SYNTHESIS AND PROPERTIES
OF INORGANIC COMPOUNDS

Synthesis, Crystal Structure, and Thermodynamic Properties of CuSm$_2$Ge$_2$O$_8$

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Abstract—Copper samarium germanate CuSm$_2$Ge$_2$O$_8$ have been synthesized by the ceramic method from CuO, Sm$_2$O$_3$, and GeO$_2$ in air at the final calcination temperature 1273 K (200 h), and its crystal structure has been determined (space group *Cm*; $a = 9.7592(2)$ Å, $b = 15.2608(4)$ Å, $c = 8.2502(2)$ Å, $\beta = 148.2566(8)°$, $V = 646.46(3)$ Å^3). The temperature dependence of the molar heat capacity $C_p = f(T)$ measured in the temperature range 350−1000 K shows a maximum at $T_{max} = 498.5$ K caused by the phase transition. Thermodynamic properties have been calculated from experimental data.

Studying the CuO−M$_2$O$_3$−EO$_2$ (M = Al, Ga, Fe, Cr, Bi, Y; E = Si, Ge) systems at 1273 K have revealed the formation of three new compounds: CuY$_2$Ge$_2$O$_8$, CuY$_2$Ge$_4$O$_{12}$, and CuY$_2$Si$_4$O$_{12}$ [1]. Later, the same researchers have synthesized CuR$_2$Ge$_2$O$_8$ (R = La−Yb) by substituting rare earth elements (except Ce and Lu) for Y (R = La−Yb) [2]. By now, they have been poorly studied. Their optical (R = Sm−Tm, Y [3], CuNd$_2$Ge$_2$O$_8$ [4]) and magnetic properties (CuNd$_2$Ge$_2$O$_8$, CuY$_2$Ge$_2$O$_8$, and CuLa$_2$Ge$_2$O$_8$ [5], CuR$_2$Ge$_2$O$_8$ (R = Pr, Nd, Sm, Eu) [6]) have been reported. According to [2], the CuY$_2$Ge$_2$O$_8$ structure is monoclinic with possible space groups $C\frac{2}{m}$, *Cm*, and *C*2. It is believed that CuY$_2$Ge$_2$O$_8$, CuLa$_2$Ge$_2$O$_8$ [5], and CuR$_2$Ge$_2$O$_8$ (R = Pr, Nd, Sm, Eu) [6] have space group *I*1*m*1. According to [2, 4−6], rare earth germanates of the same composition CuR$_2$Ge$_2$O$_8$ and even the same compounds can have different space groups (for example, [2, 4−6]). Thermophysical properties of CuR$_2$Ge$_2$O$_8$ germanates are limited only to the data on heat capacity at very low temperatures: up to 15 K for CuY$_2$Ge$_2$O$_8$ [5] and up to 20 K for CuR$_2$Ge$_2$O$_8$ (R = Pr, Nd, Sm, Eu) [6]. The phase diagrams of the CuO−R$_2$O$_3$−GeO$_2$ systems have not been drawn. To optimize the synthesis conditions and refine phase equilibria by thermodynamic modeling methods, information on the thermodynamic properties of all compounds formed in such systems is required. These data are not available in the literature.

In this context, the aim of the present work was to synthesize CuSm$_2$Ge$_2$O$_8$, determine its crystal structure, measure its high-temperature heat capacity, and calculate the thermodynamic properties.

