Prototype 1:

Thermal reference samples

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The goal of thermal reference samples is the calibration of SThM probes for the measurement of the thermal conductivity or conductance of solid materials. To date, no reference materials have been proposed for that purpose and laboratory samples have been used. Quantiheat aimed at overcoming this lack of reference samples.

Key Benefits

- *Compatible with most of the commercially available AFMs.*
- *Thermal conductivity with uncertainty provided.*
- *Calibration of SThM probe for thermal conductivity/thermal conductance measurement.*
- *Calibration of thermal characterization techniques for thermal conductivity/thermal conductance measurement.*
- *Determination of the range of sensitivity to thermal conductivity of SThM.*
- *Determination of the range of sensitivity to thermal conductivity of other thermal characterization techniques.*
- *Samples can be also used for characterizing the probe–sample interaction and facilitating the comparison between modeling and measurement results.*

Sample Specification

The sample set includes 10 bulk materials with thermal conductivity ranging from 0.1 to 100 $W.m^{-1}.K^{-1}$. The choice of samples was based on their thermophysical performance/properties assuming that thermal conductivity measured at macroscale and at micro and nanoscales are comparable and on their roughness. The identification codes, materials, providers of selected materials and their thermal properties are given in Table 1. Table 2 gives the roughness parameters measured for each sample by CMI or LNE with calibrated AFMs.

Table 1: *Thermal calibration materials and their thermal properties*.*

Material		provider	Density ($kg \cdot m^{-3}$)	Specific heat ($J \cdot kg^{-1} \cdot K^{-1}$)	Thermal diffusivity ($10^{-6}\ m^2 \cdot s^{-1}$)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
S-TH-cal1	**PMMA**	**Goodfellow**	***1180***	***1430***	***0.111***	**0.187**
S-TH-cal2	**POM-C**	**Radiospares**	***1400***	***1440***	***0.163***	**0.329**
S-TH-cal22	**Glass**	**Neyco**	***2197***	***763***	**0,663**	**1,11**
S-TH-cal3	**Fused Silicon dioxide (SiO_2)**	**Neyco**	***2190***	***738***	***0.795***	**1.28**
S-TH-cal20	**ZrO2**	**Neyco**	***5855***	***457***	**0,732**	**1,95**
S-TH-cal18	**TiO2**	**Neyco**	***4174***	***698***	**3,14**	**9,15**
S-TH-cal9	**Aluminium oxide (Al_2O_3)**	**Neyco**	***3920***	***765***	***9.93***	**29.8**
S-TH-cal21	**Al_2O_3 monocrystalline**	**Cristal**	***4002***	***769***	**12,12**	**36,9**
S-TH-cal16	**Ge undoped**	**Cristal**	***5294***	***310***	**31,09**	**52,0**
S-TH-cal13	**Silicon p++**	**Goodfellow**	***2330***	***712***	***56.3***	**93.4**

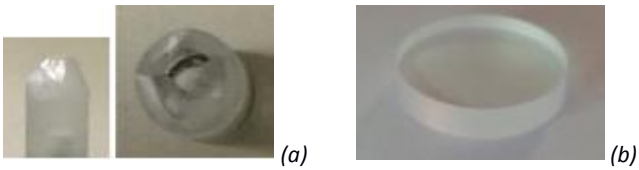
* The thermal diffusivity measurements of samples were performed at LNE by using a reference flash laser technique [1] directly traceable to the International System of Units. Specific heat values were measured with a differential scanning calorimeter (DSC), according to the "stepwise-scanning method". Sample densities were determined at 23 °C according to the Archimedean immersion method.
The relative expanded uncertainties (k=2) associated to thermal diffusivity, specific heat and density measurements performed at 23 °C by LNE have been estimated respectively equal to 4 %, 3 % and 1 %. The expanded uncertainty associated to the determination of thermal conductivity at 23 °C is estimated to 5 %.

Table 2: *Roughness parameters of the reference samples measured by CMI.***

Sample	S-TH-cal1 PMMA	S-TH-cal2 POM-C	S-TH-cal3 SiO2	S-TH-cal9 Al2O3	S-TH-cal13 Si p++	S-TH-cal22 Glass	S-TH-cal20 ZrO2	S-TH-cal18 TiO2	S-TH-cal21 Al2O3 mono	S-TH-cal16 Ge undoped
Ra [nm]	**5.04**	**11.7**	**0.56**	**7.52**	**0.75**	**1.25**	**0.80**	**0.17**	**0.53**	**0.33**
Rms [nm]	**6.43**	**15.7**	**0.73**	**10.0**	**1.47**	**1.90**	**1.58**	**0.30**	**0.69**	**0.57**

** Data presented in bold are the average values calculated by CMI on five measurements and by LNE on the three measurements performed with an area of 2x2 μm^2.

