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CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Heat Capacity of $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ in the Temperature Interval of 344–1021 K

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Abstract—The molar heat capacity of $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ is measured in the temperature interval of 344–1041 K by means of differential scanning calorimetry. Thermodynamic properties of the oxide compound are determined from the experimental data.

Keywords: rare-earth ferroborates, high-temperature heat capacity.

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INTRODUCTION

Rare-earth $ReFe_3(BO_3)_4$ (Re = Y, La–Lu) ferroborates have long attracted the attention of researchers due to their unique properties. Some ferroborates (e.g., $GdFe_3(BO_3)_4$, $NdFe_3(BO_3)_4$, etc.) are multiferroics, while others have diverse magnetic structures and phase transitions, depending on the type of rare-earth ion [1–5]. Crystals of this family have huntite structure with *R*32 symmetry [4–7]. The magnetic properties of such materials have been thoroughly studied, while information about their thermal properties is extremely scarce. Believing that the properties of the $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ crystal occupy an intermediate position between those of the $GdFe_3(BO_3)_4$ and $NdFe_3(BO_3)_4$ crystals, the authors of [5] studied its heat capacity and magnetic properties in the temperature interval of 2–300 K. It was established that this assumption was mistaken, since the magnetic properties of the $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ crystal differed strongly from those of $GdFe_3(BO_3)_4$ and $NdFe_3(BO_3)_4$.

Heat capacity is an important characteristic of all crystals and is associated with features of their composition and structure. Obtaining thermodynamic data is therefore a priority in physicochemical studies of the solid state [8].

Bearing this in mind, and that the heat capacity was measured only to 300 K, the aim of this work was to study the high-temperature (344–1021 K) heat capacity of $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ and determine its thermodynamic properties from these data.

EXPERIMENTAL

A single crystal of $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ was grown from a solution–melt based on $K_2Mo_3O_{10}$ as in [1, 5]. It was dark green and measured 7 × 6 × 5 mm. The structure of the grown crystal was determined on an XPert Pro X-ray diffractometer (Panalytical, Netherlands). It was established that at room temperature, its structure was similar to the structure of $GdFe_3(BO_3)_4$ and $NdFe_3(BO_3)_4$ crystals (space group *R*32). The resulting data are given in Table 1, where they are compared to the data of other authors for compounds $GdFe_3(BO_3)_4$ and $NdFe_3(BO_3)_4$.

The heat capacity was measured in platinum crucibles on a STA 449 C Jupiter unit (NETZSCH). Special holders were used in measuring the heat capacity. The experimental data were processed

Table 1. Parameters of the structure of $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$, $GdFe_3(BO_3)_4$ and $NdFe_3(BO_3)_4$

Compound	*a*, Å	*c*, Å	Reference
$Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$	9.557(7)	7.62(1)	[5]
	9.5602(4)	7.617(2)	this work
$GdFe_3(BO_3)_4$	9.5203(1)	7.5439(5)	[5]
	9.541	7.567	[9]
	9.560	7.583	[9]
$NdFe_3(BO_3)_4$	9.5878(3)	7.6103(3)	[5]
	9.578	7.608	[9]

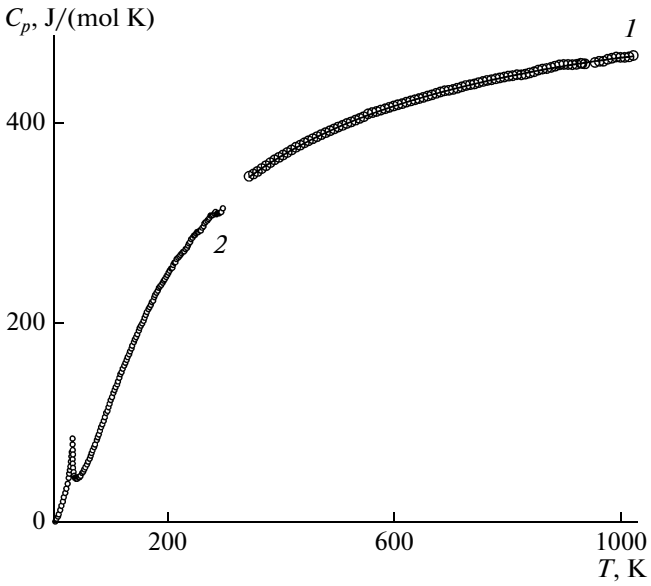

Fig. 1. Effect of temperature on the molar heat capacity of $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ single crystal: (*1*) this work, (*2*) data in [5].

