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Structure and Thermodynamic Properties of the $DyGaTi_2O_7$ and $EuGaTi_2O_7$ Titanates

L. T. Denisova[a, *], M. S. Molokeev[a, b], Yu. F. Kargin[c], V. V. Ryabov[d], L. G. Chumilina[a], N. V. Belousova[a], and V. M. Denisov[a]

[a] *Siberian Federal University, Krasnoyarsk, 660041 Russia*

[b] *Kirensky Institute of Physics, Krasnoyarsk Scientific Center (Federal Research Center), Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia*

[c] *Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Moscow, 119991 Russia*

[d] *Institute of Metallurgy, Ural Branch, Russian Academy of Sciences, Yekaterinburg, 620016 Russia*

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

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Abstract—The $DyGaTi_2O_7$ and $EuGaTi_2O_7$ titanates have been prepared by solid-state reactions in a starting mixture of Dy_2O_3 (Eu_2O_3), Ga_2O_3, and TiO_2 via firing in air at temperatures of 1273 and 1573 K, and their crystal structure has been studied by X-ray diffraction. Their high-temperature heat capacity (350–1000 K) has been determined by differential scanning calorimetry. The $C_p(T)$ experimental data have been used to calculate the thermodynamic functions of the titanates.

Keywords: solid-state synthesis, rare-earth titanates, crystal structure, high-temperature heat capacity, thermodynamic properties

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INTRODUCTION

The $R_2Ti_2O_7$ rare-earth (RE) titanates have been attracting researchers and practical workers' attention for a long time [1–4]. To modify their physicochemical properties and, hence, extend their application field, use is made of not only isomorphous substitutions, $(R'_xR''_{1-x})_2Ti_2O_7$ [4, 5], but also partial substitutions of other metals for the RE element: $RMTi_2O_7$ (M = Ga, Fe) [6]. The properties of such substituted titanates have been studied for only $RFeTi_2O_7$. There are data on the crystal structure and magnetic measurement results for $SmFeTi_2O_7$ [7], $GdFeTi_2O_7$ [8], $TbFeTi_2O_7$, $LuFeTi_2O_7$ [9], $DyFeTi_2O_7$ [10], $HoFeTi_2O_7$ [11], $TmFeTi_2O_7$ [12], and $YbFeTi_2O_7$ [13]. Genkina et al. [6] reported the preparation of the $RGaTi_2O_7$ (R = Sm–Lu, Y) titanates, but they determined the crystal structure of only one of them: $GdGaTi_2O_7$. Note that no $RMTi_2O_7$ compounds exist at M = Al or Cr, nor do their stannate or zirconate analogs exist. To optimize synthesis conditions and more accurately determine phase equilibria in the R_2O_3–M_2O_3–TiO_2 systems by thermodynamic modeling, one needs data on the thermodynamic properties of the oxide compounds existing in such systems. Little or no such data for $RMTi_2O_7$ are available in the literature, except for $LuGaTi_2O_7$ [14].

The purpose of this work was to study the crystal structure and thermophysical properties of the $DyGaTi_2O_7$ and $EuGaTi_2O_7$ substituted titanates.

EXPERIMENTAL

The $DyGaTi_2O_7$ and $EuGaTi_2O_7$ titanates were prepared by solid-state reactions as described previously [14], using reagent-grade Dy_2O_3 and Eu_2O_3 and extrapure-grade Ga_2O_3 and TiO_2 as starting materials. X-ray powder diffraction patterns of the titanates were collected at room temperature on a Bruker D8 Advance diffractometer (CuK_α radiation) equipped with a VANTEC linear detector. The scan step was 0.016° and the counting time per data point was 2 s in each step. The as-synthesized $EuGaTi_2O_7$ samples (total annealing time of 25 h) were found to contain trace levels of the starting oxides. Because of this, the firing time at 1573 K for this compound was increased by 60 h (with regrinding every 20 h). Only after that did we obtain single-phase $EuGaTi_2O_7$ samples.