Thermal reference samples are individual samples (See Figure 1): one sample of each selected material. They are available as unmounted pieces to be mounted by the microscopist. Polymeric samples (S-TH-cal1 and cal2) were cut and machined from stock rods. Their surface is of about 1 mm² and were prepared using ultramicrotomy (cryogenic cutting depending on material at Centre Technologique des Microstructures (CTμ), Lyon, France) to produce flat defect-free surface. Other samples are disks with diameter of 10 mm and thickness of 2 mm. Their surface was prepared by the sample providers.



(a) *(b)*

Figure 1: *Picture of some samples (a) S-TH-cal1 and (b) S-TH-cal3*

Cleaning and storage

- Cleaning must be performed before each of the series of measurements.
- Sensitive preparation for polymeric samples: Cleaning is possible using dry air. Keep upper surface intact: avoid touching prepared surface. Rubbing with soft tissues, or any other firm physical contact, or the use of solvents such as acetone or alcohol will damage the surface of the reference sample.
- Standard preparation by using isopropanol for the other samples. If sample is very dusty, wash it with IPA and ultrasonics (5min).
- It is recommended to store these samples under low humidity/dry air, dust free environment out of direct sunlight.

Applications

Thermal reference samples can be used for the calibration of SThM probes and setups for measurement of the effective thermal conductivity or conductance at the subsurface of unknown materials [2]. As shown in Figure 2 after the measurement of reference samples, the determination of an analytical modeling (statistical or physical) can be made by fitting SThM measurements as a function of reference sample thermal conductivity. The modeling is then used as calibration curve to study an unknown specimen.

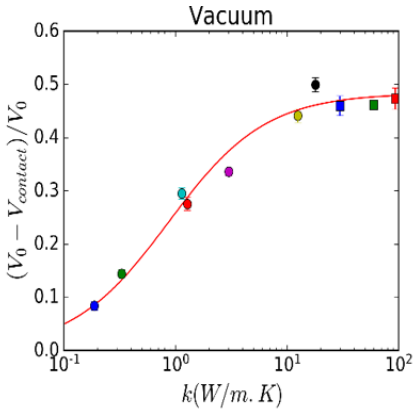


Figure2: *Calibration curve obtained from measurements performed under vacuum environment (4 Pa) on thermal reference samples with a 1.3 µm diameter wire based thermocouple probe designed at FEMTO-ST. Measurements were performed in AC mode (2 omega method) at f = 57Hz, I = 1mA). The 2ω voltages before contact V_0 and after contact $V_{contact}$ were obtained using a lock-in amplifier. V_0 = 232 µV. The probe temperature was about 39°C.*

An analytical modeling of type: $\frac{V_0 - V_{contact}}{V_0} = \frac{A + B\lambda_e}{(1-B)\lambda_e - A}$ *is used to fit the experimental data.*

Using a least squares method, we found A=1.8003 and B=1.0687

Other information

Table 4: Hardness and Young's modulus of the thermal calibration samples measured by CMI and NPL***.

Material		CMI				NPL			
		H (ave) [GPa]	H (sd) [GPa]	E (ave) [GPa]	E (sd) [GPa]	H (ave) [GPa]	H (sd) [GPa]	E (ave) [GPa]	E (sd) [GPa]
S-TH-cal1	PMMA	-	-	-	-	0.20	0.01	2.94	0.13
S-TH-cal2	POM-C	-	-	-	-	0.32	0.17	4.20	1.18
S-TH-cal3	SiO_2	5.10	0.60	46.2	2.6	5.25	0.17	71.5	1.74
S-TH-cal9	Al_2O_3	25.8	2.07	375	28.3	-	-	-	-
S-TH-cal13	Si p++	13.9	1.07	181	6.7	-	-	-	-
S-TH-cal16	Ge	8.76	0.29	101.1	2.4	-	-	-	-
S-TH-cal18	TiO2	11.0	0.8	491.1	30.1	-	-	-	-
S-TH-cal20	ZrO2	1.22	0.74	261.8	16	-	-	-	-
S-TH-cal21	Al_2O_3 monocrystalline	22.15	2.12	435.7	11.3	-	-	-	-
S-TH-cal22	Glass	6.21	0.34	58.4	1.4	-	-	-	-

***These mechanical measurements were performed by using nanoindentation. assumed Poisson's ratio 0.3.

References

[1] B. Hay, J. Hameury, N. Fleurence, P. Lacipiere, M. Grelard, V. Scoarnec and G. Davee, « New facilities for the measurements of high temperature thermophysical properties at LNE », International journal of thermophysics, vol. 35, pages 1712-1724 (2014).
[2] S. Gomès, A. Assy, and P.-O. Chapuis, "Scanning Thermal Microscopy: a review", 2015, *Physica Status Solidi (a)* 212 pp 477-494

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