Int J Thermophys (2010) 31:355–373
DOI 10.1007/s10765-010-0710-3

Pyroceram 9606, A Certified Ceramic Reference Material For High-Temperature Thermal Transport Properties: Part 2—Certification Measurements

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Received: 11 January 2010 / Accepted: 20 January 2010 / Published online: 13 April 2010

Abstract Following the characterization of the batch of Pyroceram 9606 material, a number of the partners in the European Commission (EC) supported program carried out certification measurements of thermal conductivity and thermal diffusivity. Six laboratories undertook thermal-diffusivity measurements using either the flash or the modulated beam methods. Eight laboratories measured the thermal conductivity, using either the steady-state guarded-hot-plate method or one of the transient hot-wire methods. Results from each series of measurements were provided in a standard format as an aid to simplify the statistical analysis of the data. The results were corrected to the nominal measured temperature and for change in dimension, analyzed separately, and presented in a standard format. Outliers were identified and rejected where appropriate, based on both statistical and technical evidences. The individual data sets were combined, and the grand mean data for each property analyzed further to provide the certified values together with their uncertainty limits. Finally, using the specific heat capacity and density values obtained from the characterization tests, values of thermal conductivity were calculated from the measured thermal diffusivity. The difference between the calculated and certified values is less than 2.7 %, which is well within the uncertainty limit assigned for the certified thermal property values.

Keywords Certified reference material · High temperatures · Material characterization · Pyroceram 9606 · Thermal conductivity · Thermal diffusivity · Thermal properties

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1 Introduction

Pyroceram 9606 has been used for many years as an *uncertified* reference material for thermal conductivity following recommendations based on the critical evaluation of data by the Thermophysical Properties Research Center (TPRC, now CINDAS, Purdue University, West Lafayette, Indiana, USA). While many workers have shown that its thermal properties appeared to be stable and reproducible, no organized programs of measurements of its appropriate properties appear to have been carried out to verify these attributes (see Part 1 [1]).

The results of the comprehensive characterization described in Part I of this study illustrate conclusively that the material is not only stable and reproducible but also isotropic. These three attributes are the major requirements for a certified reference material for high temperature use. This second part of the study describes the measurements and analysis of results that were undertaken to determine the final certified values of thermal conductivity and thermal diffusivity of a batch of Pyroceram 9606. In addition, the inclusion of thermal expansion, specific heat capacity, and thermal transmission properties confirm the validity of deriving thermal conductivity values from thermal-diffusivity measurements for materials in which heat transmission is predominantly due to conduction.

2 Participants, Specimen Selection, and Program

Tables 1 and 2 contain details of the individual participants involved in the different certification measurements of thermal conductivity and thermal diffusivity. The tables also include details of the specimens required by each partner for their particular methods and apparatus. Further details of the organizations involved are given in Table 1 of Part I [1].

Because the characterization study showed that the anisotropy of the material was negligible, it was decided to cut the specimens for all thermal-conductivity and thermal-diffusivity measurements in the same orientation from the individual blocks. For thermal conductivity, each participant received one set of specimens; and for thermal diffusivity, each partner received four specimens. Each specimen was required to be measured twice in separate runs. To minimize possible uncertainties due to the effect of different coatings applied to the surfaces of the thermal-diffusivity specimens, two of the four distributed specimens were identically coated with tungsten by KE. To determine the effects of different coatings, the participants coated the other two specimens using their normal coating technique.

Wherever possible, it was decided to measure at temperatures as close as possible to the nominal temperatures of 25 °C, 50 °C, and 100 to 1000 °C in increasing steps of 100 °C followed by measurements on cooling. The repeat measurements had to be carried out by removing the specimen and reassembling in the apparatus. After discussing the results from the participants, it was also decided that some laboratories would exchange their specimens and repeat the measurements. This would be useful to determine whether any observed small systematic discrepancies are caused by inhomogeneity of the material or by systematic differences in the measurements.

Table 1 Details of thermal conductivity participants and specimens

Partner	Specimen sizes			Specimen code
	Diam or square (mm)	Thickness (mm)		
Guarded hot plates				
NPL1	150 dia	50		TC17.1, TC17.2, TC17.3, TC17.4
PTB	100 dia	25		TC14.3, TC14.4, TC19.1, TC19.2
KE	200 dia	25		TC14.1, TC14.2, TC15.1, TC15.2 TC16.1, TC16.2
FIW	250 × 250	25		TC12.1, TC13.1, TC13.2, TC18.1, TC18.2, TC18.3
NIST	70	10		TC6.64
	Length (mm)	Width (mm)	Depth (mm)	
Hot wire or hot strip				
NPL	230	90	50	HW3.1, HW4.1
CERAM	230	90	50	HW9.1, HW11.1
ARCS	230	90	50	HW7.1, HW8.1
PTB	100	30	15	HW6.1, HW6.2
Corus	230	90	50	HW10.1, HW11.1

Explanation of specimen code: e.g., TC17.1, *TC* thermal conductivity (by ghp), 17.1 is the first specimen from block 17. *HW* code for hot wire or strip specimens

