

CHEMICAL THERMODYNAMICS  
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## Heat Capacity and Thermodynamic Functions of Cadmium Tellurites in the Range of 298.15–673 K

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**Abstract**—The isobaric heat capacity of cadmium tellurites is studied by dynamic calorimetry in the range of 298.15–673 K to derive the equation for the  $C_p^0 \sim f(T)$  dependence, and to determine the thermodynamic functions. The  $C_p^0 \sim f(T)$  dependences exhibit sharp  $\lambda$ -shaped anomalous effects due apparently to second-order phase transitions.

**Keywords:** calorimetry, heat capacity, magnesium–cadmium and calcium–cadmium tellurites, second-order phase transitions, thermodynamic functions.

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### INTRODUCTION

The comprehensive and systematic study of compounds based on selenium and tellurium, which have semiconductor, ferroelectric, and piezoelectric physicochemical properties, is of great interest. In addition, recent studies conducted in this field of chemistry showed that polyinorganic compounds synthesized on the basis of typical and transition metals together with nonmetals are more likely to exhibit a variety of physicochemical properties. In this respect, polyselenites, polyselenates, polytellurites, and binary selenates and tellurites of *s*- and *d*-elements are poorly studied compounds. We therefore performed a systematic study to find and development scientific bases for the targeted synthesis of new oxo compounds of selenium and tellurium with unique electrophysical properties [1, 2] that are of particular theoretical and practical interest to inorganic materials science as promising materials with valuable physicochemical properties.

Thermodynamic information about new complex oxo compounds of selenium and tellurium is required to determine the directions of the reactions in these systems, to address the possibility of the spontaneous occurrence of a reaction under given conditions, to find the equilibrium constants, and to solve some theoretical problems associated with determining the energy and nature of the chemical bonds. It is necessary to know the thermochemical and thermodynamic properties of complex oxo compounds in order to compose a bank of thermodynamic data, to simulate the synthesis of new materials with desired characteristics, and to identify the fundamental structure–energy–properties dependence in synthesized compounds. The aim of this work was to examine the heat

capacity and thermodynamic properties of binary cadmium tellurites in the range of 298.15–673 K.

### EXPERIMENTAL

Cadmium tellurites  $\text{Me}^{\text{II}}\text{Cd}(\text{TeO}_3)_2$  ( $\text{Me}^{\text{II}} = \text{Mg}, \text{Ca}$ ) were synthesized from cadmium and tellurium(IV) oxides and magnesium (calcium) carbonate by means of ceramic processing. Special purity grade  $\text{TeO}_2$  and reagent grade  $\text{CdO}$ , along with magnesium and calcium carbonates, were used to synthesize binary tellurites. Portions of the original materials were weighed to four decimal places. Stoichiometric amounts of the original materials were carefully ground in an agate mortar, then quantitatively loaded into alundum crucibles and subjected to heat treatment for solid-phase interaction in air. Our heat treatment mode was annealing at a temperature of 400–800°C for 25 h with periodic grinding in a mortar, followed by annealing at 400°C for 15 h to obtain compounds that were stable at low temperatures. The synthesized compounds were subjected to chemical analysis to determine the content of tellurium and oxides of magnesium, calcium, and cadmium [3–5]. The analysis results showed that the content of these elements in  $\text{Me}^{\text{II}}\text{Cd}(\text{TeO}_3)_2$  ( $\text{Me}^{\text{II}} = \text{Mg}, \text{Ca}$ ) was in good agreement with the calculated values.

