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High temperature heat capacity of germanate $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$

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According to the standard ceramic technology, $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$ germanate was obtained from the initial oxides of CaO, Er_2O_3 and GeO_2 by sequential firing in air in the temperature range 1223–1423 K. Its crystal structure was determined using X-ray diffraction (e.g. $P4/nbm$; $a = 9.97390(8)$ Å, $b = 5.06017(5)$ Å, $V = 503.38(1)$ Å³). The high-temperature heat capacity in the range 320–1050 K was measured by differential scanning calorimetry. Thermodynamic characteristics are calculated using experimental $C_p(T)$ data.

Keywords: calcium-erbium germanate, solid-phase synthesis, heat capacity, thermodynamic properties.

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1. Introduction

The attention of researchers to rare earth element germanates with general formula $\text{CaR}_2\text{Ge}_4\text{O}_{12}$ ($R = \text{RZE}$) is explained by the prospects of practical applications as laser conversion devices [1] and phosphors [2–4]. Therefore, researchers focused on the investigation of crystal structures and optical properties of these compounds. The data on their heat capacity and thermodynamic properties are available for a limited amount of germanates: $\text{CaY}_2\text{Ge}_4\text{O}_{12}$ [5], $\text{CaEu}_2\text{Ge}_4\text{O}_{12}$ and $\text{CaHo}_2\text{Ge}_4\text{O}_{12}$ [6]. $\text{CaO}-\text{Er}_2\text{O}_3-\text{GeO}_2$ system state diagram has not been built and input data on thermodynamic properties of all produced compounds is required for its computer-based simulation. No such findings for $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$ are available in the literature.

Considering all this, it was necessary to synthesize $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$, update its crystal structure, experimentally measure the high-temperature heat capacity within 320–1050 K and calculate its thermodynamic properties based on these findings.

2. Synthesis of samples and experimental technique

To prepare $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$, solid-phase method was used. Previously baked initial CaO and Er_2O_3 (ultra high pure), GeO_2 (99.99%) in the stoichiometric amount were homogenized in an agate mortar and pressed into pellets. They were annealed in air at 1223 K (10 h) and 1373 K (10 + 15 h). The sintered pellets were triturated after 10 h and pressed again. The single-phase state of germanate was verified by the X-ray diffraction analysis (XPA) at room temperature using Bruker D8 ADVANCE diffractometer with VANTEC-1 linear detector ($\text{CuK}\alpha$ -radiation); angle increment was 0.016° , exposition time per each increment is 2 s. The lattice cell parameters were updated by the

Rietveld method in TOPAS 3 software. XPA has shown that the sample after annealing during 35 h contained 43.37% of the major phase and $\text{Er}_2\text{Ge}_2\text{O}_7$, $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ and Er_2O_3 as impurities. Therefore, additional annealing at 1423 K (20 h) was performed. This resulted in the increase in $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$ concentration up to 70.24%. Then, CaO and GeO_2 were added up to stoichiometric ratio and annealing was performed at the same temperature (20 h). Concentration of the major phase was 93.23%. Another 90 h of annealing made it possible to achieve 97.5% of $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$ yield. CaO and GeO_2 were added again up to stoichiometric composition. Then, annealing at the same temperature was performed during 25 h with trituration every 5 h. Finally, single-phase $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$ samples were achieved. Such long-term preparation of $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$ is explained by the absence of melting temperature data for $\text{CaR}_2\text{Ge}_4\text{O}_{12}$ (the only one study [7] reports that $\text{CaY}_2\text{Ge}_4\text{O}_{12}$ has incongruent type of melting within 1503–1523 K). Therefore, the annealing temperature and time were fitted experimentally.

The heat capacity of the prepared oxide compound was measured using STA 449 C Jupiter thermal analyzer (NETZSCH, Germany) by the differential scanning calorimetry method. The experiment procedure is as described previously in [8]. The experiment error did not exceed 3%. The experimental data are polynomial smoothed by spline approximation using Systat Sigma Plot 12 (Systat Software Inc, USA) software tool.

3. Findings and discussion

Lattice cell parameters of the prepared $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$ compared with data reported by other authors are shown in Table 1. It can be seen that these values quite well agree with each other.

Table 1. Germanate lattice cell parameters $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$

Parameters	This study	[2]
Sp.gr.	$P4/nbm$	$P4/nbm$
$a = b, \text{Å}$	9.97390 (8)	9.97205(7)
$c, \text{Å}$	5.06017 (5)	5.06250(1)
$V, \text{Å}^3$	503.38 (1)	503.325

Temperature effect on the molar heat capacity of $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$ is shown in the figure.

It can be seen that an increase in temperature from 320 to 1050 K results in a consistent increase of heat capacity and $C_p(T)$ has no any extrema. This suggests that $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$ within 320–1050 K has no polymorphous transformations. The same was also observed for other $\text{CaY}_2\text{Ge}_4\text{O}_{12}$ [5], $\text{CaEu}_2\text{Ge}_4\text{O}_{12}$ and $\text{CaHo}_2\text{Ge}_4\text{O}_{12}$ [6]. It was established that among all equations describing the temperature dependence of heat capacity of solids [9] the Maier-Kelley relation better suits $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$ [10]:

