High-Temperature Heat Capacity and Thermodynamic Properties of the $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$ Germanates

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Abstract—The $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$ germanates have been synthesized by a standard ceramic processing route using $CaCO_3$, Y_2O_3, and GeO_2 as starting materials, and their crystal structure has been refined by X-ray diffraction. The high-temperature (350–1000 K) experimental heat capacity data obtained for the germanates by differential scanning calorimetry have been used to calculate their principal thermodynamic functions.

Keywords: calcium yttrium germanates, solid-state synthesis, X-ray diffraction, crystal structure, high-temperature heat capacity, thermodynamic properties

INTRODUCTION

Recent years have seen continuing interest in the $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$ germanates, whose preparation was first reported by Yamane et al. [1] in 2006. According to the differential thermal analysis and thermogravimetry data they obtained, $CaY_2Ge_3O_{10}$ is stable up to 1653 K (and, presumably, melts congruently), whereas $CaY_2Ge_4O_{12}$ decomposes in the range 1503–1523 K to give liquid phase and $CaY_2Ge_3O_{10}$ (incongruent melting). The $CaY_2Ge_3O_{10}$ germanate has a monoclinic structure (sp. gr. $P2_1/c$) and $CaY_2Ge_4O_{12}$ has a tetragonal structure (sp. gr. $P4/nbm$) [1]. The structure of the former germanate was studied by Lipina et al. [2, 3] as well. Its crystal-chemical formula was represented by Yamane et al. [1] as $(Ca_{0.45}Y_{0.55})(Ca_{0.46}Y_{0.54})(Ca_{0.09}Y_{0.01})Ge_3O_{10}$. The crystal structure of $CaY_2Ge_4O_{12}$ has been the subject of several studies [4–8]. Since the materials in question are expected to find application in photonics for laser light conversion [6], extensive research effort has focused on the optical properties of $CaY_2Ge_3O_{10}$ [2, 3, 9] and $CaY_2Ge_4O_{12}$ [4–6, 11]. These germanates are typically prepared by solid-state reactions [2, 4–10]. In a number of cases, wet-chemical methods can be used [2, 3, 9, 12].

Despite the considerable attention paid to these germanates, many of the their properties have been studied extremely little to date. This refers primarily to their thermophysical properties. The phase diagram of the $CaO-Y_2O_3-GeO_2$ system has not yet been mapped out in full detail. Data are only available for the pseudobinary system $GeO_2-CaY_2Ge_3O_{10}$ [1] and the 1473-K isothermal section of the $CaO-Y_2O_3-GeO_2$ system [13]. For computer simulation, it is necessary to have data on the thermodynamic properties of all the oxide compounds existing in the ternary system. Such data are not available in the literature.

In this paper, we report the synthesis and high-temperature heat capacity of the $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$ germanates.

EXPERIMENTAL

The germanates were synthesized by a standard ceramic processing route. Stoichiometric mixtures of precalcined starting materials—reagent-grade $CaCO_3$, extrapure-grade Y_2O_3, and 99.999%-pure GeO_2— were homogenized by grinding in a Retsch PM 100 planetary ball mill (Germany) under ethanol, using ZrO_2 grinding media and vials. After mechanical activation for 6 h at 260 rpm, the samples were dried and placed in polyethylene containers, which were then sealed under vacuum. Next, the powders were compacted on a YLJ-CIP-20B isostatic press ($P = 150$ MPa, $\tau = 5$ min). The resultant samples were fired in air: $CaY_2Ge_3O_{10}$ was fired twice for 10 h at 1423 K and