The heat capacity of the synthesized $DyGaTi_2O_7$ and $EuGaTi_2O_7$ titanates was determined using an STA 449 C Jupiter thermoanalytical system (Netzsch, Germany). The measurement procedure was described in detail elsewhere [15, 16]. The uncertainty in our measurements was within 2%.

Table 1. Unit-cell parameters and density of $DyGaTi_2O_7$ and $EuGaTi_2O_7$

Compound	$DyGaTi_2O_7$	$EuGaTi_2O_7$
Sp. gr.	*Pcnb*	*Pcnb*
a, Å	9.77917(14)	9.78426(12)
b, Å	13.5581(2)	13.62120(15)
c, Å	7.37579(11)	7.45394(9)
V, Å^3	977.94(3)	993.42(2)
d, g/cm^3	5.98	5.74
R_{wp}, %	2.21	2.61
R_p, %	1.71	2.05
R_B, %	0.52	0.51
χ^2	1.35	1.32

R_{wp}, R_p, and R_B are the weighted profile, profile, and Bragg agreement factors, respectively; and χ^2 is the goodness-of-fit index.

RESULTS AND DISCUSSION

All reflections in the X-ray diffraction patterns were indexed in an orthorhombic structure (sp. gr. *Pcnb*) with unit-cell parameters similar to those of $GdGaTi_2O_7$ [6]. Because of this, the structure of this titanate was used as an input model for Rietveld refinement with TOPAS 4.2 software [17]. The X-ray diffraction results are presented in Tables 1–3 and Fig. 1.

Figure 2 illustrates the effect of the RE ionic radius on the unit-cell parameters and density of the $RGaTi_2O_7$ titanates. It is seen that b, c, and d are linear functions of r^{3+}. The data are well represented by the equations

$$b = (11.7128 \pm 0.0639) + (1.7953 \pm 0.0623)r^{3+}, \quad (1)$$

$$c = (5.5066 \pm 0.0515) + (1.8253 \pm 0.0502)r^{3+}, \quad (2)$$

$$d = (12.0257 \pm 0.1903) + (5.8881 \pm 0.1855)r^{3+}. \quad (3)$$

At the same time, the a cell parameter is a more intricate function of the RE ionic radius. The correlation coefficients for Eqs. (1)–(3) are 0.9982, 0.9989, and 0.9985, respectively. The unit-cell parameters of the $RGaTi_2O_7$ (R = Eu, Gd, Dy, Er, Lu) compounds were determined by us, and the ionic radii of the RE elements were borrowed from Shannon [18].

Figure 3 illustrates the effect of temperature on the heat capacity of the $DyGaTi_2O_7$ and $EuGaTi_2O_7$ titanates. As the temperature is raised from 350 to 1000 K, C_p increases systematically. The $C_p(T)$ curves have no extrema, which can be interpreted as evidence that the titanates undergo no polymorphic transformations in the temperature range studied. The experimental data are well represented by the Maier–Kelley equation [19],

$$C_p = a + bT - cT^{-2}, \quad (4)$$

which has the following form for $DyGaTi_2O_7$ and $EuGaTi_2O_7$, respectively:

$$C_p = (255.30 \pm 0.56) + (30.3 \pm 0.6)\times 10^{-3}T - (33.93 \pm 0.55)\times 10^{5}T^{-2}, \quad (5)$$

$$C_p = (259.10 \pm 0.90) + (37.6 \pm 0.9)\times 10^{-3}T - (43.96 \pm 0.78)\times 10^{5}T^{-2}. \quad (6)$$

