COMPARISON OF THERMOPHYSICAL PARAMETERS OF CARBON NANOTUBES MEASURED BY VARIOUS METHODS

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Abstract

The measurements of thermophysical parameters of Single Wall Carbon Nanotubes (SWNT) HiPCO in the temperature range from –20 up to 70 °C are presented. In order to inter-compare and to validate the measured data, three different experimental techniques were used. DSC as an equilibrium method for measuring specific heat, Flash transient method for measuring the thermal diffusivity and Pulse transient method for measuring all thermophysical parameters the thermal diffusivity, the specific heat and the thermal conductivity. Good agreement of values measured by these different methods was found.

Keywords: pulse transient, flash method, DSC, carbon nanotubes, thermal conductivity, thermal diffusivity, specific heat

1 Introduction

Physical properties of carbon nanotubes have been widely investigated during last ten years. There are many papers on electrical and mechanical properties. Surprisingly, the study of thermophysical properties of single wall carbon nanotubes (SWNT) [1, 2] is still very scarce and in addition the published data show large scattering.

In this paper we present measurements of SWNT's thermophysical parameters, namely the thermal diffusivity, the specific heat and the thermal conductivity, in the temperature range from –20 up to 70 °C, using Pulse transient method [3]. To get overview on data reliability and measuring errors, we used another two measuring methods: the Flash transient method [4] for measuring the thermal diffusivity and the Differential scanning calorimetry (DSC) [5] for measuring the specific heat.

Two different kind of SWNT, a pristine SWNT and a modified SWNT (chemically treated with $SOCl_2$) were measured. To compare the absolute values of SWNT's thermophysical parameters the third kind of carbon material samples, compressed graphite powder, was measured.

2 Experimental methods

2.1 Pulse transient method

The principle of the pulse transient method is shown in Fig. 1. The method can be described as follows. The temperature of the specimen is stabilized and uniform. Then a small disturbance in the form of a heat pulse is applied to the specimen. From the temperature response the termophysical parameters can be calculated according to the model used.

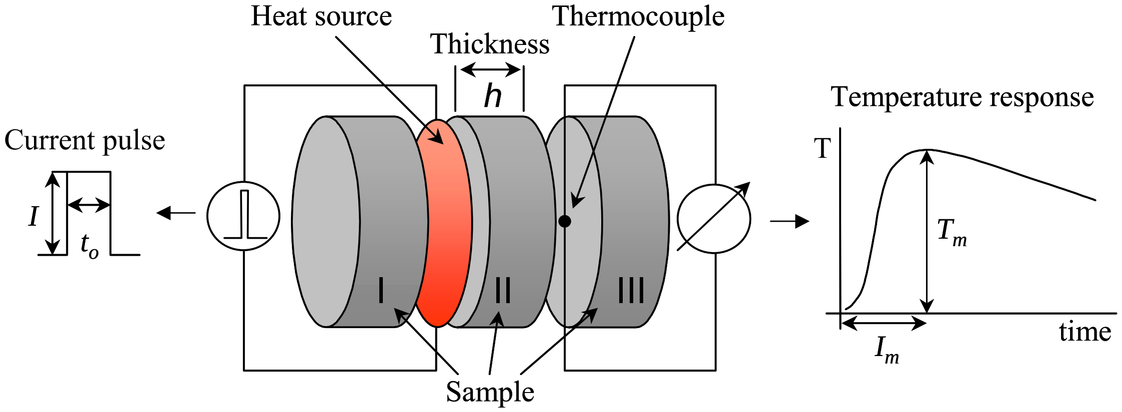

Fig 1 Experimental set up for Pulse transient method

The model of the method is characterized by the temperature function [3]

$$T(h,t) = \frac{Q}{c_p \rho \sqrt{\pi a t}} \exp\left(\frac{h^2}{4at}\right), \tag{1}$$

where $Q=RI^2t_0$ is amount of heat generated by heat source in the unit area, R is electrical resistance of the heat source, I is current supplied during time t_0, ρ is density and a, c_p are unknown thermophysical parameters (thermal diffusivity and specific heat). The temperature function (1) is the solution of the heat equation considering appropriate boundary and initial conditions. For determination of the thermophysical properties mentioned the one-point procedure was used, where the maximum of the temperature response is taken as the input. The following relations [3] for calculation of the thermophysical parameters are used:

Specific heat c_p

$$c_p = Q / T_m h \rho \sqrt{2\pi e} \tag{2}$$

Thermal diffusivity a

$$a = h^2 / 2t_m \tag{3}$$

T_m is the maximum of temperature response at the time t_m and e denotes the Euler number.

