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Crystal structure and thermodynamic properties of germanate $CuEu_2Ge_2O_8$

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Copper-europium germanate $CuEu_2Ge_2O_8$ was obtained from the initial CuO, Eu_2O_3 and GeO_2 oxides using solid-phase synthesis by annealing in air in the temperature range of 1223–1273 K. Its crystal structure was determined (space group Cm). The influence of temperature on high-temperature heat capacity of the synthesized germanate was studied by the differential scanning calorimetry method. It was found that the dependence of heat capacity on temperature has an extreme value related to a phase transition. The thermodynamic properties were calculated based on the experimental data about heat capacity.

Keywords: copper-europium germanate, solid-phase synthesis, crystal structure, thermodynamic properties.

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1. Introduction

Complex compounds containing oxides of germanium and rare earth elements attract researchers' and practitioners' attention by the possibilities of their practical application [1–4]. Along with studies of physical and chemical properties of the already known germanates, synthesis and search for new compounds is being continued. Thus, for instance, germanates $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$ were obtained in 2006 [5]. The $CuY_2Ge_2O_8$ and $CuY_2Ge_4O_{12}$ oxide compounds were synthesized slightly earlier [6]. Substituting yttrium by rare earth elements, the authors of the latter paper obtained germanates $CuR_2Ge_2O_8$ (R = La-Yb (except Ce and Lu)) [7]. By now there are no many papers dedicated to studying the properties of such compounds. The authors of [7] believe that the structure of germanate $CuY_2Ge_2O_8$ is monoclinic with possible space groups $C2/m$, Cm and $C2$. There is data that $CuY_2Ge_2O_8$, $CuLa_2Ge_2O_8$ [8] and $CuR_2Ge_2O_8$ (R = Pr, Nd, Sm, Eu) [9] have space group $I1m1$. According to [7–10], germanates of the same composition $CuR_2Ge_2O_8$, as well as one and the same compounds can have different space groups. Fragmentary data is available on measurement of the optical (R = Sm-Tm [11], Nd [10]) and magnetic properties (R = La, Nd, Y [8], Pr, Nd, Sm, Eu [9]). High-temperature heat capacity (350–1000 K) was measured only for $CuSm_2Ge_2O_8$ [12]. Data on heat capacity of $CuY_2Ge_2O_8$ [8] and $CuR_2Ge_2O_8$ (R = Pr, Nd, Sm, Eu) [9] is given only for very low temperatures. Considering the aforesaid, it seemed necessary to synthesize $CuEu_2Ge_2O_8$, revise the crystal structure and determine the influence of temperature on heat capacity.

2. Experiment

Germanate $CuEu_2Ge_2O_8$ was synthesized by the solid-phase method from the initial oxides (CuO — Alfa Aesor 99.9995%, Eu_2O_3 — 99.96%, GeO_2 — 99.999%). The baked oxides were preliminarily mixed in a stoichiometric amount and ground in an agate mortar. The powder was pressed into a tablet and annealed in a covered crucible at 1223, 1248 (for 10 h each) and 1273 K (200 h). The sintered sample was ground and pressed again in 10 h. The phase composition of the obtained sample was checked by the X-ray diffraction method using a Bruker D8 ADVANCE diffractometer (CuK_α-radiation with a graphite monochromator in the region of angles $2\theta = 11-90^\circ$) with a VANTEC linear detector. The scanning step by angle was 0.016°, and exposure time for each step was 2s. The Rietveld refinement was carried out in the TOPAS 4.2 software [13].

Dependence of heat capacity on temperature of germanate $CuEu_2Ge_2O_8$ was studied using a STA 449 C Jupiter thermoanalyzer (NETZSCH, Germany). The experiment procedure was described earlier [12,14]. The error of heat capacity measurement did not exceed 2%.

