

Heat Capacity and Thermodynamic Functions of $\text{GdGaTi}_2\text{O}_7$ in the Temperature Range of 320–1000 K

L. T. Denisova^{a,*}, M. S. Molokeev^{a,b}, L. G. Chumilina^a, V. V. Ryabov^c, and V. M. Denisov^a

^a Siberian Federal University, Krasnoyarsk, 660041 Russia

^b Kirensky Institute of Physics, Krasnoyarsk Scientific Center, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia

^c Institute of Metallurgy, Ural Branch, Russian Academy of Sciences, Yekaterinburg, 620016 Russia

*e-mail: ldenisova@sfu-kras.ru

Received December 16, 2020; revised December 16, 2020; accepted December 18, 2020

Abstract—Titanate $\text{GdGaTi}_2\text{O}_7$ has been obtained from the initial oxides Gd_2O_3 , Ga_2O_3 , and TiO_2 by the solid-state synthesis via annealing in air at temperatures of 1273 and 1573 K. The crystal structure of the titanate has been refined by X-ray diffraction. The high-temperature (320–1000 K) heat capacity of the compound has been measured by differential scanning calorimetry. Based on the experimental dependence $C_p = f(T)$, the main thermodynamic functions of the titanate have been calculated.

Keywords: rare-earth titanates, solid-state synthesis, high-temperature heat capacity, thermodynamic functions

DOI: 10.1134/S1063783421040065

1. INTRODUCTION

The interest of researchers and practitioners in rare-earth titanates with the general formula $\text{R}_2\text{Ti}_2\text{O}_7$ ($\text{R} = \text{La}–\text{Lu}$) is due to both their intriguing physical properties and prospects for application in various fields of science and technology [1–3]. The possibilities of using such materials are significantly increased by changing their physicochemical properties via doping [3], isomorphic substitution $(\text{R}'_x\text{R}''_{1-x})_2\text{Ti}_2\text{O}_7$ [4], and partial replacement of rare-earth elements by other metals with the formation of the RMTi_2O_7 compounds [5]. The later titanates are the most understudied. In particular, in [5], the synthesis of a series of the RMTi_2O_7 ($\text{R} = \text{Sm}–\text{Lu}$, Y ; $\text{M} = \text{Ga}$, Fe) compounds was reported. At the same time, data on their properties and crystal structure were not presented (the data on only the $\text{GdGaTi}_2\text{O}_7$ structure were reported). The state diagrams of the $\text{R}_2\text{O}_3–\text{M}_2\text{O}_3–\text{TiO}_2$ systems have not been completely built yet. To refine the phase equilibria in such systems by the thermodynamic modeling methods, it is necessary to obtain data on the thermodynamic properties of the coexisting phases. Literature data on the RMTi_2O_7 titanates are lacking.

In this study, we report on the synthesis of titanate $\text{GdGaTi}_2\text{O}_7$ and investigations of its structure and thermodynamic properties.

2. EXPERIMENTAL

Substituted titanate $\text{GdGaTi}_2\text{O}_7$ was obtained by the solid-state synthesis from the initial oxides Gd_2O_3 , Ga_2O_3 , and TiO_2 precalcined in air at 1173 K. The stoichiometric mixture was homogenized in an agate mortar and tableted. The tablets were sequentially burnt in air, first at 1273 K for 10 h and, then, three times at 1573 K for 5 h. To complete the solid-state reaction, after each burning the samples were ground and pressed again. The phase composition of the obtained samples was controlled by X-ray diffraction. X-ray powder diffraction patterns of $\text{GdGaTi}_2\text{O}_7$ were taken at room temperature on a Bruker D8 ADVANCE diffractometer ($\text{CuK}\alpha$ radiation) using a VANTEC linear detector. In the experiment, a 0.6-mm slit of the primary beam in the angular range of $2\theta = 11^\circ–100^\circ$ was used. A scanning step of 0.016° remained invariable over the entire angular range; the exposure time at each step was 2 s. All the reflections in the X-ray diffraction patterns were identified by the *Pcnb* rhombic cell. The Rietveld refinement was made using the TOPAS 4.2 software [6]. The refinement results are given in Table 1 and presented in Fig. 1.