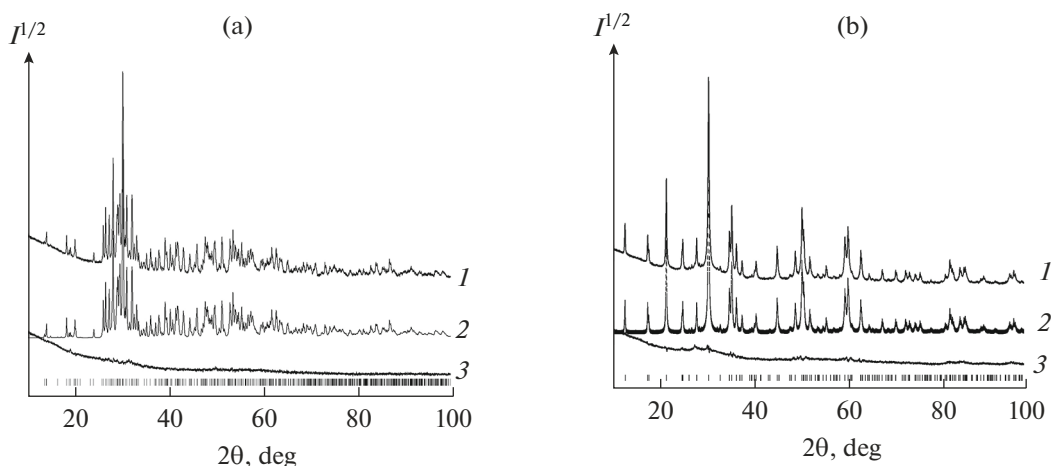**Fig. 1.** (*1*) Raw X-ray diffraction data, (*2*) calculated profiles, and (*3*) difference plots for (a) $CaY_2Ge_3O_{10}$ and (b) $CaY_2Ge_4O_{12}$ after refinement by the Rietveld method. The vertical tick marks show the calculated positions of allowed reflections.

twice for 10 h at 1473 K, and $CaY_2Ge_4O_{12}$ was fired twice for 10 h at 1423 K. After each step, the samples were reground and re-pressed. To prepare the samples for measurements, they were ground for 1 h at 260 rpm.

The phase composition of the synthesized germanates was determined by X-ray diffraction. X-ray powder diffraction patterns were obtained on a PANalytical X'Pert Pro MPD diffractometer (the Netherlands) with CuK_α radiation. Intensity data were collected using a PIXcel fast detector (scan step of 0.013°). Lattice parameters were determined by profile fitting using the derivative difference minimization method [14].

The heat capacity of the germanates was determined by differential scanning calorimetry using an STA 449 C Jupiter thermoanalytical system (Netzsch, Germany). The measurement procedure was similar to that described previously [15]. The uncertainty in our heat capacity measurements was within 2%.

Table 1. Unit-cell parameters of $CaY_2Ge_3O_{10}$

Source	This work	[1]	[2, 3]
Sp. gr.	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	6.9052(1)	6.9060(8)	6.90736(6)
b, Å	6.8363(1)	6.8329(8)	6.84276(5)
c, Å	18.7524(4)	18.752(2)	18.75830(16)
β, deg	109.078(1)	109.140(3)	108.9988(5)
V, Å³	836.60(3)	836.0(2)	838.353(12)
Z	4	4	4

RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction patterns of the synthesized $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$ germanates. Their unit-cell parameters are presented in Tables 1 and 2, respectively. It is seen that the present results agree rather well with previously reported data.

Figure 2 illustrates the effect of temperature on the molar heat capacity of $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$. As the temperature is raised from 350 to 1000 K, their C_p increases systematically. The absence of extrema in the $C_p(T)$ curves indicates that the germanates undergo no polymorphic transformations in the temperature range studied. According to our results, of all equations describing temperature-dependent heat capacity data for solids [16], the Maier–Kelley relation [17] is best suited for the compounds under study:

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

For $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$, (1) has the following form, respectively (J/(mol K)):

$$C_p = (368.40 \pm 1.05) + (28.42 \pm 1.10) \times 10^{-3}T$$
$$- (61.91 \pm 1.12) \times 10^5 T^{-2}, \quad (2)$$

$$C_p = (419.46 \pm 0.74) + (52.14 \pm 1.10) \times 10^{-3}T$$
$$- (58.11 \pm 0.80) \times 10^5 T^{-2}. \quad (3)$$

The correlation coefficient for Eqs. (2) and (3) is 0.9984, and the maximum deviation of the data points from the corresponding smoothed curves is 0.94%.

Using Eqs. (2) and (3) in combination with well-known thermodynamic relations, we evaluated the principal thermodynamic functions of the germanates studied. The results are presented in Table 3. It follows from these data that, throughout the temperature range studied, the C_p values of the germanates do not exceed the classical Dulong–Petit limit $3Rs$, where R

is the gas constant and s is the number of atoms per formula unit of the compound.

