International Journal of Thermophysics, Vol. 7, No. 4, 1986

Suggestions Regarding Thermal Diffusivity Measurements on Pyrolytic Graphite and Pyrolytic Boron Nitride by the Laser Pulse Method[1]

G. H. He,[2] X. Z. Zhang,[2] Z. Wei,[2] S. Q. Dong,[2] Z. Q. Di,[2] and B. L. Zhou[2]

The laser pulse method can be successfully applied to the measurement of thermal diffusivity of isotropic materials subject to some assumptions. For anisotropic materials, this method is applicable to the measurement of principal thermal diffusivity only on the condition that there is no difference in direction between the principal axis and that of the temperature gradient. After analyzing the heat conduction process in an anisotropic solid, it has been shown that large errors in the measurement of thermal diffusivity would exist if the direction of the principal axis deviates inconspicuously from that of the temperature gradient. The experimental results of thermal diffusivity of highly oriented pyrolytic graphite (HOPG) samples with various deviation angles have been compared with the analytical results. The laser pulse method is not applicable to measurements on semitransparent pyrolytic boron nitride (PBN). We adopted a two-layer composite sample to measure the thermal diffusivity of PBN in the c direction and a particular graphite–PBN composite sample has been prepared which has a very low thermal resistance at the interface. The thermal diffusivity and thermal conductivity of PG (below 2300°C) and PBN (below 1000°C) are given.

KEY WORDS: anisotropic materials; pyrolytic graphite; pyrolytic boron nitride; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

Pyrolytic graphite (PG) and pyrolytic boron nitride (PBN) are materials of significant technological importance. A large number of investigators have contributed to the measurement, analysis, and synthesis of the ther-

[1] Invited paper presented at the Ninth Symposium on Thermophysical Properties, June 24–27, 1985, Boulder, Colorado, U.S.A.

[2] Institute of Metal Research, Academia Sinica, Shenyang, People's Republic of China.

0195-928X/86/0700-0789$05.00/0

mal conductivity of these materials [1–4]. The thermal diffusivity of PG and its anisotropy ratio in the range 300–1600°C have been determined by Nasu *et al.* [3] using the laser pulse method [9]. In measurements of the thermal diffusivity of anisotropic materials by the pulse method, it is necessary to ensure one-dimensional heat flow. This assumption could not be completely satisfied not only because of the heat losses but also because of the devitions in the sample preparation. The reliability of the pulse method for measuring the principal thermal diffusivity of anisotropic materials could be assumed only if there is no difference between the direction of the principal axis and the temperature gradient introduced by the laser beam. One of the authors of this paper has already reported on the effect of deviations from the correct direction of the principal axis on thermal diffusivity measurements [5]. In this paper, we give briefly the theoretical analyses and the experimental results.

Another important assumption to be satisfied in the case of the laser pulse method is the requirement of opacity for the front face of the sample. The PBN material is semitransparent under the radiation of a laser beam or flash tube, and thus it is difficult to measure its thermal diffusivity directly. Simpson and Stuckes [6] used a colloidal graphite coating on the front face of the sample to protect it from the penetrating radiation of the xenon flash tube below 800 K. In our experiments, the colloidal graphite coating, however, could not prevent the penetrating radiation of the laser beam above 600 K. In the present work, we adopted the two-layer composite method [7] and measured the thermal diffusivity of PBN (in the c direction).

Thermal conductivity results of PG and PBN material calculated from thermal diffusivity, specific heat, and density are also presented.

2. MEASUREMENT OF THE THERMAL DIFFUSIVITY OF PG

2.1. Availability of Pulse Methods for Anisotropic Materials

In the general case where the heat flow is not parallel to the temperature gradient in an anisotropic solid, the heat conduction equation can be written as [8]

$$\begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix} = -\begin{pmatrix} \lambda_{11} & \lambda_{12} & \lambda_{13} \\ \lambda_{21} & \lambda_{22} & \lambda_{23} \\ \lambda_{31} & \lambda_{32} & \lambda_{33} \end{pmatrix} \begin{pmatrix} \dfrac{\partial T}{\partial X_1} \\ \dfrac{\partial T}{\partial X_2} \\ \dfrac{\partial T}{\partial X_3} \end{pmatrix} \tag{1}$$

where q_1, q_2, and q_3 are the components of the rate of heat flow along the X_1, X_2, and X_3 axes, which are mutually orthogonal, and $\partial T/\partial X_1$, $\partial T/\partial X_2$, and $\partial T/\partial X_3$ are the temperature gradients in the X_1, X_2, and X_3 directions, respectively. Here

$$\begin{pmatrix} \lambda_{11} & \lambda_{12} & \lambda_{13} \\ \lambda_{21} & \lambda_{22} & \lambda_{23} \\ \lambda_{31} & \lambda_{32} & \lambda_{33} \end{pmatrix} = \boldsymbol{\lambda} \tag{2}$$

