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A.T.Dyusekeeva[1], A.Zh.Bekturganova[1], K.T.Rustembekov[1], B.K.Kasenov[2], N.A.Makhatova[1], M.Stoev[3]

[1]Ye.A.Buketov Karaganda State University;
[2]Zh.A.Abishev Chemical-Metallurgical Institute, Karaganda;
[3]South-West University «Neofit Rilski», Blagoevgrad, Bulgaria
(E-mail: dyusekeeva_at@mail.ru)

Thermochemistry of double magnesium tellurite

The isobaric heat capacity of double magnesium tellurite is studied in the range of 298.15–673 K and used as a basis for deriving dependences $C^o_p{\sim}f(T)$ and determining their thermodynamic functions. Dependences $C^o_p{\sim}f(T)$ are found to have abnormally sharp λ-like peaks, due probably to second-order phase transitions.

Key words: calorimetry, heat capacity, magnesium tellurite, second-order phase transitions, thermodynamic functions.

Thermochemical and thermodynamic properties of the compounds present certain interest for the technological process simulation, as well as for the directed synthesis of materials with targeted properties [1]. Within this framework, the study of a system, consisting of metallic and tellurium oxides, is important to the inorganic materials science, and new tellurites, forming inside them, may have both original and unique properties.

The aim of this work was to study the heat capacities and thermodynamic properties of magnesium-cerium tellurite in the temperature range of 298.15–673 K.

Magnesium tellurite was synthesized by ceramic technology from cerium (IV) oxide, tellurium (IV) oxide, and magnesium carbonate of chemically pure grade in the stoichiometric proportion. The synthesis of this compound was described in [2]. The formation of the equilibrium composition of a compound was monitored by X-ray diffraction. The X-ray powder diffraction pattern of each compound was indexed by means of homology in [3]. The correctness of indexing was confirmed by the good reproducibility of experimental $10^4/d^2$ values and the agreement between the X-ray and pycnometric densities.

The heat capacities of tellurite were studied via dynamic calorimetry on an commercial IT-S-400 calorimeter in the temperature range of 298.15–673 K. The mean-square deviations ($\bar{\delta}$) were calculated for averaged specific heat capacities at each temperature The random error components ($\overset{o}{\Delta}$) were calculated for the average molar heat capacities. The random error components in measuring heat capacities on the IT-S-400 calorimeter does not exceed ± 10 %. Operation of the calorimeter was tested by measuring the heat capacity of α-Al_2O_3. The resulting $C^o_p(298.15)$ = 76.0 J/(mol K) was in satisfactory agreement with the reference value (79.0 J/(mol K)) [4].

We investigated the specific heat capacities of tellurite, and then we calculated its molar heat capacities based on the obtained experimental values (Table 1).

In studying the temperature dependences of the heat capacities of double magnesium tellurite at 373 and 498 K, we observed abnormally sharp λ-like peaks probably associated with second-order phase transitions (see Fig.). These transitions could be due to the redistribution of cations and changes in the magnetic moment of synthesized tellurite.

Table 1

Experimental specific and molar heat capacities of the $MgCe(TeO_3)_3$

T, K	$C_p \pm \bar{\delta}$, J/(g K)	$C^{o}_p \pm \Delta$, J/(mol K)	T, K	$C_p \pm \bar{\delta}$, J/(g K)	$C^{o}_p \pm \Delta$, J/(mol K)
298.15	0.2440±0.0036	169±4	498	0.4797±0.0036	332±8
323	0.4347±0.0030	301±8	523	0.4549±0.0033	314±8
348	0.5094±0.0036	352±9	548	0.4409±0.0021	305±8
373	0.5532±0.0038	382±10	573	0.4172±0.0022	288±7
398	0.5231±0.0039	362±9	598	0.4037±0.0033	279±7
423	0.4344±0.0039	300±8	623	0.3179±0.0047	220±6
448	0.4456±0.0032	308±8	648	0.2173±0.0035	150±4
473	0.4635±0.0025	320±8	673	0.2206±0.0036	153±4