Third termophysical parameter, thermal conductivity λ, is defined by well-known data consistency relation

$$\lambda = a c_p \rho \tag{4}$$

2.2 Flash method

In this method [4] the front face of a small disk-shaped sample is subjected to a very short burst of radiant energy, inside a vacuum or a controlled atmosphere enclosure. The source of the radiant energy is usually a laser or a xenon flash lamp and irradiation times are of the order of millisecond or less. The values of the thermal diffusivity a are computed from the temperature response using an appropriate fitting technique. The flash method is shown schematically in Fig. 2.

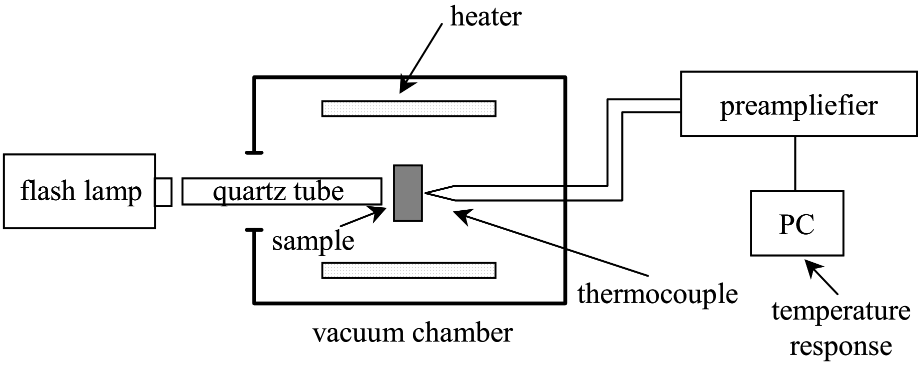

Fig 2 Experimental set up for Flash method

For opaque solids, the temperature rise at the rear face of the sample can be written as

$$T(L,t)=\frac{Q}{\rho c_p L}\left[1+2\sum_{n=1}^{\infty}(-1)^n\exp\left(-\frac{n^2\pi^2 at}{L^2}\right)\right], \tag{5}$$

where L is the sample thickness and Q is the pulse of energy per unit area which is assumed to be instantaneously and uniformly absorbed in a small depth. To compute the thermal diffusivity a, only the transient part of temperature equation (5) is taken into consideration.

2.3 Differential scanning calorimetry

DSC belongs to a large group of calorimetry methods, particularly known as equilibrium reference method. It is a relative method where the signal of the measured sample is related to the signal of a known standard sample. The method is based on a controled constant rising temperature in the sample and the reference, where inside the sample a uniform temperature distribution is assumed (equilibrium condition). In the case of a power-compensated DSC, from balance of the heat flow [5], the specific heat c_p of the measured sample is calculated as

$$c_{p,M}=\frac{Y_M(T)-Y_B(T)}{Y_S(T)-Y_B(T)}\frac{m_S}{m_M}c_{p,S}(T) \tag{6}$$

where Y_M, Y_S and Y_B are the signals from the measured sample, the standard sample and the reference sample being an empty sample pan (blanck), m_S and m_M are related masses and $c_{p,S}$ is the known specific heat of the standard sample.

3 Experiments

3.1 Samples

Three different kinds of samples were prepared for measurements (Table 1). First two, representing the investigated material made of single wall carbon nanotubes, were pristine SWNT and modified SWNT (doped with $SOCl_2$). Third one was made of compressed graphite powder.

SWNT (pristine and modified)
The samples of SWNTs consist of thin layers of SWNT (known as buckypapers) with characteristic microstructure shown in Fig 3. The carbon nanotubes form bundles of several tens of tubes. Distribution of SWNT diameters is in range (0.7-1.5) nm with a length of about 1 µm. The bundles of nanotubes are randomly ditributed in a plane reminding „spaghetti-like“ structure and keeping together either by nods or by the weak Van der Waals interaction, where the distance between bundles is about 0.35 nm. This is a reason why the samples possess strong anisotropy.

