

NETZSCH

Proven Excellence.

Thermal Properties of Ceramics

By Means of Differential Scanning Calorimetry, Thermogravimetric Analysis,
Simultaneous Thermal Analysis, Evolved Gas Analysis,
Dilatometry and Laser Flash Analysis



Thermal Properties of Ceramics

Introduction

What are Ceramics?

Ceramics is a collective term for traditional stoneware and tableware, building materials and raw materials that are composed of silicates, oxides and other high-melting inorganic compounds. In addition, glass, structural ceramics, tribological ceramics, and electrical ceramics are nowadays also included.

The production of stoneware and building materials dates back to early history and includes today materials such as superconductors, motors, fuel cells and many other high-temperature resistant materials for versatile technical applications.

Thermoanalytical methods have always played an important role in the investigation of raw materials, the optimization of manufacturing processes and the characterization of finished products. The booklet shows the wide range of applications of thermal analysis and the determination of the thermophysical properties of ceramics.



Levitating Superconductor

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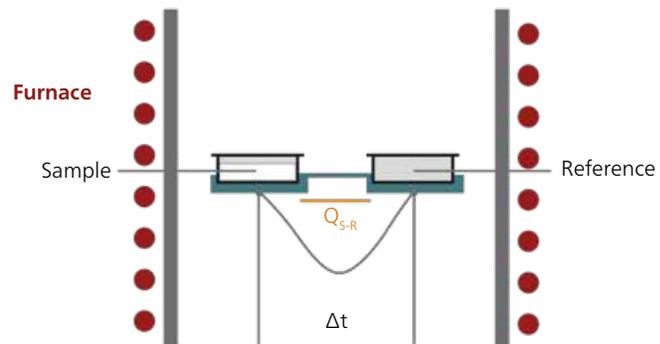
Methods

Methods

Differential Scanning Calorimetry (DSC)

As per ISO 11357-1 with this method, a sample and a reference are subjected to a controlled temperature program (heating, cooling or isothermal). The actual measured properties are the temperature of the sample and the temperature difference between sample and reference. From the raw data signals, the heat flow difference between sample and reference can be determined.

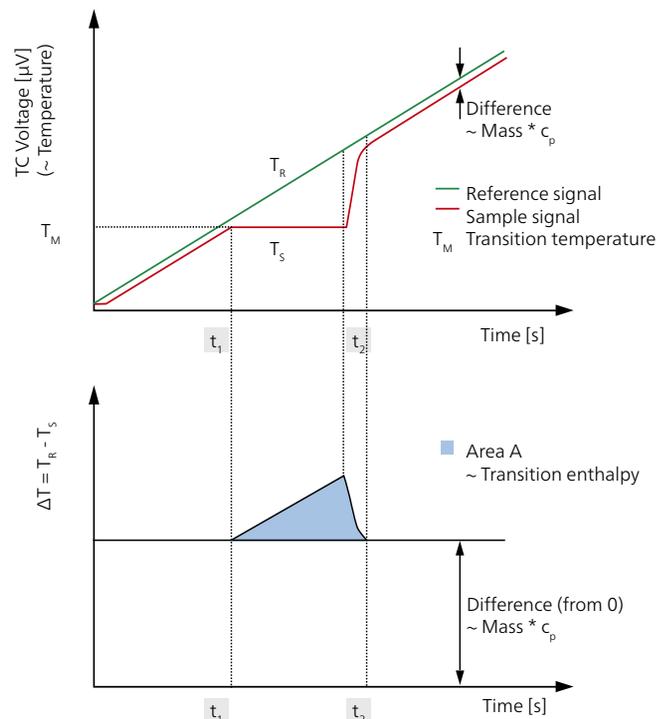
The DSC systems are based on relevant instrument and application standards, e.g., ISO 11357, ASTM E793, ASTM D3895, ASTM D3417, ASTM D3418, DIN 51004, DIN 51007.



Schematic of a heat-flux DSC cell

Measurement Results by DSC:

- Melting temperatures and enthalpies (heats of fusion)
- Crystallization temperatures and enthalpies
- Post-crystallization
- Glass transition temperatures
- Oxidative-induction time (OIT) and oxidative-onset temperature (OOT)
- Degree of crystallinity
- Solid-solid transitions
- Decomposition onset
- Polymorphism
- Phase transitions
- Liquid crystal transitions
- Eutectic purity
- Purity Determination
- Reaction temperatures and enthalpies
- Cross-linking reactions (curing)
- Degree of curing
- Specific heat capacity c_p
- Molecular weight distribution (via melting peak shape, qualitative)
- Compatibility
- Kinetic studies



Signal generation in a heat-flux DSC

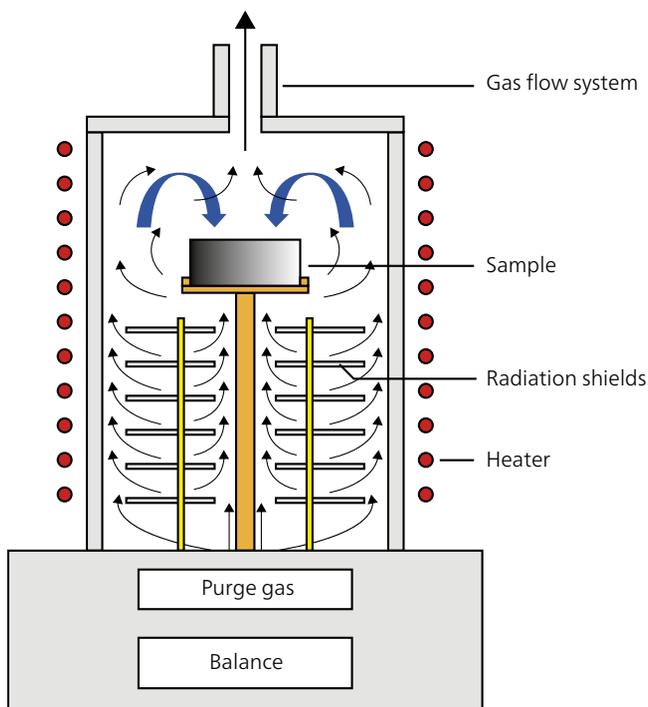
Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a method of thermal analysis in which the mass of a sample is measured versus time and/or temperature. This measurement provides information about physical phenomena, such as phase transitions, absorption and desorption; as well as chemical phenomena including thermal decomposition, and solid-gas reactions (e.g., oxidation or reduction).

NETZSCH thermobalances meet respective instrument and application standards including ISO 11358, ISO/DIS 9924, ASTM E1331, ASTM D3850 and DIN 51006.

Measurement Results by TGA:

- Mass changes
- Decomposition
- Reduction behavior
- Influence of aging
- Determination of ash content
- Reaction kinetics
- Identification
- Oxidation
- Corrosion studies
- Determination of plasticizer content and other additives
- Determination of added carbon black
- Purity Determination
- Compositional analysis
- Thermal stability
- Determination of filler content
- Determination of moisture content
- Curie temperatures



Measuring principle of the TG 209 **F1** Libra

Methods

Simultaneous Thermal Analysis (STA)

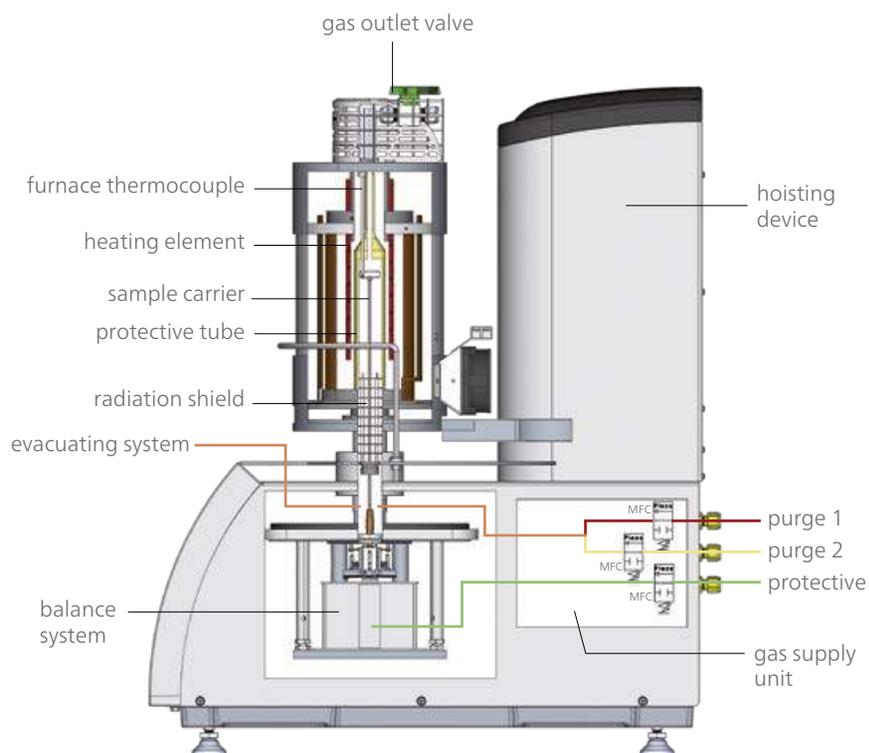
Simultaneous Thermal Analysis (STA) generally refers to the simultaneous application of Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC) to one and the same sample in a single instrument. The advantages are obvious: The test conditions are perfectly identical for the TGA and DSC signals (same atmosphere, gas flow rate, water vapor pressure on the sample, heating rate, thermal contact to the sample crucible and sensor, radiation effect, etc.). Furthermore, sample throughput is improved as more information is gathered from each test run.

