Int J Thermophys (2008) 29:1257–1266
DOI 10.1007/s10765-008-0504-z

New Measurements of the Thermal Conductivity of PMMA, BK7, and Pyrex 7740 up to 450 K

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Received: 27 May 2008 / Accepted: 3 August 2008 / Published online: 26 August 2008

Abstract New measurements of the thermal conductivity of polymethyl methacrylate (PMMA), BK7, and Pyrex 7740 are presented. The technique employed is a refined transient hot-wire technique, based on a full theoretical model with equations solved by finite elements for the exact geometry. At the 95 % confidence level, the standard deviations of the thermal conductivity measurements of PMMA, BK7, and Pyrex 7740 are 0.47 %, 1.0 %, and 0.8 %, respectively. The technique is absolute and is characterized by an uncertainty of <1 %.

Keywords BK7 · PMMA · Pyrex 7740 · Thermal conductivity · Transient hot-wire

1 Introduction

Since 2002, in a series of recent papers [1–5], a novel application of the transient hot-wire technique for thermal-conductivity measurements on solids was described. The methodology makes use of a soft-solid material between the hot wires of the technique and the solid of interest. It is based on a full theoretical model with equations solved by a finite-element method applied to the exact geometry, and thus it allows an accurate, absolute determination of the thermal conductivity of the solid. With this method, the thermal conductivity of Pyroceram 9606 [2,4], AISI 304 L [3,4], Pyrex 7740 [4], polymethyl methacrylate (PMMA), and BK7 [5] was measured as a function of tempe-

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rature. In 2008, Assael et al. [6] published further refinements of the technique reducing its uncertainty <1 %. Following these refinements, in this article the thermal conductivity of PMMA, BK7, and Pyrex 7740 is remeasured as a function of temperature.

PMMA is an amorphous, colorless thermoplastic material of excellent optical transparency, and a luminous transmittance of about 92 %. It has good abrasion resistance and dimensional stability, but is brittle and notch sensitive. Its water absorptivity is very low when compared with other polymer materials. PMMA was proposed by NPL as a possible candidate for a thermal-conductivity reference standard in 2003 [7]. However, a more recent intercomparison among 17 laboratories organized by Physikalisch-Technishe Bundesanstalt (PTB) [8], showed uncertainties of 8 % to 13 % in the thermal conductivity values, which far exceeded the laboratories' quoted uncertainties. Hence, the employment of PMMA as an acceptable thermal-conductivity standard is still under consideration.

BK7 is widely used for optical systems and can be manufactured with outstanding homogeneity. It has isotropic thermophysical properties with excellent long-term stability. In the case of BK7, a similar intercomparison among 11 European laboratories was also organized by PTB [9], aiming to qualify it as a possible candidate reference material for thermal conductivity, produced in 2004 uncertainties up to 40 %, which were far in excess of the laboratories' quoted uncertainties. Hence, this material is also still under consideration.

Finally, Pyrex 7740 is a borosilicate glass, which conforms to ASTM E-438, and since 1990 it is considered as a certified reference material for thermal conductivity, CRM 039 [10], by the European Union Institute of Reference Materials and Measurements.

2 Experimental

The actual instrument employed for the measurement of the thermal conductivity of solids at elevated temperatures, with all its new refinements, is described elsewhere [6]. Here it is only noted that, in the sensor employed, the wires act both as a heat source producing time-dependent temperature fields within the material, and as thermometers, registering the temporal resistance change and thus their temperature rise. In order to eliminate end effects, two 5 μm diameter wires differing only in length are employed. In the specific case of measurements of the thermal conductivity of solids [6], in order to minimize contact resistance between the wire sensor and the solid, the wire sensor is placed inside a flat layer of soft silicone paste, which in turn is squeezed between two blocks of the solid. A very thin Kapton film between the soft silicone paste and the solid blocks, ensures the sensor's ease of assembly. Heat is transferred from the wire via the silicone paste and the Kapton film, to the solid. During a single run, 1,000 temperature versus time points are registered usually from 20 μs up to 10 s, with a very accurate bridge. In the technique there are five unknown parameters:

- the thickness of the paste (which, in the new sensor, is set exactly equal to 1 mm by the use of steel spacers [6])
- the paste's thermal conductivity and (density × specific heat capacity) product, and
- the solid's thermal conductivity and (density × specific heat capacity) product.

