Intercomparison of thermal conductivity measurements on a calcium silicate insulation material

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Intercomparison of Thermal Conductivity Measurements on a Calcium Silicate Insulation Material

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Abstract:

The determination of reliable thermal conductivity values of insulation materials at high temperatures is important for target-oriented material research, further improvement of products and quality management. However, there is a lack of reference materials for high temperature thermal conductivity measurements which are needed to ensure and improve good measurement practise. In order to investigate porous calcium silicate as reference material for temperatures up to 1100 K, the German Thermophysics Working Group within GEFTA initiated an intercomparison of thermal conductivity measurements on a commercially available calcium silicate insulation material with seven participating laboratories. Stationary and instationary measurement methods were used to determine the effective total thermal conductivity of the calcium silicate material in the temperature range from 300 K to 1100 K. The derived weighted mean value of the thermal conductivity increases from 0.0846 $Wm^{-1}K^{-1}$ at 300 K to 0.173 $Wm^{-1}K^{-1}$ at 1100 K. Within the same temperature interval the relative uncertainty increases from 3.5% to 7%. The investigated product is commercially available and it could be therefore used in the daily laboratory work as reference material for thermal conductivity measurements at high temperatures.

Nomenclature

C	material and gas dependent parameter	$\mathrm{Pa\,K^{-1}}$
e	specific extinction coefficient	$\mathrm{m^2 kg^{-1}}$
E	deviation	1
G	geometry factor	1
n	effective complex index of refraction	1
P	pressure	Pa
T	temperature	K
U	uncertainty	$\mathrm{Wm^{-1}K^{-1}}$
x	thermal conductivity value	$\mathrm{Wm^{-1}K^{-1}}$

Greek symbols

λ	thermal conductivity	$\mathrm{Wm^{-1}K^{-1}}$
ρ	density	$\mathrm{kg\,m^{-3}}$
σ	Stefan-Boltzmann constant	$5.6704 \cdot 10^{-8}\,\mathrm{Wm^{-2}K^{-4}}$

Subscripts

b	bulk
eff	effective
g	gas
lab	experimentally determined value
$mean$	mean value
n	normalized
r	radiation
R	Rosseland-averaged
s	solid
tot	total
0	free

Acronyms

GUM	Guide to the Expression of Uncertainty in Measurement
SEM	Scanning electron microscope

1 Introduction

The German Thermophysics Working Group within GEFTA initiates and conducts several intercomparisons in the field of thermophysical properties. The objectives of this research work are to enhance the reliability of thermophysical data and to improve measurement praxis of the participating laboratories. The working group is aware of the urgent need for a reference material with low thermal conductivity values at high temperatures up to 1000 K as many members are involved in thermal conductivity measurements on high temperature insulation materials. The thermal performance of these materials is directly correlated with the improvement of energy efficiency in many industrial applications. Thus, reliable thermal conductivity data are needed to allow a target-oriented improvement of energy efficiency.

Unfortunately, there is a lack of reference materials with low thermal conductivity values at high temperatures [1, 2]. The material has to meet several conditions before it could be considered as reference material. It should be isotropic and homogeneous on a macroscopic scale to allow the use of a wide range of experimental techniques for the determination of thermal conductivity. The material should be also stiff and mechanically stable to allow easy preparation. It should be a material with a low thermal conductivity even at high temperatures. Finally, it should be easily available and inexpensive to allow laboratories easy access to this material. Insulation materials based on calcium silicate could fulfil more or less all mentioned requirements.

Therefore in the past the determination of the thermal conductivity of calcium silicate specimen were the topic of various researcher groups performing thermal conductivity measurements up to high temperatures with different methods: Schlegel concluded that the observed deviations were higher than expected from standards. The uncertainties depends not on the applied measurement method, which were guarded-hot-plate method and hot-wire method (parallel and cross array) [3]. Same methods were used by Lohmann et al. up to 1173 K which states also no influence of the applied measuring methods on the thermal conductivity values [4]. Martin et al. stated that in the case of anisotropic calcium silicate materials the used hot-wire apparatus yields higher thermal conductivity values as derived by the guarded hot plate apparatus [5]. The differences were 3 to 7% depending on the anisotropy of the material. In the mid-nineties different guarded hot plate and hot-wire apparatus of European laboratories were compared in an international intercomparison on the thermal conductivity of low density calcium silicate in the temperature range of 298 to 1173 K [2, 6]. The results of three of five laboratories were in sufficient agreement concerning the guarded hot plate apparatus. The authors mentioned that one of the most critical sources of uncertainty is the undefined thermal contact resistance between the measurement plates and the rigid specimen surface. The influence of the thermal resistance decreases with higher temperature as thermal radiation become more and more dominant and bridges this resistance. The results of hot-wire apparatus of eight laboratories show deviations in the range of 6.5 to 8.2% and fit within this uncertainty interval to the results derived by the three guarded hot plate apparatus. However, due to the general spreading of data this material was not certified. Recently, Wulf et al. performed thermal conductivity measurements on isotropic calcium silicate materials and observed a good agreement within 10 % of results obtained by stationary methods and the applied hot-wire method in a temperature range from 293 to 1923 K [7].

In summary it can be stated that the results were not satisfactory because in some cases the results were not good enough to define a reference material and it other cases results were provided by only one laboratory. Against this background in 2008 an intercomparison was initiated concerning the determination of the thermal conductivity of a calcium silicate sample to establish reference values up to temperatures of 1100 K.