Table 2 Details of thermal-diffusivity participants and specimens

Partner	Specimen sizes		Specimen code	Coating
	Diameter (mm)	Thickness (mm)		
NPL	12	1.5	TD1.42, TD1.43	Tungsten
NPL	12	1.5	TD1.44, TD1.45	NPL coating
NPL	12.5	1.5	TD2.46, TD2.47	Tungsten
NPL	12.5	1.5	TD2.48, TD2.49	NPL coating
ARCS	10	1.5	TD3.51, TD3.53	Tungsten
ARCS	10	1.5	TD3.50, TD3.52	OFZS Coating
LNE	10	1.5	TD4.54, TD4.56	Tungsten
LNE	10	1.5	TD4.55, TD4.57	LNE coating
KE	8	1.5	TD5.58, TD5.59	Tungsten
KE	8	1.5	TD5.60, TD5.61	KE coating
INSA	20	5.0	TD1.66, TD1.67	Tungsten
INSA	20	5.0	TD1.68, TD1.69	INSA coating
NETZSCH	12.5	1.5	TD2.70, TD2.71	Tungsten
NETZSCH	12.5	1.5	TD2.72, TD2.73	Netzsch coating

Specimen code example TD3.51: *TD* thermal diffusivity and 3.51 is the 51st specimen from the 3rd block

In some cases, the certification specimens were prepared from the same six blocks used for the characterization study. However, an additional eleven blocks were required to provide all the required specimens. The majority of the specimens were prepared and distributed by Ceram and NPL; however, KE was responsible for coating with tungsten and distributing specimen pairs for the thermal-diffusivity measurements.

Five specimen sets were prepared for thermal-conductivity measurements by the guarded-hot-plate (ghp) technique. In most cases as the blocks of raw material were too small to make up a complete test specimen, several individual pieces of ceramic were required. Three new specimen pairs to measure the thermal conductivity by the hot-wire technique were prepared for the following laboratories: Ceram, ARCS, and PTB. A single additional specimen was prepared for Corus since a previous specimen had cracked. NPL and SFC performed hot-wire measurements using specimens that had been prepared for the characterization phase.

Twenty-eight specimens were prepared for thermal-diffusivity testing by cutting cylindrical pieces using a core drill of the appropriate diameter or by a continuous rim diamond-cutting wheel. Specimens were sliced from the cylinders to form disks and ground flat to better than 0.05 mm. Five pairs were sent to KE for surface coating with tungsten using a special mounting device so that all specimens could be positioned in the same plane in the vacuum chamber of an electron beam welding system. The disk specimens were weighed, placed in the holder, and tungsten deposited on one surface. The deposition time had been optimized by preliminary tests to ensure that a layer of thickness of $(2 \pm 0.6)\,\mu$m was achieved. This coating thickness is sufficient to ensure that the specimen is thermally opaque but still thin enough to be neglected in the derivation of the thermal diffusivity of disks of the thickness used in these tests. The specimens were removed, reweighed, inverted, and replaced in the holder and a layer of tungsten deposited on the other surface. The specimens were removed and reweighed to check the tungsten thickness.

3 Measurements

3.1 Supplementary Testing

As discussed in Part I, measurements were carried out to determine additional properties to carry out a full characterization and evaluation of the material. These properties included thermal expansion, specific heat capacity, and thermal radiation transmissivity and emissivity.

The thermal expansion was required not only to verify isotropy but also to provide the necessary data to correct the dimensional changes and density of the specimens due to the effects of heating. The specific heat capacity (C_p) is required to derive thermal conductivity (λ) values from thermal-diffusivity (a) measurements by means of the simple relationship,

$$\lambda = \rho C_p a$$

where ρ is the density of the material.

Table 3 Details of apparatus used for specific heat measurements

Partner	Apparatus	Heating rate ($K \cdot min^{-1}$)	Holders	Environment	Estimated uncertainty (%)
ARCS	Netzsch DSC404	20	Pt/Rh	Ar	3
LNE	Setaram DSCIII	5	Al_2O_3	N_2	
PTB	Perkin Elmer DSC II				
KE	Perkin Elmer DSC II				2
Corus	Perkin Elmer Pyris I	10	Pt	N_2	2

The thermal transmissivity is required to indicate the extent of heat transfer by radiation within the material and, hence, indicate whether the above relationship applies to the material. Finally the emissivity, while not being directly required for use in the analysis of the present results, is a useful property to estimate extraneous heat transfer and heat losses which may occur in high-temperature measurements of thermophysical properties.

3.1.1 Specific Heat Capacity

Five organizations undertook the measurements using differential scanning calorimetry. Each partner measured three specimens from different blocks, all prepared in the *x*-direction since the property is independent of orientation. The specimen size for each partner was approximately 5 mm in diameter and 1 mm thick. In each case, the apparatus was calibrated with a sapphire reference material. Table 3 summarizes the experimental parameters for each measurement.

3.1.2 Thermal Expansion

Measurements were undertaken by ARCS and LNE using push rod dilatometry. Both organizations used a Netzsch 402C dilatometer with 5 mm diameter, 25 mm long specimens held in a horizontal position and heated in an inert environment at a controlled rate. The major difference in the technique was the heating rate, which varied from $5\,K \cdot min^{-1}$ for ARCS to $2\,K \cdot min^{-1}$ for LNE. In both the cases, the dilatometer was calibrated prior to the measurements using a tungsten reference material (NIST SRM 737) that has similar expansion properties to Pyroceram 9606 ($\sim 5 \times 10^{-6}\,K^{-1}$). Duplicate measurements were undertaken on each specimen.

3.1.3 Emissivity and Transmissivity

Measurements of emissivity were carried out by NPL on a Pyroceram 9606 specimen in 1996. The material was a piece from the original NBS batch and obtained from NIST. It was considered to be very similar to the present batch of material since it had the same density. It is believed that the results are still applicable and meaningful for this project since the values are of secondary importance to the major properties.