For comparison, Table 1 gives the data from [5]. It can be seen that the results obtained are in satisfactory agreement. A certain discrepancy between these data is apparently related to the fact that, in [5], single crystals were used, while, in our case, these were polycrystalline samples.

Table 1. Main parameters of the experiment and results of refinement

Parameters	This study	[5]
Space group	<i>Pcnb</i>	<i>Pcnb</i>
<i>a</i> , Å	9.7844(2)	9.7804(3)
<i>b</i> , Å	13.6078(3)	13.605(1)
<i>c</i> , Å	7.43032(18)	7.4186(2)
<i>V</i> , Å ³	989.30(4)	987.16(1)
<i>d</i> , g/cm ³	5.84	5.848
<i>R</i> _{wp} , %	2.28	
<i>R</i> _p , %	1.75	
<i>R</i> _B , %	0.52	
χ ²	1.40	

a, *b*, *c*, and β are the cell parameters, *V* is the cell volume, and *d* is the calculated density. The infidelity factors are weight profile *R*_{wp}, profile *R*_p, integral *R*_B. χ² is the fitting quality.

The heat capacity of GdGaTi₂O₇ titanate was measured by differential scanning calorimetry using an NETZSCH STA 449 C Jupiter thermal analyzer (Germany). The experimental technique was similar to that described previously in [7, 8]. The confidence interval of the experiments was no more than 5%.

3. RESULTS

The atomic coordinates and thermal parameters of the synthesized titanate are given in Table 2 and the main bond lengths, in Table 3.

Figure 2 shows the effect of temperature on the molar heat capacity of titanate GdGaTi₂O₇. As the

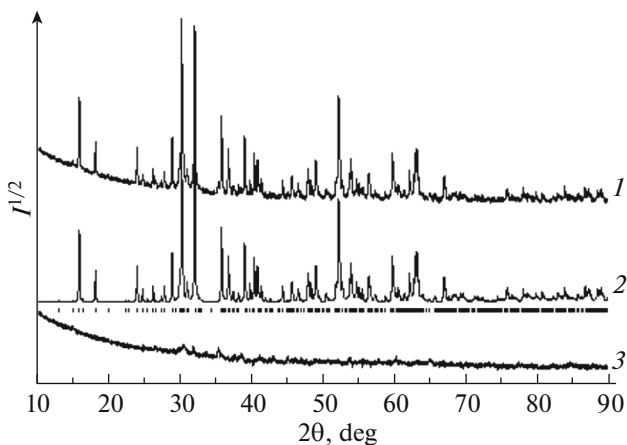


Fig. 1. (1) Differential, (2) calculated, and (3) difference profiles of the X-ray diffraction pattern of the GdGaTi₂O₇ sample after the derivative difference minimization refinement. Vertical sticks show the calculated peak positions.

Table 2. Atomic coordinates and isotropic heat parameters *B*_{iso} for the GdGaTi₂O₇ structure

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}	<i>O</i> _{cc}
Gd	0.2378(3)	0.1345(2)	0.0123(5)	0.61(19)	1
Ti1	0.2638(8)	0.3858(6)	0.5011(15)	1.2(3)	0.870(23)
Ga1	0.2638(8)	0.3858(6)	0.5011(15)	1.2(3)	0.130(23)
Ti2	0.5	0.25	0.2520(17)	1.0(5)	0.409(73)
Ga2	0.5	0.25	0.2520(17)	1.0(5)	0.591(73)
Ti3	0.004(17)	0.4906(7)	0.2732(14)	1.0(4)	0.925(43)
Ga3	0.0048(17)	0.4906(7)	0.2732(14)	1.0(4)	0.075(43)
Ga	0	0.25	0.3536(14)	1.8(4)	0.78
Gai	0.126(6)	0.280(5)	0.335(6)	1.8(4)	0.11
O1	0.1614(16)	0.3966(18)	0.223(3)	1.0(3)	1
O2	0.411(2)	0.115(2)	0.261(4)	1.0(3)	1
O3	0.109(3)	0.1518(14)	0.261(4)	1.0(3)	1
O4	0.373(3)	0.284(3)	0.439(4)	1.0(3)	1
O5	0.376(3)	0.282(2)	0.055(4)	1.0(3)	1
O6	0.377(3)	0.487(2)	0.408(4)	1.0(3)	1
O7	0.376(3)	0.490(2)	0.038(4)	1.0(3)	1

temperature increases from 320 to 1000 K, the *C*_p values naturally increase. The absence of any extrema in the *C*_p = *f*(*T*) curve is apparently indicative of the absence of polymorphic transformations in GdGaTi₂O₇ in this temperature range. The experimental data on the heat capacity of the investigated titanate are well-described by the Maier–Kelley equation [9]