2   Participants and measurement methods

The following German institutes, universities and companies participated in this intercomparison:

- Bavarian Center for Applied Energy Research (ZAE Bayern), Würzburg
- German Institute for Refractories and Ceramics (DIFK), Bonn
- Forschungsinstitut für Wärmeschutz e. V. (FIW), Munic
- Institute of Ceramic, Glass and Construction Materials (IKGB), TU Bergakademie Freiberg
- Institute of Thermal Engineering (IWTT), TU Bergakademie Freiberg
- Materialprüfungsamt Nordrhein-Westfalen (MPA NRW), Dortmund
- Netzsch Gerätebau GmbH (NGB), Selb

The thermal conductivity of the calcium silicate specimens were determined by different methods. Two groups of measurement methods have to be distinguished in principle: stationary methods, where a constant heat flow within the specimen has to be established and thermal conductivity values are derived by applying Fourier's law, and dynamic methods, where the temperature response caused by a defined thermal excitation is evaluated to yield the thermal transport properties.

Thermal conductivity measurements based on stationary conditions were performed by five participants using self-built guarded hot plate apparatuses according to DIN EN 12667. Two participants used the commercially available guarded hot plate apparatus Titan from Netzsch Gerätebau GmbH (Selb, Germany) according to DIN EN 12667 ISO 8302 and ASTM C 177. One participant used also the heat flow apparatus HFM 436 from the same company which works according to ASTM C 518, DIN EN 12939, DIN EN 13163 and DIN EN 12667. Finally one participant used a stationary measurement principle according to DIN EN 1094-7 and ASTM C 201. In the following the different experimental setups based on stationary methods will be denoted with the code 'STATx' where 'x' indicates a specific setup.

Several participants used the measurement apparatus TCT 426 from Netzsch Gerätebau GmbH (Selb, Germany) to perform hot-wire measurements according to DIN EN 993-15 (parallel method), DIN EN 993-14 (cross-array method) and to ASTM C1113 (platinum resistance thermometer technique). One participant used a self-built apparatus with an advanced data evaluation taking into account thermal end losses via the used platinum wires and thermal contact resistances between the hot wire and the specimen [8]. In the following the different experimental setups based on non-stationary methods will be denoted with the code 'DYNAx' where 'x' indicates a specific setup.
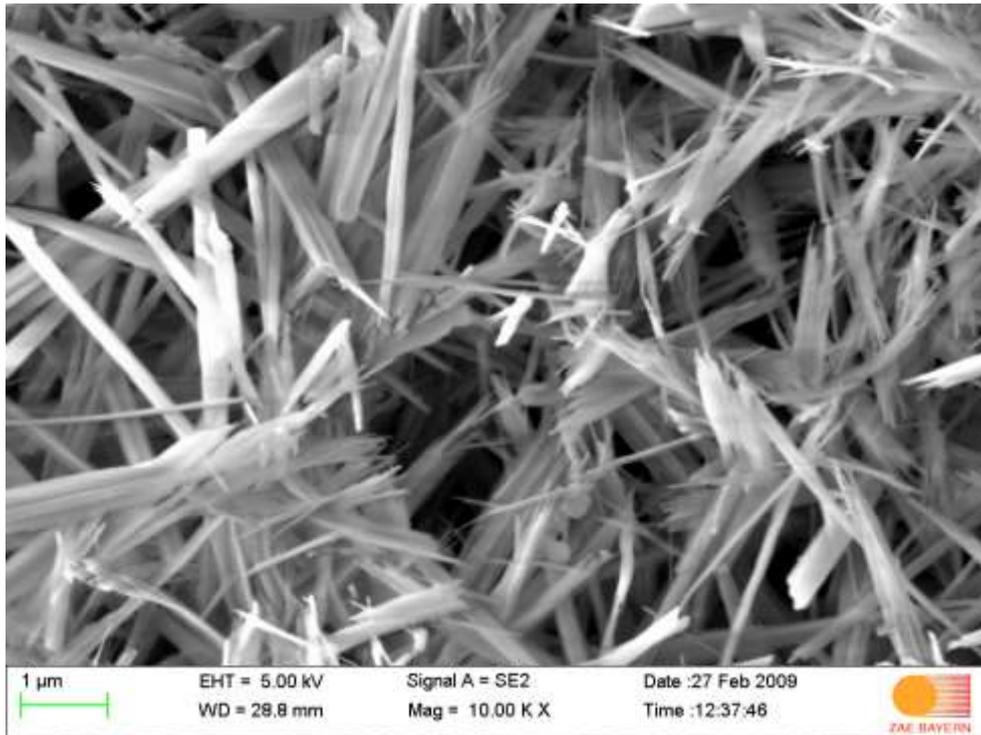
Figure 1: *SEM picture of the micro structure of the investigated calcium silicate sample*
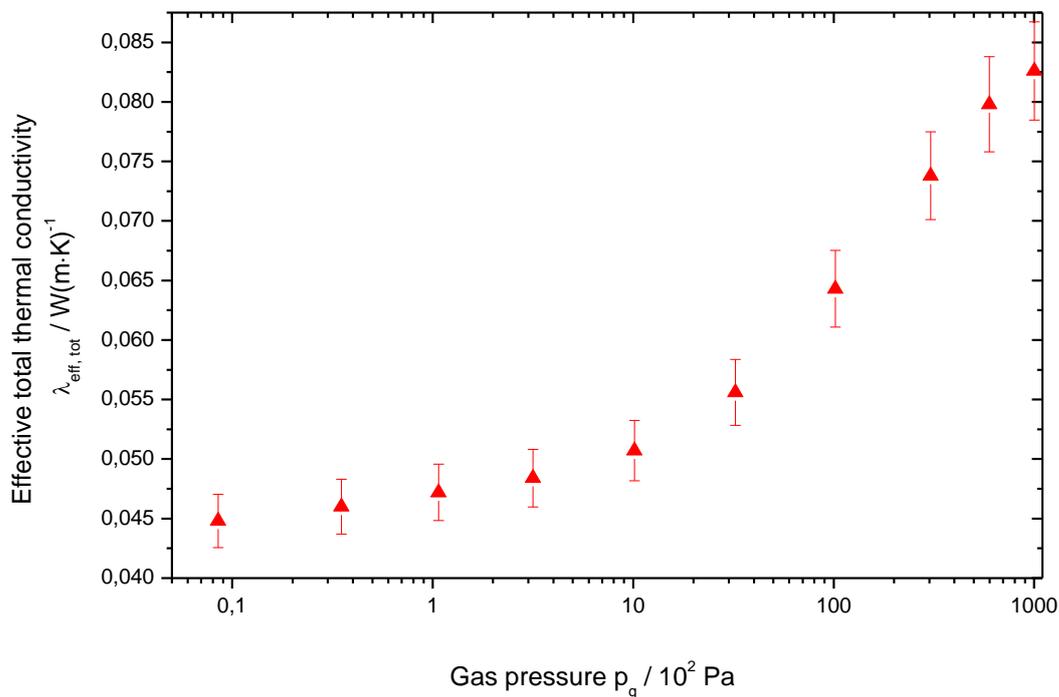
Figure 2: *Gas pressure dependent effective total thermal conductivity of the investigated calcium silicate at 300 K*

