Experimental study of boron nitride in a wide temperature interval

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Abstract. In the present work thermal conductivity (λ), thermal diffusivity (a), heat capacity (c_p) and linear thermal expansion coefficient (LTEC, α) of boron nitride (BN) with hexagonal modification were studied in a wide temperature range of 298–1273…1474 K. The experiments were performed on the samples made from the same starting material with a density of 1.64 g/cm³ at room temperature. For all studied properties the approximation equations were obtained and the tables of recommended values were developed that can be used for various scientific and practical applications.

1. Introduction

Today the binary compound of boron nitride (BN), so-called "white graphite", is widely used in manufacturing and engineering as an electrical and thermal insulator, high-temperature lubricant and lining in a variety of processes with ceramics, metals and glass. However, the data on its thermophysical properties, especially transport properties, are fragmented and vary greatly from batch to batch, since they substantially depend on the origin of the feedstock, the dispersion of the material and the method of producing BN. The purpose of this work was an experimental study of the transport, caloric and thermal properties of BN with hexagonal modification in a wide temperature range.

2. Experimental technique

The thermal diffusivity (a) of the material under study was determined using a laser flash method on an automated LFA-427 installation [1] in an atmosphere of static purified argon (Ar 99.998 vol. %) in the temperature range of 298–1474 K. A brief description of the measurement method and experimental setup is presented in [2]. The sample was a cylinder with a diameter of 12.6 mm and a thickness of 2.3 mm. Its density (ρ₀) at room temperature was 1.64±0.02 g/cm³. Measurements at a given temperature were carried out after temperature stabilization of the sample in a series of three "shots" of the laser. The interval between the "shots" was 3 minutes. The thermal expansion of the samples was not taken into account. The measurement error of a for solid samples on the LFA-427 is 2–5% depending on temperature.

The specific heat (c_p) of BN was measured by differential scanning calorimetry. The mass of the sample was 52 mg. The experiments were carried out on a DSC 404 F1 apparatus [3] using platinum crucibles with corundum liners in the temperature range of 298–1325 K with a heating rate of 10 K/min in a flowing argon atmosphere (20 ml/min). POCO graphite weighing of 50 mg was taken as
a calibration sample. The estimated error of the $c_p$ measurements confirmed by the experiments with reference samples of sapphire and platinum on the DSC 404 F1 was 2–3%.

The linear thermal expansion coefficient (LTEC, $\alpha$) of BN was investigated on horizontal dilatometer DIL-402C [4] with a holder and a pushrod made of sintered corundum. The measurements were carried out in the temperature interval of 298–1273 K in a helium atmosphere (He 99.995 vol. %) with heating-cooling of the furnace at a rate of 2 K/min and 30 minutes of isothermal holding at maximum temperature. The description of the measurement procedure and the processing of $\alpha$ data is described in [5] in detail. The measurement accuracy of DIL-402C confirmed by experiments with pure platinum and copper was 3%.

3. Results and discussion

The results of $\alpha$ are presented in Figure 1 in the temperature range of 298–1474 K. Experimental data were obtained in several series of measurements, both during heating and cooling of the sample. As it can be seen from the Figure 1, over the entire studied temperature range the $a(T)$ curve changes monotonically, without anomaly and $a(T)$ is reproduced in several cycles of the experiment. This indicates that the structure of studied material is unchanged when heated to high temperatures. It can also be noted that the thermal diffusivity value of BN decreases sharply in the temperature range from room temperature to 600...800 K, which is similar to the behavior of thermal diffusivity of dense graphites, such as, for example, MPG-6 [6]. The approximation of the experimental data gave the following equation:

$$a(T) = -7.524 + 0.0086 T - 3.091 \times 10^{-6} T^2 + 6277.3/T,$$  \hfill (1)

where $a$ is in mm$^2$/s, $T$ is in K. The root-mean-square deviation of the experimental points from (1) does not exceed 1.3%.

The $c_p$ measurement results of BN in the temperature range of 298–1325 K in comparison with the known literature data are shown in Figure 2. As it can be seen from the graph, our measured $c_p$ values are in good agreement with the most data of [7–12] within the total measurement errors. It can also be noticed that the heat capacity data of various boron nitride samples agree with each other independently of the structure and technology for BN preparation. The same situation is observed for the heat capacity of graphites [6, 13]. The approximation of the experimental data gave the following equation:

$$c_p(T) = -0.262 + 0.429 \times 10^{-2} T - 2.924 \times 10^{-6} T^2 + 7.074 \times 10^{-10} T^3,$$  \hfill (2)

where $c_p$ is in J/(g K). The root-mean-square deviation of the experimental points from (2) does not exceed 0.85%.

