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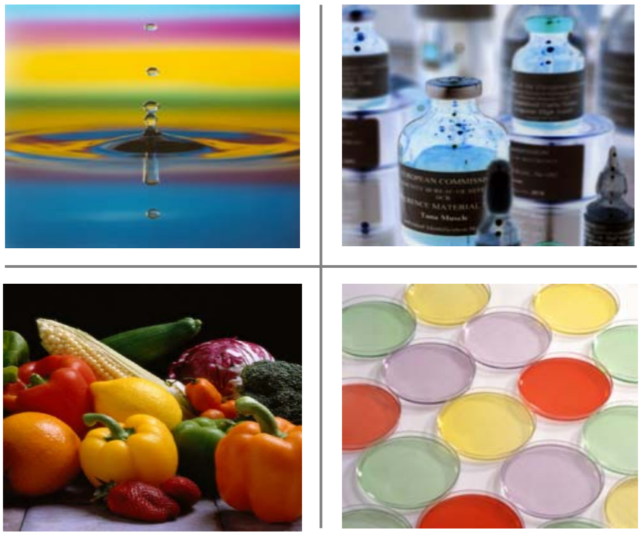
D. Salmon, G. Roebben, A. Lamberty, R. Brandt



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BCR-724

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ABSTRACT

This certification report is largely based on the final report of a research project, funded by the European Community under the 'Competitive and Sustainable Growth' program ("HTCRM – High Temperature Certified Reference Material", contract SMT4-CT98-2211 [1]). The project intended to produce a reference material with certified thermal conductivity (λ) and diffusivity (α). Samples in the shape of cylinders with different diameter and thickness were prepared from large blocks of Pyroceram 9606.

The material was tested for homogeneity. Homogeneity was found sufficient for the intended use, and the corresponding uncertainty contribution was determined. Dispatch and storage conditions were judged non-critical for this glass-ceramic material. However, stability of the samples under repeated heating cycles to elevated temperatures needed to be investigated. An uncertainty contribution was determined based on a limited use of the CRM of 10 times heating up to 1025 K. The certified values were determined through an interlaboratory exercise. Thermal diffusivity was determined using laser-flash and Xenon lamp methods. Thermal conductivity was measured using guarded hot plate apparatus and hot-wire/hot-strip methods. The following certified values and associated uncertainties were assigned.

BCR-724 glass-ceramic		
certified value [a]	unit	uncertainty [b]
$\alpha = 4.406 - 1.351.10^{-2} \cdot T + 2.133 \cdot 10^{-5} \cdot T^{2} - 1.541 \cdot 10^{-8} \cdot T^{3} + 4.147 \cdot 10^{-12} T^{4}$	$m^2/s \cdot 10^{-6}$	6.1 %
$\lambda = 2.332 + 515.1 / T$	W/(m·K)	6.5 %

[a] The certified value is valid only in a temperature range from room temperature to 1025 K. It is no longer valid when the sample has been heated up 10 times or more to 1025 K, or if it is heated up to a temperature in excess of 1025 K. In the equations, T is temperature (K).

[b] Expanded uncertainty (coverage factor k = 2, confidence level of about 95 %)

GLOSSARY

A	Area
ANOVA	Analysis of variance
c_p	Specific heat capacity
CRM	Certified Reference Material
d	Distance
EC	European Commission
GHP	Guarded Hot Plate
HTCRM	Acronym of contract SMT4-CT98-2211 (Certification of thermal conductivity and diffusivity properties of Pyroceram 9606 as a reference material up to 1000 °C)
HW	Hot-wire thermal conductivity test
IRMM	Institute for Reference Materials and Measurements
JRC	Joint Research Centre
k	Coverage factor
L	Thickness of sample
n	Number of laboratories contributing accepted data for calculation of the interlaboratory mean value
P	Electrical power
Q	Heat
s_{bb}	Standard deviation between different blocks
s_{char}	Standard deviation of laboratory means
s_m	Standard deviation of set of values measured in a specific lab
s_{wb}	Standard deviation within a block
T	Temperature
t	Time
$t_{1/2}$	Time required for rear-side of pulse method specimen to reach its maximum temperature
TC	Thermal conductivity
TD	Thermal diffusivity
u_a	Uncertainty of the values produced with a specific apparatus at a specific lab
U_a	Expanded uncertainty of the values produced with a specific apparatus at a specific lab (coverage factor k = 2 corresponding with a confidence level of about 95 %)
u_{char}	Contribution to uncertainty of certified value due to uncertainty about interlaboratory mean value

u_{h}	Contribution to uncertainty of certified value due to material heterogeneity
u_{h}^{*}	Maximum contribution to uncertainty of certified value due to material heterogeneity hidden by method repeatability
α	Thermal diffusivity
β	Linear thermal expansion coefficient
Δ	Difference
λ	Thermal conductivity
ρ	Density
Φ	Heat flux
$\varnothing$	Diameter of sample

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1 INTRODUCTION

1.1 Definitions

Thermal conductivity (symbol λ) is the ability of a material to conduct heat. Its value [unit = W/(m·K)] is defined as the quantity of heat, Q, transmitted in time t through a thickness L, in a direction normal to a surface of area A, due to a temperature difference ΔT, under steady state conditions and when the heat transfer is dependent only on the temperature gradient.

Thermal diffusivity (symbol α) is a material property, which expresses the speed of temperature change of a medium when exposed to changes in the thermal environment. The thermal diffusivity is inversely proportional to the heat capacity and proportional to the thermal conductivity. It is expressed in m^2/s.

1.2 Rationale of the certification project

Thermal conductivity and diffusivity of refractory materials are the fundamental material characteristics governing heat transport in industrial processes. For optimum economic furnace design, the knowledge of the correct thermophysical properties of a refractory material is essential. Currently, thermal conductivity at high temperatures is generally measured by some form of hot-wire method. However, some companies have used or still use either the guarded hot-plate method or more recently the laser flash method. It is well known that there can be significant differences in the thermal conductivity values obtained by the different techniques (including the three versions of the hot-wire test: resistive wire, cross wire and parallel wire). This observation was the main reason for the submission and approval of the HTCRM research project (funded by the European Community under the 'Competitive and Sustainable Growth' program, contract SMT4-CT98-2211). The project intended to produce a reference material with certified thermal conductivity and diffusivity. This certification report is based largely on the final report of the HTCRM project [1]. After the end of the HTCRM project, additional samples were prepared and tests were performed at IRMM, to complete the set of data required for the certification of the material as BCR-724.

1.3 Intended use of the certified material

A ceramic material with certified thermal properties will provide owners of comparative measurement devices in research and industry with a low thermal conductivity reference material. This is essential for those laboratories measuring insulation materials including many types of new fiber reinforced and particulate composite materials.

The use of the certified reference material for absolute measurement techniques provides a simple means for the operators of such devices to test whether their apparatus operates accurately and whether the measurement conditions are correct. Also, the CRM may be used to determine the measurement uncertainty at the certified thermal conductivity. Similarly, new or modified methods can be validated with the use of the reference material.

The material will be made available in different cylindrical shapes. The user will be required and allowed to cut samples of the geometry that suits his instrument. This must be done in full respect of the minimum sample size and the instructions for use, defined in the report and certificate.

2 PARTICIPANTS

Acronym	Institution	Laboratory or department	Country	Contact person	Sample Preparation	Measurements	Evaluation	Co-ordination
ARCS	Austrian Research Centres GmbH, (formerly OFZS) A-2444 Seibersdorf	Materials Technology	AT	Ing. G. Groboth		x	x	
CERAM	CeramRes Queen's Road Penkhull Stoke-on-Trent ST4 7LQ		UK	Sarah Baxendale	x	x		
CORUS	Corus R & D Wenckebachstraat 1 1970 CA Ijmuiden	Ceramics Research Centre	NL	Dr. S. Sinnema		x		
CPU	Constantine the Philosopher University SK-94974 Nitra	Department of Physics , Faculty of Natural Sciences	SK	Dr. L. Vozar		x		
FIW	Forschungsinstitut für Wärmeschutz Lochhamer Schlag 4 D-82166 Gräfelfing		DE	R. Schreiner		x		
INSA	Institut National des Sciences Appliquées 20, avenue Albert Einstein F-69621 Villeurbanne cedex	Centre de Thermique de Lyon	FR	Dr. D. Baillis		x		
KE	Forschungsinstitut für Kerntechnik und Energiewandlung e.V. Pfaffenwaldring 31 D-70569 Stuttgart	Energiewandlung und Wärmetechnik	DE	Dipl.-Ing. R. Brandt	x	x	x	
IRMM	Institute for Reference Materials and Measurements, Joint Research Centre, EC Retieseweg 111 B-2440 Geel	Reference Materials Unit	EU	dr. ir. G. Roebben	x	x	x	x
LNE	Laboratoire National d'Essais 29, avenue Roger Hennequin F - 78197 TRAPPES CEDEX	Division Optique et Propriétés Thermiques des Matériaux	FR	Dr. B. Hay		x		
Netzsch	Netzsch Gerätebau GmbH Wittelsbacherstrasse, 42 D-95100 Selb/Bayern	Thermische Analyse	DE	Dipl-Phys. J. Blumm		x		
NIST	National Institute of Science and Technology 100 Bureau Drive, Stop 8632 Gaithersburg, MD 20899-8632	Building and Fire Research Laboratory	US	R. Zarr		x		
NPL	National Physical Laboratory Queen's Road Teddington TW11 0LW	CBTM	UK	D. Salmon	x	x	x	x
PTB	Physikalisch-Technische Bundesanstalt Bundesallee 100, D - 38023 Braunschweig	Dept. 3.102	DE	Dr. U. Hammerschmidt		x		
SFC	Société Française de Céramique 23, rue de Cronstadt F - 75015 Paris	Ceramique Industrielles	FR	H. Le Doussal		x		

3 MATERIAL SELECTION

3.1 Candidate materials

Several materials such as zirconia and calcium silicate were considered as potential candidates to be used as a ceramic certified reference material in the temperature range up to 1300 K. These were rejected for either being potentially unstable over the temperature range of interest or having a thermal conductivity that was either too high or too low for the intended use (ref. final report of HTCRM project, [1]). The most promising available options at the start of the project were a cordierite material and Pyroceram 9606.

3.2 Cordierite

The cordierite material has the main advantages of being a commercially available material that is relatively cheap and readily available. The manufacturing process can be well controlled so that a homogeneous batch of material can be produced. Preliminary investigations of the thermal diffusivity by four different laboratories looked very promising [2]. Unfortunately the material showed signs of instability due to phase changes during thermal cycling from room temperature to temperatures around 1300 K. In particular, large specimens, such as those required for hot wire tests, crack due to differential expansion and contraction within the body of the material.

3.3 Pyroceram 9606

Pyroceram is an opaque glass-ceramic with high strength and elastic modulus and an operational temperature covering the range 75 K to 1250 K. The material is mechanically stable to 1450 K.

Corning Glass Works (now Corning Inc.) developed the material in the mid 50s and because of its excellent mechanical and dielectric properties at high temperatures it was used for the manufacture of missile radomes. Many laboratories around the world have extensively measured the thermal properties of the material and in general the material has been found to be extremely stable and reliable. The major disadvantage is its relatively high cost, especially for machining of specimens. Only a limited number of reference specimens could therefore be prepared for hot wire apparatus, which requires large specimen dimensions.

Pyroceram 9606 has been used as a reference material since 1965 by many organizations. The reference values used are generally those taken from the Purdue University series on Thermophysical Properties of Matter edited by Touloukian et al [3], [4]. These had been summarised in a National Bureau of Standards publication [5], and confirmed in a later study. A great deal of the measurement work to produce reference materials was carried out in the early 60's but no certified values have ever been published. As far as the project partners are aware no one had attempted to produce traceable reference values for Pyroceram 9606 until recently when NIST organised an intercomparison of thermal conductivity and thermal diffusivity. Unfortunately whilst much useful data were obtained from several leading laboratories throughout the world the criteria for the intercomparison measurements were not well enough defined and hence it was not possible to produce statistically valid reference values for the material at any temperature.

4 PROCESSING OF SAMPLES

4.1 Base material

30 blocks of Pyroceram 9606 of dimensions 300 mm x 75 mm x 93 mm were ordered by NPL from CORNING Inc., Corning, New York, USA.

4.2 Cutting procedure

4.2.1 Samples used in the certification procedure

The majority of samples for certification were prepared at CERAM. NPL prepared steady state thermal conductivity test samples for NPL, FIW, PTB and KE and hot wire thermal conductivity test samples for PTB.

For some tests, the dimensional sample requirements can only be met by lateral assembly of several blocks. Assembly of the blocks has a limited effect on the measured thermal property values, as long as the assembly is lateral, guaranteeing an uninterrupted heat flow between heat source and temperature detector. To reduce the gaps between the blocks, they are held together with wires. The wires used are of limited cross-section, and are aligned perpendicular to the direction in which is measured the heat flow through the sample. Therefore, heat transfer along the wires does not affect significantly the heat flow through the sample.

Each piece of Pyroceram base material was given an individual specimen code, indicating from where it was cut from which block.

To eliminate the issue of thermal anisotropy it was decided to cut the samples for all thermal conductivity and thermal diffusivity measurements in the same orientation from the individual blocks. All samples were prepared in the Y orientation (see Fig. 10, Annex 1) through the thickness of the block. (It will be shown later that the anisotropy is insignificant.)

4.2.2 Samples for distribution as CRMs

Samples were prepared with core drills of different diameter (12, 13 and 14 mm to approach 0.5 inch, 26 and 27 mm to approach 1.0 inch, and 50 and 51 mm to approach 2 inch) for the cylinder wall faces, and a continuous rim diamond cutting wheel for the end faces. Thermal conductivity specimens were then ground flat and parallel to 0.1 mm and thermal diffusivity samples to 0.05 mm.

4.3 Samples for the certification measurements

In annex 1, tables summarise the size of the samples sent out to the respective laboratories.

4.4 Tungsten coating of the samples for thermal diffusivity measurements

The samples for KE and two samples for the other partners measuring thermal diffusivity have been identically coated at KE. For that purpose a special mounting device was constructed on which all samples to be coated could be mounted in the same plane in order to be positioned in the vacuum chamber of an electron beam welding machine. Tungsten vapour is deposited at the sample surfaces by vaporising the end of a tungsten rod. The samples were then removed, their weight increase determined and then placed back in the chamber in order to coat the opposite surface. By weighing the samples three times, the thickness of the tungsten layers could be determined. The deposition time was optimised by preliminary tests so that layer thicknesses of 2 µm ± 0,6 µm could be obtained. This is thick enough to be opaque and yet thin enough so that it can be neglected in the evaluation of the thermal diffusivity measurements.

4.5 Preparation of samples for distribution as CRM

The material was cut in pieces of dimensions as required for most of the thermal conductivity and thermal diffusivity apparatuses. The various geometries available are rods or bars of diameters approximately 2 inch (51 mm), 1 inch (25 mm), and 0.5 inch (13 mm). Each rod/bar is between 50 and 90 mm long. The smaller rods are designed to be used for validation of thermal diffusivity apparatus. Each sample has been individually packed and identified by name, dimension, material block from which it is cut, and date of packing.

5 PRELIMINARY MATERIAL CHARACTERISATION

Samples from six blocks taken at random from the total number of 30, have been used to determine the chemical composition, a number of relevant physical properties, and the homogeneity and stability of thermal conductivity and diffusivity. After selection of the blocks, each block was assigned a number. The complete measurement programme is described in the HTCRM final report [1]. The most relevant results are summarised in the following sections.

5.1 Microstructure

Secondary electron microscope image analysis and Electron Probe Micro Analysis were performed at Corus. Pyroceram is shown to be a multiphase material, consisting of crystalline phases embedded in a continuous glass phase (Figure 1).

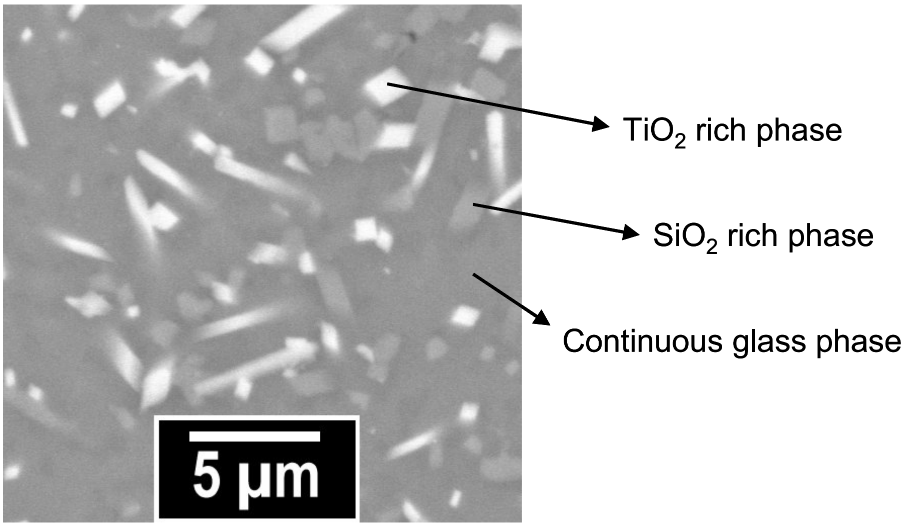


Figure 1: Microstructure of BCR-724: SEM-picture obtained on a sample from block 4, with indication of the main phases.

The microstructure (Figure 2) as well as the chemical composition [1] are homogeneous at a length scale of about 50 µm. This is much smaller than the length scale relevant for thermal conductivity and diffusivity measurements.

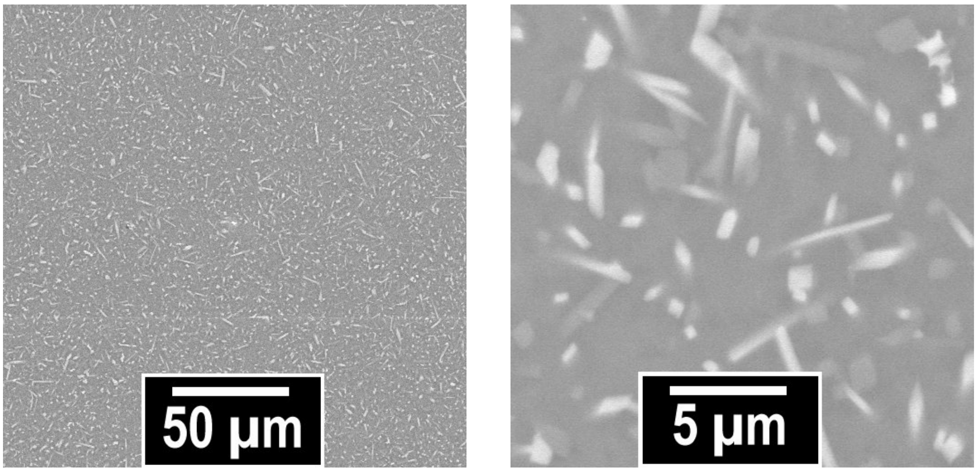


Figure 2: Low and high magnification scanning electron microscope images taken of a sample from block 3.

5.2 Physical Properties

The values of density, porosity, thermal expansion and specific heat capacity of the material are relevant for the determination of the certified thermal diffusivity and thermal conductivity. Radiative properties are required to judge the contribution to thermal conductivity by radiative heat transfer.

5.2.1 Porosity and density

The material is claimed by the manufacturer to have zero porosity. Measurements at Corus have shown that the porosity is indeed less than 0.5 vol %. Such low porosity is important for the use of the reference material at high temperatures as it reduces the possibility of radiative heat transfer within the bulk of the material; the predominant mode of heat transfer remains conductive.

The room temperature density of the material was measured on 10 samples from four different blocks and has been found to be very uniform, with a mean value of 2602 kg/m^3 and standard deviation of 0.25 %. The dependence of density on temperature was calculated using the density measured at room temperature and the linear thermal expansion measured from room temperature to 1273 K (Table 1).