EXPERIMENTAL

Germanate CuSm$_2$Ge$_2$O$_8$ was synthesized by the ceramic method from CuO (Alfa Aesor) 99.9995%, Sm$_2$O$_3$ 99.96%, and GeO$_2$ 99.999%. Stoichiometric mixtures of preliminarily calcined starting oxides were ground in an agate mortar and pressed into tablets. Being aware that at high temperatures at which solid-phase synthesis is carried out, partial evaporation of germanium oxide occurs [7], we carried out the synthesis in closed crucibles, as in [8]. The quantitative composition of complex oxide compounds was confirmed by atomic emission spectroscopy on a Perkin Elmer Optima 5300 DV inductively coupled plasma spectrometer. The pressed samples were sequentially calcined in air at 1223, 1248 (10 h each), and 1273 K (200 h). To increase the depth of the solid-phase reaction, the cake was ground every 10 h, followed by pressing. The phase composition of the samples was monitored after each stage of the compound synthesis using a Bruker D8 Advance diffractometer (CuK_α radiation) with a Vantec linear detector. It was found
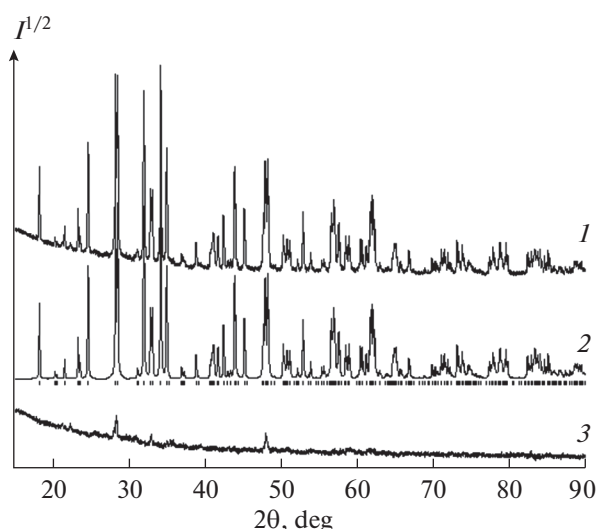
Fig. 1. (*1*) Experimental, (*2*) calculated, and (*3*) difference profiles of X-ray powder diffraction patterns of $CuSm_2Ge_2O_8$ (the tick marks show the calculated positions of reflections).

that the resulting samples contained $Sm_2Ge_2O_7$ traces. The refinement of the crystal structure and determination of the unit cell parameters of $CuSm_2Ge_2O_8$ were performed by the Rietveld method using the TOPAS 4.2 software [9].

Differential thermal analysis and measurement of the high-temperature heat capacity of $CuSm_2Ge_2O_8$ were carried out on a Netzsch STA 449 C Jupiter thermal analyzer in air. In this case, special TG + DSC 6.226.1-72 + S holders and platinum crucibles with a lid were used to measure the heat capacity. The exper-

Table 1. Unit cell parameters of $CuSm_2Ge_2O_8$

Parameter	This work	[2]
Space group	*Cm*	*Cm*
a, Å	9.7592(2)	9.675(1)
c, Å	15.2608(4)	15.259(1)
b, Å	8.2502(2)	8.25(1)
β, deg	148.2566(8)	147.95(1)
V, Å^3	646.46(3)	
Z	4	4
2θ, deg	10−105	
R_{wp}, %	5.17	
R_p, %	4.11	
R_{exp}, %	4.72	
R_B, %	0.79	
χ^2	1.07	

a, b, c, and β are the unit cell parameters; V is the unit cell volume; reliability factors: R_{wp} is the weight profile factor, R_p is the profile factor, R_{exp} is the expected factor, R_B is the integral factor; χ^2 is goodness-of-fit.

imental results were processed using the Netzsch Proteus Thermal Analysis software package. Mathematical processing of the data was carried out using the licensed program Systat Sigma Plot 12. The experimental technique was similar to that described in [10, 11]. The experimental error did not exceed 2%.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray powder diffraction pattern of the synthesized copper-samarium germanate. Almost all the peaks in the X-ray diffraction pattern were indexed in a monoclinic cell (space group *Cm*) with parameters close to those for $CuNd_2Ge_2O_8$ [4]; therefore, the structure of this crystal was taken as a starting model for refinement, in which the Nd position was replaced by the Sm ion. The thermal parameters of all atoms were refined in the isotropic approximation. The x, z coordinates of the Ge2 atom were not refined; this is required to fix the origin in the *Cm* group. Refinement was smooth and led to low R values (Table 1). The atomic coordinates and selected bond lengths in the unit cell of the $CuSm_2Ge_2O_8$ crystal are presented in Tables 2 and 3, respectively.