The quantity $\boldsymbol{\lambda}$ is the thermal conductivity tensor. According to the relation $\lambda = \alpha\rho c$ (α is thermal diffusivity, c is specific heat, and ρ is density; the latter two parameters are scalars), the thermal diffusivity tensor $\boldsymbol{\alpha}$ can be written as

$$\boldsymbol{\alpha} = \begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{pmatrix} = \frac{1}{\rho c} \begin{pmatrix} \lambda_{11} & \lambda_{12} & \lambda_{13} \\ \lambda_{21} & \lambda_{22} & \lambda_{23} \\ \lambda_{31} & \lambda_{32} & \lambda_{33} \end{pmatrix} \tag{3}$$

It is possible to obtain a symmetrical tensor by a transformation of axes. We have

$$\boldsymbol{\alpha} = \begin{pmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{22} & 0 \\ 0 & 0 & \alpha_{33} \end{pmatrix} \tag{4}$$

where α_{11}, α_{22}, and $_{33}$ are the thermal diffusivity of the three principal axes, respectively. The heat conduction equation for the transient mode can be written as

$$\begin{aligned} \left.\frac{\partial T}{\partial t}\right|_{x_1} &= \alpha_{11} \frac{\partial^2 T}{\partial X_1^2} \\ \left.\frac{\partial T}{\partial t}\right|_{x_2} &= \alpha_{22} \frac{\partial^2 T}{\partial X_2^2} \\ \left.\frac{\partial T}{\partial t}\right|_{x_3} &= \alpha_{33} \frac{\partial^2 T}{\partial X_3^2} \end{aligned} \tag{5}$$

If the principal axes of an anisotropic sample are parallel to this set of axes, the one-dimensional heat flow could be obtained and the laser pulse method can be used to measure the principal thermal diffusivity by the

known relation $\alpha = 0.139L^2/t_{1/2}$ (where L is the thickness of the sample and $t_{1/2}$ is the time at which the half-maximum excursion temperature of the sample is reached) [9].

2.2. Analysis of Measurement Error

In order to express the measurement error caused by improper sample preparation, it is necessary to make a transformation. We specify principal coordinates as an old set of axes $(0X_1, 0X_2, 0X_3)$ and the arbitrary coordinates as a new one $(0X'_1, 0X'_2, 0X'_3)$ (Fig. 1). According to the transformation of the components of a second-rank tensor, we obtain

$$\alpha'_{ij} = a_{ir} a_{jr} \alpha_{rr} \qquad \begin{pmatrix} r = X_1, X_2, X_3 \\ i, j = X'_1, X'_2, X'_3 \end{pmatrix} \tag{6}$$

where α'_{ij} are the components of the thermal diffusivity tensor in the new set of axes, and a_{ir} and a_{jr} are the direction cosines of axes i and j with respect to axis r, respectively. For the pyrolytic graphite with its hexagonal structure, there are two principal thermal diffusivities i.e., α_c in the c direction (parallel to the hexagonal axis) and α_a in the a direction (parallel to the

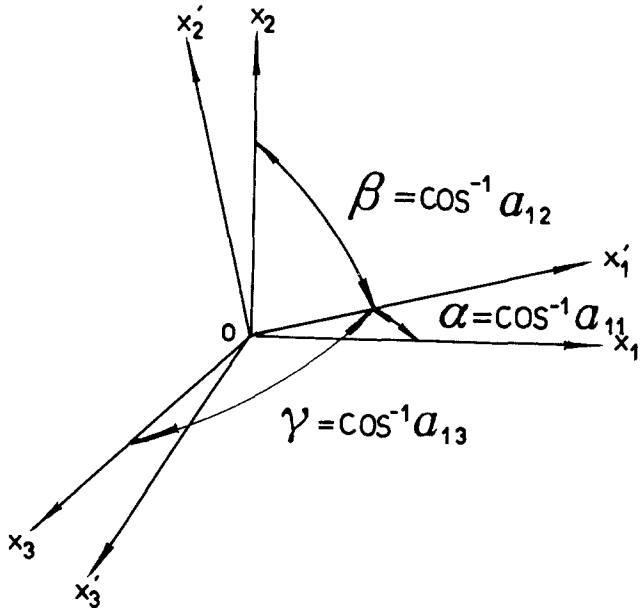

Fig. 1. Indication of two sets of axes and direction cosines.

basal plane). Both α_c and α_a can be measured by the laser pulse method if the c axis and the a axis are parallel to the measurement direction (X_1), respectively.

