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Karaganda State University named after academician E.A. Buketov,
Karaganda, the Republic of Kazakhstan**THERMODYNAMIC PROPERTIES
OF YTTRIUM-MAGNESIUM BISMUTHITE**

Abstract. The possibility of obtaining bismuthite of yttrium with an s-element in a solid-phase method from yttrium (III) oxides, bismuth (III) and magnesium carbonate is shown. Using X-ray diffraction analysis determined that yttrium-magnesium bismuthite crystallizes in cubic syngony, and also the parameters of primitive cell, X-ray and pycnometric densities. To investigate the isobaric heat capacity of the compound used dynamic calorimetry in the interval from 298.15 to 673 K. The λ -shaped jump at 473 K on the curve of the temperature dependence of the heat capacity of the compound indicates a second-order phase transition due to valuable electrophysical properties

Keywords: yttrium-magnesium bismuthite, calorimetry, heat capacity, second-order phase transition, thermodynamic functions.

The study of systems consisting of alkaline-earth oxides, bismuth and rare-earth elements is of great importance for inorganic materials science. The new bismuthites formed in these systems can possess both original and unique properties.

The paper presents the results of the synthesis and calorimetric study of the heat capacity of yttrium-magnesium bismuthite. The synthesis was carried out by a solid-phase method. The stoichiometric amounts of yttrium oxide, bismuth and magnesium carbonate were mixed and thoroughly rubbed in an agate mortar [1]. The heat treatment of the mixture was carried out in an alundum crucible in a selitic furnace in 3 stages in the temperature range 600 – 1200°C for 30 hours. After each step, the mixture was blended and grinded in an agate mortar.

The formation of the equilibrium composition of the compound was monitored by X-ray diffraction analysis using a DRON-2.0 setup and CuK_α – radiation filtered by a Ni-filter ($U = 30$ kV, $I = 10$ mA, pulse counter scale 1000 pulses per second, counter rotation rate 2 grad/min, rotation speed of 1000 pulses per second, time constant $\tau = 5$ seconds, angular interval 2θ from 10 to 90°). The intensity of the diffraction peaks was estimated from the hundred-point scale. The X-ray powder diffraction patterns of the research compound were determined by the homology method [2].

The reliability of the results of the X-ray display indicates a satisfactory agreement between the experimental and theoretical values of the reciprocals of the squares of the interplanar distances (table 1).

The density of the resulting compound was determined by a pycnometric method [3]. It is established that the compound under consideration crystallizes in a cubic system with the following parameters of a primitive cell: $a = 10.84 \text{ \AA}$, $V^0 = 1272 \text{ \AA}^3$, $Z = 16$, $V_{\text{primit. cell}} = 79.5 \text{ \AA}^3$, $\rho_{\text{x-ray}} = 8.06$, $\rho_{\text{pycn}} = 7.98 \text{ g/cm}^3$.

Table 1 – X-ray indication of YMgBiO₄

I/I_0	$d, \text{Å}$	$10^4/d^2_{\text{exp.}}$	hkl	$10^4/d^2_{\text{teor.}}$
100	3.1212	1026	222	1022
43	2.7054	1366	400	1363
6	2.0934	2292	333	2300
45	1.9141	2729	440	2726
37	1.6323	3753	622	3748
9	1.5629	4094	444	4089
3	1.4885	4513	641, 720	4515, 4514
5	1.3537	5457	800	5451
11	1.2429	6473	662	6474
9	1.2113	6815	840	6815

The heat capacity of the synthesized substance was investigated on a serial ITC-400 calorimeter [4, 5]. From the experimental values, the molar heat capacities of YMgBiO₄ were calculated (table 2).

Table 2 – Experimental values of the heat capacities YMgBiO₄

T, K	$C_p \pm \bar{\delta}, \text{J/(g·K)}$	$C_p^0 \pm \Delta, \text{J/(mol·K)}$
298.15	0.2063 ± 0.0064	80 ± 7
323	0.2527 ± 0.0055	98 ± 6
348	0.2931 ± 0.0087	113 ± 9
373	0.3121 ± 0.0055	120 ± 6
398	0.3293 ± 0.0075	127 ± 8
423	0.3416 ± 0.0069	132 ± 7
448	0.4010 ± 0.0086	156 ± 9
473	0.4582 ± 0.0072	177 ± 8
498	0.4036 ± 0.0121	156 ± 13
523	0.3781 ± 0.0099	146 ± 11
548	0.3736 ± 0.0119	144 ± 13
573	0.3689 ± 0.0067	142 ± 7
598	0.3707 ± 0.0097	143 ± 10
623	0.3790 ± 0.0062	146 ± 7
648	0.3844 ± 0.0087	148 ± 9
673	0.3908 ± 0.0103	151 ± 11

When researching the dependence of the heat capacity of YMgBiO_4 on the temperature at 473 K, a sharp anomalous jump was observed, probably connected with a second-order phase transition. These transitions can be associated with cation redistributions, with changes in the coefficients of thermal expansion and changes in the magnetic moments of the synthesized compound. In connection with the presence of a phase transition, the dependence $C_p^0 \sim f(T)$ was described by several equations (table 3).

