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A New Method for the Determination of the Specific Heat Capacity Using Laser-Flash Calorimetry Down to 77 K

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Abstract A new method for evaluation of the specific heat capacity in the temperature regime between 77 K and 330 K using laser-flash calorimetry is presented. Usually, laser-flash calorimetry is accomplished by performing an additional laser-flash measurement on a reference specimen with a known specific heat capacity and by comparing the maximum rear-side temperatures rises. In this study, the calibration is achieved by comparison of the rear-side temperature rise to specific-heat-capacity data determined by other methods in an adjacent temperature regime. Subsequently, the thus yielded proportional factor is used for the evaluation of the specific heat capacity from laser-flash measurements at temperatures where no specific-heat-capacity data are available. The reliability of this method is shown by performing measurements on a material with known specific heat capacity, aluminum oxide. Furthermore, the specific heat capacity and thermal conductivity of borosilicate crown glass (BK7) was determined experimentally.

Keywords Aluminum oxide · BK7 glass · Laser-flash · Low temperature · Specific heat capacity

1 Introduction

The laser-flash method is a standard method for the determination of the thermal diffusivity of solids [1]. One side of a thin specimen is heated by a short laser pulse, and the subsequent temperature rise at the opposite side of the specimen is recorded as a function of time. As the temperature rise is usually measured contact-free using an

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infrared detector, this method is mostly used at temperatures above room temperature due to the rapidly declining sensitivity of infrared detectors at lower temperatures. In our study, we are using the temperature-dependent resistance of a thin gold strip which is sputtered onto the rear side of the specimen as an alternative temperature probe below room temperature [2,3].

Using the thermal diffusivity which was determined by the laser-flash method, the thermal conductivity can be calculated by multiplying the thermal diffusivity $a(T)$, the specific heat capacity $c_p(T)$, and the density $\rho(T)$ of the specimen

$$\lambda(T) = a(T)c_p(T)\rho(T) \tag{1}$$

Besides the thermal diffusivity, the specific heat capacity can also be obtained by the laser-flash experiment, which is also known as laser-flash calorimetry [1]. Not only the absolute rear-side temperature rise but also the amount of energy absorbed by the specimen must be known for calculation of the specific heat capacity. As the latter can hardly be determined experimentally, usually measurements on a reference material with known specific heat capacity and similar thermophysical properties are performed [4,5]. It is of great importance that not only the temperature of both specimens, the reference and sample material, is the same during the measurement but also the amount of energy that is absorbed by the specimens. However, one big problem in performing laser-flash calorimetry with a reference specimen is the fact that even when the surfaces of both specimens are coated with graphite, the spectral emissivities of the different materials are mostly unequal, for example, due to differences in surface roughness [6]. This problem could be solved using a calibrated surface, the so-called absorption disk, which is a thin layer of glassy carbon glued to the front side of the specimen [7]. One disadvantage of this method is the contact resistance between the absorption disk and the specimen which changes every time the absorption disk is glued to another specimen.

A new approach to determine the specific heat capacity over a wide temperature range with the laser-flash technique is to calibrate the maximum rear-side temperature rise using an averaged temperature-independent proportional factor. This factor is calculated by comparison of the maximum rear-side temperature rise to specific-heat-capacity data which is already available in an adjacent temperature range. Afterward, this calibration can be extrapolated to temperatures where no specific-heat-capacity data are available, but laser-flash measurements can be performed. An advantage of this method is that there is no need to perform laser-flash measurements on a reference specimen. This method is very promising as the gold strip temperature probe used in this study is quite suitable for this evaluation method, especially at low temperatures. In comparison to infrared detectors, the detector signal height during the laser-flash measurement is not influenced by environmental factors such as the different infrared optical properties of the specimen and reference.

Thus, the objective of this study is to test the method described above with our low-temperature laser-flash apparatus, to gather values for the specific heat capacity between 77 K and 300 K.