For the sake of completeness it has to be mentioned that also the applicability of the Laserflash method for the determination of the thermal diffusivity of porous calcium silicate specimens was tested. Therefore three laboratories, all well experienced in the Laserflash technique, consented to perform Laserflash measurements beside the intercomparison.

However the results were not reliable. The relative deviations between the thermal diffusivity data were more than 30%. The relative deviations between the calculated thermal conductivity values based on Laserflash measurement, using known values of specific heat and density, and the results presented in this paper were in some cases about 100%. A future publication is planned to discuss these results in detail, e.g. penetrations depth of the laser pulse.

3   Heat transfer within calcium silicate insulation materials

Heat transfer in optically thick, highly porous insulation materials is caused by the conduction of heat via the solid backbone and the gaseous phase and by diffusive radiative heat transfer. Under the assumption of independent transport processes, an effective total thermal conductivity $\lambda_{tot,eff}$ can be defined as function of temperature for constant gas pressure [9]:

$$\lambda_{tot,eff}(T) = \lambda_s(T) + \lambda_g(T) + \lambda_r(T) \tag{1}$$

with λ_s: thermal conductivity of the solid backbone, λ_g: contribution of the pore gas to the effective total thermal conductivity and λ_r: radiative conductivity. The thermal conductivity of the solid backbone is proportional to the thermal conductivity of the bulk material [10]:

$$\lambda_s(T) = G(\rho) \cdot \lambda_b(T) \tag{2}$$

with λ_b: temperature dependent thermal conductivity of the bulk material and G: geometry factor, which describes the influence of the structure of the solid backbone and the density of the porous material on the solid thermal conductivity. The thermal conductivity contribution of the gas phase can be expressed by [11]:

$$\lambda_g(T, p_g) = \frac{\Phi \cdot \lambda_{g,0}(T)}{1 + \dfrac{C \cdot T}{P_g}} \tag{3}$$

with Φ: porosity of the porous material, $\lambda_{g,0}$: thermal conductivity of the free gas, C: material and gas dependent parameter, p_g: gas pressure. The radiative thermal conductivity λ_r is given by [12]:

$$\lambda_r(T) = \frac{16}{3} \frac{n^2 \cdot \sigma \cdot T^3}{\rho \cdot e_R^*(T)} \tag{4}$$

With n: effective index of refraction, σ: Stefan-Boltzmann constant and e_R^*: Rosseland-averaged effective specific extinction coefficient.

