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Measurements and data of thermophysical properties traceable to a metrological standard

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Abstract
In order to improve the performance of devices, components and systems, where heat is generated, transported, stored or converted to other types of energy, reliable thermal design and simulation are required using reliable thermophysical property data. In order to produce reliable thermophysical property data systematically and continually, the international and national standards of thermophysical properties must be established and the measurement methods should be evaluated and standardized, and the measuring instruments must be calibrated by reference materials traceable to the international or national standard.

Users search for and purchase a particular grade of material which satisfies the properties, performances and technical specifications required. In order to guarantee fair commerce and trade, values of thermophysical properties should be measured traceable to the national standard. Thus, the establishment of an international standard is required satisfying the global CIPM MRA under the metric convention, and then, the global and regional framework to examine calibration and measurement capability of national metrology institutes (NMIs). A domestic traceability system in each country should be established and the quality management system of the NMI and calibration laboratories should be constructed based on ISO 17025.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

An *ad hoc* Working Group (WG) on metrology applicable to the measurement of material properties was established in 2005 by the CIPM in order to include materials metrology in the formal international measurement structure under the Metre Convention [1] following a proposal by the Versailles Project on Advanced Materials and Standards (VAMAS) G7 pre-normative organization. The Working Group on Materials Metrology (WGMM) agreed to scope its materials metrology activities as follows [2].

Materials metrology covers the application of measurement knowledge to the determination of the intrinsic and procedural properties of materials, including compositional and micro-structural properties.

The establishment of WGMM may enable the extension of the Mutual Recognition Arrangement (MRA) of CIPM to material metrology [3]. The WGMM has recommended extending the work of the CIPM's Consultative Committees to include calibration and measurement capabilities (CMCs) for a number of important materials properties in the Key Comparison Database (KCDB) of BIPM [4].

The present author was a member of the WG representing the National Metrology Institute of Japan (NMIJ) and served as the leader of Task Group 2 (TG2) for Thermophysical Properties (physical and chemical) in the WGMM. The author is also the chairman of the Working Group 9 (WG-9), thermophysical property, of the Consultative Committee for Thermometry (CCT). Accordingly, this report is based on the integration of the information created by TG2 of the WGMM, WG9 of the CCT and the thermophysical properties section of NMIJ.

Reliable values of thermophysical properties are particularly important for the reduction of global energy consumption, which is an urgent international issue [5]. It is expected that improvement of the insulation of buildings, houses, furnaces, kilns, boilers, refrigerators, pipelines and chemical plants will reduce the tremendous amount of heat losses in the world [6]. Thermal conductivity is a direct index of the performance of insulating materials. Fire resistance and non-toxicity of the material are of primary importance for this application. Degradation of insulation induced by precipitation of moisture or ageing should be predicted. Mechanical strength, density, heat capacity, cost and environmental load are indispensable information.

Efficient use of electric energy can reduce the emission of carbon dioxide [7]. One of the key technologies is power electronics to control high current for inverters, power transmission, hybrid cars, electric vehicles and electric trains [8]. High thermal conductivity heat spreaders are necessary to reduce overheating of power devices under high current operations. The thermal expansion of the heat spreader must not deviate from that of the device, which is made of silicon (or silicon dioxide, etc). The electrical resistivity or conductivity of the heat spreader is also important.

In order to develop advanced industrial technologies, such as highly integrated electric devices, optical disks, magneto-optical disks and thermoelectric devices, reliable thermophysical property values of thin films are important. In the ITRS (International Technology Roadmap for Semiconductors) 2006 Update 'Package Substrate Physical Properties (table 98) have been updated to incorporate additional parameters for thermal properties that are increasingly critical for higher temperature, smaller form factor packages' in the assembly and packaging parts. It is also mentioned that one of the difficult challenges $\geqslant$32 nm is 'Thermal-mechanical-electrical modeling for interconnections and packaging' in the modelling and simulation part and Difficult Challenges (table 122) have been updated as 'Model thermal-mechanical, thermodynamic and electronic properties of low κ, high κ, and conductors for efficient in-chip package layout and power management, and the impact of processing on these properties especially for interfaces and films under 1 micron dimension' in the modelling and simulation part [9].

In optical recording storage media, a small area is heated by a laser beam and it is recorded by changing the state (magnetization, crystal phase or an amorphous phase) of the area. The thermal assist recording technology is under development for next-generation hard disks. Therefore, the control of a temperature change in recording media by pulse heating becomes a key technology [10].

Thermal properties of such thin films do not agree with those of bulk materials of the same name/same composition. Consequently, it is necessary to measure these thin films *in situ* in the shape of circuit elements or recording media, or to measure thin film specimens which are synthesized to the same thickness by the same deposition method as the thin films in the device [11].

In order to establish the national standard and traceability system to measure thermophysical properties of functional solid materials including thin films, a national project 'Development of measurement technology of thermophysical properties and reference materials for functional materials' was conducted in Japan from 1997 to 2002 for a five-year term involving more than ten participating laboratories and universities [12]. The approach and effort of the project have been continued and evolved for developing primary methods for measuring thermophysical properties, developing and supplying reference materials and reference data for industrial and academic communities, developing new measurement methods applicable to advanced materials, standardizing methods for evaluating the uncertainty in practical measurement methods, producing property data for selected technologically important materials and developing a prototype network database system.

2. Thermophysical property measurement as material metrology

2.1. Scope

Since the WGMM is focused mainly on solid materials, liquids and gases (e.g. water, oils, lubricants) were agreed to be out of the scope of the report of the WGMM. Consequently, they are not discussed in this report either although thermophysical properties of liquids and gases are as important as the study of thermophysical properties of solids and there are comprehensive needs for liquid and gas properties from industry, trade, commerce, regulation and science. However, materials in their molten state, such as for example a metal, semiconductor, glass or polymer melts, are included in the report.

2.2. Uncertainty in measurement and non-uniformity of material

Concept, definition and evaluation procedure of 'uncertainty in measurement' are clearly stated in the '*Guide to the Expression of Uncertainty in Measurement, GUM*' [13]. If measurements are made for only one specimen, variation of the measured property values can be entirely attributed to the uncertainty in measurement. However, in most cases, measurements of material properties are made to give some representative values to a set of materials, such as a lot or a grade. In some cases, the property of a local area on the specimen is measured instead of an integrated property over the specimen, such as mass. In these cases, the measured values scatter not only by reproducibility of the measurements, but also through non-uniformity of the material. In the process of evaluation of the reference value for a reference material for metrology, the evaluated non-uniformity and instability of the material are eventually merged into the uncertainty of the reference value of the reference material since reference materials are used as measures for metrological traceability.

In contrast, evaluation of non-uniformity and instability of the materials over a lot or a grade is primarily important for materials of practical use in order to be used for a guaranteed value for safety and regulation, quality control of the material, quantitative design or simulation using property values of material, specification for commerce and trade [14–17], and basic data for environmental load and energy saving. Therefore, uncertainty in measurement and non-uniformity of material should be separated as key information of material metrology as shown in figure 1.

