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Thermochemistry of new holmium-calcium tellurite

The new double holmium-calcium tellurite was synthesized by the ceramic technology. The formation of the equilibrium composition of the compound was monitored by X-ray diffraction. Double tellurite of holmium $HoCaTeO_{4.5}$ has been synthesized according to the results of X-ray analysis. Calorimetric investigation of the heat capacity of the new double tellurite $HoCaTeO_{4.5}$ was carried out for the first time in the range of 298.15–673 K. Calibration of the device was carried out on the basis of determining the thermal conductivity of a heat meter. The calorimeter performance was checked by measuring the heat capacity of α-Al_2O_3. The experimental data and the specific molar heat capacities have been processed by methods of mathematical statistics. The dependence equation $C_p^0 \sim f(T)$ has been derived on the basis of experimental data. According $C_p^0 \sim f(T)$ and the calculated value of $S^0(298.15)$ of tellurite the temperature dependence of the thermodynamic functions $H^0(T)–H^0(298.15)$, $S^0(T)$ and $\Phi^{xx}(T)$ have been determined. Abnormal jumps have been observed on the dependence $C_p^0 \sim f(T)$ associated probably with the phase transitions of the second order. The thermodynamic characteristics of the new tellurite can serve as source materials for inclusion in fundamental data banks and reference books, used to predict the thermochemical constants of similar compounds.

Keywords: calorimetry, holmium-calcium tellurite, heat capacity, phase transitions, thermodynamic functions.

Almost all processes observed in nature are associated with the transformation of energy by the absorption or release of heat. Knowledge in this area allows to understand better the structure of molecules, thermal effects of physical processes or chemical reactions and many biological phenomena, to optimize production processes and, and taking into account entropy, to identify the conditions of chemical equilibria. Information about the values of thermal effects and the nature of their occurrence is one of the main in the practice of research and in the optimization or control of many industrial processes.

Compounds of tellurium, which include little-studied complex oxo-compounds, in particular, double tellurites of *s-f*-elements, raise some interest because of their semiconducting, piezoelectric and ferroelectric properties.

At the Department of inorganic and technical chemistry of the Karaganda State University named after academician Ye.A. Buketov systematic research on search and the development of scientific bases of directed synthesis of new oxo-compound of tellurium and selenium which have unique physical properties has been carried out [1, 2].

The aim of this work was to study the calorimetry of new tellurite $HoCaTeO_{4.5}$ in the temperature range of 298.15–673 K.

Double holmium-calcium tellurite with $HoCaTeO_{4.5}$ composition was synthesized by the ceramic technology from holmium (III) oxide, tellurium (IV) oxide, and calcium carbonate of «chemically pure» grade. In our previous work [3] the method of synthesis and radiographic characteristics of this compound were described. Formation of the equilibrium composition of the compound was monitored by the X-ray analysis. The powder X-ray diffraction pattern of each compound was indexed by means of homology. The correctness of the indication is confirmed by the good agreement between the experimental and calculated values $10^4/d^2$ and the agreement between the X-ray and pycnometric densities.

The heat capacities of double holmium-calcium tellurite were studied via dynamic calorimetry on an commercial IT-S-400 calorimeter in the temperature range of 298.15–673 K. The calibration of an instrument was carried out on the basis of determination of thermal conductivity of the calorimeter K_t [4]. Several experiments with copper sample and an empty vial were carried out for this purpose. The thermal conductivity of the calorimeter was determined by the formula

$$K_T = C_{\text{cop. sample}} / (\bar{\tau}_{TM} - \bar{\tau}^0{}_T), \tag{1}$$

where $C_{\text{cop. sample}}$ — full heat capacity of the copper sample, J/(mol·K); $\bar{\tau}_{TM}$ — the average time delay in the calorimeter in experiments with a copper sample, s; $\bar{\tau}^0{}_T$ — the average value of the time delay in experiments with an empty ampoule, s.

Full heat capacity of the copper sample was calculated by the formula

$$C_{\text{cop.sample.}} = C_M \cdot m_{\text{sample}}, \tag{2}$$

where C_M — the tabular value of the specific heat capacity of copper, kJ/(kg·K); $m_{\text{sample.}}$ — the mass of the copper sample, kg.