5.2.2 Linear thermal expansion

Thermal expansion data are required to determine corrections to the specimen thickness for the thermal conductivity and thermal diffusivity measurements at high temperatures. Therefore, partners LNE and ARCS both measured the thermal expansion of BCR-724, using similar equipment. The mean values of the linear thermal expansion at the certification temperatures with reference to the dimensions at 298 K are given in Table 1. The measurement uncertainty of the thermal expansion measurements was estimated at 0.5 × 10^{-6}/K, corresponding with 8 % to 10 % over the measured temperature range.

Cylindrical samples were cut with a long axis of length 25 mm parallel with directions X, Y and Z. This was done for blocks 1, 2, and 3. ARCS measured the expansion for two samples from each block (1, 2, and 3) in each direction (X, Y and Z). LNE measured a third sample for each direction of block 3. In view of the standard measurement uncertainty (5 %), the observed differences between the thermal expansion in x-, y- and z- orientations (2 %) and between the three blocks (2 %), are less significant.

However, both partners observed a difference between the thermal expansion measured in the first and the second run. The difference is between 2 and 3 % at low or moderate temperatures, but increases with temperature and reaches values of approximately 3 % to 5 % at 973 K. This change does not progress with increasing number of thermal cycles.

Combined, the standard uncertainty contributions from measurement uncertainty, dependence on orientation, between-block variation and change between first and second run, amount to 8 %. This uncertainty value will be used when assessing the effect of sample geometry on the measured diffusivity and conductivity values.

Table 1: Linear thermal expansion, density, and specific heat capacity of BCR-724

Test temperature [K]	**Thermal strain between room and test temperature [10^{-3} m/m]**	**Density calculated from measured linear expansion [kg/m^3]**	**Specific heat capacity [J/(g·K)]**
298	0	2602	0.821
373	0.59	2598	0.902
473	1.28	2593	0.982
573	1.66	2590	1.038
673	2.05	2587	1.079
773	2.46	2584	1.110
873	2.88	2580	1.135
973	3.36	2577	1.156
1073	3.89	2574	1.177
1173	4.43	2571	1.195
1273	4.94	2568	1.211

5.2.3 Specific heat capacity

Six partners measured the specific heat of three samples from three different blocks. For convenience, and since the specific heat is not affected by orientation, all samples were prepared in the X-direction. The difference in heat capacity between samples taken from the same block is less than 2 %. Likewise, the variation between blocks is less than 2 %. Within the temperature range [298 K – 1273 K] the average values over all laboratories can be represented by the polynomial function given in Eq. 1:

$$c_p = 0.2334 + 2.923 \cdot 10^{-3} \cdot T - 3.878 \cdot 10^{-6} \cdot T^2 + 2.497 \cdot 10^{-9} \cdot T^3 - 6.1295 \cdot 10^{-13} \cdot T^4 \quad \text{Eq. 1}$$

The average values are listed in Table 1 (uncertainty at 95 % confidence interval = 7 %).

5.2.4 Thermal radiative properties

Emissivity of the material may affect the analysis of the thermal diffusivity of the material since one should take account of heat losses from the specimen at high temperatures. However, for thermal diffusivity measurements, the samples have to be coated as described in 4.4, i. e. the emissivity of BCR-724 is not relevant.

One has to take account of radiative heat transfer within and through the specimen when we compare transient and steady state values of thermal conductivity. Therefore, thermal transmissivity measurements were performed and the dominant modes of heat transfer in BCR-724 determined. PTB and INSA have found the material to be essentially opaque to wavelengths in the range 4 μm to 20 μm corresponding to that of radiation transmitted from bodies at temperatures of the order of 1250 K. This indicates that the main heat transport mechanism in the material is conduction, and rules out any possibility of coupled radiative and conductive heat transmission.

6 MACHINING OF SUBSAMPLES AND MINIMUM SAMPLE SIZE

6.1 Machining of sub-samples

The BCR-724 samples are produced in different sizes. Nevertheless, the available sizes will not fit the sample holders of all instruments. Most users will therefore be required to cut parts from the BCR-724 samples to their instrument's needs. This additional machining is to be performed with sufficient care, since the accuracy of the dimensions of the sample affects the accuracy of the thermal property measurements. The effect of sample shape imperfections is not covered by the uncertainty of the certified value. Its contribution to the uncertainty can be calculated in a straightforward manner from the estimates of the uncertainty of the dimensions.

6.2 Minimum sample size

In addition, splitting of the BCR-724 samples in smaller samples can cause 'sampling' effects, that is: the volume of material in the smaller sample might not be representative for the bulk of the BCR-724 material. This issue is tackled by the definition of a minimum sample intake. For a material with a certified property value, the minimum sample intake is the smallest sample volume or mass intake for which the sample-to-sample variation of the certified property value does not significantly increase the total measurement uncertainty.

6.2.1 Minimum sample size for thermal diffusivity measurements

Since no dedicated minimum sample size study was performed, the required information will be extracted from the characterisation tests.

Most characterisation tests were performed on cylindrical samples of nominal diameter 10 mm and nominal thickness 1.5 mm. Very good agreement is observed between the thermal diffusivity results obtained in Lab A2 (see Annex 2) using the smallest amount of material (cylinder of Ø 8 mm, thickness 1.0 mm) and the certified value (Section 11). This suggests that the samples used were sufficiently large to be representative of the BCR-724 material. However, given the limited number of tests performed on samples of 1.0 mm thickness, it is chosen to increase the minimum value of the most critical dimension (thickness) and set it at 1.5 mm.

Therefore, the minimum sample size is defined at 1.5 mm thickness and 8 mm diameter. This conclusion is supported by the earlier reported observation that, qualitatively, the microstructure is homogeneous at a length scale of about 50 µm.

6.2.2 Minimum sample size for thermal conductivity measurements

High-accuracy thermal conductivity methods require relatively large samples, to reduce undesired heat loss from the surfaces, and establish a uniform unidirectional heat flow throughout a large fraction of the sample. Therefore, it is difficult to assess directly the minimum sample intake in terms of thermal conductivity.

Physically, thermal diffusivity and thermal conductivity are directly related, as both properties are determined by the transport of heat throughout the material. Therefore, it is decided to use the thermal diffusivity minimum sample intake also for the thermal conductivity property. Additional evidence for this approach is provided in the following section (Homogeneity study).

7 HOMOGENEITY STUDY

The within- and between-block homogeneity of the material was assessed on specimens prepared from 6 out of the 30 blocks.

7.1 Preliminary qualitative investigation

7.1.1 Density

Density was measured on samples from blocks 1, 2, 3 and 4 at Corus and NPL. The smallest samples used were cylinders with thickness and diameter of 20 mm. The highest difference in density within the same block is found in block 4 which shows a standard deviation of 0.23 % from the mean value. Similarly, the difference in density between the blocks is very small. The standard deviation of all measurements is 0.25 %.

7.1.2 Thermal diffusivity

KE measured thermal diffusivity of samples taken from blocks 4, 5 and 6 in three orthogonal directions testing the material's anisotropy. No significant differences in thermal diffusivity can be observed in the three orientations. This confirms the absence of anisotropy indicated by linear thermal expansion and ultra sound velocity studies [1].

7.2 Quantitative investigation

In the absence of a dedicated homogeneity study on a random selection of samples in repeatability conditions, a conservative but quantitative estimate of the between- and within-block homogeneity is obtained from the interlaboratory comparison results. These existing data were subject to an ANOVA analysis.

7.2.1 Within and between block heterogeneity of thermal diffusivity

Samples for thermal diffusivity tests were taken from blocks 1 to 6 and distributed to several labs. Not all laboratories tested at the same temperatures. Yet, at the temperatures 673 K, 873 K and 1073 K, results were obtained from at least 3 samples of every single block of the 6 blocks. A one-way ANOVA analysis allows estimation of the variance within and between blocks. Unfortunately, since samples assigned to a particular lab also belonged to one particular block, the between-block variance also contains the lab-to-lab variance. Hence the results, presented in Table 2 provide a conservative measure of the between-block material heterogeneity.

The within- and between-block standard deviations are combined to obtain u_h, an estimate of the standard uncertainty contribution from the material's heterogeneity. The value of u_h varies with temperature. Taking into account the fact that the between-block material heterogeneity is overestimated, an average u_h of 2.5 % can be safely used in the calculation of the uncertainty of the certified value over the whole of the temperature range covered in this certification.

Table 2: Thermal diffusivity results and result of ANOVA analysis to determine the within-block heterogeneity (s_{wb}), the between-block heterogeneity (s_{bb}); u_h is the combined within- and between-block heterogeneity.

Test temperature		**400**	**600**	**800**
block	sample	thermal diffusivity (10^{-6} x m²/s)		
1	42	1.163	1.014	0.933
1	43	1.164	1.044	0.943
1	44	1.193	1.048	0.943
1	45	1.171	1.035	0.946
2	70	1.116	0.990	0.914
2	71	1.120	0.996	0.918
2	72	1.100	0.986	0.908
2	73	1.097	0.977	0.909
3	50	1.146	1.031	0.956
3	51	1.161	1.055	0.982
3	52	1.137	1.028	0.954
4	54	1.136	1.017	0.946
4	55	1.135	1.011	0.953
4	56	1.127	1.017	0.948
4	57	1.147	1.025	0.950
5	17	1.123	0.993	0.917
5	18	1.116	1.014	0.935
5	19	1.130	1.012	0.934
5	24	1.096	1.000	0.914
6	3	1.079	0.973	0.926
6	6	1.103	1.005	0.938
6	9	1.106	0.998	0.927
mean-of-means		**1.130**	**1.012**	**0.937**
	s_{wb} (%)	**1.12**	**1.17**	**0.89**
	s_{bb} (%)	**2.44**	**2.00**	**1.87**
	u_h (%)	**2.68**	**2.31**	**2.08**

7.2.2 Heterogeneity of thermal conductivity

The thermal conductivity measurements were all performed on samples that are larger than the size of the BCR-724 samples that will be made available as CRM. Therefore, the available test results do not allow a correct estimation of the heterogeneity of the material in terms of thermal conductivity. As explained in section 6.2.2, it is difficult to perform accurate thermal conductivity measurements on small samples. Therefore, it is not possible to do a thermal conductivity homogeneity study that is equally detailed as the one performed for thermal diffusivity. Instead, to assess the homogeneity of the thermal conductivity, λ, use is made of the previously mentioned (see Section 6.2.2) physical link between λ and the thermal diffusivity, α.

Mathematically, the relation between λ and α is captured by the relation $\lambda = \alpha \cdot c_p \cdot \rho$ (with c_p = specific heat capacity and ρ = density). The physical link between λ and α suggests that the value of u_h assessed with thermal diffusivity tests can also be used as an estimate of the heterogeneity of the thermal conductivity. Mathematically, however, the heterogeneity in terms of λ is a combination of the heterogeneity in terms of α, c_p and ρ. One can assume that the effect of the material's heterogeneity on the static properties c_p and ρ is smaller than its effect on a dynamic property such as λ or α [6]. In this case, the contributions of heterogeneity in c_p and ρ can be neglected in comparison with the values of u_h determined in Section 7.2.1 (2.1 to 2.7 %). To verify this, the homogeneity in terms of ρ and c_p was determined at IRMM.

A combined between and within block heterogeneity was already reported in section 5.2.1. Results on 10 samples from 4 different blocks had a standard deviation of 0.25 %. This information needed to be confirmed at a smaller sample scale. The homogeneity of the density of BCR-724 was therefore calculated from the mass and dimensions of 6 disk shaped samples ($\varnothing$ = 6.3 mm, L between 0.4 mm and 3.0 mm) accurately machined (grinding and laser cutting) from 2 blocks. A standard deviation of 0.4 % was achieved, indicating that indeed the contribution from density can be neglected.

The heat capacity was determined at 273 K, 298 K and 373 K, with modulated temperature differential scanning calorimetry (TA Instruments Q1000, temperature oscillation 1.0 K, period 80 seconds, heating rate 5 K/min). 12 discs (nominal thickness 0.5 mm, nominal diameter 6 mm) were tested from 10 different BCR-724 samples. The repeatability of the tests was approximately 3 %. Three replicates were performed on each sample. The variation between samples was not large enough to be detected with the method. However, using the approach proposed by Linsinger et al. [7], the maximum heterogeneity hidden by the method variability was estimated at $u_h^* = 0.77$ %. Again, this is supporting evidence for the assumption that the material heterogeneity in terms of α can be used as an estimate of the material heterogeneity in terms of λ.

8 STABILITY

In order to determine the proper storage and transport conditions for a CRM and the corresponding shelf-life during which the certified value remains valid within its uncertainty, the stability of the certified properties needs to be assessed. However, given the stability of the Pyroceram 9606 microstructure at ambient temperatures, no such study was required.

On the other hand, the use of this CRM will lead to repeated exposure to elevated temperatures. The effect of this thermal cycling is critical and was therefore investigated.

8.1 Qualitative study of the stability on thermal cycling

The stability of the BCR-724 material on thermal cycling has been studied at Corus by combining measurements on thermal conductivity with measurements on sound velocity and acoustic attenuation. The sample size used is 230 mm x 92 mm x 50 mm. NPL has carried out several measurements on hot wire samples of 34 mm thickness in order to check that thin samples can be measured using the hot wire technique. In addition conclusions are drawn from linear thermal expansion measurements described above in Section 5.2.2.

8.1.1 Thermal expansion and density

Thermal expansion and density measurements reveal a permanent linear expansion of 0.28 % after heating the material to 1273 K and cooling back to room temperature. This effect is unlikely to have a significant effect on the thermal properties of the material.

8.1.2 Sound velocity and attenuation

No noticeable difference was observed in sound velocity and attenuation before and after three temperature cycles, indicating that the stability on thermal cycling is good after three cycles.

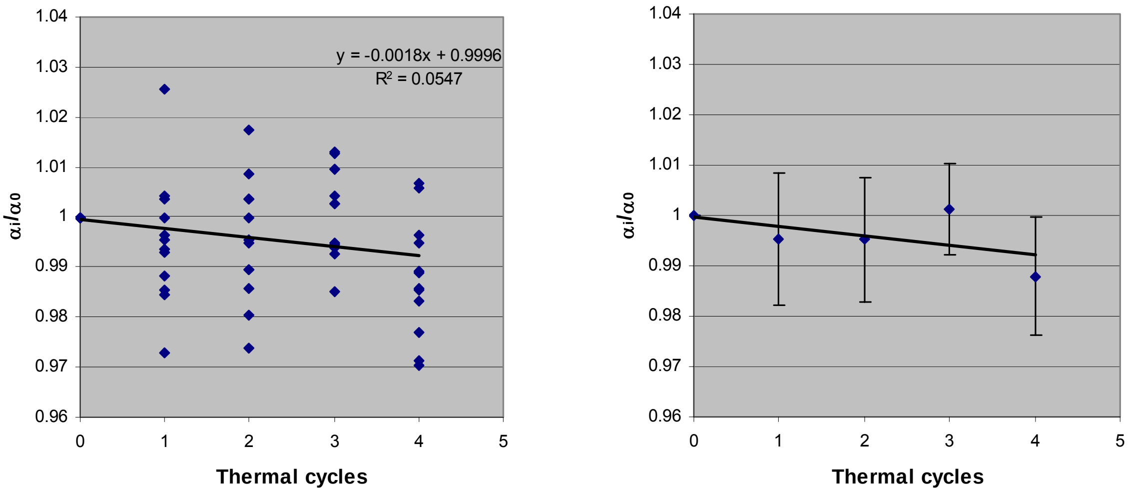
8.1.3 Thermal conductivity

At NPL 35 mm and 50 mm thick hot wire specimens were exposed to temperature cycles up to 1273 K and back several times in carrying out measurements using the parallel wire and resistive wire mode in order to obtain the best operating conditions for the measurement of thermal conductivity. No visible detrimental effect to the specimens was observed.

On the other hand, Corus found that after one thermal cycle, one of their 35 mm thick hot wire specimens cracked along the groove machined in the specimen surface for the thermocouple. This was unfortunate but it is thought that the crack was initiated by micro-cracks introduced during the machining of the specimen. So far no problems have been experienced with cracking of the NPL specimens. It would appear that specimens prepared from this hard glassy ceramic, as with all materials of this type, are always susceptible to cracking if sufficient care is not taken in machining and handling.

8.2 Quantitative analysis of the stability of the thermal diffusivity

Long term stability of the material was monitored at LNE by measuring thermal diffusivity of four samples on receipt (January 2000), at 3 months, 6 months, 1 year and after two years. Measurements were performed at room temperature, 673 K and 1073 K. The results [1] are analysed in accordance with the stability assessment procedures described by Linsinger et al. [8].



a) b)

Figure 3: Change of thermal diffusivity α with number i of thermal cycles; a) all data, b) averages per thermal cycle, with indication of standard deviation.

For the analysis of the results, the measured thermal diffusivity values α_i of thermal cycle *i* are normalised to the value α_0 obtained in the first thermal cycle. The results obtained at the three investigated test temperatures on the 4 samples are pooled. The results (12 data points per thermal cycle) are shown in Figure 3.

The observed slope (-0.182 %/cycle) is statistically not significant (t-test, confidence level 95 %), because of the rather high standard uncertainty associated with the slope (0.099 %/cycle). In such case, the stability contribution to the uncertainty of the certified value is obtained directly from the uncertainty of the measured slope. The uncertainty resulting from an extrapolation of the use to 10 test cycles is 0.99 %. This value will therefore be used as the repeated-use uncertainty of the CRM and included in the combined uncertainty of the certified value.

8.3 Conclusions

1) There is no doubt about the stability of BCR-724 at room temperature even for extended shelf-lifes, or under extreme transport conditions (temperatures varying realistically not outside the range 260 K to 325 K).

2) The analytical results obtained so far do not guarantee that the certified thermal diffusivity value is stable over many repeated uses of the CRM at elevated temperatures. Until additional information is obtained, it is required to limit the use of the CRM to no more than 10 repeated uses up to 1025 K, the maximum temperature used during the stability tests. The corresponding uncertainty of 1 % is added to the uncertainty of the certified value of the thermal diffusivity.

3) As for the homogeneity study, the direct relationship between diffusivity and thermal conductivity is called upon to justify use of the uncertainty determined for the stability of the thermal diffusivity under repeated thermal cycling in the calculation of the uncertainty of the certified thermal conductivity.

9 BATCH CHARACTERISATION ANALYSES

9.1 Description of methods used at participating laboratories

The labs participating in the characterisation tests are indicated with an anonymous code (a letter), as is common practice in reports about the interlaboratory comparison parts of IRMM certification studies. When different test methods are used at a particular lab, the lab code consists of a letter and number.

9.1.1 Thermal diffusivity

Thermal diffusivity is determined by means of transient heating of one side of a specimen and measurement of the temperature response at another side of the specimen. Thermal diffusivity is proportional to the square of the sample thickness and inversely proportional to the measured propagation time of the temperature wave through the sample. Corrections need to be made for heat losses from the sample and for finite pulse rise time (in the case of laser flash technique). Models presume a uniform absorption of the heating beam at the front surface of the sample and one-dimensional heat flow through the sample.

Six laboratories have measured the thermal diffusivity all using different techniques of heating by thermal radiation (either by a laser flash or modulated light beam), and using different mathematical models for data evaluation. The measurement capability of each participating laboratory has been confirmed by participation in intercomparison measurement programs [9, 10, 11, 12, 13, 14].