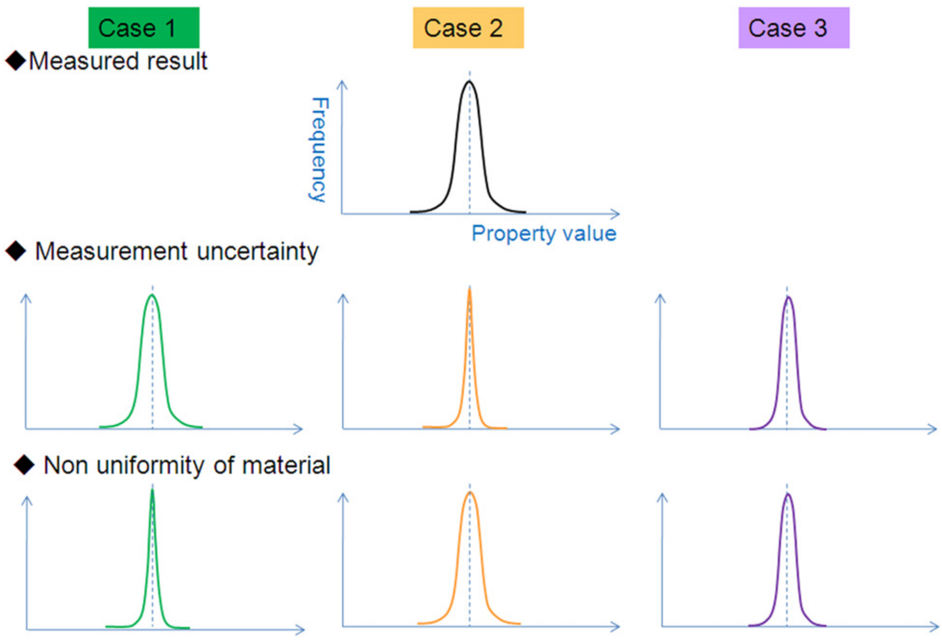

Figure 1. Measurement uncertainty and non-uniformity of material.

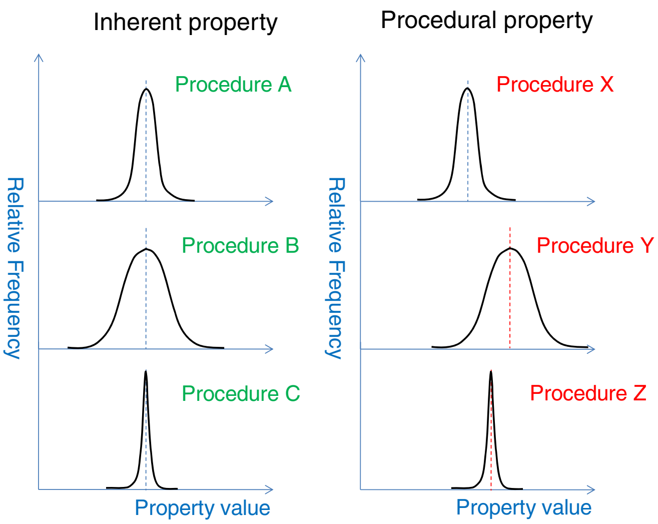

Figure 2. Distribution of measured property value for inherent property and procedural property.

2.3. *Inherent properties and procedural properties*

It is mentioned in the report 'Data Evaluation Theory and Practice for Material Properties' by Dr Munro of NIST that measurands of materials metrology can be classified into two categories, measurable quantities and procedural quantities [18]. And two terms have been introduced to distinguish the material properties that belong to the two categories. Micro-structures of materials are considered as a special class of measurable quantities.

Inherent material property: a material property that is a measurable quantity.

Procedural material property: a material property that is a procedural quantity.

This classification has been succeeded by the *ad hoc* WGMM of CIPM [2]. Figure 2 shows the distribution of measured property values for inherent property and procedural property, respectively. In the case of inherent property, the measured values of the same property of the same specimen (or specimens which are guaranteed to have the same property value) by different procedures are expected to distribute around the peak located at the same position although the width of the distribution might be different. In the case of procedural property, not only the width but also the peak position of the distribution changes depend on the procedure.

In this paper, the inherent thermophysical properties such as thermal conductivity, specific heat capacity, thermal diffusivity, emissivity, thermal expansion coefficient and density are mainly discussed. Among the procedural thermophysical properties glass transition temperature will be mentioned briefly.

2.4. *Consistency of inherent thermophysical properties obtained by different measurement methods*

Since thermal conductivity, specific heat capacity, thermal diffusivity and density are inherent thermophysical properties, the thermal conductivity value directly measured by a steady state method should agree with the value calculated as the product of thermal diffusivity, specific heat capacity and density as shown in the following equation (1):

$$\lambda = \alpha c \rho. \qquad (1)$$

This kind of consistency was investigated in a research project to produce a reference material with certified thermal conductivity (λ) and diffusivity (α), funded by the European Community under the 'Competitive and Sustainable Growth' programme ('HTCRM—High Temperature Certified Reference Material', contract SMT4-CT98-2211 [19]).

The thermal diffusivity was measured using the laser flash and xenon lamp methods. The thermal conductivity was measured using a guarded hot plate apparatus and the hot-wire/hot-strip methods. The heat capacity was measured at 273 K, 298 K and 373 K, with the modulated temperature differential scanning calorimetric method. The material is claimed by the manufacturer to have zero porosity. 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.

Consistency between the directly measured thermal conductivity value and the value calculated from other properties including thermal diffusivity and specific heat capacity was investigated and it was confirmed that both values agree with each other considering the uncertainty of both values.

A glass–ceramic reference material BCR-724 with certified thermal conductivity (λ) and diffusivity (α) was established and supplied by the European Commission Joint Research Centre Institute for Reference Materials and Measurements (IRMM) as the accomplishment of this joint project.

2.5. Non-uniformity of material

Each thermophysical property measurement is performed for a specific specimen. If a series of measurements is made for a set of specimens randomly sampled from a specified lot based on statistics, a set of statistical information about the thermophysical property of the lot including the mean value and the standard deviation of scattering of the thermophysical property value originated by non-uniformity of the lot is obtained. It should be noted that both non-uniformity in the lot and uncertainty of the measurements cause scattering of the measured thermophysical property values. An ANOVA analysis of variance is necessary to derive the non-uniformity of the material separating the measurement uncertainty from the measured scattering as shown in figure 1.

Material producers control and specify the process for a grade of material and supply the material to users with the grade name. Examples of grade names are Corning Pyrex® 7740, Toray TORACA® T300 carbon fibre, etc. Manufacturers usually release data sheets corresponding to the grade for their products. If the material is produced according to a special order from the customer, properties will be given to the lot delivered to the customer.

As mentioned above, it is not difficult to obtain information for the specified lot from which sampling of specimens for measurements can be made by routine operation of realistic cost and time based on statistics as shown in figure 3. It is much more difficult to obtain information for scattering of material properties under a specified process corresponding to the grade name since complete sampling cannot be made from all production by the specified process which has been and will be operated for a long time including the future.

However, it is important to point out that the mean value is not enough for material properties when the property varies in the lot because of non-uniformity or under the specified production process which varies or fluctuates over a long time of operation. Therefore, standard deviation representing

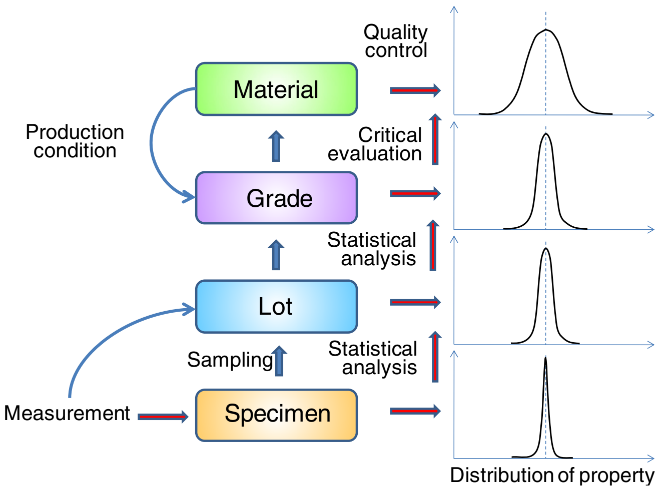

Figure 3. Evaluation process of material property from the measured data for specimens to lot and grade materials.

non-uniformity of thermophysical properties over the lot or the grade is expected to be presented. Stability or drift of the thermal property should be considered as indispensable information.

