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A new reference material for high-temperature thermal transport properties – LNE participation in the certification process of Pyroceram 9606†

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Pyroceram 9606 has been distributed since May 2007 by the Institute of Reference Materials and Measurements (IRMM) as certified reference material (BCR-724) for thermal conductivity and thermal diffusivity measurements from room temperature up to 1025 K. LNE participated with ten other partners to the certification of this new reference material in the framework of an European metrology research programme entitled "HTCRM – High Temperature Certified Reference Material". The objective of this project was to provide direct traceability to thermal conductivity and thermal diffusivity standards for measurement and testing laboratories throughout Europe. The present paper describes the LNE measurements contribution, as well as the apparatus and the measurement methods used. The results are discussed and compared to the final certified values.

Keywords: Certified reference material, high temperature, Pyroceram 9606, specific heat, thermal conductivity, thermal diffusivity, thermal expansion.

1 INTRODUCTION

To meet the growing need for traceable standards useful for thermal transport properties, the European Commission launched a few years ago a project aiming to produce a reference material with certified values of thermal

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conductivity and thermal diffusivity up to 1000°C. This research project was funded under the « Competitive and Sustainable Growth » programme Contract SMT4-CT98-2211 and involved eleven organisations coming from five countries [1]: ARCS (A), CERAM (UK), CORUS (NL), FIW (D), INSA (F), KE (D), LNE (F), Netzsch (D), NPL (UK), PTB (D) and SFC (F). Such reference material could be used to validate techniques and apparatuses based on absolute measurement method (hot-wire method, guarded hot plate method, laser flash method...) and to perform the calibration of comparative measurement devices (heat flow meter apparatus...).

Several materials such as cordierite, zirconia and Pyroceram 9606 were considered as potential candidates. Pyroceram 9606 was chosen because previous works [2,3] showed the stability and reproducibility of its thermal properties in a large temperature range. Pyroceram 9606 is an opaque glass-ceramic with high strength and elastic modulus and an operational temperature covering the range 75 K to 1250 K. A specific batch of 30 blocks of this material was purchased for this project from Corning Inc. Samples in the shape of cylinders with different diameter and thickness were prepared from these blocks.

This project was structured into two main parts, a preliminary phase of characterization and a certification phase. The first phase was performed to check the suitability of the selected material as a reference material. It involved in particular an investigation of:

– *homogeneity* by measurements of density, porosity, specific heat and thermal diffusivity,

– *anisotropy* by measuring thermal diffusivity, thermal expansion and ultrasonic velocity,

– *long-term stability and reproducibility* of thermal conductivity and thermal diffusivity over the duration of the project,

– *stability on thermal cycling* between 20°C and 1000°C by measuring thermal diffusivity and thermal expansion.

Density ρ and specific heat c_p measurements were used in addition in the assessment of the thermal conductivity λ of the material by indirect approach, from its thermal diffusivity a by means of the simple relationship $\lambda = \rho \cdot c_p \cdot a$. These thermal conductivity values calculated from thermal diffusivity results were compared in the certification phase with those obtained by direct measurements. The thermal expansion data were used for the thermal diffusivity measurements at high temperature, in order to calculate the corrections on the specimen thickness due to expansion. All the specimens tested during this characterization phase were machined from six blocks randomly selected from the batch of 30.

The second phase of the project consisted of direct measurements of thermal conductivity and thermal diffusivity on different specimens machined in several blocks of Pyroceram 9606. Six laboratories measured the thermal diffusivity using either the laser flash method or the modulated beam method. Eight laboratories undertook thermal conductivity measurements using guarded hot plate method or hot wire method. The goal of this certification phase was to establish reference values for both properties with associated uncertainties. The contribution of LNE to these two parts of the project is presented hereafter.

2 CHARACTERISATION OF THE BATCH OF PYROCERAM 9606

LNE participated in several tasks of the characterization phase, such as anisotropy, reproducibility and long-term stability studies. It also contributed to the determination of the specific heat and thermal expansion.

2.1 Anisotropy

Several techniques (ultra-sound velocity, thermal diffusivity and thermal expansion measurements) were used to investigate the anisotropy of the material. LNE examined it in particular by measuring the thermal expansion on 3 specimens taken from a same block of Pyroceram 9606 in different orientations. Two successive measurements were undertaken on each specimen between 23°C and 1000°C by means of a push-rod dilatometer Netzsch 402.