3. Results and discussion

Almost all the peaks of the synthesized $CuEu_2Ge_2O_8$ were indexed by a monoclinic cell (space group Cm) with parameters close to $CuNd_2Ge_2O_8$. Therefore, the structure

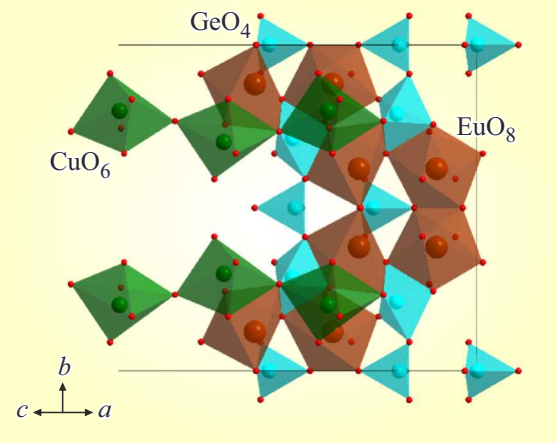

Figure 1. Crystal structure $CuEu_2Ge_2O_8$.

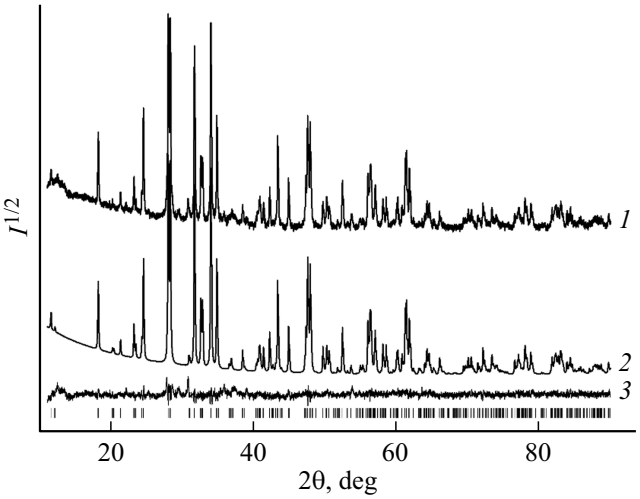

Figure 2. Experimental (*1*), calculated (*2*) and difference (*3*) profiles of radiographs for $CuEu_2Ge_2O_8$ after the Rietveld refinement; the dash lines show the calculated position of reflections.

of this crystal was taken as a starting model for refinement. The Nd position was substituted by an Eu ion for conversion (Fig. 1).

The thermal parameters of all atoms were refined in the isotropic approximation. Refinement was stable and gave low values of *R*-factors (Table 1, Fig. 2).

The atom coordinates and the main bond lengths for the studied germanate are given in Tables 2 and 3 respectively.

Fig. 3 shows the influence of temperature on heat capacity of copper-europium germanate. It can be seen that molar heat capacity increases non-monotonically with a temperature rise from 350 to 1000 K. The dependence $C_P = f(T)$ has a small extreme value with $T_{max} = 548.7$ K. It should be noted that a similar phenomenon was observed when studying the temperature dependence of heat capacity of $CuSm_2Ge_2O_8$ ($T_{max} = 498.5$ K) [12]. Thereat, the curve of differential thermal analysis shows a very small blurred extreme value in the region of 475–518 K, which was also noted for $CuLa_2Ge_2O_8$ [7].

According to [12], an extreme value in the curve of $C_p = f(T)$ is not related to thermal instability of $CuSm_2Ge_2O_8$. At the same time, a study of temperature influence on the unit cell parameters of $CuLa_2Ge_2O_8$ showed the presence of a smooth transition of the monoclinic structure into an orthorhombic one, which ends at 548 K [7]. According to the latter paper, a body-centered orthorhombic cell is relatively simply obtained from a face-centered monoclinic cell, while the possible monoclinic space groups are subgroups of orthorhombic ones. It can be assumed that a similar situation is also observed for $CuEu_2Ge_2O_8$. In this case, taking into account the closeness of the structures of this germanate before and after a phase

Table 1. Main shooting and refinement parameters $CuEu_2Ge_2O_8$

Parameters	$CuEu_2Ge_2O_8$
Space group	*Cm*
a, Å	9.8613(2)
b, Å	15.3679(3)
c, Å	8.3523(2)
β, deg	148.4658(6)
V, Å^3	662.00(3)
Z	4
R_{wp}, %	4.11
R_p, %	3.12
R_{exp}, %	2.43
R_B, %	1.69
χ^2	1.23

Note. a, b, c, β are the cell parameters; V is the cell volume, Z is the number of formula units in a cell; factors of unreliability: R_{wp} — weight profile, R_p — profile, R_{exp} — expected, R_B — integral; χ^2 — quality of fit.