Since the ISO Guide 34 series presents procedures to evaluate uniformity and stability of reference materials, uniformity and stability of a lot or a grade of material can be evaluated by referring to the Guide 34 as a precedent example [20].

Mechanical strength, electrical conductivity or resistivity, melting temperature, glass transition temperature and degradation temperature in possible environments are also key information.

Cost, limitation of resource, corrosiveness, toxicity, environmental load and machinability are also universally requested information.

3. Present effort for traceable thermophysical property measurements

3.1. Task group for thermophysical properties (physical and chemical) in WGMM

At the first meeting of the *ad hoc* WG in CIPM, task groups (TGs) were established related to five material property areas: mechanical, thermophysical (phys–chem), composition and micro-structural, functional and electrochemical. The members of the TGs were Tetsuya Baba (Leader), NMIJ (Japan), Wolfgang Buck, PTB (Germany), and Philippe Charlet, LNE (France) [21].

The conclusions from TG2 are as follows:

- There were extensive needs for metrology of thermophysical properties from science, industry, energy conservation, safety and trade.
- Thermophysical properties are inherent and represented by SI-traceable derived units.
- Temperature dependence of a thermophysical property is essential information.

- Thermophysical properties are covered by CCT WG9 'Thermophysical properties'.
- Thermophysical properties can be a good area of collaboration between an existing CC and material metrology activity in areas such as reference materials, thermophysical properties for design and for advanced materials, such as nanomaterials.

The recommendation of the *ad hoc* WG of material property is as follows [22]:

The WG recommends that CC WGs should be established to stimulate comparisons, establish measurement capabilities in NMIs and identify suitable certified reference materials with known uncertainties.

The WG recommends that materials WGs established by CCs should encourage participation of all important stakeholders, including ISO/IEC, ILAC and VAMAS.

3.2. WG-9 of the CCT

In order to establish an international standard for thermophysical property measurements, WG-9 was founded under CCT from 2002. John Redgrove of the National Physical Laboratory, UK, served as the chairman until 2005. Tetsuya Baba of the National Metrology Institute of Japan succeeded to the chairmanship at the 23rd meeting of the CCT, June 2005. The present member NMIs of WG-9 are CENAM, Mexico; INRIM, Italy; KRISS, Korea; LNE, France; NIM, China; NIST, USA; NMIJ, Japan; NPL, UK; PTB, Germany; VNIIM, Russia.

The terms of reference of WG-9 were revised at the 24th meeting of the CCT, May 2008, according to the recommendation to CCs stated in the report of the CIPM *ad hoc* WGMM as follows:

> To advise the CCT on matters related to thermophysical properties, to assess the need for key comparisons in this field, and to develop and maintain an effective liaison with the international materials science community, including the Versailles Project on Advanced Materials and Standards (VAMAS).

WG-9 is tasked with continuing the production of a document on uncertainty, and with identifying and undertaking suitable pilot studies to establish the state of measurement and maturity of the field.

Three pilot studies for limited comparison in the following three fields have been carried out from 2006 and are now in the final stage.

(1) Thermal conductivity of insulating materials

Temperature range	0 °C to 100 °C
Measurement technique	the guarded hot plate method
Pilot institute	LNE, France

(2) Thermal diffusivity of dense materials

Temperature range	RT to 1000 °C
Measurement technique	the laser flash method
Pilot institute	NMIJ, Japan

(3) Normal spectral emissivity of solids

Pilot institute	NIST, USA (succeeded from NPL, UK)

3.3. Specific heat capacity

The TG2 reported that C_p of heat exchanger fluids is necessary for determining the efficiency of thermal engines and of building materials for fire protection. An uncertainty of 5% is often sufficient. Accredited testing laboratories for C_p testing need traceability [23].

Thermodynamic properties such as specific heat capacity and enthalpy of fusion have been studied mainly by the academic community of chemical research related to the International Union of Pure and Applied Chemistry (IUPAC) [24], the International Confederation for Thermal Analysis and Calorimetry (ICTAC) and the International Association of Chemical Thermodynamics (IACT). Since a huge accumulation of careful measurements and critical evaluation has been achieved, it is expected to declare CMC of these properties by collaboration with CCT under CIPM-MRA [3].

3.4. Thermal expansion coefficient

The TG2 reported that supply of certified reference materials is usually the traceability route for thermal expansion (suppliers—NMIJ (Japan), NIST (USA), PTB (Germany)). Uncertainty budgets have been developed for these measurements by NMIJ, Japan [23].

A supplementary comparison on the thermal expansion coefficient of gauge blocks was performed in 2004–2006 [25]. The comparison was carried out by members in the Discussion Group (DG8): Thermal expansion of Working Group on Dimensional Metrology (WGDM) in the Consultative Committee for Length (CCL). The four gauge blocks, which were three ceramic blocks and one steel block, were calibrated by seven organizations in turn. Most reported results corresponded with each other within their expanded uncertainties ($k = 2$).

Five countries have declared CMC of thermal expansion coefficient registered on appendix C of the KCDB of BIPM [5].

3.5. Thermal conductivity

The TG2 reported that traceability is well established for low conductivities, where reference materials exist. For medium to high conductivities, a demand for reference materials was identified, but few are available on the market. A need is especially expressed for the characterization of ceramics and new polymers. Manufacturers of instruments also require reference materials for the calibration of their instruments. For classic materials, no specific problem of metrological traceability was identified. Reference methods exist (available at NMIs), but a lack of reference materials was observed. Nevertheless, for new materials linked to micro- and nanoscale a real traceability problem has been identified. Emergent sectors (electronic and bio) have expressed their needs for conductivity measurements [23].

The standard method for thermal conductivity measurements for a low thermal conductivity material is the guarded hot plate method. The guarded hot plate method is simply

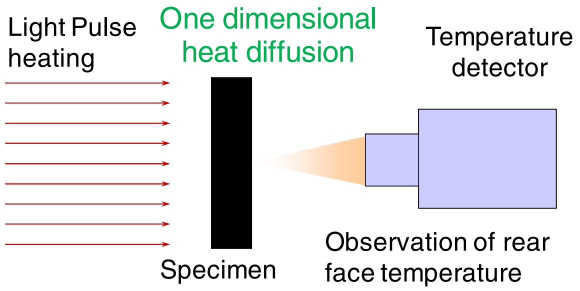

Figure 4. Basic configuration of the light pulse heating method for thermal diffusivity measurements.

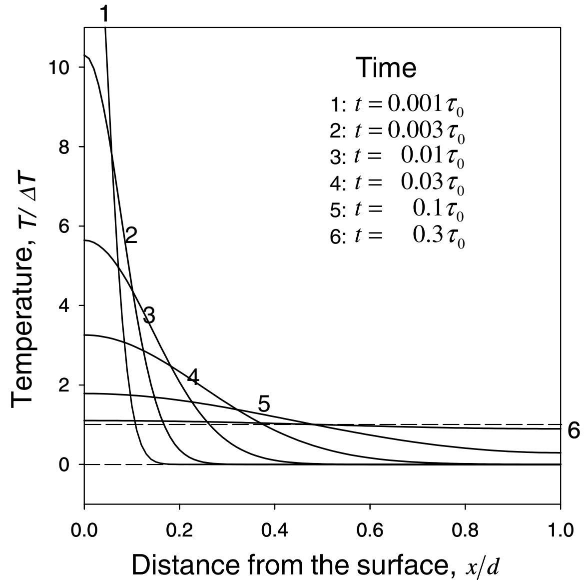

Figure 5. Chronological change in temperature distribution inside the specimen after impulse heating to the surface.