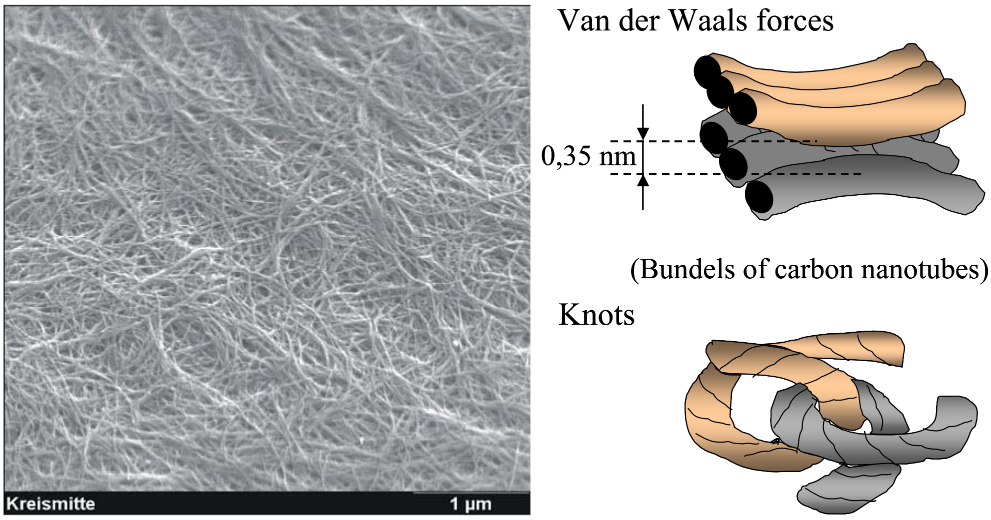

Fig 3 SEM picture of thin layer of SWNT (left) and schematically drawing of SWNT bundles (right)

For the transient methods the thermophysical parameters are determined in direction of heat flow. For measurements using the Pulse transient and Flash method, heat flows in direction perpendicular to the layers of the SWNT's bundles as it is shown in Fig 4.

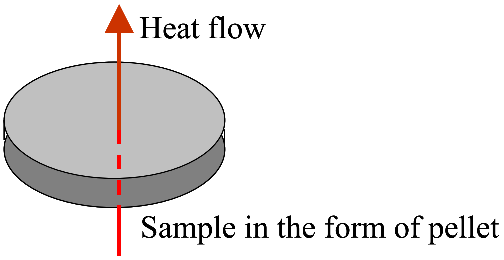

Fig 4 The heat flow perpendicular to the thin layers of the SWNT compressed into the pellet

Modified SWNT doped with $SOCl_2$ show increase of electrical conductivity by factor of 5. Therefore, a question arise how the dopant would influence the thermophysical parameters of sample.

Graphite

In order to compare the thermal properties of SWNT to other carbon structures, graphite pellets made of compressed graphite powder were prepared. Unlike the SWNT's samples the graphite samples are isotropic.

Table 1 Parameters of samples considering used measuring method

Sample	Method	Density [kg.m^{-3}]	Diameter [mm]	Thickness [mm]
1. Pristine SWNT	Transient	1024	12.2	1.54
	DSC	1040	6.1	0.6
2. Modified SWNT	Transient	1294	12.2	1.54
	DSC	1059	6.1	0.74
3. Graphite	Transient	1451	12.1	3.16
	DSC	1392	6.1	1.45

Since each of the methods has specific requirements on the sample geometry, the samples were prepared in two different sizes (see Table 1). The density variations of individual samples are caused by non-reproducible compression condition at samples preparation.

3.2 Experimental set-up and conditions

Pulse transient method

The thermophysical transient tester RT 1.02 (Institute of Physics SAS) is used for measurement of the specific heat, thermal diffusivity and thermal conductivity. A heat source made of thin metallic foil (Nickel) of thickness 20 μm in a form of meander is used. Due to electrical conductivity of specimen the heat source is isolated with thin Kapton foil. The electrical resistance of the heat source is ≈ 2 Ω. A thermocouple made of insulated Chromel and Alumel wires with the thickness of 50 μm was used for measuring the temperature response. The following measuring parameters were used:
Temperature range: -20 to 70 °C
Surrounding atmosphere: vacuum
Cooling rate: -0.1 °C/min