The specimen was polished prior to measurement, and measurements were undertaken in vacuum using the standard NPL apparatus at temperatures of 800 °C and 950 °C and at wavelengths of 2.26 μm and 5.06 μm.

PTB and INSA undertook measurements of the spectral transmittance through the material. At the former laboratory, the spectral transmittance, $\tau = \tau(\lambda)$, measurements were carried out on specimens of thicknesses of 1 mm, 2 mm, 3 mm, 4 mm, and 5 mm by means of a Fourier IR-spectrometer, Bruker IFS 48, for wavelengths between $\lambda = 1.5\,\mu$m and $\lambda = 20\,\mu$m. Wien's displacement law for a blackbody radiating its maximum emissive power is

$$\lambda_{\max} T = 2.897 \times 10^{-3} \mathrm{m} \cdot \mathrm{K}$$

and, for the wavelengths given above, the equivalent temperature, T, ranges from 1727 °C to −128 °C.

The measurement uncertainty of the instrument, $U(\tau) = ku(\tau)$, is assessed according to the ISO "Guide to the Expression of Uncertainty in Measurement" [2]:

$$\text{For } 1.5 \leq \lambda/\mu\mathrm{m} \leq 2, \quad U(\tau) = 0.1\,\%, \quad k = 2$$
$$\text{For } 2 < \lambda/\mu\mathrm{m} \leq 20, \quad U(\tau) = 0.02\,\%, \quad k = 2$$

INSA also measured two specimens of each thickness (1 mm, 2 mm, 3 mm, 4 mm, and 5 mm) using a Fourier–transform infrared spectrometer (FTS60A BioRad Inc.). A ceramic source characterized by a blackbody emission spectrum at 1300 °C was used as the source of radiation.

3.2 Measurements of Properties to be Certified

3.2.1 Thermal Diffusivity

Overall measurements were carried out on sets of four specimens by each of six participants, five used the established flash method in one form or the other [3–6], while the sixth, KE, used the modulated light–beam technique [7]. The specimen sizes ranged from 8 mm to 20 mm in diameter and 1.5 mm to 5 mm in thickness depending on the particular apparatus and energy source. In all cases the apparatus had been proven separately by participation in inter-comparisons or regular tests on a known material.

According to the different mathematical models used for evaluation, the thermal diffusivity is roughly proportional to the square of the specimen thickness and inversely proportional to the measured propagation time of the temperature wave through the specimen. Corrections are made for heat losses from the specimen and for the finite pulse rise time (by the laser-flash technique only). The models presume total absorption of the heating beam at the front surface and one-dimensional heat flow through the specimen.

Since Pyroceram 9606 is known to be semitransparent to the incident laser or light beam, the heated specimen face must be coated with an opaque layer to ensure absorption of the heating beam at the surface. Where the temperature variation of the

rear specimen face is recorded by means of radiation thermometers, it is also necessary to coat this face. The coating should be as thin as possible and should have a high thermal diffusivity to avoid errors in the measurement of the propagation time. Each partner has identified and verified their own special techniques to meet these requirements. However, in order to be able to exclude discrepancies between the individual measurements by the laser-flash technique, it was decided that two of the four specimens sent to the partners would have identical tungsten coatings, as described earlier.

Since the thermal diffusivity is proportional to the square of the thickness, this quantity must be measured very carefully at room temperature and corrected for the thermal expansion at elevated temperatures. All partners applied this correction using the linear thermal expansion coefficients obtained during the characterization of the material.

Results of measurements on individual specimens were provided on proforma sheets supplied by NPL to assist in analysis. In most cases, the thermal diffusivity has been measured at temperatures diverging by some degrees from the nominal temperatures. In order to facilitate comparison of the results and to allow calculation of a mean thermal diffusivity at the nominal temperatures, the original thermal-diffusivity data measured at the actual temperatures were corrected to values at the nominal temperatures taking into account the differences between actual and nominal temperatures and the slopes of the thermal-diffusivity/temperature curves at the nominal temperatures. The slope at each nominal temperature has been determined iteratively from the mean thermal diffusivity values of all measurements. The resulting thermal-diffusivity/temperature curve has been found by fitting the values to an inverse fourth-order polynomial. The slope at the nominal temperatures has been estimated by differentiating this function. Due to coating adhesion problems experienced with the specimens measured by KE, their measurements were subsequently made on four specimens used for the earlier characterization phase of the project. In all cases, the final certified values were based on the results obtained from the heating cycles only.

3.2.2 Thermal Conductivity

Two separate methods involving nine partners were used for this evaluation. The first was the steady-state ghp method, and the second was the transient hot-wire technique that also included one partner who used the hot-strip variation.

One of the basic problems with the ghp measurements was due to the size of the specimens. Because of limitations in the overall size of the original stock available from the manufacturer, most specimens had to be fabricated from separate smaller pieces described as follows.

The FIW double-sided ghp apparatus required specimens with dimensions of 500 mm × 500 mm and a metering area of 250 mm × 250 mm. The actual specimen consisted of two sets consists of two rectangular pieces 90 mm wide, and one piece 60 mm wide, each piece being 250 mm long and 25 mm thick. These were carefully arranged on either side of the heater to cover the metering area, and the guard zone surrounding the specimen built-up with a thermal insulation material. Measurements could only be made in the temperature range from 200 °C to 750 °C with a temperature difference restricted to 5 °C and 15 °C.

