

Synthesis, Crystal Structure, Luminescence, and Thermophysical Properties of TbGaGe₂O₇

L. T. Denisova^{a,*}, M. S. Molokeev^{a,b}, A. S. Krylov^b, A. S. Aleksandrovsky^{a,b},
L. A. Irtyugo^a, V. V. Beletskii^a, 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

*e-mail: antluba@mail.ru

Received September 7, 2020; revised September 7, 2020; accepted September 16, 2020

Abstract—Germanate TbGaGe₂O₇ has been obtained from the initial Tb₂O₃, Ga₂O₃, and GeO₂ oxides by the solid-phase synthesis. The germanate structure has been established by X-ray diffraction. Room-temperature luminescence spectra of the compound have been recorded. The effect of temperature on the heat capacity of the oxide compound has been investigated by differential scanning calorimetry. The thermodynamic properties of the compound have been calculated from the experimental $C_p = f(T)$ data.

Keywords: terbium gallogermanate, solid-state synthesis, crystal structure, luminescence, high-temperature specific heat, thermodynamic properties

DOI: 10.1134/S106378342101008X

1. INTRODUCTION

The complex oxide compounds with a general formula RMGe₂O₇ (R is a rare-earth element and M is Al, Ga, In, or Fe) can be identified in the two crystal structure types: thortveitite-like and thortveitite. The compounds with a thortveitite structure crystallize in the monoclinic syngony (sp. gr. $C2/m$), while the compounds with a thortveitite-like structure, in different space groups ($C2$, $P2_1/m$, $P2_1/c$, and $C2/c$) [1]. Interest of researchers and practitioners in such compounds is due not only to their structural features, but also to their application potential [1, 2]. The latter concerns laser materials [1, 3], luminophores, X-ray laser screens, and nuclear industry [1, 2]. This class of materials includes TbGaGe₂O₇. For this compound, only the data on the unit cell parameters are available [4]. Literature data on its luminescence and thermophysical properties are lacking. TbGaGe₂O₇ seems to be the most unexplored among the RMGe₂O₇ compounds. In view of the aforesaid, we found it necessary to synthesize TbGaGe₂O₇ and study its structural, luminescent, and thermophysical properties.

2. EXPERIMENTAL

Germanate TbGaGe₂O₇ was obtained by the solid-phase synthesis from the initial Tb₂O₃, Ga₂O₃, and GeO₂ oxides. A stoichiometric mixture was prepared from the oxides precalcined at 1173 K. After homoge-

nization in an agate mortar, the mixture was tableted. The tablets were burnt in air sequentially at 1273 K (40 h), 1373 K (100 h), and 1473 K (70 h). To ensure the completeness of the solid-state reaction, the tablets were ground every 20 h and pressed again. Since relatively high temperatures lead to partial evaporation of GeO₂ [5], the synthesis was performed in crucibles with lids. The synthesis time and the amount of additionally embedded GeO₂ were chosen experimentally. The phase composition of the samples was controlled by X-ray structural analysis.

The X-ray powder diffraction pattern of TbGaGe₂O₇ was obtained at room temperature on a Bruker D8 ADVANCE diffractometer (CuK_α radiation) with a VANTEC linear detector. In the experiment, a 0.6-mm primary beam slit was used in the angular range of $2\theta = 11^\circ\text{--}120^\circ$. A scanning step of 0.016° was kept constant over the entire angular range and the time of exposure at each step was 2 s.

The luminescence spectra were recorded on a HORIBA Jobin Yvon T6400 spectrometer at room temperature.