The specific heat capacity of the test substance calculated by the formula

$$C_{sp.} = \frac{K_T}{m_0} \cdot (\tau_T - \tau_T^0), \tag{3}$$

where K_T — the thermal conductivity of the calorimeter; m_0 — the mass of the test substance, kg; τ_T — the time delay of the temperature in the calorimeter, s; τ_T^0 — the time delay of the temperature of the calorimeter in experiments with an empty ampoule, s.

Then, values of the molar heat capacity were calculated from the values of specific heat by the formula

$$C_M = C_{sp.} \cdot M, \tag{4}$$

where $C_{sp.}$ — specific heat of a substance, J/(g·K); M — the molecular weight of substance, g/mol.

Five parallel experiments were carried out at each fixed temperature, the results of which were processed by methods of mathematical statistics [5]. For the average values of the specific heat capacities at each temperature the standard deviation δ [J/(g·K)] was calculated according to the formula

$$\bar{\delta} = \sqrt{\sum_{i=1}^{n} \frac{(c_i - \bar{c})^2}{n-1}}, \tag{5}$$

where n — the number of experiments; c_i — the measured specific heat capacity; $\bar{c}$ — the arithmetic mean of the values of the specific heat capacity.

Random component of error was calculated for average values of molar heat capacity

$$\dot{\Delta}, \% = \frac{\delta t_P}{\bar{c}} \cdot 100, \tag{6}$$

where $\dot{\Delta}$ — the random component of error; t_P — Student's ratio is equal to 2.78 for $n = 5$ at $p = 0.95$. The random component of the error ($\dot{\Delta}$) is expressed in J/(mol·K).

Operation of the calorimeter was tested by measuring the heat capacity of α-Al_2O_3. The resulting $C_p^0(298.15)$ for α-$Al_2O_3 = 76.0$ J/(mol·K) was in satisfactory agreement with the reference value (79.0 J/(mol·K) [6]. The results of the study of the heat capacity of the synthesized holmium-calcium tellurite are presented in the Table 1.

From the results given in the Table 1, it is seen that error components in measuring heat capacities on the IT-S-400 calorimeter does not exceed (±10 %) in the entire temperature range [7].

In studying the temperature dependences of the heat capacities of double holmium — calcium tellurite at 398 and 548 K, we observed abnormally peaks associated probably with second-order phase transitions (see Fig.). These transitions could be due to the redistribution of cations, with the change in the coefficient of thermal expansion and changes in the magnetic moment of the double tellurite synthesized.

Based on the experimental data (Table 1) with considering the temperatures of second-order transitions there has been derived the equation of temperature dependence for the compounds heat capacity C_p^0 [J/(mol K)]

$$C_p^0 = a + bT + cT^{-2}, \tag{7}$$

the coefficients of which are given in the Table 2. The error in the coefficients of dependences $C_p^0 \sim f(T)$ was determined using average values of random errors for the considered interval of temperatures.

Table 1

Experimental specific and molar heat capacities of $HoCaTeO_{4.5}$

T, K	$C_p \pm \bar{\delta}$, J/(g·K)	$C_p \pm \dot{\Delta}$, J/(mol·K)
298.15	0.7530 ± 0.0008	305 ± 0
323	0.8063 ± 0.0253	326 ± 10
348	0.8441 ± 0.0013	342 ± 1
373	0.9793 ± 0.0475	396 ± 19
398	1.0406 ± 0.0001	421 ± 0
423	0.5664 ± 0.0004	229 ± 0
448	0.6059 ± 0.0177	245 ± 7
473	0.6324 ± 0.0046	256 ± 2
498	0.6830 ± 0.0009	276 ± 0
523	0.7898 ± 0.0409	320 ± 17
548	0.8262 ± 0.0007	334 ± 0
573	0.6583 ± 0.0609	266 ± 25
598	0.6376 ± 0.0000	258 ± 0
623	0.5696 ± 0.0062	230 ± 3
648	0.5080 ± 0.0233	206 ± 9
673	0.5016 ± 0.0001	203 ± 0