KE used a commercial apparatus with a plate size of 200 mm diameter and a metering area of 100 mm diameter. The specimen was supplied in the form of two semi-circular pieces that were carefully butted together for the measurements. The cold plates and power supply had to be modified to enable successful measurements to be made in the overall range from 50 °C to 650 °C.

NPL measurements were carried out using a 305 mm diameter ghp apparatus with a nominal metering area of 150 mm diameter [8]. The specimens in two semicircular pieces were 148 mm in diameter and fitted exactly onto the metering area. The guard and gap area were filled with low-density calcium silicate of the same thickness. Tests were run with a temperature difference across the specimens of 30 K measured with thermocouples firmly embedded in grooves cut into the surfaces of the specimen, and the overall uncertainty in thermal conductivity measurement was estimated to be 5 %.

PTB used a single-sided plate that was designed by PTB for measurements on hard cylindrical specimens [9]. Specimens were provided as two semi-cylindrical pieces that were wired together at the edges to form a 100 mm diameter piece. In this particular case, the temperature range was limited to −60 °C to +200 °C with temperature drops across the specimen of 5 K; the absolute uncertainty was estimated to be better than 3 % based on measurements on other hard materials.

NIST-Boulder measurements were carried out using a 70 mm diameter plate apparatus capable of operating up to 1200 °C [10]. Measurements were made with thermocouples mounted in the plates and the use of specimens of different thicknesses to minimize or eliminate the effect of the contact resistances between the plates and the specimen.

For the hot-wire and hot-strip measurements, five of the original six partners undertook the tests with NPL carrying out a separate series of tests by operating the hot-wire apparatus in the resistive wire in addition to the parallel wire mode to form the sixth participant. It is acceptable to consider the two modes as representing different methodology due to the different means of measuring the temperature rise and data analysis.

Both NPL and Corus used a Netzsch 426 commercial apparatus for the measurements on the brick-shaped specimens of dimensions 230 mm × 90 mm × 50 mm having the main surfaces carefully machined to a flatness of better than 0.1 mm. Repeat measurements were made on the same and additional specimens. PTB used the hot–strip version of the basic technique for measurements up to 800 °C on thinner bricks measuring 100 mm × 30 mm × 30 mm. Both Ceram [11] and SFC used a hot-wire apparatus developed in-house to the ISO8894-2 standard.

4 Results

4.1 Supplementary Testing

4.1.1 Specific Heat Capacity

The results of measurements by the six partners are shown in Table 4. Differences between measured values for specimens from each block are less than 2 %, and the

Table 4 Specific heat capacity results of all partners

Temp. (°C)	Specific heat capacity ($J \cdot g^{-1} \cdot K^{-1}$)					
	ARCS	LNE	KE	PTB	Corus	NPL
50						0.854
100	0.887	0.904	0.887	0.890	0.897	0.915
150	0.934	0.946	0.937	0.942	0.947	0.965
200	0.974	0.976	0.977	0.980	0.987	1.005
250	1.007	1.000	1.009	1.012	1.018	1.038
300	1.035	1.019	1.036	1.039	1.043	1.064
350	1.057	1.035	1.058	1.063	1.064	1.085
400	1.076	1.050	1.077	1.085	1.083	1.103
450	1.093	1.064	1.094	1.105	1.102	1.118
500	1.106	1.078	1.109	1.122	1.123	1.130
550	1.119	1.092	1.124	1.136		1.142
600	1.130	1.104	1.137	1.148		1.152
650	1.140	1.114	1.148			1.163
700	1.150	1.118	1.157			1.173
750	1.160					1.182
800	1.169					1.192
850	1.179					1.200
900	1.189					1.207
950	1.198					1.213
1000	1.207					
1050	1.215					
1100	1.222					

differences for each block are also less than 2 %. The overall uncertainty of the average values represented by the polynomial equation,

$$C_p = 0.7904 + 1.306 \times 10^{-3}T - 2.0853 \times 10^{-6}T^2 + 1.8011 \times 10^{-9}T^3 \\ -6.0185 \times T^{-13}T^4$$

is ±4 % based on 95 % confidence limits. These average values are shown in Table 5.

4.1.2 Thermal Expansion

The results for the nine specimens from block 3 are summarized in Fig. 1, which also contains values obtained from the TPRC Data Series for comparison [12]. As discussed in Part I, ARCS found that there was no significant evidence of anisotropy. Deviations between the blocks are less than 2 %. Both partners observed a difference between the first and repeat heating runs, indicating a small fixed change in length. The LNE results gave values to within ±4 % in the first runs and ±7 % in the repeat

Table 5 Final values of linear thermal expansion, density, and specific heat capacity of Pyroceram 9606

Temp. (°C)	Linear thermal expansion (%)	Density ($kg \cdot m^{-3}$)	Specific heat capacity ($J \cdot g^{-1} \cdot K^{-1}$)
25	0	2606	0.821
50		2604	0.851
100	0.59	2598	0.902
200	1.28	2593	0.982
300	1.66	2590	1.038
400	2.05	2587	1.079
500	2.46	2584	1.110
600	2.88	2580	1.135
700	3.36	2577	1.156
800	3.89	2574	1.177
900	4.43	2571	1.195
1000	4.94	2568	1.211