2 Experimental Setup

2.1 Low-Temperature Laser-Flash Device

All measurements were performed in the low-temperature laser-flash setup which was already presented in an earlier study[3]. The specimen is positioned in a cryostat which is surrounded by liquid nitrogen and filled with a nitrogen atmosphere. The temperature of the specimen is monitored with a Pt 100 resistance thermometer and can be adjusted between 77 K and 330 K. A Nd:YAG laser with a wavelength of 1064 nm, a beam diameter of approximately 15 mm, pulse lengths between 0.3 ms and 20 ms, and accordingly pulse energies between 1 J and 20 J is used. A photodiode detects the starting time and shape of the laser pulse and starts the data acquisition which is performed by a digital storage oscilloscope. A thin gold strip which is sputtered onto the rear side of the specimen is used as a temperature probe for the laser-flash experiment. The temperature-dependent resistance change of this gold strip is measured using a Kelvin bridge circuit in contrary to Ref. [3] where a simple Wheatstone bridge circuit was used. An advantage of the Kelvin bridge is that this bridge circuit is especially suitable for the measurement of small resistance changes as the resistances of the feed lines can be neglected [8].

Before each measurement, the Kelvin bridge is adjusted to zero so that the change of the bridge voltage, ΔU_{B}, is proportional to the resistance change of the gold strip, ΔR_{GS}. In the entire temperature range during our measurements, this resistance change is linearly proportional to the rear-side temperature rise ΔT,

$$\Delta U_{\mathrm{B}} \propto \Delta T. \tag{2}$$

To prevent the specimen from being heated too much by the laser pulse during the low-temperature measurements, calibrated infrared filters were used to weaken the laser pulse. By performing infrared optical measurements using an FTIR spectrometer, the transmittance of the filters at the laser pulse wavelength was determined. With the known transmittance of the filters, the detector signal can be scaled to the signal height in case of an unweakened laser pulse. For example, at 77 K only 5 % of the pulse energy which is used for measurements at 300 K is needed to yield a similarly strong laser-flash signal.

2.2 Temperature Modulated Differential Scanning Calorimetry (MDSC)

For determination of the specific heat capacity in the temperature range from 190 K to 330 K, the MDSC technique was used. In this method, the specimen and a reference specimen are positioned in crucibles and are successively exposed to the same temperature program in an oven [9]. An empty crucible is exposed to the same temperature variation, and the temperature difference between the empty crucible and the crucible filled with a specimen is determined as a function of time. As the temperature difference can be correlated directly to a heat flow, the specific heat capacity of the specimen can be determined by calibration with the known specific heat capacity of the

reference specimen. In order to yield a higher resolution, the MDSC method utilizes a temperature regime consisting of a linear and a sinusoidally oscillating portion.

The apparatus we used was the Q2000 by TA Instruments Inc. which enables the determination of the specific heat capacity in the temperature range between 190 K and 800 K. All measurements were performed in aluminum crucibles and a dynamic helium atmosphere to minimize the thermal contact resistance between the crucibles and the measurement cell. As a reference specimen, a sapphire disc was used which was supplied by the manufacturer of the MDSC apparatus and is thus a secondary standard. The relative measurement uncertainty of the thus determined specific-heat-capacity values was 5 %.

3 Analysis of Laser-Flash Measurements

3.1 Determination of the Thermal Diffusivity

In order to determine the thermal diffusivity from a laser-flash detector signal, a mathematical model is fitted to the experimentally determined relative rear-side temperature rise. Thus, the entire measurement signal is used for evaluation of the thermal diffusivity. The mathematical model we are using does not only incorporate the influence of radiative heat losses from the surfaces of the specimen but also the effect of finite pulse lengths [10,11]. An estimation of the measurement uncertainties according to GUM yields a relative measurement uncertainty of 5 % [12]. This estimation includes, for example, uncertainties in the determination of the thickness of the specimen or inaccuracies due to the nonlinear fit.