The TbGaGe₂O₇ heat capacity was measured on an STA 449 C Jupiter thermal analyzer (NETZSCH, Germany). The experimental technique was similar to that described in [6]. The results obtained were processed using the NETZSCH Proteus Thermal Analysis software package and a Systat Sigma Plot 12

Table 1. Main parameters of the shot and refinement of the TbGaGe₂O₇ crystal structure (sp. gr. $P2_1/c$)

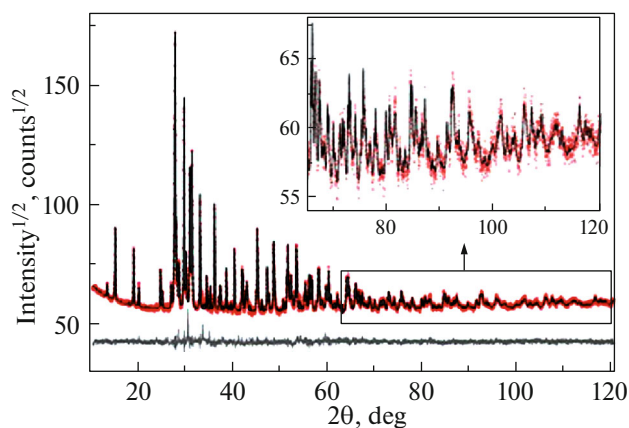
Parameter	Value
a , Å	7.1342(1)
b , Å	6.5451(1)
c , Å	12.7131(2)
β , deg	117.4824(9)
V , Å ³	526.64(2)
Z	4
d , g/cm ³	6.13
2θ angle range, deg	11–120
R_{wp} , %	2.71
R_p , %	1.90
R_{exp} , %	1.87
χ^2	1.95
R_B , %	0.71

a , b , c , and β are the cell parameters, V is the cell volume, and d is the calculated density. The criteria of fit are weight profile R_{wp} , profile R_p , expected R_{exp} , integral R_B , and goodness of fit χ^2 .

licensed software tool (Systat Software Inc, US). The experimental error was no more than 2%.

3. RESULTS

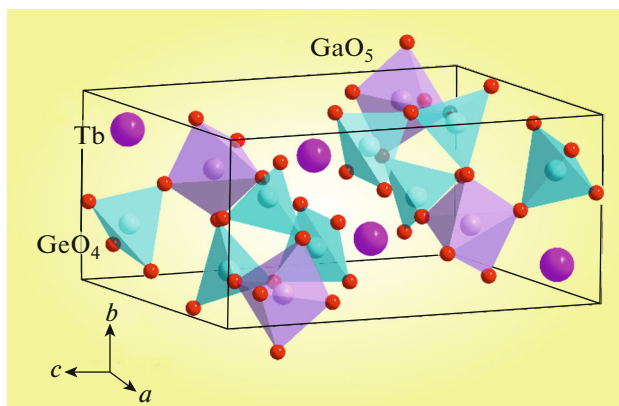
Almost all the reflections, except for weak impurity peaks, were indexed with a monoclinic cell with the parameters similar to those of SmFeGe₂O₇ [7]; therefore, this structure was used as initial one. The Sm ion was replaced by Tb and the Fe ion, by Ga. The Rietveld refinement was made in the TOPAS 4.2 program [8]. The refinement results are given in Table 1 and illustrated in Fig. 1. The atomic coordinates and thermal parameters are given in Table 2 and the main bond

**Fig. 1.** Rietveld refinement difference X-ray diffraction pattern for TbGaGe₂O₇.**Table 2.** Atomic coordinates and isotropic heat parameters (B_{iso}) of the TbGaGe₂O₇ structure

Atom	x	y	z	B_{iso}
Tb	0.7603(4)	0.1477(3)	0.02535(17)	0.72(14)
Ga1	0.7928(5)	0.3981(7)	0.2709(3)	0.43(15)
Ge1	0.7816(6)	0.6528(6)	0.0416(3)	0.40(16)
Ge2	0.3019(6)	0.4111(6)	0.2234(3)	0.52(16)
O1	0.574(3)	0.845(3)	0.0192(12)	0.7(2)
O2	0.772(2)	0.117(3)	0.2125(13)	0.7(2)
O3	0.560(2)	0.387(3)	0.3092(13)	0.7(2)
O4	0.005(3)	0.322(3)	0.4192(13)	0.7(2)
O5	0.732(3)	−0.004(2)	0.4119(14)	0.7(2)
O6	0.796(3)	0.459(2)	0.1399(15)	0.7(2)
O7	0.150(3)	0.184(2)	0.1939(15)	0.7(2)