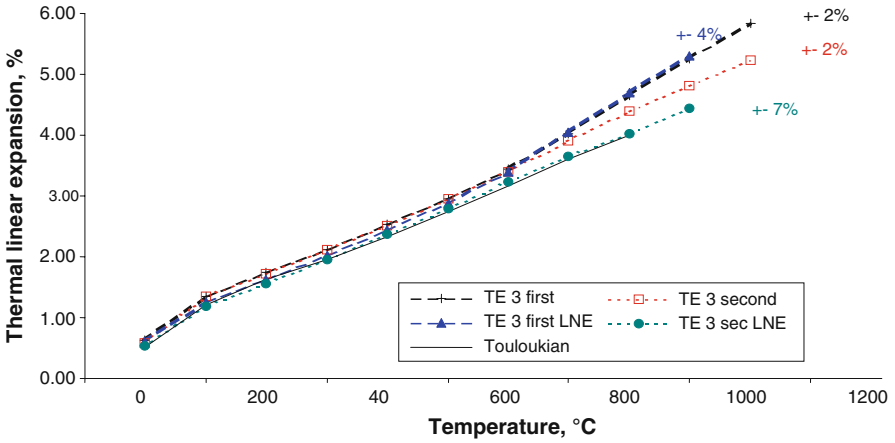

Fig. 1 Thermal expansion measurements on nine specimens from block 3, three from each direction ($\Delta L/L \times 10^3$)

measurements. The overall averaged values are contained in Table 5 together with values of density based on the correction for expansion at each of the selected temperatures.

4.1.3 Emissivity and Transmissivity

Table 6 contains results of the emissivity measurements at 800 °C and 950 °C for different wavelengths. Figure 2 shows a typical curve for the transmittance of the material for a specimen thickness of 5 mm showing limited transparency up to wavelengths of 4 μm, but essentially zero for longer wavelengths. Very similar curves were

Table 6 NPL emissivity results

Wavelength (μm)	Emissivity	
	800 °C	950 °C
5.06	0.902	0.891
3.79	0.458	0.463
3.43	0.373	0.388
3.18	0.313	0.346
2.26	0.205	0.271

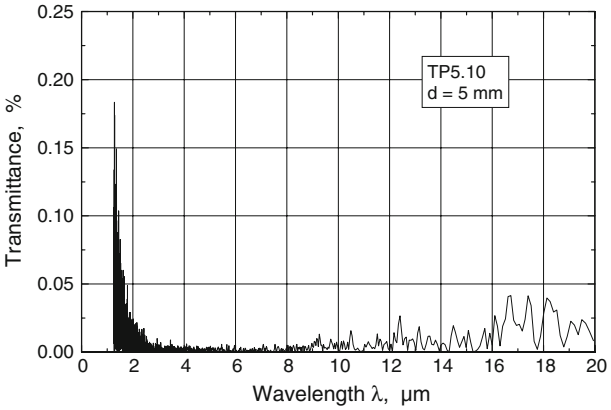

Fig. 2 PTB transmittance values for 5 mm thick specimen

obtained by both the partners for specimens ranging from 1 mm to 5 mm in thickness, indicating that the material is essentially opaque to thermal radiation and that conduction processes dominate the heat transfer modes. This important result eliminates any complications in the analysis of the results by removing the possibility of coupling of radiative and conductive heat transfer modes.

4.2 Properties to be Certified

4.2.1 Thermal Diffusivity

The results were corrected for temperature and thickness and presented in a standard format for each partner for subsequent certification analysis. Table 7 and Fig. 3 show this format for one of the participants as a typical example.

A preliminary examination of the results indicated that there were no significant differences in the data from each of the partners. Where repeat measurements were made, it was found that overall differences between them were less than 1 % except for the INSA results where the difference was 3.3 % and application of the Grubbs test showed that one value was an outlier. As a result, the INSA data were discarded from the certification process. The differences between the coating techniques were

Table 7 Thermal diffusivity results of LNE arranged for analysis of data

LNE specimen	4.55(Au)		4.57(Au)		4.54(W)		4.56(W)	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
T (°C)	$a1$	$a2$	$a3$	$a4$	$a5$	$a6$	$a7$	$a8$
	$(10^{-6}\mathrm{m}^2 \cdot \mathrm{s}^{-1})$		$(10^{-6}\mathrm{m}^2 \cdot \mathrm{s}^{-1})$		$(10^{-6}\mathrm{m}^2 \cdot \mathrm{s}^{-1})$		$(10^{-6}\mathrm{m}^2 \cdot \mathrm{s}^{-1})$	
Measurement results								
25	1.894	1.927	1.924	1.949	1.926	1.924	1.952	1.947
50								
100	1.549	1.595	1.586	1.602	1.577	1.581	1.596	1.589
200	1.332	1.354	1.367	1.371	1.360	1.351	1.357	1.363
300	1.217	1.219	1.229	1.235	1.227	1.218	1.218	1.223
400	1.132	1.138	1.149	1.144	1.146	1.126	1.129	1.124
500	1.062	1.073	1.080	1.080	1.066	1 065	1.075	1.068
600	1.006	1.017	1.024	1.026	1.024	1.010	1.017	1.016
700	0.977	0.978	0.980	0.982	0.976	0.977	0.980	0.975
800	0.950	0.955	0.948	0.953	0.951	0.941	0.946	0.949
900								
1000								

T (°C)	Measurements (a1–a8)			Apparatus		Mean deviations	
	Mean value $(10^{-6}\mathrm{m}^2 \cdot \mathrm{s}^{-1})$	Max. scatter (%)	Standard deviation (%)	Uncertainty (%)	95 % conf. interval	Run 2/1 (%)	Au/W (%)
Evaluation							
25	1.930	2.97	0.91	2.45	4.90		−0.72
50							
100	1.584	3.34	0.97	2.20	4.40	0.93	−0.17
200	1.357	2.89	0.83	1.85	3.70	0.43	−0.14
300	1.223	1.49	0.50	1.85	3.70	0.09	0.28
400	1.136	2.18	0.79	1.85	3.70	−0.52	0.83
500	1.071	1.68	0.61	1.95	3.90	0.06	0.50
600	1.018	2.06	0.67	2.10	4.20	−0.05	0.10
700	0.978	0.72	0.23	2.25	4.50	−0.03	0.21
800	0.949	1.51	0.43	2.35	4.70	0.08	0.50
900							
1000							
Averages		2.09	0.66	2.09	4.19	0.12	0.16

again less than 1 %, indicating that the results for all specimens could be given equal weight.

