Heat capacity of neodymium- and gadolinium-gallium garnets

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Abstract. In the present article an experimental study of neodymium- and gadolinium-gallium garnets (NGG and GGG) heat capacity was carried out by the method of differential scanning calorimetry. The measurements were performed in the temperature interval from 300 to 975 K, and the estimated error of the received data was 2–3%. The fitting equations for specific heat temperature dependences have been received. The table of recommended values for investigated gallium garnets heat capacity has been developed for the use in various theoretical and applied problems.

1. Introduction
Synthetic crystals with a garnet structure, along with the traditional use in quantum electronics, are widely used in various fields of science and technology. In this regard, there is a need to investigate the thermophysical properties of garnets, without knowledge of which carrying out engineering calculations in the design of the corresponding devices is difficult. In addition to purely applied, technical use, data on the thermophysical properties of single crystals are necessary when studying the features of energy transfer mechanisms and changes in the intensity of thermal motion in polyatomic structural compounds, which contributes to the development of theoretical concepts. A review of the literature has revealed that currently there are three works [1–3], in which the heat capacity of GGG and NGG garnets was studied in the temperature range not exceeding 300 K, and there are practically no data on the heat capacity of gallium garnets in the temperature range above 300 K with a single exception [4]. But it is exactly the area that becomes interesting when using garnets as functional elements of apparatus for various purposes, and, especially, as active elements of optical quantum generators, when operating temperatures can significantly exceed room temperatures. Based on the foregoing, the aim of the present work was to experimentally investigate neodymium- and gadolinium-gallium garnets heat capacity in the range from room temperature up to 975 K of the solid state.

2. Experimental technique
The measurements of gallium garnets heat capacity coefficient \( c_p \) were carried out by the method of differential scanning calorimetry (DSC) using DSC 404 F1 calorimeter [5] produced in Germany by NETZSCH Company. Experiments were performed on samples of gadolinium-gallium (GGG) and neodymium-gallium (NGG) garnets, represented by the single crystals of Gd\(_3\)Ga\(_5\)O\(_{12}\) and Nd\(_3\)Ga\(_5\)O\(_{12}\). The specimens under study had the shape of cylinders with up to 1.5 mm thickness and 5 mm diameter with plane base for better thermal contact with the crucible bottom. The masses of the samples were 205.96 mg and 176.90 mg for Gd\(_3\)Ga\(_5\)O\(_{12}\) and Nd\(_3\)Ga\(_5\)O\(_{12}\), respectively. The analytical balances AND GH-252 [6] was used for mass measurements. The control measurements of the sample mass were carried out directly before and after the experiments. Experiments to determine \( c_p \) were
conducted in the temperature range of 300–975 K with a heating rate of 10 K/min in the flow-through argon atmosphere (20 ml/min). The argon purity was 99.998 vol. %, and the main impurities were: O₂ – 0.0001%; N₂ – 0.0005%; H₂O – 0.0004%; CO₂ – 0.00002%; CH₄ – 0.0001%; H₂ – 0.0001%. The furnace working volume of the unit was pumped out to a vacuum of 1 Pa and several times washed with argon before the experiments. The sapphire weighting of 85.26 mg was used as a standard sample for \( c_p \) calibration. All the investigated specimens of garnets and sapphire were placed in platinum crucibles with corundum inserts and platinum lids. It was taken into account that the sample should not interact with the material of the measuring cell and protective gas atmosphere when choosing the crucible material. The measurement error of \( c_p \) data on DSC 404 F1 calorimeter was 2–3%, which was confirmed by experiments with reference samples of high-purity platinum and sapphire.

3. Results and discussion

Figure 1 presents the heat capacity measurement results for the gadolinium-gallium garnet. The experiments have shown that no anomalous changes were recorded in the temperature dependence of \( c_p \) in the entire studied temperature range. Our Gd₃Ga₅O₁₂ \( c_p \) data, obtained in successive thermal heating cycles, were reproduced among themselves within the limits of the estimated measurement errors. A similar situation was observed in experiments with Nd₃Ga₅O₁₂ sample.

The heat capacity temperature dependence of investigated garnets was approximated by a single equation over the entire studied temperature range (300–975 K). Approximation of \( c_p \) experimental values of GGG by the least squares method gave the equation:

\[
c_p(T) = 0.8731 - 7.416 \times 10^{-4} T + 7.179 \times 10^{-7} T^2 - 2.550 \times 10^{-10} T^3 - 100.83 T^{-1},
\]

(1)

where \( T \) is the temperature in K, and \( c_p \) is in J (g K)\(^{-1}\). The standard deviation of the experimental points from the approximation dependence (1) is 0.12%.
For NGG, approximation of \( c_p \) experimental data by the least squares method yielded the following equation:

\[
c_p(T) = 1.002 - 1.131 \times 10^{-3} T + 1.3854 \times 10^{-6} T^2 - 6.022 \times 10^{-10} T^3 - 108.53 T^{-1}.
\] (2)

The standard deviation of the experimental values from (2) does not exceed 0.12%. Recommended data for \( c_p \) of investigated GGG and NGG garnets, obtained using equations (1) and (2), are given in the table.

A comparison of recommended \( c_p \) values of \( \text{Gd}_3\text{Ga}_5\text{O}_{12} \) and \( \text{Nd}_3\text{Ga}_5\text{O}_{12} \) with known literature data [1–4] is shown in figure 2. As can be seen, our values obtained for both gallium garnets are in good agreement with all published data within the limits of measurement error. It should also be noted, that the data of this study extend the previously investigated temperature range by 275 K.

![Figure 2](image)

**Figure 2.** Comparison of the heat capacity experimental results for GGG and NGG garnets.  
1 – [1], 2 – [2], 3 – GGG [3], 4 – NGG [3], 5 – GGG [4], 6 – NGG [4], 7, 8 – our recommended values for GGG and NGG, respectively.
Table 1. The recommended values of gallium garnets heat capacity.

| $T$, K | $c_p$, J (g K)$^{-1}$ | $T$, K | $c_p$, J (g K)$^{-1}$ |
|-------|-----------------------|-------|-----------------------|
|       | GGG                   | NGG   | GGG                   | NGG   |
| 300   | 0.372                 | 0.409 | 700                   | 0.474 | 0.528 |
| 350   | 0.402                 | 0.440 | 750                   | 0.479 | 0.534 |
| 400   | 0.423                 | 0.461 | 800                   | 0.483 | 0.540 |
| 450   | 0.437                 | 0.478 | 850                   | 0.486 | 0.544 |
| 500   | 0.448                 | 0.491 | 900                   | 0.489 | 0.547 |
| 550   | 0.457                 | 0.502 | 950                   | 0.492 | 0.547 |
| 600   | 0.463                 | 0.511 | 975                   | 0.493 | 0.547 |
| 650   | 0.469                 | 0.520 | —                     | —     | —     |

Conclusion
New reliable experimental data on the heat capacity of neodymium- and gadolinium-gallium garnets were obtained in the temperature range 300–975 K of the solid state. A comparison of the results with the available literature data were carried out. The data were received for the first time for the temperature interval of 700–975 K.

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