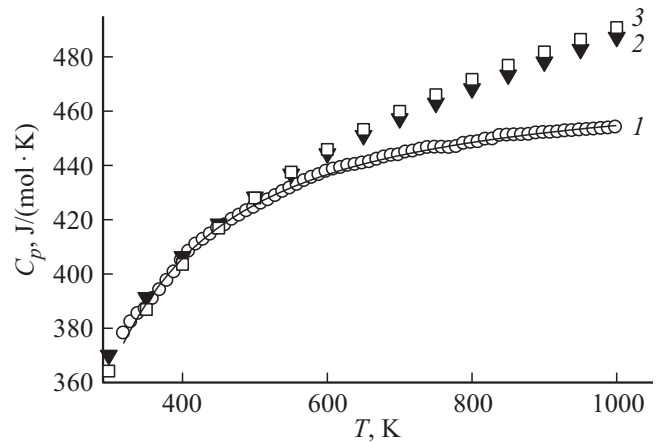
$$C_p = a + bT - cT^{-2}. \quad (1)$$

For the analyzed germanate, equation (1) is written as (J/K mol):

$$C_p = (455.70 \pm 1.22) + (7.53 \pm 0.13) \cdot 10^{-3}T - (84.81 \pm 1.17) \cdot 10^5 T^{-2}. \quad (2)$$

The correlation coefficient for equation (2) is 0.9990, and the maximum deviation of the experimental points from the smoothing curve is 0.93%.

There is no other heat capacity data for $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$, therefore the obtained data, like in [5,6], will be compared with the values calculated using various model representations: by Neumann–Kopp method (NK) [11,12] and Kumok



Temperature dependence of molar heat capacity of $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$: 1 — experiment, 2 — NK₂ calculation, 3 — NK₁ calculation, solid line — approximating curve (equation (2)).

increment method (KIM) [13]. The Neumann–Kopp method used two options: calculation of $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$ heat capacity by simple oxide data (NK₁) [11] and by heat capacity of $\text{Er}_2\text{Ge}_2\text{O}_7$ [14], CaO and GeO_2 [11] (NK₂). It was established that at 298 K the calculated value of C_p for NK₁ (362.4 J/K mol) is lower by 1.02% than that calculated using equation (2) and equal to 364.2 J/K mol. At the same time, NK₂ calculation gives a higher value by 2.12% ($C_{p,298} = 370.1$ J/K mol). The maximum deviation from $C_{p,298}$ calculated using equation (2) gives KIM — $C_{p,298} = 379.8$ J/K mol which is equal to +4.28%.

The temperature dependences of heat capacity of $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$ was calculated by the Neumann–Kopp method. For NK₁, $C_p(T)$ of simple CaO [15], Er_2O_3 [16] and GeO_2 were used [17]. For NK₂, similar dependences were used for $\text{Er}_2\text{Ge}_2\text{O}_7$ [14], CaO [15] and GeO_2 [17]. The obtained results are shown in Figure 1. It can be seen

Table 2. Thermodynamic properties $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$

T, K	$C_p, \text{J}/(\text{mol} \cdot \text{K})$	$H^\circ(T) - H^\circ(320 \text{K}), \text{kJ/mol}$	$S^\circ(T) - S^\circ(320 \text{K}), \text{J}/(\text{mol} \cdot \text{K})$	$-\Delta G/T^*, \text{J}/(\text{mol} \cdot \text{K})$
320	375.3	—	—	—
350	389.1	11.47	34.26	1.48
400	405.7	31.37	87.37	8.95
450	417.2	51.96	135.9	20.40
500	425.5	73.03	180.3	34.19
550	431.8	94.47	221.1	49.36
600	436.6	116.2	258.9	65.26
650	440.5	138.1	294.0	81.53
700	443.6	160.2	326.8	97.89
750	446.2	182.5	357.5	114.2
800	448.4	204.8	386.3	130.3
850	490.3	227.3	413.6	146.2
900	452.0	249.9	439.4	161.7
950	453.4	272.5	463.9	177.0
1000	454.7	295.2	487.1	191.9

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

that the calculated values of C_p (\mathbf{NK}_1 and \mathbf{NK}_2) are close to each other. At the same time, they are higher than the experimental values at $T > 600$ K.

It can be pointed out that as the radius of REM ion in the octahedral position ($r(\text{Eu}^{3+}) = 0.947$ Å, decreases, $r(\text{Ho}^{3+}) = 0.901$ Å, $r(\text{Er}^{3+}) = 0.89$ Å [18]) reduction of heat capacity of $C_{p,298}$, J/(mol·K): 380.6, 365.9 and 364.2 for $\text{CaEu}_2\text{Ge}_4\text{O}_{12}$, $\text{CaHo}_2\text{Ge}_4\text{O}_{12}$ [6], $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$, respectively, is observed. Similar pattern is also observed for the temperature dependence of molar heat capacity.

Using equation (2) and known thermodynamic relations [11], thermodynamic properties of $\text{CaEr}_2\text{Ge}_4\text{O}_{12}$ were calculated. This data is shown in Table 2. It may be noted that the calculated values of C_p do not exceed the classical Dulong–Petit limit $3Rs$ (R is the universal gas constant, s is the number of atoms in the formula unit of the oxide compound) throughout the investigated temperature range.

4. Conclusion

$\text{CaEr}_2\text{Ge}_4\text{O}_{12}$ was prepared by the solid-phase synthesis. The effect of temperature on its molar heat capacity was studied by the differential scanning calorimetry method. It was found that the experimental data was well described by the Mayer–Kelley equation within 320–1050 K. The data was used to calculate thermodynamic properties (enthalpy, entropy and Gibbs energy variation) of the oxide compound. The calculated data may be used for thermodynamic calculations and optimization of processes for production of luminescent materials based on calcium erbium germanate.

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Conflict of interest

The authors declare that they have no conflict of interest.

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