It was also found that the mean values obtained by ARCS at temperatures in excess of 400 °C were higher than the mean values of the other participants. As a result because LNE specimens were of the same dimensions as ARCS, they exchanged specimens

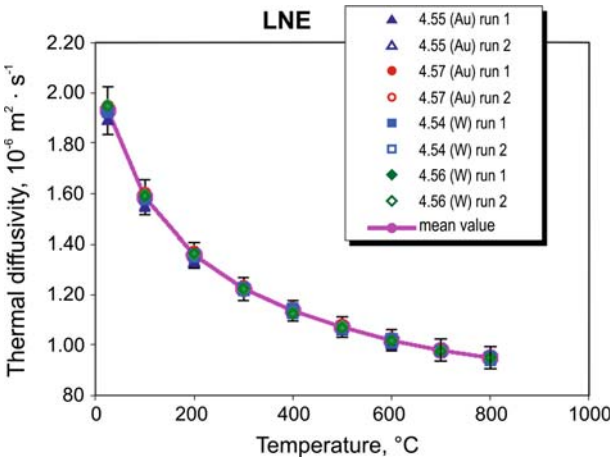

Fig. 3 Thermal-diffusivity results of LNE

and repeated all measurements. The results are shown in Table 8. They indicate that the original difference (column 2, 1.7 % average) is composed of a systematic difference between the two participants on the same specimens (column 5, ranging from 0.7 % to 1.8 % at higher temperatures) and a difference between specimens from blocks 3 and 4 (column 8) of approximately 1 %. Both differences are within the overall experimental uncertainties.

4.2.2 Thermal Conductivity

Two different basic methods were used for this property, and the individual experimental values are shown in Figs. 4 and 5 for the ghp and hot-wire/hot-strip methods, respectively. Smoothed values calculated from a least-squares fit to each set of data are shown in Tables 9 and 10. Application of the Grubbs test to the data sets indicated that both the FIW and the NIST-Boulder results are outliers. As a result, these sets were not used in the certification process.

5 Certification

The final certification of the material was carried out by the European Commission's Joint Research Centre Institute for Reference Materials and Measurement (IRMM), Geel, Belgium who are responsible for sales of the Reference Material designated BCR-724 with the certified values given in the respective equations below valid over the temperature range from 25 °C to 752 °C.

Since all the results indicated that this batch of Pyroceram 9606 was homogeneous, reproducible, and stable, certification was based on the evaluation of the respective mean values of all the measurements of the two properties with the exclusion of the three sets of data discussed earlier. The interlaboratory mean values are summarized in Table 11. The associated measurement uncertainties, which are valid over

Table 8 Thermal diffusivity of specimens exchanged between ARCS and LNE

Column 1	2	3	4	5	6	7	8
	Original distribution		Samples exchanged				
Laboratorium	ARCS	LNE	ARCS	LNE			
samples (block)	ARCS (3)	LNE (4)	LNE (4)	ARCS (3)			
meas. No.	1	2	3	4			
T (°C)	a $(10^{-6}\mathrm{m}^2 \cdot \mathrm{s})^{-1}$						
Mean measurement results							
25	1.953	1.930	1.921	1.946			
50	1.773		1.749				
100	1.605	1.584	1.550	1.596			
200	1.352	1.357	1.356	1.373			
300	1.245	1.223	1.238	1.240			
400	1.155	1.136	1.156	1.149			
500	1.094	1.071	1.087	1.082			
600	1.045	1.018	1.042	1.034			
700	1.002	0.978	0.996	0.985			
800	0.970	0.949	0.958	0.958			
900	0.943		0.931				
1000	0.909		0.906				

Laboratorium	ARCS/LNE	ARCS/LNE	ARCS/LNE	ARCS/LNE	ARCS	LNE	Mean
samples (block)	3/4	3	4	mean	3/4	3/4	3/4
meas. No.	1/2	1/4	3/2		1/3	4/2	
T (°C)	Deviation (%)						
Evaluation							
25	1.2	0.3	−0.5	−0.1	1.6	0.8	1.2
50					1.4		1.4
100	1.3	0.6	−2.2	−0.8	3.6	0.7	2.1
200	−0.3	−1.5	−0.1	−0.8	−0.3	1.2	0.4
300	1.8	0.4	1.2	0.8	0.6	1.4	1.0
400	1.6	0.5	1.7	1.1	−0.1	1.1	0.5
500	2.2	1.1	1.5	1.3	0.6	1.1	0.8
600	2.7	1.1	2.4	1.7	0.3	1.6	1.0
700	2.4	1.8	1.9	1.8	0.6	0.7	0.6
800	2.2	1.2	1.0	1.1	1.2	1.0	1.1
900					1.2		1.2
1000					0.3		0.3
Mean values	1.7			0.7			1.0