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

which, for the investigated compound, has the form

$$C_p = (266.7 \pm 0.50) + (15.91 \pm 0.50) \times 10^{-3}T - (45.39 \pm 0.48) \times 10^5 T^{-2}. \quad (2)$$

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

The presence of a temperature dependence of the heat capacity of GdGaTi₂O₇ in the form of Eq. (2) allows us to calculate its basic thermodynamic functions using the known thermodynamic relations. These results are given in Table 4.

We could not compare our data on the GdGaTi₂O₇ heat capacity with results of other authors because of the absence of the later. Therefore, Fig. 2 shows the heat capacity of titanate Gd₂Ti₂O₇ [10]. Note that the partial replacement of Gd by Ga reduces the heat capacity over the entire investigated temperature range. In addition, the *C*_{p, 298} values can be compared with the calculated data according to different model representations: the additive Neumann–Kopp (NK)

Table 3. Main bond lengths (Å) in the GdGaTi₂O₇ structure

Bond length	Value	Bond length	Value
Gd–O2	2.52(3)	Ga–O1	2.03(2)
Gd–O2 ⁱ	2.38(3)	Ga3–O2 ^v	1.90(3)
Gd–O3	2.25(3)	Ga3–O3 ^{vi}	2.24(2)
Gd–O3 ⁱ	2.41(3)	Ga3–O6 ^{vii}	1.86(3)
Gd–O4 ⁱ	2.38(3)	Ga3–O7 ^{iv}	2.29(4)
Gd–O5	2.44(3)	Ga3–O7 ^{vii}	1.90(4)
Gd–O6 ⁱⁱ	2.35(3)	Ga–O3	1.84(2)
Gd–O7 ⁱⁱⁱ	2.42(3)	Ga–O5 ^{iv}	1.97(3)
(Ti1/Ga1)–O1	2.30(3)	Gai–O1	1.82(6)
(Ti1/Ga1)–O1 ^{iv}	1.81(3)	Gai–O3	1.84(6)
(Ti1/Ga1)–O4	1.81(3)	Gai–O5 ^{iv}	1.64(5)
(Ti1/Ga1)–O5 ^{iv}	2.01(3)	(Ti3/Ga3)–O1	2.03(2)
(Ti1/Ga1)–O6	1.92(3)	(Ti3/Ga3)–O2 ^v	1.90(3)
(Ti1/Ga1)–O7 ^{iv}	1.99(3)	(Ti3/Ga3)–O3 ^{vi}	2.24(2)
(Ti2/Ga2)–O2	2.03(3)	(Ti3/Ga3)–O6 ^{vii}	1.86(3)
(Ti2/Ga2)–O4	1.92(3)	(Ti3/Ga3)–O7 ^{iv}	2.29(4)
Ti2/Ga2)–O5	1.93(3)	(Ti3/Ga3)–O7 ^{vii}	1.90(4)

Symmetry elements (i) $x + 1/2, y, z - 1/2$; (ii) $x + 1/2, y - 1/2, -z + 1/2$; (iii) $x, y - 1/2, -z$; (iv) $x + 1/2, y, z + 1/2$; (v) $x + 1/2, y + 1/2, -z + 1/2$; (vi) $x, -y + 1/2, z$; (vii) $x - 1/2, -y + 1, -z + 1/2$.

Table 4. Thermodynamic properties of GdGaTi₂O₇

T, K	$C_p, J K^{-1} mol^{-1}$	$H^\circ(T) - H^\circ(320 K), kJ mol^{-1}$	$S^\circ(T) - S^\circ(320 K), J K^{-1} mol^{-1}$	$-\Delta G/T^*, J K^{-1} mol^{-1}$
320	227.4	–	–	–
350	235.2	6.94	20.74	0.90
400	244.7	18.96	52.80	5.41
450	251.4	31.37	82.03	12.33
500	256.5	44.07	108.8	20.65
550	260.4	57.00	133.4	29.80
600	263.6	70.10	156.2	39.40
650	266.3	83.35	177.4	49.21
700	268.6	96.72	197.3	59.09
750	270.5	110.2	215.9	68.93
800	272.3	123.8	233.4	78.66
850	273.9	137.4	249.9	88.25
900	275.4	151.2	265.6	97.68
950	276.8	165.0	280.6	106.9
1000	278.1	178.8	294.8	115.9

