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High temperature heat capacity and thermodynamic properties of $CaEu_2Ge_4O_{12}$ and $CaHo_2Ge_4O_{12}$ germanates in the range of 320−1050 K

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The germanates $CaEu_2Ge_4O_{12}$ and $CaHo_2Ge_4O_{12}$ were synthesized from stoichiometric mixtures of CaO, Eu_2O_3 (Ho_2O_3) and GeO_2 by sequential firing in air in the temperature range 1223−1373 K. Their crystal structure has been refined using X-ray diffraction. The heat capacity C_p of the obtained germanates was measured by differential scanning calorimetry in the region of 320−1050 K. Based on the experimental dependence of $C_p(T)$, the thermodynamic characteristics of the analyzed oxide compounds are calculated.

Keywords: calcium germanates of europium and holmium, solid-phase synthesis, differential scanning calorimetry, high-temperature heat capacity, thermodynamic properties.

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1. Introduction

After the announcement in 2006 about the preparation of calcium tetrametagermanate of yttrium $CaY_2Ge_4O_{12}$ [1] many papers appeared relating the preparation and study of other isostructural compounds (space group $P4/nbm$, the number of formula units in the cell $Z = 2$) [2–7]. From the data obtained it follows that these compounds are promising for practical use as laser radiation converters [2] and luminophores [3–7]. Therefore, in previously published papers the main attention was paid to the study of both the optical properties of such germanates and their crystal structure. Despite the attention paid to such compounds, many of their properties were not yet studied. First of all, this relates to thermophysical properties. At that keep in mind that the use of such materials in practice presupposes knowledge of their behavior under operating conditions. State diagrams of $CaO-Eu_2O_3-GeO_2$ and $CaO-Ho_2O_3-GeO_2$ were not completely plotted, and the available information refers to adjacent binary systems: $CaO-Eu_2O_3(Ho_2O_3)$ [8], $Eu_2O_3(Ho_2O_3)-GeO_2$ [9–11], $CaO-GeO_2$ [12,13]. Computer simulation of phase equilibrium in these systems requires reliable information about the thermodynamic properties of all formed compounds. Publications does not contain such information for systems $CaO-Eu_2O_3-GeO_2$ and $CaO-Ho_2O_3-GeO_2$.

Considering the above said it seems necessary to determine experimentally the high temperature heat capacity of germanates $CaEu_2Ge_4O_{12}$ and $CaHo_2Ge_4O_{12}$ (in temperature range 320−1050 K) and to calculate their thermodynamic properties based on them.

2. Experimental procedure

The germanates $CaEu_2Ge_4O_{12}$ and $CaHo_2Ge_4O_{12}$ were received by solid-phase method. For this we used CaO (extra pure), Eu_2O_3 and Ho_2O_3 (chem. pure), GeO_2 (99.99%). They were precalcinated: CaO — at temperature of 1173 K for 2 h; Eu_2O_3, Ho_2O_3 and GeO_2 — at temperature of 773 K for 1 h. Then they were ground in stoichiometric ratios in an agate mortar. After this, the tablets were pressed and fired in air at 1223 K (for 10 h) and 1373 K (seven times for 10 h). After each firing, the samples were ground and pressed again. The phase composition of the synthesized samples was monitored by X-ray phase analysis (Bruker D8 ADVANCE diffractometer with VANTEC linear detector, CuK_α-radiation) similar to [14].

The heat capacity of germanates $CaEu_2Ge_4O_{12}$ and $CaHo_2Ge_4O_{12}$ was measured using thermal analyzer STA 449 C Jupiter (NETZSCH, Germany) by method of differential scanning calorimetry. The experiment procedure is as described earlier in [15]. The experimental results were processed using program package NETZSCH Proteus Thermal Analysis and licence program Sistat Sigma Plot (Sistat Software Inc., USA). The experiment error did not exceed 2%.

3. Results and discussion

The diffraction patterns of the studied germanates were indexed on the basis of a tetragonal lattice (space group $P4/nbm$). The data obtained on the parameters of latice cells in comparison with the results of other authors are given in Table 1. It can be seen that they well agree with each other.