3.2 Determination of the Specific Heat Capacity

According to Parker et al. [1], the specific heat capacity c_p can be calculated from laser-flash measurements using the equation

$$c_p = \frac{Q}{\rho d A} \frac{1}{\Delta T_{\max}} \tag{3}$$

with the amount of energy absorbed by the specimen, Q, the thickness d of the specimen, the surface area A of the specimen, and the maximum rear-side temperature rise $\Delta T_{\max}$.

Equation 3 is only valid for the adiabatic case which means it is assumed that there are no radiative heat losses from the specimen surfaces. However, usually there are temperature-dependent radiative heat losses which are also dependent on the thermal diffusivity. Hence, a heat loss correction must be performed on the experimentally determined laser-flash signal. In our study, a heat loss correction according to Cowan was used which assumes heat losses following an exponential decay [10]. In Fig. 1, an example for the heat loss correction of a measured laser-flash signal is shown. Thus, the maximum bridge voltage $\Delta \widetilde{U}_{\mathrm{B,max}}$ for the theoretical adiabatic case can be determined. This quantity is subsequently divided by the transmittance of the optical filter used in the measurement to yield the scaled maximum bridge voltage $\Delta U_{\mathrm{B,max}}$.

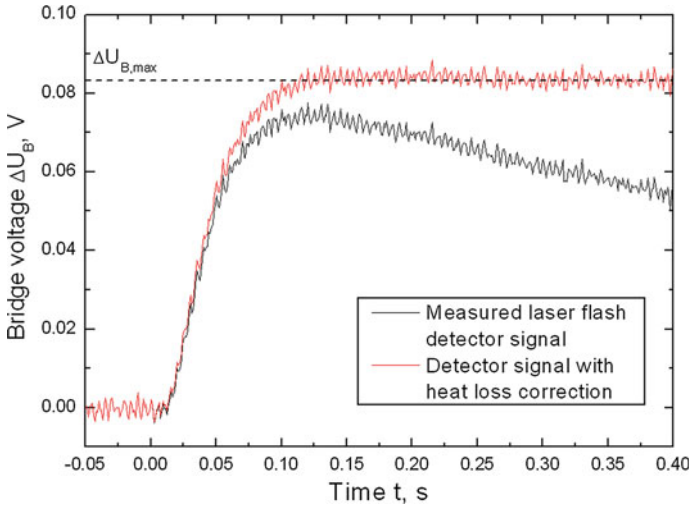

Fig. 1 Heat-loss correction of an experimentally determined laser-flash curve according to Cowan [10]

Comparing Eqs. 2 and 3, it is obvious that $c_p(T) \propto Q(\Delta U_{\mathrm{B,max}}(T))^{-1}$.

Assuming that the emissivity of the graphite coating on the front side of the specimen is hardly temperature dependent, Q is regarded as temperature independent as the pulse length used in the experiment is the same for each measurement temperature. Thus, it can be presumed that

$$c_p(T) = \bar{A}\left(\Delta U_{\mathrm{B,max}}(T)\right)^{-1} \tag{4}$$

with a temperature-independent, mean proportional factor $\bar{A}$.

In order to yield this proportional factor, the inverse of the maximum bridge voltage, $(\Delta U_{\mathrm{B,max}})^{-1}$, is compared to already available specific-heat-capacity data for the material under investigation. The averaged proportional factor is determined over the whole temperature range where data for the specific heat capacity are available to minimize the influence of stray data points. Assuming that this mean proportional factor remains temperature independent, the specific heat capacity of the specimen can be obtained from the maximum bridge voltage at temperatures where no specific-heat-capacity data are available. In our case, we use the mean proportional factor for the determination of the specific heat capacity down to 77 K as only measurements down to 190 K are possible using our MDSC apparatus.