* $(\Delta G^\circ/T) = (H^\circ(T) - H^\circ(320 K))/T - (S^\circ(T) - S^\circ(320 K))$.

method [11], the increment Kumok method (IKM) [12], Kellog (Kel) tables [13], and group contributions (GC) [14]. These results are given in Table 5. It follows from the later that the best agreement with the experiment (Eq. (2)) is obtained using the Kumok method. The heat capacities of binary oxides Gd₂O₃, Ga₂O₃, and TiO₂ required for the calculations at $T = 298 K$ were borrowed from the literature [11].

The temperature dependence of the heat capacity can be estimated by the method of group contributions [14] (Fig. 2). For GdGaTi₂O₇, the calculated C_p values from 320 to 600 K coincide with the experimental values. At $T > 600 K$, the difference between them increases with temperature. The C_p values calculated for Gd₂Ti₂O₇ are lower than the experimental values, but this difference decreases with increasing temperature. When analyzing the prediction of the temperature dependence of the heat capacity of oxide compounds by the group contribution method, Leiner et al. [15] found that it yields reasonable C_p values at 298 K, while, at other temperatures, deviations from the experimental data can be observed. This was noted by the authors of the method of group contributions [14].

We calculated the temperature dependence of the heat capacity of GdGaTi₂O₇ by the Erdos and Cherny method [16, 17] using the equation

$$C_p = a + kbT - k^{-2}cT^{-2}, \quad (3)$$

where k is the coefficient of similarity equal to the ratio between the temperatures of the reference and

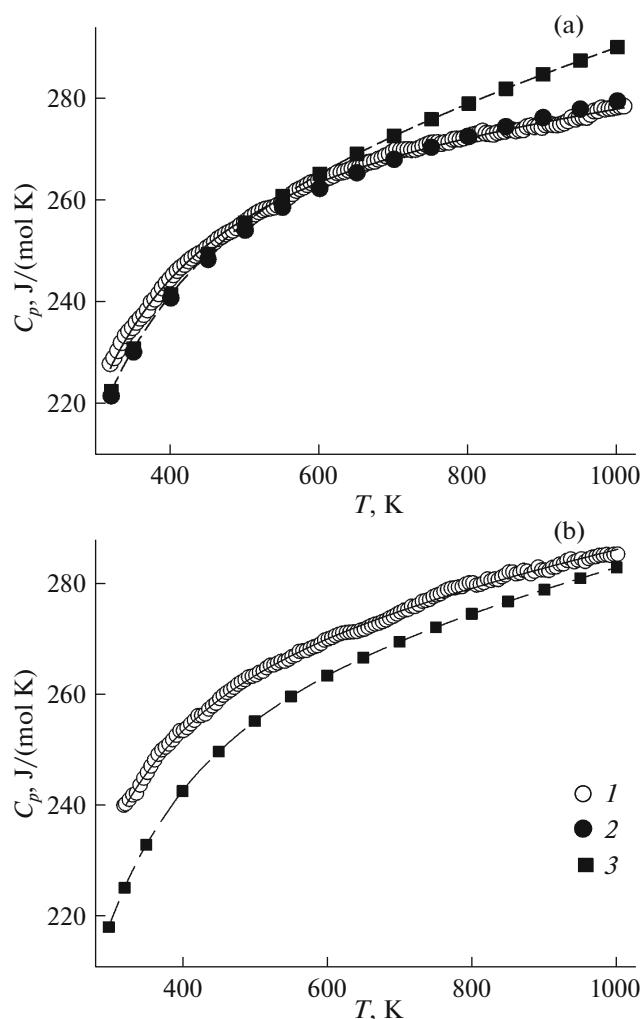


Fig. 2. Dependences $C_p = f(T)$ for (a) GdGaTi₂O₇ and (b) Gd₂Ti₂O₇ (1) obtained experimentally and calculated using (2) the Erdos–Cherny method and (3) model representations of the group contributions.

investigated substance at which their heat capacities are equal. Titanate Gd₂Ti₂O₇ was taken as a reference (the data on its high-temperature heat capacity were reported in [10]). The heat capacities of Gd₂Ti₂O₇ and GdGaTi₂O₇ are equal at 650 and 800 K ($k = 0.8125$). The results are shown in Fig. 2. It can be seen that, in this case, agreement with the experimental data is better than when using the method of group contributions.