lengths, in Table 3. The TbGaGe₂O₇ structure is shown in Fig. 2. The comparison of our data on the TbGaGe₂O₇ structure with the data reported in [4] ($a = 7.12(1)$ Å, $b = 6.53(1)$ Å, $c = 12.72(1)$ Å, $\beta = 117.4(2)^\circ$, and $d = 6.15$ g/cm³) showed their satisfactory agreement.

Figure 3 presents the luminescence spectrum of the nonresonantly excited germanate TbGaGe₂O₇. For comparison, the spectrum of the resonantly excited β' -Tb₂(MoO₄)₃ crystal is shown [9]. In both spectra, one can clearly see the main luminescence transitions of the Tb³⁺ ion. In particular, in the investigated TbGaGe₂O₇ crystal, the transitions $^5D_4-^7F_5$, $^5D_4-^7F_4$, $^5D_4-^7F_3$, $^5D_4-^7F_2$, $^5D_4-^7F_1$, and $^5D_4-^7F_0$ were observed. The luminescence intensity of the nonresonantly excited terbium ion is low (the luminescence was excited by a semiconductor laser with a central wavelength of 450 nm; detuning of this wavelength from the resonant transitions of terbium is large, so the effective excitation of the luminescence of this ion

**Fig. 2.** TbGaGe₂O₇ crystal structure.

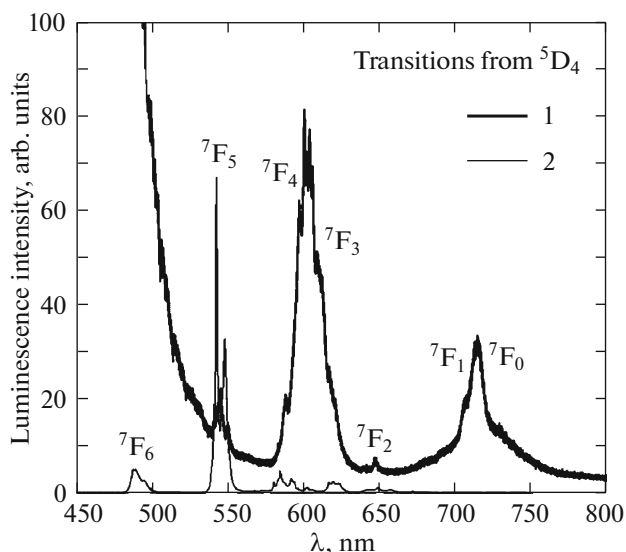


Fig. 3. Comparison of the luminescence spectra of (1) the nonresonantly excited germanate $\text{TbGaGe}_2\text{O}_7$ and (2) the resonantly excited β' - $\text{Tb}_2(\text{MoO}_4)_3$.

should not be expected). Obviously, the excitation of the terbium ion should be attributed to the nonresonant population of the $^5\text{D}_4$ level. At the same time, no luminescence traces were observed on the $^5\text{D}_4$ – $^7\text{F}_6$ transition. Since this transition of the terbium ion is hypersensitive, it should be assumed that the terbium ion in the $\text{TbGaGe}_2\text{O}_7$ crystal lattice is in the local environment similar to the environment with the inversion center. In addition, it is noteworthy that the maximum luminescence intensity is observed on the $^5\text{D}_4$ – $^7\text{F}_4$ and $^5\text{D}_4$ – $^7\text{F}_3$ transitions, the bands of which