The parameters concerning the paste properties are obtained from measurements at short times (20 μs to 0.3 s). Having acquired those, the parameters related to the solid can be obtained from measurements at longer times (0.3 s to 10 s).

The COMSOL Multiphysics V.3.2b finite-element package is employed to fully describe the complete geometry of the sensor. The COMSOL package has the advantage that its mesh can consist of either triangular or quadrilateral elements. This allows precise modeling of the sensor, i.e., the wire, the silicone paste, the Kapton film (negligible effect), and the solid, resulting in perfect agreement between the experimental points and the calculated temperature versus time curve from 20 μs to the last time measurement. Hence, full advantage of the whole temperature versus time curve is obtained, as will be seen in the figures of this article.

3 Validation of Technique

As already discussed elsewhere [6], an advantage of the proposed configuration is that it can also be employed to measure the thermal conductivity of fluids. Liquid toluene has been proposed by the Subcommittee on Transport Properties of the International Union of Pure and Applied Chemistry as a standard thermal-conductivity liquid with an uncertainty of 0.6 % [11].

In this case, the two 25-μm diameter wires in their support were placed in toluene at 302 K and 1,000 temperature versus time points were obtained over a period of 1 s. In order to calculate the thermal conductivity of toluene, the COMSOL package was employed, but instead of the properties of the silicone layer, the Kapton film, and the solid, the properties of liquid toluene were used. In Fig. 1 the temperature rise versus the logarithm of time is shown. The thermal-conductivity value obtained from the superimposition of the COMSOL calculated values and the experimental ones deviates by 0.4 %.