2.1.1 Method of measurement

The specimen (5 mm diameter, 25 mm long) is held in a horizontal position and heated in nitrogen atmosphere at a heating rate of 2 K/min. An inductive displacement transducer detects dimensional changes, which are transmitted from the specimen via a fused silica push-rod. Temperature is measured by means of a type S thermocouple situated close to the specimen. The dilatometer is calibrated prior to the measurements using a tungsten reference material (NIST SRM 737) that has similar expansion properties ($\sim 5 \times 10^{-6}\,\mathrm{K}^{-1}$) to Pyroceram 9606. Uncertainties on linear thermal expansion coefficient between 23°C and 1000°C are estimated to be $\pm\,0.5 \times 10^{-6}\,\mathrm{K}^{-1}$.

2.1.2 Results

The results obtained for the 3 specimens are summarised Table 1. The measurements in the 3 directions give values within $\pm\,0.3 \times 10^{-6}\,\mathrm{K}^{-1}$ for the first run and $\pm\,0.4 \times 10^{-6}\,\mathrm{K}^{-1}$ for the repeated measurements. These results show that within the measurement uncertainty there is no difference between the thermal expansion of specimens taken from different orientations. This conclusion, which was confirmed by the results obtained by other partners [1] using ultra-sound velocity, thermal diffusivity or thermal expansion measurements, highlights that the material can be considered as isotropic.

2.2 Reproducibility study

The reproducibility study consisted of examining the influence of the specimen thickness, the environment (vacuum or inert atmospheres) and the nature

Coefficient of thermal expansion (10^{-6} K^{-1})								
	Cycle 1				*Cycle 2*			
Temp. °(C)	*X direction*	*Y direction*	*Z direction*	*Mean Value*	*X direction*	*Y direction*	*Z direction*	*Mean Value*
23	/	/	/	**0.00**	/	/	/	**0.00**
200	7.26	7.14	6.72	**7.04**	7.00	7.14	6.03	**6.72**
300	6.06	5.86	5.61	**5.84**	5.83	5.86	5.13	**5.60**
400	5.50	5.40	5.17	**5.36**	5.31	5.37	4.80	**5.16**
500	5.26	5.17	4.93	**5.12**	5.14	5.14	4.67	**4.98**
600	5.12	5.02	4.79	**4.98**	4.99	4.97	4.56	**4.84**
700	5.18	5.05	4.85	**5.03**	4.88	4.90	4.52	**4.77**
800	5.41	5.22	5.03	**5.22**	4.82	4.82	4.47	**4.70**
900	5.55	5.38	5.16	**5.36**	4.67	4.70	4.36	**4.58**
1000	5.89	5.26	5.14	**5.43**	4.93	4.50	4.24	**4.55**

TABLE 1
Thermal expansion coefficient of Pyroceram 9606 measured by LNE.

of coating on the thermal diffusivity measurements. LNE measured the thermal diffusivity at 23°C, 200°C, 400°C, 600°C and 800°C of 12 specimens, which all were machined in only one direction of the same block. One set of 6 specimens was tested under argon and the other one under vacuum, each set containing 3 specimens (1.5 mm, 2 mm and 3 mm thick) coated on both sides with gold (Au) and 3 specimens (1.5 mm, 2 mm and 3 mm thick) coated with tungsten (W).

2.2.1 Method of measurement

LNE performs thermal diffusivity measurements up to 1400°C in argon or vacuum environments by using a set-up based on the principle of the “laser flash method” [4,5]. A specimen (10 mm in diameter and about 1 to 5 mm thick) is isothermally heated at a uniform temperature in one of the furnaces (depending on the test temperature). A short (around 450 μs) laser pulse of 1054 nm wavelength irradiates the front face of the specimen (see Figure 1). The induced transient temperature rise on its rear face is measured by optical means with infrared detectors. The acquisition of the temperature versus time curve is performed with a NI PXI-6052 data acquisition device. In the case of solid homogeneous isotropic opaque materials, the thermal diffusivity is estimated according to the “partial time moments method” proposed by Degiovanni [6]. A new “front face detection” system has been recently fitted, in order to allow the study of multilayered materials.