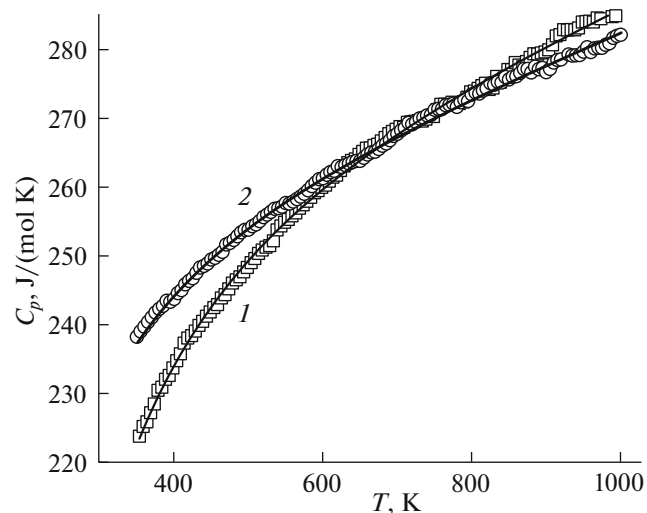


Fig. 4. Temperature dependences of the molar specific heat of (1) $\text{Tb}_2\text{Ge}_2\text{O}_7$ and (2) $\text{TbGaGe}_2\text{O}_7$

have approximately the same intensity and merge into a single band, while the $^5\text{D}_4$ – $^7\text{F}_5$ transition often dominates [9]. This points out additional possibilities for controlling the Judd–Ofelt intensity parameters implemented in the materials of the investigated class of gallogermanates.

Figure 4 illustrates the effect of temperature on the $\text{TbGaGe}_2\text{O}_7$ heat capacity. It can be seen that, as the temperature rises from 350 to 1000 K, the C_p values regularly increase and the dependence $C_p = f(T)$ does not contain various extrema. This suggests that $\text{TbGaGe}_2\text{O}_7$ does not undergo polymorphic transformations in this temperature range. The data obtained can be described by the Maier–Kelley equation [10]

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

which, for $\text{TbGaGe}_2\text{O}_7$, has the form (J/(mol K))

$$C_p = (246.80 \pm 0.76) + (43.91 \pm 0.80) \times 10^{-3}T - (48.78 \pm 0.83) \times 10^5 T^{-2}. \quad (2)$$

The correlation coefficient for Eq. (2) is 0.9992 and the maximum deviation of the experimental points from the smoothing curve is 0.67%.

Since there has been a lack of literature data on the $\text{TbGaGe}_2\text{O}_7$ heat capacity, Fig. 4 shows, for comparison, the measured heat capacity of $\text{Tb}_2\text{Ge}_2\text{O}_7$ [11]. It can be seen that the C_p values for these compounds are similar. At the same time, they are higher for $\text{TbGaGe}_2\text{O}_7$ at low temperatures and lower for this germanate at high temperatures.

Using Eq. (2), we calculated the thermodynamic properties of $\text{TbGaGe}_2\text{O}_7$ from the known thermodynamic relations. The results are given in Table 4. It follows from these data that the C_p values obtained at

Table 3. Main bond lengths (Å) in the $\text{TbGaGe}_2\text{O}_7$ structure

Bond length	Value	Bond length	Value
Tb–O1 ⁽ⁱ⁾	2.365(17)	Ga1–O4 ^(vi)	1.836(15)
Tb–O1 ⁽ⁱⁱ⁾	2.183(11)	Ga1–O6	1.721(16)
Tb–O2	2.352(14)	Ga1–O7 ^(vii)	1.926(16)
Tb–O3 ⁽ⁱⁱⁱ⁾	2.454(15)	Ge1–O1	1.864(15)
Tb–O4 ^(iv)	2.599(15)	Ge1–O4 ^(vii)	1.756(14)
Tb–O4 ^(v)	2.691(12)	Ge1–O5 ⁽ⁱⁱⁱ⁾	1.803(16)
Tb–O5 ⁽ⁱⁱⁱ⁾	2.702(15)	Ge1–O6	1.753(16)
Tb–O6	2.446(15)	Ge2–O2 ^(vii)	1.777(17)
Tb–O7 ^(vi)	2.623(15)	Ge2–O3	1.657(12)
Ga1–O2	1.961(19)	Ge2–O5 ^(vii)	1.714(16)
Ga1–O3	1.938(9)	Ge2–O7	1.772(15)