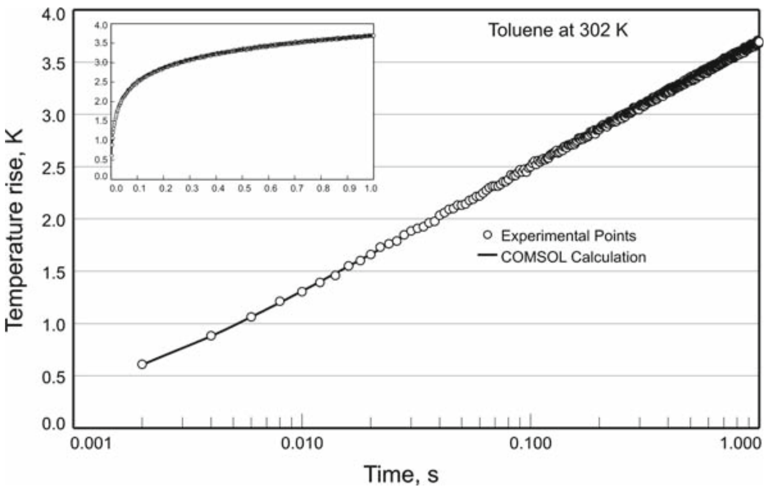

Fig. 1 Temperature rise as a function of time of toluene at 302 K

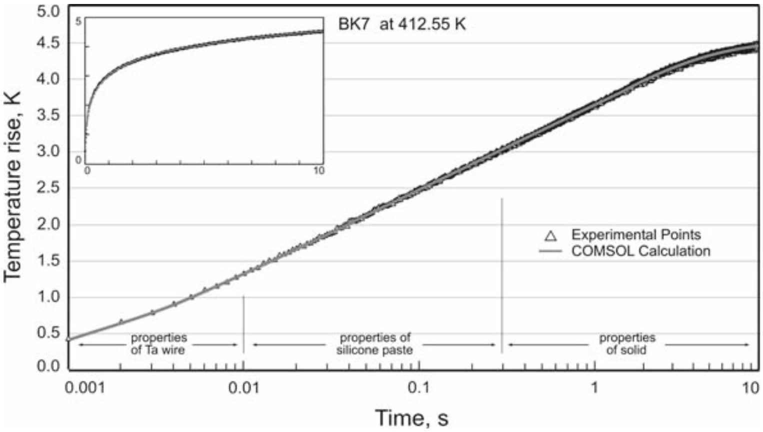

Fig. 2 Temperature rise as a function of time of BK7 at 412.55 K

Figure 2 shows a typical run of BK7 at 412.55 K. One thousand measurements between 0.001 s and 10 s are shown. The first part of the curve is related to the properties of the tantalum wire, the second part refers to the silicone paste, and the last part to the properties of the solid. The full agreement of the COMSOL calculated values with the experimental temperature rise values, over five orders of magnitude in time, is observed. Thus, the heat transfer model developed for the description of the hot-wire sensor is entirely consistent with the practical operation of the sensor over a time range of five orders of magnitude as the heat pulse transmits through four different materials. Following the uncertainty analysis described elsewhere [6], it is possible to assert that the uncertainty in the thermal conductivity of the solid determined by this technique is better than 1 %.

4 Results and Discussion

The blocks of PMMA investigated in this article, produced by casting and supplied by Degussa Rohm Plexiglas GmbH, were also made available to our laboratory by PTB. Their density was found by weighing them and determining their volume, equal to 1,200 kg $\cdot$ m^{-3} at 293.15 K. Further properties of this specific material can be found in the literature [8]. The two samples of BK7 employed in this article were manufactured and supplied by Schott AG, and were also made available to our laboratory by PTB. Their density was found by weighing them and determining their volume, equal to 2,504 kg $\cdot$ m^{-3} at 293.15 K. Further properties of this specific material can also be found in the literature [9]. Finally, the blocks of Pyrex 7740 were supplied by Anter Corporation, Pittsburgh, PA, USA. Their density was found by weighing them and determining their volume, equal to 2,227 kg $\cdot$ m^{-3} at 293.15 K.

The present measurements of the thermal conductivity, λ, of the three solids are shown in Table 1. The thermal conductivity, λ(W $\cdot$ m^{-1} $\cdot$ K^{-1}), values shown in

Table 1 Measured properties of solids as a function of temperature

T(K)	$\lambda(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$	$\Delta\lambda^{a}(\%)$
PMMA		
314.61	0.1920	−0.11
324.32	0.1940	−0.10
333.89	0.1970	0.43
343.94	0.1980	−0.10
353.67	0.2000	−0.10
BK7		
315.87	1.080	−0.67
333.91	1.120	0.90
353.15	1.135	0.42
372.70	1.146	−0.08
392.40	1.155	−0.38
412.55	1.164	−0.34
433.04	1.178	0.49
Pyrex 7740		
314.44	1.150	−0.18
333.70	1.170	−0.52
353.55	1.210	0.76
372.87	1.230	0.42
393.26	1.250	−0.02
413.02	1.270	−0.39
432.81	1.300	0.03

[a] $\Delta\lambda = 100 \times (\lambda_{\mathrm{exp}} - \lambda_{\mathrm{fit}})/\lambda_{\mathrm{fit}}$

Table 1 were fitted as a function of the absolute temperature T (K) with an equation,

$$\lambda = \lambda(298.15\ \mathrm{K}) \sum_i a_i \left(\frac{T}{298.15}\right)^i, \tag{1}$$

where the coefficients a_i and the values of λ (298.15 K) are shown in Table 2. The maximum deviations of the experimental points, presented in Table 1, from the above equation, are 0.43 %, 0.90 %, and 0.76 % for PMMA, BK7, and Pyrex 7740, respectively. At the 95 % confidence level, the standard deviations of the thermal conductivity measurements of PMMA, BK7, and Pyrex 7740 are 0.42 %, 1.0 %, and 0.8 %, respectively, which are well within the standard uncertainty of the technique.