Flash method

The experimental apparatus constructed at Institute of Physics SAS is used for measurement of the thermal diffusivity. The flash lamp is used as the heat source of the radiant energy. The length of heat pulse is 5 milliseconds. A thermocouple made of Chromel and Constantan wires having the thickness of 25 μm was used for measuring the temperature response. The following measuring parameters were used:
Temperature range: room temperature
Surrounding atmosphere: air

DSC
An commercial experimental apparatus Perkin-Elmer power-compensated DSC 7 is used for measurement of the specific heat. The Sapphire is used as the standard sample. The following measuring parameters were used:
Temperature range: 10 to 150 °C
Surrounding atmosphere: argon
Heating rate: +10 °C/min

3.3 Results

Thermal diffusivity of the SWNT (pristine and modified) and of the Graphite as a function of temperature measured by Pulse transient and Flash method is shown in Fig. 5. The thermal diffusivity measurement using Flash method was performed just for the modified SWNT at room temperature only. The difference of 6% was found, comparing the values for the modified SWNT obtained by Pulse transient and by Flash method.

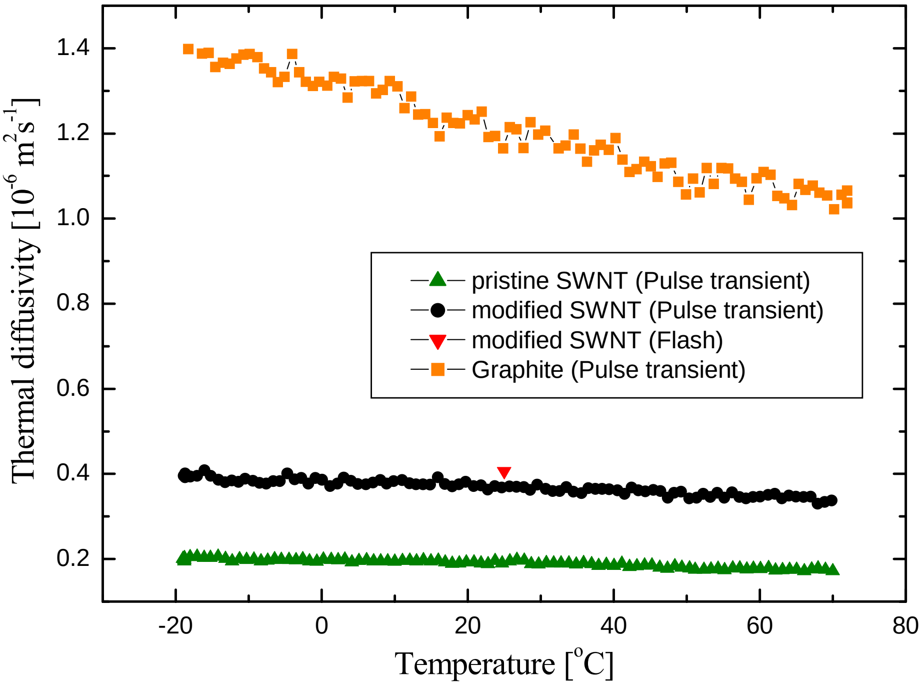

Fig 5 Thermal diffusivity of various samples measured by Pulse transient and Flash method

Fig. 6. represents the specific heat as a function of the temperature obtained by Pulse transient and DSC method. Comparison between Pulse transient and DSC data shows an excellent agreement for the samples made of graphite and pristine SWNT. A large difference of about 25 % was found for the results obtained by Pulse transient and DSC methods for the modified SWNT samples. The more detailed study by DSC method (fig. 7. right) indicates that the discrepancy is caused by presence of water in the modified SWNT during the Pulse transient measurement. Water absorbed into the sample by air is step by step desorbed during the DSC measurements, which manifests as endothermic peak in the specific heat curve, shown in Fig. 7 (left). A much smaller desorption effect is

noticed for pristine SWNT and graphite samples. The rate of desorption is dependent on the heating rate of measurements (here +10 °C per minute).