Since Pyroceram is known to be semitransparent to the incident laser or light beam, the heated sample faces must be coated with an opaque layer to ensure absorption of the heating beam at the sample surface. If the temperature variation of the rear sample face is recorded by means of radiation thermometers it is also necessary to coat the non-heated face of the sample. The coating should be as thin as possible and should have a high thermal diffusivity in order to avoid errors in the measurement of the propagation time. Different laboratories usually apply different coating types. However, in order to be able to assess discrepancies between different coating types, it was decided to distribute to all partners in addition to the two uncoated samples two further samples with identical tungsten coatings as described in 4.4.

Since the thermal diffusivity is proportional to the square of the sample thickness, this quantity must be measured very carefully (at room temperature) and must be corrected for thermal expansion at elevated temperatures. Since all partners have applied this correction using the linear thermal expansion given in Section 5.2.2, the effect of the uncertainty of the thermal expansion correction (8 %) must be included in the uncertainty of the certified properties. The maximum thermal expansion over the temperature range [298 K – 1273 K] is 0.5 %. Given the fact that thermal diffusivity is proportional to (sample thickness)^2, the standard uncertainty of the thermal expansion (8 %) results at most in an additional uncertainty of the thermal diffusivity of $(0.005 \times 0.08 \times 2) = 0.0008 = 0.08\ \%$, which will be shown to be negligible in comparison with other uncertainty contributions.

In the tables in Annex 2, the measurement techniques of the participants are described.

9.1.2 Thermal conductivity using steady state methods

All the measurements were carried out using guarded hot plate (GHP) apparatus. This steady state technique involves placing a solid sample of fixed dimension between two temperature-controlled plates. One plate is heated while the other plate is cooled, and their temperatures are monitored until they are constant. The steady state temperatures, the thickness of the sample and the heat input are used to calculate the thermal conductivity. GHP can be operated either in the single sided or double-sided mode. In the double-sided mode, the central heater plate is placed between two test samples. Most partners embedded the thermocouples in grooves cut in the surfaces of the specimens. The partners who did not do this adopted correction factors to remove the effect of the interface resistance between the specimens and the plates of the apparatus.

Laboratory A1

A 200 mm diameter commercial double-sided hot-plate apparatus (Holometrix, USA) with a metering area of 100 mm diameter was used for the measurements. The device is designed for measurements in the temperature range 50 °C to 650 °C on specimens 5 to 50 mm thick having thermal conductivities from 0.02 to 2 W/(m·K). However, modifications had to be made to the cold plates. Also the power output to the heater plate had to be increased to accommodate the higher thermal conductivity specimens of BCR-724. The specimen was supplied in two hemi-cylindrical shapes that were butted together during the test.

Laboratory B1

The measurements were carried out in a double-sided high temperature 305 mm diameter guarded hot-plate apparatus with a metering area of 150 mm diameter operating in the single sided mode. The apparatus was designed for thermal conductivity measurements in the range up to 0.5 W/(m·K) over the temperature range 100 °C to 850 °C with an uncertainty of about 5 %. However, for the measurement of BCR-724, which has a higher thermal conductivity, the thermocouples used to measure surface temperature were embedded in grooves cut in the specimen surface. The specimens measured were 148 mm diameter and fitted exactly onto the metering area of the heater plate. During a test the metering area was filled with low-density calcium silicate of the same thickness. The temperature difference across the specimen was 30 K.

Laboratory C1

A single specimen guarded hot-plate apparatus was used which was designed at lab C1 for thermal conductivity measurements in the range from 0.1 to about 5 W/m K. The computer-controlled instrument is designed to accommodate cylindrical samples from 80 to 100 mm in diameter and up to 25 mm thick. However, best results are obtained using samples 100 mm in diameter and 10 to 15 mm thick. The BCR-724 specimens were supplied at this diameter but in two hemi-cylindrical pieces that had to be held together during a test with wire tied around the circumference. The thermal conductivity was measured over the temperature range from –60 °C to +200 °C and the temperature drop across the sample controlled to be 5 K. The measurement uncertainty is better than 3 % with a repeatability of 0.1 %.

Laboratory D

Measurements were carried out using a double-sided guarded hot-plate apparatus with sample dimensions of 500 x 500 mm and a metering area of 250 x 250 mm. The BCR-724 sample consisted of two sets of three rectangular pieces 250 mm long and 25 mm thick. Pieces were 70 to 90 mm wide. These were arranged either side of the heater to cover the metering area. The annular zone surrounding the sample was built up with insulating material. The temperature range covered was about 200 °C to 750 °C with a temperature drop in the samples of between 5 °C and 15 °C.

Laboratory E

The measurements were carried out using a 70 mm diameter single-sided guarded hot plate apparatus capable of operating up to 1200 °C. These measurements were carried out using plate thermocouples; two specimens of different thickness are required for the test in order to eliminate the contact resistance between the plates and the specimen.

9.1.3 Thermal conductivity using hot wire or hot strip methods

This transient technique involves placing an electrically heated wire into a material. This intrusive method is limited to testing foams, fluids and melted plastics. The heat flows out radially from the wire into the sample and the temperature of the wire is measured. By plotting the temperature of the wire versus the logarithm of time, thermal conductivity can be calculated.

Originally six partners were to carry out the measurements of thermal conductivity using a hot wire apparatus. Lab F had problems with its apparatus and was not able to complete any measurements. However, lab B2 was able to carry out additional measurements by operating this hot wire apparatus in the resistive wire mode as described below. It is safe to accept this as a different method as the measurement of the temperature rise was determined using the change in resistance of the heater wire rather than the additional thermocouple and the data analysis was different.

Five of the participating laboratories used the hot wire technique whilst lab C2 used the slightly different hot strip method that has some benefits over the hot wire approach.

Laboratory G

This partner used a parallel hot-wire method built in house according to ISO 8894-2: "Refractory materials - Determination of thermal conductivity."

Laboratory B2

Lab B2 used a commercial apparatus (Netzsch 426) capable of measuring thermal conductivity up to 25 W/(m·K) in the parallel wire mode over the temperature range from room temperature to 1500 °C. The apparatus at Lab B2 could also measure thermal conductivity in the resistive wire mode where the temperature rise of the hot wire is measured by observing its change in resistance as it is heated during a test. The method is then less sensitive to inhomogeneities in the specimen. In the parallel wire mode if the wire separation is known then the specific heat capacity and thermal diffusivity can also be determined. Two sets of bricks were used for the measurement whose surfaces were flat to better than 0.1 mm thus ensuring good thermal contact at the interfaces.

Laboratory H

The same type of apparatus as lab B2 was used, that is a Netzsch hot wire operated in the parallel wire mode.

Laboratory C2

A transient hot strip set-up was used to measure thermal conductivity and diffusivity simultaneously at working temperatures from room temperature up to 800 °C. A set of two nearly identical bricks, each of 80 mm in length and 30 mm x 30 mm in cross section are required for the measurement. The measurement uncertainty is not less than 5 % for thermal conductivity and 10 % for diffusivity.

Laboratory I

Lab I used an apparatus built in house for carrying out the measurements. The apparatus is normally used for carrying out tests on ceramic based materials so it was ideal for these measurements. It is not easy to control the test temperature in this apparatus. Therefore, the results are obtained at temperatures not so close to the nominal temperatures.

9.1.4 Correction of values for difference between nominal and actual test temperature

In most cases diffusivity and conductivity have 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 mean thermal diffusivity and conductivity values at the nominal temperatures, the original data measured at the actual temperature had to be corrected to the value at nominal temperature taking into account the difference between actual and nominal temperature and the slope of the property/temperature curve at the nominal temperatures.

For diffusivity tests, the slope at each nominal temperature has been determined from the mean thermal diffusivity values of all measurements across all labs. The resulting diffusivity/temperature curve iteratively has been found by fitting the values with a fourth order hyperbola. The slope at the nominal temperatures has been estimated by differentiating this hyperbolic function. The deviations from the nominal temperature were in most cases less than 2 K, and the corresponding diffusivity corrections were in most cases less than 1 %.

For conductivity tests, a similar approach was followed, but using a linear model of thermal conductivity versus the reciprocal of the absolute temperature. This function is predicted to fit the thermal conduction in a crystalline material by phonons (lattice vibration). Whereas Pyroceram 9606 is indeed a good electrical insulator (so no free electrons for thermal conduction) and while, over the temperature range considered in this project, the thermal transmission by radiation has been shown to be negligible, Pyroceram is not fully crystalline. Nevertheless, the linear function fits the data very well ($R^2 = 0.998$), and allows a reliable calculation for each lab of the values of thermal conductivity at the nominal temperatures.

9.2 Results

9.2.1 Thermal diffusivity results

Each of the six partners involved in thermal diffusivity measurements had four specimens for measurement. These four samples were measured at the predetermined nominal temperatures (298 K, 323 K, 373 K and up in steps of 100 K to 1273 K) during a first heating cycle (run 1), in some cases followed by a measurement during cooling, and in a repeated heating cycle (run 2). Repeat measurements had to be carried out by removing the specimen and re-assembling in the apparatus.

The interlaboratory mean values were calculated using the results from the heating cycles. For each lab, the measurement results on the four samples are presented in the tables in Annex 2.

For each partner two graphs are shown (Figure 12 to Figure 23). One graph shows the dependency of the thermal diffusivity, averaged over all accepted data of the four measured samples, on temperature. The second graph indicates the scatter of the results on the four samples compared to the mean values of the four measurements.

- Note on measurements of partner A

A first round of measurements at samples 5.58 to 5.61 showed bad adhesion of the tungsten layers for all 4 samples. The deposited tungsten film contained in some regions a high number of holes that caused measurement errors leading to too high diffusivity values. It was therefore decided that the results on all these samples should be rejected and a second round of measurements should be performed on four samples already measured during the preliminary characterisation phase of the project. These four samples (5.17-5.19, 5.24) had been cut also from block 5, had a thickness of about 1.0 mm and had shown no defects in tungsten layers. They had been measured in the first round at 673 K, 873 K, 1073 K, and 1273 K during heating and subsequent cooling. They were now re-measured in the second round between 573 K and 1273 K, during heating and subsequent cooling. The results obtained on these samples are presented in Annex 2.

9.2.2 Thermal conductivity results

- Thermal conductivity measurements by steady-state methods

None of the apparatus used by the laboratories were of the same size. Therefore each partner was supplied with a specimen - usually made of several pieces - that was unique for their apparatus. The number of pieces used to make each specimen was determined by the size of the raw blocks of Pyroceram and the size of the partner's guarded hot plate. Every attempt was made to minimise the number of joints in the metering area and generally this was kept down to one joint. Some of the partners carried out additional machining on the specimens to mount thermocouples in grooves to measure the surface temperature more accurately. It was therefore not possible to exchange specimens.

Each partner was requested to carry out a repeat measurement of their own specimens in order to assess their repeatability. The raw data results from the thermal conductivity measurements are shown in the tables in annex 3.

- Thermal conductivity measurements by hot wire/strip methods

The size of the large hot wire specimens for this test as recommended in ISO 8894-2:1990 is 200 x 100 x 50 mm. Because of the size of the Pyroceram blocks the maximum size specimen that could be made was 230 x 90 x 50 mm. This should not affect the measured value of the thermal conductivity. However it makes the measurement more difficult as there is less data on the temperature rise time curve for analysis. In order to conserve material stocks it was decided that only three pairs of samples plus a smaller pair for Lab C2 would be produced. The three larger samples were passed around the other 5 partners for measurement.

Lab F dropped out of the measurements as their apparatus broke and could not be repaired in time to complete their measurements. Their place was taken by Lab B2 who carried out additional tests using the resistive wire mode of operation and analysis. Apart from Lab C2 and Lab I the other partners managed to carry out measurements on two specimens.

The raw data results from individual laboratories using the transient technique are shown in annex 4.

10 TECHNICAL AND STATISTICAL EVALUATION OF THE BATCH CHARACTERISATION

10.1 Thermal diffusivity

10.1.1 Technical-statistical evaluation

Thermal diffusivity has been measured by six partners on 5 different blocks of the material. Each partner has measured four samples of the same block in one or two cycles. Two of the samples were coated with tungsten, the other two coated by the partner's own technique.

From the results of those partners, who repeated measurements (Labs F2, A2, L), it can be seen that the mean deviation between run 1 and run 2 is less than 1 % for most measurements. Only the results of Lab K showed greater differences up to 3.3 %. Positive as well as negative deviations are observed, indicating that there is no systematic difference between the two cycles, i.e. no irreversible change in the material due to thermal treatment could be found.

The mean diffusivity data (run 1 + run 2) of all samples coated with the own coating technique of each partner are compared to the results obtained at the samples coated by KE with tungsten. With the exception of Lab F2 the difference between these two coating techniques was 1 % or less, with values both positive and negative. Hence, there is no systematic bias due to the type of coating.

From the above, we conclude that the results of all samples and of both heating cycles can be pooled.

- Note to results Lab F2

The instrument of lab F2 is very sensitive to scattered light (from the laser beam). For exact measurements the sample faces have to be coated with a high absorption material like graphite. Therefore it was decided that the data obtained on the tungsten-coated sample 3.53(W) (printed Table 16 in italic) should not be used for the calculation of the certified value.

- Note to results Lab K

The highest scatter of diffusivity data is obtained at 373 K (14.6 %), which is caused by a very low value for specimen 1.68 (run 2) and a very high value of 1.69 (run 1), as can be seen from Table 17. According to the Grubbs' outlier test the low value is an outlier. However, at the other temperatures the results on these data sets are not extreme, indicating that the outlier values do not stem from the sample but from the apparatus performance. The bad reproducibility of measurements is greater than the given apparatus uncertainty. Therefore, data from lab K were withdrawn.

- Exchange of samples between laboratories

For lab F2 the mean diffusivity values at temperatures above 673 K are higher than the grand mean values of all laboratories. Since lab L uses samples of the same dimensions, it was decided that these laboratories should exchange their specimens. The samples of lab F2 had been cut from block 4, those of lab L from block 3.

The diffusivity results obtained at the exchanged samples are compared to those before exchanging (see annex 5). The original difference observed in diffusivity data between lab F2 and lab L (about 1.7 % averaged over all measured temperatures) reveals to be composed of a systematic difference between the results of lab F2 and lab L on the same samples (about 0.7 %, but increasing with temperature to about 1.8 % at higher temperatures) and a difference in thermal diffusivity between block 3 and block 4 of about 1.0 %. This is consistent with the previously assessed between-block heterogeneity value (of about 2 %), which is confirmed to be a conservative estimate.

10.1.2 Interlaboratory mean thermal diffusivity and the associated uncertainty

The mean diffusivity values of all laboratories are summarised in Table 3. The interlaboratory mean values are plotted versus temperature together with the mean values of the laboratories in Figure 4.

Table 3: Overview of thermal diffusivity data, interlaboratory means and standard deviations. (Note: data from lab K are excluded from the calculation of mean and standard deviation; see section 10.1.1)

column 1	2	3	4	5	6	7	8	9
Labs	**F2**	**K**	**A**	**L**	**M**	**B3**		
block	**3**	**1**	**5**	**4**	**2**	**1**		
	lab-mean of measured thermal diffusivity							
T	a1	a2	a3	a4	a5	a6	overall mean	s
K	10^{-6} m^2/s						10^{-6} m^2/s	%
298	1.934	*1.865*		1.930	1.923	1.918	**1.926**	0.38
323	1.755				1.785	1.772	**1.771**	0.86
373	1.583	*1.554*		1.584	1.575	1.644	**1.596**	2.00
473	1.353	*1.373*		1.357	1.341	1.409	**1.365**	2.21
573	1.238		1.223	1.223	1.204	1.278	**1.233**	2.26
673	1.148		1.116	1.136	1.108	1.173	**1.136**	2.28
773	1.086		1.055	1.071	1.042	1.090	**1.069**	1.89
873	1.038		1.005	1.018	0.987	1.035	**1.017**	2.09
973	0.993		0.963	0.978	0.946	0.980	**0.972**	1.82
1073	0.964		0.925	0.949	0.912	0.941	**0.938**	2.16
1173	0.937		0.898		0.889	0.901	**0.906**	2.33
1273	0.903		0.871		0.866	0.868	**0.877**	2.02

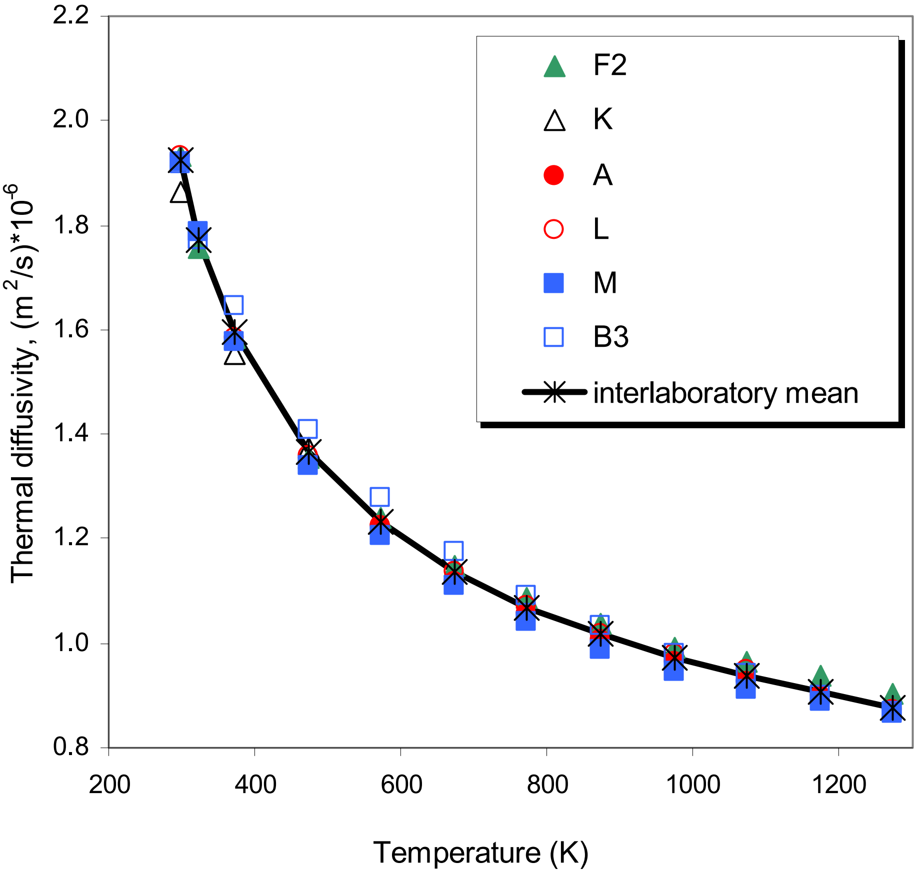


Figure 4: Mean thermal diffusivity data of all labs, and interlaboratory mean (interlaboratory mean was calculated excluding data from lab K; see section 10.1.1).