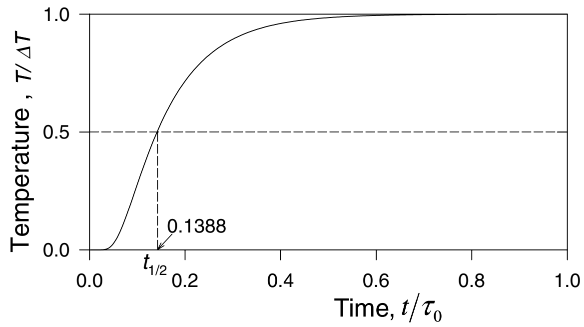

Figure 6. Temperature response at the rear face of the specimen after impulse heating to the front face.

based on the definition of thermal conductivity. A definite amount of heat is generated by an electric heater uniformly over a fixed area.

Many NMIs have been engaged in the establishment of a thermal conductivity standard of insulating materials by the guarded hot plate method. The thermal conductivity standard is maintained by organizations other than an NMI in several countries. International round robin measurements have been organized several times in order to investigate consistency among countries [26].

Round robin measurements of thermal conductivity of insulating materials by the guarded hot plate method organized by WG9/CCT are in progress.

3.6. Thermal diffusivity

The TG2 reported that basic information for thermal design (e.g. production control in metallurgy and ceramic industries) depends on reliable diffusivity data, and accredited testing laboratories for thermal diffusivity measurements need traceability [23].

Since heat capacity measurements by adiabatic calorimetry and thermal conductivity measurements by the steady state method are both direct realizations of the definition, variations of their design such as heating methods and geometrical configuration are limited. In contrast, transient measurement methods of thermal diffusivity are more flexible and there are varieties of design with options of specimen size, shape, geometrical configuration of heating and temperature detection. An electrical heater or light of pulse-wise, step-wise or sinusoidal modulation can be used to heat the specimen. These transient heating methods can be an absolute measurement method or a relative measurement method and for each method it must be explained how the method can determine the corresponding thermophysical property value based on the definition.

The basic and simplest method for thermal diffusivity is the pulsed light heating method represented by 'the laser flash method' where the front face of a planar specimen kept at constant temperature is uniformly light-pulse-heated as shown in figure 4 [27]. Heat diffuses one-dimensionally from the front face of the heated specimen to the rear face, and eventually the temperature of the entire specimen becomes uniform as shown in figure 5. Because the rate of temperature change of the specimen's rear face is proportional to its thermal diffusivity and inversely proportional to the square of its thickness, thermal diffusivity can be calculated from the thickness of the specimen and the heat diffusion time as shown in figure 6.

The following conditions are assumed to be ideal:

(1) The duration of the laser pulse is negligible compared with the heat diffusion time.
(2) The specimen is adiabatic to the environment.
(3) The specimen front face is heated uniformly.
(4) The temperature change of the specimen's rear face is measured precisely.
(5) The specimen is dense, uniform and opaque.
(6) The change in thermal diffusivity following a rise in temperature of the specimen after pulse heating is negligible.

Under the assumptions mentioned above, when the front face of a plate of thermal diffusivity α, specific heat capacity c,

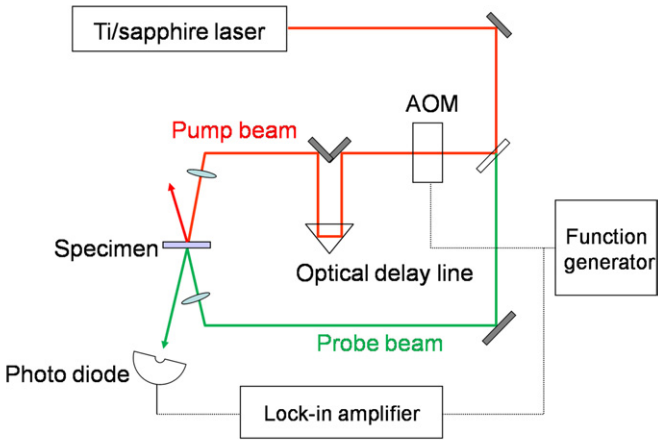

Figure 7. Block diagram of an ultrafast laser flash system for measuring thin film thermophysical properties by picosecond pulsed laser heating.

density ρ and thickness d is light-pulse-heated at a uniform energy density, the temperature change of the specimen's rear face is expressed as

$$T(t) = \Delta T \cdot \left\{ 1 + 2\sum_{n=1}^{\infty} (-1)^n \exp\left[-(n\pi)^2 \frac{t}{\tau} \right] \right\}, \qquad (2)$$

where $\Delta T = Q/C$, Q is the total energy absorbed by the specimen, C is the heat capacity of the specimen and $\tau = d^2/\alpha$ is the characteristic time for heat diffusion across the specimen. A graph of equation (2) is shown in figure 6.

When 0.1388 of the characteristic time for heat diffusion across the specimen has passed after pulse heating, the specimen's rear face temperature reaches half of the maximum temperature rise. This time is called the half rise time, $t_{1/2}$. The characteristic time is determined by fitting a theoretical curve to the rear face transient temperature curve, and the thermal diffusivity is calculated [28]. The conventional standard data analysis algorithm is the half-time method, where thermal diffusivity is calculated as [2]

$$\alpha = 0.1388 d^2/t_{1/2}. \qquad (3)$$

Geometrical configuration of the laser flash method can be evolved to measure thermal diffusivity values across thin films if the heating light pulse is of shorter pulse duration and rear face temperature is observed with a much faster temperature detector [29]. Fast light pulse heating thermoreflectance methods by picosecond pulse heating and by nanosecond pulse heating have been developed to measure thin films synthesized on transparent substrates as shown in figure 7 [30]. These high-speed pulsed light heating thermoreflectance methods observe heat diffusion across a well-defined length of the specimen thickness under one-dimensional heat flow. Since the geometry is very simple, thermal diffusivity can be determined reliably with uncertainty evaluation based on GUM [13].

Upon the establishment of the regular laser flash method and the ultrafast laser flash methods (the picosecond and nanosecond thermoreflectance methods), the thermal diffusivity of materials ranging from thin films of several tens of nanometres thickness to bulk specimens of several tens of millimetres thickness can be measured by the light pulse heating methods using the same configuration of one-dimensional heat diffusion after impulse heating as shown in figure 8.

The ultrafast laser flash method can be widely used if commercial instruments are available. The reliability of the measurements can be checked by the reference materials of thermal diffusivity traceable to the national standard and/or the international standard.

NMIJ/AIST established the national standard in Japan of the laser flash method in 2002 [31]. Uncertainty of thermal diffusivity standard by the laser flash method was evaluated based on the '*Guide to the Expression of Uncertainty in Measurement, GUM*' and a quality system corresponding to ISO 17025 was constructed [32]. Now, evaluation of homogeneity and stability of high density isotropic graphite is in progress. The standard value of thermal diffusivity of graphite is to be determined with uncertainty evaluation based on GUM and it has been supplied as a reference material from 2006.