It should be mentioned that heat transfer by vapour transport driven by a temperature gradient is not relevant for the discussion of measurement results obtained within this intercomparison and therefore is not considered.
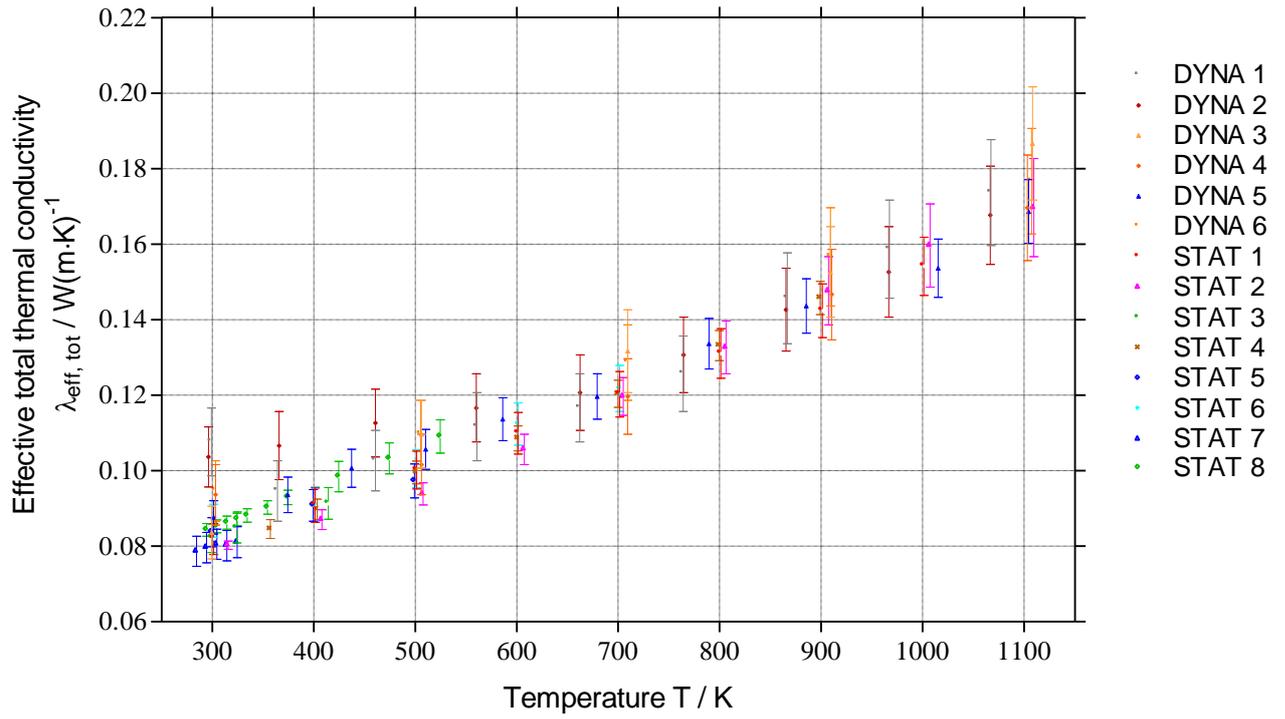
Figure 3: *Effective total thermal conductivity values as delivered by the participants*
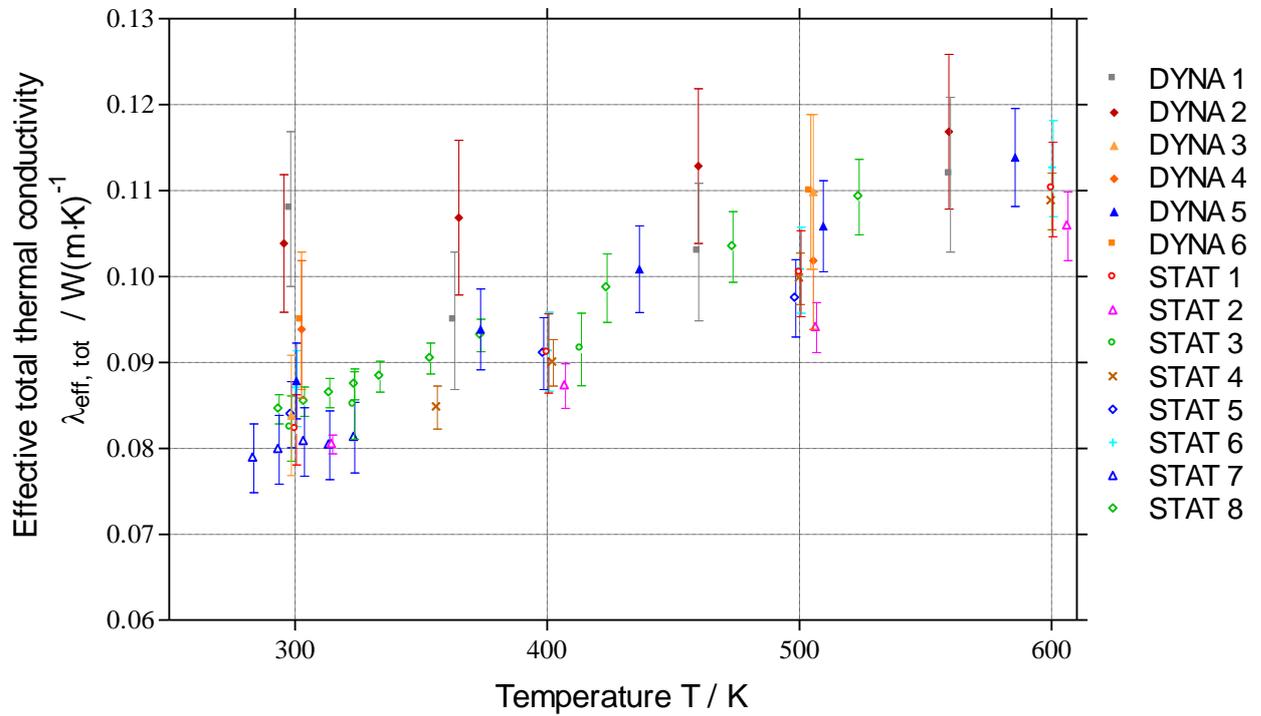
Figure 4: *Effective total thermal conductivity values as delivered by the participants in temperature range 300 K to 600 K*

4 Sample description and preparation of specimens

Calcium silicate insulation materials are synthesized from the precursor limestone and quartz in a hydrothermal batch process. The sample material investigated in this work was prepared by CALSITHERM Silikatbaustoffe GmbH, Germany, and is commercially treated under the product name SILCAL 1100. The main components of this highly porous calcium silicate are 46-47% CaO and 44-45% SiO_2 which forms a three-dimensional crystalline backbone (see Figure 1). Typical effective pore diameters are in the range of microns.