Comparison of the $CuSm_2Ge_2O_8$ crystal structure parameters obtained by us with the available data [2] shows (Table 1) that they generally agree with each other.

The effect of temperature on the heat capacity of $CuSm_2Ge_2O_8$ in the temperature range 350−1000 K is shown in Fig. 2. It can be seen from the figure that the $C_p = f(T)$ curve has an extremum at $T_{max} = 498.5$ K ($\Delta H_{pt} = 506$ J/mol, $\Delta S_{pt} = 1$ J/(mol K)). Its appearance can be due to thermal instability of the compound or a phase transition. There are no literature data on the effect of temperature on the Cu(II) $\rightarrow$ Cu(I) transformation in the $CuSm_2Ge_2O_8$ compound. There are numerous data on phase equilibria and thermodynamics of the Cu−O and CuO−Cu_2O systems [12−18]. The only relevant paper [1] contains information on the thermal stability of the isoformular compound $CuY_2Ge_2O_8$ in an argon atmosphere (decomposition is observed starting from $T = 1253$ K). In that paper, it has been noted that for many oxide compounds containing CuO in their composition, decomposition in an air atmosphere begins at temperatures 100−200 K higher than in an argon atmosphere. Therefore, it can be assumed that the presence of an extremum on the $C_p = f(T)$ curve is not associated with the instability of $CuSm_2Ge_2O_8$. The latter is supported by our gravimetric study of this compound. In the temperature range 320−1000 K, no change in the weight of the samples was recorded. The differential thermal analysis curve for $CuSm_2Ge_2O_8$ has a very small diffuse extremum in the range from 472 to 518 K ($\Delta H = -0.15$ kJ/mol). It should be noted that similar results have been obtained for the $CuLa_2Ge_2O_8$ compound [2].

A study of the effect of temperature on the unit cell parameters of $CuLa_2Ge_2O_8$ has revealed a smooth transition of the monoclinic structure to the orthorhombic structure, which ends at 548 K [2]. It has been noted [2] that a body-centered orthorhombic cell is easily obtained from a face-centered monoclinic cell, and possible monoclinic space groups are orthorhombic subgroups. It cannot be ruled out that a similar picture is observed in our case for $CuSm_2Ge_2O_8$.

Taking into account the closeness of the $CuSm_2Ge_2O_8$ structures before and after the transition, the $C_p = f(T)$ dependence in the temperature range studied (350−1000 K) is described by the Maier−Kelley equation [19]:

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

For the given germanate, without considering the phase transition, this equation takes the form (J/(mol K)):

$$C_p = (302.3 \pm 1.1) + (45.54 \pm 1.10) \times 10^{-3}T - \\ - (32.30 \pm 1.19) \times 10^5 T^{-2}. \quad (2)$$

The correlation coefficient for Eq. (2) is 0.9973, and the maximum deviation of the experimental points from the approximating curve is 0.96%.

Using polynomial (2) and well-known equations [20] for $CuSm_2Ge_2O_8$, its thermodynamic properties were calculated (Table 4).

Since the available information on the heat capacity of $CuSm_2Ge_2O_8$ is limited only by temperatures up to 20 K [6], our results were compared with the values calculated using various models: Neumann−Kopp (NK) model [21, 22] (in this case, two options were taken into account: calculation using data on the heat capacity of the CuO, Sm_2O_3, and GeO_2 oxides [21] (NK1) or CuO [21] and $Sm_2Ge_2O_8$ [23] (NK2)), the Kumok incremental method (KIM) [24], group contributions (GC) [25], and Kellogg (Kel) model [26]. According to the results summarized in Table 5, the best agreement with experiment is obtained by the Kumok method.