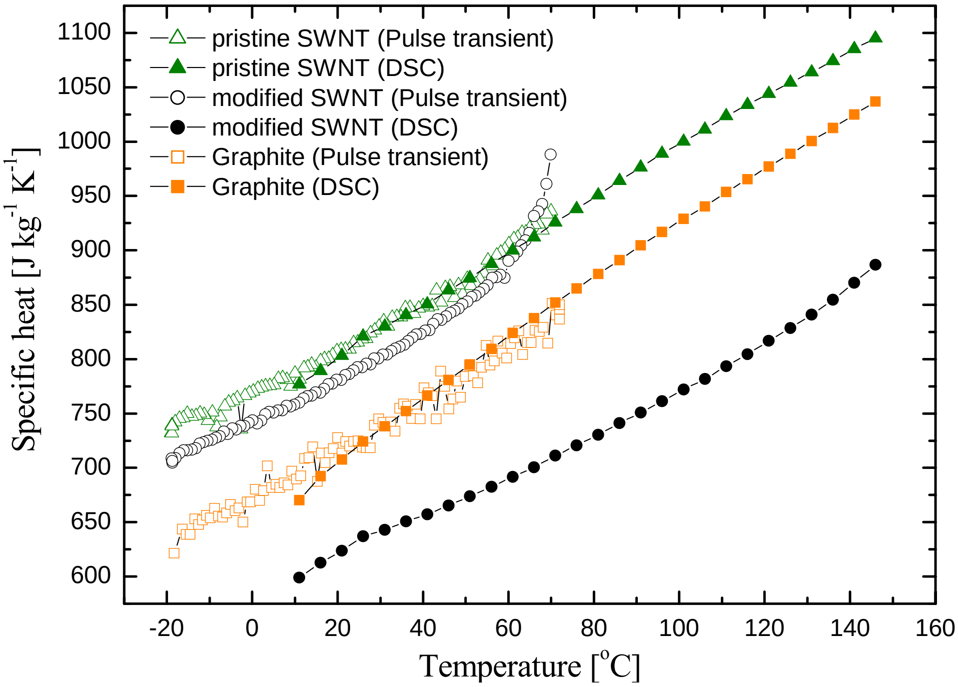

Fig 6 Specific heat of various samples measured by Pulse transient and DSC method

The desorption effect on the modified SWNT is depicted in Fig. 7 (right), where the specific heat reached equilibrium values after several measurement‘s runs (DSC). Comparison of the curve measured by Pulse transient with DSC curves denotes, that the

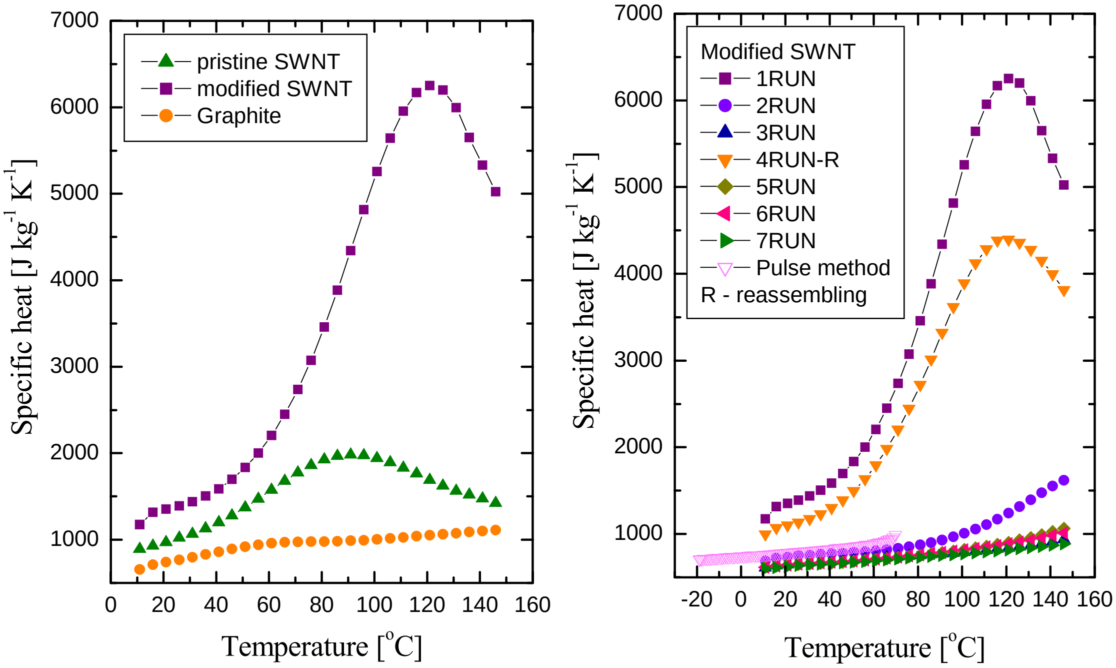

Fig 7 Desorption effect as the specific heat (DSC) for various material samples (first run, only – left) and different runs (modified SWNT – right)

curve of specific heat measured by Pulse transient method represents the values that correspond to sample partly saturated with water.