In Figs. 2 and 3 it is shown that the normals of samples are not in the x_1 direction but in the X_1' direction over which a temperature gradient would be established by the laser pulse.

According to the principle of conservation of energy, we have

$$\rho c \frac{\partial T}{\partial t} = -\nabla q \tag{7}$$

where the rate of the heat flow q has to be expressed by Eq. (1) in the new set of axes, so Eq. (7) can be written as

$$\rho c \frac{\partial T}{\partial t} = \lambda'_{11} \frac{\partial^2 T}{\partial X_1'^2} + \lambda'_{22} \frac{\partial^2 T}{\partial X_2'^2} + \lambda'_{33} \frac{\partial^2 T}{\partial X_3'^2} + (\lambda'_{23} + \lambda'_{32}) \frac{\partial^2 T}{\partial X_2' \partial X_3'} + (\lambda'_{13} + \lambda'_{31}) \frac{\partial^2 T}{\partial X_1' \partial X_3'} + (\lambda'_{12} + \lambda'_{21}) \frac{\partial^2 T}{\partial X_1' \partial X_2'} \tag{8}$$

If the sample is an infinite plate, then

$$\frac{\partial T}{\partial X_2'} = 0, \qquad \frac{\partial T}{X_3'} = 0 \tag{9}$$

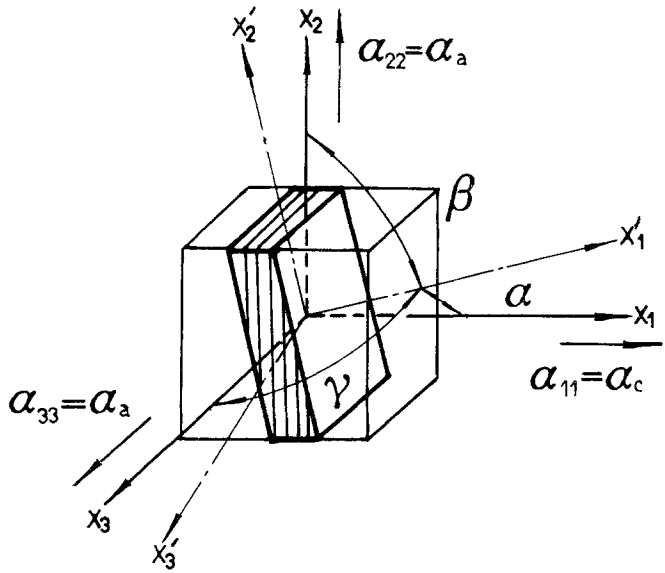

Fig. 2. Deviation of sample preparation (in the c direction).

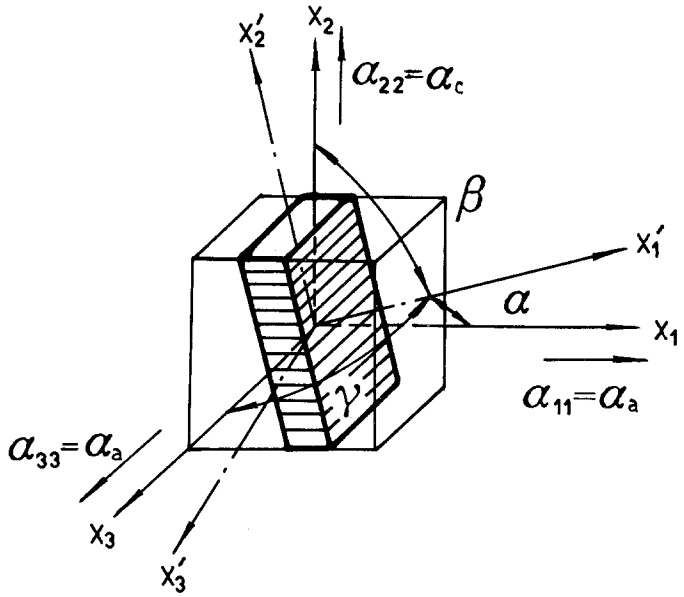

Fig. 3. Deviation of sample preparation (in the a direction).