NMIJ/AIST is also developing the standard of thin film thermophysical property by the ultrafast laser flash method under the same scheme. The national standards for picosecond and nanosecond thermoreflectance methods were established in 2005 and 2008, respectively. Thin film reference material is under development and to be supplied for the nanosecond thermoreflectance method.

3.7. Glass transition temperature

The TG2 reported that measurement of the glass transition temperature, which is an important method for checking the cure state of reinforced plastics, especially high performance polymer matrix composites, is measured by changes in many other properties such as dielectric, thermal expansion, stiffness and acoustics (ultrasonics), as a function of temperature. Comparability, as well as traceability to SI, of the different methods is of concern to industry and needs attention. There

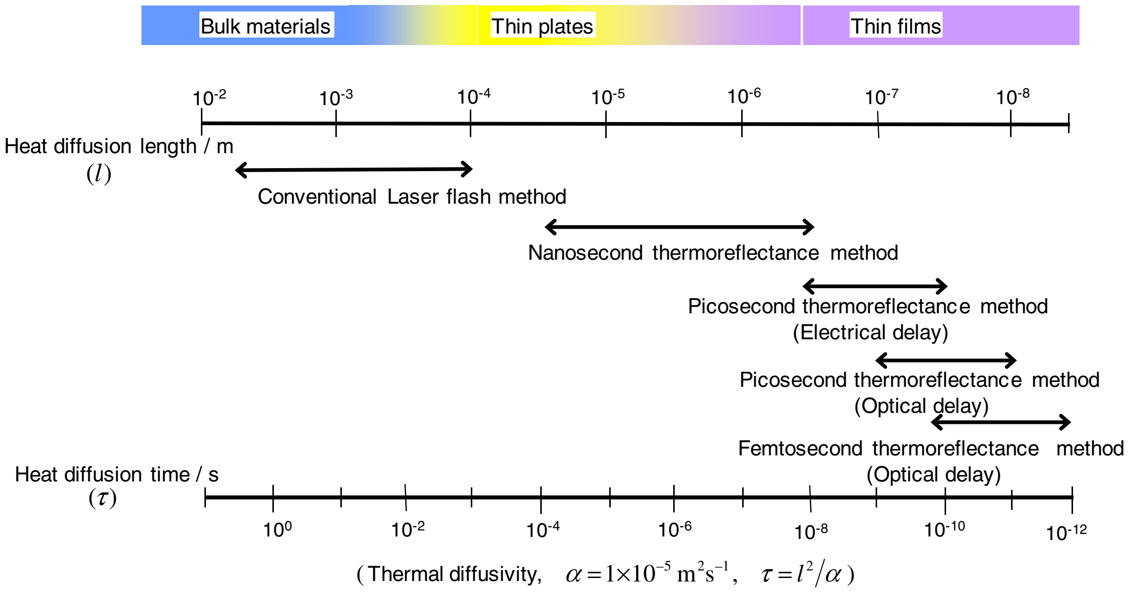

Figure 8. Observable heat diffusion time and observable thickness of the specimen covered with four types of light pulse heating methods with a thermal diffusivity of 10^{-5} m^2 s^{-1}.

is a need to show that all these alternative methods measure the same glass transition temperature and a pilot study should be proposed. Improved traceability and calibration of temperature, in particular, length and force should be included [23].

4. Global metrology system for thermophysical properties

4.1. Measurement standards of thermophysical properties

It is well known that measurement standards have been prepared for material metrology of mechanical properties by the International Organization for Standardization (ISO), regional and national standardization organizations (CEN, ASTM, JIS, etc). There are also many international, regional and national measurement standards for thermophysical properties. The remarkable difference between mechanical properties and thermophysical properties is that the typical and major thermophysical properties, such as thermal conductivity, specific heat capacity and thermal expansion coefficient, are inherent whereas the typical and measurable mechanical properties, such as yield strength, fracture toughness, hardness and creep rate, are procedural.

Conventionally, these measurement standards required neither traceability to the national or international standard nor evaluation of uncertainty in measurement. Recently, when Japanese industrial standard (JIS) 'Measurement methods of thermal diffusivity, specific heat capacity, and thermal conductivity for fine ceramics by flash method' was harmonized to ISO 18755 : 2005 [33], the procedures to establish traceability to SI standard by calibrating instruments by thermal diffusivity reference materials and to evaluate uncertainty based on the GUM have been described in the revised version.

Thus, in order to establish an internationally harmonized metrology system as shown in figure 9, the following subjects should be achieved.

The first step for a measurement standard is the following:

- Establish the national metrological standard and build and operate a quality management system according to ISO 17025 in each country.
- Organize or participate in the key comparison or supplementary comparison of the property.
- Get accreditation for the quality management system.
- Registration of CMCs [3] of member countries or economies to the KCDB of BIPM [4]

The second step is required for the production of certified reference materials:

- Development of reference materials according to ISO Guide 34 and determination of the reference value and uncertainty of the thermophysical property based on the registered CMC.

The third step is specially required for material metrology where measurement standards have been popularly used but SI traceability of the standards has not been established yet:

- The measurement standard should be revised to state the procedures to calibrate the instrument by SI-traceable reference material and to evaluate uncertainty of the measurement.

In some cases, there is no measurement standard available for thermophysical property measurement for materials, such as thermal barrier coatings. Further, it is important to collaborate with VAMAS based on the Memorandum of Understanding (MOU) on Cooperation to identify key metrological traceability issues affecting the comparability and accuracy of the measurement of material properties between the BIPM and VAMAS signed in 2008 [34].

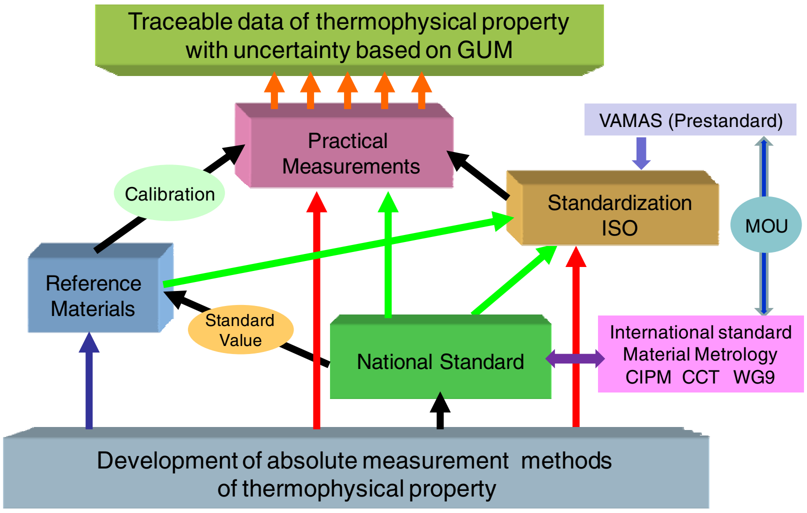

Figure 9. The global system of the international and national standards and traceability system of the thermophysical property measurements in order to accelerate production efficiency of the reliable thermophysical property data.

Many researchers have contributed to the production of reliable thermophysical property data for a long time. Many careful measurements for a variety of materials have been made according to contemporary needs. There have been efforts to present recommended values for basic materials and important materials from the viewpoint of application. Unfortunately, most of these efforts were completed before the concept of uncertainty and SI traceability was established.

Once an international standard of thermophysical properties is established within the framework of CIPM MRA, it can be the hub of all previous efforts and a global metrology system to produce universally reliable data with uncertainty traceable to the international standard can be created.

