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Calorimetry of new double dysprosium tellurite

New dysprosium-barium double tellurite was synthesized based on ceramic technology. The formation of the equilibrium composition of the compound is controlled by X-ray phase analysis, the results of which revealed that $DyBaTeO_{4.5}$ dysprosium tellurite was synthesized. For the first time, a calorimetric study of the heat capacity of the new double tellurite $DyBaTeO_{4.5}$ was carried out in the temperature range of 298.15–673 K. The calibration of the instrument was carried out on the basis of the determination of the heat meter thermal conductivity. The operation of the calorimeter was checked by measuring the α-Al_2O_3 heat capacity. The experimental data of the specific and molar heat capacity were processed by the methods of mathematical statistics. The equation for the dependence $C_p^o \sim f(T)$ is derived based on the experimental data. The temperature dependences of the thermodynamic functions $H^o(T)$–$H^o(298.15)$, $S^o(T)$ and, $F^{xx}(T)$ are determined from $C_p^o \sim f(T)$ and the calculated value of $S^o(298.15)$ of tellurite. Anomalous jumps are observed on the dependence $C_p^o \sim f(T)$, which are probably related to second-order phase transitions. The thermodynamic characteristics of new tellurite can serve as background information for fundamental data banks and reference books, and also used to predict the thermochemical constants of similar compounds.

Keywords: dysprosium-barium tellurite, calorimetry, heat capacity, phase transitions, thermodynamic functions.

Modern electronic technology poses the problem of searching for new compounds with valuable electrophysical properties and their in-depth physical and chemical research. Criteria for assessing the prospects of using a particular material put forward the relative cheapness and simplicity of their production, environmental safety as priority requirements, and also one of the decisive factors when choosing a new material is availability of such valuable properties as semiconductor, ferroelectric, piezoelectric and pyroelectric, radioluminescent and superconducting.

Therefore, compounds formed in systems consisting of REE oxides, alkaline earth metals and tellurium are of particular interest for inorganic materials science, since they have promising physical and physicochemical properties [1]. The purpose of this work is a calorimetric study of the heat capacity of new dysprosium double tellurite in the temperature range of 298.15–673 K.

Dysprosium (III), tellurium (IV) and barium carbonate («chemically pure» oxides) were used as starting components for the synthesis in a stoichiometric ratio. Dysprosium-barium tellurite $DyBaTeO_{4.5}$ was synthesized by the method of ceramic technology. The method of synthesis is similar to that given by us earlier in [2]. The formation of the equilibrium composition of the compound was monitored by X-ray phase analysis on a DRON-2.0 diffactometer. X-ray data show that the synthesized compound crystallizes in the structural type of distorted perovskite P_m3_m [3].

The heat capacity of dysprosium-barium double tellurite was studied by dynamic calorimetry on an IT-C-400 serial device in the 298.15–673 K temperature range. The limit of the permissible error of the device is ± 10 % according to passport data [2]. The calibration of the instrument was carried out on the basis of determining the thermal conductivity of the heat meter K_T [4]. For this, several experiments were carried out with a copper sample and an empty ampoule. Thermal conductivity of the heat meter was determined by the formula:

$$K_T = C_{cs} / (\overline{\tau}_{TC} - \overline{\tau}_T^0),$$

where C_{cs} is the total heat capacity of the copper sample, J/(mol×K); $\overline{\tau}_{TC}$ is the average value of the lag time on the heat meter in experiments with a copper sample, s; $\overline{\tau}_T^0$ is the average value of the lag time in experiments with an empty ampoule, s.

The total heat capacity of the copper sample was calculated by the formula:

$$C_{cs} = C_C \times m_s,$$

where C_C is the tabular value of the specific heat capacity of copper, kJ/(kg×K); m_s is the mass of the copper sample, kg.

The value of the specific heat capacity of the analyte was calculated by the formula:

$$C_s = \frac{K_T}{m_0} \times (\tau_T - \tau_T{}^0),$$

where K_T is the heat conductivity of the heat meter; m_0 is the mass of the test substance, kg; τ_T is the lag time of the temperature at the heat meter, s; $\tau_T{}^0$ is the lag time of the temperature on the heat meter in experiments with an empty ampoule, s.