The formation of an equilibrium composition of the compound was monitored by X-ray diffraction analysis. The X-ray diffraction pattern of the powder of the compound under study was indexed via homology [6]. The correctness of the indexing was confirmed by the good agreement between the experimental and

**Table 1.** Experimental data on the specific and molar heat capacities of the investigated compounds

$T, \text{K}$	$C_p \pm \bar{\delta}, \text{J/(g K)}$	$C_p^\circ \pm \bar{\Delta}, \text{J/(mol K)}$	$T, \text{K}$	$C_p \pm \bar{\delta}, \text{J/(g K)}$	$C_p^\circ \pm \bar{\Delta}, \text{J/(mol K)}$
$\text{MgCd}(\text{TeO}_3)_2$					
298.15	$0.3144 \pm 0.0082$	$153 \pm 11$	498	$0.5853 \pm 0.0031$	$286 \pm 4$
323	$0.3745 \pm 0.0067$	$184 \pm 9$	523	$0.5882 \pm 0.0061$	$287 \pm 8$
348	$0.4159 \pm 0.0044$	$203 \pm 6$	548	$0.5134 \pm 0.0049$	$251 \pm 7$
373	$0.4609 \pm 0.0045$	$225 \pm 6$	573	$0.4368 \pm 0.0031$	$213 \pm 4$
398	$0.4991 \pm 0.0028$	$244 \pm 4$	598	$0.4822 \pm 0.0022$	$235 \pm 3$
423	$0.5322 \pm 0.0047$	$260 \pm 6$	623	$0.5399 \pm 0.0115$	$263 \pm 16$
448	$0.5535 \pm 0.0044$	$270 \pm 6$	648	$0.5833 \pm 0.0035$	$285 \pm 5$
473	$0.5734 \pm 0.0071$	$280 \pm 10$	673	$0.6140 \pm 0.0081$	$300 \pm 11$
$\text{CaCd}(\text{TeO}_3)_2$					
298.15	$0.3152 \pm 0.0111$	$159 \pm 16$	498	$0.7057 \pm 0.0065$	$355 \pm 9$
323	$0.4664 \pm 0.0070$	$235 \pm 10$	523	$0.7465 \pm 0.0066$	$376 \pm 9$
348	$0.4241 \pm 0.0059$	$214 \pm 8$	548	$0.6571 \pm 0.0066$	$331 \pm 9$
373	$0.3774 \pm 0.0061$	$190 \pm 9$	573	$0.5490 \pm 0.0067$	$277 \pm 9$
398	$0.3583 \pm 0.0053$	$180 \pm 7$	598	$0.4938 \pm 0.0066$	$249 \pm 9$
423	$0.5163 \pm 0.0063$	$260 \pm 9$	623	$0.6340 \pm 0.0069$	$319 \pm 10$
448	$0.6100 \pm 0.0060$	$307 \pm 8$	648	$0.6837 \pm 0.0076$	$344 \pm 11$
473	$0.6407 \pm 0.0065$	$323 \pm 9$	673	$0.7378 \pm 0.0078$	$372 \pm 11$

calculated values of  $10^4/d^2$  and the consistency of the X-ray and pycnometric densities.

The heat capacity of the tellurites was studied by dynamic calorimetry using an IT-400 commercial instrument in the temperature range of 298.15–673 K (Table 1). Our experiments were performed with the monotonic heating of the sample at an average rate of about 0.1 K/s and a temperature difference between the sample and the environment of 3–30 K. These temperature difference values were used to measure the times of temperature delay on heat meters. The instrument's measuring circuit yields measurements of temperature at fixed points up through 25 K. Use of the instrument is limited to a volumetric heat capacity of  $C_p = 1 \times 10^7 \text{ J/(K m}^3\text{)}$ . The heat meter was a heat flux transducer that measured fluxes, equalized the surface temperature of the sample, and made enabled calibration directly in the thermal unit to allow for errors. Liquid nitrogen was employed as a refrigerating agent. The time for measuring over the temperature range with the processing of the experimental data was no more than

2.5 h. The maximum allowable error of the instrument according to its rated values was  $\pm 10\%$  [7, 8].