4.2. Complementary role of measurements and data for thermophysical properties

If the temperature of a solid material is measured, the measured temperature value is just for this body at the measured time. On the other hand, the same thermal conductivity is expected for the same solid material under the same temperature, pressure and environment where it is not degraded even if the measurement is made at different times.

Since the thermophysical property of each specimen is measured, data obtained by individual measurements are assigned to the specimen. After a series of measurements is completed for a set of specimens of the same material and ANOVA analysis to separate measurement uncertainty from the non-uniformity, the representative value and the non-uniformity of the thermophysical property can be assigned to the lot.

Uniformity of a grade of material is controlled by the process of the material producers and it is expected that a thermophysical property of the material set of the specified grade follows a predictable distribution. As mentioned in section 2.5, it is not easy to obtain information for scattering of material properties under a specified process corresponding to the grade name since complete sampling is impossible for all materials which have been produced by the specified process for a long time and will be produced in the future. It is important to develop a universal procedure to evaluate uniformity and stability of a grade of material referring to the Guide 34 which has been successful in evaluating reference materials as a precedent example [20].

4.3. Thermophysical property database

These thermophysical property data of materials can be widely and repeatedly accessible by data users across the world if they are stored in the database open to the internet.

Until now, many thermophysical databases have been developed and there are a few prominent databases which are worthy of special mention not only in the field of thermophysical property research but also in data science, such as the thermophysical property data developed by the Center for Information and Numerical Data Analysis and Synthesis (CINDAS) at Purdue University [35] compiled from the well-known TPRC data series [36].

However, a database under the concept of traceability and uncertainty of thermophysical property data has not yet been developed. Another restriction of the conventional thermophysical database is the identification of the material to which a thermophysical property data set is assigned.

A new type of database, which is optimized to store and evaluate traceable thermophysical property data with uncertainty and material identification based on hierarchical classification, has been developed by the National Metrology Institute of Japan (NMIJ) in the National Institute of Advanced Industrial Science and Technology (AIST) [37]. Figure 10 shows the hierarchical classifications of substances and materials which can be operated by a graphical user interface. The highest level is named ‘Domain’ and classified into ‘Fluids’ and ‘Solids and Melts’ since many substances are used by alternating the gas phase and the liquid phase, such as a working fluid for energy technology which vaporizes from the liquid phase to the gas phase and condenses from the gas phase to the liquid phase. On the other hand, most metals and semiconductors are solidified from the melt phase.

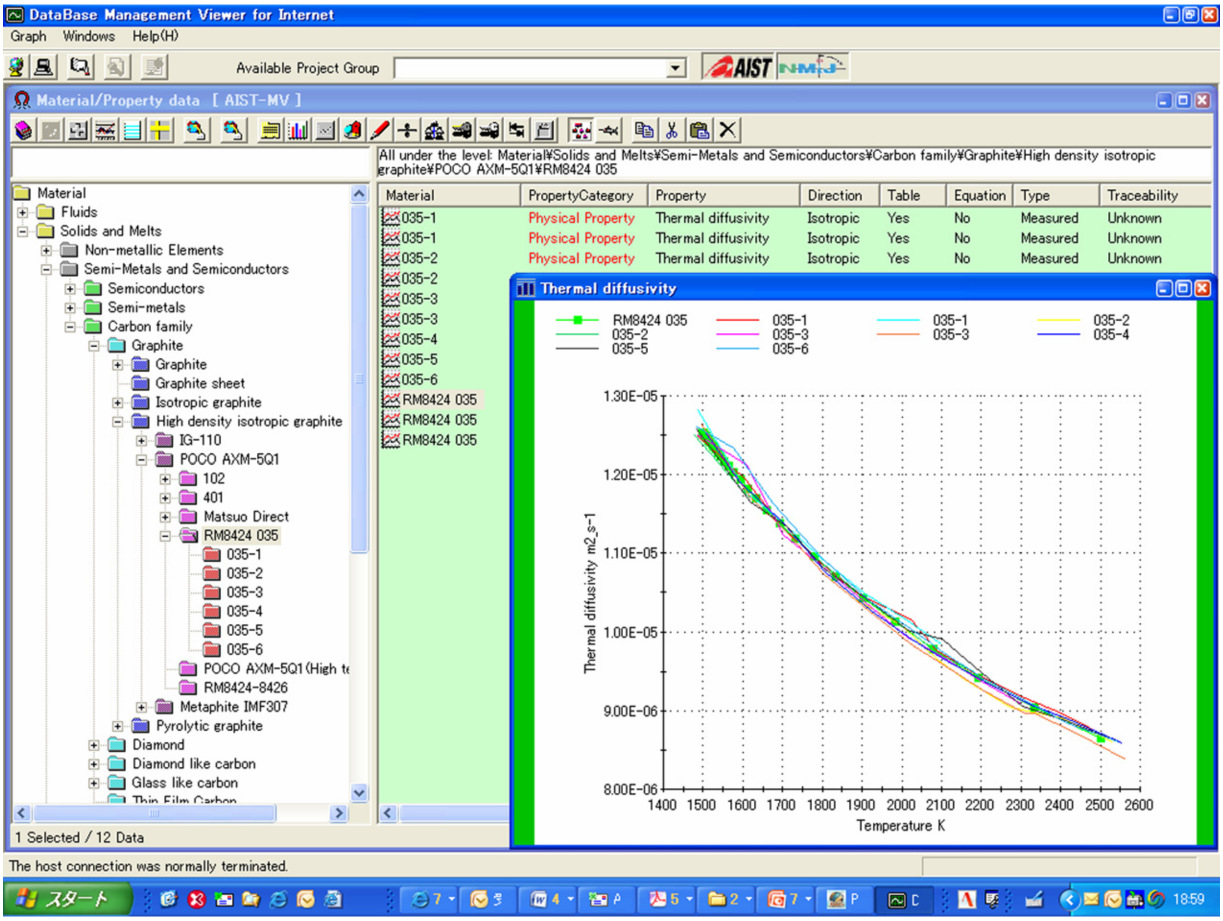

Figure 10. Graphical user interface of the network database for thermophysical properties. Hierarchical classification and graph are displayed for POCO AXM-5Q1 graphite.

The class of the second layer is named 'Group', and classification below the groups is optimized depending on the group. Examples of groups are metals, ceramics, semiconductors and polymers under the 'Solids and Melts' Domain.

The third level is named 'Material Class 1'. Examples of material class 1 are oxides, carbides and nitrides under the ceramics group.

The fourth level is named 'Material Class 2' where the substance name is stated with the information of chemical composition, IUPAC name of the main component and CAS registry number. Examples of material class 2 are aluminium oxide and silicon oxide under the oxide folder.

The fifth level is named 'Material Class 3' where the material name is assigned with the information of crystalline or non-crystalline structure and microstructure. If the material is a single crystal or a polycrystal, the crystal system is specified by the space group. Examples of material class 3 are quartz and fused quartz under the silicon oxide folder.

The sixth level is named 'Grade' where the grade name is stated with the information of product name, material producer, composition and so forth. Examples of grade are POCO AXM 5Q1, IG 110 under the high density isotropic graphite folder.

The seventh level is named 'Lot' where the lot name is stated with the information of lot characters and the parameters for process control under which the lot was produced.

The eighth level is named 'Specimen' where the specimen name is stated with the information of dimensions such as thickness and diameter for disc-shaped specimens, machining method and procedure for specimen preparation, surface finish and specimen characters.