Taking into account the molar mass, the molar heat capacity was calculated using the specific heat capacity by the formula:

$$C_M = C_s \times M,$$

where C_s is the specific heat capacity of substance, J/(g×K); M is the molar mass of the substance, g/mol.

Five parallel experiments were carried out at each fixed temperature, the results of which were averaged and processed by methods of mathematical statistics [5].

At each temperature, the standard deviation $\overline{\delta}$ was estimated for the averaged values of the specific heat capacity using the formula:

$$\overline{\delta} = \sqrt{\sum_{i=1}^{n} \frac{(C_i - \overline{c})^2}{n-1}},$$

where n is the number of experiments; C_i is the measured value of the specific heat capacity; $\overline{c}$ is arithmetic average of the measured values of specific heat capacity.

The random error component was calculated for the average values of the molar heat capacity:

$$\overset{\circ}{\Delta} = \frac{\delta t_p}{\overline{c}} \cdot 100,$$

where $\overset{\circ}{\Delta}$ is the random component of the error in %; t_p is the Student's coefficient (for $n = 5$ $t_p = 2.78$ with $p = 0.95$ confidence interval).

The systematic component of the error was calculated by the formula:

$$\Delta_c = \frac{\overline{C} - C_0}{C_0} \cdot 100,$$

where Δ_c is the systematic component of the error in %; C_0 is the heat capacity value of the model measure taken at the temperature at which the heat capacity was determined.

In our studies, the systematic error and errors in temperature measurements were not included in the calculation, since they were negligible compared to the random component.

The work of the calorimeter was tested by determining the α-Al_2O_3 heat capacity. The resulting value of $C_p{}^0(298.15)$ for α-Al_2O_3, which is equal to 76.0 J/(mol×K), is in satisfactory agreement with its recommended value of 79.0 J/(mol×K) [6]. These data show not only the reliability of the results obtained, but also the negligible value of the systematic error, such as the measurement of the temperature error.

The results of calorimetric studies of the heat capacity of tellurite are shown in Table 1.

Table 1

Experimental values of specific and molar heat capacities $DyBaTeO_{4,5}$

T, K	$C_p \pm \bar{\delta}$, J/(g×K)	$C_p^0 \pm \overset{0}{\Delta}$, J/mol×K
298.15	0.5361±0.0312	250±15
323	0.5061±0.0811	260±24
348	0.5464±0.0643	280±26
373	0.6393±0.0521	310±27
398	0.7721±0.0251	360±1
423	0.9352±0.0651	420±29
448	1.1234±0.0721	500±34
473	1.3293±0.0452	620±2
498	0.8582±0.0187	400±4
523	0.6650±0.0335	310±16
548	0.6891±0.0295	330±12
573	0.7932±0.0445	370±19
598	0.9651±0.0362	450±16
623	0.8154±0.0257	380±10
648	0.7283±0.0452	350±21
673	0.6961±0.0329	325±2

It can be seen from the data presented in Table 1 that the random components of the error of the experimental values of the heat capacities are within the limits of the error of the device over the entire temperature range. The Figure shows the temperature dependence of the heat capacity of the tellurite synthesized.