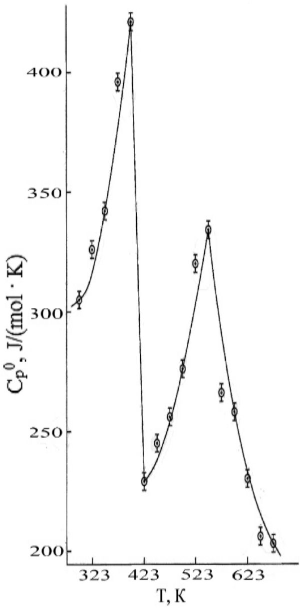

Figure. The temperature dependence of heat capacity of $HoCaTeO_{4.5}$

Table 2

Coefficients of equation (7) in the range of 298.15–673 K for holmium-calcium tellurite

Coefficients			ΔT, K
a	$b \cdot 10^{-3}$	$c \cdot 10^{5}$	
–(1089.9±33)	315.7±0.09	402.9±12	298.15–398
3475.3±104	–(767.4±0.23)	–	398–423
–(1171.2±35)	226.8±0.07	789.4±24	423–548
–(1405.2±42)	146.9±0.04	2806.7±84	548–673

Due to the fact that the technical characteristics of the device do not allow direct calculation of the standart entropy $S^0(298.15)$ of tellurites from the experimental data on $C_p^0 \sim f(T)$, it was estimated by means of Kumok's ion increments [8].

Based on known correlations using experimental data on $C_p^0 \sim f(T)$, and the estimated values of $S^0(298.15)$ the temperature dependences of thermodynamic functions were calculated. The thermodynamic functions $H^0(T)–H^0(298.15)$, $S^0(T)$ and $\Phi^{xx}(T)$ was calculated by the following formulas:

$$H^0(T) - H^0(298.15) = \int_{298.15}^{T} C_p^0 dT\,; \tag{8}$$

$$S^0(T) = S^0(298.15) + \int_{298.15}^{T} \frac{C_p}{T} dT\,; \tag{9}$$

$$\Phi^{xx}(T) = S^0(T) - \frac{H^0(T) - H^0(298.15)}{T}\,. \tag{10}$$

The results are presented in the Table 3.

Table 3

Thermodynamic properties of tellurite $HoCaTeO_{4.5}$ in the range of 298.15–673 К

T, K	$C_p^0(T) \pm \overset{\circ}{\Delta}$, J/(mol·K)	$S^0(T) \pm \overset{\circ}{\Delta}$, J/(mol·K)	$H^0(T) - H^0(298.15) \pm \overset{\circ}{\Delta}$, J/mol	$\Phi^{xx}(T) \pm \overset{\circ}{\Delta}$, J/(mol·K)
298.15	305 ± 0	188 ± 19	-	188 ± 19
323	316 ± 10	211 ± 21	7383 ± 464	189 ± 19
348	341 ± 1	234 ± 23	14967 ± 941	191 ± 19
373	377 ± 19	257 ± 26	23373 ± 1470	195 ± 19
398	421 ± 0	283 ± 28	33102 ± 2082	199 ± 20
423	229 ± 0	302 ± 30	41227 ± 2593	205 ± 20
448	238 ± 7	316 ± 32	47044 ± 2959	211 ± 21
473	254 ± 2	329 ± 33	53175 ± 3345	217 ± 22
498	276 ± 0	343 ± 34	59787 ± 3761	223 ± 22
523	303 ± 17	357 ± 36	67015 ± 4215	229 ± 23
548	334 ± 10	372 ± 37	74970 ± 4716	235 ± 23
573	291 ± 25	386 ± 39	82762 ± 5206	241 ± 24
598	258 ± 0	397 ± 40	89608 ± 5636	248 ± 25
623	233 ± 3	407 ± 41	95730 ± 6021	254 ± 25
648	215 ± 9	416 ± 42	101318 ± 6373	260 ± 26
673	203 ± 0	424 ± 42	106533 ± 6701	266 ± 27

For all values of heat capacity and enthalpy over the whole range of temperatures there were evaluated average random components of the error, and for the values of entropy and thermodynamic potential the accuracy of the calculation of entropy (±3 %) was included to the estimation of error.