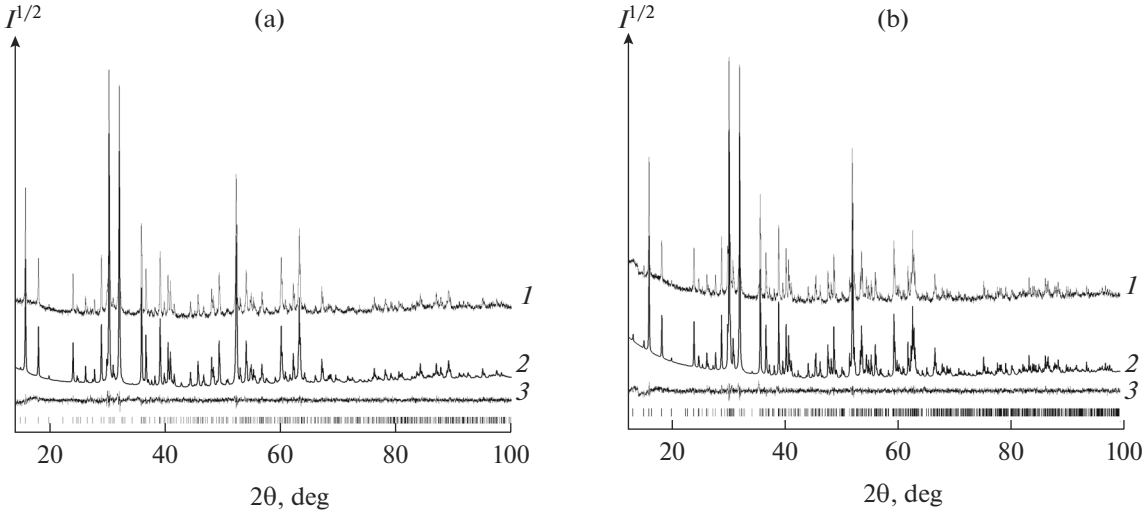

Fig. 1. (*1*) Raw X-ray diffraction data, (*2*) calculated profile, and (*3*) difference plot after refinement by the Rietveld method for (a) $DyGaTi_2O_7$ and (b) $EuGaTi_2O_7$ at room temperature. The vertical tick marks show the calculated positions of allowed reflections.

Table 2. Atomic position coordinates and isotropic thermal parameters (Å) in the structure of the titanates

Atom	*x*	*y*	*z*	B_{iso}	O*cc*
			$DyGaTi_2O_7$		
Dy	0.2412(4)	0.13445(18)	0.0075(5)	0.39(18)	1
Ti1	0.2608(10)	0.3850(5)	0.4978(16)	1.0(2)	0.865(20)
Ga1	0.2608(10)	0.3850(5)	0.4978(16)	1.0(2)	0.135(20)
Ti2	0.5	0.25	0.252(2)	1.0(5)	0.592(71)
Ga2	0.5	0.25	0.252(2)	1.0(5)	0.408(71)
Ti3	0.0018(14)	0.4893(6)	0.2630(14)	1.0(4)	0.839(41)
Ga3	0.0018(14)	0.4893(60)	0.2630(14)	1.0(4)	0.161(41)
Ga	0	0.25	0.3461(14)	1.6(30)	0.78
Gai	0.090(5)	0.292(4)	0.315(7)	1.6(3)	0.11
O1	0.1625(14)	0.3977(14)	0.233(4)	0.3(2)	1
O2	0.406(2)	0.113(2)	0.257(4)	0.3(2)	1
O3	0.104(3)	0.1550(120)	0.231(4)	0.3(2)	1
O4	0.379(3)	0.287(2)	0.445(4)	0.3(2)	1
O5	0.368(3)	0.276(2)	0.052(4)	0.3(2)	1
O6	0.364(3)	0.488(2)	0.427(4)	0.3(2)	1
O7	0.381(4)	0.494(2)	0.058(4)	0.3(2)	1
			$EuGaTi_2O_7$		
Eu	0.2360(2)	0.13454(17)	0.0137(3)	0.45(19)	1
Ti1	0.2673(6)	0.3863(5)	0.4994(11)	1.4(2)	0.872(19)
Ga1	0.2673(6)	0.3863(5)	0.4994(11)	1.4(2)	0.128(19)
Ti2	0.5	0.25	0.2523(13)	1.2(4)	0.609(59)
Ga2	0.5	0.25	0.2523(13)	1.2(4)	0.391(59)
Ti3	0.0061(11)	0.4874(5)	0.2786(9)	1.1(3)	0.824(35)
Ga3	0.0061(11)	0.4874(5)	0.2786(9)	1.1(3)	0.176(35)
Ga	0	0.25	0.3543(12)	1.5(3)	0.78
Gai	0.078(5)	0.286(4)	0.372(7)	1.5(3)	0.11
O1	0.1655(13)	0.4002(12)	0.222(2)	0.4(2)	1
O2	0.4102(18)	0.1175(18)	0.267(3)	0.4(2)	1
O3	0.109(2)	0.1562(11)	0.259(3)	0.4(2)	1
O4	0.376(2)	0.2795(18)	0.430(3)	0.4(2)	1
O5	0.379(2)	0.2888(16)	0.053(3)	0.4(2)	1
O6	0.373(3)	0.4891(15)	0.409(3)	0.4(2)	1
O7	0.373(2)	0.4901(14)	0.037(3)	0.4(2)	1