Since no heat capacity data had been previously reported for $CaY_2Ge_3O_{10}$ or $CaY_2Ge_4O_{12}$, the present results were compared to heat capacity calculated using various model notions: Neumann–Kopp (NK) additivity rule [18, 19] in two versions ((1) calculation with the use of heat capacity data for the CaO, Y_2O_3, and GeO_2 oxides [18] (NK_1) and (2) calculation with the use of heat capacity data for CaO, GeO_2 [18], and $Y_2Ge_2O_7$ [20] (NK_2)), Kumok increment method (KIM) [21], group contribution (GC) method [22], Kellog (K) method [23], and Ivanova (I) method [24]. It follows from the data in Table 4 that the best agreement with the experimental data is ensured by the KIM and NK_2. To calculate C_p by the Ivanova method, data on the melting point (phase transition temperature) are needed, which are not available for $CaY_2Ge_3O_{10}$ in the literature (the melting point of $CaY_2Ge_4O_{12}$ was reported by Yamane et al. [1]). Note that the specific features of the use of these model notions for calculating the heat capacity of solid inorganic materials were described by us previously [25].

The temperature dependence of heat capacity for solid inorganic substances can be predicted by various methods, including the Erdos–Cherny [26, 27], Kubaschewski [23, 26, 27], NK [19], and GC [22] methods. Since no additional information is required in the last case for $C_p(T)$ calculation (the coefficients a, b, c, and d for the equation $C_p = a + bT + cT^{-2} + dT^2$ are presented in tabular form), we calculated heat capacity as a function of temperature for $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$ (not shown in Fig. 2). The C_p calculation results were found to agree well with the corresponding experimental data obtained at low temperatures (350–450 K). At higher temperatures, the calculated heat capacity exceeds the measured one (the higher the temperature, the larger the difference). A similar effect was reported by not only Mostafa et al.

Table 2. Unit-cell parameters of $CaY_2Ge_4O_{12}$

Source	This work	[1]	[6, 8]
Sp. gr.	*P4/nbm*	*P4/nbm*	*P4/nbm*
$a = b$, Å	9.9926(2)	9.99282(6)	9.98757(9)
c, Å	5.0654(1)	5.0670(4)	5.06434(6)
V, Å	505.79(2)	505.97(6)	505.175
Z	2	2	2

[22], who proposed the GC method, but also Leitner et al. [28], who analyzed the applicability of this method to $C_p(T)$ calculation for various mixed oxide compounds. This leads us to assume that the GC method is not universally applicable, despite its simplicity.

Figure 2 compares the experimental $C_p(T)$ data with the NK_2 calculation results. It is seen that, in the case of $CaY_2Ge_3O_{10}$, there is better agreement with the experimental data. In the case of $CaY_2Ge_4O_{12}$, there is some discrepancy at low temperatures (below 750 K). Data necessary for the calculations were borrowed from the literature: $C_p(CaO) = f(T)$ [23, 29], $C_p(GeO_2) = f(T)$ [30], and $C_p(Y_2Ge_2O_7) = f(T)$ [20]. It should be especially pointed out that $C_p(T)$ calculations for $CaY_2Ge_4O_{12}$ using the present temperature-dependent heat capacity data for $CaY_2Ge_3O_{10}$ (Eq. (2)) and literature data for GeO_2 [30] (NK_3) ensure better agreement with the experimental data than do the NK_2 calculations (Fig. 2). Note that both positive and negative observed deviations from values corresponding to the NK additivity rule are commonly attributed to changes in vibrational frequencies of atoms in mixed oxides in comparison with binary oxides [31].
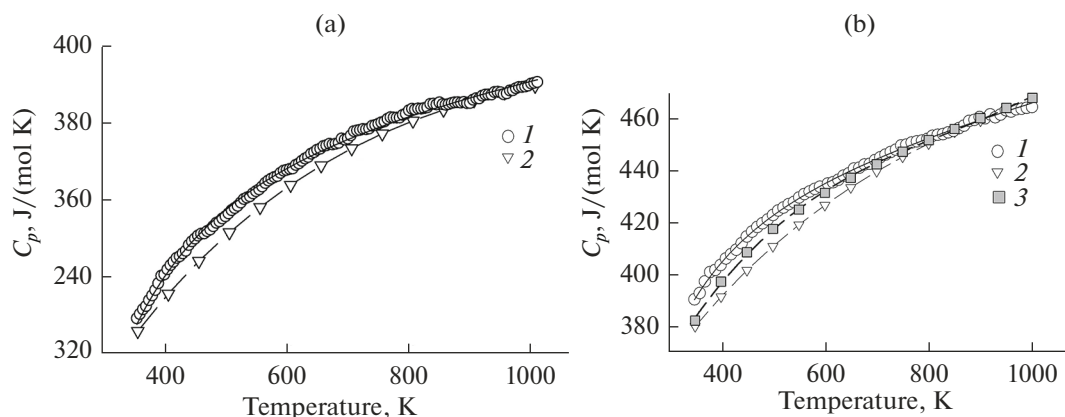

