

CHEMICAL THERMODYNAMICS
AND THERMOCHEMISTRY

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

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Abstract—The isobaric heat capacity of double thulium tellurites is studied via dynamic calorimetry in the range of 298.15–673 K. It is used as the basis for deriving the equation $C_p^\circ \sim f(T)$ and determining the thermodynamic functions. Dependences $C_p^\circ \sim f(T)$ are found to have second-order phase λ -transitions.

Keywords: sodium–thulium tellurites, potassium–thulium tellurites, heat capacity, thermodynamic functions.

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INTRODUCTION

Due to the large-scale introduction of electronic devices in different branches of science and industry, inorganic chemistry encounters the problem of searching for new compounds with valuable electro-physical characteristics, e.g., semiconducting, ferroelectric, radioluminescent, superconducting, and piezo- and pyroelectric properties. The study of complex perovskite-structured oxides of transition 3d- and 4f-elements is therefore also of great importance to inorganic material science [1].

The aim of this work was thus to synthesize double thulium tellurites and study their heat capacity and thermodynamic properties within the range of 298.15–673 K.

EXPERIMENTAL

Thulium tellurites $\text{Me}^{\text{I}}\text{TmTeO}_4$ (Me^{I} —Na, K) were synthesized via the ceramic method with allowance for stoichiometric amounts of thulium oxide, tellurium(IV) oxide, and sodium (potassium) carbonate (chemically pure grade). The samples were carefully ground in an agate mortar and subjected to thermal treatment in air in a SNOL furnace. The regime of thermal treatment was annealing for 10 h at a temperature of 500°C and then within a range of 700–1000°C for 24 h. The mixtures were cooled and repeatedly ground before each temperature increase. Equilibrium

phases stable at low temperatures were obtained by annealing at a temperature of 400°C for 20 h.

The X-ray powder diffraction analysis of the prepared tellurites was performed on a DRON-2.0 diffractometer. The X-ray powder diffraction patterns of the studied compounds were indexed according to homology to establish that the synthesized tellurites crystallized in tetragonal symmetry with the unit cell parameters NaTmTeO_4 , $a = 8.93 \text{ \AA}$, $c = 19.76 \text{ \AA}$, $V^0 = 1575.76 \text{ \AA}^3$, $V_{\text{cell}}^0 = 196.97 \text{ \AA}^3$, $Z = 8$, $\rho_{\text{X-ray}} = 3.23 \text{ g/cm}^3$, $\rho_{\text{pycn}} = 3.19 \pm 0.04 \text{ g/cm}^3$; KTmTeO_4 , $a = 8.95 \text{ \AA}$, $c = 19.88 \text{ \AA}$, $V^0 = 1592.44 \text{ \AA}^3$, $V_{\text{cell}}^0 = 199.05 \text{ \AA}^3$, $Z = 8$, $\rho_{\text{X-ray}} = 3.33 \text{ g/cm}^3$, and $\rho_{\text{pycn}} = 3.26 \pm 0.77 \text{ g/cm}^3$. The data from our X-ray diffraction studies showed that the synthesized compounds crystallize in the distorted perovskite structure $Pm3m$.

The isobaric heat capacities of tellurites were studied via dynamic calorimetry on an IT-S-400 commercial calorimeter in the temperature range of 298.15–673 K. The methods used in our experiments and processing of the result were the same as described in [2–4].

RESULTS AND DISCUSSION

The experimental heat capacities of double tellurites are listed in Table 1. When studying the temperature dependences of the heat capacities of double tellurites, second-order phase λ -transitions presumably associated with the Curie point, changes in dielectric permeability and electrical conductivity, and other

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

T, K	$C_p \pm \bar{\delta}, J/(g K)$	$C_p^\circ \pm \bar{\Delta}, J/(mol K)$	T, K	$C_p \pm \bar{\delta}, J/(g K)$	$C_p^\circ \pm \bar{\Delta}, J/(mol K)$
NaTmTeO₄					
298.15	0.2760 ± 0.0089	106 ± 4	498	0.5472 ± 0.0057	210 ± 9
323	0.5987 ± 0.0071	230 ± 9	523	0.5827 ± 0.0087	223 ± 9
348	0.4348 ± 0.0066	166 ± 7	548	0.5090 ± 0.0077	195 ± 8
373	0.3756 ± 0.0054	144 ± 6	573	0.4583 ± 0.0063	176 ± 7
398	0.2956 ± 0.0046	113 ± 5	598	0.3463 ± 0.0078	133 ± 5
423	0.4142 ± 0.0051	159 ± 6	623	0.4565 ± 0.0059	175 ± 7
448	0.4203 ± 0.0057	161 ± 7	648	0.5082 ± 0.0043	195 ± 8
473	0.4660 ± 0.0062	179 ± 7	673	0.5753 ± 0.0041	221 ± 9
KTmTeO₄					
298.15	0.3117 ± 0.0071	125 ± 5	498	0.5056 ± 0.0064	202 ± 8
323	0.3559 ± 0.0080	142 ± 6	523	0.3866 ± 0.0067	154 ± 6
348	0.4073 ± 0.0055	163 ± 7	548	0.3519 ± 0.0063	141 ± 6
373	0.4395 ± 0.0045	176 ± 7	573	0.4491 ± 0.0077	179 ± 8
398	0.4635 ± 0.0034	185 ± 8	598	0.5456 ± 0.0103	218 ± 9
423	0.2965 ± 0.0060	118 ± 5	623	0.5618 ± 0.0062	225 ± 9
448	0.4470 ± 0.0085	179 ± 8	648	0.6524 ± 0.0088	261 ± 11
473	0.4989 ± 0.0056	199 ± 8	673	0.7091 ± 0.0042	283 ± 12