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

Table 4. Thermodynamic properties of TbGaGe₂O₇

T , K	C_p , J/(mol K)	$H^\circ(T) - H^\circ(350 \text{ K})$, kJ/mol	$S^\circ(T) - S^\circ(350 \text{ K})$, J/(mol K)	$\Phi^\circ(T)$, J/(mol K)
350	222.4	—	—	—
400	233.9	11.42	30.49	1.93
450	242.5	23.34	58.56	6.69
500	249.3	35.64	84.47	13.19
550	254.7	48.25	108.5	20.77
600	259.6	61.12	130.9	29.03
650	263.8	74.20	151.8	37.68
700	267.6	87.49	171.5	46.54
750	271.1	100.9	190.1	55.50
800	274.3	114.6	207.7	64.47
850	277.4	128.4	224.4	73.39
900	280.3	142.3	240.4	82.23
950	283.1	156.4	255.6	90.95
1000	285.9	170.6	270.2	99.55

$T > 800$ K exceed the classical Dulong–Petit limit $3Rs$, where R is the universal gas constant and s is the number of atoms per oxide compound formula unit ($s = 11$).

4. CONCLUSIONS

The oxide compound TbGaGe₂O₇ was synthesized by the solid-state reaction. Its crystal structure was refined and its luminescence spectra were recorded. Using the experimental data on the high-temperature specific heat, the thermodynamic properties of the germanate were calculated.

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

1. E. A. Juarez-Arellano, J. Campa-Molina, S. Ulloa-Godinez, L. Bucio, and E. Orozco, *Mater. Res. Soc. Symp. Proc.* **848**, FF6.15.1 (2005).
2. L. N. Dem'yanets, A. N. Lobachev, and E. A. Emel'chenko, *Hermites of Rare Earth Elements* (Nauka, Moscow, 1980) [in Russian].
3. A. A. Kaminskii, H. Rhee, O. Lux, A. Kaltenbach, H. J. Eichler, J. Hanuza, S. N. Bagayev, H. Uonea, A. Shirakawa, and K. Ueda, *Laser. Phys. Lett.* **10**, 075803 (2013).
4. A. A. Kaminskii, B. V. Mill, A. V. Butashin, E. L. Belokoneva, and K. Rurbanov, *Phys. Status Solidi A* **103**, 575 (1987).
5. V. W. Becker and J. Felsche, *J. Less-Commun. Met.* **128**, 269 (1987).
6. L. T. Denisova, L. A. Irtyugo, Yu. F. Kargin, V. V. Beletskii, and V. M. Denisov, *Inorg. Mater.* **53**, 93 (2017).
7. T. V. Drokina, G. A. Perakovskii, D. A. Velikanov, and M. S. Molokeev, *Phys. Solid State* **56**, 1131 (2014).
8. *Bruker AXS TOPAC V4: General Profile and Structure Analysis Software for Powder Diffraction Data, User's Manual* (Bruker AXS, Karlsruhe, Germany, 2008).
9. V. V. Atuchin, A. S. Aleksandrovsky, O. D. Chimitova, A. S. Krylov, M. S. Molokeev, B. G. Bazarov, J. G. Bazarova, and Z. Xia, *Opt. Mater.* **36**, 1631 (2014).
10. C. G. Maier and K. K. Kelley, *J. Am. Chem. Soc.* **54**, 3243 (1932).
11. L. T. Denisova, Yu. F. Kargin, N. V. Belousova, L. A. Irtyugo, V. M. Denisov, and V. V. Beletskii, *Inorg. Mater.* **55**, 952 (2019).

Translated by E. Bondareva