Pyroceram 9606 being semitransparent to the laser wavelength, all the specimens were coated with a thin (1 to 3 μm) opaque layer of tungsten or gold (on which a thin layer of graphite was deposited), in order to ensure absorption of the laser beam on the front face. One of the objectives of the

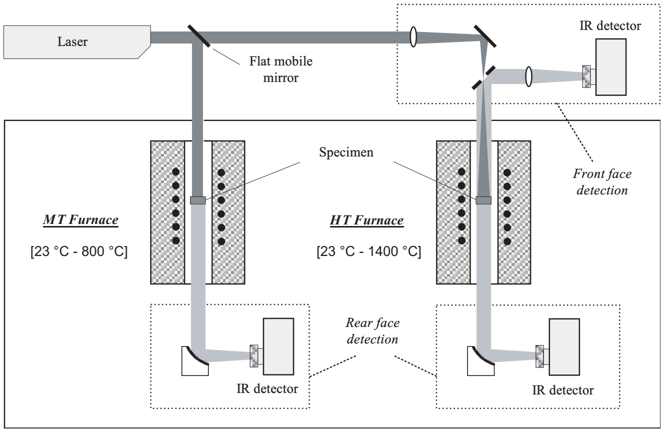

FIGURE 1
Schematic diagram of LNE laser flash set-up.

reproducibility study was to check that the influence of the coating on the heat transfer could be considered as negligible, because of its high thermal diffusivity and its low thickness in comparison with that of the specimen.

2.2.2 Results

All thermal diffusivity values presented hereafter result from the average of three successive measurements carried out on repeatability conditions. The scattering of measurements performed for the three different specimen thicknesses in the same experimental conditions (atmosphere, temperature and coating) is lower than 3%. These results show that the thermal diffusivity is independent of the specimen thickness, indicating good homogeneity within the block. Table 2 presents the results for each of the four experimental configurations [coating – atmosphere]. The standard deviations of these mean values are less than 2% in the whole temperature range, and are within the

Thermal Diffusivity (10^{-6} m^2/s)						
Temperature (°C)	Au coating Argon	W coating Argon	Au coating Vacuum	W coating Vacuum	Mean Value	Standard deviation (%)
23	1.908	1.921	1.951	1.949	**1.932**	1.1
200	1.326	1.328	1.369	1.352	**1.344**	1.5
400	1.105	1.128	1.147	1.136	**1.129**	1.6
600	1.000	1.010	1.033	1.029	**1.018**	1.5
800	0.962	0.943	0.971	0.943	**0.955**	1.5

TABLE 2
Thermal diffusivity of Pyroceram 9606 block 5 – LNE measurements.

measurement uncertainties (given in Table 4). No significant difference was observed between measurements carried out with different coatings and in different environments.

2.3 Long term stability

The long-term stability was monitored by LNE measuring periodically the thermal diffusivity of a set of four specimens during the lifetime of the project. The measurements were performed on tungsten-coated specimens (1.5 or 3 mm thick) from the same block under argon or vacuum (10^{-3} mbar) atmosphere at 23°C, 400°C and 800°C. The results given Table 3 show that there is no significant drift over two years in the measured values of thermal diffusivity obtained for the four specimens. The standard deviation of these values is less than 2% whatever the conditions (atmosphere, temperature, thickness). These tests proved that no reaction occurred with the environment during a long series of measurements at high temperatures. Pyroceram 9606 can be consequently considered as thermally stable over a long period.

2.4 Specific heat measurements

LNE determined specific heat under nitrogen atmosphere from 23°C to 800°C using a Differential Scanning Calorimeter DSC111 (Setaram). These measurements were performed on a disk specimen (5 mm in diameter and 1 mm thick) applying the stepwise-scanning method. The total temperature range was divided into intervals of 5 K, which were successively scanned at a heating

		Thermal diffusivity (10^{-6} m^2/s)						
Specimen / Conditions	Temp. (°C)	T_0	$T_0 + 3$ months	$T_0 + 6$ months	$T_0 + 1$ year	$T_0 + 2$ years	Mean Value	Stand. dev. (%)
n° 1	23	1.905	1.912	1.912	1.923	1.898	**1.910**	0.5
1.5 mm	400	1.125	1.121	1.125	1.119	1.106	**1.119**	0.7
Argon	800	0.940	0.934	0.930	0.926	0.912	**0.928**	1.1
n° 2	23	1.939	1.947	1.946	1.964	1.955	**1.950**	0.5
1.5 mm	400	1.159	1.142	1.147	1.152	1.131	**1.146**	0.9
Vacuum	800	0.968	0.953	0.949	0.961	0.938	**0.954**	1.2
n° 3	23	1.956	1.947	1.928	1.961	1.935	**1.945**	0.7
3.0 mm	400	1.132	1.132	1.126	1.135	1.116	**1.128**	0.7
Argon	800	0.944	0.933	0.952	0.953	0.917	**0.940**	1.6
n° 4	23	1.907	1.956	1.940	1.931	1.920	**1.931**	1.0
3.0 mm	400	1.130	1.122	1.125	1.124	1.121	**1.124**	0.3
Vacuum	800	0.958	0.932	0.933	0.962	0.936	**0.944**	1.5