Table 3. Principal bond lengths (Å) in the structure of the titanates

		$DyGaTi_2O_7$	
Dy–O2	2.46(3)	Ga–O3	1.84(2)
Dy–O2[1]	2.36(3)	Ga–O5[4]	2.02(3)
Dy–O3	2.15(3)	Gai–O1	1.71(6)
Dy–O3[1]	2.56(3)	Gai–O3	1.97(6)
Dy–O4[1]	2.42(30)	Gai–O3[6]	2.12(6)
Dy–O5	2.31(3)	Gai–O5[4]	1.81(6)
Dy–O6[2]	2.28(3)	(Ti2/Ga2)–O4	1.92(3)
Dy–O7[3]	2.39(3)	(Ti2/Ga2)–O5	1.99(30)
(Ti1/Ga1)–O1	2.18(3)	(Ti3/Ga3)–O1	2.02(2)
(Ti1/Ga1)–)1[4]	1.90(3)	(Ti3/Ga3)–O2[5]	1.91(3)
(Ti1/Ga1)–O4	1.81(3)	(Ti3/Ga3)–O3[6]	2.22(2)
(Ti1/Ga1)–O5[4]	1.98(3)	(Ti3/Ga3)–O6[7]	1.97(3)
(Ti1/Ga1)–O6	1.80(3)	(Ti3/Ga3)–O7[4]	2.46(3)
(Ti1/Ga1)–O7[4]	2.08(3)	(Ti3/Ga3)–O7[7]	1.79(3)
(Ti2/Ga2)–O2	2.07(3)		
		$EuGaTi_2O_7$	
Eu–O2	2.553(19)	Ga–O3	1.811(19)
Eu–O2[1]	2.343(19)	Ga–O5[4]	1.97(2)
Eu–O3	2.23(2)	Gai–O1	2.10(5)
Eu–O3[1]	2.45(2)	Gai–O3	1.98(5)
Eu–O4[1]	2.34(2)	Gai–O3[6]	2.17(6)
Eu–O5	2.54(2)	Gai–O5[4]	2.41(6)
Eu–O6[2]	2.32(2)	Gai–O5[8]	2.58(5)
Eu–O7[3]	2.41(2)	(Ti2/Ga2)–O4	1.84(2)
(Ti1/Ga1)–O1	2.302(19)	(Ti2/Ga2)–O5	1.97(2)
(Ti1/Ga1)–)1[4]	1.795(19)	(Ti3/Ga3)–O1	2.005(17)
(Ti1/Ga1)–O4	1.87(3)	(Ti3/Ga3)–O2[5]	1.98(3)
(Ti1/Ga1)–O5[4]	1.99(2)	(Ti3/Ga3)–O3[6]	2.263(18)
(Ti1/Ga1)–O6	1.87(2)	(Ti3/Ga3)–O6[7]	1.94(3)
(Ti1/Ga1)–O7[4]	1.99(2)	(Ti3/Ga3)–O7[4]	2.26(2)
(Ti2/Ga2)–O2	2.01(2)	(Ti3/Ga3)–O7[7]	1.92(2)

Symmetry code: (1) $-x + 1/2, y, z - 1/2$; (2) $-x + 1/2, y - 1/2, -z + 1/2$; (3) $x, y - 1/2, -z$; (4) $-x + 1/2, y, z + 1/2$; (5) $-x + 1/2, y + 1/2, -z + 1/2$; (6) $-x, -y + 1/2, z$; (7) $x - 1/2, -y + 1, -z + 1/2$; (8) $x - 1/2, -y + 1/2, z + 1/2$.