The instrument was calibrated by determining heat conduction  $K_t$  of the heat meter. To accomplish this, several experiments were conducted with a copper sample and an empty tube. Five parallel experiments were performed at each temperature; their results were averaged and processed using mathematical statistics techniques. We found the root-mean-square deviations ( $\bar{\delta}$ ) for the averaged values of the specific heat capacity at each temperature and random components of error  $\bar{\Delta}$  for the molar heat capacities [9, 10]. The random components of the error of the experimental values of heat capacities did not exceed the instrument's maximum allowable error. The operation of the calorimeter was verified by measuring the heat capacity of  $\alpha\text{-Al}_2\text{O}_3$ . The experimentally found value of  $C_p^\circ(298.15)$  for  $\alpha\text{-Al}_2\text{O}_3$  was  $76.0 \text{ J/(mol K)}$ , which is fairly consistent with the reference value ( $79.0 \text{ J/(mol K)}$ ) [11].

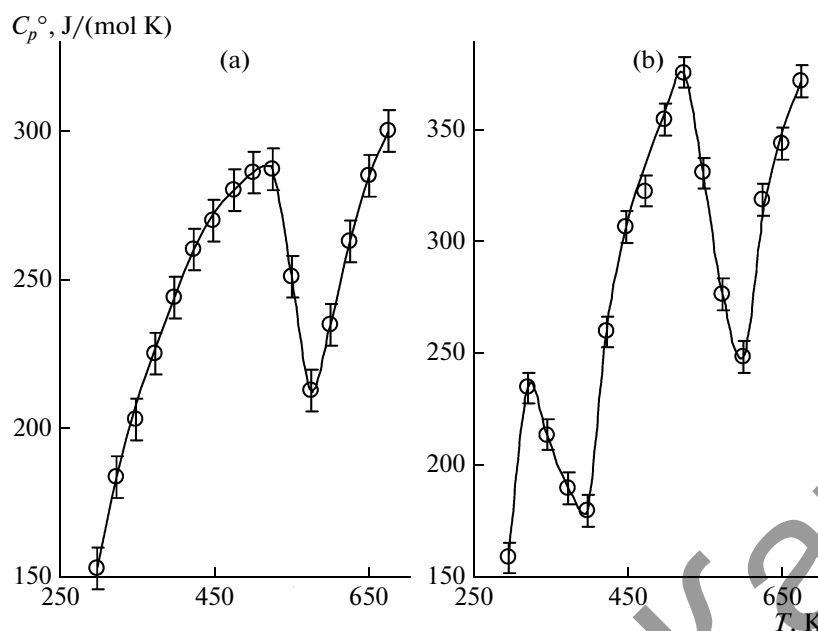


Fig. 1. Temperature dependences of the heat capacities of tellurites: (a)  $\text{MgCd}(\text{TeO}_3)_2$  and (b)  $\text{CaCd}(\text{TeO}_3)_2$ .

## RESULTS AND DISCUSSION

Our study of the temperature dependences of the heat capacity of binary tellurites at 523 K for  $\text{MgCd}(\text{TeO}_3)_2$  and at 323 and 523 K for  $\text{CaCd}(\text{TeO}_3)_2$  revealed sharp abnormal  $\lambda$ -shaped jumps, due apparently to second-order phase transitions (see Fig. 1). These transitions could be associated with cation redistribution, with a change in the coefficient of thermal expansion, or with a change in the magnetic moment of the synthesized tellurites.

The equation for the temperature dependence of the heat capacity of the compounds was derived on the

basis of the experimental data (Table 1) and allowing for the temperatures of the second-order phase transitions:

$$C_p^\circ, \text{J}/(\text{mol K}) = a + b + cT^{-2}, \quad (1)$$

the coefficients of which are listed in Table 2. To determine the accuracy of the coefficients in our equation for the  $C_p^\circ \sim f(T)$  dependences, we used the average random errors for the investigated temperature ranges. Since the instrument's performance capability prevented us from calculating the standard entropy  $S^\circ(298.15)$  of tellurites directly from the experimental data according to  $C_p^\circ(T)$ , it was estimated using via ion increment. Based on the known relationships, the temperature dependences of the functions  $C_p^\circ(T)$ ,  $S^\circ(T)$ ,  $H^\circ(T) - H^\circ(298.15)$ , and  $\Phi^{xx}(T)$  were calculated using the experimental data on  $C_p^\circ \sim f(T)$  and the calculated values of  $S^\circ(298.15)$ . The results are shown in Table 3.