features were observed at 323 and 523 K for NaTmTeO₄ and at 398 and 498 K for KTmTeO₄ (Fig. 1).

The temperature dependences of the heat capacities of compounds were derived with allowance for second-order phase transitions and using the experi-

mental data in Table 1. Their coefficients are listed in Table 2.

The standard entropy of compounds was estimated using ion entropy increments [5]. The thermodynamic functions $S^\circ(T)$, $H^\circ(T) - H^\circ(298.15)$, and $\Phi^{xx}(T)$

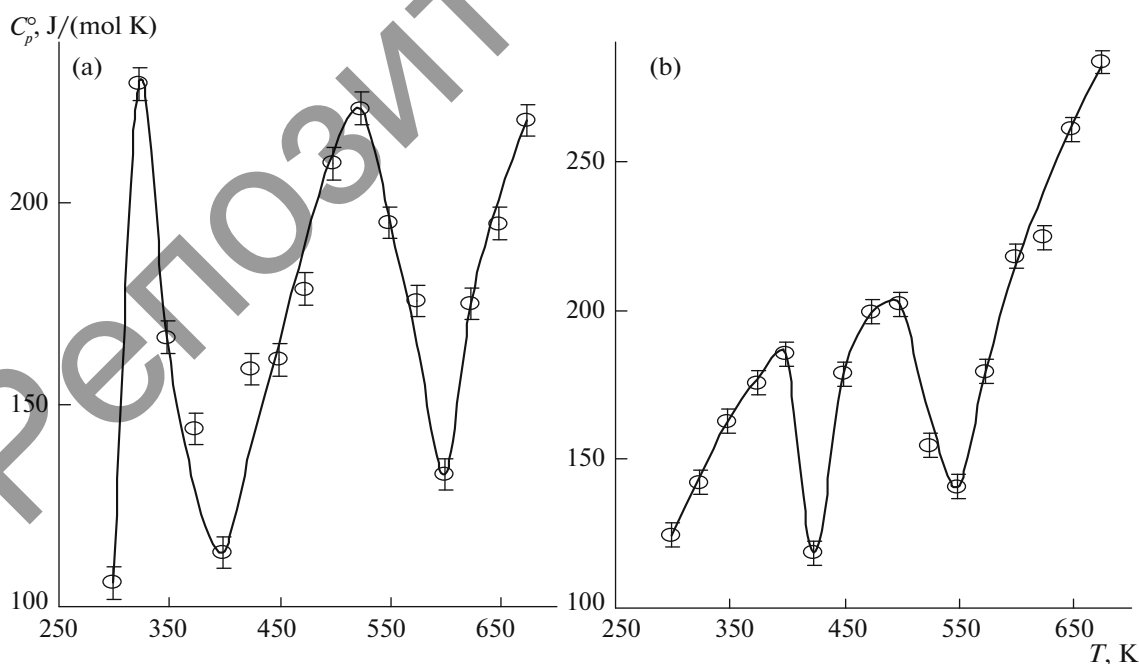
**Fig. 1.** Temperature dependences of the heat capacities of tellurites (a) NaTmTeO₄ and (b) KTmTeO₄.

Table 2. Coefficients for the equation C_p° , (J/(mol K)) = $a + bT + cT^{-2}$ in the range of 298.15–673 K

T, K	a	$b \times 10^{-3}$	$c \times 10^5$
NaTmTeO ₄			
298–323	-1369.4 ± 55.6	4950.4 ± 201.0	–
323–398	730.0 ± 29.6	-1549.6 ± 62.9	374.4 ± 15.2
398–523	-279.9 ± 11.4	942.2 ± 38.3	28.9 ± 1.2
523–598	855.8 ± 34.7	-1209.1 ± 49.1	–
598–673	618.7 ± 25.1	71.9 ± 2.9	1583.8 ± 64.3
KTmTeO ₄			
298–398	329.9 ± 13.9	-128.0 ± 5.4	-148.5 ± 6.1
398–423	1247.6 ± 52.4	-2669.3 ± 112.2	–
423–498	4948.5 ± 207.9	-6543.6 ± 274.9	-3689.6 ± 155.0
498–548	813.7 ± 34.2	1228.2 ± 51.6	–
548–673	-665.7 ± 28.0	1338.3 ± 56.2	219.0 ± 9.2