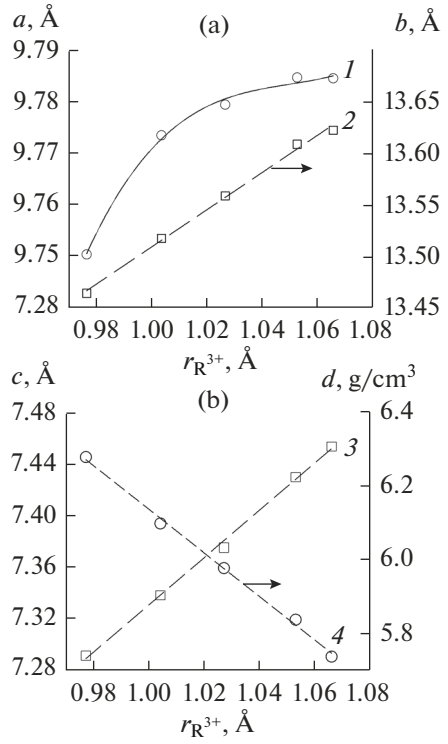

Fig. 2. Effect of the RE ionic radius r^{3+} on the (*1*) *a*, (*2*) *b*, and (*3*) *c* cell parameters and (*4*) density *d* of the $RGaTi_2O_7$ titanates.

The correlation coefficients for Eqs. (5) and (6) are 0.9990 and 0.9988, respectively, and the maximum deviations of the data points from the corresponding smoothed curves are 0.58 and 0.83%, respectively.

The present molar heat capacity data for the $DyGaTi_2O_7$ or $EuGaTi_2O_7$ titanate cannot be compared to previously reported results because no such data for these compounds are available in the literature. This can be done by comparing $C_{p,298}$ values calculated using Eqs. (5) and (6) and different model notions: Neumann–Kopp (NK) additive rule [20, 21] and Kumok increment method (KIM) [22]. The results are summarized in Table 4. It is seen these data that, on the whole, there is good agreement between the calculated heat capacity and experimental data. The heat capacity data for the binary oxides Dy_2O_3, Eu_2O_3, Ga_2O_3, and TiO_2, necessary for NK calculations, were borrowed from Leitner et al. [20].

Figure 3 shows the temperature dependences of the measured molar heat capacity for the $DyGaTi_2O_7$ and $EuGaTi_2O_7$ titanates in comparison with the NK calculation results. It is seen that the $C_p(T)$ experimental data and calculation results agree well. The $C_p(T)$ data necessary for calculation were borrowed from Gordienko et al. [23] for Dy_2O_3 and Eu_2O_3, from Zinkevich and Aldinger [24] and Guo et al. [25] for Ga_2O_3, and from Ref. [26] for TiO_2 (rutile).

Using Eqs. (5) and (6) in combination with well-known thermodynamic relations, we evaluated the principal thermodynamic functions of $DyGaTi_2O_7$ and $EuGaTi_2O_7$ (Table 5). Above 800 K, the C_p values of these titanates 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 oxide compound.