Note that the NK, KIM, and Kel models have been described in detail in monographs [26−28]. At the same time, the group contribution method [25] is not so often used in practice. It is based on the equation:

$$C_p = a + bT + cT^{-2} + dT^2. \quad (3)$$

The a, b, c, and d coefficients for a particular compound are found by summing the ionic contributions of the constituent ions forming this compound (the values of the a, b, c, and d coefficients for ions are given in [25]). The analysis of the GC method proposed for predicting the heat capacity of solid oxides [25] has been performed in [29]. It has been found that for 113 oxides, the average error in calculating C_p at 298 K is 4.8%, and the maximum error is 26.3%. Based on

**Table 2.** Atomic coordinates and isotropic thermal parameters (Å^2) of the $CuSm_2Ge_2O_8$ crystal

Atom	x	y	z	B_{iso}
Sm1	0.479(13)	0.1199(6)	0.227(17)	0.2(3)
Sm2	0.488(14)	0.1199(6)	0.742(18)	0.2(3)
Ge1	0.427(7)	0.5	0.431(9)	0.2(12)
Ge2	0.509	0.5	0.0106	0.2(12)
Ge3	0.490(13)	0.290(2)	0.504(19)	0.2(7)
Cu1	0.494(14)	0.292(3)	0.962(18)	0.2(10)
O1	0.21(3)	0.5	0.05(4)	0.3(5)
O2	0.21(3)	0	0.38(4)	0.3(5)
O3	0.23(4)	0	0.06(5)	0.3(5)
O4	0.22(4)	0.5	0.39(5)	0.3(5)
O5	0.14(3)	0.091(8)	0.63(3)	0.3(5)
O6	0.15(3)	0.330(9)	0.16(3)	0.3(5)
O7	0.31(3)	0.404(8)	0.80(3)	0.3(5)
O8	0.32(3)	0.170(10)	0.34(4)	0.3(5)
O9	0.19(2)	0.237(5)	0.52(3)	0.3(5)
O10	0.160(17)	0.236(4)	0.85(2)	0.3(5)

Table 3. Selected bond lengths in the $CuSm_2Ge_2O_8$ structure

Bond	d, Å	Bond	d, Å
Sm1−O3	2.34(8)	Ge1−O4	1.74(5)
Sm1−O4^i	2.30(7)	Ge1−O5^{vi}	1.77(12)
Sm1−O5^{ii}	2.77(14)	Ge2−O2^{vi}	1.72(16)
Sm1−O6^{iii}	2.29(9)	Ge2−O3^{vi}	1.82(5)
Sm1−O7^{iii}	2.63(14)	Ge2−O7^{ii}	1.79(12)
Sm1−O8	2.51(6)	Ge3−O5^{iii}	1.98(13)
Sm1−O9^{iii}	2.53(10)	Ge3−O6	1.85(14)
Sm1−O10^{ii}	2.46(9)	Ge3−O8	2.03(16)
Sm1−O1^{iv}	2.27(11)	Ge3−O9^{iii}	1.89(3)
Sm2−O2	2.42(12)	Ge3−O10^{iii}	1.73(11)
Sm2−O5	2.69(9)	Cu1−O6^v	2.05(15)
Sm2−O6^v	2.39(13)	Cu1−O7	1.96(13)
Sm2−O7^{iii}	2.77(9)	Cu1−O8^v	1.82(18)
Sm2−O8	2.24(16)	Cu1−O9	2.10(14)
Sm2−O9	2.44(8)	Cu1−O10	2.66(4)
Sm2−O10^{iii}	2.43(6)	Cu1−O10^{iii}	2.49(4)
Ge1−O1	1.74(17)		

Symmetry codes: (i) $x + 1/2, y − 1/2, z$; (ii) $x, y, z − 1$; (iii) $x + 1/2, −y + 1/2, z$; (iv) $x + 1/2, y − 1/2, z + 1$; (v) $x + 1/2, −y + 1/2, z + 1$; (vi) $x + 1/2, y + 1/2, z$.

