

SHORT
COMMUNICATIONS

High-Temperature Heat Capacity of $\text{YbAl}_3(\text{BO}_3)_4$

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Abstract—The isobaric heat capacity $C_p(T)$ of $\text{YbAl}_3(\text{BO}_3)_4$ grown by spontaneous crystallization from solution (100 – n) wt % ($\text{Bi}_2\text{Mo}_3\text{O}_{12}$ + 2.5% B_2O_3 + 0.75% Li_2MoO_4) + n wt % $\text{YbAl}_3(\text{BO}_3)_4$ is studied experimentally in the region of 344–1016 K. It is established that there are no extrema on the $C_p(T)$ dependence, and the obtained data can be described using the Berman–Brown polynomial. The temperature variations of enthalpy and entropy are calculated from the $C_p(T)$ dependence.

Keywords: ytterbium aluminum borate, high-temperature heat capacity, thermodynamic properties.

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INTRODUCTION

In $\text{RAl}_3(\text{BO}_3)_4$ ($\text{R} = \text{Y}, \text{Nd}, \text{Sm}, \text{etc.}$) crystals with huntite structure, the effective transformation of laser radiation frequencies strongly exceeds the similar parameters of familiar media [1–5]. Using these materials, we can create lasers safe for performing delicate operations in ophthalmology and neurosurgery [5, 6]. Despite the obvious success in the field of growing and studying the structural, optical, and other properties of such materials, there are no data on their thermodynamic properties. We should remember that crystals of these compounds, including $\text{YbAl}_3(\text{BO}_3)_4$, have an incongruent character of melting. $\text{YbAl}_3(\text{BO}_3)_4$ crystals can be obtained via solid-phase synthesis and solution–melt crystallization. Thermodynamics plays an important role in understanding the processes for obtaining phases of a given composition. However, the thermodynamic study of synthesis is possible only with thermodynamic databases, of which there are none for $\text{YbAl}_3(\text{BO}_3)_4$. We should also remember that heat capacity is a bulk thermodynamic characteristic of any material [7].

The aim of this work was to study the high-temperature heat capacity of $\text{YbAl}_3(\text{BO}_3)_4$, and to determine its thermodynamic properties on the basis of these data.

EXPERIMENTAL

Molar heat capacity C_p was measured on single crystals grown via spontaneous crystallization from a solution–melt (100 – n) wt % ($\text{Bi}_2\text{Mo}_3\text{O}_{12}$ + 2.5% B_2O_3 + 0.75% Li_2MoO_4) + n wt% $\text{YbAl}_3(\text{BO}_3)_4$. The crystal growth technique is similar to that the one

described in [8, 9]. X-ray patterns were recorded on an X'Pert Pro (Panalytical, Netherlands) diffractometer using $\text{CuK}\alpha$ radiation. Data was recorded on a PIXEL high-speed detector equipped with a graphite monochromator. At room temperature, the sample had the lattice parameters $a = 9.269(2)$ Å, $b = 7.210(3)$ Å. This allowed us to conclude that our results were in good agreement with the data in [9] ($a = 9.274(3)$ Å, $b = 7.212(3)$ Å) and somewhat different from those given in [10, 11]: $a = 9.251(2)$ Å, $b = 7.189(3)$ Å.

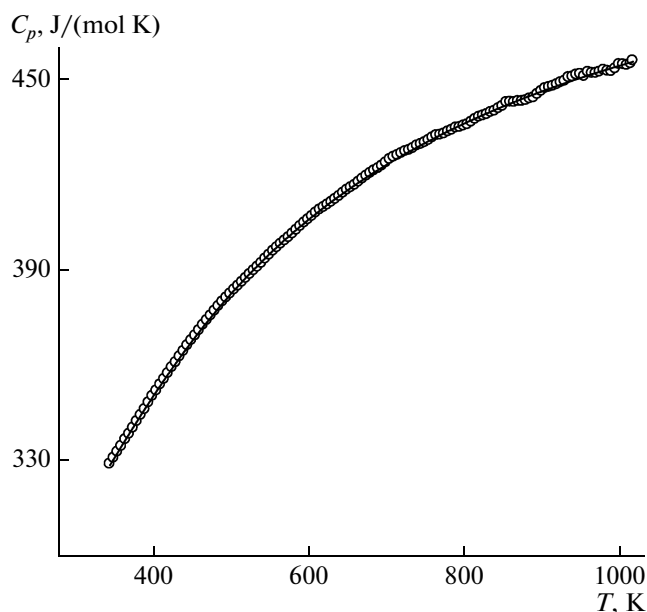
Measurements for C_p ($\text{YbAl}_3(\text{BO}_3)_4$) were performed in platinum crucibles on a STA 449 C Jupiter device (NETZSCH). The experimental technique was similar to the one described in [12]. The experimental data were processed using the Systat Sigma Plot 12 program package.

RESULTS AND DISCUSSION

The figure shows the effect temperature has on the molar heat capacity of $\text{YbAl}_3(\text{BO}_3)_4$. It can be seen that as the temperature rises, C_p grows smoothly, and there are no extrema on the $C_p(T)$ dependence. Our data can be described by the Berman–Brown polynomial [13]

$$\begin{aligned} C_p &= k_0 + k_1 T^{-0.5} + k_2 T^{-2} + k_3 T^{-3} \\ &= 552.1 - 2.49 \times 10^3 T^{-0.5} \\ &\quad - 23.17 \times 10^6 T^{-2} + 43.49 \times 10^8 T^{-3}, \end{aligned}$$

allowing us to obtain good results in the high-temperature extrapolation of the heat capacity. The scatter of



Effect of temperature on the heat capacity of YbAl₃(BO₃)₄.

the experimental point against the approximating curve did not exceed 0.2%.

Using these data, we calculated the variations in enthalpy ($H_T^\circ - H_{344}^\circ$) and entropy ($S_T^\circ - S_{344}^\circ$) from the known thermodynamic equations. The results from

Thermodynamic properties of YbAl₃(BO₃)₄

T, K	$C_p, J/(mol K)$	$(H_T^\circ - H_{344}^\circ), kJ/mol$	$(S_T^\circ - S_{344}^\circ), J/(mol K)$
344	329.0	—	—
350	331.4	1.981	5.710
400	350.9	19.05	51.25
450	368.1	37.03	93.60
500	383.0	55.82	133.2
550	395.6	75.29	170.3
600	406.3	95.35	205.2
650	415.5	115.9	238.1
700	423.5	136.9	269.2
750	430.4	158.2	298.6
800	436.4	179.9	326.6
850	441.8	201.9	353.2
900	446.5	224.1	378.6
950	450.8	246.5	402.9
1000	454.6	269.1	426.1

our calculations are given in the table. Note that at all of the investigated temperatures, the molar heat capacity 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 YbAl₃(BO₃)₄ ($s = 20$).

We cannot compare the obtained the C_p values for YbAl₃(BO₃)₄ to other data because there is no such information. We nevertheless obtained the heat capacities $C_p(T)$ for YAl₃(BO₃)₄ [14]. The latter compound has the same structure as YbAl₃(BO₃)₄. To disregard the difference of the molecular masses of these compounds, we compare the specific heat capacity C_p° at room temperature. C_p° for YAl₃(BO₃)₄ is 0.66 J/(g K), while for YbAl₃(BO₃)₄ $C_p^\circ = 0.64 J/(g K)$. We may conclude that these values are quite close.

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