Table 3. Thermodynamic functions of tellurites in the temperature range of 298.15–673 K

T, K	$C_p^\circ(T) \pm \Delta$, J/(mol K)	$S^\circ(T) \pm \Delta$, J/(mol K)	$H^\circ(T) - H^\circ(298.15) \pm \Delta$, J/mol	$\Phi^{xx}(T) \pm \Delta$, J/(mol K)
NaTmTeO ₄				
298.15	106 ± 4	179 ± 5	–	179 ± 5
300	116 ± 5	180 ± 13	222 ± 9	179 ± 13
325	240 ± 10	194 ± 14	4662 ± 189	179 ± 13
350	178 ± 7	209 ± 15	9690 ± 393	181 ± 13
375	141 ± 6	220 ± 16	13672 ± 555	183 ± 13
400	111 ± 5	228 ± 16	16816 ± 683	186 ± 13
425	137 ± 6	235 ± 17	19961 ± 810	189 ± 13
450	158 ± 6	244 ± 17	23648 ± 960	191 ± 14
475	181 ± 7	253 ± 18	27883 ± 1132	194 ± 14
500	203 ± 8	263 ± 19	32674 ± 1327	198 ± 14
525	225 ± 9	273 ± 19	38025 ± 1544	201 ± 14
550	191 ± 8	283 ± 20	43174 ± 1753	204 ± 14
575	161 ± 7	291 ± 21	47567 ± 1931	208 ± 15
600	130 ± 5	297 ± 21	51205 ± 2079	212 ± 15
625	168 ± 7	303 ± 21	55013 ± 2234	215 ± 15
650	197 ± 8	310 ± 22	59588 ± 2419	219 ± 15
675	223 ± 9	318 ± 23	64840 ± 2633	222 ± 16
KTmTeO ₄				
298.15	125 ± 5	192 ± 6	–	192 ± 6
300	127 ± 5	192 ± 14	251 ± 11	192 ± 14
325	148 ± 6	203 ± 15	3691 ± 155	192 ± 14
350	164 ± 7	215 ± 15	7596 ± 319	193 ± 14
375	176 ± 7	227 ± 16	11855 ± 498	195 ± 14
400	186 ± 8	238 ± 17	16388 ± 689	197 ± 14
425	113 ± 5	247 ± 18	20051 ± 842	200 ± 14
450	182 ± 8	256 ± 18	23962 ± 1007	203 ± 15
475	205 ± 9	267 ± 19	28860 ± 1213	206 ± 15
500	201 ± 8	277 ± 20	33984 ± 1428	209 ± 15
525	169 ± 7	286 ± 21	38591 ± 1621	213 ± 15
550	138 ± 6	293 ± 21	42429 ± 1783	216 ± 16
575	170 ± 7	300 ± 22	46339 ± 1947	220 ± 16
600	198 ± 8	308 ± 22	50940 ± 2140	223 ± 16
625	227 ± 10	317 ± 23	56251 ± 2363	227 ± 16
650	256 ± 11	326 ± 24	62286 ± 2617	231 ± 17
675	286 ± 12	337 ± 24	69058 ± 2901	234 ± 17

were calculated from the experimental heat capacities of tellurites and their standard entropies (Table 3).

CONCLUSIONS

Tellurites $\text{Me}^{\text{I}}\text{TmTeO}_4$ ($\text{Me}^{\text{I}} = \text{Na, K}$) were synthesized by the ceramic method from thulium and tellurium(IV) oxides and sodium (potassium) carbonate. Their symmetry, unit cell parameters, and X-ray and pycnometric densities were determined. The isobaric heat capacities of new double thulium tellurites with s -elements were estimated via dynamic calorimetry in the temperature range of 298.15–673 K for the first time. The dependences $C_p^\circ \sim f(T)$ for sodium–thulium and potassium–thulium tellurites were found to have λ -effects attributable to second-order phase transitions. The existence of such transitions allows us to hypothesize that these compounds can have unique electrophysical properties. The thermodynamic functions $S^\circ(T)$, $H^\circ(T) - H^\circ(298.15)$, and $\Phi^{\text{ex}}(T)$ were also calculated.

The second-order phase transition effects accompanied by the emergence of semiconducting and ferro-

electric properties were found for the double selenates of s - d -elements and tellurites of s - d - and s - f -elements in [2, 3, 6] and for mixed metal manganiferites [4].

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