Measurement Results by DSC:

- Melting behavior
- Crystallization behavior
- Melting and crystallization enthalpy
- Solid-solid transitions
- Polymorphism
- Degree of crystallinity
- Glass transitions
- Cross-linking reactions
- Oxidative stability
- Purity Determination
- Specific heat capacity
- Thermokinetics

Measurement Results by TGA:

- Mass changes
- Temperature stability
- Oxidation/reduction behavior
- Decomposition
- Corrosion studies
- Compositional analysis
- Thermokinetics



Schematic of the STA 449 **F1** Jupiter®

Hyphenated Techniques (Evolved Gas Analysis – EGA)

By coupling a Thermobalance (TG, TGA), Simultaneous Thermal Analyzer (STA, TGA-DSC) or Dilatometer (DIL) with a Quadrupole Mass Spectrometer (QMS), it is possible to detect and identify evolved gases in exact time correlation with TGA or STA signals.

The combination with an FT-IR (Fourier Transform Infrared Spectrometer) has become a must, especially in the polymer-producing, chemical and pharmaceutical industries.

The GC (gas chromatograph) separates gas mixtures based on the differences in component distribution between a stationary phase (e.g., inner coating of a capillary) and a mobile phase (e.g., He). The purge gas rapidly carries away gas components with a low affinity for the stationary phase. Gases with a high affinity for the stationary phase will follow with a significant time delay (“retention time”).

Measurement Results by Coupling:

Decomposition

- Dehydration
- Stability
- Residual solvent
- Pyrolysis

Solid-Gas Reactions

- Combustion
- Oxidation
- Adsorption
- Desorption
- Catalysis
- Corrosion

Compositional Analysis

- Polymer content
- Proximate analysis
- Binder burnout
- Dewaxing
- Ash content
- Coal analysis

Identification

- Gas composition
- Fingerprint
- Partial pressure
- Fragmentation
- Solid-gas interactions

Evaporation

- Vapor pressure
- Sublimation



STA 449 **F1** Jupiter®, coupled to an FT-IR (left, BRUKER OPTICS) with external gas cell and QMS Aeolos® (right)

Methods

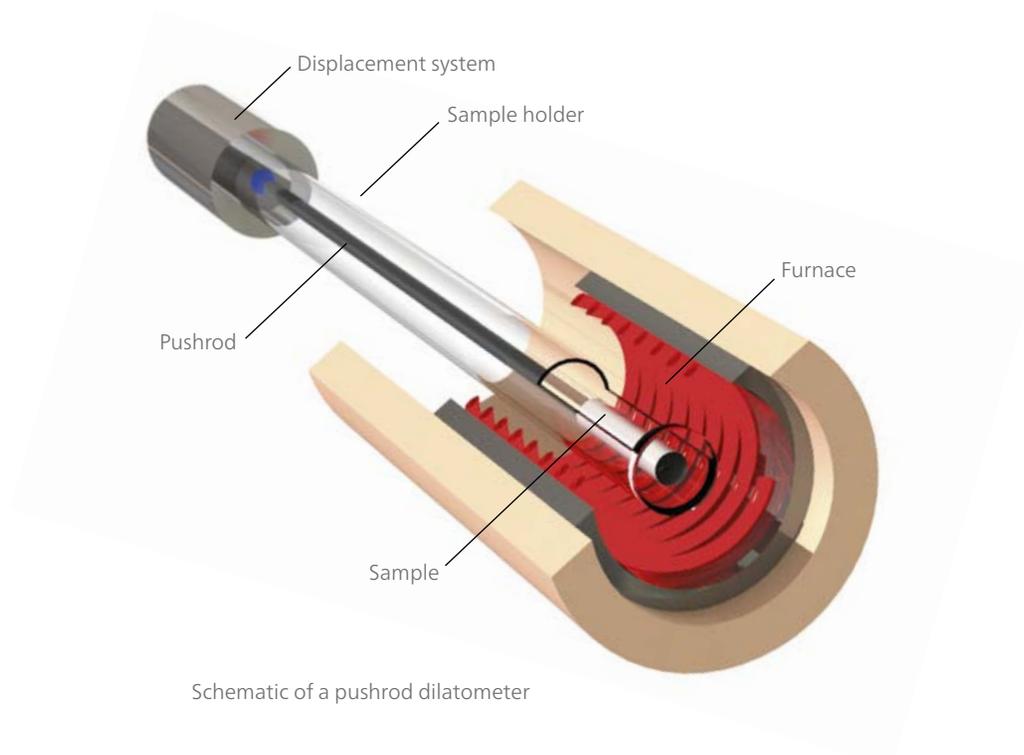
Dilatometry

Dilatometry (DIL) is the method of choice to study length change phenomena of ceramics, glasses, metals, composites, and polymers as well as other construction materials, thus revealing information regarding their thermal behavior and about process parameters or sintering (and curing) kinetics.

All NETZSCH dilatometers are based on, e.g., DIN EN 821, DIN 51045, ASTM E831, ASTM E228.

Measurement Results by DIL:

- Linear thermal expansion
- Coefficient of thermal expansion (CTE)
- Volumetric expansion
- Shrinkage steps
- Softening point
- Glass transition temperature
- Phase transitions
- Sintering temperatures and steps
- Density change
- Influence of additives and raw materials
- Decomposition temperature of, e.g., organic binders
- Anisotropic behavior
- Optimizing of firing process
- Caloric effects by using c-DTA®
- Rate-Controlled Sintering (RCS)
- Thermokinetics
- Debinding



Laser Flash Analysis (LFA)

The laser or light flash (LFA) method dates back to studies by Parker* et al. in 1961.

In carrying out a measurement, the lower surface of a plane-parallel sample (see scheme of flash technique) is first heated by a short energy pulse. The resulting temperature change on the upper surface of the sample is then measured with an infrared detector. The typical course of the signals is presented in the bottom picture (red curve). The higher the sample's thermal diffusivity, the steeper the signal increase.

Using the half time ($t_{1/2}$, time value at half signal height) and sample thickness (d), the thermal diffusivity (a) and finally the thermal conductivity (λ) can be calculated by means of the formula below. Furthermore, the specific heat capacity (c_p) of solids can be determined using the signal height (ΔT_{\max}) compared to the signal height of a reference material.

$$\lambda(T) = a(T) \cdot c_p(T) \cdot \rho(T)$$

where

λ = thermal conductivity [W/(m·K)]

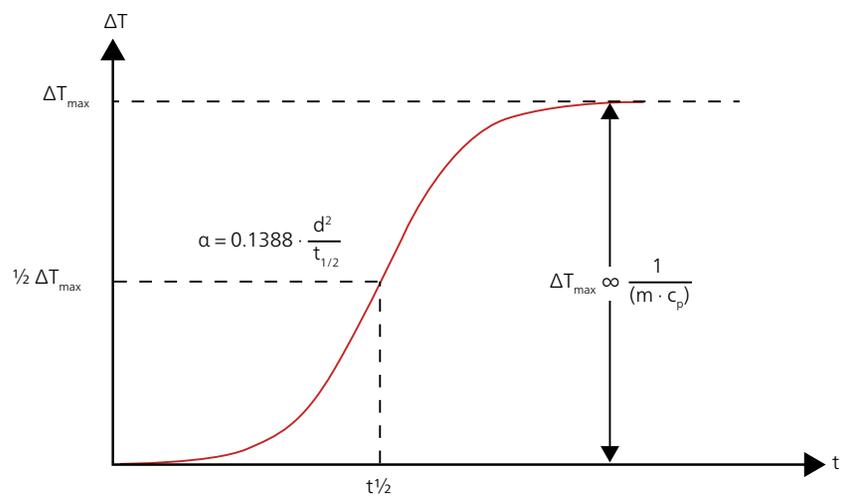
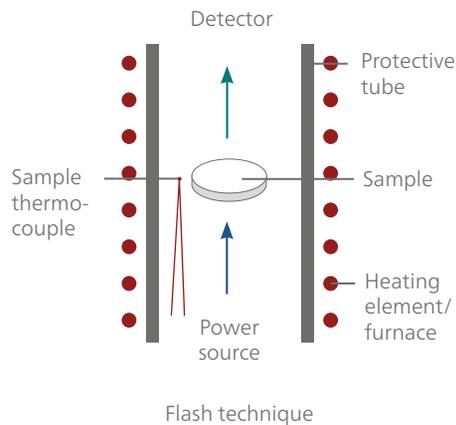
a = thermal diffusivity [mm²/s]

c_p = specific heat capacity [J/(g·K)]

ρ = bulk density [g/cm³].