So Eq. (8) can be simplified as

$$\rho c \frac{\partial T}{\partial t} = \lambda'_{11} \frac{\partial^2 T}{\partial X_1'^2}$$

or

$$\frac{\partial T}{\partial t} = \alpha'_{11} \frac{\partial^2 T}{\partial X_1'^2} \tag{10}$$

Comparing Eq. (10) with Eq. (5), measurement error δ caused by improper sample preparation can be expressed as

$$\delta = \frac{\alpha'_{11} - \alpha_{11}}{\alpha_{11}} \tag{11}$$

According to Eq. (6) and Fig. 1, we have

$$\alpha'_{11} = \alpha_{11} \cos^2 \alpha + \alpha_{22} \cos^2 \beta + \alpha_{33} \cos^2 \gamma \tag{12}$$

The relation among α, β, and γ is

$$\cos^2 \gamma = 1 - \cos^2 \alpha - \cos^2 \beta \tag{13}$$

Replacing Eq. (12) by Eq. (13), we obtain

$$\alpha'_{11} = \alpha_{11} \cos^2 \alpha + \alpha_{22} \cos^2 \beta + \alpha_{33}(1 - \cos^2 \alpha - \cos^2 \beta) \tag{14}$$

and then the error δ in Eq. (11) becomes

$$\delta = \cos^2 \alpha + \frac{\alpha_{22}}{\alpha_{11}} \cos^2 \beta + \frac{\alpha_{33}}{\alpha_{11}} (1 - \cos^2 \alpha - \cos^2 \beta) - 1 \tag{15}$$

From Fig. 2, $\alpha_{22}/\alpha_{11} = \alpha_{33}/\alpha_{11} = \alpha_a/\alpha_c$, and from Fig. 3, $\alpha_{22}/\alpha_{11} = \alpha_c/\alpha_a$, $\alpha_{33}/\alpha_{11} = \alpha_a/\alpha_a = 1$; thus

$$\delta_c = (\cos^2 \alpha - 1)\left(1 - \frac{\alpha_a}{\alpha_c}\right) \tag{16}$$

and

$$\delta_a = \cos^2 \beta \left(\frac{\alpha_c}{\alpha_a} - 1\right) \tag{17}$$

Equations (16) and (17) show the effect of improper sample preparation on the results.

2.3. Results

The details of the thermal diffusivity equipment used in our experiments can be found elsewhere [10, 11]. Its main features are as follows. The pulse radiation source is a Nd–glass laser with a maximum output of about 50 J and a pulse duration of 0.6–0.7 ms. The high-temperature furnace (up to 2500°C) is a tungsten or graphite tube. The detector is a thermocouple or a lead sulfide element. The signal is amplified and recorded with an oscilloscope.

At first, a piece of highly oriented pyrolytic graphite (HOPG) ($22 \times 18 \times 1.5$ mm) made at our institute was prepared to make three samples with different deviation angles ($\alpha \approx 0°$, $\alpha \approx 1.1°$, $\alpha \approx 4.2°$), which were tested by the X-ray diffraction method. The experimental results are shown in Fig. 4 and are compared with the analytical results given in Table I. Thermal diffusivity α_a and measurement error δ_a for another PG sample are also given in Table I. From Table I it may be seen that the experimental and analytical results would be similar for the assumed anisotropy ratio of 200–250.

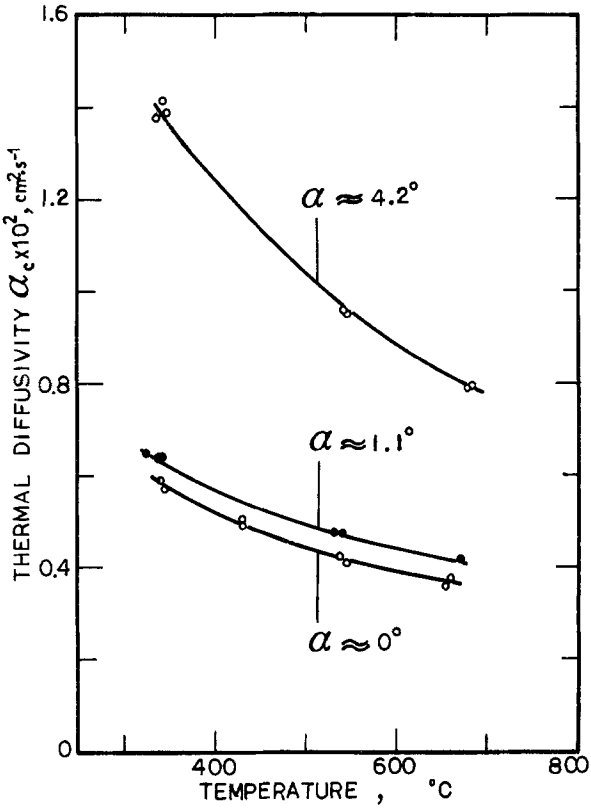

Fig. 4. Thermal diffusivity α_c of PG for different deviation angles.