Table 3 – Equations of the temperature dependence of the heat capacities YMgBiO_4 in the interval 298.15 – 673K

ΔT , K	The coefficients of equation $C_p^0 = a + bT + cT^{-2}$, J/(mol·K)		
	a	$b \cdot 10^{-3}$	$c \cdot 10^5$
298 – 473	-101.25 ± 6.65	581.78 ± 38.20	6.70 ± 0.44
473 – 573	-332.53 ± 21.84	515.83 ± 33.90	590.00 ± 38.80
573 – 673	-133.87 ± 8.79	319.95 ± 21.02	310.00 ± 20.40

Table 4 – Thermodynamic functions of yttrium-magnesium bismuthite

T, K	$C_p^0(T) \pm \Delta$, J/(mol·K)	$S^0(T) \pm \Delta$, J/(mol·K)	$H^0(T) - H^0(298,15) \pm \Delta$, J/mol	$\Phi^{xx}(T) \pm \Delta$, J/(mol·K)
298.15	80 ± 5	147 ± 4	–	147 ± 4
300	81 ± 5	147 ± 14	160 ± 10	147 ± 14
325	94 ± 6	154 ± 15	2350 ± 150	147 ± 14
350	108 ± 7	162 ± 15	4870 ± 320	148 ± 14
375	122 ± 8	170 ± 16	7740 ± 510	149 ± 14
400	136 ± 9	178 ± 17	10960 ± 720	151 ± 14
425	150 ± 10	187 ± 18	14520 ± 950	152 ± 14
450	164 ± 11	196 ± 19	18440 ± 1210	155 ± 15
475	178 ± 12	205 ± 20	22720 ± 1490	157 ± 15
500	161 ± 10	213 ± 20	26900 ± 1770	160 ± 15
525	152 ± 10	221 ± 21	30820 ± 2020	162 ± 15
550	146 ± 9	228 ± 22	34540 ± 2270	165 ± 16
575	142 ± 9	234 ± 22	38150 ± 2510	168 ± 26
600	144 ± 9	241 ± 23	41750 ± 2740	171 ± 16
625	145 ± 9	246 ± 23	45370 ± 2980	174 ± 17
650	147 ± 10	252 ± 24	49030 ± 3220	177 ± 17
675	150 ± 10	258 ± 25	52740 ± 3470	180 ± 17

Based on the known relationships and the values of the coefficients, the thermodynamic functions $S^\circ(T)$, $H^\circ(T) - H^\circ(298.15)$ и $\Phi^{xx}(T)$. were calculated from the equations for the temperature dependence on the heat capacity of the compound in question. The obtained results are given in table 4. For all values of the heat capacity and enthalpy, the average random components of the error were estimated over the whole temperature range, and for entropy values and the reduced thermodynamic potential, the accuracy of calculating the entropy ($\pm 3\%$) is included in the error estimate.

The results are of definite theoretical and practical interest for the directed synthesis of compounds with valuable physicochemical properties.

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Резюме

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ТЕРМОДИНАМИЧЕСКИЕ СВОЙСТВА ВИСМУТИТА ИТТРИЯ-МАГНИЯ

Твердофазным способом получен двойной висмутит иттрия-магния. Результаты рентгенофазового анализа показывают, что соединение кристаллизуется в кубической сингонии. Параметры элементарной ячейки: $a = 10.84 \text{ \AA}$, $V^0 = 1272 \text{ \AA}^3$, $Z = 16$, $V_{\text{эл.ячейки}} = 79.5 \text{ \AA}^3$, $\rho_{\text{рентг}} = 8.06$, $\rho_{\text{пикн}} = 7.98 \text{ г/см}^3$. Методом динамической калориметрии исследована изобарная теплоемкость висмутита, на основе которой выведены уравнения зависимости $C_p^\circ \sim f(T)$ и определены термодинамические функции.

Ключевые слова: висмутит иттрия-магния, калориметрия, теплоемкость, фазовый переход II рода, термодинамические функции.

Резюме

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ИТТРИЙ-МАГНИЙ ВИСМУТИТТІҢ ТЕРМОДИНАМИКАЛЫҚ ҚАСИЕТТЕРІ

Қатты фазалық синтез әдісімен иттрий-магний висмутиті алынды. Рентгенфазалық анализ нәтижелері бойынша жаңа қосылыс кубты сингонияда кристалданатыны анықталды. Элементарлы ұяшық параметрлері: $a = 10.84 \text{ \AA}$, $V^0 = 1272 \text{ \AA}^3$, $Z = 16$, $V_{\text{эл.ұяшық}} = 79.5 \text{ \AA}^3$, $\rho_{\text{рентг}} = 8.06$, $\rho_{\text{пикн}} = 7.98 \text{ г/см}^3$. Динамикалық калориметрия әдісімен висмутиттің изобаралық жылусыйымдылығы зерттеліп, $C_p^\circ \sim f(T)$ тәуелділіктің теңдеулері шығарылып, термодинамикалық функциялары анықталды.

Түйін сөздер: иттрий-магний висмутиті, калориметрия, жылусыйымдылық, II текті фазалық ауысу, термодинамикалық функциялар.