LFA investigations generally take much less time than thermal conductivity measurements by means of GHP (Guarded Hot Plate) or HFM (Heat Flow Meter).

NETZSCH LFA instruments are based on the respective instrument and application standards for LFA, e.g., ASTM E1461, DIN EN 821, BS EN 1159-2, ASTM C714, etc.



$$\lambda(T) = a(T) \cdot c_p(T) \cdot \rho(T)$$

Typical course of the signals of an LFA

*W.J. Parker; R.J. Jenkins; C.P. Butler; G.L. Abbott (1961). "Method of Determining Thermal Diffusivity, Heat Capacity and Thermal Conductivity". Journal of Applied Physics. **32**

TRADITIONAL CERAMICS



Building Materials

Gypsum (Calcium Sulfate Dihydrate)

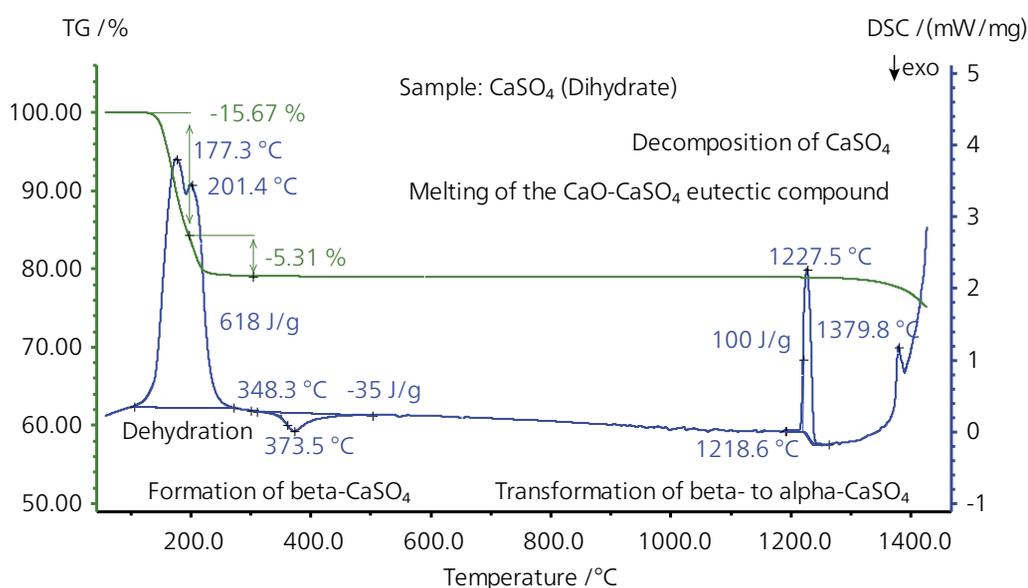
Calcium sulfate materials (gypsum, plaster) are popular materials used in several building applications. When calcium sulfate halfhydrate is mixed with water, it reforms into gypsum (dihydrate), initially as a paste but eventually hardening into a solid. The structure consists of sheets of Ca^{2+} and SO_4^{2-} ions held together by hydrogen bonds of the water molecules. The grip between these sheets can easily be broken, so gypsum is fairly soft. Gypsum is used as a building material similar to mortar or cement.

Like those materials plaster starts as a dry powder that is mixed with water to form a paste which then hardens. Unlike those materials, plaster remains quite soft after drying, and can easily be manipulated with metal tools or even sandpaper. These characteristics make plaster suitable for a finishing rather than a load-bearing material.

Test Results

Between 100 and 300°C, the double-step dehydration of the calcium sulfate-dihydrate occurred. In the first step, 1.5 out of 2 water molecules were released from the system and halfhydrate was formed. In the second step, the half-hydrate dehydrates further on and forms anhydrate. Starting at 348°C, the anhydrate converts to β -calcium sulfate (exothermal effect). At 1219°C, the β -calcium sulfate converts to α -calcium sulfate, clearly visible as a sharp endothermal effect in the DSC curve. At temperatures above 1250°C, a further mass loss can be seen. This mass loss refers to the sulfate decomposition. Calcium sulfate converts into calcium oxide. The endothermal peak at 1380°C is due to melting of an eutectic mixture of calcium sulfate and calcium oxide.

Test Conditions	
Instrument	STA 409
Temperature range	RT ... 1500°C
Heating/cooling	20 K/min
Atmosphere	Air at 60 ml/min
Sample mass	38.68 mg
Crucible	Pt with lid
Sensor	DSC type S



STA measurement on calcium sulfate dihydrate: dehydration, phase transitions and decomposition

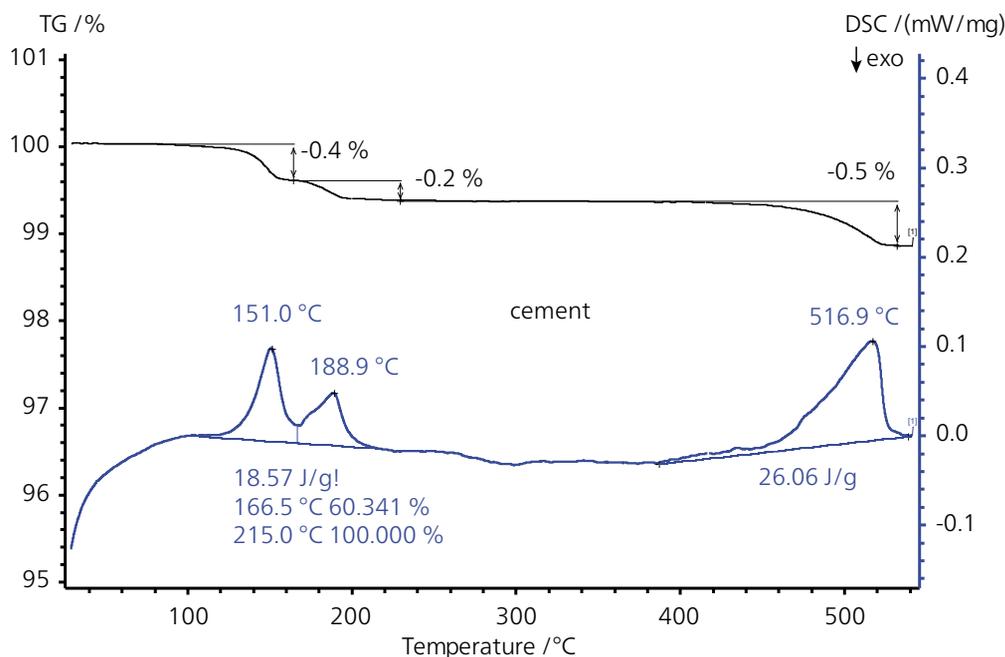
Cement / Gypsum

Portland cement is the most common type of cement. It consists of a mixture of oxides of calcium, silicon and aluminum. The main phases are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and a ferrite phase C_4AF . Portland cement is produced by heating of limestone with clay and/or sand up to about 1480°C. To the resulting clinker, 4-5% gypsum is mixed and then grinded and milled to a fine grain size. The additives gypsum, anhydrite, etc., influence the setting time of the cement.