From the above results it may be seen that the serious measurement errors in the c direction would exist even for small deviations of the normal of the sample from the principal axis (for example, $\alpha \approx 1.1°$). Therefore, preparation of the sample is an important consideration for α_c measurements of anisotropic materials, especially of highly oriented pyrolytic graphite.

In addition, the thermal diffusivity of one kind of PG material used in a high-power tube as a grid had been measured after preparing the sample carefully and performing heat loss corrections [12]. The thermal diffusivity results are given in Fig. 5. The results for thermal conductivity, determined from measured thermal diffusivity, specific heat (measured at this institute [13]), and density corrected for thermal expansion are shown in Fig. 6.

Table I. Comparison of the Experimental δ_c and δ_a with the Analytical Values According to Eqs. (16) and (17) for PG

Temp. (°C)	$\alpha_c \times 10^3$ (cm$^2 \cdot$ s^{-1})			$\delta_c \times 10^2$ (α: 1.1°)			$\delta_c \times 10^2$ (α: 4.2°)			α_a^b (cm$^2 \cdot$ s^{-1})		$\delta_a \times 10^2$ (β: 8.2°)		
	α				Anal. η^a			Anal. η^a		β			Anal. η^a	
	0°	1.1°	4.2°	Exp.	200	250	Exp.	200	250	90°	82°	Exp.	200	250
350	5.7	6.2	13.8	+8.8			+142							
500	4.5	4.9	10.5	+8.8	+7.3	+9.2	+133	+107	+133	2.05	2.00	−2.4	−2.0	−2.0
650	3.7	4.1	8.4	+10.8			+137							

[a] η is the ratio of α_a to α_c (assumed).
[b] α_a is measured at room temperature.

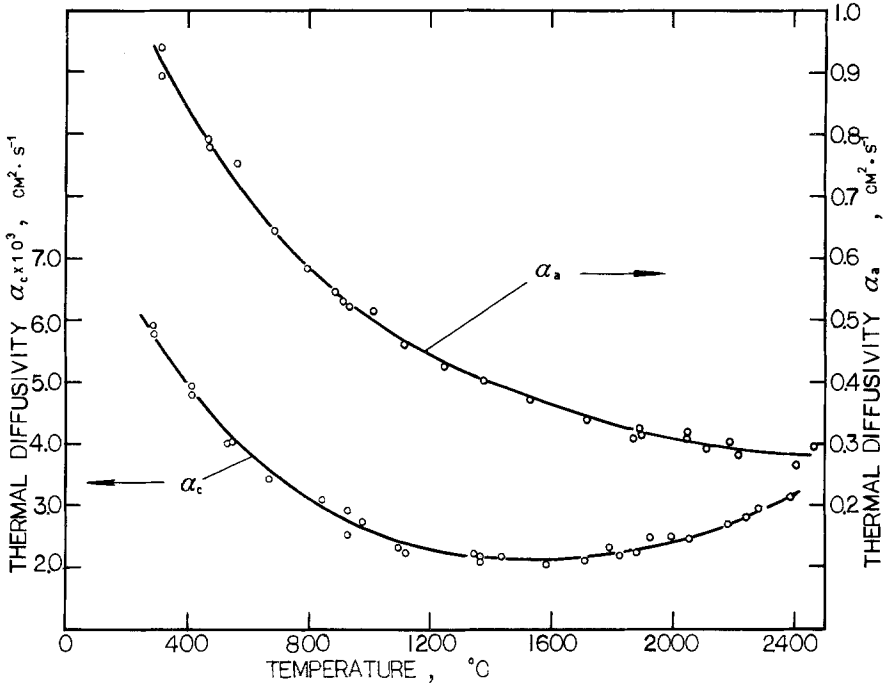

Fig. 5. Thermal diffusivity α_a and α_c of one kind of PG material.