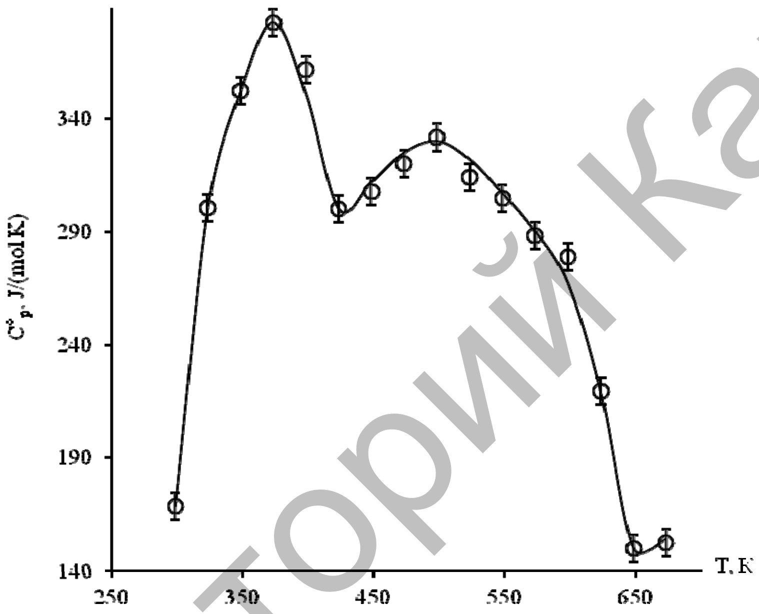

Figure. The temperature dependence of specific heat capacity of the magnesium-cerium tellurite

Based on the experimental data (Table 1) and considering the temperatures of second-order transitions, we derived the following temperature dependence for the compound' heat capacities:

$$C^{o}_{p}, \text{J/(mol K)} = a + bT + cT^{-2}, \quad (1)$$

the coefficients of which are given in Table 2. The error in the coefficients of dependences $C^{o}_{p}\sim f(T)$ was determined using the average random errors for the considered temperature ranges. Since the technical characteristics of the calorimeter do not allow direct calculation of the standard entropy S°(298.15) of tellurites from the experimental data on $C^{o}_{p}(T)$, it was estimated by means of ion increments.

Table 2

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

T, K	a	$b\cdot10^{-3}$	$c\cdot10^{5}$
298–373	4545.0 ± 114.4	–7490.9 ± 188.5	–1904.0 ± 47.9
373–423	994.8 ± 25.0	–1641.8 ± 41.3	–
423–648	3112.3 ± 78.3	–3770.9 ± 94.9	–2177.3 ± 54.8
648–673	90.3 ± 2.3	92.4 ± 2.3	–

Using known relationships, the experimental data on $C^{o}_{p}\sim f(T)$, and the estimated values of S°(298.15), we calculated the temperature dependences of functions $C^{o}_{p}(T)$, $S°(T)$, $H°(T) - H°(298.15)$, and $\Phi^{xx}(T)$. Our results are presented in Table 3.

Table 3

Thermodynamic functions of the $MgCe(TeO_3)_3$ in the temperature range of 298.15–673 K