From a batch of several cubic meters plates were prepared with the dimensions of (3 x 1.25 x 0.1) m^3. From these plates the specimens different in shape and size were prepared for the participants. All specimens were thermally treated at 1123 K during 12 hours before shipping to forestall phase changes occurring during the first heating of the specimens. The mean density of the delivered sample material determined by the participants of the intercomparison test was (250 ± 15) kgm^{-3}.

5 Measurement and evaluation procedure

All participants were asked to provide one set of thermal conductivity data at predefined temperatures from 300 K to 1100 K in steps of 100 K. The participants were instructed to start the measurements at the highest temperature and to measure in descending order to avoid the absorption of water at lower temperatures. Only two participants were able to measure at the given temperatures. In the other cases a polynomial of third order was fitted to the measurement data and the interpolated thermal conductivity data used for the further evaluation. This interpolation procedure induced an additionally maximum uncertainty less then 1% to derived thermal conductivity values.

All measurements should be performed under atmospheric pressure with air or nitrogen. The intercomparison is aligned to the rules for comparison measurements valid at present; especially to the guidance laid down by the CIPM (Comité International des Poids et Mesures) for comparison measurements. Every participant had to deliver measurement values with stated uncertainties according to GUM [13].

Reference values were derived from the delivered measurement values by calculating the arithmetic mean. Therefore the measurement values were weighted with their stated uncertainties. The uncertainty of the weighted mean value was also calculated using the weighted arithmetic mean of the delivered uncertainties for the single measurement values. The deviation function E_n was introduced to provide a measure about the quality of a measurement value and whether it could be taken into account for calculating the weighted mean value or not. The deviation E_n, normalized with respect to the experimental uncertainty U_{lab} stated by the participant, is defined by [14]:

$$E_n = \frac{x_{lab} - x_{mean}}{\sqrt{\left(U_{lab}^2 + U_{mean}^2\right)}} \quad , \tag{5}$$

with the measurement value x_{lab}, the calculated mean value x_{mean} and the uncertainty of the mean value U_{mean}. An absolute value of E_n less then 1 indicates that the uncertainty stated by the laboratory concerned is reliable. If the absolute value E_n was larger than 1, the corresponding measurement value was excluded from the calculation of the mean value. This procedure was repeated unless the quality criterion $-1 < E_n < 1$ was fulfilled for the remaining measurement values.
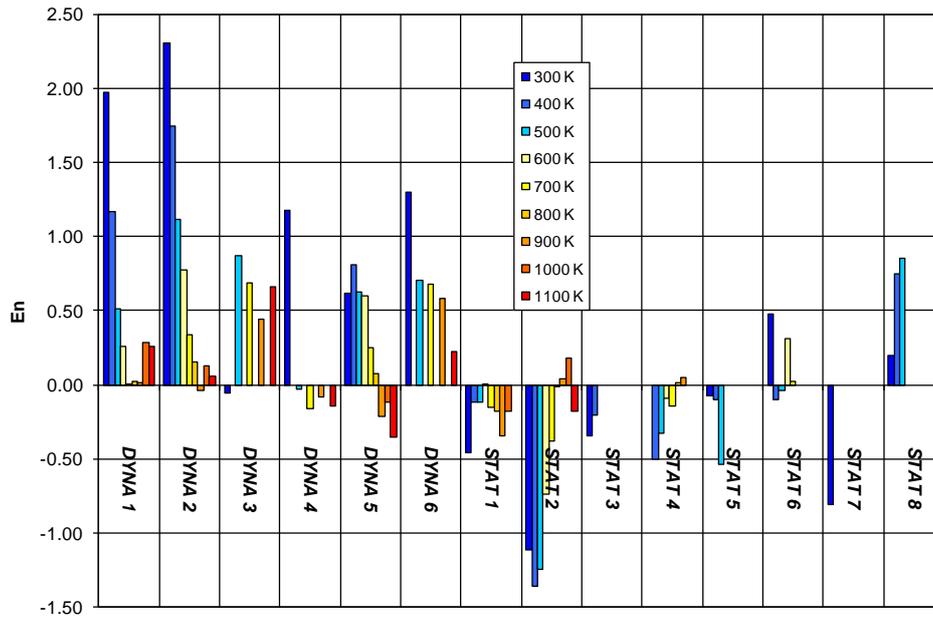
Figure 5: *Values of the normalized deviation calculated according to Eq. (5) from all delivered experimental results from different setups as a function of specimen temperature (cf. key)*
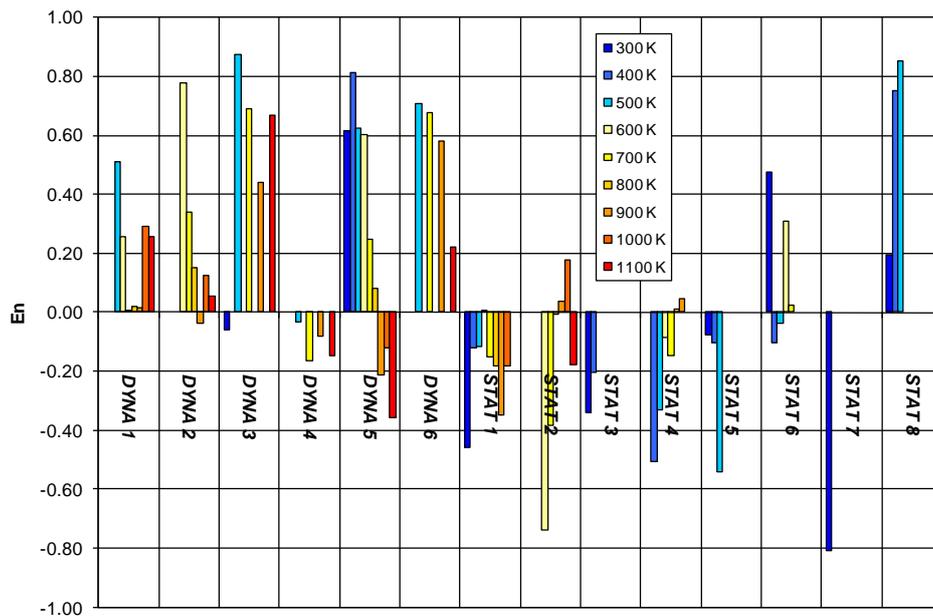
Figure 6: *Values of the normalized deviation calculated according to Eq. (5) of the remaining experimental results after the exclusion process from different setups as a function of specimen temperature (cf. key)*