Figures 3–5 show the present thermal-conductivity measurements and their percentage deviations from the values calculated by Eq. 1. In the same figures, our previous measurements on the same samples of PMMA, BK7 [5], and Pyrex 774 [4], as well as measurements of other investigators, are also shown. We have chosen not to present here the values of investigators who report only one measurement and that at “room temperature” quoting no exact reference temperature, and no uncertainty in their measurements. Also, measurements presented only in graphical form have not been included. In all three cases, our previous measurements [4,5] performed with an uncertainty of 1.5 % agree very well with the present measurements performed with

Table 2 Coefficients and standard deviation of Eq. 1

	PMMA	BK7	Pyrex 7740
λ(298.15 K) ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)	0.1889	1.0617	1.1318
$a_0(-)$	0.6771	0.11921	0.6718
$a_1(-)$	0.3226	1.32874	0.3282
$a_2(-)$	0	−0.44795	0
$\sigma(-)$	0.0004	0.006	0.005
σ(%)95 % confidence level	±0.42	±1.0	±0.8

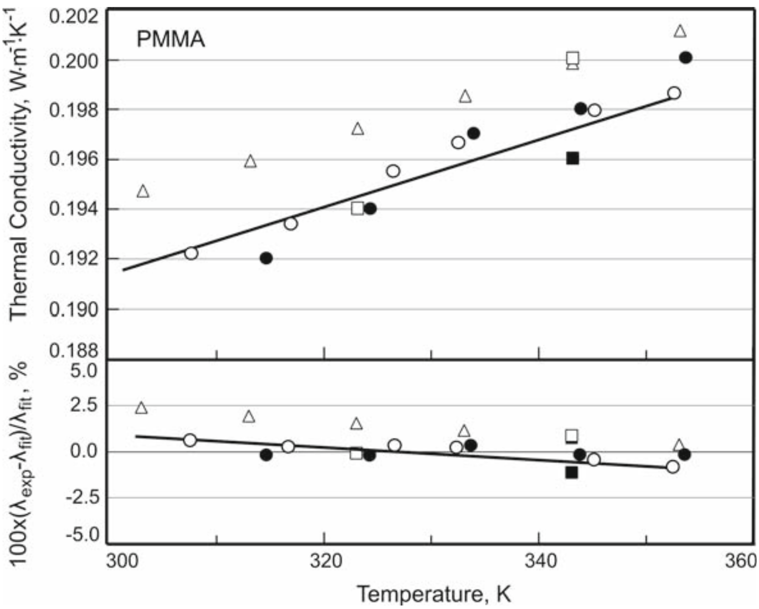

Fig. 3 Thermal-conductivity measurements of PMMA as a function of temperature, and their percentage deviations from the values calculated by Eq. 1: ●, present work; ○, Assael et al. [5]; –, Tye and Salmon [7]; △, Rudtsch and Hammerschmidt [8]: ■, guarded hot-plate data; □, transient plane source data; Boumaza and Redgrove [12]

the lower uncertainty of 1 %. Only at one temperature in BK7, the measurements are just over the mutual uncertainties of the two instruments.

In 2003, Tye and Salmon [7], after a very careful investigation aiming to produce a candidate thermal-conductivity reference polymer, proposed an equation for the thermal conductivity of PMMA with an uncertainty of 1 % at the 95 % confidence level. The deviations of this equation, also shown in Fig. 3, from present values calculated by Eq. 1 are in excellent agreement with the present measurements.

In 2004, Rudtsch and Hammerschmidt [8], also aiming to propose a thermal conductivity reference material candidate, coordinated in PTB an intercomparison project for PMMA involving 17 European laboratories. Unfortunately the thermal conductivity values produced even at 30 °C ranged from 0.16 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ to 0.21 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$.