Test Results

Separation and quantification of calcium sulfate dihydrate (DH) and hemihydrate (HH) in cement samples is only possible when a certain water vapor pressure over the sample can be created. A possibility is to use closed aluminum crucibles with a small pinhole of about 40 to 50 μm . From the TG curve, the DH amount can be calculated to 2.5% and the HH amount to 1.8%. The TG step (0.5%) starting at about 420°C is due to the decomposition of $\text{Ca}(\text{OH})_2$ (content approx. 2.2%).

Test Conditions	
Instrument	STA 449
Temperature range	RT ... 550°C
Heating/cooling	10 K/min
Atmosphere	Air at 50 ml/min
Sample mass	39.5 mg
Crucible	Al with 50 μm hole
Sensor	TG-DSC type S



STA measurement on calcium sulfate dihydrate shows the separation of the dihydrate and hemihydrate between 100°C and 220°C

Building Materials

Cement Raw Material

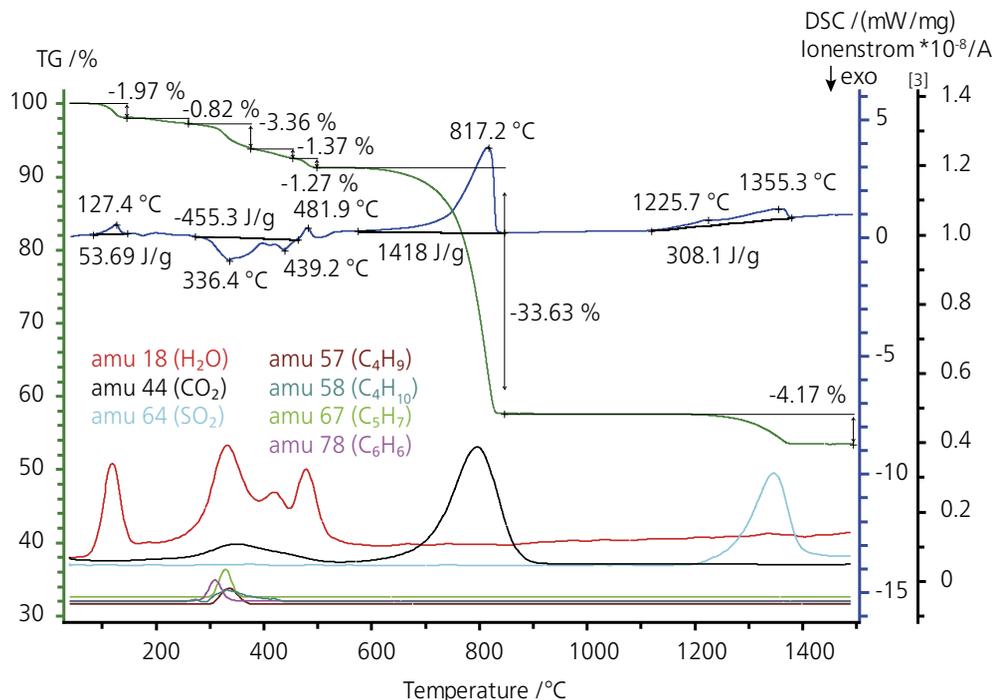
Building materials such as bricks or cement are classical application fields for thermal analysis coupled to mass spectroscopy. Cement raw materials are mostly complex mixtures of ceramic components like gypsum and calcium carbonate. Organic components and clay, however, can also be present. On the one hand, thermal analysis along with mass spectroscopy enables investigation and quantification of the different components of the raw material. It also features a tool for the simulation of the manufacturing process of the later building material on the other.

Test Results

Using simultaneous thermogravimetry (TG), differential scanning calorimetry (DSC) and mass spectroscopy (MS), a

cement raw material was studied. Upon heating to 1500°C, several mass-loss steps as well as endothermic and exothermic effects were observed. The mass spectrometer signals allow for identification of the evolved gases and thus of the components of the cement raw material. H₂O was released most probably from gypsum at low temperatures and from Ca(OH)₂ at ~480°C. In the temperature range between ~300°C - 400°C, organic components were partially decomposed and burned which can be concluded from the mass spectrometer signals as well as from the exothermic DSC peaks. At ~800°C, the evolution of CO₂ indicates the decomposition of CaCO₃ while SO₂ indicates the decomposition of CaSO₄ at highest measuring temperatures.

Test Conditions	
Instrument	STA 449 Jupiter® - QMS 403 Aëolos®
Temperature range	RT ... 1500°C
Heating/cooling	10 K/min
Atmosphere	Synth. air at 70 ml/min
Sample mass	16.06 mg
Crucible	Pt with pierced lid
Sensor	TG-DSC type S



Measurement on a cement raw material using simultaneous TGA-DSC (STA) and mass spectroscopy (MS). The monitored MS data correlate well with the mass loss behavior.

Cement

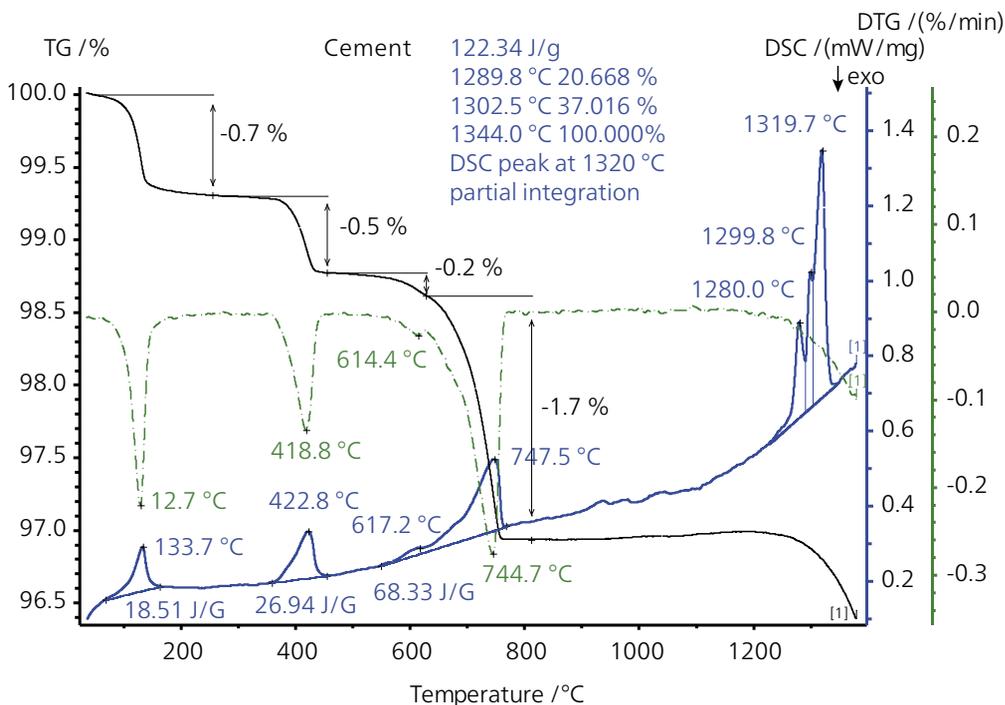
The cement world production in 2018 was estimated to be 4.1 billion tons*. The top three producers were China with 2370, India with 290, and the United States with 88.5 billion tons. Portland cement is the most common type of cement and widely used for the construction of buildings, bridges, etc. Cement is also one of the main components of concrete, which is a mixture of sand, stones and cement as binder.

Test Results

With the STA, the components (additives) of cement can be identified and quantified. The 1st TG step is due to the water loss of CaSO₄ dihydrate and hemihydrate. At about 419°C (DTG peak), the water loss of Ca(OH)₂ shows its maximum. The decomposition of carbonates (calcite, dolomite) was found in the temperature range between 600°C and 750°C. The MgCO₃ amount of dolomite decomposes prior to CaCO₃. At about 1200°C, CaSO₄ starts melting and decomposing.