6 Measurement results

Two institutes, DIFK and ZAE Bayern, investigated the isotropy of the delivered sample material by measuring the ultrasonic speed in different directions. The ultrasonic speed is directly correlated with the thermal conductivity of the solid backbone. In two directions an ultrasonic speed of (1080 ± 20) ms^{-1} could be determined and (1130 ± 10) ms^{-1} in the third direction with a 5% enhanced ultrasonic speed, which can be explained by the influence of gravity during the preparation process of the material. However anisotropy of this magnitude will not affect the effective total thermal conductivity to be determined. The maximum influence could be expected at the lowest measurement temperatures, because the thermal

conductivity of the crystalline backbone decreases whereas the thermal conductivity of the gas and the radiative conductivity increase with temperature.
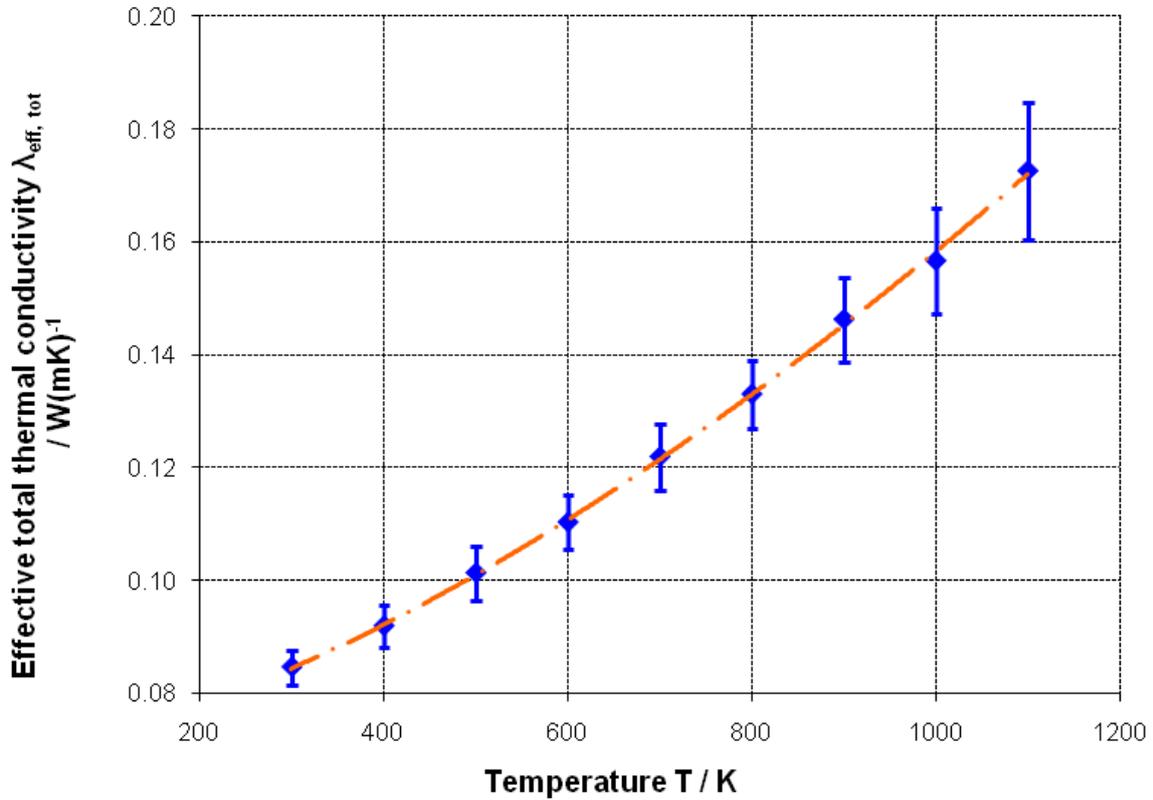
Figure 7: *Weighted mean value of all considered measurement results of the investigated calcium silicate as a function of temperature. Additionally a non-linear regression line is depicted according to a polynomial of third order $\lambda = (9 \cdot 10^{-12} \cdot T^3 / K^3 + 6 \cdot 10^{-08} \cdot T^2 / K^2 + 4 \cdot 10^{-05} \cdot T / K + 0.0674)$ W·m⁻¹·K⁻¹*

Figure 2 shows the gas pressure dependent total effective thermal conductivity of the investigated calcium silicate at 300 K determined by hot-wire method. The thermal conductivity values increase from about 0.045 Wm⁻¹K⁻¹ at $0.1 \cdot 10^2$ Pa to 0.0826 Wm⁻¹K⁻¹ at $1000 \cdot 10^2$ Pa. A constant value of the thermal conductivity at higher pressures can not be observed because the average mean pore size is in the range of about one micron (cf. Figure 1).

