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SEMICONDUCTORS

# High-Temperature Heat Capacity of $YFe_3(BO_3)_4$

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**Abstract**—The molar heat capacity of $YFe_3(BO_3)_4$ has been measured using differential scanning calorimetry in the temperature range 339–1086 K. It has been found that the dependence $C_p = f(T)$ exhibits an extremum at a temperature of 401 K due to the structural transition.

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## 1. INTRODUCTION

Borate compounds with a generalized formula $RM_3(BO_3)_4$ ($R \equiv$ Y, La–Tm, $M \equiv$ Al, Ga, Sc, Cr, Fe) attract attention as materials with a potential for nonlinear optics and laser technology applications [1–6]. They are believed to hold forth considerable promise in development of compact, diode-pumped solid-state lasers which generate radiation simultaneously in the near-infrared and visible spectral regions as a result of second harmonic generation in the active medium [7]. It was established that rare-earth ferroborates ($R \equiv$ Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er) belong to a new family of magnetoelectric materials [1, 2, 8]. Their crystals have the huntite orthorhombic structure with a high-temperature $R32$ ($D_3^7$) spatial structure, which in crystals with a small ionic radius $R^{3+}$ transforms into $P3_121$ ($D_3^4$) with decreasing temperature [1, 8, 9]. Best studied of the rare-earth ferroborates $RFe_3(BO_3)_4$ is the gadolinium ferroborate $GdFe_3(BO_3)_4$, whose properties have been studied by magnetic, resonance, thermodynamic, magnetoelectric, and magnetoelastic methods [1, 2]. Other $RFe_3(BO_3)_4$ compounds, including $YFe_3(BO_3)_4$, enjoyed moderate interest. As for the latter compound, one studied its magnetic [3, 10–12], structural [12, 13], and thermodynamic characteristics [10, 11, 14]. Incidentally, the heat capacity of $YFe_3(BO_3)_4$ was measured only in the temperature range 0–300 K. Therefore, the goal of the present work is to investigate the high-temperature (339–1086 K) heat capacity.

## 2. EXPERIMENT

The $YFe_3(BO_3)_4$ single crystals were grown from $Bi_2Mo_3O_{12}$-based melts by the technique described elsewhere [12]. The X-ray diffraction patterns were recorded with an X'Pert Pro diffractometer (Panalytical, The Netherlands). The values of the unit cell parameters obtained were found to practically coincide with those listed in [12] while being slightly smaller than those specified in [15]. The molar heat capacity $C_p$ was measured by the technique described earlier [15]. All experiments were performed in platinum crucibles by differential scanning calorimetry with an STA 449 C Jupiter (NETZSCH) instrument.

## 3. RESULTS AND DISCUSSION

The effect of temperature on the molar heat capacity of $YFe_3(BO_3)_4$ crystals is illustrated graphically in Fig. 1. The values of $C_p$ are seen to grow regularly with increasing temperature. In the region of 401 K the $C_p = f(T)$ curve exhibits an extremum, which starts at 376 K, passes through a maximum at 401 K, and damps at 426 K ($\Delta T = 50$ K). This value of $\Delta T$ and the clearly pronounced λ-shaped extremum may evidence a second-order transition.

Presented in Fig. 1 for comparison are data obtained by other authors as well. Note that the results of $C_p = f(T)$ measurements cited in [10, 14, 16] fully coincide. This gives grounds to limit ourselves to the data presented in [14] where this curve underwent a more comprehensive analysis. As seen from Fig. 1, our data agree best of all with the results reported in [14]. The values of $C_p$ for $YFe_3(BO_3)_4$ cited in [10] practi-

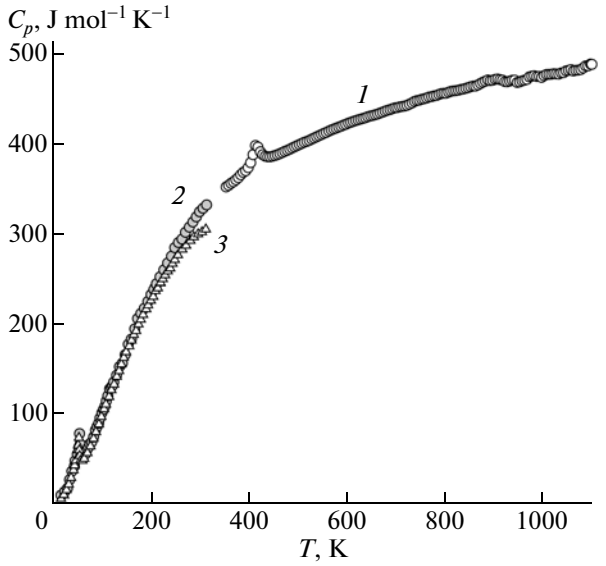


**Fig. 1.** Temperature dependence of the heat capacity of $YFe_3(BO_3)_4$ according to (*1*) our data, (*2*) [14], and (*3*) [10].