Fig. 2. Effect of temperature on the molar heat capacity of (a) $CaY_2Ge_3O_{10}$ and (b) $CaY_2Ge_4O_{12}$: (*1*) experimental data, (*2*) NK_2 and (*3*) NK_3 calculation results.

Table 3. Thermodynamic properties of $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$

T, K	C_p, J/(mol K)	$H°(T) - H°(350\ K)$, kJ/mol	$S°(T) - S°(350)$, J/(mol K)	$-\Delta G/T^*$, J/(mol K)
		$CaY_2Ge_3O_{10}$		
350	327.8	–	–	–
400	341.1	16.74	44.70	2.84
450	350.7	34.0	85.45	9.79
500	357.9	51.77	122.8	19.25
550	363.6	69.81	157.2	30.25
600	368.3	88.11	189.0	42.16
650	372.3	106.6	218.7	54.61
700	375.7	125.3	246.4	67.33
750	378.7	144.2	272.4	80.14
800	381.5	163.2	296.9	92.93
850	384.0	182.3	320.1	105.6
900	386.4	201.6	342.2	118.2
950	388.6	221.0	363.1	130.5
1000	390.7	240.4	383.1	142.6
		$CaY_2Ge_4O_{12}$		
350	390.3	–	–	–
400	404.0	19.87	53.06	3.37
450	414.2	40.34	101.3	11.61
500	422.3	61.26	145.3	22.81
550	428.9	82.55	185.9	35.82
600	434.6	104.1	223.5	49.91
650	439.6	126.0	258.6	64.62
700	444.1	148.1	291.2	79.65
750	448.2	170.4	322.0	94.79
800	452.1	192.9	351.0	109.9
850	455.7	215.6	378.6	124.9
900	459.2	238.5	404.7	139.7
950	462.5	261.5	429.6	154.3
1000	465.8	284.7	453.4	168.7

* $\Delta G/T = [H°(T) - H°(320\ K)]/T - [S°(T) - S°(320\ K)]$.

Table 4. Comparison of the experimental heat capacity data for $CaY_2Ge_3O_{10}$ (Eq. (2)) and $CaY_2Ge_4O_{12}$ (Eq. (3)) with calculation results at 298 K

	C_p, J/(mol K)					
experiment	NK_1	NK_2	KIM	GC	K	I
			$CaY_2Ge_3O_{10}$			
307.2(2)	300.8 (−2.1)	313.9 (−2.2)	311.3 (+1.3)	304.2 (−1.0)	318.9 (+3.8)	–
			$CaY_2Ge_4O_{12}$			
369.6(3)	352.7 (−4.6)	366.0 (−1.0)	367.7 (−0.5)	358.8 (−2.9)	375.8 (+1.7)	380 (+2.8)

The numbers in parentheses indicate the deviation Δ, %.

CONCLUSIONS

The $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$ germanates have been prepared by solid-state reactions using $CaCO_3$, Y_2O_3, and GeO_2 as starting materials, and their crystal structure has been refined by X-ray diffraction. The effect of temperature on the molar heat capacity of the germanates has been studied using differential scanning calorimetry. The $C_p(T)$ experimental data have been shown to be well represented by the Maier–Kelley equation in the temperature range 350–1000 K. The experimental heat capacity data have been used to calculate the thermodynamic functions of the mixed oxide compounds $CaY_2Ge_3O_{10}$ and $CaY_2Ge_4O_{12}$.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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