Since the thermophysical property of each specimen is measured, data obtained by individual measurements are registered to the specimen folders at the eighth level. After a series of measurements has been completed for a set of specimens of the same lot, the obtained set of data for the lot has been analysed and evaluated and the representative data for the lot presented, it can be registered to the lot folder at the seventh level.

Catalogue values of thermophysical properties given to specific grades of commercial materials by manufacturers are registered to the grade folder at the sixth level. Certified values for reference materials are also registered to the grade folder. Thus, thermophysical property data are registered to the folders located between the fifth level and the eighth level and uncertainty can be assigned to each data point in this database.

Data categories of thermophysical property data stored in this database range over different types such as directly measured, derived from the relationship between other known physical properties, synthesized by curve fitting, calculated by numerical simulation or predicted in value by material physics.

One type from these listed categories is assigned to each data as 'Data type'.

The levels of traceability are classified into international standard, national standard, industrial standard and other standards traceable to an established standard and assigned for measured data and original measurement data from which data are derived or synthesized. Information regarding how and by whom the data are authorized is also assigned to each data. For example, if the data are reported in a reviewed scientific journal, they are authorized by the reviewers and the editorial board of the journal. The national standard data based on CMC of a NMI should be approved by CIPM.

Browsing software called TPDS-web and InetDBGV has been developed to access the database via the Internet. TPDS-web enables us to access the database very easily without user registration (it needs only a contents license agreement) and software installation.

TPDS-web can be accessed at the following URL [38]: http://riodb.ibase.aist.go.jp/TPDB/DBGVsupport/English/.

InetDBGV has a much more intelligent and versatile user interface than TPDS-web. The latest version of it can be downloaded from the following URL: http://www.aist.go.jp/RIODB/TPDB/DBGVsupport/.

This database is equipped with the function to analyse correlation between properties and to calculate and display graphically the property derived from other properties [37].

For example, the Lorentz number L is defined by the following equation according to the Wiedemann–Franz law:

$$L = \lambda\rho/T, \tag{4}$$

where λ is the thermal conductivity, ρ is the electrical resistivity and T is the absolute temperature. The Lorentz number can be calculated from the thermal conductivity data, the electrical resistivity data and their temperature. For metals such as magnesium, aluminium, copper and silver Lorentz numbers calculated from the new edition of *Thermophysical Property Handbook* are close to the ideal value based on the free electron model by the Drude theory (2.44×10^{-8} W Ω K^{-2}) at temperatures above 600 K [39]. If the Lorentz number calculated from a set of thermal conductivity and electrical resistivity data at the same temperature for the same metal is quite different from the ideal Lorentz number, the reliability of these data or characterization of the measured specimen should be carefully examined.

4.4. Evaluation of data

The importance of 'critical evaluation' of thermophysical property data from already published data has long been emphasized [40]. However, the majority of these data are not traceable to the national or international standards nor has uncertainty been given. Further, critical evaluation must be performed by the experts on thermophysical property research and measurements, who must start from the investigation of the measurement method and uncertainty by which the literature data were obtained and the identification of the material of the specimens on which the measurements were performed as shown in figure 11. Thus, critical evaluation is a quite intelligent, creative, careful and time-consuming task to be performed specially and ingeniously corresponding to a variety of evaluated materials. Therefore, there is the academic journal the *Journal of Physical and Chemical Reference Data*, published by the American Institute of Physics (AIP) for the National Institute of Standards and Technology (NIST), to provide critically evaluated physical and chemical property data [41]. Consequently, critically evaluated data can be given for a limited number of materials of high priority from the metrological, academic or technological point of view since they cost a lot of effort and time of intelligent and experienced persons.

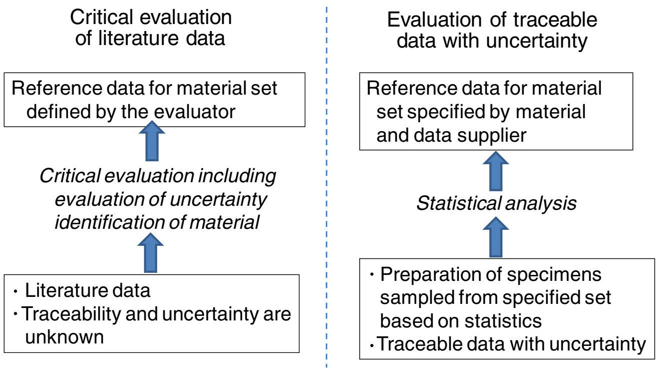

Figure 11. Evaluation processes of thermophysical property data.

However, critical evaluation will face the challenge of meeting the rapid growth and speed of huge requirements for reliable thermophysical property data from industrial needs such as for thermal design and heat transfer simulation, basic data to calculate heat management efficiency to reduce carbon dioxide generation or fair commerce and trade. It is not easy to overcome this challenge since the conventional approach of critical evaluation is very expensive and time consuming.

The global system of the international and national standards and the traceability system of the thermophysical property measurements can accelerate the production efficiency of the reliable thermophysical property data as shown in figure 9. Hence, thermophysical property data produced under the global traceability system are supplied with uncertainty based on globally agreed procedures. Uncertainty of the measurement is already given before critical evaluation by the experts.

If the lot or grade, to which the reference value is given, is clearly identified, the specimens should be sampled following the established statistical procedure as shown in figure 11. Then, the reference value can be derived by just following the procedure given by the GUM. Even if the series of measurements is claimed to be traceable to the national standard with uncertainty, it is desirable that the result be confirmed by round robin measurements among institutes, which can make measurements traceable to the national or international standard.

It is much more difficult to give a reference value to a material that is not specified by grade as shown in figure 3. For example, first of all, the term 'single crystal pure iron' must be defined quantitatively, in order to assign the reference value of thermal conductivity to 'single crystal pure iron'.

It is of primary importance to specify purity, such as 99.9% or seven nine, etc. The dependence of thermal conductivity on species of impurity should be investigated at the same impurity concentration. The effect of isotope ratio on thermal conductivity should be known for materials with high thermal conductivity like diamond.

In the case of sintered ceramics, carbon materials or sputtered thin films, the situation is especially complicated due to grain size, shape and orientation of grains, structure and property of grain boundary, crystalline structure in the grain and miscellaneous factors, in addition to purity. Then, critical evaluation is still indispensable to derive a reference value or a reference equation.

Considering this situation, as a special class of measurable quantities of materials, structures are defined in the report by Dr Munro, 'Data Evaluation Theory and Practice for Material Properties' [18]. The report of the CIPM *ad hoc* WGMM, 'Evolving Need for Metrology in Material Property Measurements', also covered structures in the scope of material metrology [2]. If the methods to measure and characterize material structure are standardized and calibrated by reference materials traceable to the international standard, more quantitative and systematic analysis can be applied to investigate correlation between thermophysical properties and structures.

Versatile functions of the thermophysical property database, such as display of multiple data on the same graph, display of uncertainty on the graph, fitting an analytical function to specified data plots and their graphical display, analysis of correlation between properties, compositions, structures and process parameters for material production are expected to innovate critical evaluation.

5. Summary

There are extensive needs for metrology of thermophysical properties from science, industry, energy conservation, safety and trade. Thermophysical properties are inherent and represented by SI-traceable derived units. Since typical thermophysical properties such as thermal conductivity, specific heat capacity, thermal diffusivity and density are inherent thermophysical properties and temperature dependence of thermophysical properties is essential information, it is natural that the WG-9 devoted to thermophysical properties is established under the CCT tasked with the establishment of the international standard of thermophysical properties under the Metric system. International collaboration among member NMIs and important stakeholders, including ISO/IEC, ILAC and VAMAS, is essential to create a global metrological system optimized to thermophysical properties in the new field of material metrology.

