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## 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 electrophysical characteristics, e.g., semiconducting, ferroelectric, radioluminescent, superconducting, and piezo- and pyroelectric properties. The study of complex perovskite-structured oxides of transition 3*d*- and 4*f*-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 $\mathrm{Me^{I}TmTeO_4}$ ($\mathrm{Me^{I}}$–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 $\mathrm{NaTmTeO_4}$, $a = 8.93$ Å, $c = 19.76$ Å, $V^0 = 1575.76$ Å$^3$, $V^0_{\text{cell}} = 196.97$ Å$^3$, $Z = 8$, $\rho_{\text{X-ray}} = 3.23\ \text{g/cm}^3$, $\rho_{\text{pycn}} = 3.19 \pm 0.04\ \text{g/cm}^3$; $\mathrm{KTmTeO_4}$, $a = 8.95$ Å, $c = 19.88$ Å, $V^0 = 1592.44$ Å$^3$, $V^0_{\text{cell}} = 199.05$ Å$^3$, $Z = 8$, $\rho_{\text{X-ray}} = 3.33\ \text{g/cm}^3$, 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 *Pm*3*m*.

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) | $C_p^\circ \pm \overset{\circ}{\Delta}$, J/(mol K) | $T$, K | $C_p \pm \bar{\delta}$, J/(g K) | $C_p^\circ \pm \overset{\circ}{\Delta}$, J/(mol K) |
|---|---|---|---|---|---|
| | | $NaTmTeO_4$ | | | |
| 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 |
| | | $KTmTeO_4$ | | | |
| 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 $NaTmTeO_4$ and at 398 and 498 K for $KTmTeO_4$ (Fig. 1).

The temperature dependences of the heat capacities of compounds were derived with allowance for second-order phase transitions and using the experimental 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 $S°(T)$, $H°(T) - H°(298.15)$, and $\Phi^{xx}(T)$

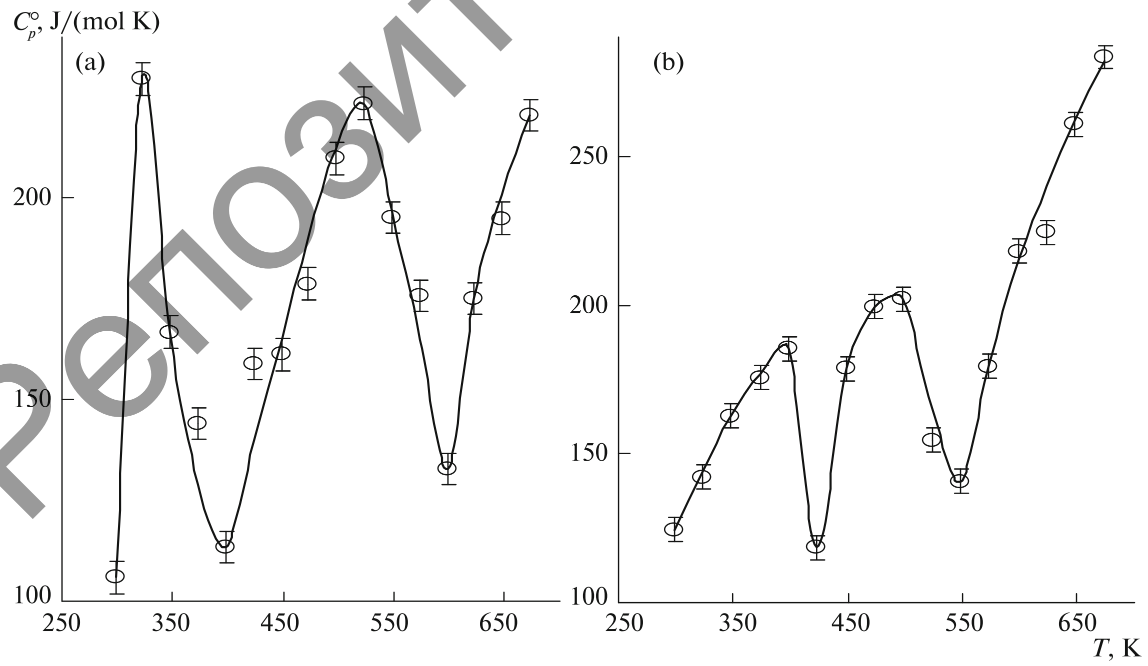

**Fig. 1.** Temperature dependences of the heat capacities of tellurites (a) $NaTmTeO_4$ and (b) $KTmTeO_4$.

**Table 2.** Coefficients for the equation $C_p^\circ$, (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 | $C_p^\circ(T) \pm \mathring{\Delta}$, 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) |
|---|---|---|---|---|
| | | $NaTmTeO_4$ | | |
| 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 $Me^ITmTeO_4$ ($Me^I$ = 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 $\Phi^{xx}(T)$ were also calculated.

The second-order phase transition effects accompanied by the emergence of semiconducting and ferroelectric 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 manganitoferrites [4].

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