The thermal conductivities of measured samples as a function of the temperature are shown in Fig. 8. The values were calculated using relation (4).

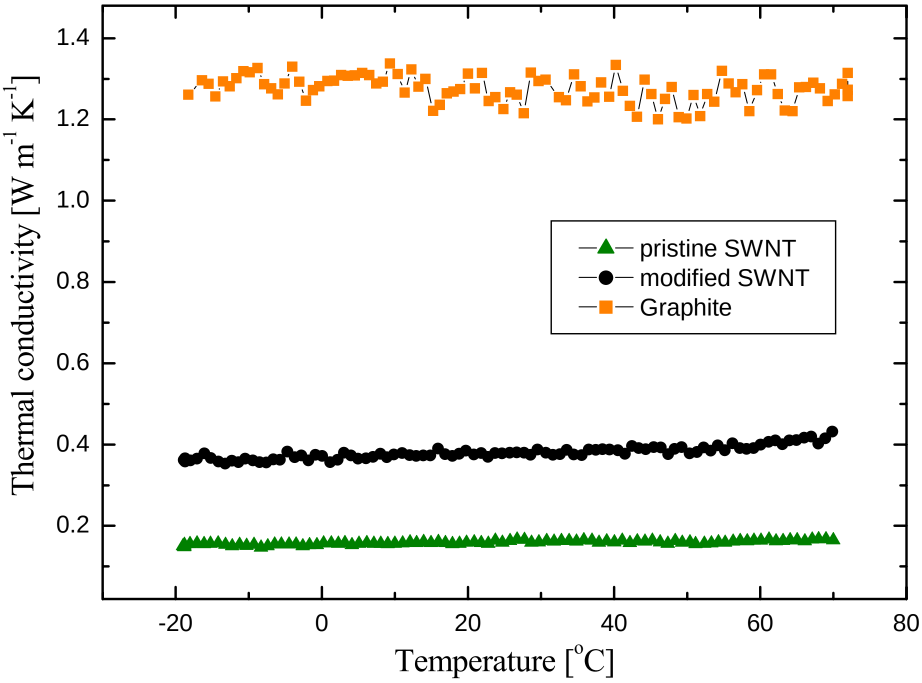

Fig 8 Thermal conductivity of various samples measured by Pulse transient method

Finally, the thermophysical parameters of the measured materials corresponding to the room temperature are given in Table 2. In the case of modified SWNT, the specific heat of the desorbed sample measured by DSC method was taken into calculation of thermal conductivity (see Fig. 7 right).

Table 2 Thermophysical parameters in room temperature (25 °C)

Sample	Thermal diffusivity [10^{-6} m^2 s^{-1}]	Specific heat [J kg^{-1} K^{-1}]	Thermal conductivity [W m^{-1} K^{-1}]
1. Pristine SWNT	0.19	816	0.16
2. Modified SWNT	0.37	637*	0.30*
3. Graphite	1.17	725	1.25

* The specific heat measured by DSC method was taken into consideration

4 Conclusions

The thermophysical parameters of SWNT (pristine and modified) and graphite samples were measured by Pulse transient, Flash and DSC method. A good agreement for the values measured by these different methods was found. Large scattering of the thermophysical data measured on the graphite samples by Pulse transient method is noticed (see Fig. 5, 6 and 8). Probably, it was caused by a low temperature stabilization during the measurements.

The presented transport thermophysical properties (thermal conductivity and diffusivity) of the SWNT samples correspond more to the inter-layer transport properties, because the heat applied in transient methods flew in direction perpendicular to the layers of SWNT. This could explain the low values of thermal conductivities of SWNT in comparison to the graphite sample (Fig. 8.). In order to get the „in-plane“ values of the thermophysical parameters of SWNT, the additional measurements within the layers of the SWNT should be performed using appropriate methods.

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