4 Specimens

4.1 Aluminum Oxide (Al_2O_3)

Aluminum oxide is a frequently used reference material which is already well-documented. Specific-heat-capacity values are available in the literature down to

lowest temperatures [13]. The specimen we used was a non-porous specimen with a thickness of 1.027 mm, a diameter of 13 mm, and a determined density of $\rho = (3761 \pm 113)\,\mathrm{kg \cdot m^{-3}}$. Energy dispersive X-ray (EDX) measurements indicate a purity of the aluminum specimen of at least 98 %. A gold strip with a width of approximately 400 µm and a height of <100 nm was sputtered onto the rear side of the specimen using magnetron sputtering. For easier contacting of the gold strip with the spring-loaded contact pins, two contact pads were applied on the specimen using conductive silver varnish. Afterwards, the specimen was exposed to temperature cycling between 290 K and 350 K to induce curing of the gold strip. In the examined temperature region between 77 K and 330 K, the resistance of the cured gold strip at a temperature T is given by the relation $R(T) = R_0(1 + \alpha T)$ with $R_0 = 25.36\,\Omega$ and the temperature coefficient $\alpha = 1.23 \times 10^{-3}\,\mathrm{K^{-1}}$. The front side of the specimen was coated with a thin layer of graphite using graphite spray for better absorption of the laser pulse energy.

4.2 Borosilicate Crown Glass (BK7)

BK7 is a standard glass for optical applications and has in the past been used for an intercomparison test on thermophysical properties initiated by the Thermophysics Working Group [14]. Although there are already several publications on thermophysical properties of BK7 glass, the specific heat capacity and thermal conductivity have never been determined experimentally before at temperatures below 190 K [3,15,16]. The thickness of the investigated specimen was 1.183 mm, the diameter was 20 mm, and the density was determined to be $\rho = (2460 \pm 74)\,\mathrm{kg \cdot m^{-3}}$. The preparation and curing of the gold strip and the contact pads was carried out analogous to the aluminum oxide specimen. Between 77 K and 330 K, the resistance of the gold strip follows the relation $R(T) = R_0(1 + \alpha T)$ with $R_0 = 94.92\,\Omega$ and the temperature coefficient $\alpha = 9.05 \times 10^{-4}\,\mathrm{K^{-1}}$. The front side of this specimen was also coated with graphite using graphite spray.

5 Results

5.1 Measurements on Aluminum Oxide (Al_2O_3)

The thermal diffusivity of the aluminum oxide specimen was determined experimentally in the temperature range between 77 K and 330 K using a 0.3 ms laser pulse. Figure 2 shows the thereby obtained results with a relative uncertainty of 5 %.

The specific heat capacity was measured between 190 K and 330 K by the MDSC technique. In order to perform the above-described method of calculating the specific heat capacity from the maximum temperature rise during the laser-flash experiment, the temperature dependence of the inverse of the maximum bridge voltage is depicted in comparison to the specific-heat-capacity values determined by MDSC measurements in Fig. 3. The mean proportional factor between the inverse of the maximum bridge voltage and the specific heat capacity was determined to be $\bar{A} = 6.40 \times 10^{-2}\,\mathrm{J \cdot V \cdot g^{-1} \cdot K^{-1}}$.