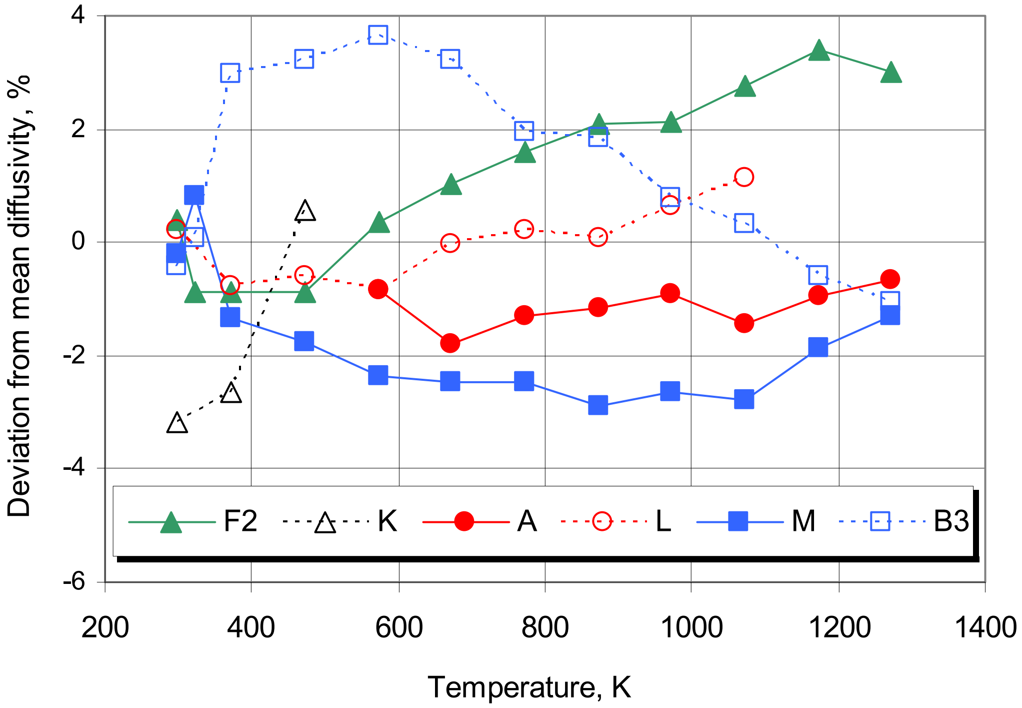


Figure 5: Differences between within-lab mean thermal diffusivities and interlaboratory mean.

The deviation of the results of the individual laboratories from the interlaboratory mean is plotted as a function of temperature in Figure 5. The lowest values were measured by lab M on samples of block 2 and are up to 2.8 % lower than the grand mean values. The highest values were measured by lab B3 on block 1 at medium temperatures (up to 3.6 % higher than the grand mean) and by lab F on block 3 at high temperatures (maximum 3.4 % higher than grand mean). In any case the differences between the results of the partners and the grand mean values are within the method uncertainties of the individual labs shown in. shows also the uncertainty u_{char} of the grand mean values, calculated as $u_{char} = \frac{s_{char}}{\sqrt{n}}$, with s_{char} the standard deviation of the lab means at a particular temperature, and n the number of labs that produced an accepted thermal diffusivity value at that temperature. For each of the measured temperatures, u_{char} is near to or less than 1 %. The largest value is 1.16 % (for the data obtained at 1173 K), the average value is 0.93 %.

Table 4: Calculation of uncertainty of interlaboratory mean thermal diffusivity, and comparison with uncertainty values of individual labs.

column	2	3	4	5	6	7	8	9
Labs	**F2**	**A**	**L**	**M**	**B3**	interlaboratory **mean**	**st.dev**	**u_{char}**
U_A (specified by lab, 95 % confidence level)								
T (K)	%	%	%	%	%	$(m^2/s)*10^{-6}$	%	%
298	4,30		4,90	6,02	6	1,93	0,38	0,19
323	4,20			6,10	6	1,77	0,86	0,49
373	4,10		4,40	6,04	6	1,60	2,00	1,00
473	4,00		3,70	6,00	6	1,37	2,21	1,11
573	3,00	6,48	3,70	6,04	6	1,23	2,26	1,01
673	4,20	6,46	3,70	6,10	6	1,14	2,28	1,02
773	2,60	6,50	3,90	6,12	6	1,07	1,89	0,85
873	4,10	5,84	4,20	6,20	6	1,02	2,09	0,93
973	3,30	6,08	4,50	6,22	6	0,97	1,82	0,82
1073	3,30	4,28	4,70	6,30	6	0,94	2,16	0,97
1173	4,20	4,04		6,36	6	0,91	2,33	1,16
1273	4,20	4,70		6,32	6	0,88	2,02	1,01
						maximum	**2,33**	**1,16**

10.2 Thermal conductivity

10.2.1 Steady state thermal conductivity values

The GHP results obtained at laboratory D (Table 22) were very much lower than those from the other partners and the spread between repeat runs was greater than 10 %. A statistical analysis of these results showed that they were outliers and could not be considered as part of the same data set as the other measurements. The data were rejected as the apparatus, which is designed for measuring insulating materials, had been heavily modified to carry out the tests.

A statistical examination using the Grubb’s outlier test shows that the results of laboratory E (Table 26) are statistical outliers. Closer inspection of the technical details of the test method revealed suspicion about the correction made for the interface resistance between the apparatus (increasing with temperature), and about the assumptions being made about radiative heat transmission within the sample. This is why the data were rejected for inclusion in the analysis.

The first set of data from lab B1 (run 1, see Table 24) was omitted from the analysis because the measurements were carried out with bare wire thermocouples that had not been used in this apparatus before and it was more difficult to determine the exact position of the thermocouple tip in the groove cut in the specimen surface.

10.2.2 Transient thermal conductivity

From the original raw data for the hot wire and strip measurements none was rejected.

10.2.3 Pooling of results from steady-state and transient test methods

There is reasonably good agreement between the results from steady state and transient methods. The steady state values are usually within the spread of transient values. It was decided to pool the two sets of data and to obtain a single interlaboratory mean thermal conductivity.

10.2.4 Interlaboratory mean thermal conductivity and the associated uncertainty

All the thermal conductivity data from both transient and steady state methods used to determine the interlaboratory mean value are summarised in Table 5, which shows the mean value of thermal conductivity at each temperature level, the standard deviation of all mean values at a particular temperature, and the resulting u_{char} (calculated as $u_{char} = \frac{s_{char}}{\sqrt{n}}$). With the exception of the results at 298 K, the values of u_{char} are always smaller than 1.8 %. For each of the data points, the interlaboratory mean and the laboratory mean agree within the respective uncertainties u_{char} and u_a.

Table 5: Calculation of interlaboratory mean thermal conductivity and associated uncertainty.

	GHP			**Hot Wire or Hot Strip**						**average and uncertainty**			
						parallel wire	resistive wire						
Temperature	A1	B1	C1	G	H	B2	B2	C2	I	**mean**	**s_{char}**	**s_{char}**	**u_{char}**
K	**(W/m.K)**									**(W/m.K)**		**%**	
223			4.42							**4.42**	-	-	**-**
273			4.09							**4.09**	-	-	**-**
298	3.99		3.96	3.94	3.97	4.28	3.93	4.03	4.54	**4.08**	0.22	5.33	**1.88**
323	3.88		3.86		3.84	4.13	3.82	3.89		**3.90**	0.11	2.92	**1.19**
373	3.70		3.69	3.58	3.63	3.89	3.64	3.67		**3.69**	0.10	2.68	**1.01**
473	3.46		3.46	3.28	3.34	3.57	3.40	3.37	3.68	**3.45**	0.13	3.76	**1.33**
573	3.30	3.27		3.09	3.15	3.36	3.24	3.17		**3.23**	0.09	2.91	**1.10**
673	3.19	3.16		2.95	3.01	3.21	3.13	3.03	3.25	**3.12**	0.11	3.44	**1.22**
773	3.11	3.08		2.85	2.91	3.10	3.05	2.93		**3.00**	0.11	3.50	**1.32**
873	3.05	3.02		2.78	2.84	3.01	2.99	2.85	3.01	**2.94**	0.10	3.50	**1.24**
973		2.97		2.71	2.78	2.95	2.94	2.78		**2.86**	0.11	3.89	**1.59**
1073		2.92		2.66	2.73	2.89	2.90	2.73	2.86	**2.81**	0.10	3.68	**1.39**
1173				2.62	2.69	2.85	2.87	2.69		**2.74**	0.11	4.01	**1.79**
1273				2.59	2.65	2.81	2.84		2.76	**2.73**	0.11	3.90	**1.75**
												mean u_{char}	1.40
												max u_{char}	1.88

The deviations of the thermal conductivity values measured at individual laboratories from the interlaboratory mean thermal conductivity values are shown in Figure 6 for each laboratory, for each investigated temperature. The values obtained by steady state methods are indicated with solid shapes (diamond, square, triangle). The graph shows that the steady state thermal conductivity values tend to be amongst the higher values obtained using the transient technique.

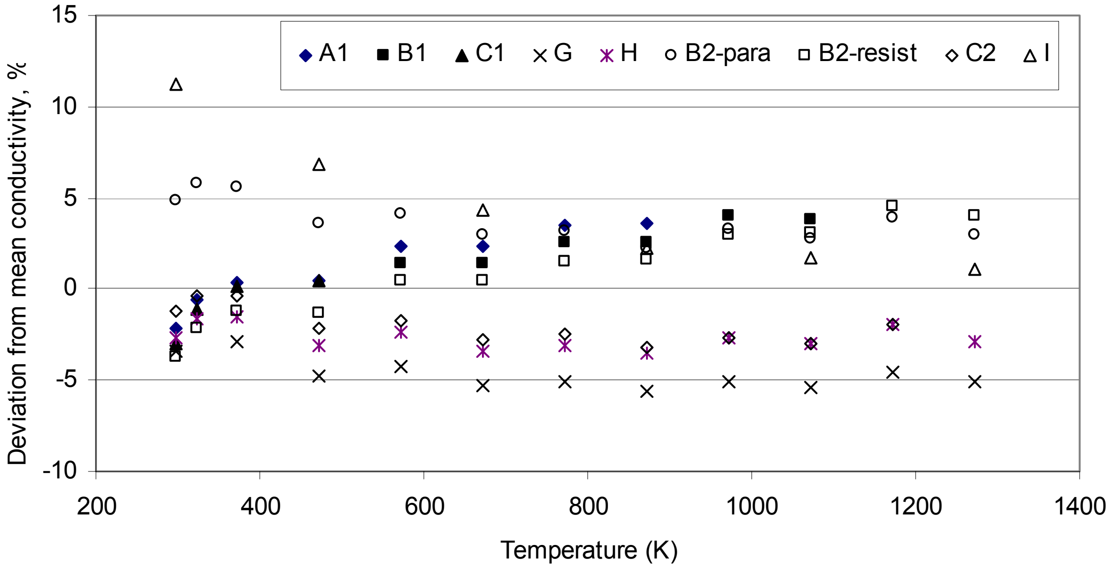


Figure 6: Percentage deviations for each laboratory from the mean value of thermal conductivity.

10.3 Comparison of thermal conductivity values calculated from thermal diffusivity results with GHP- and hot wire measurements.

Applying the first law of thermodynamics and combining with Fourier's law it can be shown that the following relationship, Eq. 2, between the thermal diffusivity α and the thermal conductivity λ applies in conditions of transient temperatures:

$$\lambda = \alpha \cdot c_p \cdot \rho \qquad \text{Eq. 2}$$

The specific heat capacity c_p and the density ρ have been determined for the BCR-724 (see 5.2). The measured values and the calculated thermal conductivity are presented in Table 6. The agreement between calculated and interlaboratory mean thermal conductivity is clearly within the uncertainty of the individual values (Figure 7). This is an important observation because thermal diffusivity measurements are very often used to determine thermal conductivity indirectly.

Table 6: Comparison of thermal conductivity results obtained from thermal diffusivity, from GHP- and Hot-wire measurements.

Temperature	**Interlaboratory mean TD**	**Specific heat capacity**	**Density**	**TC calculated from TD**	**GHP mean TC**	**Hot wire mean TC**	**Interlaboratory mean TC**
K	$(m^2/s)*10^{-6}$	J/(g K)	kg/m^3	W/(m K)	W/(m K)	W/(m K)	W/(m K)
298	1.926	0.821	2606	4.121	3.975	4.115	**4.080**
323	1.771	0.851	2604	3.924	3.870	3.920	**3.903**
373	1.596	0.902	2598	3.741	3.695	3.682	**3.686**
473	1.365	0.982	2593	3.476	3.460	3.440	**3.445**
573	1.233	1.038	2590	3.316	3.285	3.202	**3.226**
673	1.136	1.079	2587	3.172	3.175	3.097	**3.116**
773	1.069	1.110	2584	3.065	3.095	2.968	**3.004**
873	1.017	1.135	2580	2.977	3.035	2.913	**2.944**
973	0.972	1.156	2577	2.896	2.970	2.832	**2.855**
1073	0.938	1.177	2574	2.843	2.920	2.795	**2.813**
1173	0.906	1.195	2571	2.784		2.744	**2.744**
1273	0.877	1.211	2568	2.727		2.730	**2.730**

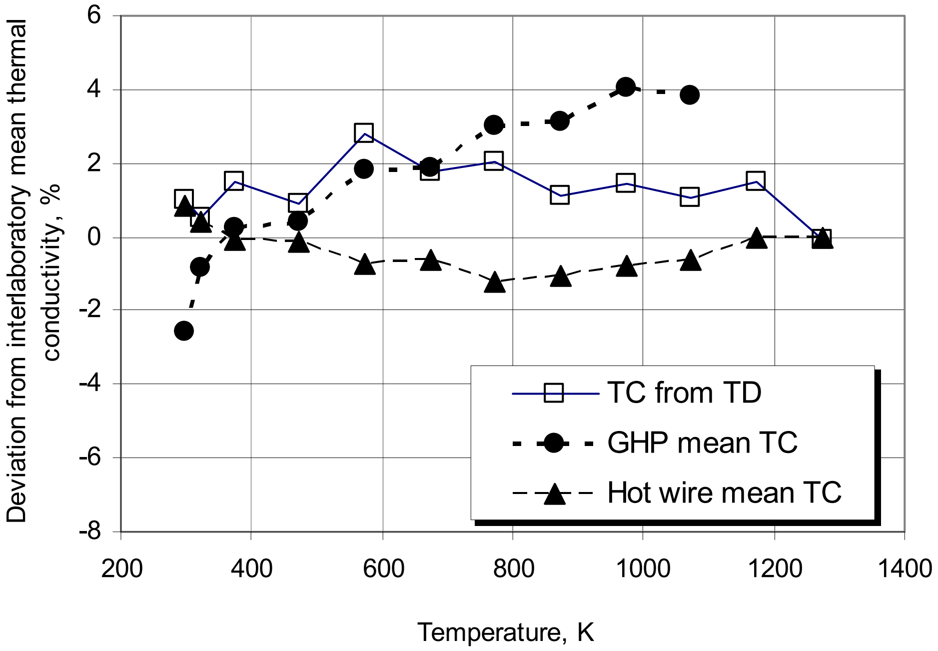


Figure 7: Deviations of the thermal conductivity values calculated from diffusivity, GHP-, and Hot-wire-measurement results respectively from the interlaboratory mean thermal conductivity.

11 CERTIFIED VALUES OF THERMAL CONDUCTIVITY AND THERMAL DIFFUSIVITY FOR BCR-724

The certified values of thermal conductivity, λ, and thermal diffusivity, α, of BCR-724 are presented in the form of an equation of α and λ versus temperature. The equations are obtained by fitting to the interlaboratory mean values over the full range of test temperatures [298 K – 1273 K]. However, for reasons of stability, the temperature range over which the certified values are valid is limited to [298 K – 1025 K]. It is chosen to estimate the uncertainty as 1 particular relative value, valid over the whole temperature range.

11.1 Thermal diffusivity

The certified value of the thermal diffusivity, α, is represented by the following 4th order polynomial function in T (K):

$$\alpha = 4.406 - 1.351 \cdot 10^{-2} \cdot T + 2.133 \cdot 10^{-5} \cdot T^2 - 1.541 \cdot 10^{-8} \cdot T^3 + 4.147 \cdot 10^{-12} T^4 \qquad \text{Eq.3}$$

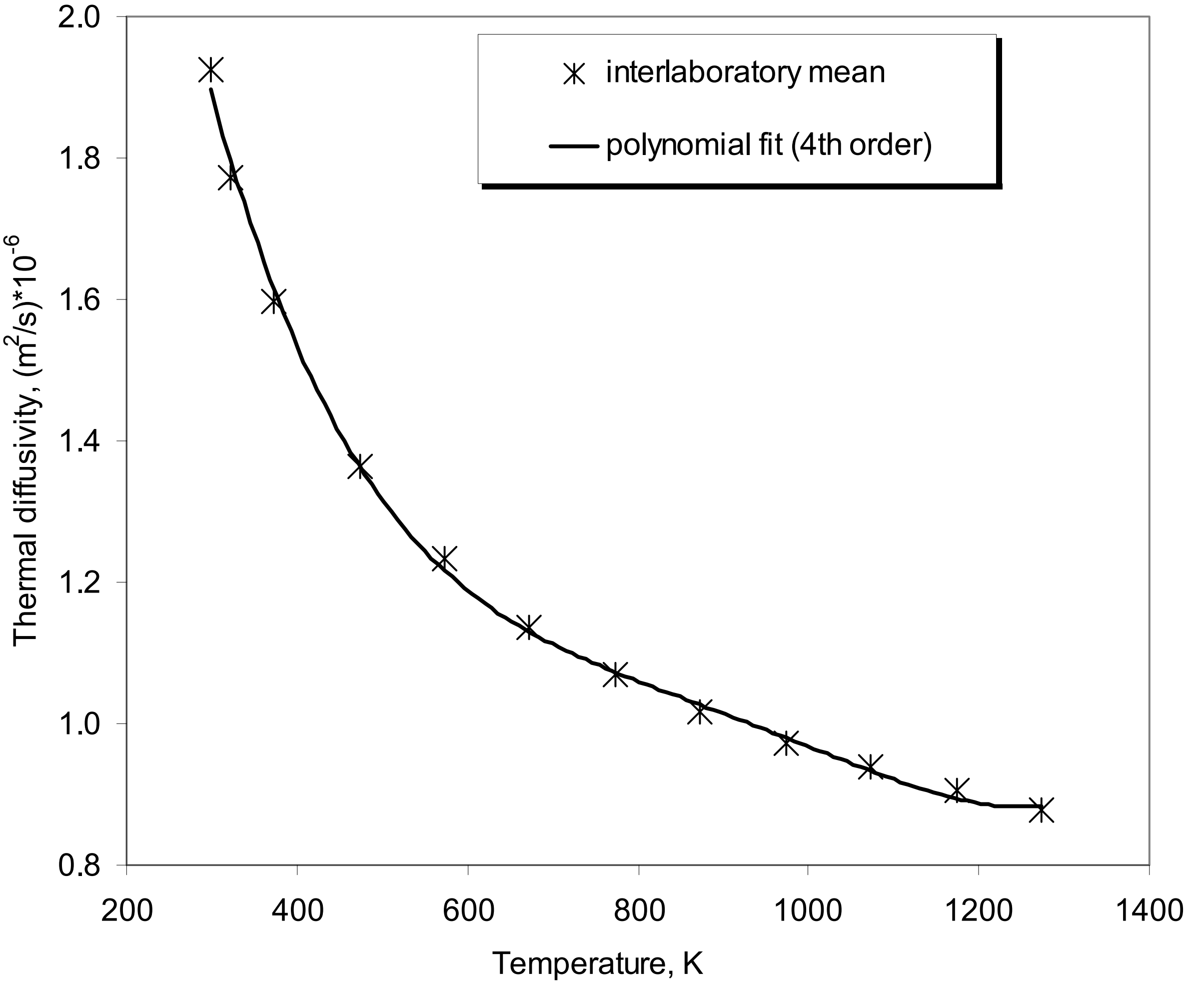


Figure 8: Fit of 4th-order polynomial curve to interlaboratory mean values as a function of temperature (in K).

The equation represents the interlaboratory mean values to better than 0.5 % (Figure 8). The combined uncertainty of the certified value of the thermal diffusivity therefore consists of the following contributions:

- Uncertainty associated with fitting equation through measured values: 1.0 %
- Uncertainty associated with the estimate of the interlaboratory mean value: 1.0 %
- Uncertainty associated with material heterogeneity: 2.5 %
- Uncertainty associated with stability: 1.0 %
- Uncertainty associated with correction for thermal expansion: 0.1 %

The combined uncertainty is the square root of the sum of squares of all uncertainty contributions, and therefore is 3.04 %. The expanded uncertainty, equal to the combined uncertainty multiplied by a coverage factor equal to 2, providing a level of confidence of approximately 95 %, is 6.1 %.