The thermodynamic functions  $H^\circ(T) - H^\circ(298.15)$ ,  $S^\circ(T)$ , and  $\Phi^{xx}(T)$  were calculated using the formulas

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

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

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

Table 2. Coefficients of Eq. (1) in the range of 298.15–673 K

$T, \text{K}$	$a$	$b \times 10^{-3}$	$c \times 10^5$
$\text{MgCd}(\text{TeO}_3)_2$			
298–523	$394.7 \pm 12.2$	$-68.9 \pm 2.1$	$196.0 \pm 6.0$
523–573	$641.0 \pm 19.7$	$676.9 \pm 20.9$	—
573–673	$818.4 \pm 25.2$	$-310.6 \pm 9.6$	$-1402.9 \pm 43.2$
$\text{CaCd}(\text{TeO}_3)_2$			
298–323	$-749.1 \pm 27.8$	$3046.4 \pm 113.0$	—
323–398	$469.5 \pm 17.4$	$-726.1 \pm 26.9$	—
398–523	$2237.1 \pm 83.0$	$-2290.8 \pm 85.0$	$-1813.5 \pm 67.3$
523–598	$1263.6 \pm 46.9$	$-1697.1 \pm 63.0$	—
598–673	$3836.3 \pm 142.3$	$-3147.4 \pm 116.8$	$-6098.9 \pm 226.3$

**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)
$MgCd(TeO_3)_2$				
298.15	155 ± 5	247 ± 7	–	247 ± 15
300	156 ± 5	248 ± 15	310 ± 10	247 ± 15
325	188 ± 6	262 ± 16	4611 ± 142	248 ± 15
350	211 ± 6	277 ± 17	9588 ± 295	249 ± 15
375	230 ± 7	292 ± 18	15096 ± 465	252 ± 15
400	245 ± 8	307 ± 19	21028 ± 648	255 ± 15
425	258 ± 8	323 ± 20	27302 ± 841	258 ± 16
450	268 ± 8	338 ± 21	33852 ± 1043	262 ± 16
475	276 ± 8	352 ± 21	40629 ± 1251	267 ± 16
500	282 ± 9	366 ± 22	47593 ± 1466	271 ± 16
525	287 ± 9	380 ± 23	54710 ± 1685	276 ± 17
550	269 ± 8	393 ± 24	61638 ± 1898	281 ± 17
575	252 ± 8	405 ± 25	68144 ± 2099	286 ± 17
600	241 ± 7	415 ± 25	73876 ± 2275	291 ± 18
625	265 ± 8	425 ± 26	80226 ± 2471	297 ± 18
650	284 ± 9	436 ± 26	87102 ± 2683	302 ± 18
675	301 ± 9	447 ± 27	94424 ± 2908	307 ± 19
$CaCd(TeO_3)_2$				
298.15	159 ± 6	263 ± 10	–	263 ± 18
300	165 ± 6	264 ± 18	324 ± 12	263 ± 18
325	241 ± 9	280 ± 19	5397 ± 200	263 ± 18
350	215 ± 8	297 ± 20	11008 ± 408	265 ± 18
375	197 ± 7	311 ± 21	16164 ± 600	268 ± 18
400	179 ± 7	323 ± 22	20867 ± 774	271 ± 18
425	259 ± 10	337 ± 23	26501 ± 983	274 ± 18
450	311 ± 12	353 ± 24	33667 ± 1249	278 ± 19
475	345 ± 13	371 ± 25	41896 ± 1554	283 ± 19
500	366 ± 14	389 ± 26	50815 ± 1885	288 ± 19
525	376 ± 14	407 ± 27	60120 ± 2230	293 ± 20
550	330 ± 12	424 ± 28	68905 ± 2556	298 ± 20
575	288 ± 11	437 ± 29	76629 ± 2843	304 ± 20
600	245 ± 9	449 ± 30	83292 ± 3090	310 ± 21
625	308 ± 11	461 ± 31	90347 ± 3352	316 ± 21
650	347 ± 13	473 ± 32	98562 ± 3657	322 ± 22
675	373 ± 14	486 ± 33	107590 ± 3992	328 ± 22