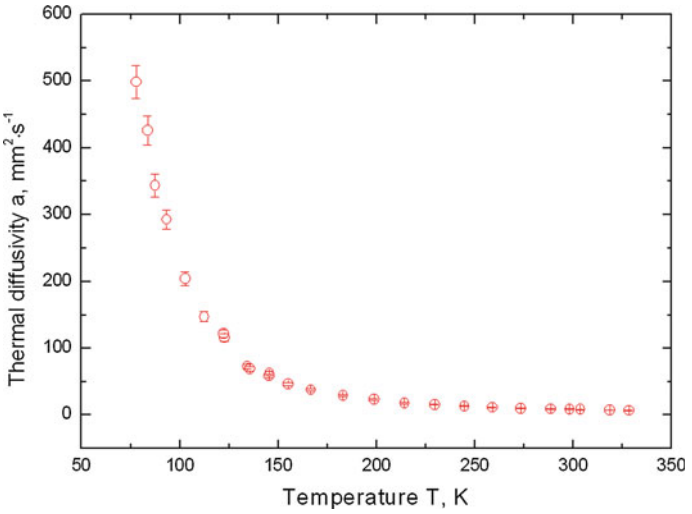

Fig. 2 Thermal diffusivity of aluminum oxide, determined by laser-flash method

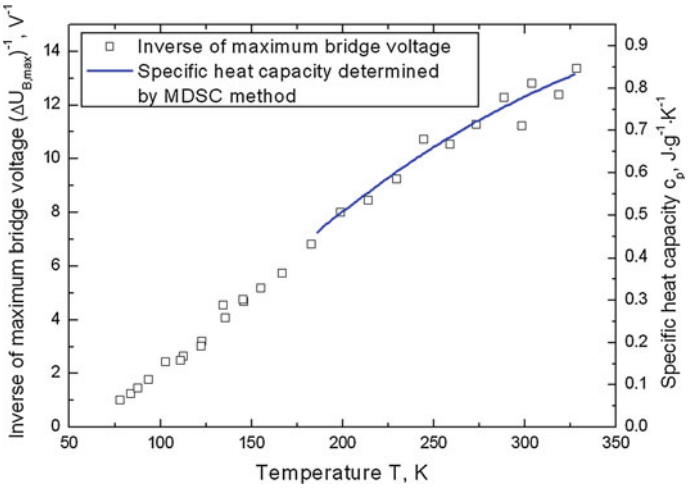

Fig. 3 Comparison of the temperature dependence of the inverse of the maximum bridge voltage during the laser-flash experiment and the experimentally determined specific heat capacity for the determination of the mean proportional factor

Finally, the specific heat capacity was calculated from all laser-flash curves down to 77 K using the mean proportional factor yielded by the calibration with MDSC results. The results of this calculation as well as the specific-heat-capacity values determined by the MDSC technique and literature data from Ditmars [13] are shown in Fig. 4. The relative uncertainty of the data determined by laser-flash calorimetry was estimated to be 10 %.

For a better comparison of the specific-heat-capacity values determined by laser-flash calorimetry to literature data, the relative deviation was calculated and is depicted

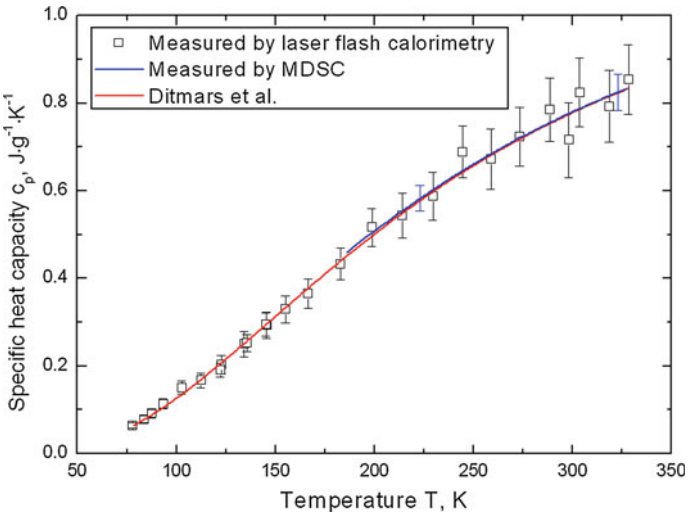

Fig. 4 Specific heat capacity of aluminum oxide, determined by MDSC technique and laser-flash calorimetry. Literature values were taken from Ditmars [13]