11.2 Thermal conductivity

BCR-724 is a good electrical insulator, so there are no free electrons for thermal conduction. Also, over the temperature range considered, the thermal transmission by radiation is negligible. Therefore the thermal conduction in the material is predominantly by phonons and the conductivity should vary linearly with the reciprocal of the absolute temperature. Hence, the certified value of the thermal conductivity, λ, is represented by the following linear function of the inverse of the absolute temperature (T in K).

$$\lambda = 2.332 + 515.1/T \qquad \text{Eq. 4}$$

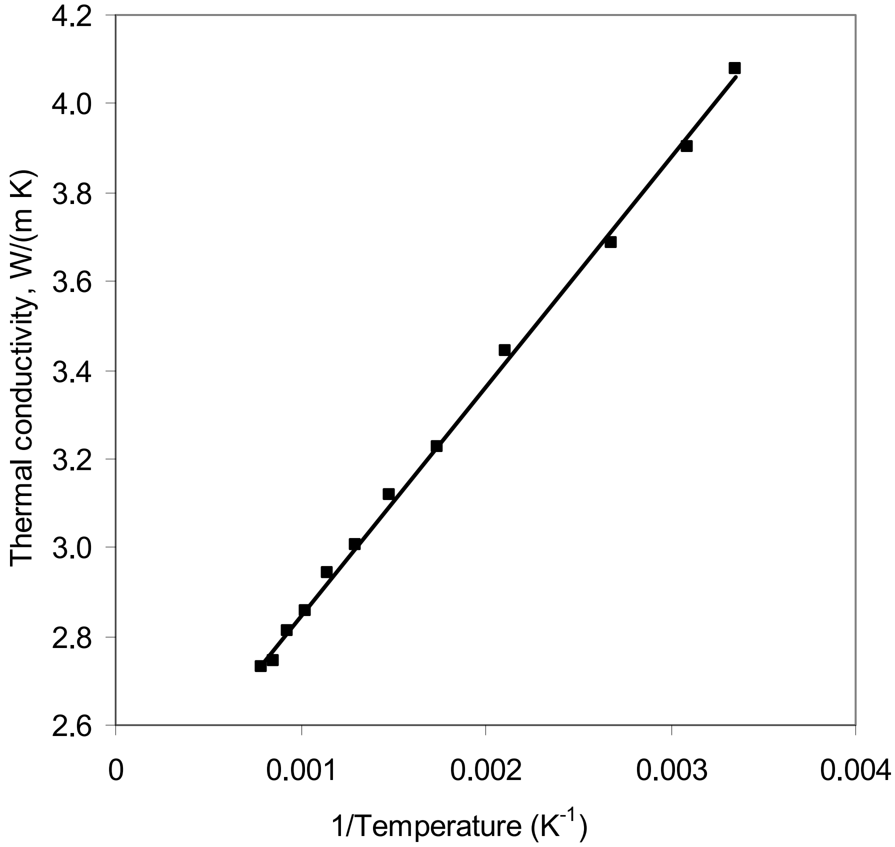


Figure 9: Fit of linear curve to interlaboratory mean values as a function of 1/Temperature (x = 1/(Temperature in Kelvin)).

The fitted equation approaches all of the interlaboratory mean values to within 1.0 % (Figure 9). The combined uncertainty of the certified value of the thermal diffusivity therefore consists of the following contributions:

- Uncertainty associated with fitting equation through measured values: 1.0 %
- Uncertainty associated with the estimate of the interlaboratory mean value: 1.5 %
- Uncertainty associated with material heterogeneity: 2.5 %
- Uncertainty associated with stability: 1.0 %

The combined uncertainty therefore is 3.24 %. The expanded uncertainty, equal to the combined uncertainty multiplied by a coverage factor equal to 2, providing a level of confidence of approximately 95 %, is 6.5 %.

12 TRACEABILITY

12.1 Thermal diffusivity

The certified thermal diffusivity of the BCR-724 material has been calculated using data obtained with instruments based on the laser flash or Xenon-lamp pulse methods. In these methods, the specimen is supported in a furnace to assure the desired reference temperature. A short uniform heat pulse is deposited on the front side of the sample where thermal energy is absorbed within a thin surface layer. The energy diffuses through the sample and after some time reaches the rear side. Here, it produces a characteristic temperature vs. time-shape. The rear-side temperature excursion is measured. In general, the thermal diffusivity, α, is calculated from the sample thickness, d, and the characteristic time, $t_{1/2}$, needed for the rear-side temperature to reach 50% of its maximum value:

$$\alpha = C\frac{d^2}{t_{1/2}} \tag{1}$$

The dimensional constant C equals 0.1388 m^2/s; the half-time, $t_{1/2}$, should stay within 0.04 to 0.25 s limits, and the temperature increase reaches values from 1 K up to 5 K [15]. Eq. 1 is directly resulting from the definition of thermal diffusivity (ref. section 1.1). Also, the measurements involved (thickness of sample, temperature of rear-side, and time) can be performed in an SI-traceable manner. Therefore, the laser-flash method can be considered a primary method.

As a conclusion, since the certified thermal diffusivity value has been deduced from measurements at 6 independent laboratories, each using a primary method, the certified value is traceable to SI.

12.2 Thermal conductivity

The certified thermal conductivity of the BCR-724 material has been calculated from results obtained at 9 different laboratories, using several types of analysis instruments. Three of the retained data sets were obtained on instruments that are based on the guarded hot plate method. In the guarded hot plate method, the thermal conductivity is directly determined using a simple equation for one-dimensional heat flow along the longitudinal axis of a sample:

$$\lambda = \frac{\Phi}{\Delta T}\frac{d}{A} \tag{2}$$

According to this equation, a heat flow is applied normal to the sample's cross-sectional area, A, to give rise to planar isotherms. The heat flow-rate, Φ, is controlled to be small enough for reasonable thermal stability but large enough to produce an accurately measurable temperature difference, $\Delta T = T_1 – T_2$, across the heat path length, $d = x_2-x_1$. Whereas the measurement in itself is a common task, the major difficulties arise from the realization of the appropriate boundary conditions. These have to be adiabatic for the following two reasons: A one-dimensional and uniform heat flow pattern within the sample, as assumed by Eq.(2), can only be reached in practice if there are no heat losses from the sample's lateral surface. Otherwise, these would distort the planar temperature profile at the edges. Furthermore, since Φ can not be measured directly, it is usually evaluated from the (electric) power, P, to the applied heater. This is trivial only if all measured power is entirely fed into the sample and thus, Φ = P is valid. Hence, both the sample's lateral surface, as well as the edges of the heater, must be thermally isolated to the surroundings to prevent any stray heat flows. In order to establish adiabatic conditions to the sample, suitable auxiliary guard heaters are required in addition to effective thermal insulations. Each guard heater has to be balanced carefully to minimize its temperature drop to the specimen.

A steady-state determination of λ is a laborious and time-consuming task because measurements can only be started after having accomplished a proper temperature matching of all heaters. However, the underlying principle of steady-state techniques is given in terms of a very simple mathematical model. Since only measurements of power and the base units length and temperature are required, these methods are absolute ones [15].

Considering that the certified thermal conductivity of the BCR-724 material has been calculated from data obtained at 9 different laboratories, amongst which three have used a primary method, the certified value is traceable to SI.

13 INSTRUCTIONS FOR USE

13.1 Instruction for storage and transport

BCR-724 samples can be stored in a normal laboratory environment. No special temperature or humidity conditions are required. For transportation it should be protected against cracking or chipping by packing between foam or polystyrene chips. However, the European Commission cannot be held responsible for changes that take place during storage of the material at the customer's premises, especially of opened samples.

13.2 Physical handling and sample preparation

The user is allowed to drill holes or slots in the sample, provided that the amount of material removed is negligibly small in comparison with the dimensions of the sample. The material is very hard and difficult to machine. When it is necessary to cut a smaller sample from a rod, the following hints should be considered:

- Use a high speed cutting tool that has plenty of water cooling and move the cutting tool slowly across the work piece taking small cuts at a time.
- For grinding, a typical amount to remove in one cut would be of the order of 0.1 mm.
- Thickness of the sample when measured at a minimum of 4 positions on the specimen should not vary by more than 1 %.

13.3 Restrictions for use of the BCR-724 samples

The user should keep within the following guidelines:

- Never heat the sample above the maximum temperature of 1025 K. Until additional evidence for stability is obtained, the certified reference material samples are not to be heated more than 10 times up to 1025 K.
- Both heating and cooling rate should not exceed 50 K/min.
- After the first heating run to the upper temperature at least two measurement runs should be carried out in order to check repeatability.

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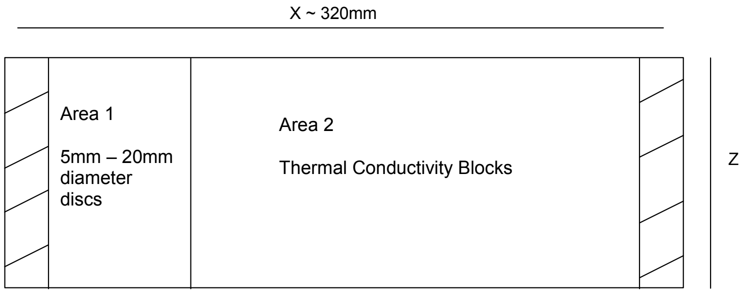
ANNEX 1: CUTTING SCHEME AND DISTRIBUTION OF SAMPLES USED FOR CERTIFICATION STUDY (BLOCKS 1-6)

Orientation – top face of block



Side view - block tapers in length from top to bottom

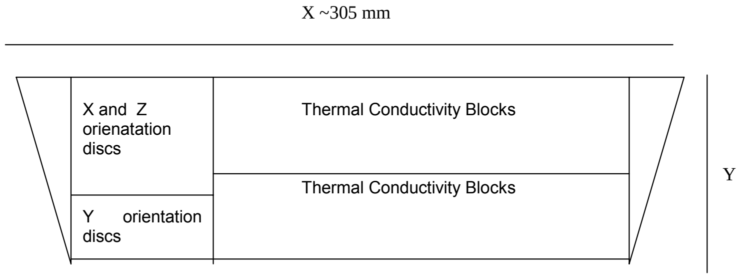
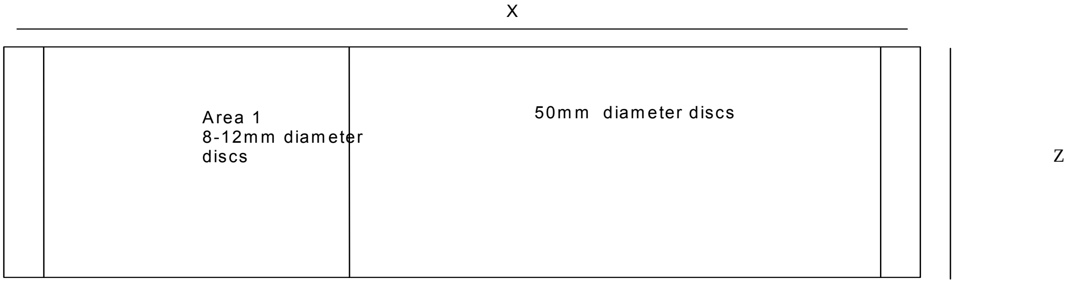


Figure 10: Cutting plan for blocks 1-4.

Orientation – top face of block



Side view - block tapers in length from top to bottom

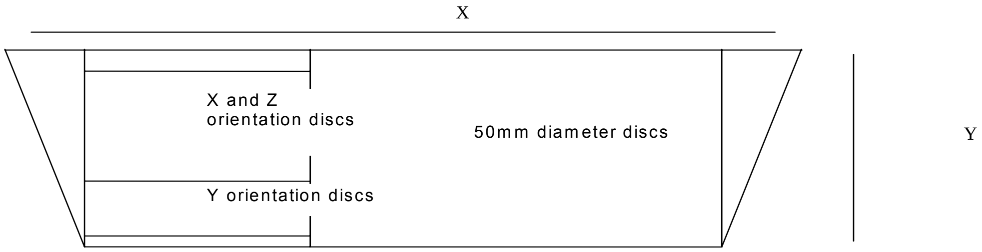


Figure 11: Cutting plan for blocks 5-6.

Table 7: Samples selected for the Guarded-Hot-Plate thermal conductivity certification measurements

Partner	**Specimen dimensions (mm)**		**Specimen Code**
	Diameter or Sides	**Thickness**	
A1	Ø 200	25	TC14.1, TC14.2, TC15.1, TC15.2 TC16.1, TC16.2
B1	Ø 150	50	TC17.1, TC17.2, TC17.3, TC17.4
B1	Ø 20	70	TC17.5, TC17.6
C1	Ø 100	25	TC14.3, TC14.4, TC19.1, TC19.2
D	250 x 250	25	TC12.1, TC13.1, TC13.2, TC18.1, TC18.2, TC18.3
E	Ø 70	10	TC6.64

(Note: TC = Thermal Conductivity; 14.3 = third sample from block 14.)

Table 8: Samples selected for hot-wire (HW) thermal conductivity certification measurements

Partner	**Specimen dimensions (mm)**			**Specimen Code**
	Length	**Width**	**Depth**	
B2	230	90	50	HW3.1, HW4.1
G	230	90	50	HW9.1, HW11.1
F1	230	90	50	HW7.1, HW8.1
C2	100	30	15	HW6.1, HW6.2
H	230	90	50	HW10.1, HW11.1
I	230	90	50	HW7.1, HW8.1

Table 9: Samples selected for thermal diffusivity certification measurements

Partner	**Specimen Code**	**Nominal dimensions (mm)**		**Coating**
		Diameter	**Thickness**	
B3	TD1.42, TD1.43	12	1.5	Tungsten
B3	TD1.44, TD1.45	12	1.5	B3 coating
B3	TD2.46, TD2.47	12.5	1.5	Tungsten
B3	TD2.48, TD2.49	12.5	1.5	B3 coating
F2	TD3.51, TD3.53	10	1.5	Tungsten
F2	TD3.50, TD3.52	10	1.5	F Coating
L	TD4.54, TD4.56	10	1.5	Tungsten
L	TD4.55, TD4.57	10	1.5	L coating
A2	TD5.58, TD5.59	8	1.5	Tungsten
A2	TD5.60, TD5.61	8	1.5	A coating
A2	TD5.17, TD5.18, TD5.19, TD5.24	8	1.0	Tungsten
K	TD1.66, TD1.67	20	5.0	Tungsten
K	TD1.68, TD1.69	20	5.0	K coating
M	TD2.70, TD2.71	12.5	1.5	Tungsten
M	TD2.72, TD2.73	12.5	1.5	M coating

ANNEX 2: THERMAL DIFFUSIVITY INSTRUMENTS AND TEST RESULTS

A2.1 Characteristics of the thermal diffusivity instruments

Table 10: Thermal diffusivity measurement device of laboratory F2

Measurement method	Laser flash technique Additional heating of the sample at the desired temperature by a short laser pulse (0.5 ms) of 1.06 µm wavelength to one side of the sample. Diffusivity is calculated from the temperature rise on the opposite sample face.
Manufacturer and type of instrument	Self constructed (1980)
Temperature range	Room temperature to 2175 K
Sensor used to detect sample temperature variations	Infrared sensor HCT-80, HgCdTe, 8 - 13 µm region
Sample dimensions	Diameter × thickness: 10 mm × 1.5 mm
Sample coating (thickness)	Graphite spray (1 - 3 µm)
Atmosphere (pressure)	Vacuum (1 x 10^{-5} mbar)
Evaluation procedure	Clark & Taylor
Estimation of heat losses	Calculation according to definitions of Clark & Taylor, Degiovanni [16, 17]
Finite laser pulse time correction	Calculation according to Azumi [18]
Measurement of sample temperature	Thermocouples Ni/NiCr on the rear face
Verification of traceability	Periodical test measurements of ARMCO Iron and Stainless steel 1.4970. Participation in inter-comparison program

Table 11: Thermal diffusivity measurement device of laboratory K

Measurement method	Xenon-lamp pulse method; absorbed pulse energy by sample front face; measurement of the temperature increase of the rear face; pulse length 5-6 ms. Pulse energy 1-2 J cm^{-2}.
Manufacturer and type of instrument	Self constructed (1983)
Temperature range	Room temperature to 473 K
Sensor used to detect sample temperature variations	Bi_2Te_3 thermocouples coated on the sample
Sample dimensions	Diameter × thickness: 20 mm × 5 mm
Sample coating (thickness)	Front face: paint with high emissivity (2-3 µm) Back face: Ag (silver) lacquer (2-3 µm)
Atmosphere (pressure)	Air (1013 hPa)
Evaluation procedure	Partial time method [17]
Estimation of heat losses	Calculated by the partial time method [17]
Measurement of sample temperature	Estimated from the measured resistance of a Pt100 resistor mounted close to the specimen rear face
Verification of traceability	Participation on intercomparison programs

Table 12: Thermal diffusivity measurement device of laboratory A

Measurement method	Modulated light beam (Xenon lamp); heating of the sample on one face with periodic modulated light; measurement of phase shifts between heating beam, temperature oscillation of front face (heated), and temperature oscillation of rear face at least at 3 different modulation frequencies between 0.2 Hz and 1 Hz.
Manufacturer and type of instrument	Self constructed (1974)
Temperature range	523 K to 2173 K
Sensor used to detect sample temperature variations	Radiation thermometer (PbSe-detector between 573 K and 1073 K, photo-multiplier above 873 K)
Sample dimensions	Diameter × thickness: 8 mm × 1.0 mm
Sample coating (thickness)	Physical vapour deposited tungsten (2-3 µm)
Atmosphere (pressure)	Vacuum (1×10^{-5} mbar)
Evaluation procedure	Cowan [19]
Estimation of heat losses	Calculation according to definitions of Cowan [19] or alternate calculating of heat loss parameters and thermal diffusivity from both measured phase shifts
Measurement of sample temperature	Radiation thermometer on the rear face
Verification of traceability	Internal calibration of radiation thermometer (DKD-laboratory No. 13501). Participation in two intercomparison programs.