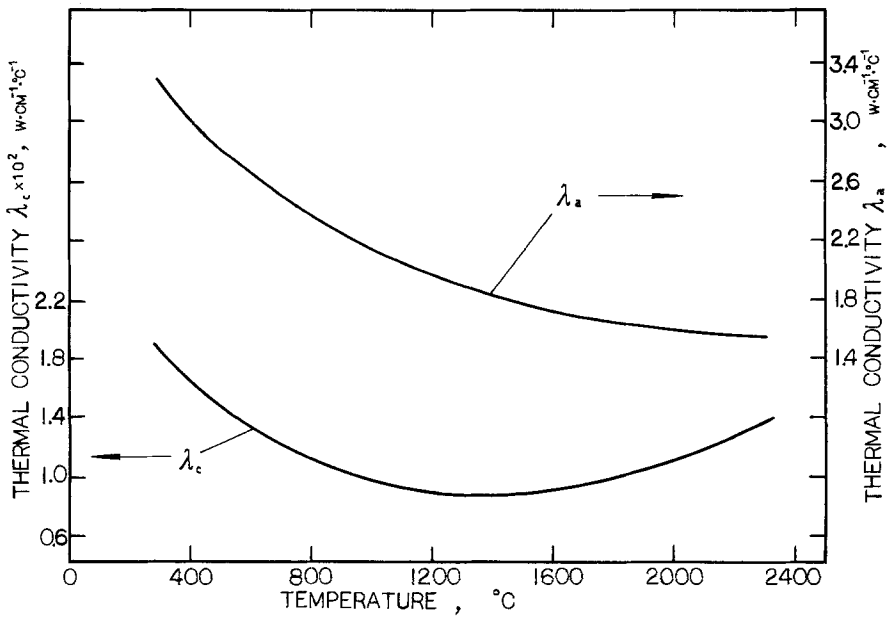

Fig. 6. Thermal conductivity λ_a and λ_c of one kind of PG material.

3. MEASUREMENT OF THE THERMAL DIFFUSIVITY OF PBN

3.1. Application of the Two-Layer Composite Method

In order to meet the opacity condition required by the laser pulse method, we used the two-layer composite sample proposed by Bulmer and Taylor [7]. The dimensionless temperature history of the rear face of the sample $V(t)$ can be written as

$$V(t) = 1 - 2R_2 \sum_{k=1}^{\infty} \frac{[1 - \exp(\beta_k^2/R_2)] \exp(-\beta_k^2 t/U_2)}{\beta_k^2[\cos(\beta_k X) \cos \beta_k - \Omega(X) \sin(\beta_k X) \sin \beta_k]}, \qquad t > \tau_p \tag{18}$$

where $U_2 = L_2^2/\alpha_2$, $R_2 = U_2/\tau_p$, $X = L_1/L_2(\alpha_2/\alpha_1)^{1/2}$, $\Omega(X) = (X + H/X)/(H+1)$, $H = \rho_1 c_1 L_1/\rho_2 c_2 L_2$, and τ_p is the pulse duration of the laser beam. The α_1, ρ_1, c_1, and L_1 and α_2, ρ_2, c_2, and L_2 are the thermal diffusivity, density, specific heat, and thickness for two layers, respectively. In Eq. (18), β_k is the kth positive root of

$$H \cos \beta \sin(\beta X) + X \cos(\beta X) \sin \beta = 0 \tag{19}$$

In Eq. (18), only α_1 (or α_2) is the unknown parameter. We prepared a program to calculate α_1 (or α_2) when $t = t_{1/2}$, $V(t) = 0.5$, and checked the program using the data given in Ref. 7. An additional important consideration in the case of the two-layer composite sample is the satisfaction of the condition of a very small interface thermal resistance.

3.2. Preparation of a Composite Sample and Experimental Results

The PBN crucible used for crystal growth can be manufactured by depositing PBN on a graphite base at our institute. The method of preparation of a two-layer composite sample is the same as that of preparation of a crucible with the same depositing conditions. The composite sample consists of a graphite sample with known α_2, ρ_2, c_2, and L_2 (2.50 mm) and a depositing layer of PBN with known ρ_1, c_1, and L_1 (0.53 mm). Metallographic studies indicated the close binding at the interface. The α_c of PBN could be obtained by means of Eq. (18) using the above sample.