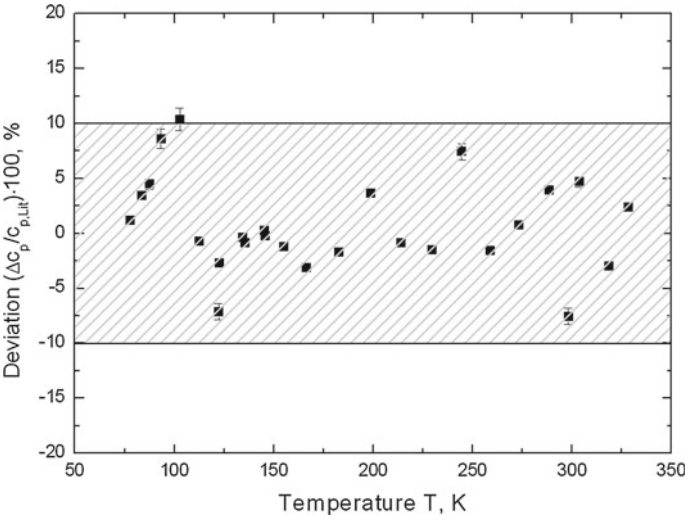

Fig. 5 Relative deviation of experimentally derived specific heat capacity determined by laser-flash calorimetry from literature data from Ditmars [13]

in Fig. 5. In the entire examined temperature region, the deviation of laser-flash calorimetry data from literature data is <10 % which can be seen as a proof for the reliability of our evaluation procedure.

Using Eq. 1, the thermal conductivity can be calculated. Figure 6 shows the temperature dependence of the thus yielded thermal conductivity with a relative uncertainty of 7.7 % and 11.6 %, depending on whether the specific heat capacity was determined by the MDSC method or laser-flash calorimetry.

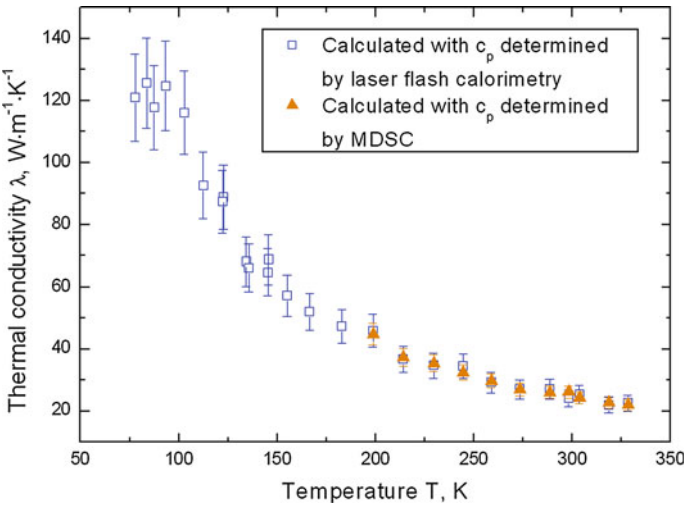

Fig. 6 Temperature dependence of the calculated thermal conductivity of aluminum oxide

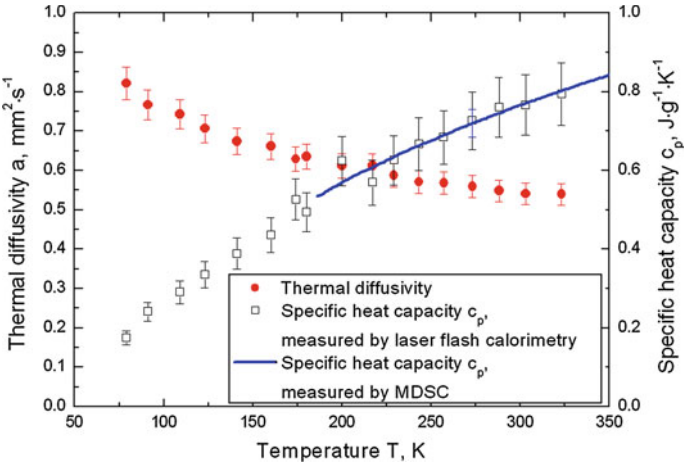

Fig. 7 Thermal diffusivity and specific heat capacity of BK7 glass, determined by laser-flash method, laser-flash calorimetry, and MDSC technique