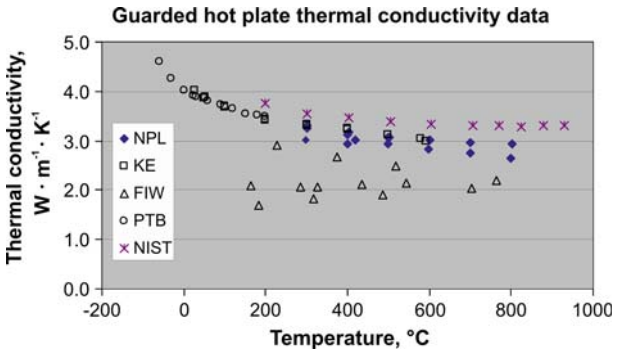

Fig. 4 Original guarded-hot-plate (ghp) thermal-conductivity raw data from each partner before rejecting values

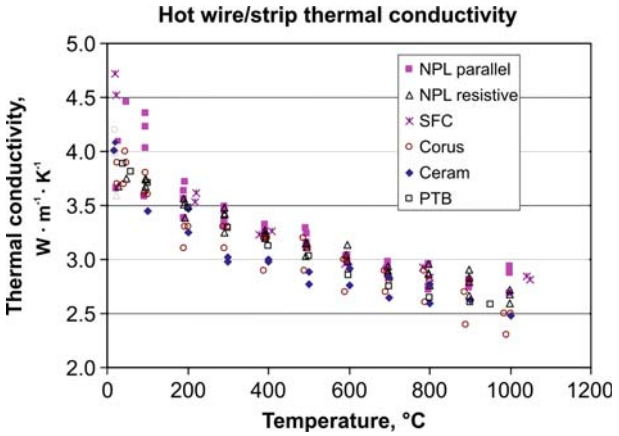

Fig. 5 Original hot-wire/hot-strip thermal-conductivity results from each partner

the whole temperature range, are calculated with components related to fitting the equation through the measured values, the estimate of the interlaboratory mean value, the material heterogeneity, material stability, and for thermal diffusivity, a small error associated with the correction for thermal expansion.

The certified value of the thermal diffusivity, a, is represented by the following fourth-order polynomial function in T (K):

$$a = 4.406 - 1.351 \times 10^{-2}T + 2.133 \times 10^{-5}T^2 - 1.541 \times 10^{-8}T^3 + 4.147 \times 10^{-12}T^4$$

The equation represents the interlaboratory mean values of the thermal diffusivity, a, shown in Table 11 to better than 0.5 % and has an expanded uncertainty of 6.1 % within a confidence level of 95 %

Table 9 Smoothed values of steady-state thermal conductivity calculated from a fit to a linear equation for each partner

Temp (°C)	NPL	KE	PTB	NIST	FIW	Mean	SD ($W \cdot m^{-1} \cdot K^{-1}$)
	Fitted thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)						
−50			4.424			4.424	
0			4.089			4.089	
25		3.988	3.963			3.976	0.018
50		3.877	3.857			3.867	0.014
100		3.700	3.687			3.694	0.009
200		3.459	3.456	3.703		3.539	0.142
300	3.271	3.301		3.577	2.774	3.231	0.334
400	3.161	3.191		3.488	2.626	3.116	0.359
500	3.079	3.109		3.422	2.516	3.031	0.377
600	3.015	3.046		3.371		3.144	0.197
700	2.965			3.330		3.148	0.258
800	2.924			3.297		3.111	0.264
900				3.270		3.270	

The mean of all the results is shown before rejecting data

Table 10 Thermal-conductivity values at set temperatures calculated from curve fitting; values used to calculate the mean value for thermal conductivity using hot-wire/strip

Temp. (°C)	CERAM	NPL parallel	NPL resistive	PTB	CORUS	SFC	MEAN	SD ($W \cdot m^{-1} \cdot K^{-1}$)
	Fitted thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)							
25	3.935	4.278	3.927	4.033	3.973	4.543	4.115	0.246
50		4.129	3.817	3.894	3.840		3.920	0.143
100	3.581	3.892	3.641	3.671	3.627		3.682	0.122
200	3.284	3.568	3.401	3.367	3.335	3.682	3.439	0.153
300	3.090	3.357	3.244	3.170	3.145		3.201	0.103
400	2.954	3.209	3.134	3.031	3.012	3.246	3.098	0.117
500	2.853	3.099	3.053	2.927	2.913		2.969	0.103
600	2.775	3.014	2.990	2.848	2.837	3.010	2.912	0.105
700	2.713	2.947	2.940	2.785	2.776		2.832	0.105
800	2.663	2.892	2.899	2.733	2.727	2.862	2.796	0.101
900	2.621	2.847	2.866	2.691	2.686		2.742	0.108
1000	2.586	2.808	2.837		2.652	2.760	2.729	0.107

The last column shows the standard deviation of the experimental points from the mean value

The certified values of the thermal conductivity, λ, are represented by the following linear function of the inverse of the absolute temperature (T in K):

$$\lambda = 2.332 + 515.1/T$$

Table 11 Interlaboratory mean values of the thermal diffusivity and thermal conductivity of Pyroceram 9606

	Thermal diffusivity Interlaboratory	Thermal conductivity Interlaboratory
Temp. (°C)	Mean value (10^{-6}m$^2 \cdot$ s^{-1})	Mean value (W $\cdot$ m$^{-1} \cdot$ K^{-1})
25	1.93	4.080
50	1.77	3.903
100	1.60	3.686
200	1.37	3.445
300	1.23	3.226
400	1.14	3.116
500	1.07	3.004
600	1.02	2.944
700	0.97	2.855
800	0.94	2.813
900	0.91	2.744
1000	0.88	2.730

This equation agrees with the interlaboratory mean values shown in Table 11 to within 1 %. The expanded uncertainty is 6.5 % within a confidence level of 95 %.

