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SEMICONDUCTORS

High-Temperature Heat Capacity of $TbFe_3(BO_3)_4$

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Abstract—The molar heat capacity of $TbFe_3(BO_3)_4$ in the temperature range of 346–1041 K has been measured by differential scanning calorimetry. It has been found that the $C_p = f(T)$ curve does not show extremes. The thermodynamic properties of the oxide compound have been determined from the experimental data.

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1. INTRODUCTION

In recent years, continuing interest has been expressed in rare-earth ferroborates with the general formula $LnM_3(BO_3)_4$, where Ln is a rare-earth element and M = Fe, Cr, Al, Ga, or Sc [1–5]. These compounds are promising for laser techniques and generation of optical second harmonics [6]. The crystals have a huntite structure and belong to the space group $R32$ [2]. Compounds of this type include $TbFe_3(BO_3)_4$, the properties of which are poorly studied. There are data on its structure [7], magnetic properties [2, 7] and low-temperature heat capacity [8]. Therefore, this work is aimed at studying high-temperature (346–1041 K) heat capacity of $TbFe_3(BO_3)_4$.

2. EXPERIMENT

$TbFe_3(BO_3)_4$ single crystals were grown from $Bi_2Mo_3O_{12}$-based melts according to the procedure similar to that described in [9]. The grown crystals were analyzed on a Panalytical X'Pert Pro X-ray diffractometer with a semiconductor detector and a graphite monochromator (CuK_α radiation). The found parameters of the crystal lattice of $TbFe_3(BO_3)_4$ are presented in Table 1 in comparison with the results of other authors. It can be concluded that there is good agreement with the other data.

The molar heat capacity was measured in platinum crucibles on a NETZSCH STA 449 C Jupiter instrument. The experimental technique was described in our previous paper [10].

3. RESULTS AND DISCUSSION

The temperature dependence of the molar heat capacity of $TbFe_3(BO_3)_4$ is shown in Fig. 1. Clearly, C_p increases regularly with increasing temperatures and the $C_p = f(T)$ curve does not have extremes in the temperature range of measurements. The data can be approximated by the relation (in units of J/(mol K))

$$C_p = 377.18 + 13.90 \times 10^{-2} T - 78.51 \times 10^5 T^{-2}. \quad (1)$$

Equation (1) was found by fitting the experimental data with the use of the authentic Systat Sigma Plot 12 software. The maximum deviation of the experimental points from the fitting curve was no greater than 0.3% up to T = 900 K and 0.7% at T > 900 K.

Figure 1 also presents the C_p results of [8]. As is seen, these data agree well with our values of the heat capacity of $TbFe_3(BO_3)_4$. It can be mentioned that the data of the same authors on C_p of $YFe_3(BO_3)_4$ [11] also agree well with our results [12].

The presence of the temperature dependence of C_p allows finding the changes in the enthalpy $H_T^0 - H_{346}^0$ and the entropy $S_T^0 - S_{346}^0$ from the thermodynamic

Table 1. Parameters of the crystal lattice of $TbFe_3(BO_3)_4$

a, Å	c, Å	References
9.55236(7)	7.57370(8)	[2]
9.5466(2)	7.5704(1)	[7]
9.5511(4)	7.5699(3)	This work

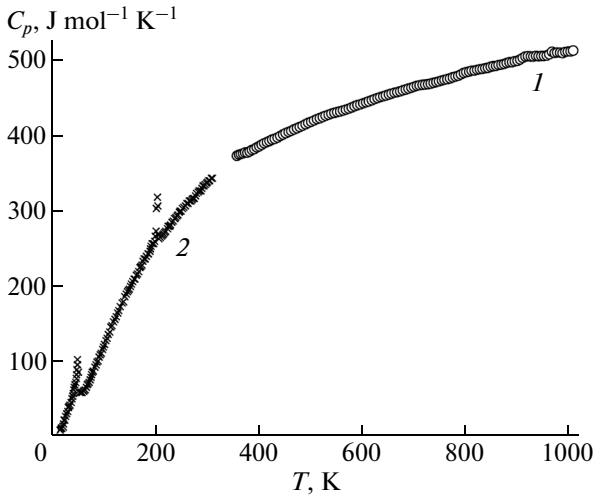

Fig. 1. Temperature dependence of the heat capacity of $TbFe_3(BO_3)_4$ according to the data of (*1*) this work and (*2*) [8].