5.2 Measurements on BK7 Glass

The thermal diffusivity of BK7 glass was determined experimentally using the laser-flash method with a laser pulse of 0.3 ms duration. The specific heat capacity was determined by the MDSC technique and by laser-flash calorimetry calibrated with the results from the MDSC measurements. The mean proportional factor was calculated to be $\bar{A} = 6.80 \times 10^{-2}\,\mathrm{J \cdot V \cdot g^{-1} \cdot K^{-1}}$. In Fig. 7, the derived thermal diffusivity and specific heat capacity are depicted.

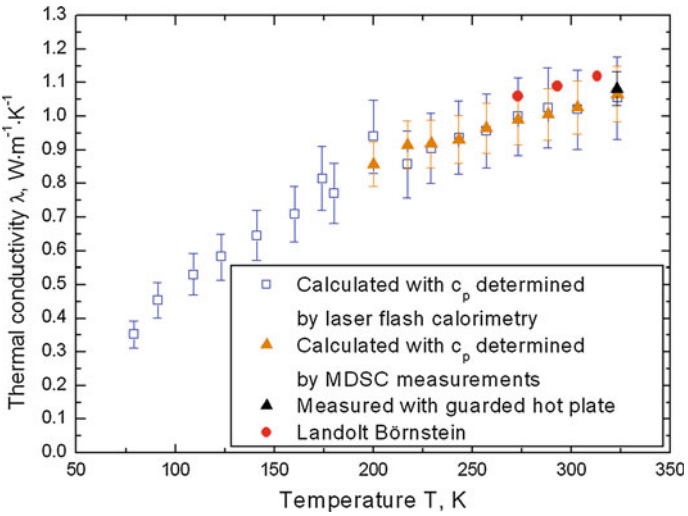

Fig. 8 Thermal conductivity of BK7 glass, calculated from MDSC and laser-flash measurements. Also shown is the thermal conductivity determined by a guarded hot-plate method as well as literature data taken from Hausen [14,17]

The thermal conductivity of BK7 glass was calculated using Eq. 1. Using the rule of the propagation of uncertainties, the relative uncertainties of the thermal conductivity are 7.7 % and 11.6 % for the specific heat capacity measured by the MDSC method and laser-flash calorimetry, respectively. The results as well as the literature data in the temperature range from 270 K and 310 K are shown in Fig. 8 [17]. Also depicted is a value determined by a stationary measurement using a guarded hot-plate apparatus [14].

Within the estimated measurement uncertainties, the thermal conductivity determined by laser-flash measurements and the literature data coincide.

6 Conclusion

A new experimental method for the determination of the specific heat capacity from laser-flash measurements was presented. This procedure uses known values for the specific heat capacity in a limited temperature range to calibrate the laser-flash signal at lower temperatures. Thus, the specific heat capacity of aluminum oxide and BK7 glass was determined down to 77 K using laser-flash calorimetry. Comparison with literature data of the specific heat capacity of aluminum oxide showed a relative deviation of our results of <10 % from literature values which is already quite satisfactory and can be seen as a demonstration of the functionality of the new method. Using the specific heat capacity and the thermal diffusivity which was also determined by laser-flash measurements, the thermal conductivity could be calculated in a temperature range between 77 K and 330 K. Until now, no experimentally determined values of the thermal conductivity and specific heat capacity of BK7 glass have been published for temperatures below 190 K [3].

An extension of the experimentally accessible temperature range down to lower temperatures is planned using a cold head device with which laser-flash measurements down to at least 30 K can be performed. Additionally, measurements on an electrically conductive specimen using intrinsic thermocouples are planned.

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