Test Conditions	
Instrument	STA 449 Jupiter®
Temperature range	RT ... 1350°C
Heating/cooling	10 K/min
Atmosphere	Argon at 50 ml/min
Sample mass	39.5 mg
Crucible	Pt/Rh with lid
Sensor	TG-DSC type S

*<https://de.statista.com/statistik/daten/studie/153695/umfrage/produktion-von-zement-nach-laendern/>



Quantification of cement additives using STA

Building Materials

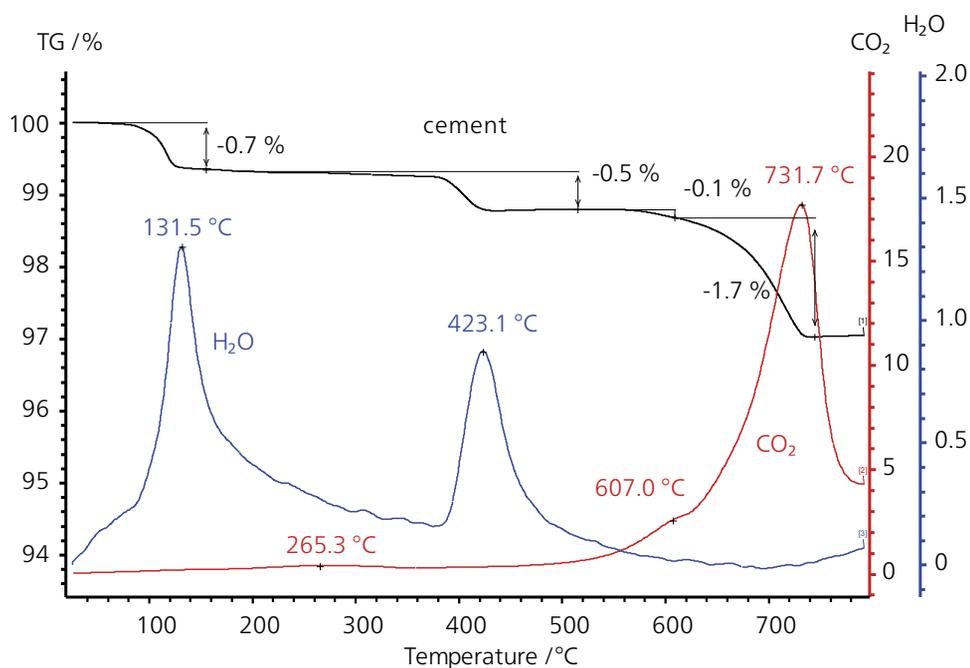
Portland Cement

Portland cement is produced by heating of limestone with clay and/or sand up to about 1480°C. To the resulting clinker, 4-5% gypsum is mixed and then grinded and milled to a fine grain size of approx 10 µm. The additives gypsum, anhydrite, etc., influence the setting time of the cement. Impurities in the raw material can have a negative influence on the quality of the cement. Magnesia, e.g., causes expansion and deterioration of cements on long exposure, and its presence of more than 5% is not desirable.

Test Results

With thermoanalytical methods, the components (additives) of cement can be identified and quantified. The combination of thermogravimetry with an evolved gas analysis method (i.e., mass spectrometry or Fourier transform infrared spectroscopy) is a very powerful method since the evolved gases can be identified. The water evolved from the CaSO_4 dihydrate and hemihydrate (1st TG step) and $\text{Ca}(\text{OH})_2$ (2nd TG step) can be verified by FT-IR analysis. The decomposition of carbonates (calcite, dolomite) is found in the temperature range between 600°C and 750°C. The MgCO_3 amount of the dolomite decomposes before CaCO_3 and is also seen as a shoulder in the CO_2 trace of the FT-IR signal.

Test Conditions	
Instrument	TG 209 F1 Iris®- FT-IR
Temperature range	RT ... 800°C
Heating/cooling	10 K/min
Atmosphere	Air at 40 ml/min
Sample mass	43.6 mg
Crucible	Pt/Rh with pierced lid
Sensor	TG-DSC type S



TGA-FT-IR measurement on Portland cement; the FT-IR traces for water (blue) and CO_2 (red) correspond very well to the single mass-loss steps

Floor Tiles

Tiles are often used to form wall and floor coverings, and can range from simple square tiles to complex mosaics. Tiles are most often made of ceramic. The raw material is mainly based on mixtures of clay minerals, quartz, calcite and feldspar.

For cost efficiency, mainly local mineral deposits were used to reduce transportation costs. Therefore, the mineral content could be very different. After the forming process, the tile raw material has to be fired to approx. 1000°C to produce the final product. The firing temperature influences also the porosity of the tile.

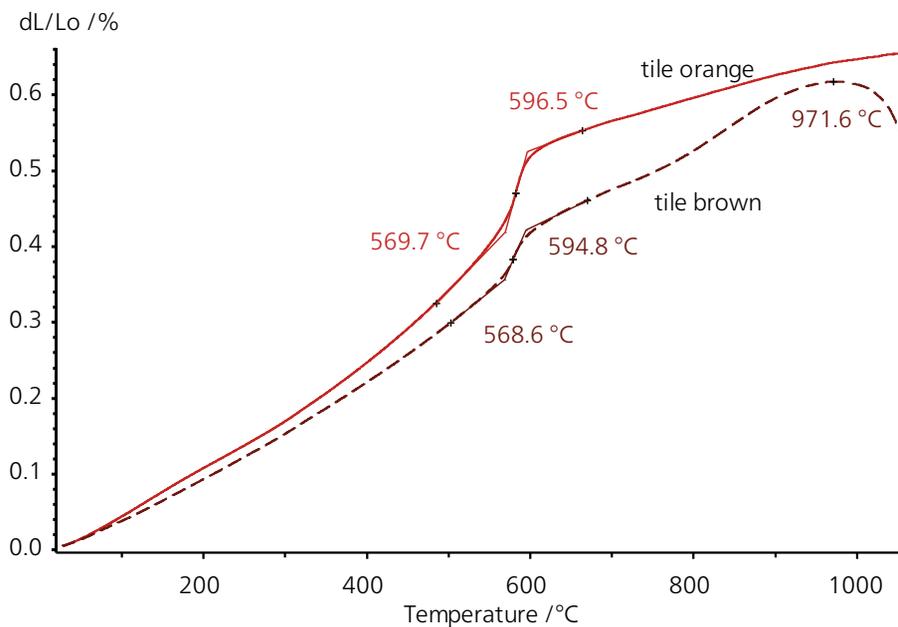
Test Results

Two different tiles were simultaneously measured with the Double Dilatometer DIL 402 CD. Both tiles show the phase transition of the quartz amounts indicated by the expansion increase starting at approx. 570°C. The "orange" tile seems to have a higher quartz amount since the step is more distinctive. The "brown" tile shows a shrinkage starting at approx. 972°C most probably due to a high amorphous amount in the material.

The DIL 402 allows very fast and precise characterization of ceramic products because of the high resolution and the possibility to measure two samples simultaneously.

Test Conditions

Instrument	DIL 402
Temperature range	RT ... 1050°C
Heating/cooling	5 K/min
Atmosphere	Air, static
Sample mass	25 mg
Sensor	Alumina



Dilatometer measurement on two different floor tiles

Building Materials

Mineral Wool

Mineral wool consists of fibers made from minerals or metal oxides. This includes fiberglass, ceramic fibers and rock wool also known as stone wool. Mineral wool is mainly used for filtering and insulation since batts, sheets and roll made of mineral wool are poor conductors of heat and also of sound. Mineral wool can generally contain a binder and oil to reduce dusting.

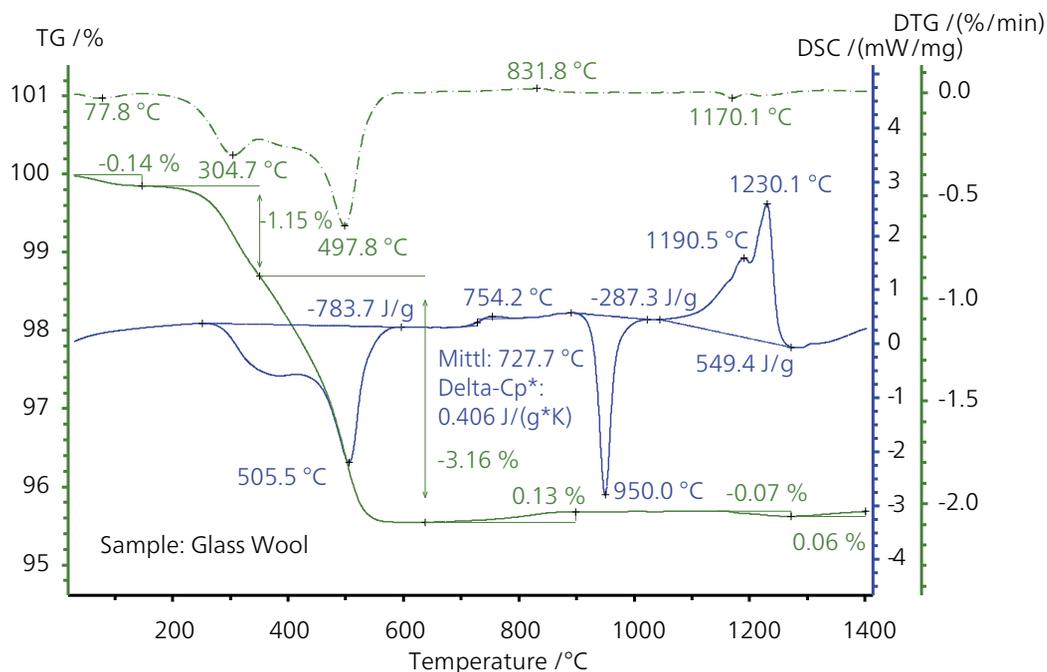
Test Results

The STA measurement shows three mass-loss steps below approx. 600°C which are due to the evaporation of

humidity and the burn-up of organic binder. The latter can be seen from the strongly exothermic DSC signal in this temperature range. The step in the DSC signal at 728°C with an increase in specific heat capacity of 0.41 J/(g·K) is due to the glass transition. The exothermic DSC peak at 950°C with an enthalpy of -287 J/g is due to crystallization; the endothermic effects between approx.