this analysis, it has been concluded [29] that the group contribution method does not always provide reliable prediction of the temperature dependence of the heat capacity of oxides. It should be noted that the GC method can be used to calculate $C_p = f(T)$ of complex oxides when there is no other additional information.
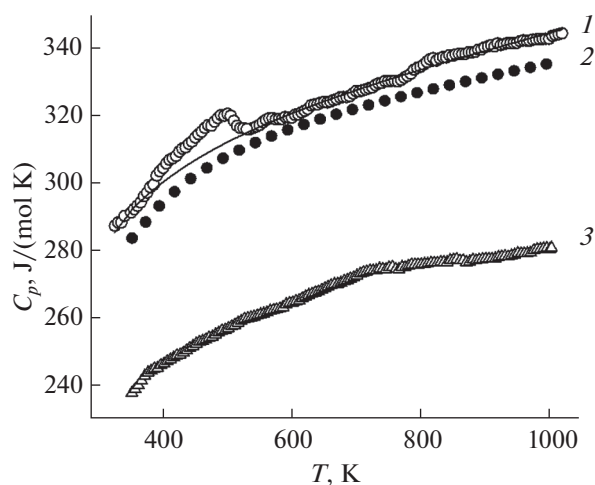
Fig. 2. Temperature dependence of molar heat capacity of (*1, 2*) CuSm$_2$Ge$_2$O$_8$ and (*3*) Sm$_2$Ge$_2$O$_7$; (*1*) experimental data (solid line is the approximating curve) and (*2*) calculated data.

Figure 2 shows the dependence $C_p = f(T)$ for Sm$_2$Ge$_2$O$_7$ [23]. It can be noted that in this case the molar heat capacity values are lower than those for CuSm$_2$Ge$_2$O$_8$. Using the data on the temperature dependence of the heat capacity of CuO [30] and Sm$_2$Ge$_2$O$_7$ [23], we calculated $C_p = f(T)$ for CuSm$_2$Ge$_2$O$_8$ (Fig. 2, curve *2*). The obtained values are close to the experimental ones, except for the region of the extremum caused by the phase transformation. The latter could be expected a priori, since there are no extrema on the $C_p = f(T)$ curves for CuO and Sm$_2$Ge$_2$O$_7$.

CONCLUSIONS

A complex oxide compound CuSm$_2$Ge$_2$O$_8$ has been synthesized, and its crystal structure has been determined. The effect of temperature in the range 350−1000 K on the molar heat capacity of copper samarium germanate has been studied. The temperature dependence of the molar heat capacity $C_p = f(T)$ shows the presence of an extremum with a maximum at $T_{max} = 498.5$ K, associated with a phase transition. The experimental data have been used to calculate the key thermodynamic functions (temperature dependences of entropy, enthalpy increments, and Gibbs energy) of copper samarium germanate.

Table 4. Smoothed heat capacities and thermodynamic properties of CuSm$_2$Ge$_2$O$_8$

T, K	C_p, J/(mol K)	$H°(T) − H°(350\ \mathrm{K})$, kJ/mol	$S°(T) − S°(350)$, J/(mol K)	$−\Delta G/T^*$, J/(mol K)
350	291.9	−	−	−
400	300.0	14.82	39.55	2.50
450	306.8	30.00	75.32	8.65
500	312.1	45.48	107.9	16.94
550	316.6	61.20	137.9	26.63
600	320.6	77.14	165.6	37.03
650	324.2	93.26	191.4	47.92
700	327.5	109.6	215.6	59.03
750	330.7	126.0	238.3	70.30
800	333.6	142.6	259.7	81.45
850	336.5	159.4	280.0	92.47
900	339.2	176.3	299.3	103.1
950	341.9	193.3	317.8	114.3
1000	344.5	210.5	335.4	123.9

* $\Delta G/T = [H°(T) − H°(350\ \mathrm{K})]/T − [S°(T) − S°(350)]$.

Table 5. Comparison of the obtained data on the heat capacity of $CuSm_2Ge_2O_8$ at 298 K (Eq. (2)) with calculated values $(J/(mol\ K))$

Eq. (2)	NK$_1$	Δ, %	NK$_2$	Δ, %	KIM	Δ, %	GC	Δ, %	Kel	Δ, %
279.5	262.0	−6.2	264.0	−5.5	273.4	−2.2	265.9	−4.9	262.5	−6.1

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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