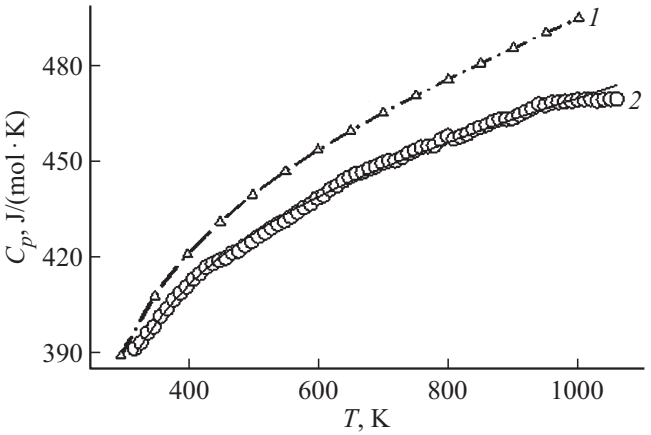

Figure 1. Temperature effect on molar heat capacity $CaEu_2Ge_4O_{12}$. *1* — calculation by Neumann method–Kopp, *2* — experiment, solid line — approximating curve.

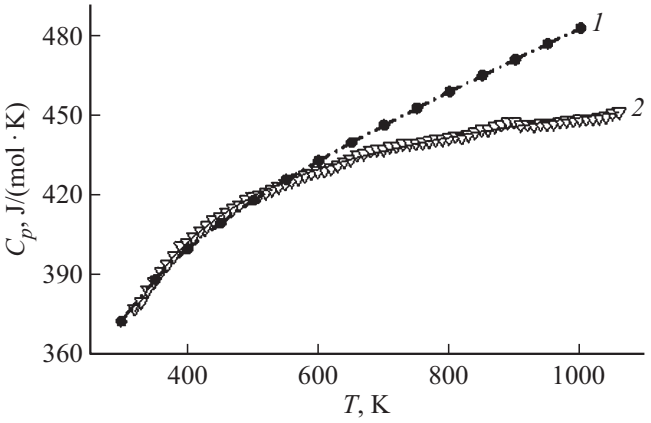

Figure 2. Temperature effect on molar heat capacity $CaHo_2Ge_4O_{12}$. *1* — calculation by Neumann method–Kopp, *2* — experiment.

Figures 1 and 2 show the temperature effect on molar heat capacity $CaEu_2Ge_4O_{12}$ and $CaHo_2Ge_4O_{12}$. Smoothing of experiment curves $C_p(T)$ was performed using program Sistat Sigma Plot, selecting the approximation equations. The best polynomial describing the temperature dependences of the heat capacity in the temperature range under study is Mayer–Kelly equation [16]:

$$C_p = a + bT - cT^{-2}, \quad (1)$$

which for $CaEu_2Ge_4O_{12}$ and $CaHo_2Ge_4O_{12}$ has, respectively, the following form (J/(K mol):

$$C_p = (418.10 \pm 1.74) + (56.27 \pm 1.80) \cdot 10^{-3}T - (48.24 \pm 1.72) \cdot 10^{5}T^{-2}, \quad (2)$$

$$C_p = (438.02 \pm 0.91) + (18.31 \pm 0.90) \cdot 10^{-3}T - (68.89 \pm 0.91) \cdot 10^{5}T^{-2}. \quad (3)$$

The correlation coefficients between the experimentally measured heat capacity values and the points of the smoothing curves (2) and (3) are equal to 0.9978, 0.9992, and the maximum deviation of the experimental values from the smoothing curves is 1.50 and 0.79%.

Absence of different type of extrema in the dependences $C_p(T)$ is the basis to consider that in region 320–1050 K these compounds do not have polymorphic transformations.

It was not possible to compare the obtained heat capacity values of $CaEu_2Ge_4O_{12}$ and $CaHo_2Ge_4O_{12}$ with the data provided by other authors due to the absence of such data. So the calculation of $C_p(T)$ of these germanates was carried out by the Neumann–Kopp method [17]. For this the input data were taken from publications: $Eu_2Ge_2O_7$ — from paper [18], $Ho_2Ge_2O_7$ — from [19], CaO — from [20], GeO_2 — from [21].

Figures 1 and 2 show that the calculated heat capacity values are close to the experimental values only at temperatures only.

The calculation of C_p germanates under study at 298 K were made using Neumann–Kopp (NK) method [17], Kumok incremental method (KIM) [22] and by Kellogg (Kel) method [23] (in latter case only for $CaHo_2Ge_4O_{12}$, as for Eu no input data are available). A comparison of these results with the values calculated using equations (2) and (3) is given in Table 2 (in brackets — deviation, %).

Note that the best agreement with experiment is observed for $CaEu_2Ge_4O_{12}$.

Using relations (2) and (3) and known thermodynamic equations [17] for calcium germanates of europium and holmium the enthalpy changes $(H^\circ(T) - H^\circ(320\,\mathrm{K}))$, entropy $(S^\circ(T) - S^\circ(320\,\mathrm{K}))$ and Gibbs energy ΔG were calculated.