T, K	$C_p^0(T) \pm \overset{0}{\Delta}$, J/(mol K)	$S^0(T) \pm \overset{0}{\Delta}$, J/(mol K)	$H^0(T) - H^0(298,15) \pm \overset{0}{\Delta}$, J/(mol)	$\Phi^{xx}(T) \pm \overset{0}{\Delta}$, J/(mol K)
298.15	169 ± 4	293 ± 9	–	293 ±20
300	182 ± 5	294 ± 20	351 ± 8	293 ± 20
325	308 ± 8	314 ± 22	6633 ± 167	294 ± 20
350	369 ± 9	340 ± 23	15207 ± 383	296 ± 20
375	382 ± 10	366 ± 25	24680 ± 621	300 ± 21
400	338 ± 9	389 ± 27	33644 ± 847	305 ± 21
425	297 ± 7	408 ± 28	41582 ± 1046	310 ± 21
450	340 ± 9	427 ± 30	49683 ± 1250	316 ± 22
475	356 ± 9	446 ± 31	58422 ± 1470	323 ± 22
500	356 ± 9	464 ± 32	67351 ± 1695	329 ± 23
525	343 ± 9	481 ± 33	76106 ± 1915	336 ± 23
550	318 ± 8	496 ± 34	84390 ± 2124	343 ± 24
575	285 ± 7	510 ± 35	91956 ± 2314	350 ± 24
600	245 ± 6	521 ± 36	98600 ± 2481	357 ± 25
625	198 ± 5	530 ± 37	104149 ± 2621	364 ± 25
650	146 ± 4	537 ± 37	108458 ± 2729	370 ± 26
675	153 ± 4	543 ± 38	112246 ± 2824	376 ± 26

The average random error components were estimated for all heat capacities and enthalpies over the range of temperatures. The error in calculating entropy (± 3 %) was incorporated into the estimated error for entropy and the reduced thermodynamic potential. The standard entropies were estimated using Kumok's ion entropy increments [5].

The isobaric heat capacities of new double magnesium-cerium tellurite were determined by dynamic calorimetry in the temperature range of 298.15–673 K for the first time. Equations describing their temperature dependences were derived. Dependences C^{o}_{p}~$f(T)$ for magnesium–cerium tellurite were found to have sharp abnormal peaks, i.e., λ-like effects attributable to a second-order phase transition. Thermodynamic functions $C^{o}_{p}(T)$, $S^{\circ}(T)$, $H^{\circ}(T)$–$H^{\circ}(298.15)$, and $\Phi^{xx}(T)$ were calculated. The existence of a second-order phase transition indicates that this compound could have unique electrophysical properties.

It should be noted that the abnormal effects of second-order phase transitions were observed earlier for the double selenates and tellurites of *s*-*d*-elements [6–8]. Classes of these compounds in the range of second-order phase transitions exhibit semiconducting and segnetoelectrical properties.

The results from our studies could be of interest for inorganic material science, the targeted synthesis of chalcogenites with specified properties, and the physicochemical modeling of chemical and metallurgical processes with the participation of tellurium compounds. They could also serve as initial data for basic reference works and information databases on the thermodynamic constants of inorganic compounds.

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А.Т.Дүйсекеева, А.Ж.Бектұрғанова, К.Т.Рүстембеков,
Б.Қ.Қасенов, Н.А.Махатова, М.Стоев

Магний қос теллуритінің термохимиясы

298,15–673 К температура аралығында динамикалық калориметрия әдісі арқылы магний қос теллуритінің изобаралық жылу сыйымдылығы зерттелді. Оның C^{o}_{p}~$f(T)$ температуралық тәуелділігін сипаттайтын теңдеулері келтірілді және термодинамикалық функциялары анықталды. C_p^0~$f(T)$ тәуелділік қисықтарында II-текті фазалық ауысуға жатуы мүмкін λ-тәрізді эффектілер байқалды.

А.Т.Дюсекеева, А.Ж.Бектурганова, К.Т.Рустембеков,
Б.К.Касенов, Н.А.Махатова, М.Стоев

Термохимия двойного теллурита магния

Методом динамической калориметрии в интервале 298,15–673 К исследована изобарная теплоемкость двойного теллурита магния, на основе которой выведены уравнения зависимости C^{o}_{p}~$f(T)$ и определены термодинамические функции. На зависимостях C^{o}_{p}~$f(T)$ наблюдаются резкие аномальные λ-образные эффекты, связанные, вероятно, с фазовыми переходами II рода.

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