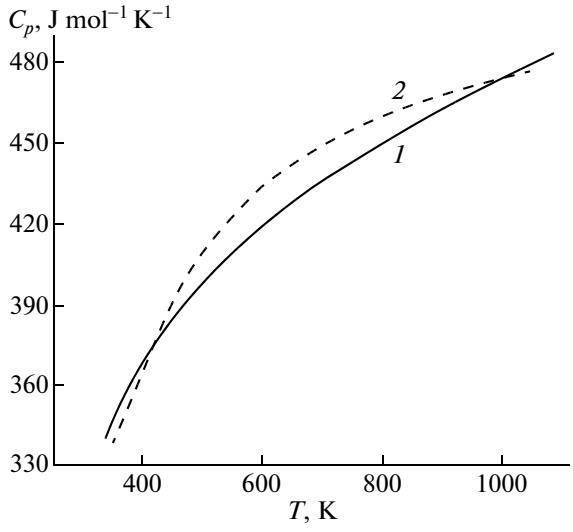


**Fig. 2.** Temperature dependence of the heat capacity according to (*1*) calculation from Eq. (1) and (*2*) calculation from the Debye model.

cally reproduce the other measurements while being slightly smaller.

The $C_p = f(T)$ graph [10, 11, 14] at 37 K demonstrates a λ-peak reflecting the antiferromagnetic ordering of the iron subsystem (regretfully, the temperature interval in which $C_p$ was measured in these studies was restricted by 300 K).

$YFe_3(BO_3)_4$ was shown [10, 14, 17] to undergo at 445 K an $R32$ structural transition into $P3_121$, which manifests itself in the DTA curve as well [10]. One cannot rule out the possibility that the peak observed by us in the $C_p(T)$ curve at 401 K (Fig. 1) likewise can be traced to this transition.

Neglecting the additional contribution to $C_p$ in the region of the extremum, the temperature dependence of the heat capacity can be described by the Mayer–Kelley equation (in units of J/(mol K))

$$C_p = 389.4 + 93.30 \times 10^{-3} T - 92.28 \times 10^5 T^{-2}. \quad (1)$$

Relation (1) can be used to calculate with standard thermodynamic equations the changes of the enthalpy $H_T^0 - H_{339}^0$ and entropy $S_T^0 - S_{339}^0$ for $YFe_3(BO_3)_4$. The results obtained are listed in the table.

We note that at all the temperatures studied, the molar heat capacity does not exceed the classical Dulong–Petit limit $3Rn$, where $R$ is the universal gas constant, and $n$ is the number of atoms in the formula unit of $YFe_3(BO_3)_4$ ($n = 20$). We used the characteristic Debye temperature obtained by us, $\Theta_D = 1020$ K, and the tabulated Debye functions $(\Theta_p/T)$ [18] to calculate the values of $C_p$, which we assumed in the first approximation to be close to those of $C_v$. The results are compared with the experimental data in Fig. 2. Recalling that by the Debye model one calculates $C_v$ rather than $C_p$, as well as that the Debye theory of heat capacity should be considered for quite a number of complex oxide compounds as an approximation [19], the close coincidence of experimental with calculated values of the heat capacity for $YFe_3(BO_3)_4$ should be considered

Smoothed values of the molar heat capacity and the calculated thermodynamic functions of $YFe_3(BO_3)_4$

| $T$, K | $C_p$, J mol$^{-1}$ K$^{-1}$ | $H_T^0 - H_{339}^0$, kJ mol$^{-1}$ | $S_T^0 - S_{339}^0$, J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| 339 | 340.7 | – | – |
| 350 | 346.7 | 3.781 | 10.98 |
| 400 | 369.0 | 21.70 | 58.81 |
| 450 | 385.8 | 40.59 | 103.3 |
| 500 | 399.1 | 60.23 | 144.6 |
| 550 | 410.2 | 80.47 | 183.2 |
| 600 | 419.7 | 101.2 | 219.3 |
| 650 | 428.2 | 122.4 | 253.3 |
| 700 | 435.9 | 144.0 | 285.3 |
| 750 | 443.0 | 166.0 | 315.6 |
| 800 | 449.6 | 188.3 | 344.4 |
| 850 | 455.9 | 211.0 | 371.9 |
| 900 | 462.0 | 233.9 | 398.1 |
| 950 | 467.8 | 257.1 | 423.2 |
| 1000 | 473.5 | 280.7 | 447.4 |
| 1050 | 479.0 | 304.5 | 470.6 |

satisfactory (the maximum disagreement among the values of $C_p$ is 2.6%).

Note that, taking due account of the fact that at high temperatures the magnetic susceptibility of $YFe_3(BO_3)_4$ obeys the Curie–Weiss law with an effective magnetic moment corresponding to the $s = 5/2$ spin of $Fe^{3+}$ ions, and assuming the total magnetic entropy of the iron subsystem released in antiferromagnetic ordering to be $S_{mag} = 3R\ln(2s + 1) = 44.7$ J/(mol K), the authors of [14] expressed the lattice contribution to the total heat capacity in the form of a sum of Debye functions (which dominates at a low temperature) and four Einstein functions.

The calculation of the specific heat capacity $C_p^0$ of $YFe_3(BO_3)_4$ by the additive Neumann–Kopp method [20] yields 0.76 J/(g K). Since it turned out to be somewhat larger than the experimental value (0.64 J/(g K), this brings us to the conclusion that in some cases estimation by the additive method may end up with an error which will affect the values of the thermodynamic quantities calculated with these data as well. The data needed for calculation by the Neumann–Kopp method were taken from [21].

## 4. CONCLUSIONS

The temperature dependence of the molar heat capacity of $YFe_3(BO_3)_4$ has been studied. The extremum revealed in the $C_p = f(T)$ curve is assigned to the $R32$–$P3_121$ transition. The Debye model has been established to describe satisfactorily the temperature dependence of the heat capacity in the 339–1086 K region.

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