1050°C and 1250°C with an entire enthalpy of 549 J/g are due to melting. The slight mass changes above 700°C are most probably due to oxidation and evaporation of impurities.

Test Conditions	
Instrument	STA 449 F3 Jupiter®
Temperature range	RT ... 1400°C
Heating/cooling	20 K/min
Atmosphere	Synth. air at 70 ml/min
Sample mass	49.71 mg
Crucible	Pt
Sensor	TG-DSC type S



STA measurement on mineral wool delivers an overview of the thermal behavior. Binder burnout, glass transition, crystallization and melting can be observed.

Clay Brick

Clay bricks are mass-produced articles where the costs had to be kept low. Therefore, only locally available clays are employed. The mineral content of the raw materials can be mixtures of fireclays, illites, montmorillonite, chlorite, quartz, etc. After forming and drying, the raw brick is fired in kilns up to 1000°C to its final consistency. Often additives are also included like sawdust or polystyrene to increase the porosity of clay bricks. The pollution of brick production can be very high dependent on the raw material used. Not only the emission of CO₂, CO, NO_x, but also the emission of HF and SO₂ has to be considered and limited by primary solutions (optimization of the firing process, additives etc.) or secondary procedures (dust filter, fluorine filter etc.).

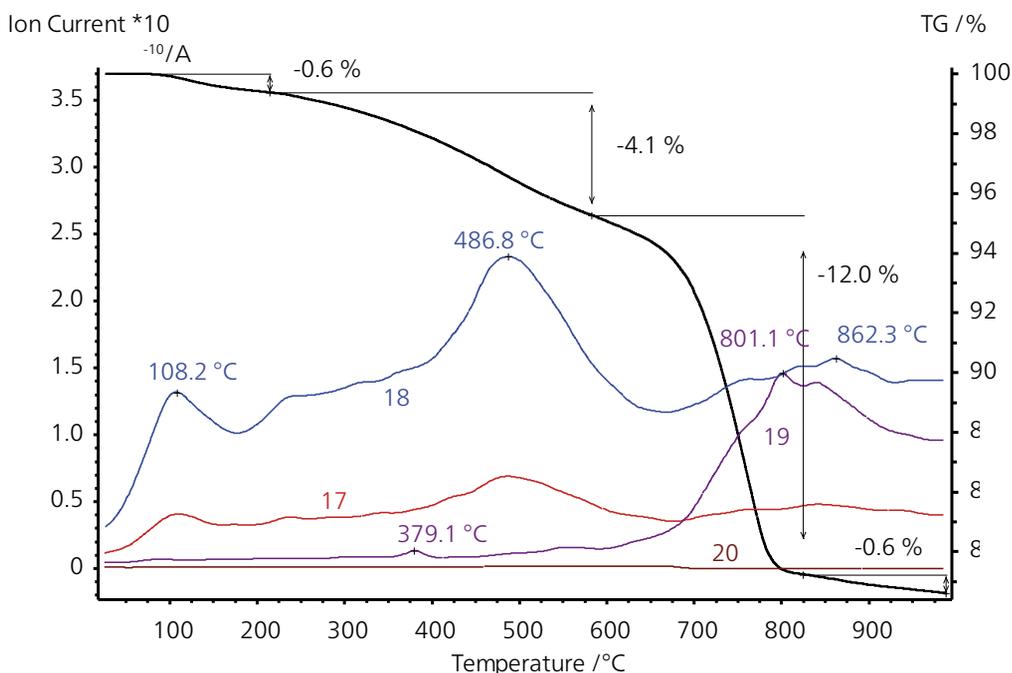
Test Results

Clay materials used for the brick production often contain fluorine in small amounts. The detection of fluorine or HF with MS or FT-IR is often problematic because of the small amounts evolved. Fluorine has mass number 19 and HF mass number 20.

These mass numbers also occur when higher amounts of water are evolved because of the generation of H₃O⁺ (19 amu) and the oxygen isotope 18, this means H₂¹⁸O⁺ (20 amu). The measured brick clay shows the evolution of fluorine at about 380°C and 800°C (peak temperatures) indicated by mass number 19 and no corresponded high intensity of mass number 18 representing water.

Test Conditions

Instrument	TG 209 F1 - QMS 403 Aëolos®
Temperature range	RT ... 1000°C
Heating/cooling	10 K/min
Atmosphere	Air at 40 ml/min
Sample mass	21.7 mg
Crucible	Alumina
Sensor	TG type Platinel



TGA-MS measurement on a clay brick allows for the detection of fluorine (mass number 19) and HF (mass number 20)



Building Materials

Clay

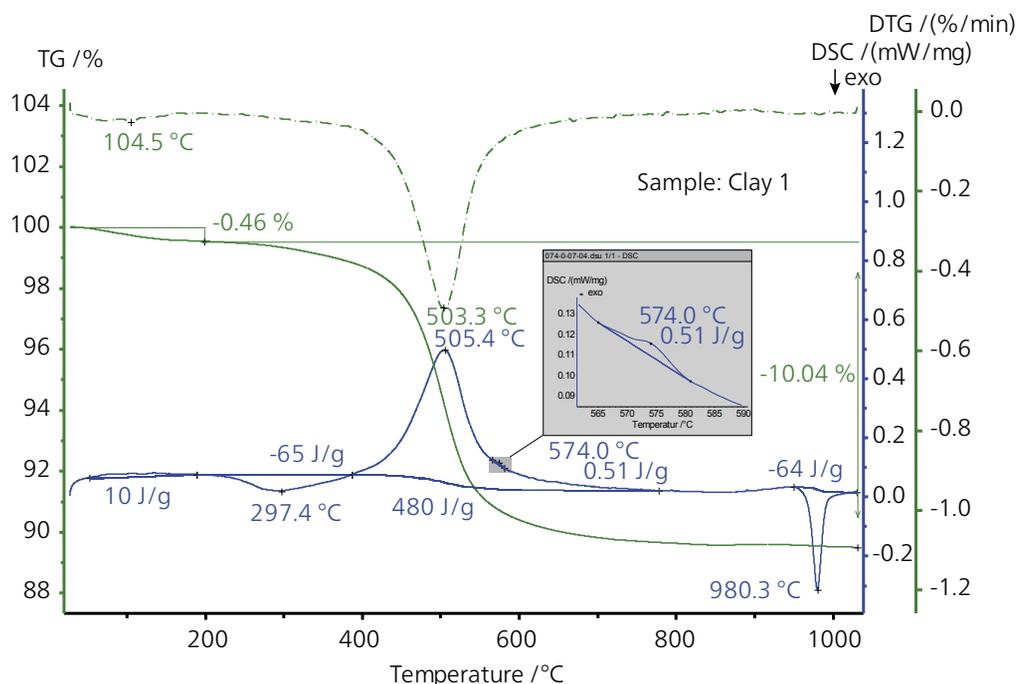
Clays are water-containing aluminosilicates with small contents of Mg, Fe, Na, K and Ca. The most familiar clays are illite, montmorillonite and kaolinite. Clay is one of the most important raw materials for the ceramic and cement industries. Flagon, bowls, cups, (roof) tiles as well as bricks can furthermore be made directly out of clay. Such bricks are nowadays produced highly porous in order to obtain good insulation properties which make them ideal for building applications. By means of STA (simultaneous TGA-DSC) and dilatometry (DIL), the composition and expansion

properties of clay can be investigated.

Test Results

The first figure depicts the temperature-dependent mass change (TG), rate of mass change (DTG) and calorific effects (DSC) of a clay sample. Two mass-loss steps of 0.5% and 10.0% were observed which are most probably due to the evaporation of humidity at low temperatures, the burnout of organics between 200°C and 400°C and dehydration of the clay above ~400°C.