A Rosseland-averaged effective specific extinction of e^*_R = 23.6 m²kg⁻¹ at 300 K was determined by performing infrared-optically directional-hemispherical transmission and reflection measurements [15]. According to Eq. (4) a radiative conductivity of 0.0014 Wm⁻¹K⁻¹ can be derived for this optically thick material, assuming an effective index of refraction of 1. The gaseous and the radiative contribution to the effective total thermal conductivity are not influenced by the anisotropy of the sample material. Considering the derived values for the thermal conductivity of the evacuated material and the radiative conductivity the influence on the effective total thermal conductivity of the observed anisotropy is according to Eq. (1) less than 2.6 % at 300 K and even smaller at higher temperature.
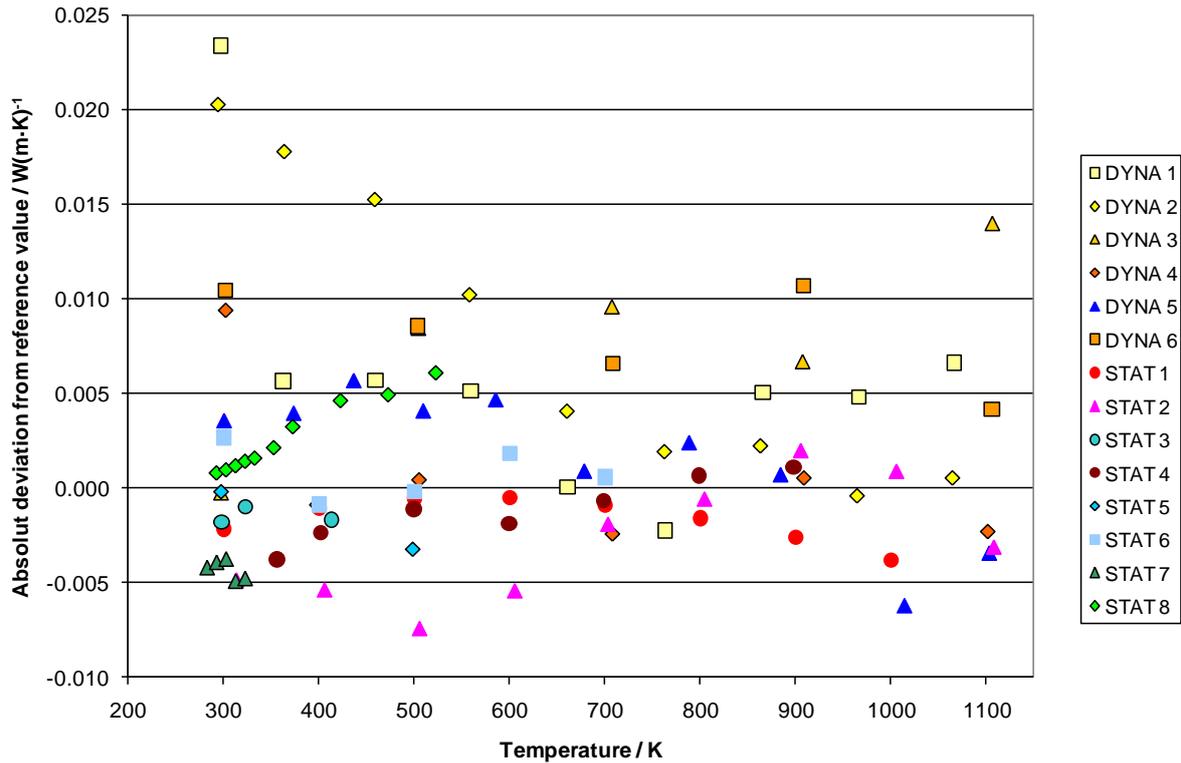
Figure 8: *Absolute deviation of all delivered thermal conductivity values from the derived weighted mean value (cf. Table 1)*

Figure 3 and Figure 4 show the delivered measurement results of all participants. The effective total thermal conductivity increases in the investigated temperature range. In most cases a good agreement of the delivered data values could be observed within the stated uncertainties. Exceptions could be observed at temperatures below 600 K (cf. **Fehler! Verweisquelle konnte nicht gefunden werden.**). For some dynamic experimental setups (DYNA 1, DYNA 2) significantly higher thermal conductivity values were determined. One participant delivers thermal conductivity values with exceptional low uncertainties for the used stationary setup (STAT 2).

Above 700 K more data from dynamic set ups were delivered. At 900 K three stationary set ups, e.g. guarded hot plate apparatus, and six dynamic methods were used by the participants. At 1100 K only one guarded hot plate could be used for the measurement.

7   Discussion and conclusion

From the thermal conductivity values, derived by interpolation of the measurement results for the requested temperatures, the normalized deviation E_n-values were calculated accordingly to Eq. 5 (cf. Figure 5). In a second step, thermal conductivity values leading to absolute E_n-values above 1 were excluded from averaging and the E_n-value was again calculated based on the reduced data set. After this procedure all thermal conductivity values passed the quality criteria (cf. Figure 6).