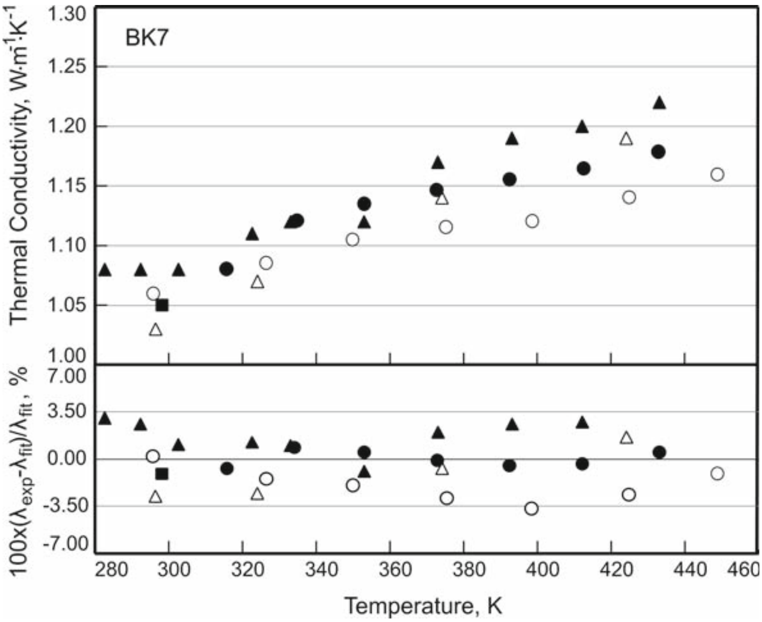

Fig. 4 Thermal-conductivity measurements of BK7 as a function of temperature, and their percentage deviations from the values calculated by Eq. 1: ●, present work; ○ Assael et al. [5]; ■, Kubicar et al. [15]; ▲, double-plate data; △, laser-flash data; Ebert [16]

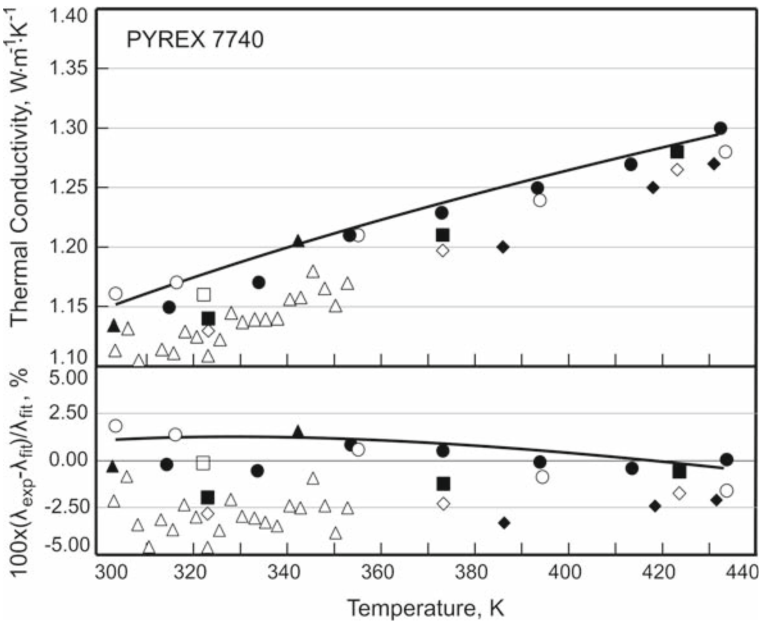

Fig. 5 Thermal-conductivity measurements of Pyrex 7740 as a function of temperature, and their percentage deviations from the values calculated by Eq. 1: ●, present work; ○, Assael et al. [5]; –, CRM 039 [10]; ◇, Hulstrom et al. [17]; ■, Powell et al. [18]; ▲, Milano et al. [19]; △, Matsumoto and Ono [20]; ◆, Pillai and George [21]; □, Log and Metallinov [22]

It was argued that the most probable reason for this discrepancy was the improperly treated effect of contact resistance. In order to prove independently that the thermal contact resistance was adequately taken into account, in the same article, values obtained at PTB by two different methods (guarded hot plate, transient hot strip) were also reported [8]. The deviations of these values, shown in Fig. 3, from the present values calculated by Eq. 1, are well within the mutual uncertainty of the instruments.