Table 5. Comparison of the experimental values of the heat capacity of GdGaTi₂O₇ with the calculated values using different models

$C_{p, 298}$ (exp)	NK	$\Delta, \%$	IKM	$\Delta, \%$	Kel	$\Delta, \%$	GC	$\Delta, \%$
220.3	209.9	-4.7	217.3	-1.4	228.2	+3.6	228.2	+3.6

ACKNOWLEDGMENTS

We are grateful to the Krasnoyarsk Regional Center for Collective Use, Krasnoyarsk Scientific Center, Siberian Branch of the Russian Academy of Sciences.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

- L. N. Komissarova, V. M. Shatskii, G. Ya. Pushkina, L. G. Shcherbakova, L. T. Mamsurova, and G. E. Sukhanova, *Compounds of Rare Earth Elements. Carbonates, Oxalates, Nitrates, Titanates* (Nauka, Moscow, 1984) [in Russian].
- M. F. Vasil'eva, A. K. Gerasyuk, A. I. Goev, V. V. Potelov, B. N. Senik, A. B. Sukhachev, B. M. Zhigarnovskii, V. V. Kirilenko, and A. V. Nozrachev, *Prikl. Fiz.*, No. 5, 91 (2007).
- C. Li, H. Xiang, J. Chen, and L. Fang, *Ceram. Int.* **42**, 11453 (2016).
- C. Chen, Z. Gao, H. Yan, and M. Reece, *J. Am. Ceram. Soc.* **99**, 523 (2016).
- E. A. Genkina, V. I. Andrianov, E. L. Belokoneva, B. V. Mill', B. A. Maksimov, and R. A. Tamazyan, *Sov. Phys. Crystallogr.* **36**, 796 (1991).
- Bruker AXS TOPAS V4: General Profile and Structure Analysis Software for Powder Diffraction Data, User's Manual* (Bruker AXS, Karlsruhe, Germany, 2008).
- V. M. Denisov, L. T. Denisova, L. A. Irtyugo, and V. S. Biron, *Phys. Solid State* **52**, 1362 (2010).
- L. T. Denisova, L. A. Irtyugo, Yu. F. Kargin, V. V. Beletskii, and V. M. Denisov, *Inorg. Mater.* **53**, 93 (2017).
- C. G. Maier and K. K. Kelley, *J. Am. Chem. Soc.* **54**, 3243 (1932).
- L. T. Denisova, L. G. Chumilina, V. V. Ryabov, Yu. F. Kargin, N. V. Belousova, and V. M. Denisov, *Inorg. Mater.* **55**, 477 (2019).
- J. Leitner, P. Chuchvalec, D. Sedmidubský, A. Strejc, and P. Abrman, *Thermochim. Acta* **395**, 27 (2003).
- V. N. Kumok, *Direct and Inverse Problems of Chemical Thermodynamics* (Nauka, Novosibirsk, 1987), p. 108 [in Russian].
- C. B. Alcock and O. Kubaschewski, *Metallurgical Thermochimistry* (Pergamon, Oxford, 1979).
- A. T. M. G. Mostafa, J. M. Eakman, M. M. Montoya, and S. L. Yarbrow, *Ind. Eng. Chem. Res.* **35**, 343 (1996).
- J. Leiner, D. Sedmidubský, and P. Chuchvalec, *Ceram.-Silikaty* **46**, 29 (2002).
- A. G. Morachevskii, I. B. Sladkov, and E. G. Firsova, *Thermodynamic Calculations in Chemistry and Metallurgy* (Lan', St. Petersburg, 2018) [in Russian].
- G. K. Moiseev, N. A. Vatolin, L. A. Marshuk, and N. I. Il'inykh, *Temperature Dependences of the Reduced Gibbs Energy of Some Inorganic Substances (Alternative Databank ASTRA.OWN)* (UrO RAN, Yekaterinburg, 1997) [in Russian].

Translated by E. Bondareva