In addition, for measuring the α_a of PBN, another PBN sample was made up of separate pieces (thickness, about 2 mm each piece) bound together with wires to form a cylinder with a thickness of 5.39 mm and a diameter of 10 mm. The sample was deposited on a thin carbon layer (only

Table II. Typical α_c Results for PBN Calculated by Eq. (18)[a]

Temp. (°C)	C_1 (cal·g^{-1}·°C^{-1})	C_2 (cal·g^{-1}·°C^{-1})	α_2 (cm^2·s^{-1})	$t_{1/2}$ (s)	α_c (cm^2·s^{-1})	V_1	V_2
260	0.374	0.303	0.33	0.151	0.0085	0.4999	0.5003
442	0.387	0.372	0.225	0.177	0.0081	0.4999	0.5003
644	0.404	0.422	0.162	0.212	0.0074	0.4999	0.5003
854	0.432	0.455	0.132	0.238	0.0070	0.4999	0.5003
961	0.452	0.462	0.125	0.255	0.0066	0.4999	0.5002

[a] Subscript 1 represents PBN; subscript 2 represents graphite. $L_1 = 0.053$ cm, $L_2 = 0.25$ cm, $\rho_1 = 2.1$ g·cm^{-3}, $\rho_2 = 1.8$ g·cm^{-3}, $\alpha_c(V_1) < \alpha_c(0.5) < \alpha_c(V_2)$.

a few micrometers) which could protect the sample from the penetrating radiation of the laser beam conveniently. Thus, the α_a of PBN was determined by the laser pulse method used as for isotropic materials using the above sample.

The typical α_c results for PBN by the two-layer composite method according to Eq. (18) are presented in Table II. The results for α_a and α_c and calculated λ_a and λ_c of PBN are shown in Fig. 7 and Fig. 8, respectively.

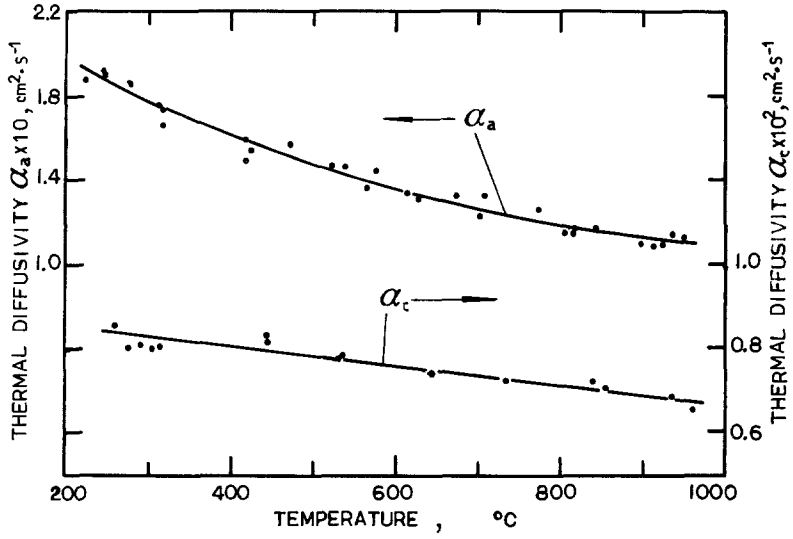

Fig. 7. Thermal diffusivity α_a and α_c of one kind of PBN material.

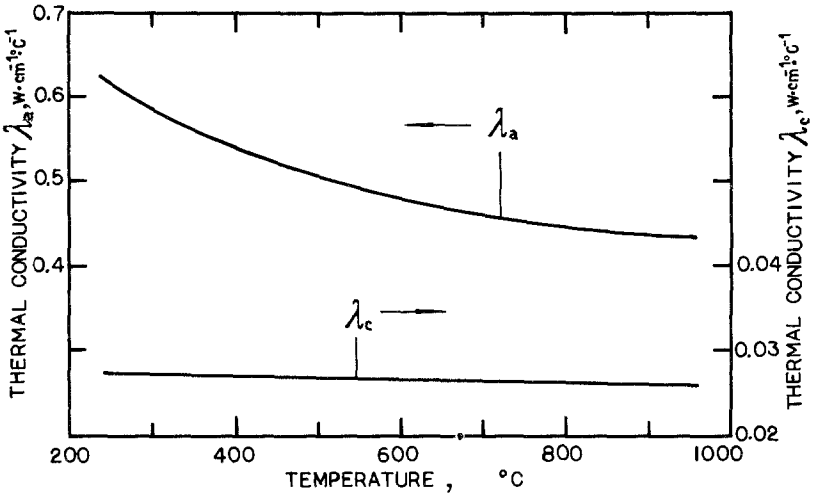

Fig. 8. Thermal conductivity λ_a and λ_c of one kind of PBN material.