TABLE 3
Long term stability – Thermal diffusivity measurement.

rate of 5 K/min. LNE results are in general 2% lower than those obtained by the other laboratories, but within the estimated measurement uncertainty of ±3%.

3 CERTIFICATION OF PYROCERAM 9606 AS REFERENCE MATERIAL

The certification phase was then engaged, since the characterization phase showed that Pyroceram 9606 had all the needed characteristics (homogeneity, stability, isotropy) of a Reference Material. Eleven laboratories performed direct measurements of thermal diffusivity and/or thermal conductivity on specimens coming from different blocks. The obtained results were analyzed and combined by the Institute of Reference Materials and Measurements in order to express the certified values in the form of equations giving thermal diffusivity a and thermal conductivity λ versus temperature [7], as follows:

$$a = 4.406 - 1.351 \times 10^{-2}T + 2.133 \times 10^{-5}T^2 - 1.541 \times 10^{-8}T^3 + 4.147 \times 10^{-12}T^4 \quad (1)$$

$$\lambda = 2.332 + 515.1/T \quad (2)$$

The relative expanded uncertainties (coverage factor $k = 2$) of the certified values given by equations (1) and (2) were estimated to be respectively ± 6.1% and ± 6.5%.

LNE contributed to the phase of certification by measuring twice in separate runs the thermal diffusivity of four samples (1.5 mm thick) under vacuum

Thermal diffusivity (10^{-6} m^2 /s)									
	Mean value of the two runs								
Temp. (°C)	Spec. n°1 W coating	Spec. n°2 Au coating	Spec. n°3 W coating	Spec. n°4 Au coating	Mean Value	Standard Deviation (%)	Expanded # Uncertainty (%)	Certified Value	Relative Deviation (%)
23	1.925	1.911	1.950	1.937	**1.930**	0.9	4.9	1.907	1.2
100	1.579	1.572	1.593	1.594	**1.584**	0.7	4.4	1.614	−1.9
200	1.356	1.343	1.360	1.369	**1.357**	0.8	3.7	1.364	−0.6
300	1.223	1.218	1.221	1.232	**1.223**	0.5	3.7	1.216	0.6
400	1.136	1.135	1.127	1.147	**1.136**	0.7	3.7	1.128	0.7
500	1.066	1.068	1.072	1.080	**1.071**	0.6	3.9	1.071	0.0
600	1.017	1.012	1.017	1.025	**1.018**	0.5	4.2	1.024	−0.6
700	0.977	0.978	0.978	0.981	**0.978**	0.2	4.5	0.976	0.2
800	0.946	0.953	0.948	0.951	**0.949**	0.3	4.7	0.927	2.3

#These measurement uncertainties (estimated according to [8]) correspond to two standard deviations.

TABLE 4
Certification phase – Thermal diffusivity measured by LNE on four specimens.

atmosphere on the temperature range 23°C to 800°C. The difference between the first and the second measurements is lower than 2% for the 4 samples. Table 4 presents for each specimen the average of the measurement obtained for the two runs. The standard deviations of these mean values are less than 1% in the whole temperature range, and are within the uncertainty of measurement. The relative deviation of mean values determined by LNE from the certified value calculated from the expression (1) is less than $\pm$ 2.5%.

4 CONCLUSION

LNE was involved with ten other European laboratories in the qualification of Pyroceram 9606 as a certified reference material for high-temperature thermal transport properties. The characterization phase indicated clearly that this batch of material was stable, homogeneous and isotropic. The expanded uncertainties of the certified values of thermal diffusivity and thermal conductivity determined during the certification phase were estimated to be respectively $\pm$ 6.1% and 6.5% in the temperature range from 298 K to 1025 K. This new reference material is available, as BCR-724, since May 2007 at the Institute of Reference Materials and Measurements (www.irmm.jrc.be), the European body in charge in particular of the spreading of CRMs (Certified Reference Materials).

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