![Figure 1. Thermal diffusivity coefficient of BN: 1 – experimental data, 2 – approximation by (1).](image1)

![Figure 2. Specific heat of BN: 1 – [7], 2 – [8], 3 – [9], 4 – [10], 5 – [11], 6 – [12], 7 – our recommended data.](image2)
A total of three LTEC experiments were conducted in the temperature range of 298–1273 K. The obtained data showed a good reproducibility. BN is stable in a wide range of temperatures and it is similar to graphites by the nature of LTEC temperature dependence. To obtain the approximation dependence of LTEC, the results were combined and processed by the least squares method with the following polynomial:

$$\alpha(T) = -2.559 + 6.34 \times 10^{-3} T - 2.479 \times 10^{-6} T^2,$$  \hspace{1cm} (3)

where $\alpha$ is in $10^{-6} \text{K}^{-1}$. The recommended values for the relative elongation ($\varepsilon$) were calculated by integrating equation (3) with the condition that the value of $\varepsilon(T)$ is zero at room temperature. The obtained curves for $\alpha(T)$ and $\varepsilon(T)$ are shown in Figure 3.

The thermal conductivity coefficient ($\lambda$) of BN has been calculated in the temperature interval of 298–1474 K by the formula:

$$\lambda = a \rho c_p,$$  \hspace{1cm} (4)

where $a$ is the thermal diffusivity experimental data; $\rho$ is the density, which was found from $\varepsilon$ values and the density at room temperature $\rho_0$; $c_p$ is the calculated data from (2). Equations for $\varepsilon$ and $c_p$ were extrapolated to a temperature of 1474 K. The error in the $\lambda$ calculation is 3–5% taking into account the errors of $a$, $\rho$ and $c_p$. The approximation of the calculated thermal conductivity data gave the following equation:

$$\lambda(T) = 24.075 - 0.0146 T + 2.96 \times 10^{-6} T^2,$$  \hspace{1cm} (5)

where $\lambda$ is in W/(m K). The root-mean-square deviation of the calculated points from (5) does not exceed 1%.

The calculated thermal conductivity results are presented in Figure 4 in comparison with the data from [11]. As it can be seen from the figure, our $\lambda$ values differ greatly from [11]. As mentioned above, the transport properties of boron nitride, as well as graphite, vary greatly from batch to batch and depend largely on the origin of the raw material and its density. The technical report [11] could not be found, therefore it is unknown what modification of studied BN and its density were. The data have been taken from the handbook of Touloukian Y.S. et al [14], in which it is indicated that thermal conductivity was measured by the radial heat flux method for two samples. Points 1 and 2 in Figure 4 correspond to two experimental cycles for the first sample, points 3 do for the second sample. The data error is not given. As it can be seen from the figure, the results of [11] have a fairly strong scatter, while our $\lambda$ values lie on a single curve.
In Table 1 the recommended values for $a$, $\lambda$, $c_p$, $\alpha$ and $\varepsilon$ of BN are presented.

**Table 1.** Recommended values of BN thermophysical properties

| $T$, K | $a$, mm$^2$/s | $\lambda$, W/(m K) | $c_p$, J/(g K) | $\alpha$, $10^{-6}$ K$^{-1}$ | $\varepsilon$, $10^{-6}$ |
|--------|---------------|-------------------|----------------|-----------------|-----------------|
| 298.15 | 15.82         | 19.98             | 0.776          | $-0.89$         | $-4.51$         |
| 400    | 11.11         | 18.71             | 1.031          | $-0.42$         | $-70.73$        |
| 500    | 8.55          | 17.51             | 1.240          | $-0.01$         | $-91.76$        |
| 600    | 6.98          | 16.38             | 1.412          | 0.35            | $-74.17$        |
| 700    | 5.94          | 15.30             | 1.551          | 0.66            | $-22.94$        |
| 800    | 5.22          | 14.28             | 1.661          | 0.93            | 56.99           |
| 900    | 4.68          | 13.32             | 1.746          | 1.14            | 160.64          |
| 1000   | 4.25          | 12.43             | 1.811          | 1.30            | 283.08          |
| 1100   | 3.89          | 11.59             | 1.860          | 1.42            | 419.32          |
| 1200   | 3.56          | 10.81             | 1.898          | 1.48            | 564.42          |
| 1300   | 3.25          | 10.09             | 1.927          | 1.49            | 713.43          |
| 1400   | 2.93          | 9.42              | -              | -               | -               |
| 1474   | 2.68          | 8.97              | -              | -               | -               |

**Conclusion**

New experimental data on thermal diffusivity, thermal conductivity, heat capacity and thermal expansion of BN in the temperature range of 298–1273…1474 K were obtained. For all studied properties the approximation equations and the table of recommended values were developed.

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