CONCLUSIONS

The $DyGaTi_2O_7$ and $EuGaTi_2O_7$ titanates have been prepared by solid-state reactions and their crystal structure has been determined. The effect of temperature on their molar heat capacity has been studied by differential scanning calorimetry. The $C_p(T)$ experi-

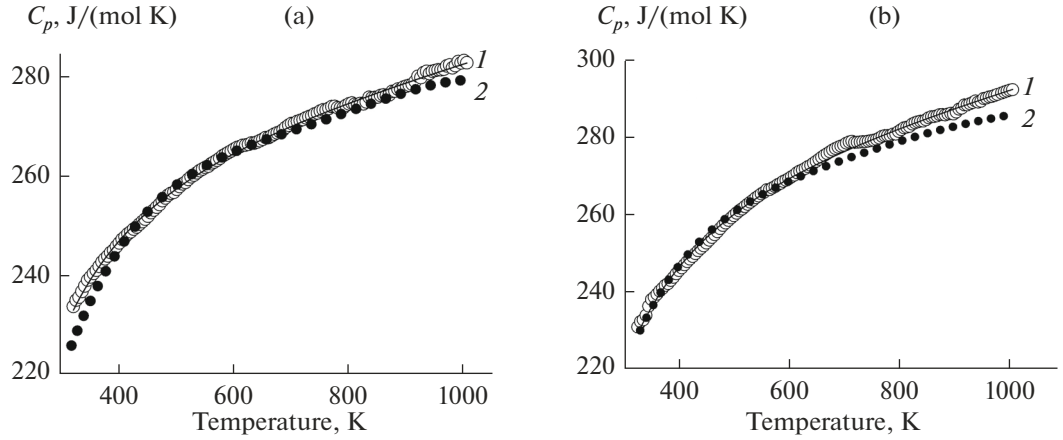

Fig. 3. Temperature dependences of molar heat capacity for the (a) $DyGaTi_2O_7$ and (b) $EuGaTi_2O_7$ titanates: (*1*) experimental data, (*2*) Neumann–Kopp calculation results.

Table 4. Comparison of the measured heat capacity $C_{p,298}$ (J/(mol K)) of $DyGaTi_2O_7$ and $EuGaTi_2O_7$ with calculation results

Compound	C_p (meas)*	C_p (NK)	Δ, %	C_p (KIM)	Δ, %
$DyGaTi_2O_7$	226.2	215.3	−4.8	220.5	−2.5
$EuGaTi_2O_7$	220.8	219.5	−0.6	222.8	+0.9

* Obtained from Eqs. (5) and (6) for $T = 298$ K.

Table 5. Thermodynamic properties of the $DyGaTi_2O_7$ and $EuGaTi_2O_7$ titanates

T, K	C_p, J/(mol K)	$H°(T) - H°(320\ K)$, kJ/mol	$S°(T) - S°(320\ K)$, J/(mol K)	$-(\Delta G°/T)$, * J/(mol K)
		$DyGaTi_2O_7$		
320	231.93	–	–	–
350	238.3	7.056	21.07	0.91
400	246.3	19.18	53.44	5.49
450	252.2	34.65	82.80	12.47
500	256.9	44.38	109.6	20.87
550	260.8	57.33	134.3	30.07
600	264.1	70.45	157.1	39.72
650	267.0	83.73	178.4	49.58
700	269.6	97.15	198.3	59.50
750	272.0	110.7	217.0	69.38
800	274.3	124.4	234.6	79.16
850	276.4	138.1	251.3	88.80
900	278.4	152.0	267.1	98.27
950	280.4	166.0	282.2	107.6
1000	282.3	180.0	269.7	116.6
		$EuGaTi_2O_7$		
320	228.2	–	–	–
350	236.3	6.97	20.82	0.90
400	246.6	19.06	53.09	5.44
450	254.3	31.59	82.60	12.40
500	260.3	44.46	109.7	20.79
550	265.2	57.60	134.6	30.03
600	269.4	70.97	158.0	39.73
650	273.1	84.54	179.7	49.68
700	276.4	98.27	200.1	59.70
750	279.4	112.1	219.2	69.71
800	282.3	126.2	237.4	79.62
850	284.9	140.4	254.6	89.42
900	287.5	154.7	270.9	99.05
950	289.9	169.1	286.5	108.5
1000	292.3	183.7	301.5	117.8

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

mental data have been shown to be well represented by the Maier–Kelley equation in the range 350–1000 K. These data have been used to calculate the principal thermodynamic functions of the titanates.

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