There are a few other investigators who have measured the thermal conductivity of PMMA. Boumaza and Redgrove in 2003 [12] employed a transient plane-source (Gustaffson probe) and a guarded hot-plate instrument to investigate the thermal conductivity of PMMA with temperature. Their results, characterized by 5 % reproducibility, shown in Fig. 3, agree very well with the present measurements. We should finally mention the very interesting comparisons of various methods of measurements employed for the thermal conductivity of PMMA, done by Kubicar and Bohac [13] and Lockmuller et al. [14].

In the case of BK7, Rurdtsch et al. in 2004 [9], aiming to propose a thermal-conductivity reference-material candidate, coordinated in PTB an intercomparison project involving 11 laboratories. The results for the thermal conductivity showed typically an 8 % spread in the low-temperature range, while at higher temperatures this rose to 40 %. It was thus concluded that further investigation was necessary.

The only other data for the thermal conductivity of BK7 available to our knowledge are the measurements of Kubicar et al. in 2005 [15] and of Ebert [16] in 2002. Kubicar et al. [15] employed a pulse transient method with a quoted uncertainty of 5 %. The deviation of their values, shown in Fig. 4, from that calculated by Eq. 1, is well within the mutual uncertainties. Ebert [16] employed a double-plate instrument and a laser-flash instrument. No uncertainty was specified. His results for both methods, shown in Fig. 4, deviate by up to 3 % from the values calculated by Eq. 1.

Pyrex 7740 is a well-known borosilicate glass that has been in use for many years as a reference material. In September 1990, the European Community Bureau of Reference (BCR) finally issued a certificate for Pyrex glass material [10]. This certified material is now available as CRM 039 from the European Union Institute of Reference Materials and Measurements (IRRM) in Geel, Belgium. However, it should be noted that this certificate refers only to a Pyrex glass and not specifically the 7740 grade. These certified values, characterized by a 1.7 % standard deviation at the 95 % confidence level, are presented in Fig. 5. As can be seen, the present measurements are in excellent agreement with these values.

In Fig. 5, also, the recommended values of Hulstrom et al. in 1988 [17], from round-robin tests, characterized by a 10.3 % standard deviation at the 95 % confidence level, are shown, together with the previously reported values of Powell et al. in 1966 [18], of 5 % maximum uncertainty. The agreement with all these sets is excellent. More recent values are also included in the same figure:

(a) The measurements of Milano et al. in 1991 [19] were performed in a transient double-plate instrument. No uncertainty is quoted, but the measurements deviate by <1 % from the present values calculated by Eq. 1.
(b) The measurements of Matsumoto and Ono in 1991 [20] were performed by applying a perpendicular heat flow to a thin-plate sample. Although the technique is

described as an absolute technique, no uncertainty is quoted. These values show a spread of 2.5 %, and differ by up to 5 % from the present values calculated by Eq. 1.

(c) The measurements of Pillai and George in 1991 [21] were performed in a steady-state axial heat-flow comparative instrument with an uncertainty of 2 %. The deviations of these measurements from the present values calculated by Eq. 1 are within the mutual uncertainties of the two instruments.

(d) The thermal-conductivity measurements of Log and Metallinov in 1992 [22], at 322.15 K, performed with the transient hot-strip method, and with a claimed uncertainty of 3 % (no confidence level was specified), are in excellent agreement with the present values calculated by Eq. 1.

From the above presentation it is apparent that the present set of thermal-conductivity values agree well with the previous sets of measurements, while at the same time exhibiting a smaller uncertainty.

5 Conclusions

New thermal-conductivity measurements of lower uncertainty for PMMA, BK7, and Pyrex 7740 up to 450 K are presented. The technique employed is a refined transient hot-wire technique based on a full theoretical model with equations solved by finite elements for the exact geometry. At the 95 % confidence level, the standard deviations of the thermal-conductivity measurements of PMMA, BK7, and Pyrex 7740 are 0.47 %, 1.0 %, and 0.8 %, respectively. The technique is absolute and is characterized by an uncertainty of <1 %.

Acknowledgment The authors would like to thank Dr. Ulf Hammerschmidt in Physikalisch-Technishe Bundesanstalt (PTB) for his help in providing the solid samples.

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