The derived weighted mean values of the effective total thermal conductivity of the investigated calcium silicate are compiled in Table 1 and Figure 7. The effective total thermal conductivity increases from $0.0846\,Wm^{-1}K^{-1}$ at 300 K to $0.173\,Wm^{-1}K^{-1}$ at 1100 K. The relative uncertainty increases from 3.5% to 7% within the same temperature interval. The

absolute and relative deviations of the delivered thermal conductivity values from the weighted mean value are depicted in Figure 8 and Figure 9.
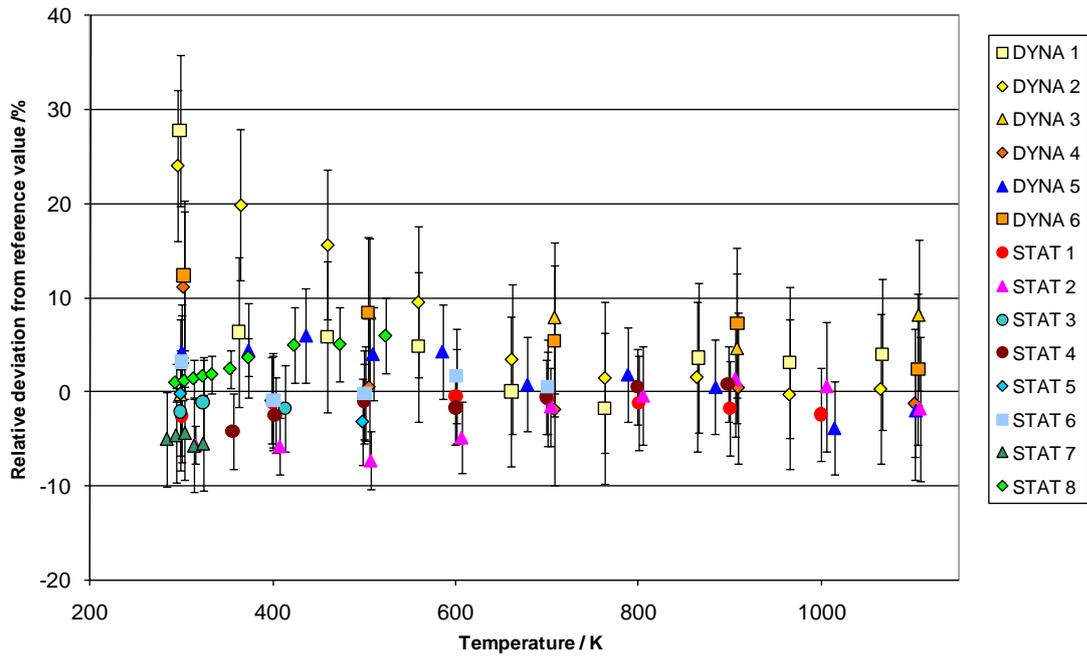
Figure 9: *Relative deviation of all delivered thermal conductivity values from the derived weighted mean value (cf. Table 1)*

Table 1 Weighted mean value of all considered measurement results of the investigated calcium silicate as a function of temperature

Temperature (K)	Effective total thermal conductivity $(W \cdot m^{-1} \cdot K^{-1})$
300	0.0846 ± 0.0030
400	0.0919 ± 0.0038
500	0.101 ± 0.005
600	0.110 ± 0.005
700	0.122 ± 0.006
800	0.133 ± 0.006
900	0.146 ± 0.008
1000	0.157 ± 0.009
1100	0.173 ± 0.012

The resulting uncertainties are in the same range or even lower as stated for other intercomparison tests [2, 5-7].

A main reason for increasing uncertainty of the thermal conductivity values at higher temperature is the increasing uncertainty of measured temperature values. This fact makes it more difficult to control the necessary temperature boundary conditions during the experiment and to receive precise temperature data needed for the evaluation of the thermal conductivity. At low temperatures, i.e. below 600 K, thermal contact resistances between specimen and measuring areas of the measurement device (e.g. plates of a guarded hot plate or wire in a hot-wire experiment) could lead to higher uncertainty values. In the case of stationary guarded hot plate experiment this effect will lead in an underestimation of the true thermal conductivity value. For the experiments based on the hot-wire method thermal contact resistances between the wire and the specimen could lead to an overestimation of the thermal conductivity value [8]. In principle, also humidity transport could lead to an enhanced heat transfer and therefore to higher thermal conductivity values. However, this effect should be minimized due to the fact that the participants were asked to perform measurements only on thermally treated specimens. This could be done by starting the thermal conductivity measurements at the highest possible temperature and performing the other measurements at descending order of temperature. Another possibility to avoid the influence of humidity was the thermal treatment of the specimen immediately before the measurement and using a dry nitrogen atmosphere during the experiment.

Generally it could be stated that the measurement capability of the community of the participants is reduced at higher temperatures, i.e. more measurement values are available at moderate temperatures and the dynamic hot-wire method is dominant at the highest temperatures. The deviations of the delivered thermal conductivity values used for the calculated weighted mean value are spread homogenously around the weighted mean. A significant influence neither on the applied measurement methods nor on the temperature could not be found. The maximum absolute deviation is about $\pm$ 0.010 $\mathrm{Wm^{-1}K^{-1}}$ which corresponds to a maximum relative deviation of $\pm$ 7%.

Finally, it can be concluded that the results of this intercomparison are consistent and the given weighted mean values and the related uncertainties are reliable. The values are determined by state-of-the-art measuring and evaluation methods. The investigated calcium silicate material is commercially available in a constant quality and it could be therefore used as reference material for thermal conductivity measurements at high temperatures.

Acknowledgement

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