the specific heat capacity of the compound, J/(kg K), and M is the molar mass of the compound, g/mol.

RESULTS AND DISCUSSION

In studying the temperature dependences of the heat capacities of double tellurites at 323 and 448 K for $CaCeTe_3O_9$ and 398 and 498 K for $SrCeTe_3O_9$, we observed abnormally sharp λ-like peaks probably associated with second-order phase transitions (see Fig. 1). These transitions could be due to the redistribution of cations and changes in the magnetic moment of synthesized tellurites.

Based on the experimental data (Table 1) and considering the temperatures of second-order transitions, we derived the following temperature dependence for the compounds' heat capacities:

$$C_p^\circ\text{, J/(mol K)} = a + bT + cT^{-2}, \qquad (7)$$

the coefficients of which are given in Table 2. The error in the coefficients of dependences $C_p^\circ \sim f(T)$ was determined using the average random errors for the considered temperature ranges. Since the technical characteristics of the calorimeter do not allow direct calculation of the standard entropy $S°(298.15)$ of tellurites from the experimental data on $C_p^\circ(T)$, it was estimated by means of ion increments. Using known relationships, the experimental data on $C_p^\circ \sim f(T)$, and the estimated values of $S°(298.15)$, we calculated the temperature dependences of functions $C_p^\circ(T)$, $S°(T)$, $H°(T) - H°(298.15)$, and $\Phi^{xx}(T)$. Our results are presented in Table 3.

The average random error components were estimated for all heat capacities and enthalpies over the range of temperatures. The error in calculating entropy (±3%) was incorporated into the estimated error for entropy and the reduced thermodynamic potential. The standard entropies were estimated using Kumok's ion entropy increments [14].

The hypothesis of a second-order phase transition in the above temperature ranges agrees with the data from studying the temperature dependences of the electrical resistance of synthesized tellurites in the range of 300–600 K [7]. This takes the form of an

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Table 2. Coefficients of Eq. (7) in the range of 298.15–673 K

T, K	a	$b \times 10^{-3}$	$c \times 10^{5}$
	CaCeTe$_3$O$_9$		
298–323	−4046.7 ± 290.2	14527.8 ± 1041.6	–
323–348	4974.8 ± 356.7	−13402.5 ± 961.0	–
348–448	254.8 ± 18.3	960.9 ± 68.9	−337.3 ± 24.2
448–473	4404.5 ± 315.8	−8676.9 ± 622.1	–
473–673	518.7 ± 37.2	203.4 ± 14.6	−703.7 ± 50.5
	SrCeTe$_3$O$_9$		
298–398	−402.0 ± 33.9	2075.3 ± 174.7	–
398–443	1219.7 ± 102.7	−1999.3 ± 168.3	–
443–498	−986.2 ± 83.0	2924.7 ± 246.3	–
498–523	3584.0 ± 301.8	−6252.5 ± 526.5	–
523–673	1287.4 ± 108.4	−450.4 ± 37.9	−2018.5 ± 170.0

Table 3. Thermodynamic functions of tellurites 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)
		CaCeTe$_3$O$_9$		
298.15	285 ± 20	351 ± 11	–	351 ± 36
300	312 ± 22	353 ± 36	594 ± 43	351 ± 36
325	675 ± 48	392 ± 40	12925 ± 927	353 ± 36
350	284 ± 20	426 ± 43	24211 ± 1736	357 ± 36
375	375 ± 27	450 ± 46	32865 ± 2356	362 ± 37
400	428 ± 31	476 ± 48	42924 ± 3078	368 ± 37
425	476 ± 34	503 ± 51	54244 ± 3889	376 ± 38
450	521 ± 37	532 ± 54	66715 ± 4783	383 ± 39
475	283 ± 20	553 ± 56	76502 ± 5485	392 ± 40
500	339 ± 24	569 ± 58	84540 ± 6062	400 ± 41
525	370 ± 27	587 ± 60	93410 ± 6698	409 ± 42
550	398 ± 29	605 ± 61	103017 ± 7386	417 ± 42
575	423 ± 30	623 ± 63	113281 ± 8122	426 ± 43
600	445 ± 32	641 ± 65	124136 ± 8901	434 ± 44
625	466 ± 33	660 ± 67	135526 ± 9717	443 ± 45
650	484 ± 35	679 ± 69	147404 ± 10569	452 ± 46
675	502 ± 36	697 ± 71	159729 ± 11453	461 ± 47
		SrCeTe$_3$O$_9$		
298.15	216 ± 18	362 ± 11	–	–
300	221 ± 19	364 ± 42	437 ± 37	362 ± 41
325	272 ± 23	383 ± 44	6600 ± 556	362 ± 41
350	324 ± 27	405 ± 46	14061 ± 1184	363 ± 41
375	376 ± 32	430 ± 49	22818 ± 1921	365 ± 42
400	428 ± 36	455 ± 52	32872 ± 2768	369 ± 42
425	370 ± 31	479 ± 55	42747 ± 3599	373 ± 43
450	320 ± 27	499 ± 57	51372 ± 4325	379 ± 43
475	403 ± 34	519 ± 59	60532 ± 5097	385 ± 44
500	476 ± 40	541 ± 62	71520 ± 6022	391 ± 45
525	301 ± 25	560 ± 64	81009 ± 6821	398 ± 46
550	372 ± 31	534 ± 61	89666 ± 7550	406 ± 46
575	418 ± 35	551 ± 63	99562 ± 8383	370 ± 42
600	457 ± 38	570 ± 65	110506 ± 9305	378 ± 43
625	489 ± 41	589 ± 67	122338 ± 10301	386 ± 44
650	517 ± 44	609 ± 70	134924 ± 11361	393 ± 45
675	540 ± 46	629 ± 72	148149 ± 12474	401 ± 46

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abnormal change in electrical resistance depending on the temperature, indicating that these compounds have semiconducting and segnetoelectrical properties.

It should be noted that the abnormal effects of second-order phase transitions were observed earlier for the double selenates and tellurites of *s–d* elements [15, 16] and mixed-metal manganese ferrites [17]. Classes of these compounds in the range of second-order phase transitions exhibit semiconducting and segnetoelectrical properties.

CONCLUSIONS

The isobaric heat capacities of new double cerium tellurites with *s* elements were determined by dynamic calorimetry in the temperature range of 298.15–673 K for the first time. Equations describing their temperature dependences were derived. Dependences $C_p^\circ \sim f(T)$ for calcium–cerium and strontium–cerium tellurites were found to have sharp abnormal peaks, i.e., λ-like effects attributable to a second-order phase transition. Thermodynamic functions $C_p^\circ(T)$, $S^\circ(T)$, $H^\circ(T) - H^\circ(298.15)$, and $\Phi^{xx}(T)$ were calculated. The existence of a second-order phase transition indicates that these compounds could have unique electrophysical properties.

The results from our studies could be of interest for inorganic material science, the targeted synthesis of chalcogenites with specified properties, and the physicochemical modeling of chemical and metallurgical processes with the participation of tellurium compounds. They could also serve as initial data for basic reference works and information databases on the thermodynamic constants of inorganic compounds.

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