Test Conditions STA	
Instrument	STA 409
Temperature range	RT ... 1000°C
Heating/cooling	5 K/min
Atmosphere	Synth. air at 70 ml/min
Sample mass	38.91 mg
Crucible	Pt
Sensor	TG-DSC type S



Comparison of the different thermoanalytical results for a deeper insight into the behavior of sample clay 1

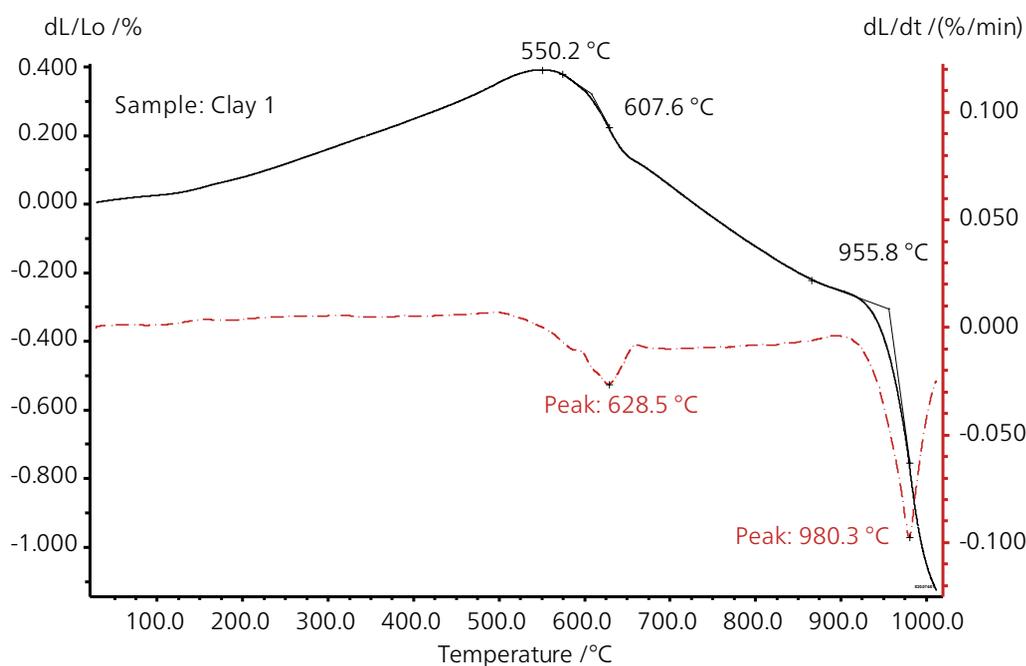
Clay... continued

These mass-loss steps are accompanied by endothermic effects with enthalpies of 10 J/g and 480 J/g. The DSC signal exhibited furthermore an exothermic peak at 297°C which is most probably due to the burn-up of organics in the range between ~200°C and ~400°C. At

574°C, an endothermic DSC peak with an enthalpy of 0.5 J/g indicates the structural $\alpha \rightarrow \beta$ transition of the quartz content. The exothermic DSC peak at 980°C is due to a structural solid-solid transformation of kaolin.

Test Conditions DIL

Instrument	DIL 402
Temperature range	30 ... 1000°C
Heating/cooling	5 K/min
Atmosphere	Static air
Sample mass	18 mm
Calibration length	with Al ₂ O ₃



Dilatometer measurement for detection of the expansion and shrinkage behavior of brick clay 1

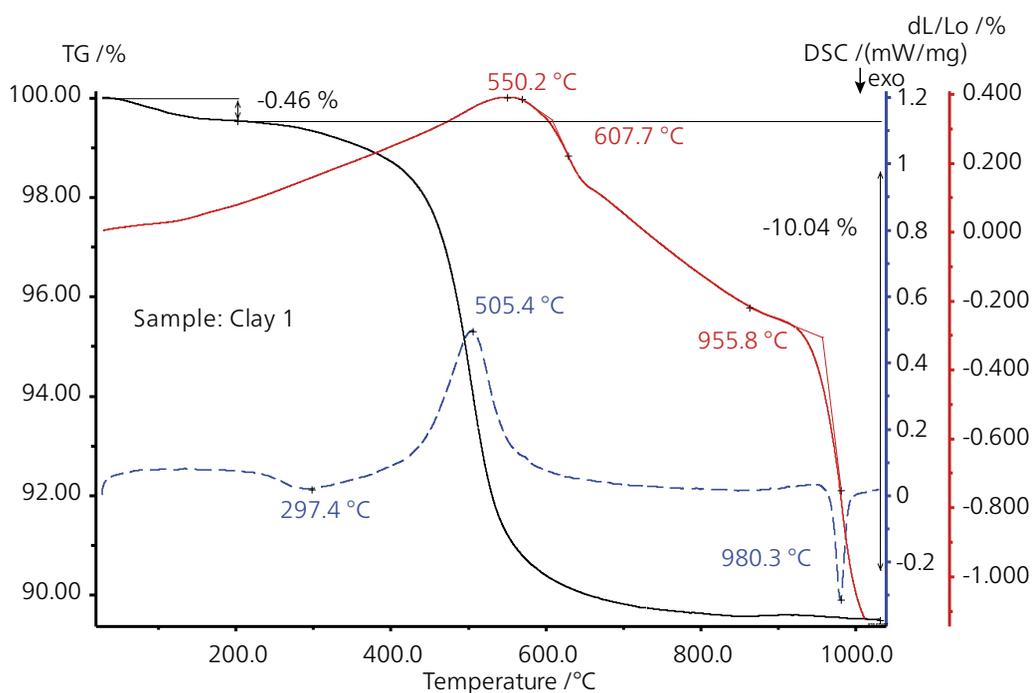
Building Materials

Clay ... continued

The next figure shows the linear thermal expansion and the rate of expansion of the same clay sample. At the beginning, the material expanded with an almost constant rate of expansion (red curve) and reached a maximum length at 550°C. Subsequently, two steps were detected during shrinkage. The first step was at 608°C (extrapolated onset), the second

one at 956°C (extrapolated onset). The corresponding minima in the rate of expansion were observed at 629°C and 980°C.

A comparison of the STA and DIL results is shown in figure 3.



Comparison of the DIL and STA measurements on sample clay 1



Whiteware

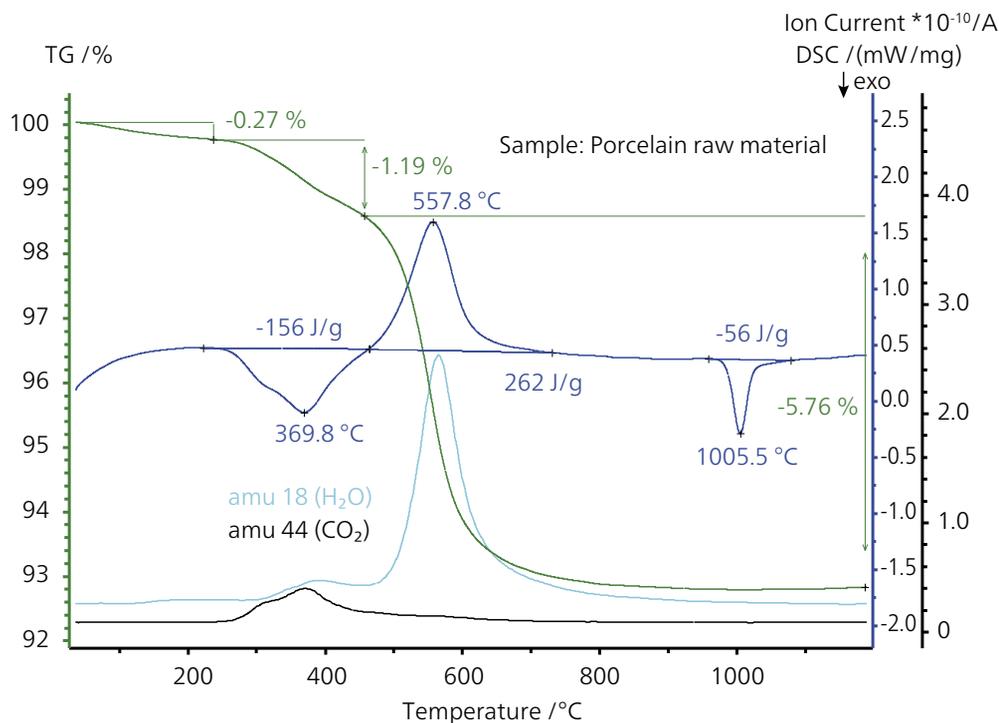
Porcelain Raw Material

Porcelain, which is often called the white gold, consists basically of kaolin, feldspar and quartz in well defined ratios. Tableware, glazed tiles and electrical isolators are the most popular forms of appearance of porcelain. It can also be used as a high-tech coating of, e.g., engine cylinders. Porcelain was invented already in the year 620 in China and was brought to Europe around 1300 by Marco Polo. It took until 1708 before the first porcelain could be produced in Europe, too. Porcelain is a classical application field of thermal analysis since the raw materials can be characterized and the burning process of the porcelain can be simulated.