Table 2. Atomic coordinates and isotropic thermal parameters (Å^2) of the $CuEu_2Ge_2O_8$ crystal

Atom	*x*	*y*	*z*	B_{iso}
Eu1	0.452(4)	0.1202(4)	0.203(5)	0.2(3)
Eu2	0.447(4)	0.1202(4)	0.712(5)	0.2(3)
Ge1	0.446(5)	0.5	0.444(6)	0.2(6)
Ge2	0.509	0.6	0.0106	0.2(5)
Ge3	0.452(5)	0.2877(8)	0.468(7)	0.2(4)
Cu1	0.448(5)	0.2977(11)	0.920(6)	1.9(6)
O1	0.20(3)	0.5	0.06(3)	0.3(4)
O2	0.23(2)	0	0.40(3)	0.3(4)
O3	0.23(2)	0	.05(3)	0.3(4)
O4	0.201(19)	0.05	0.37(2)	0.3(4)
O5	0.128(11)	0.089(4)	0.628(13)	0.3(4)
O6	0.143(11)	0.333(4)	0.160(11)	0.3(4)
O7	0.318(11)	0.412(4)	0.803(12)	0.3(4)
O8	0.312(12)	0.167(3)	0.344(14)	0.3(4)
O9	0.180(11)	0.244(3)	0.540(13)	0.3(4)
O10	0.165(11)	0.234(3)	0.852(13)	0.3(4)

Table 3. Main bond lengths (Å) in $CuEu_2Ge_2O_8$

Eu1−O3	2.23(4)	Ge1−O4	1.94(3)
Eu1−O4^{i}	2.35(4)	Ge1−O5^{i}	1.66(6)
Eu1−O5^{ii}	2.71(6)	Ge1−O6	3.01(5)
Eu15i−O6^{i}	2.31(3)	Ge2−O2^{i}	1.79(10)
Eu1−O7^{i}	2.75(6)	Ge2−O3^{i}	1.95(2)
Eu1−O8	2.57(3)	Ge2−O7^{ii}	1.68(6)
Eu1−O9^{i}	2.55(6)	Ge2−O8^{i}	3.01(5)
Eu1−O10^{ii}	2.35(5)	Ge3−5^{i}	2.11(6)
Eu2−O1^{iii}	2.39(8)	Ge3−O6	1.74(5)
Eu2−O2	2.31(7)	Ge3−O8	2.00(5)
Eu2−O5	2.62(2)	Ge3−O9^{i}	1.83(2)
Eu2−O6^{iii}	2.44(5)	Ge3−O10^{i}	1.82(6)
Eu2−O7^{i}	3.08(3)	Cu1−O6^{iii}	2.28(6)
Eu2−O8	2.18(5)	Cu1−O7	1.89(6)
Eu2−O9	2.49(5)	Cu1−O8^{iii}	2.01(6)
Eu2−O10^{i}	2.60(4)	Cu1−O9	1.85(6)
Ge1−O1	1.72(12)	Cu1−O10	2.53(2)
Ge1−O3^{iii}	3.03(10)	Cu1−O10^{i}	2.68(2)

Note. Symmetry elements: (i) $x + 1/2, -y + 1/2, z$; (ii) $x, y, z - 1$; (iii) $x + 1/2, -y + 1/2, z + 1$.

transition, the temperature dependence of heat capacity in the region of 350−1000 K can be described by a Maier–Kelley equation [15]:

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

which has the following form without taking into account the phase transition for $CuEu_2Ge_2O_8$:

$$C_p = (311.3 \pm 0.95) + (29.5 \pm 1.0) \cdot 10^{-3}T - (31.92 \pm 0.86) \cdot 10^{5}T^{-2}\,(\text{J/mol} \cdot \text{K}). \quad (2)$$

The correlation coefficient for equation (2) is 0.9992, and the maximum deviation from the smoothing curve is 0.54%.