Table 13: Thermal diffusivity measurement device of laboratory L

Measurement method	Laser Flash Method - Measurement of the temperature rise on the rear face of a thin disk sample caused by a short laser pulse (450 µs) of 1.06µm wavelength on the front face.
Manufacturer and type of instrument	Self constructed (1990)
Temperature range	Room temperature to 1073 K (will be expanded up to 1773 K)
Sensor used to detect sample temperature variations	Infrared detector (HgCdTe)
Sample dimensions	Diameter × thickness: 10 mm × 1-5 mm
Sample coating (thickness)	Physical vapour deposited gold (2-3 µm)
Atmosphere (pressure)	Vacuum (1×10^{-3} mbar)
Evaluation procedure	Partial temporal moment method [20]
Estimation of heat losses	Calculated by the partial temporal moment method
Finite laser pulse time correction	Calculated according to Azumi method [18]
Measurement of sample temperature	S-type thermocouple in the immediate vicinity of the specimen
Verification of traceability	Periodical test measurements of ARMCO Iron

Table 14: Thermal diffusivity measurement device of laboratory M

Measurement method	Laser Flash Method: The front side of a plane parallel sample is heated by a short laser pulse. The resulting temperature rise on the rear side of the sample is measured versus time.
Manufacturer and type of instrument	NETZSCH-Gerätebau GmbH (2001)
Temperature range	233 K to 2273 K
Sensor used to detect sample temperature variations	InSb-IR-detector
Sample dimensions	Diameter × thickness: 12.5 mm × 1.5 mm
Sample coating (thickness)	Physical vapour deposited tungsten (2-3 µm) and graphite (10-20 µm)
Atmosphere (pressure)	Argon (1013 hPa)
Evaluation procedure	Cape and Lehmann fit routine
Estimation of heat losses	Calculation according to Cape and Lehmann including radial and facial heat losses
Measurement of sample temperature	Type S (Pt/Pt10%Rh) sample thermocouple
Verification of traceability	Internal verification on the basis of various NIST thermal conductivity standards

Table 15: Thermal diffusivity measurement device of laboratory B3

Measurement method	Laser flash technique; Pulsed laser beam (Nd:Glass, 1064 nm wavelength); heating of the sample on one face with pulsed laser beam; measurement of temperature rise of the other face (non-heated), by using an InSb infrared detector.
Manufacturer and type of instrument	Self constructed (1982)
Temperature range	Room temperature to 1873 K
Sensor used to detect sample temperature variations	Infrared detector (InSb)
Sample dimensions	Diameter × thickness: 12 mm × 1-4 mm
Sample coating (thickness)	Colloidal graphite spray (10-20 µm)
Atmosphere (pressure)	Vacuum (1 × 10^{-5} mbar)
Evaluation procedure	Cowan $10t_{0.5}$ [21] for correcting heat loss effect; Taylor and Clark's method for correcting pulse duration effect [22]
Estimation of heat losses	Calculation according to definitions of Cowan [22]
Estimation of sample temperature	type-R thermocouple located in vicinity of the sample, with temperature calibration.
Verification of traceability	Annual internal calibration of micrometer and data acquisition system. Annual thermal diffusivity measurement on a POCO-graphite (AXM-5Q1) reference material. Participation on two intercomparison programmes

A2.2 Thermal diffusivity test results

The measurement results on the four samples tested at each lab are presented in the tables and graphs below. In the upper part of the tables, first the two samples being coated by the partner's own technique are shown. The latter two samples are coated with tungsten. The sample numbers, type of coating in brackets, are tabulated in the second row. In the lower part of the tables the following data are shown:

- column 1: nominal temperature
- column 2: mean value of accepted thermal diffusivity measurements
- column 3: difference between maximum and minimum of accepted values
- column 4: standard deviation s_m between all accepted values
- column 5: apparatus uncertainty u_a (values given by lab)
- column 6: 95 % confidence interval $U_a = 2 \cdot u_a$
- column 8: deviation between mean of all repeated cycles (run 2) compared to mean of all first cycles (run 1)
- column 9: deviation between mean of all results (run 1+2) of the samples coated by the partners own coating technique, and mean of the samples coated at KE with W.

After each table, two graphs are shown (Figure 12 to Figure 23). One graph shows the dependency of the thermal diffusivity, averaged over all accepted data of the four measured samples, on temperature. The second graph indicates the scatter of the results on the four samples compared to the mean values of the four measurements.

Table 16: Thermal diffusivity results of lab F2 (results in italics not used for certification because the instrument was disturbed by the light scattered from the W coating.)

F2								
Specimen	3.50(C)		3.52(C)		3.51(W+C)		3.53(W)	
Meas-No.	run 1	run 2	run 1	run 2	run 1	run 2	run 1	run 2
Measurement results								
T (K)	a1 (m^2/s)*10^{-6}	a2	a3 (m^2/s)*10^{-6}	a4	a5 (m^2/s)*10^{-6}	a6	a7 (m^2/s)*10^{-6}	a8
298	1.944	1.918	1.919	1.894	1.998	1.932	*2.014*	*2.002*
323	1.746	1.742	1.760	1.757	1.763	1.764	*1.743*	*1.912*
373	1.582	1.569	1.597	1.547	1.599	1.601	*1.650*	*1.695*
473	1.355	1.345	1.356	1.344	1.351	1.368	*1.351*	*1.349*
573	1.237	1.231	1.239	1.211	1.262	1.248	*1.269*	*1.263*
673	1.154	1.139	1.144	1.129	1.173	1.150	*1.172*	*1.177*
773	1.086	1.073	1.083	1.055	1.102	1.116	*1.111*	*1.127*
873	1.034	1.027	1.035	1.021	1.058	1.051	*1.070*	*1.063*
973	0.993	0.982	0.984	0.973	1.017	1.007	*1.037*	*1.024*
1073	0.960	0.952	0.962	0.946	0.986	0.979	*0.982*	*0.992*
1173	0.931	0.924	0.936	0.925	0.951	0.954	*0.959*	*0.961*
1273	0.896	0.900	0.899	0.890	0.919	0.916	*0.917*	*0.932*

Evaluation								
	measurements (a1-a6)			apparatus			mean deviations	
T (K)	**mean value** (m^2/s)*10^{-6}	max. scatter %	standard deviation %	un-certainty %	95% conf. interval %		run 2 / 1 %	C / W %
298	**1.934**	5.41	1.84	2.15	4.3		-1.63	-3.44
323	**1.755**	1.25	0.53	2.10	4.2		2.32	-2.46
373	**1.583**	3.44	1.35	2.05	4.1		-0.24	-3.83
473	**1.353**	1.83	0.67	2.00	4.0		-0.13	-0.35
573	**1.238**	4.08	1.37	1.50	3.0		-1.08	-2.45
673	**1.148**	3.81	1.30	2.10	4.2		-1.03	-2.27
773	**1.086**	5.66	1.98	1.30	2.6		-0.25	-3.55
873	**1.038**	3.61	1.37	2.05	4.1		-0.84	-2.94
973	**0.993**	4.51	1.68	1.65	3.3		-1.15	-3.72
1073	**0.964**	4.22	1.61	1.65	3.3		-0.58	-3.01
1173	**0.937**	3.23	1.37	2.10	4.2		-0.34	-2.81
1273	**0.903**	3.19	1.28	2.10	4.2		0.18	-2.69
averages		**3.69**	**1.36**	**1.90**	**3.79**		**-0.40**	-2.79

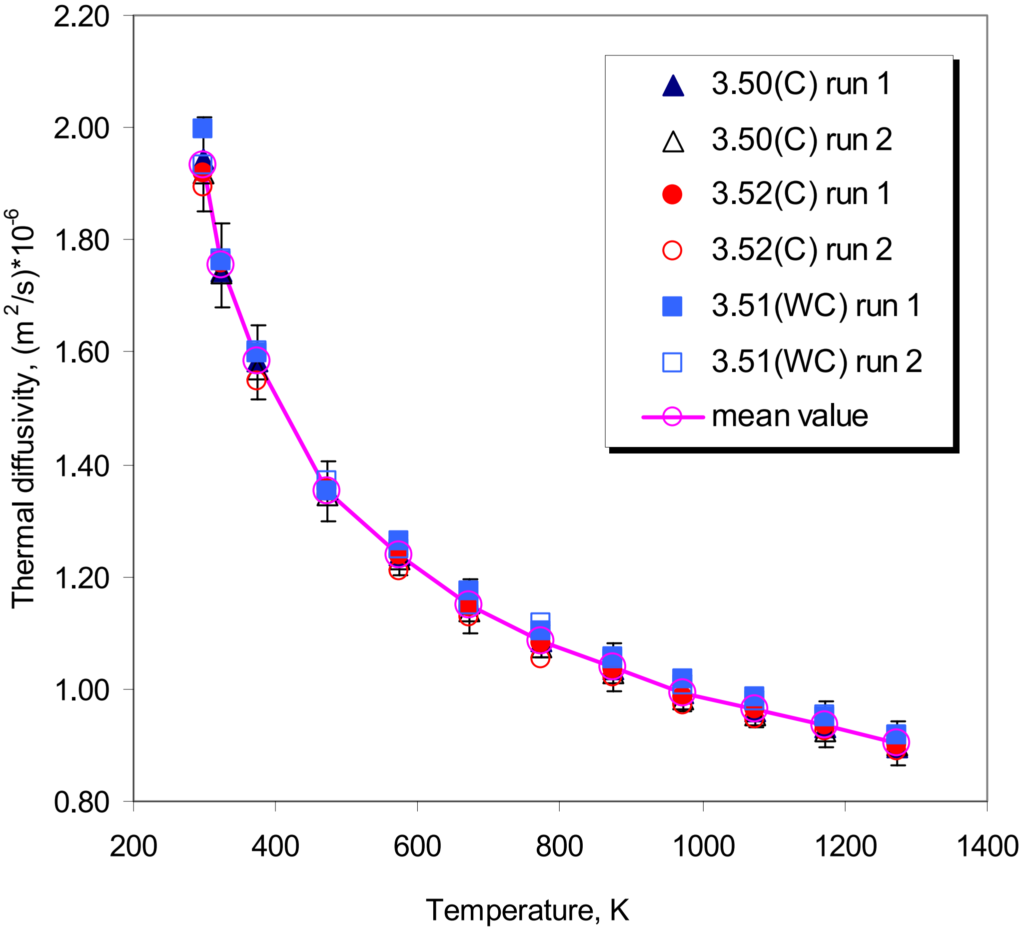


Figure 12: Thermal diffusivity results of Lab F2.

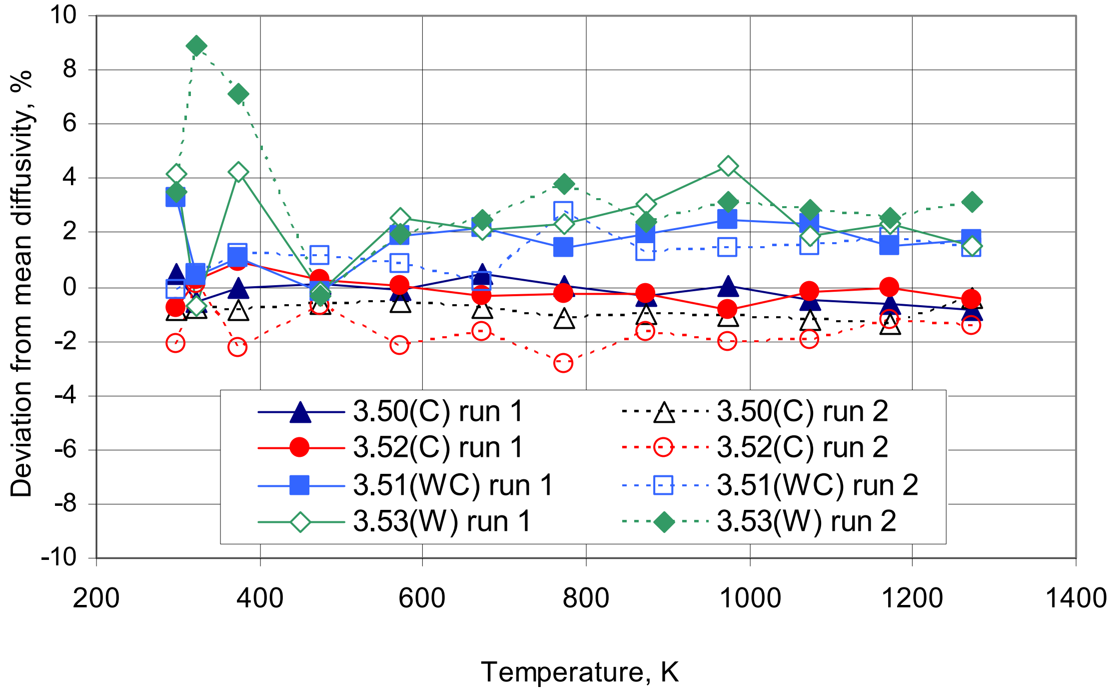


Figure 13: Deviation of individual diffusivity results from the mean value of Lab F2

Table 17: Thermal diffusivity results of lab K (samples 1.68(I) and 1.69(I): (I) denotes coating at lab K).

K								
Specimen	1.68(I)		1.69(I)		1.66 (W)		1.67(W)	
Meas-No.	run 1	run 2	run 1	run 2	run 1	run 2	run 1	run 2
Measurement results								
T (K)	a1 $(m^2/s)*10^{-6}$	a2	a3 $(m^2/s)*10^{-6}$	a4	a5 $(m^2/s)*10^{-6}$	a6	a7 $(m^2/s)*10^{-6}$	a8
298	1.935	1.900	1.793	1.793	1.817	1.813	1.935	1.937
323								
373	1.506	1.436	1.663	1.533	1.527	1.506	1.627	1.636
473	1.410	1.390	1.398	1.400	1.328	1.360	1.348	1.350
573								
673								
773								
873								
973								
1073								
1173								
1273								
Evaluation								
	measurements (a1-a8)			apparatus			mean deviations	
T (K)	**mean value** $(m^2/s)*10^{-6}$	max. scatter %	standard deviation %	un-certainty %	95% conf. interval %		run 2 / 1 %	I / W %
298	**1.865**	7.75	3.61	5	10		-0.49	-1.07
323								
373	**1.554**	14.60	5.08	5	10		-3.34	-2.50
473	**1.373**	5.95	2.19	5	10		0.28	3.93
573								
673								
773								
873								
973								
1073								
1173								
1273								
averages		**9.43**	**3.63**	**5**	**10**		**-1.18**	0.12

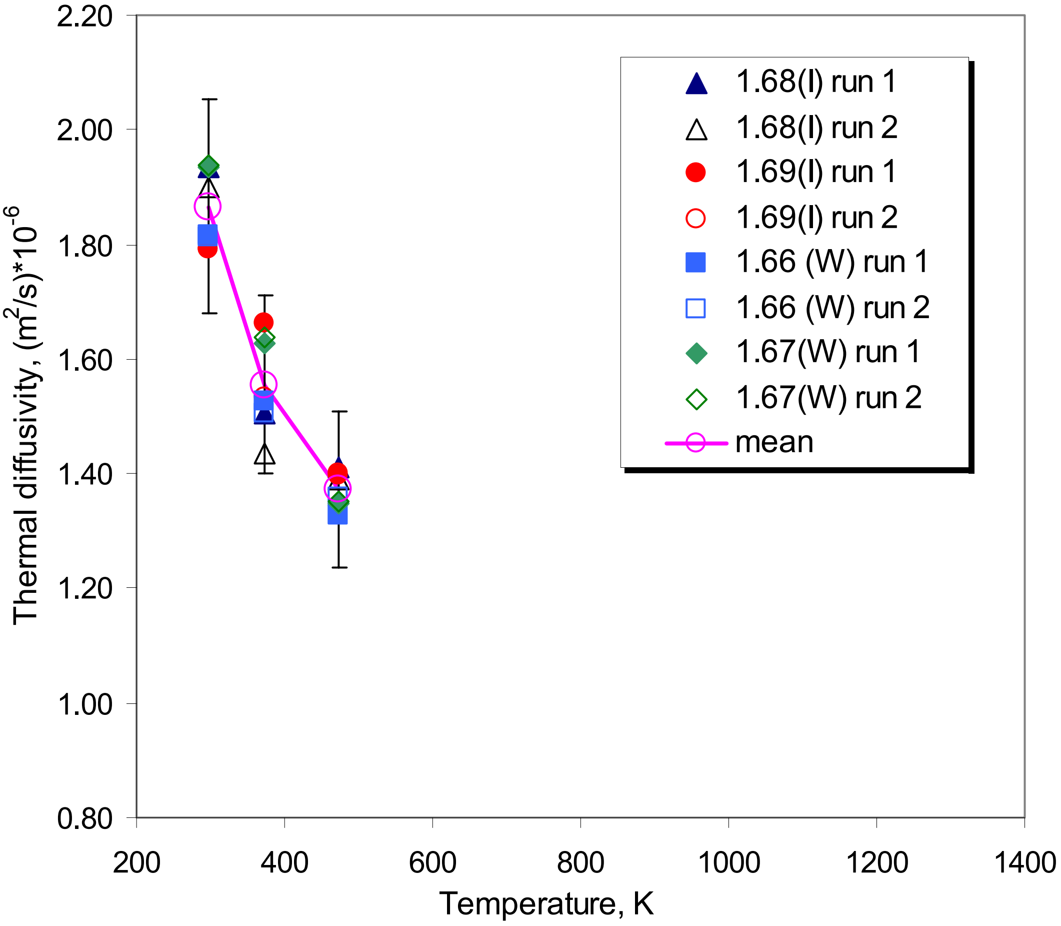


Figure 14: Thermal diffusivity results of lab K.

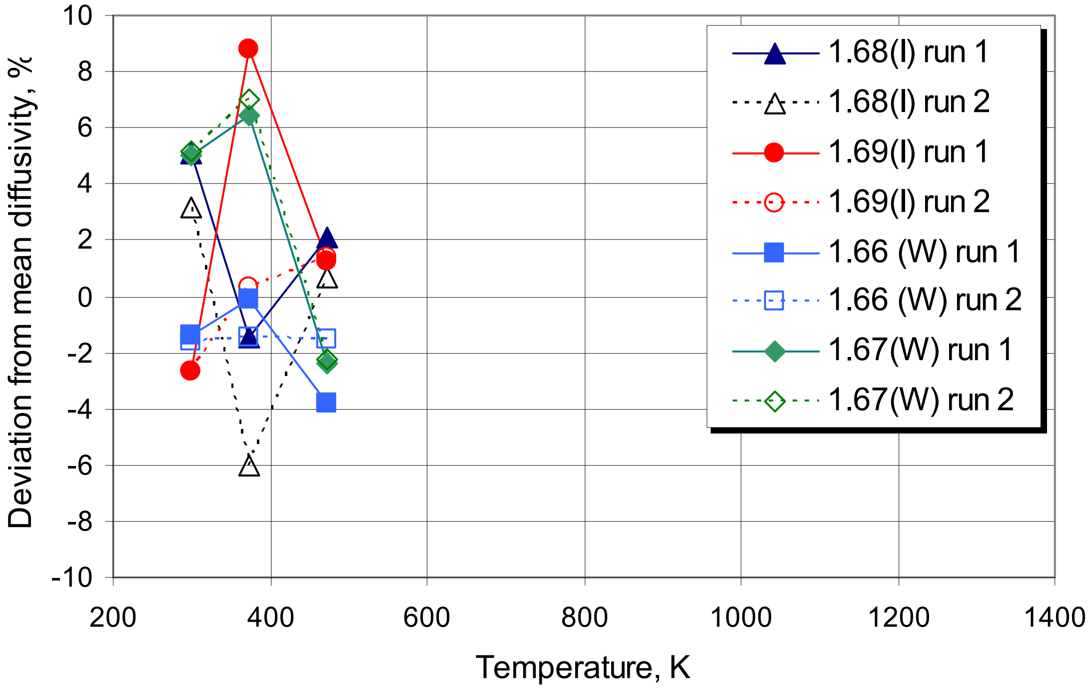


Figure 15: Deviation of individual diffusivity results from the mean value of lab K.