4. DISCUSSION

In analyzing the measurement error resulting from deviation in the sample preparation, we assume that the sample is an infinite plate and no temperature gradient exists in the X_2' and X_3' directions. In fact, the dimension of the sample is always finite and both $\partial T/\partial X_2'$ and $\partial T/\partial X_3'$ are not zero. The term $\lambda_{11}'(\partial^2 T/\partial X_1'^2)$ in Eq. (8), however, may still be the essential term for small deviations in sample preparation. So it could be acceptable to use Eq. (9) for simplifying Eq. (8) because the goal of our study is mainly to investigate the effect of sample preparation on measurements and not to measure thermal diffusivity exactly.

For any kind of CVD (chemical vapor deposition) material including HOPG materials, the preferred orientation could not always be the ideal plane. The mosaic spread $\Delta\omega$ is about 0.7–1.4° for our HOPG material. From the above analyses (Sections 2.2 and 2.3), the higher the anisotropy ratio (i.e., the smaller the $\Delta\omega$), the larger the δ_c and δ_a, especially δ_c. So careful sample preparation is necessary; the best way to check the deviation angle is by the X-ray diffraction technique.

Equation (18) was derived for a square-wave pulse resulting from a ruby laser. For the Nd–glass laser used in our experiments, the pulse would nearly be a triangular wave. The more complicated solution of $V(t)$ for a triangular-wave pulse has been obtained and its validity has been checked using a certain composite sample [14]. The results calculated by this

solution for the same PBN sample as used above approach those calculated by Eq. (18) but the difference between $V_1(0.5)$ and $V_2(0.5)$ using this solution is larger than that obtained using Eq. (18).

5. CONCLUSIONS

The large measurement errors of the principal thermal diffusivity for HOPG material in the c direction would exist due to unnoticed normal deviation by the laser pulse method. Therefore, it is necessary to pay more attention to the sample preparation. The useful way to check the sample preparation would be by the X-ray diffraction technique. The two-layer composite sample laser pulse method for measuring the thermal diffusivity of semitransparent PBN material would be available for protecting penetrating radiation from a laser beam. It is important to reduce the thermal resistance of the interface of the two-layer composite sample.

ACKNOWLEDGMENTS

The authors gratefully thank Dr. Z. Q. Yan for providing HOPG material and testing deviation of the sample preparation. We would like to express our thanks to Dr. F. M. Zhao for providing the PBN samples.

REFERENCES

1. Y. S. Touloukian, R. W. Powell, C. Y. Ho, and P. G. Klemens, *Thermophysical Properties of Matter, Vol. 2, Thermal Conductivity, Nonmetallic Solids* (Plenum, New York, 1970), pp. 30–41.
2. M. R. Null, W. W. Lozier, and A. W. Moore, *Carbon* **10**:352 (1972).
3. S. Nasu, T. Takahashi, and T. Kikuchi, *J. Nucl. Mat.* **43**:72 (1972).
4. J. E. Parrott and A. D. Stuckes, *Thermal Conductivity of Solids* (Pion, London, 1975), pp. 127–128.
5. X. Z. Zhang, *The Method to Measure Thermal Diffusivity of Anisotropic Materials by Laser Pulse Technique*, M.S. thesis (IMR, Academia Sinica, Shenyang, 1983) (Chinese).
6. A. Simpson and A. D. Stuckess, *J. Phys. C Solid State Phys.* **4**:1710 (1971).
7. R. F. Bulmer and R. Taylor, *High Temp. High Press.* **6**:491 (1974).
8. J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, London, 1957), p. 195.
9. W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbott, *J. Appl. Phys.* **32**:1679 (1961).
10. G. H. He, Q. H. Ye, Z. Q. Di, and B. L. Zhou, *J. Eng. Therm.* **2**:283 (1981) (Chinese).
11. G. H. He, Q. H. Ye, S. Q. Dong, Z. Q. Di, and B. L. Zhou, *Acta Metrol. Sin.* **4**:168 (1983) (English).
12. R. D. Cowan, *J. Appl. Phys.* **34**:926 (1963).
13. P. W. Zhang, Z. H. Li, R. Z. Chang, X. N. Zhou, and L. B. Lou, *J. Eng. Therm.* **3**:413 (1982) (Chinese).
14. X. Z. Zhang, G. H. He, Z. Wei, and B. L. Zhou, Private communication (1985).