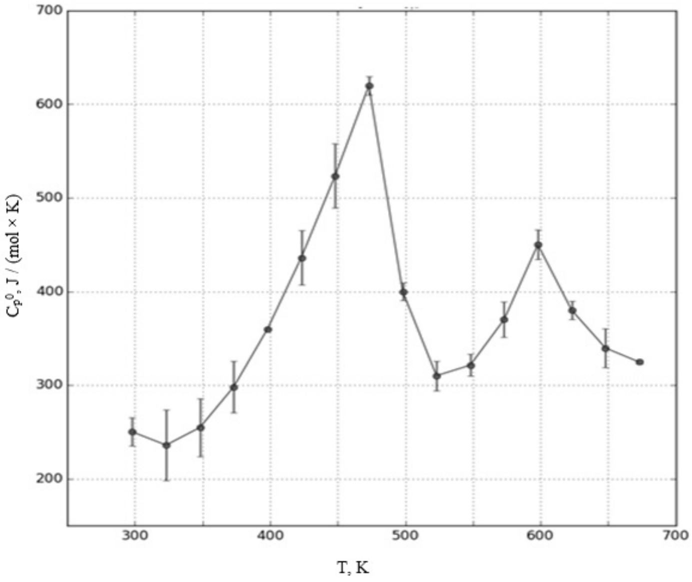

Figure. Temperature dependence of the $DyBaTeO_{4.5}$ heat capacity

Based on the data in Table 1 and the Figure, it was found that the curve of the temperature dependence of the heat capacity of double tellurite $DyBaTeO_{4.5}$ at 473 and 598 K revealed abrupt anomalous λ–shaped jumps, probably due to the second-order phase transitions. These transitions can be associated with cationic redistribution, with changes in the coefficient of thermal expansion, as well as changes in the magnetic moment of the tellurite synthesized or changes in the dielectric constant, electrical resistivity, etc. Due to the presence of the second-order phase transition, the dependence of the compound was described by several equations, the coefficients of which are given in Table 2.

Table 2

Equations of the temperature dependence of the heat capacity of double tellurite $DyBaTeO_{4.5}$

Equation coefficients $C_p^0 = a + bT + cT^{-2}$, J/mol×K			ΔT, K
a	$b \cdot 10^{-3}$	$c \cdot 10^{5}$	
–(2550.8±76.5)	5804.6±174.1	951.3±28.5	298.15–473
–(22283.2±668.5)	28357.0±850.7	21232.6±637.0	473–523
–(9319.0±279.6)	12143.1±364.3	8966.9±269.0	523–598
–(7443.4±223.3)	7646.6±229.4	11875.2±356.3	598–673

There were used the values of average random errors for all considered temperature ranges to determine the error coefficients in the equations of dependencies $C_p^0 \sim f(T)$. Due to the fact that the technical characteristics of the device do not allow us to directly calculate the standard entropy *S*°(298.15) of the test compound from the experimental data on $C_p^0(T)$ it was evaluated using the Kumok ion increment method [7]. Based on the known relations [8, 9] the temperature dependences of the functions were calculated *S*°(*T*), *H*°(*T*)–*H*°(298.15) and $F^{xx}(T)$ using experimental data on $C_p^0 \sim f(T)$ and calculated values for *S*°(298.15). The results are shown in Table 3.

Table 3

Thermodynamic functions of tellurite $DyBaTeO_{4.5}$ in the temperature range of 298.15–673 K

ΔT, K	$C_p^0(T) \pm \overset{\circ}{\Delta}$, J/(mol×K)	$S^0(T) \pm \overset{\circ}{\Delta}$, J/(mol×K)	$H^{\circ}(T) - H^{\circ}(298{,}15) \pm \overset{\circ}{\Delta}$, J/mol	$F^{xx}(T) \pm \overset{0}{\Delta}$, J/(mol×K)
298,15	250±15	210±8	-	210±6
323	260±24	229±7	5959±60	211±7
348	280±26	247±8	12033±146	213±7
373	310±14	266±9	18899±187	216±8
398	360±7	288±11	27092±216	216±9
423	420±33	312±13	37018±270	226±9
448	500±32	339±16	48996±357	230±10
473	620±15	370±19	63275±478	237±11
498	400±15	396±12	75726±597	244±12
523	310±9	413±19	84357±788	252±12
548	330±17	427±10	92163±898	260±13
573	370±17	443±11	100733±8	267±13
598	450±17	460±14	110923±998	275±14
623	380±18	477±11	121231±1109	282±14
648	350±17	491±10	130170±1181	290±15
673	325±17	503±20	138424±1219	298±15

The errors in the temperature dependence of enthalpy were estimated with the average random component of the error in heat capacity, and the errors in temperature dependence *S*°(*T*) and $F^{xx}(T)$ were calculated by summing the average error of the experimental determination of heat capacity and the accuracy of the calculation of entropy (±3 %).

Thus, for the first time, the isobaric heat capacity of new double dysprosium tellurite $DyBaTeO_{4.5}$ was investigated by the dynamic calorimetry method in the range of 298.15–673 K.