In conclusion, the measured specific heat and thermal expansion values have been utilized together with the measured thermal diffusivities to derive thermal-conductivity values using the relationship,

$$\lambda = aC_p\rho$$

and the calculated results are compared with the thermal conductivities measured by both steady-state and transient methods in Table 12. The agreement between calculated and certified thermal conductivities is clearly within the quoted uncertainties of the individual values. This is one of the most important results of the certification work because thermal-diffusivity measurements are very often used to determine thermal conductivities indirectly. It also probably indicates that the overall uncertainty for the certified values is better than that indicated, possibly because the laboratories overestimated their measurement uncertainties.

6 Conclusions

A large batch of Pyroceram 9606 was purchased from Corning Inc. to carry out the characterization and certification of the material. There is sufficient material to provide reference specimens for at least 10 years for the calibration of axial heat flow equipment and for the validation of thermal-diffusivity apparatus within Europe. The reference material will be available as short bars or rods of diameters of 12.7 mm, 25.4 mm, and 50.8 mm.

Table 12 Comparison of thermal-conductivity results obtained by calculation from thermal diffusivity and from GHP and hot-wire/strip measurements

	Calculated from diffusivity				GHP	Hot wire	Interlab
Temp (°C)	a (10^{-6} m^2·s^{-1})	C_p (J·g^{-1}·K^{-1})	ρ (kg·m^{-3})	λ (W·m^1·K^{-1})	λ (W·m^1·K^{-1})	λ (W·m^1·K^{-1})	λ (W·m^1·K^{-1})
25	1.926	0.821	2606	4.12	3.98	4.11	4.08
50	1.771	0.851	2604	3.92	3.87	3.92	3.90
100	1.596	0.902	2598	3.74	3.69	3.68	3.69
200	1.365	0.982	2593	3.48	3.46	3.44	3.44
300	1.233	1.038	2590	3.31	3.29	3.20	3.23
400	1.136	1.079	2587	3.17	3.18	3.10	3.12
500	1.069	1.110	2584	3.07	3.09	2.97	3.00
600	1.017	1.135	2580	2.98	3.03	2.91	2.94
700	0.972	1.156	2577	2.90	2.97	2.83	2.86
800	0.938	1.177	2574	2.84	2.92	2.80	2.81
900	0.906	1.195	2571	2.78		2.74	2.74
1000	0.877	1.211	2568	2.73		2.73	2.73
	Deviation from interlab mean value						
Temp (°C)				(%)	(%)	(%)	
25				0.98	− 2.45	0.74	
50				0.51	− 0.77	0.51	
100				1.36	0.00	− 0.27	
200				1.16	0.58	0.00	
300				2.48	1.86	− 0.93	
400				1.60	1.92	− 0.64	
500				2.33	3.00	− 1.00	
600				1.36	3.06	− 1.02	
700				1.40	3.85	− 1.05	
800				1.07	3.91	− 0.36	
900				1.46		0.00	
1000				0.00		0.00	

In the characterization phase, described in Part I of this article, it was shown that the material was stable, homogeneous, and isotropic. This glass–ceramic material was shown to have a uniform fine-grained crystalline structure throughout the batch; similarly, the chemical composition was shown to be consistent between several blocks of material. As part of the characterization, physical properties such as specific heat, thermal expansion, and density were determined. These parameters are essential for calculating the thermal conductivity from thermal-diffusivity values and also enabled comparisons to be made between measured and calculated values of thermal conductivity.

In the certification phase of the project, six partners provided data for the determination of the thermal diffusivity from direct measurements and 11 partners, using either steady-state or transient methods, provided data for the determination of the thermal conductivity. The thermal conductivity was also calculated from the thermal-diffusiv-

ity values using data for the specific heat and density determined in the characterization phase; the agreement between the two sets of values was between +2.7 % and −0.3 %. Similarly, three partners used the hot-wire method to determine the specific heat and thermal diffusivity above 100 °C; these values also agreed with the directly measured values to between +3 % to −4.8 % and +3 % to −6.3 %, respectively. These results show good internal consistency among all the measurements carried out by the partners on the thermal properties of the material.

Finally, full certification of the thermal conductivity and thermal diffusivity of the batch of Pyroceram 9606 was carried out by IRMM [11], resulting in certified values of the thermal diffusivity and thermal conductivity with expanded uncertainties of better than 6.1 % and 6.5 %, respectively, being assigned to the material over the temperature range from 25 °C to 752 °C.

Acknowledgments We would like to acknowledge the help and co-operation of the following partners involved in this project: Sarah Baxendale, Ceram, UK; Gerhard Groboth, ARCS, Austria; Bruno Hay, LNE, France; Ulf Hammerschmidt, PTB, Germany; Rüdiger Brandt and Guenther Neuer, KE Stuttgart, Germany; Sido Sinnema, Corus R and D, The Netherlands; Dominique Baillis and Michel Laurent, INSA Lyon, France; Roland Schreiner, FIW, Germany; Ludwig Hagemann and Juergen Blumm, Netzsch Geratebau GmbH, Germany; Gerrard Bisson and Edgar Dossou, SFC, France; Andy Slifka, NIST Boulder, USA (Co-opted partner); Carlos Saraiva Martins (European Commission Technical Representative (RTD)).

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