Table 18: Thermal diffusivity results of partner A2

A2								
Specimen	5.17(W)		5.18(W)		5.19(W)		5.24(W)	
Meas-No.	run 1	run 2	run 1	run 2	run 1	run 2	run 1	run 2
Measurement results								
T (K)	a1 (m^2/s)*10^{-6}	a2	a3 (m^2/s)*10^{-6}	a4	a5 (m^2/s)*10^{-6}	a6	a7 (m^2/s)*10^{-6}	a8
298								
323								
373								
473								
573		1.234		1.227		1.242		1.190
673	1.116	1.131	1.114	1.118	1.129	1.130	1.088	1.103
773		1.061		1.061		1.059		1.038
873	0.989	0.997	1.013	1.016	1.014	1.009	1.004	0.997
973		0.958		0.977		0.969		0.948
1073	0.919	0.915	0.931	0.938	0.933	0.935	0.913	0.915
1173		0.888		0.909		0.904		0.889
1273	0.867	0.864	0.873	0.882	0.877	0.878	0.868	0.861

Evaluation								
	measurements (a1-a8)			apparatus			mean deviations	
T (K)	**mean value** (m^2/s)*10^{-6}	max. scatter %	standard deviation %	un-certainty %	95% conf. interval %		run 2 / 1 %	C / W %
298								
323								
373								
473								
573	**1.223**	4.18	1.86	3.24	6.48			
673	**1.116**	3.80	1.33	3.23	6.46		0.76	
773	**1.055**	2.24	1.08	3.25	6.50			
873	**1.005**	2.60	0.96	2.92	5.84		-0.06	
973	**0.963**	2.94	1.29	3.04	6.08			
1073	**0.925**	2.69	1.11	2.14	4.28		0.18	
1173	**0.898**	2.30	1.17	2.02	4.04			
1273	**0.871**	2.41	0.85	2.35	4.70		0.03	
averages		**2.89**	**1.20**	**2.77**	**5.55**		**0.23**	

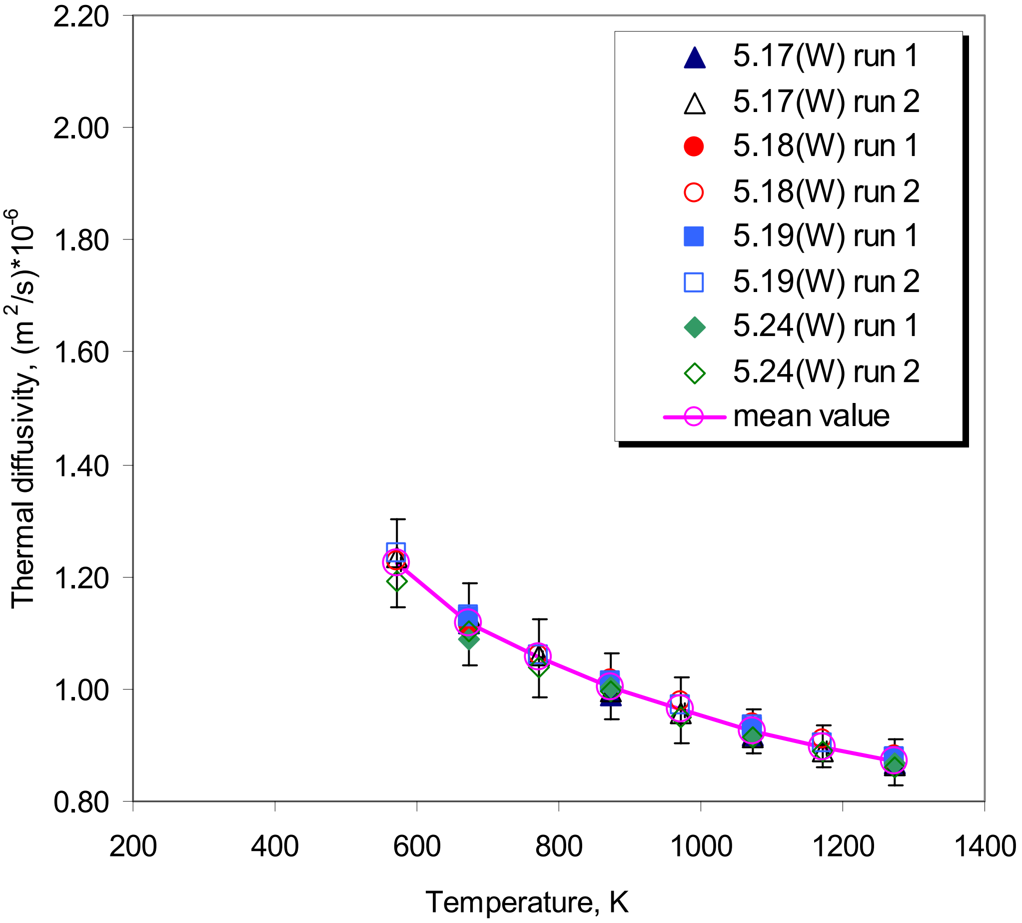


Figure 16: Thermal diffusivity results of lab A2.

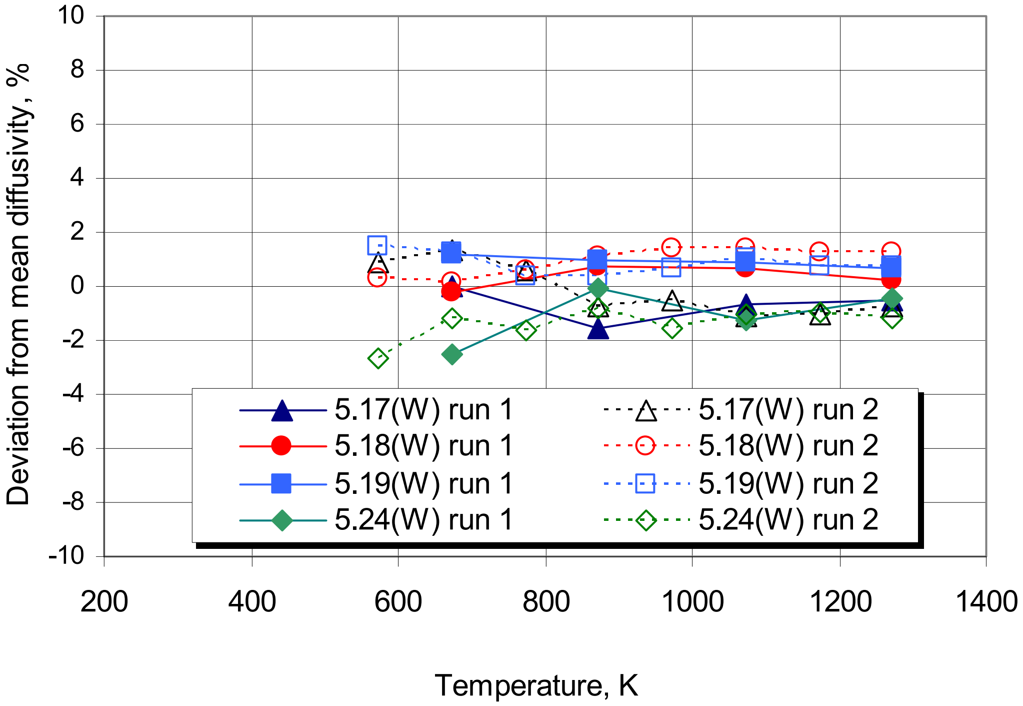


Figure 17: Deviation of individual diffusivity results from the mean value of lab A2.

Table 19: Thermal diffusivity results of partner L

L								
Specimen	4.55(Au)		4.57(Au)		4.54(W)		4.56(W)	
Meas-No.	run 1	run 2	run 1	run 2	run 1	run 2	run 1	run 2
Measurement results								
T	a1	a2	a3	a4	a5	a6	a7	a8
(K)	$(m^2/s)*10^{-6}$		$(m^2/s)*10^{-6}$		$(m^2/s)*10^{-6}$		$(m^2/s)*10^{-6}$	
298	1.894	1.927	1.924	1.949	1.926	1.924	1.952	1.947
323								
373	1.549	1.595	1.586	1.602	1.577	1.581	1.596	1.589
473	1.332	1.354	1.367	1.371	1.360	1.351	1.357	1.363
573	1.217	1.219	1.229	1.235	1.227	1.218	1.218	1.223
673	1.132	1.138	1.149	1.144	1.146	1.126	1.129	1.124
773	1.062	1.073	1.080	1.080	1.066	1.065	1.075	1.068
873	1.006	1.017	1.024	1.026	1.024	1.010	1.017	1.016
973	0.977	0.978	0.980	0.982	0.976	0.977	0.980	0.975
1073	0.950	0.955	0.948	0.953	0.951	0.941	0.946	0.949
1173								
1273								
Evaluation								
	measurements (a1-a8)			apparatus			mean deviations	
T (K)	**mean value** $(m^2/s)*10^{-6}$	max. scatter %	standard deviation %	un-certainty %	95% conf. interval %		run 2 / 1 %	Au / W %
298	**1.930**	2.97	0.97	2.45	4.9			-0.72
323								
373	**1.584**	3.34	1.04	2.20	4.4		0.93	-0.17
473	**1.357**	2.89	0.89	1.85	3.7		0.43	-0.14
573	**1.223**	1.49	0.54	1.85	3.7		0.09	0.28
673	**1.136**	2.18	0.84	1.85	3.7		-0.52	0.83
773	**1.071**	1.68	0.65	1.95	3.9		0.06	0.50
873	**1.018**	2.06	0.71	2.10	4.2		-0.05	0.10
973	**0.978**	0.72	0.24	2.25	4.5		-0.03	0.21
1073	**0.949**	1.51	0.46	2.35	4.7		0.08	0.50
1173								
1273								
averages		**2.09**	**0.70**	**2.09**	**4.19**		**0.12**	0.16

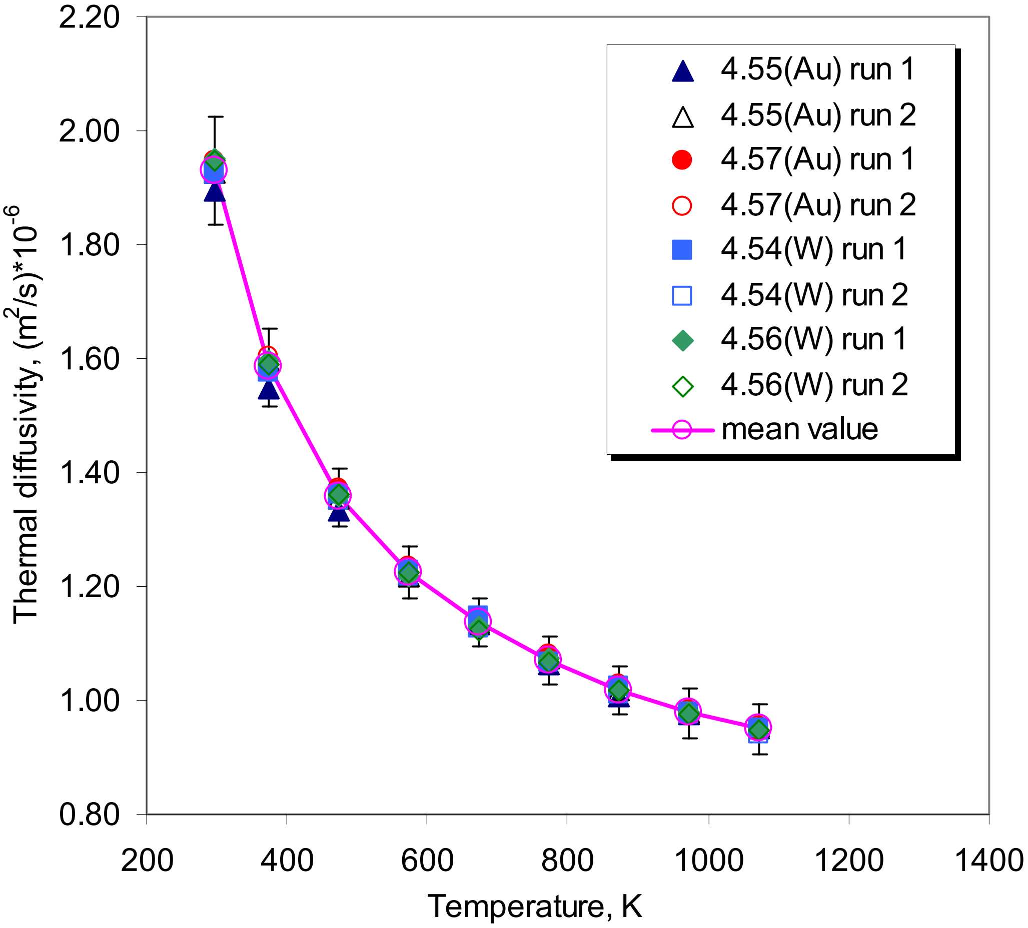


Figure 18: Thermal diffusivity results of lab L.

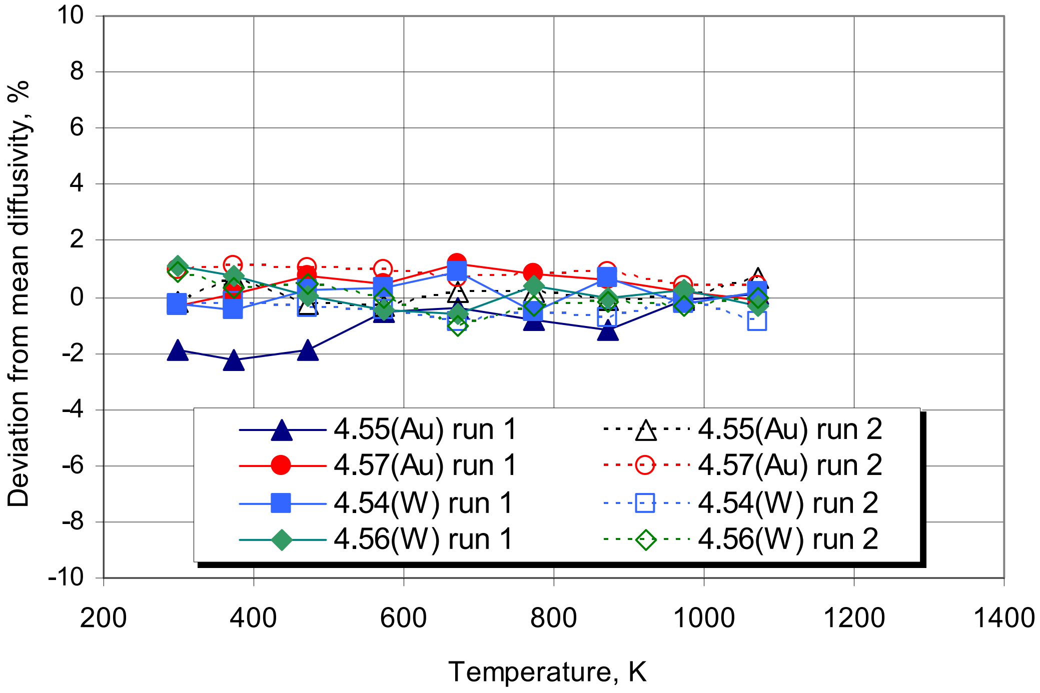


Figure 19: Deviation of individual diffusivity results from the mean value of lab L.

Table 20: Thermal diffusivity results of lab M

M								
Specimen	2.72(C)		2.73(C)		2.70(W)		2.71(W)	
Meas-No.	run 1	run 2	run 1	run 2	run 1	run 2	run 1	run 2
Measurement results								
T (K)	a1 $(m^2/s)*10^{-6}$	a2	a3 $(m^2/s)*10^{-6}$	a4	a5 $(m^2/s)*10^{-6}$	a6	a7 $(m^2/s)*10^{-6}$	a8
298	1.921		1.938		1.922		1.910	
323	1.790		1.788		1.785		1.779	
373	1.575		1.571		1.593		1.561	
473	1.334		1.331		1.350		1.351	
573	1.197		1.193		1.214		1.213	
673	1.100		1.097		1.116		1.120	
773	1.041		1.036		1.045		1.047	
873	0.986		0.977		0.990		0.996	
973	0.946		0.942		0.947		0.951	
1073	0.908		0.910		0.914		0.918	
1173	0.894		0.892		0.886		0.886	
1273	0.867		0.867		0.863		0.866	
Evaluation								
	measurements (a1-a8)			apparatus			mean deviations	
T (K)	**mean value** $(m^2/s)*10^{-6}$	max. scatter %	standard deviation %	un-certainty %	95% conf. interval %		run 2 / 1 %	C / W %
298	**1.923**	1.44	0.59	3.01	6.02			0.70
323	**1.785**	0.63	0.27	3.05	6.10			0.40
373	**1.575**	2.01	0.84	3.02	6.04			-0.24
473	**1.341**	1.45	0.77	3.00	6.00			-1.32
573	**1.204**	1.68	0.88	3.02	6.04			-1.49
673	**1.108**	2.08	1.03	3.05	6.10			-1.74
773	**1.042**	1.03	0.46	3.06	6.12			-0.72
873	**0.987**	1.92	0.81	3.10	6.20			-1.16
973	**0.946**	1.01	0.41	3.11	6.22			-0.53
1073	**0.912**	1.07	0.49	3.15	6.30			-0.80
1173	**0.889**	0.88	0.43	3.18	6.36			0.73
1273	**0.866**	0.49	0.23	3.16	6.32			0.30
averages		**1.31**	**0.60**	**3.08**	**6.15**			-0.49

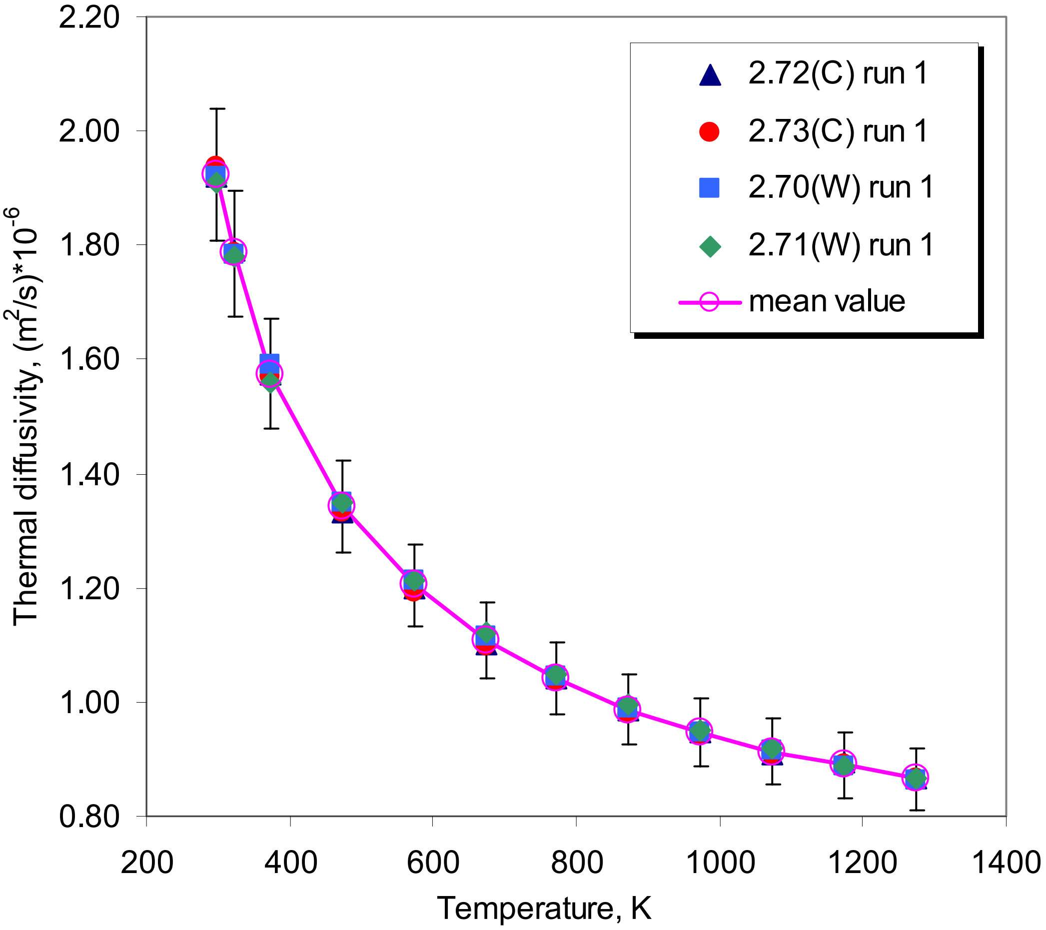


Figure 20: Thermal diffusivity results of lab M.