The results obtained are given in Tables 3 and 4, respectively.

Table 1. Parameters of lattice cell of germanates $CaEu_2Ge_4O_{12}$ and $CaHo_2Ge_4O_{12}$

Parameters	$CaEu_2Ge_4O_{12}$		$CaHo_2Ge_4O_{12}$	
	Present paper	[4]	Present paper	[2,4]
Sp. gr.	$P4/nbm$	$P4/nbm$	$P4/nbm$	$P4/nbm$
$a = b$, Å	10.10223(6)	10.09892(8)	9.99693(5)	9.99176(4)
c, Å	5.11576 (5)	5.11491(5)	5.06974(4)	5.06810(2)
V, Å^3	522.089	521.660	506.663	505.975

Table 2. Comparison of approximation of heat capacity experminatal values according to Mayer–Kelly (MK) germanates $CaEu_2Ge_4O_{12}$ and $CaHo_2Ge_4O_{12}$ at 298 K with calculated by different methods (J/(mol · K))

Germanate	KM	NK	KIM	Kel
$CaEu_2Ge_4O_{12}$	380.6	386.9 (1.66)	386.3 (1.50)	–
$CaHo_2Ge_4O_{12}$	365.9	377.18 (3.08)	378.9 (3.55)	371.95 (1.65)

Table 3. Thermodynamic properties $CaEu_2Ge_4O_{12}$

T, K	C_p, J/(mol · K)	$H^\circ(T)-H^\circ(320\,\mathrm{K})$ kJ/mol	$S^\circ(T)-S^\circ(320\,\mathrm{K})$ J/(mol · K)	$-\Delta G/T^*$, J/(mol · K)
320	389.0	–	–	–
350	398.5	11.82	35.29	1.53
400	410.5	32.06	89.32	9.18
450	419.6	52.82	138.2	20.85
500	427.0	73.99	182.8	34.85
550	433.1	95.50	223.8	50.19
600	438.5	117.3	261.7	66.26
650	443.3	139.3	297.0	82.67
700	447.7	161.6	330.1	99.18
750	451.8	184.1	361.1	115.6
800	455.6	206.8	390.4	131.9
850	459.3	229.6	418.1	147.9
900	462.8	252.7	444.4	163.6
950	466.3	275.9	469.6	179.1
1000	469.6	299.3	493.6	194.2
1050	472.8	322.9	516.6	209.3

Note. $^*\Delta G/T = [H^\circ(T)-H^\circ(320\,\mathrm{K})]/T - [S^\circ(T)-S^\circ(320\,\mathrm{K})]$.

Table 4. Thermodynamic properties $CaHo_2Ge_4O_{12}$

T, K	C_p, J/(mol · K)	$H^\circ(T)-H^\circ(320\,\mathrm{K})$ kJ/mol	$S^\circ(T)-S^\circ(320\,\mathrm{K})$ J/(mol · K)	$-\Delta G/T^*$, J/(mol · K)
320	376.6	–	–	–
350	388.2	11.5	34.28	1.48
400	402.3	31.3	87.10	8.94
450	412.2	51.6	135.1	20.33
500	419.6	72.4	178.9	34.03
550	425.3	93.6	219.2	49.06
600	429.9	115.0	256.4	64.80
650	433.6	136.5	291.0	80.89
700	436.8	158.3	323.2	97.06
750	439.5	180.2	353.4	113.1
800	441.9	202.2	381.9	129.1
850	444.0	224.4	408.7	144.7
900	446.0	246.6	434.2	160.1
950	447.8	269.0	458.3	175.2
1000	449.4	291.4	481.3	189.9
1050	451.0	313.9	503.3	204.3

Note. $^*\Delta G/T = [H^\circ(T)-H^\circ(320\,\mathrm{K})]/T - [S^\circ(T)-S^\circ(320\,\mathrm{K})]$.

From the presented data it follows that at all studied temperatures the values C_p for these germanates do not exceed the Dulong–Petit limit $3Rs$, where R — universal gas constant, s — number of atoms in the formula unit of the corresponding oxide compound.

4. Conclusion

The germanates $CaEu_2Ge_4O_{12}$ and $CaHo_2Ge_4O_{12}$ were received by solid-phase synthesis. The effect of temperature on its molar heat capacity is studied. It was identified that in the temperature range 320–1050 K the dependence $C_p = f(T)$ is well described by Mayer–Kelly equation. The thermodynamic properties of oxide compounds were calculated based on the experimental data about heat capacity.

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Conflict of interest

The authors declare that they have no conflict of interest.

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