The average random components of the error were estimated for all values of heat capacity and enthalpy over the range of temperatures; for the entropy and reduced thermodynamic potential, our estimate of the error included the accuracy of calculating the entropy ( $\pm 3\%$ ). The standard entropies were determined using the Kumok ion entropy increment [12].

### CONCLUSIONS

The isobaric heat capacities of new binary cadmium tellurites with *s*-elements were determined for the first time by dynamic calorimetry in the temperature range of 298.15–673 K. An equation that describes their temperature dependences was derived. Sharp anomalous jumps, i.e.,  $\lambda$ -shaped effects attributable to a second-order phase transition, were found in the  $C_p^\circ \sim f(T)$  dependences of magnesium–cadmium and calcium–cadmium tellurites. The values of the thermodynamic functions  $C_p^\circ(T)$ ,  $S^\circ(T)$ ,  $H^\circ(T) - H^\circ(298.15)$ , and  $\Phi^{xx}(T)$  were calculated. The occurrence of a second-order phase transition suggests that these compounds have unique electrophysical properties.

The results from our research could be of interest in the targeted synthesis of chalcogenites with desirable properties and physicochemical simulations of chemical and metallurgical processes involving tellurium compounds. They could also be employed as input data for fundamental reference books and data banks on the thermodynamic constants of inorganic materials.

### REFERENCES

1. A. T. Dyusekeeva, Extended Abstract of Candidate's Dissertation in Chemistry (E. A. Buketov Karagand. State Univ., Karaganda, 2008).
2. K. T. Rustembekov and A. T. Dyusekeeva, *Izv. Tomsk. Politekh. Univ.* **315** (3), 20 (2009).
3. G. Charlot, *Les méthodes de la chimie analytique: Analyse quantitative minérale* (Masson, Paris, 1961; Khimiya, Moscow, 1966).
4. N. S. Poluektov, *Methods of Analysis Using Flame Photometry* (Khimiya, Moscow, 1967) [in Russian].
5. S. Yu. Fainberg and I. A. Filippova, *Analysis of Non-Ferrous Metal Ores* (Metallurgizdat, Moscow, 1963) [in Russian].
6. L. M. Kovba and V. K. Trunov, *X-ray Analysis* (Mosk. Gos. Univ., Moscow, 1976) [in Russian].
7. E. S. Platunov, S. E. Buravoi, V. V. Kurepin, and G. S. Petrov, *Thermophysical Measurements and Devices* (Mashinostroenie, Leningrad, 1986) [in Russian].
8. *Technical Description and Operating Instructions on IT-S-400* (Etalon, Aktyubinsk, 1986) [in Russian].
9. V. P. Spiridonov and A. A. Lopatkin, *Mathematical Processing of Physicochemical Data* (Mosk. Gos. Univ., Moscow, 1970) [in Russian].
10. L. A. Reznitskii, *Calorimetry of Solids* (Mosk. Gos. Univ., Moscow, 1981) [in Russian].
11. R. A. Robie, B. S. Hewingway, and I. R. Fisher, *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and  $10^5$  Pa Pressure and at Higher Temperatures* (United States Government Printing Office, Washington, DC, 1978).
12. V. N. Kumok, *Direct and Inverse Problems of Chemical Thermodynamics* (Nauka, Sib. Otd., Novosibirsk, 1987) [in Russian].