Thus, for the first time the capacity of the new holmium-calcium tellurite in the range of 298.15–673 K has been investigated by the method of dynamic calorimetry. Equations of temperature dependence were derive and thermodynamic functions $C_p^0(T)$, $S^0(T)$, $H^0(T) - H^0(298.15)$ and $\Phi^{xx}(T)$ of the double tellurite synthesized were determined. λ-Like effects attributable to a second-order phase transition were detected on the curve of dependences $C_p^0 \sim f(T)$. The existence of a second-order phase transition indicates that this compound could have unique electrophysical properties. Thermodynamic characteristics of the new tellurite can serve as the starting materials for inclusion in basic data banks and references and can also be used for directed synthesis of new derivatives of chalcogens with desired properties.

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Гольмий-кальций жаңа теллуритінің термохимиясы

Керамикалық технологиямен жаңа гольмий-кальций қос теллуриті синтезделді. Қосылыстың тепе-теңдік құрамының түзілуі рентгенфазалық талдау әдісімен бақыланды. Рентгенфазалық талдау нәтижесі бойынша $HoCaTeO_{4.5}$ гольмий қос теллуритінің синтезделгені анықталды. Алғаш рет 298,15–673 К аралығында жаңа $HoCaTeO_{4.5}$ қос теллуритінің жылу сыйымдылығы калориметрлік әдіспен зерттелді. Құрылғының градуирленуі жылу өлшеуіштің жылулық өткізгіштігін анықтау негізінде жүзеге асырылды. Калориметрдің жұмысы α-Al_2O_3-тің жылу сыйымдылығын өлшеумен тексерілді. Меншікті және мольдік жылу сыйымдылықтарының тәжірибелік мәліметтері математикалық статистика әдістерімен өңделді. Тәжірибелік мәліметтердің негізінде $C_p^0 \sim f(T)$ тәуелділік теңдеуі шығарылды. $C_p^0 \sim f(T)$ және теллуриттің есептелген $S^0(298.15)$ мәні бойынша $H^0(T) - H^0(298.15)$, $S^0(T)$ және $\Phi^{xx}(T)$ термодинамикалық функцияларының температуралық тәуелділіктері анықталды. $C_p^0 \sim f(T)$ тәуелділігінде, II текті ауысумен болуы мүмкін, күрт аномалды секірулер байқалды. Жаңа теллуриттің термодинамикалық сипаттамалары іргелі мәліметтер банкіне және анықтамаларға бастапқы материалдар болуы ықтимал, сол сияқты ұқсас қосылыстардың термохимиялық константаларын болжауда қолданылуы мүмкін.

Кілт сөздер: калориметрия, гольмий-кальций теллуриті, жылу сыйымдылығы, фазалық түрленулер, термодинамикалық функциялар.

К.Т. Рустембеков, Е.С. Лазарева, М. Стоев, В.Н. Фомин, Д.А. Кайкенов

Термохимия нового теллурита гольмия-кальция

На основе керамической технологии синтезирован новый двойной теллурит гольмия-кальция. Образование равновесного состава соединения контролировали методом рентгенофазового анализа, по результатам которого было установлено, что синтезирован двойной теллурит гольмия $HoCaTeO_{4.5}$. Впервые в интервале 298,15–673 К проведено калориметрическое исследование теплоемкости нового двойного теллурита $HoCaTeO_{4.5}$. Градуировку прибора осуществляли на основании определения тепловой проводимости тепломера. Проверку работы калориметра проводили измерением теплоемкости α-Al_2O_3. Экспериментальные данные удельной и мольной теплоемкостей обработаны методами математической статистики. На основе экспериментальных данных выведено уравнение зависимости $C_p^0 \sim f(T)$. По $C_p^0 \sim f(T)$ и вычисленного значения $S^0(298,15)$ теллурита, определены температурные зависимости термодинамических функций $H^0(T) - H^0(298,15)$, $S^0(T)$ и $\Phi^{xx}(T)$. На зависимости $C_p^0 \sim f(T)$ наблюдаются аномальные скачки, связанные, вероятно, с фазовыми переходами II рода. Термодинамические характеристики нового теллурита могут служить исходной информацией для включения в фундаментальные банки данных и справочники, а также использованы для прогнозирования термохимических констант аналогичных соединений.

Ключевые слова: калориметрия, теллурит гольмия-кальция, теплоемкость, фазовые переходы, термодинамические функции.

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