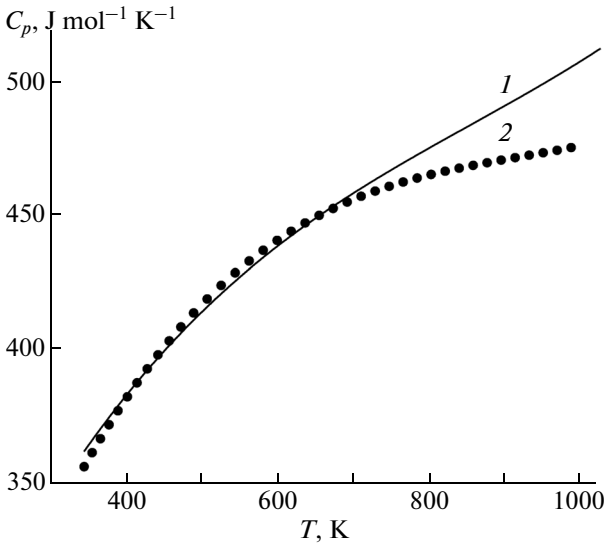

Fig. 2. Temperature dependence of the heat capacity of $TbFe_3(BO_3)_4$ according to (*1*) calculation using Eq. (1) and (*2*) calculation in the Debye model.

equations. The corresponding data are listed in Table 2.

As follows from Table 2, the C_p values above 900 K exceed the classical Dulong–Petit limit $3Rs$, where R is the universal gas constant and s is the number of atoms in the formula unit of $TbFe_3(BO_3)_4$ ($s = 20$).

Assuming C_p and C_V of $TbFe_3(BO_3)_4$ to be close to each other, we calculated the Debye temperature to be $\Theta_D = 948$ K. Using the obtained value of Θ_D and the tabulated Debye function of Θ_D/T [13], we calculated C_p. The corresponding data are shown in Fig. 2. As is seen, there is some discrepancy between the experimental and calculated values of C_p at $T > 650$ K and the discrepancy increases with temperature. This can be associated with the fact that the Debye theory is poorly applicable to polyatomic compounds [13] and with the variation of Θ_D with temperature [14].

Table 2. Approximated values of the molar heat capacity and the thermodynamic functions of $TbFe_3(BO_3)_4$ calculated from these data

T, K	C_p, J mol^{-1} K^{-1}	$H_T^0 - H_{346}^0$, kJ mol^{-1}	$S_T^0 - S_{346}^0$, J mol^{-1} K^{-1}
346	359.7	–	–
350	361.7	1.44	4.15
400	383.7	20.10	53.95
450	401.0	39.74	100.2
500	415.3	60.15	143.2
550	427.7	81.23	183.4
600	438.8	102.9	221.1
650	448.9	125.1	256.6
700	458.5	147.8	290.2
750	467.5	170.9	322.1
800	476.1	194.5	352.6
850	484.4	218.5	381.7
900	492.6	243.0	409.6
950	500.5	267.8	436.5
1000	508.3	293.0	462.3

Let us compare the heat capacity of $TbFe_3(BO_3)_4$ with the corresponding data for $YFe_3(BO_3)_4$ found in our previous work [12]. It should be mentioned that the latter compound has the same structure as $TbFe_3(BO_3)_4$. It was found that the molar heat capacities of $TbFe_3(BO_3)_4$ and $YFe_3(BO_3)_4$ at 298 K are 330 and 313 J/(mol K), respectively. Taking into account the difference in the molecular masses of these compounds, it can be concluded that the C_p values are quite close to each other.

4. CONCLUSIONS

The temperature dependence of the molar heat capacity of $TbFe_3(BO_3)_4$ has been investigated. It has been shown that the Debye model does not describe the temperature dependence of the heat capacity in the range of 346–1041 K.

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