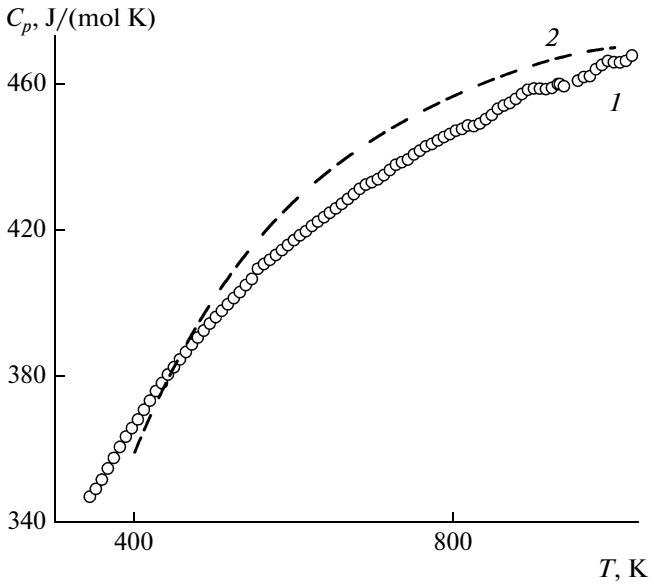

Fig. 2. Temperature dependence of the heat capacity of $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$: (*1*) experimental data, (*2*) calculations according to the Debye model.

with the NETZSCH Proteus Thermal Analysis software package. The experimental technique was similar to the one described in [10].

Table 2. Thermodynamic properties of $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$

T, K	C_p, J/(mol K)	$H°(T) - H°(344)$, kJ/mol	$S°(T) - S°(344)$, J/(mol K)
344	342.2	–	–
400	367.8	19.92	53.61
450	384.4	38.75	97.93
500	397.5	58.31	139.1
550	408.3	78.46	177.6
600	417.5	99.11	213.5
650	425.6	120.2	247.2
700	432.9	141.7	279.0
750	439.6	163.5	309.1
800	445.9	185.6	337.7
850	451.8	208.1	364.9
900	457.4	230.8	390.9
950	462.8	253.8	415.8
1000	468.1	277.8	439.7

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the molar heat capacity of $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ single crystal. It follows from these data that the C_p grows continuously as the temperature rises, and there are no extrema on the $C_p = f(T)$ dependence. The resulting data can be described by the Maier–Kelley equation

$$C_p = (393.36 \pm 0.99) + (84.20 \pm 1.00) \times 10^3 T - (94.81 \pm 1.07) \times 10^5 T^{-2}. \quad (1)$$

The experimental results were processed using the Systat Sigma Plot 12 licensed software package. The correlation coefficient for Eq. (1) was $r = 0.9992$. The maximum deviation of the experimental data from the values obtained according to Eq. (1) for temperatures up to 800 K did not exceed 0.1%, and at $T > 800$ K was 0.2%.

For comparison, Fig. 1 shows data for C_p of $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ [5] at lower temperatures. It can be seen that there is good agreement between our data and the results in [5]. The temperature dependence of the heat capacity in the form of relation (1) allowed us to calculate the variation in enthalpy ($H°(T) - H°(344)$) and entropy ($S°(T) - S°(344)$) for $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ using standard thermodynamic equations. Our results are given in Table 2.

On the basis of Table 2, we may conclude that at all of the investigated temperatures, the molar heat capacity of $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ did not exceed the

classical Dulong–Petit limit of $3Rs$, where R is the universal gas constant and s is the number of atoms in the formula unit of the oxide compounds.

On the basis of the experimental C_p values, we calculated the characteristic Debye temperature Θ_D = 1060 K. In the first approximations, we assumed that C_p and C_V are close. Using our Θ_D value and tables of Debye functions (Θ_D/T) [11], we calculated C_p for $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$. In Fig. 2, these data are compared to the experimental C_p values. It can be seen that the calculated and experimental C_p values are quite close, with a maximum deviation from the experimental results of 2.9% in the region of 650 K.

Note that we obtained similar results for $YFe_3(BO_3)_4$ in [12]. The Θ_D values (1020 K for the latter compound) and the shape of the experimental and calculated dependences $C_p = f(T)$ were close.

It was specified above that the magnetic properties of $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ crystals are not intermediate between such properties of $GdFe_3(BO_3)_4$ and $NdFe_3(BO_3)_4$ crystals [5]. Comparison of the data on the heat capacity C_p(298 K) of these crystals reveals that a similar phenomenon is observed in this case as well: $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$—312 J/(mol K)) (our data); $GdFe_3(BO_3)_4$—316 J/(mol K)) [13]; $NdFe_3(BO_3)_4$–339 J/(mol K)) [7]. Our data on the heat capacity thus confirm the results of [5], in which individual features of the $Gd_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ crystal were established by studying its magnetic properties.

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