Thus, thermophysical properties can be a good area of collaboration between an existing CC and material metrology activity in areas such as reference materials, thermophysical properties for design and for advanced materials, such as nanomaterials.

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References

[1] Wallard A 2007 Measurement principles and structures *Handbook of Materials Measurement Methods* ed H Czichos *et al* (Berlin: Springer) chapter 1

[2] Bennett S and Sims G D (ed) 2007 Evolving need for metrology in material property measurements *Report of the CIPM ad hoc Working Group on Materials Metrology (WGMM)* October 2007

[3] 1999 *Mutual Recognition of National Measurement Standards and of Calibration and Measurement Certificates Issued by National Metrology Institutes* BIPM, October 1999

[4] http://kcdb.bipm.org/

[5] http://www.ipcc.ch/

[6] Watson R T, Zinyowera M C and Moss R H (eds) 1996 Technologies, policies and measures for mitigating climate change *IPCC Technical Paper I* IPCC, Geneva, Switzerland, November 1996, p 20 http://www.ipcc.ch/pdf/technical-papers/paper-I-en.pdf

[7] Watson R T, Zinyowera M C and Moss R H (eds) 1996 Technologies, policies and measures for mitigating climate change *IPCC Technical Paper I* IPCC, Geneva, Switzerland, November 1996, p 34 http://www.ipcc.ch/pdf/technical-papers/paper-I-en.pdf

[8] 2007 *Annual Progress Report for the Advanced Power Electronics and Electric Machinery Program FY 2007* US Department of Energy Office of Vehicle Technologies, December 2007 http://www1.eere.energy.gov/vehiclesandfuels/pdfs/program/2007_apeem_report.pdf

[9] 2006 Modeling and simulation *The International Technology Roadmap for Semiconductors* 2006 Update, p 3 http://www.itrs.net/Links/2006Update/FinalToPost/15_Modeling2006Update.pdf

[10] Baba T (ed) 2009 Thermal design and thermophysical property for electronics *Japan. J. Appl. Phys.* **48** (5) (special issue) http://jjap.ipap.jp/journal/JJAP-48-5S2.html

[11] Taketoshi N, Yagi T and Baba T 2009 Effect of synthesis condition on thermal diffusivity of molybdenum thin films observed by a picosecond light pulse thermoreflectance method *Japan. J. Appl. Phys.* **48** 05EC01

[12] Ono A, Baba T and Fujii K 2001 Traceable measurements and data of thermophysical properties for solid materials: a review *Meas. Sci. Technol.* **12** 2023–30

[13] *ISO/IEC Guide 98-1:2009* Uncertainty of measurement: 1. Introduction to the expression of uncertainty in measurement
ISO/IEC NP Guide 98-2 Uncertainty of measurement: 2. Concepts and basic principles
ISO/IEC Guide 98-3:2008 Uncertainty of measurement: 3. Guide to the expression of uncertainty in measurement (GUM,1995)

[14] WTO 2002 A compilation and summary of the responses received to the questionnaire for a survey to assist

developing country members to identify and prioritize their specific needs in the TBT field *Report G/TBT/W/186* World Trade Organization Committee for Technical Barriers to Trade, October 2002
[15] WTO website (www.WTO.org)
[16] CIPM 2003 *Evolving Needs for Metrology in Trade, Industry and Society and the Role of the BIPM* (Sèvres: BIPM)
[17] Kaarls R (ed) 2007 *Evolving Needs for Metrology in Trade, Industry and Society and the Role of BIPM* (Sèvres: BIPM)
[18] Munro R G 2003 *Data Evaluation Theory and Practice for Materials Properties, NIST Recommended Practice Guide* (Washington, DC: US Government Printing Office) SP 960-11
[19] Salmon D, Roebben G, Lamberty A and Brandt R 2007 Certification of thermal conductivity and thermal diffusivity up to 1025 K of a glass–ceramic reference material BCR-724 *EUR Report* 21764 EN, ISBN 92-894-9920-6, ISSN 1018-5593
[20] *ISO Guide* 34:2009 General requirements for the competence of reference material producers
[21] Bennett S and Sims G D (ed) 2007 Evolving need for metrology in material property measurements *Report of the CIPM ad hoc Working Group on Materials Metrology (WGMM)* October 2007, p 38
[22] Bennett S and Sims G D (ed) 2007 Evolving need for metrology in material property measurements *Report of the CIPM ad hoc Working Group on Materials Metrology (WGMM)* October 2007, p 52
[23] Bennett S and Sims G D (ed) 2007 Evolving need for metrology in material property measurements *Report of the CIPM ad hoc Working Group on Materials Metrology (WGMM)* October 2007, p 39
[24] Gatta G D, Richardson M J, Sarge S M and Stølen S 2006 Standards, calibration, and guidelines in microcalorimetry: 2. Calibration standards for differential scanning calorimetry (IUPAC Technical Report) *Pure Appl. Chem.* **78** 1455–76
[25] Yamada N *et al* 2008 Final report on the thermal expansion coefficient of gauge blocks (APMP.L-S1) *Metrologia* **45** (Tech. Suppl.) 04001
[26] Zarr R R and Filliben J J 2002 International comparison of guarded hot plate apparatus using national and regional reference materials *NIST Technical Note* 1444
[27] Parker W J, Jenkins R J, Butler C P and Abbott G L 1961 Flash method of determining thermal diffusivity, heat capacity, and thermal conductivity *J. Appl. Phys.* **32** 1679–84
[28] Baba T and Ono A 2001 Improvement of the laser flash method to reduce uncertainty in thermal diffusivity measurements *Meas. Sci. Technol.* **12** 2046–57
[29] Baba T 2009 Analysis of one-dimensional heat diffusion after light pulse heating by the response function method *Japan. J. Appl. Phys.* **48** 05EB04
[30] Taketoshi N, Baba T and Ono A 2001 Development of a thermal diffusivity measurement system for metal thin films using a picosecond thermoreflectance technique *Meas. Sci. Technol.* **12** 2064–73
[31] Akoshima M and Baba T 2006 Study on a thermal-diffusivity standard for laser flash method measurements *Int. J. Thermophys.* **27** 1189–203
[32] *ISO/IEC 17025* 1999 General requirements for the competence of testing and calibration laboratories ISO/IEC
[33] *ISO 18755:2005* 2005 Fine ceramics (advanced ceramics, advanced technical ceramics)—determination of thermal diffusivity of monolithic ceramics by laser flash method
[34] 2008 *Memorandum of Understanding on Cooperation between the BIPM and VAMAS*
[35] https://cindasdata.com/ (accessed 1 August 2009)
[36] Touloukian Y S *et al* 1970–1972 *Thermophysical Properties of Matter* (*TPRC Data Series*) (New York: IFI-Plenum)
[37] Baba T, Yamashita Y and Nagashima A 2009 Function sharing and systematic collaboration between a networking database system and printed media on thermophysical properties data *J. Chem. Eng. Data* **54** 2745–57
[38] http://riodb.ibase.aist.go.jp/TPDB/DBGVsupport/English/
[39] Japan Society of Thermophysical Properties 2008 *Thermophysical Properties Handbook* 2nd edn (Tokyo: Yokendo) pp 23–5
[40] Lide D R Jr 1981 Critical data for critical needs *Science* **212** 1343–9
[41] http://jpcrd.aip.org/ (accessed 1 August 2009)