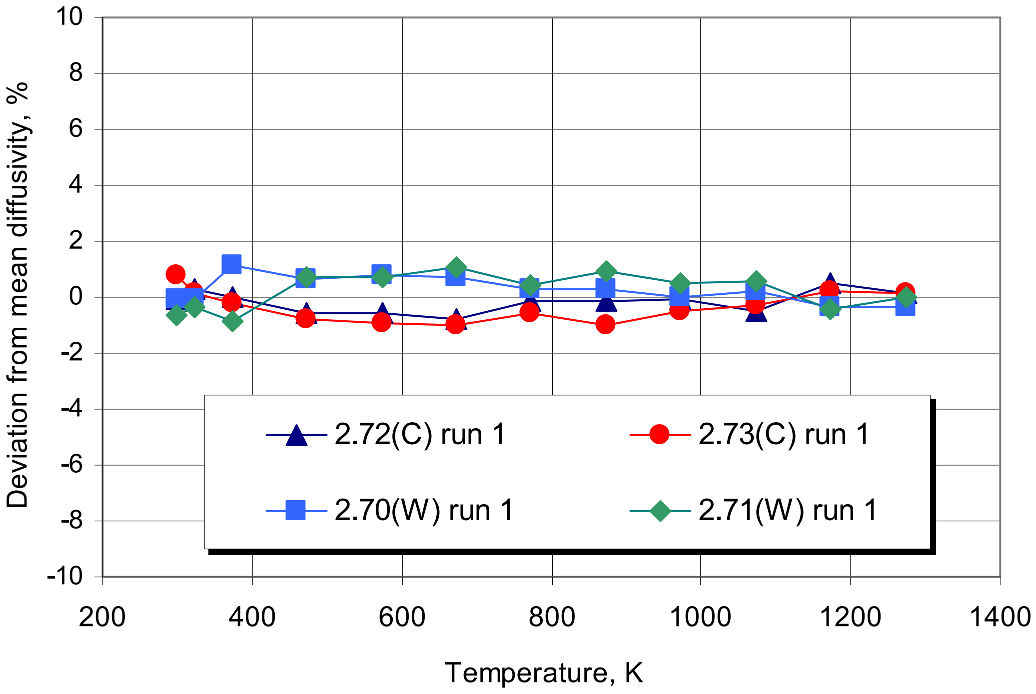


Figure 21: Deviation of individual diffusivity results from the mean value of lab M.

Table 21: Thermal diffusivity results of lab B3.

B3								
Specimen	1.44(C)		1.45(C)		1.42(W)		1.43(W)	
Meas-No.	run 1	run 2	run 1	run 2	run 1	run 2	run 1	run 2
Measurement results								
T (K)	a1 $(m^2/s)*10^{-6}$	a2	a3 $(m^2/s)*10^{-6}$	a4	a5 $(m^2/s)*10^{-6}$	a6	a7 $(m^2/s)*10^{-6}$	a8
298	1.909		1.912		1.915		1.938	
323							1.772	
373	1.686		1.638		1.652		1.599	
473	1.434		1.401		1.396		1.406	
573	1.294		1.275		1.269		1.277	
673	1.193		1.171		1.163		1.165	
773	1.103		1.089		1.079		1.087	
873	1.048		1.035		1.014		1.044	
973	0.989		0.982		0.967		0.980	
1073	0.943		0.946		0.933		0.943	
1173					0.890		0.912	
1273	0.884		0.878		0.849		0.861	

Evaluation

	measurements (a1-a8)			apparatus			mean deviations	
T (K)	**mean value** $(m^2/s)*10^{-6}$	max. scatter %	standard deviation %	un-certainty %	95% conf. interval %		run 2 / 1 %	C / W %
298	**1.918**	1.53	0.70	3	6			-0.84
323	**1.772**			3	6			
373	**1.644**	5.29	2.19	3	6			2.26
473	**1.409**	2.72	1.22	3	6			1.21
573	**1.278**	1.91	0.82	3	6			0.87
673	**1.173**	2.55	1.19	3	6			1.56
773	**1.090**	2.22	0.92	3	6			1.21
873	**1.035**	3.21	1.44	3	6			1.17
973	**0.980**	2.22	0.93	3	6			1.23
1073	**0.941**	1.32	0.59	3	6			0.66
1173	**0.901**	2.42	1.71	3	6			
1273	**0.868**	4.08	1.86	3	6			3.08
averages		**2.68**	**1.23**	**3**	**6**			1.24

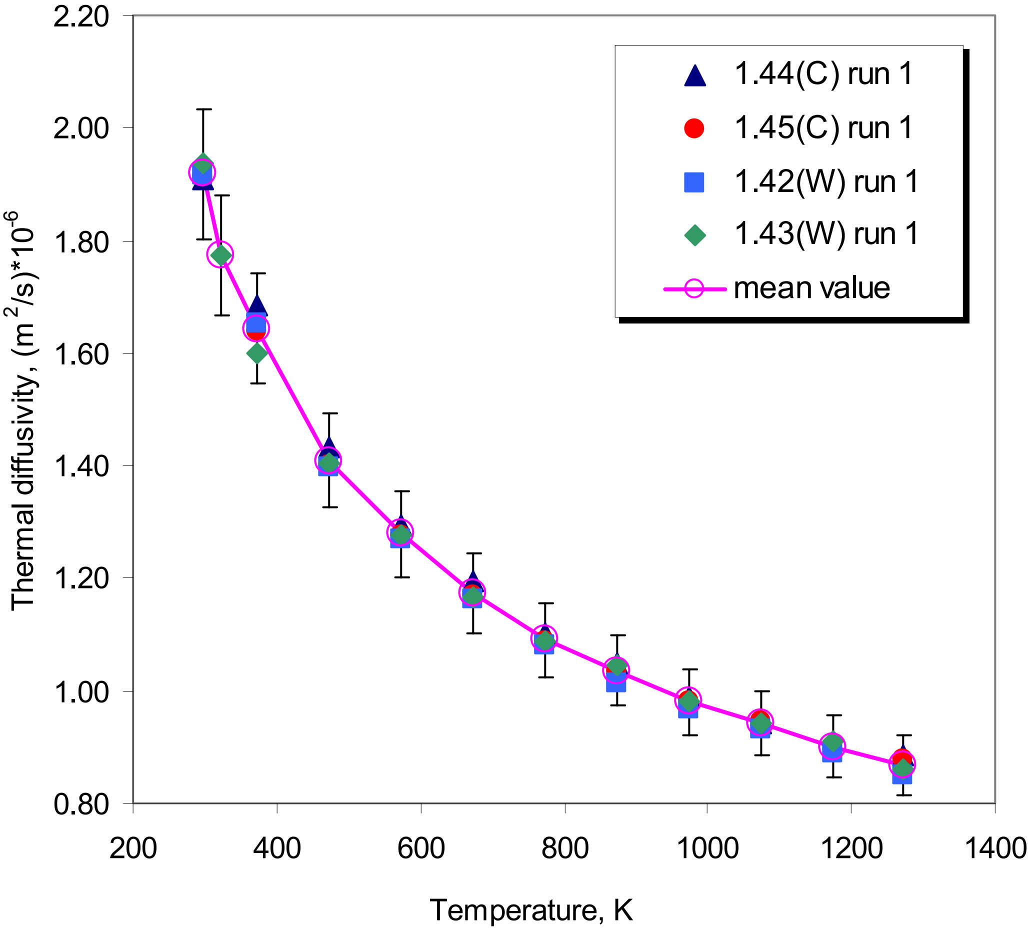


Figure 22: Thermal diffusivity results of lab B3.

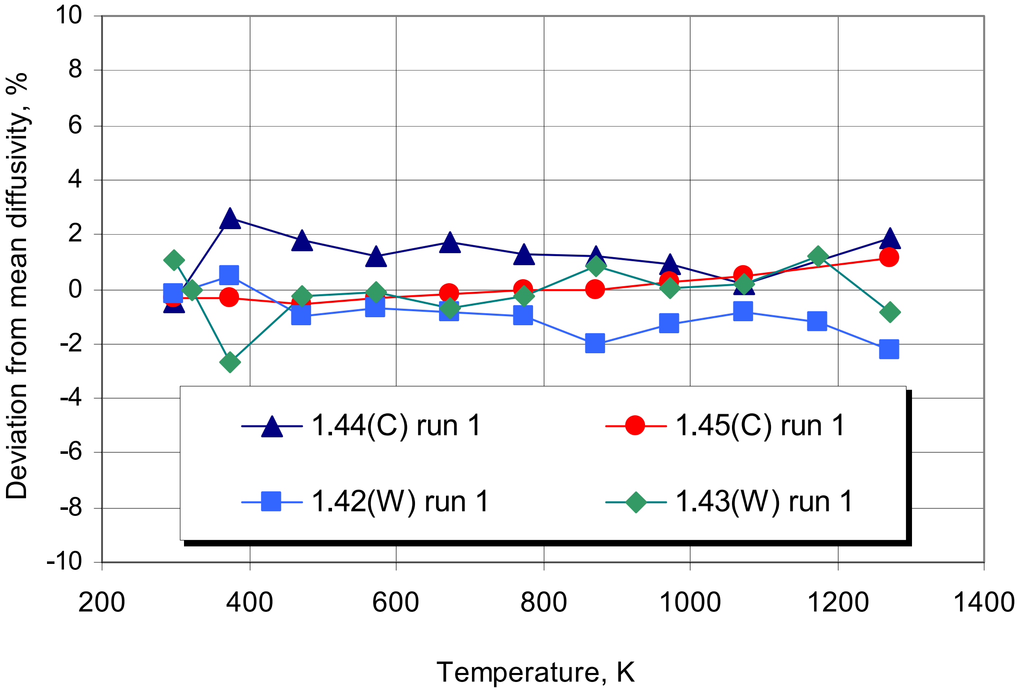


Figure 23: Deviation of individual diffusivity results from the mean value of lab B3.

ANNEX 3: GUARDED HOT PLATE THERMAL CONDUCTIVITY DATA

Table 22: Original raw data of thermal conductivity from lab D (guarded hot plate).

Laboratory: **D**					
Sample ID: TC18.1-3, TC12.1, TC13.1+2					
Run 1		Run 2		Run 3	
Temperature	Thermal Conductivity	Temperature	Thermal Conductivity	Temperature	Thermal Conductivity
K	W/(m·K)	K	W/(m·K)	K	W/(m·K)
437.9	2.083	455.0	1.684	499.9	2.920
557.6	2.074	590.6	1.832	646.7	2.660
708.0	2.118	758.6	1.899	790.8	2.500
818.3	2.132	977.3	2.042		
1038.1	2.189				
600.8	2.076				

Table 23: Original raw data of thermal conductivity from lab A1 (guarded hot plate).

Laboratory: **A1**			
Sample ID:TC14.1+2, TC15.1+2, TC 16.1+2			
Run 1		Run 2	
Temperature	Thermal Conductivity	Temperature	Thermal Conductivity
K	W/(m·K)	K	W/(m·K)
297.9	3.995	298.2	4.014
324.0	3.876	323.0	3.865
373.4	3.692	372.0	3.670
472.9	3.424	473.4	3.446
573.7	3.316	573.7	3.327
673.3	3.234	673.4	3.241
773.2	3.130	773.3	3.113
863.3	2.985	853.0	3.030

Table 24: Original raw data of thermal conductivity from lab B1 (guarded hot plate).

Laboratory: **B1**					
Sample ID:TC17.1 to TC17.4					
Run 1		Run 2		Run 3	
Temperature	Thermal Conductivity	Temperature	Thermal Conductivity	Temperature	Thermal Conductivity
K	W/(m·K)	K	W/(m·K)	K	W/(m·K)
572.55	3.018	573.25	3.306	574.35	3.263
672.95	2.926	675.65	3.163	673.45	3.131
693.75	3.021				
772.55	2.930	774.05	3.073	773.55	3.069
871.25	2.832	873.55	3.016	873.45	3.005
972.55	2.752	974.35	2.951	974.45	2.952
1072.75	2.657	1075.45	2.942	1074.75	2.949

Table 25: Original raw data of thermal conductivity from lab C1 (guarded hot plate).

Laboratory **C1**	
Sample ID :TC19.1,TC19.2	
Run 1	
Temperature	Thermal Conductivity
K	W/(m·K)
213	4.600
243	4.260
273	4.030
296	3.920
303	3.900
333	3.800
363	3.730
393	3.650
423	3.550
453	3.525
473	3.495

Table 26: Original raw data of thermal conductivity from lab E (guarded hot plate).

Laboratory **E**	
Sample ID: TC6.64	
Run 1	
Temperature	Thermal Conductivity
K	W/(m·K)
471	3.755
574	3.549
677	3.458
779	3.399
876	3.330
980	3.316
1044	3.315
1098	3.290
1153	3.300
1204	3.305

ANNEX 4: HOT WIRE THERMAL CONDUCTIVITY DATA

Table 27: Original raw data of thermal conductivity from Lab G (hot-wire apparatus).

Lab G - specimen 1		**Lab G - specimen 2**	
Temperature	Thermal conductivity	Temperature	Thermal conductivity
K	W/(m·K)	K	W/(m·K)
292	4.08	291	4.01
373	3.45	373	3.45
473	3.25	473	3.47
573	3.02	573	2.98
673	3.00	673	2.98
773	2.89	773	2.77
873	2.92	873	2.76
973	2.83	973	2.65
1073	2.77	1073	2.59
1273	2.48	1173	2.63

Table 28: Original raw data of thermal conductivity from Lab H (hot-wire apparatus).

Lab H		**Lab H - repeat**		**Lab H - sample 2**	
Temperature	Thermal conductivity	Temperature	Thermal conductivity	Temperature	Thermal conductivity
K	W/(m·K)	K	W/(m·K)	K	W/(m·K)
293	4.2	297	3.9	298	3.7
318	4.0	321	3.9	315	3.7
367	3.8	375	3.6	366	3.6
465	3.3	474	3.3	464	3.1
562	3.3	572	3.3	563	3.1
661	3.2	670	3.2	663	2.9
761	3.2	770	3.1	763	2.9
861	3.0	870	3.0	863	2.7
961	2.9	972	2.8	963	2.7
1060	2.9	1073	2.8	1063	2.6
1159	2.7	1174	2.8	1163	2.4
1259	2.5	1275	2.5	1263	2.3

Table 29: Original raw data of thermal conductivity from lab B2 (hot-wire apparatus).

Lab B2 - parallel		**Lab B2 - parallel repeat**		**Lab B2 - resistive**		**Lab B2 - resistive repeat**	
Temperature	Thermal conductivity	Temperature	Thermal conductivity	Temperature	Thermal conductivity	Temperature	Thermal conductivity
K	W/(m·K)	K	W/(m·K)	K	W/(m·K)	K	W/(m·K)
301	4.10	296	3.66	296	3.60	300	3.68
367	4.03	366	3.59	366	3.65	367	3.68
464	3.56	464	3.38	464	3.51	465	3.39
564	3.36	565	3.31	563	3.48	564	3.43
665	3.32	665	3.24	665	3.24	665	3.20
766	3.29	767	3.11	766	3.15	766	3.03
867	3.03	868	3.01	867	3.04	868	3.14
969	2.98	968	2.92	969	2.94	969	2.90
1070	2.96	1070	2.72	1070	2.87	1069	2.96
1171	2.82	1171	2.78	1171	2.91	1171	2.83
1272	2.94	1272	2.88	1272	2.68	1271	2.72

Table 30: Original raw data of thermal conductivity from Lab I (hot-wire apparatus).

Lab I		**Lab I repeat**	
Temperature	Thermal conductivity	Temperature	Thermal conductivity
K	W/(m·K)	K	W/(m·K)
293	4.72	294	4.52
494	3.61	490	3.53
650	3.23	681	3.26
863	2.96	871	2.92
1057	2.92	1073	2.84
1322	2.814	1313	2.85

Table 31: Original raw data of thermal conductivity from lab C2 (hot-strip apparatus).

Lab C2	
Temperature	Thermal conductivity
K	W/(m·K)
293	3.98
313	3.89
333	3.81
373	3.71
473	3.48
573	3.29
673	3.13
773	3.03
873	2.85
973	2.75
1073	2.65
1173	2.60
1223	2.58

ANNEX 5: RESULTS OF THE EXCHANGE OF THERMAL DIFFUSIVITY SAMPLES BETWEEN LAB F2 AND LAB L

Table 32: Comparison of results of thermal diffusivity tests obtained on exchanged samples at laboratories F2 and L.

column 1	2	3	4	5	6	7	8
Mean measurement results							
	original distribution		**after samples exchange**				
Laboratory	F2	L	F2	L			
Samples (block)	F2 (3)	L (4)	L (4)	F2 (3)			
Meas. No.	1	2	3	4			
T (K)	a (m^2/s)*10^{-6}						
298	1.953	1.930	1.921	1.946			
323	1.773		1.749				
373	1.605	1.584	1.550	1.596			
473	1.352	1.357	1.356	1.373			
573	1.245	1.223	1.238	1.240			
673	1.155	1.136	1.156	1.149			
773	1.094	1.071	1.087	1.082			
873	1.045	1.018	1.042	1.034			
973	1.002	0.978	0.996	0.985			
1073	0.970	0.949	0.958	0.958			
1173	0.943		0.931				
1273	0.909		0.906				
Evaluation							
Laboratory	F2 / L	F2 / L	F2 / L	F2 / L	**F2**	**L**	**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 (K)	deviation %						
298	**1.2**	0.3	-0.5	**-0.1**	1.6	0.8	**1.2**
323					1.4		**1.4**
373	**1.3**	0.6	-2.2	**-0.8**	3.6	0.7	**2.1**
473	**-0.3**	-1.5	-0.1	**-0.8**	-0.3	1.2	**0.4**
573	**1.8**	0.4	1.2	**0.8**	0.6	1.4	**1.0**
673	**1.6**	0.5	1.7	**1.1**	-0.1	1.1	**0.5**
773	**2.2**	1.1	1.5	**1.3**	0.6	1.1	**0.8**
873	**2.7**	1.1	2.4	**1.7**	0.3	1.6	**1.0**
973	**2.4**	1.8	1.9	**1.8**	0.6	0.7	**0.6**
1073	**2.2**	1.2	1.0	**1.1**	1.2	1.0	**1.1**
1173					1.2		**1.2**
1273					0.3		**0.3**
mean values	**1.7**			**0.7**			**1.0**

European Commission

EUR 21764 EN – DG Joint Research Centre, Institute for Reference Materials and Measurements –
Certification of thermal conductivity and thermal diffusivity up to 1025 K of a glass-ceramic reference material, BCR-724
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Abstract

This certification report is largely based on the final report of a research project, funded by the European Community under the 'Competitive and Sustainable Growth' program ("HTCRM – High Temperature Certified Reference Material", contract SMT4-CT98-2211 [1]). The project intended to produce a reference material with certified thermal conductivity (λ) and diffusivity (α). Samples in the shape of cylinders with different diameter and thickness were prepared from large blocks of Pyroceram 9606.

The material was tested for homogeneity. Homogeneity was found sufficient for the intended use, and the corresponding uncertainty contribution was determined. Dispatch and storage conditions were judged non-critical for this glass-ceramic material. However, stability of the samples under repeated heating cycles to elevated temperatures needed to be investigated. An uncertainty contribution was determined based on a limited use of the CRM of 10 times heating up to 1025 K. The certified values were determined through an interlaboratory exercise. Thermal diffusivity was determined using laser-flash and Xenon lamp methods. Thermal conductivity was measured using guarded hot plate apparatus and hot-wire/hot-strip methods. The following certified values and associated uncertainties were assigned.

BCR-724 glass-ceramic		
certified value [a]	unit	uncertainty [b]
$\alpha = 4.406 - 1.351.10^{-2} \cdot T + 2.133 \cdot 10^{-5} \cdot T^2 - 1.541 \cdot 10^{-8} \cdot T^3 + 4.147 \cdot 10^{-12} T^4$	$m^2/s \cdot 10^{-6}$	6.1 %
$\lambda = 2.332 + 515.1 / T$	W/(m·K)	6.5 %

[a] The certified value is valid only in a temperature range from room temperature to 1025 K. It is no longer valid when the sample has been heated up 10 times or more to 1025 K, or if it is heated up to a temperature in excess of 1025 K. In the equations, T is temperature (K).

[b] Expanded uncertainty (coverage factor k = 2, confidence level of about 95 %)

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