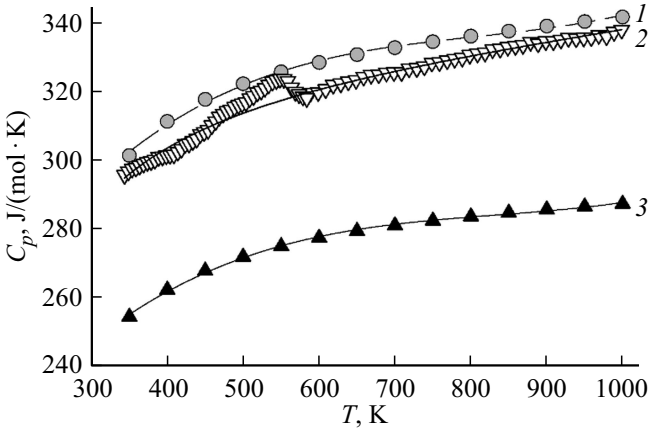

Figure 3. Temperature dependence of heat capacity of $CuEu_2Ge_2O_8$ (*1, 2*) and $Eu_2Ge_2O_7$ (*3*). *1* — the data calculated according to Neumann–Kopp, *2* — the experiment.

Fig. 3 shows for comparison the data on the temperature dependence of $Eu_2Ge_2O_7$ [16]. It can be seen that the values of C_p in this case are lower. A calculation of heat capacity of $CuEu_2Ge_2O_8$ by the Neumann–Kopp method [17], as a sum of molar heat capacities of CuO [18] and $Eu_2Ge_2O_7$ [16], shows that the values of C_P are close to the experimental ones (except the extreme value). This could be expected because the curves of $C_p = f(T)$ for copper oxide and europium germanate do not have such extreme values.

The temperature dependence of heat capacity of $CuEu_2Ge_2O_8$ (equation (2)) was used to calculate its thermodynamic properties according to the known thermodynamic correlations (neglecting the phase transition). These results are given in Table 4. It can be noted that the values of C_p at the temperature of > 350 exceed the classical Dulong–Petit limit $3Rs$, where R is the universal

Table 4. Thermodynamic properties $CuEu_2Ge_2O_8$

T, K	C_p, J/(K mol)	$H^\circ(T) - H^\circ(350\,\text{K})$, kJ/mol	$S^\circ(T) - S^\circ(350\,\text{K})$, J/(K mol)	$-\Delta G/T^*$, J/(K mol)
350	303.1	–	–	–
400	308.8	14.98	39.99	2.54
450	313.3	30.28	76.03	8.74
500	317.0	45.84	108.8	17.13
550	320.1	61.60	138.8	26.85
600	322.9	77.53	166.5	37.35
650	325.4	93.60	192.3	48.29
700	327.7	109.8	216.3	59.45
750	329.9	126.1	238.8	70.67
800	332.0	142.6	260.1	81.85
850	33.9	159.1	280.1	92.93
900	335.8	175.8	299.2	103.9
950	337.6	192.5	317.3	114.6
1000	339.4	209.4	334.5	125.2

Note. * — $\Delta G/T = [H^\circ(T) - H^\circ(350\,\text{K})]/T - S^\circ(T) - S^\circ(350\,\text{K})]$.

gas constant, s is the number of atoms in a formula unit of germanate.

4. Conclusion

Germanate $CuEu_2Ge_2O_8$ was synthesized and its crystal structure was determined. It was found that the temperature dependence $C_p = f(T)$ in the region of $T = 548.7$ K has an extreme value related to a phase transition. The thermodynamic functions of the studied complex oxide compound were calculated based on the experimental results on heat capacity.

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Conflict of interest

The authors declare that they have no conflict of interest.

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