The standard heat capacity C_p°(298.15) = 250 ± 15 (J/mol×K) was determined for tellurite $DyBaTeO_{4.5}$ experimentally. The equations of temperature dependences of the heat capacity for the compound under study were derived based on the experimental values.

Abrupt anomalous jumps of λ–shaped effects related to the second-order phase transition were detected for the tellurite under study, at 473 and 598 K, on the dependence curve $C_p{}^0(T) \sim f(T)$. The standard entropy of the double tellurite under study was calculated by the method of ionic increments. The temperature dependences of the heat capacity were calculated in the range of 298.15–673 K $C_p^0(T)$ and thermodynamic functions such as entropy $S°(T)$, enthalpy $H°(T)–H°(298.15)$ and reduced thermodynamic potential $F^{xx}(T)$ of tellurite $DyBaTeO_{4.5}$.

The presence of the second-order phase transition in the temperature dependence curve of the heat capacity suggests that this compound may have unique electrophysical properties [10]. Thermochemical and thermodynamic characteristics of tellurite can be initial information files of fundamental reference books and data banks and are of interest for chemical informatics, and also have theoretical and practical interest for inorganic materials science in the field of directional synthesis of compounds with polyfunctional properties.

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Диспрозий жаңа қос теллуритінің калориметриясы

Керамикалық технологиямен жаңа диспрозий-барий қос теллуриті синтезделді. Қосылыстың тепетеңдік құрамының құрылысы рентгенфазалық талдау әдісімен бақыланды. Рентгенфазалық талдау нәтижесі бойынша $DyBaTeO_{4,5}$ қос теллуритінің синтезделгені анықталды. Алғаш рет 298,15–673 К аралығында жаңа $DyBaTeO_{4,5}$ диспрозий қос теллуритінің жылусыйымдылығы калориметрлік әдіспен зерттелді. Құрылғының градуирленуі жылуөлшеуіштің жылуөткізгіштігін анықтау негізінде жүзеге асырылды. Калориметрдің жұмысы α-Al_2O_3-тің жылу сыйымдылығын өлшеумен тексерілді. Меншікті және мольдік жылусыйымдылықтарының тәжірибелік мәліметтері математикалық статистика әдістерімен өңделді. Тәжірибелік мәліметтердің негізінде $C_p°{\sim}f(T)$ тәуелділік теңдеуі шығарылды. $C_p°{\sim}f(T)$ және теллуриттің есептелген $S°(298,15)$ мәні бойынша $H°(\mathrm{T})–H°(298,15)$, $S°(T)$ және $\Phi^{xx}(T)$ термодинамикалық функцияларының температуралық тәуелділіктері анықталды. $C_p°{\sim}f(T)$ тәуелділігінде, II-текті фазалық 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: диспрозий-барий теллуриті, калориметрия, жылусыйымдылығы, фазалық түрленулер, термодинамикалық функциялар.

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Калориметрия нового двойного теллурита диспрозия

На основе керамической технологии синтезирован новый двойной теллурит диспрозия-бария. Образование равновесного состава соединения контролировано методом рентгенофазового анализа, по результатам которого было установлено, что синтезирован двойной теллурит диспрозия $DyBaTeO_{4,5}$. Впервые в интервале 298,15–673 К проведено калориметрическое исследование теплоемкости нового двойного теллурита $DyBaTeO_{4,5}$. Градуировку прибора осуществляли на основании определения тепловой проводимости тепломера. Проверку работы калориметра проводили измерением теплоемкости α-Al_2O_3. Экспериментальные данные удельной и мольной теплоемкости обработаны методами математической статистики. На основе экспериментальных данных выведено уравнение зависимости $C_p^o \sim f(T)$. По $C_p^o \sim f(T)$ и вычисленному значению $S^o(298{,}15)$ теллурита определены температурные зависимости термодинамических функций $H^o(T)$–$H^o(298{,}15)$, $S^o(T)$ и $\Phi^{xx}(T)$. На зависимости $C_p^o \sim f(T)$ 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 могут быть использованы для прогнозирования термохимических констант аналогичных соединений.

Ключевые слова: теллурит диспрозия-бария, калориметрия, теплоемкость, фазовые переходы, термодинамические функции.

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