Test Results

The STA measurement on porcelain raw material shows three mass-loss steps: below approx. 250°C, the evaporation of humidity occurred and at temperatures between 250°C and 450°C, the burn-up of organic binder was observed which released an energy of 156 J/g. The dehydration of kaolin occurred above 450°C which required 262 J/g. The mass spectrometer signals for mass numbers 18 and 44 reflect the corresponding evolution of H₂O and CO₂. The exothermic effect detected at 1006°C with an enthalpy of -56 J/g is due to a solid-solid reaction in the kaolin content in the porcelain raw mixture.

Test Conditions	
Instruments	STA 449 F3 Jupiter® - QMS 403 Aeolos®
Temperature range	RT ... 1200°C
Heating/cooling	20 K/min
Atmosphere	Synth. air at 70 ml/min
Sample mass	37.14 mg
Crucible	Pt
Sensor	TG-DSC type S



The main mass-loss step in the STA-MS measurement is due to the dehydration of kaolin above 450°C.

Bone China

Bone china for very special and expensive tableware has an outstanding translucency and is totally dense after firing. Isostatic dry pressing and fast firing require exact knowledge of its thermal behavior.

The spray-dried bone china with a mixture of organic additives for dry pressing shows characteristic thermal effects in the TGA and DTA curves as compared to a porcelain body.

Endothermal DTA signals are again due to water release (81.3°C) and dehydroxylation of the clay content (522.0°C). The organic additives are burnt out at 302.5°C (exothermal reaction).

Some carbonate content decomposes at 780°C in an endothermal reaction.

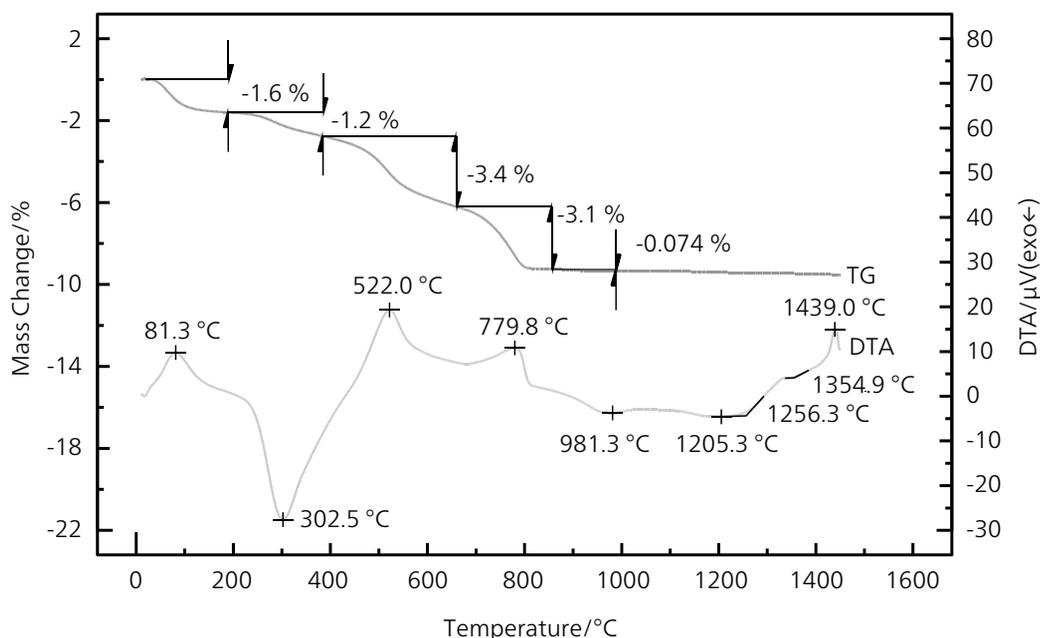
These thermal processes are all related to mass-loss steps.

A bone china body forms a large amount of melting phase starting at 1256°C, appearing as an endothermal signal in the DTA curve within a relatively narrow temperature range.

Therefore, determination and control of the exact firing temperature is extremely important for the production of tableware. If the maximum temperature is too low, the content of the glass phase is not sufficient to obtain translucency. On the other hand, a final temperature that is too high leads to deformation of the product.

Test Conditions

Instrument	STA 409 C
Temperature range	RT ... 1420°C
Heating/cooling	10 K/min
Atmosphere	air (100 ml/min)
Sample holder	TGA-DTA, type S
Crucible	Pt
Sample mass	110 mg
Sample preparation	powder, loosely filled



STA measurement on bone china in the temperature range RT to 1420°C

Whiteware

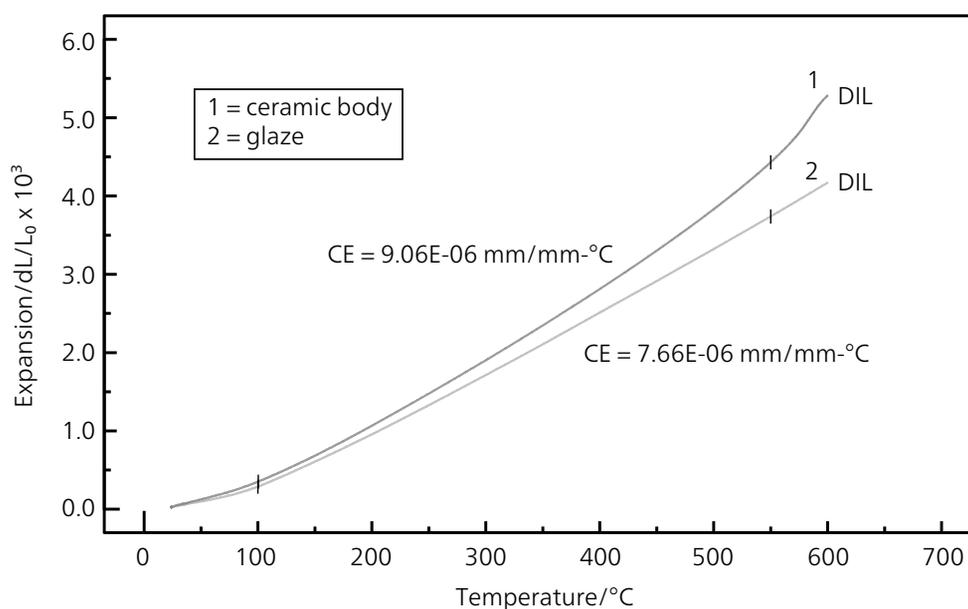
Porcelain with Glaze

When firing a ceramic body (curve 1) together with its glaze (curve 2), e.g., in the production of porcelain for tableware, the coefficients of thermal expansion must be appropriately adjusted.

The thermal expansion of the glaze should be somewhat lower than the expansion of the body. In that way, the glaze is under a slight compressive stress after cooling, thus enhancing the mechanical strength of the product and preventing cracks from appearing in the glaze.

In the expansion curve of the ceramic body (1), the influence of the quartz content is observed above 550°C through the deviation of the curve to higher values.

Test Conditions	
Instrument	DIL 402 ES
Temperature range	RT ... 600°C
Heating/cooling	5 K/min
Atmosphere	air (static)
Sample holder	Al ₂ O ₃
Sample length	44 mm (porcelain)
Sample length	39.5 mm (glaze)
Sample preparation	Green bars, end faces polished parallel



Thermal expansion of a ceramic body and glaze by means of the DIL 402



Refractories

Oxide Refractory

Refractory materials retain their strength at high temperatures. They are used to make crucibles and refractory linings which line furnaces, kilns and incinerators. The oxides of magnesite and dolomite are the most important refractory materials, though fireclay is also widely used. Zircon is used when the material must withstand extremely high temperatures. Silicon carbide is another refractory material. It is very strong at high temperatures, but burns in the presence of oxygen, if the protective silica coating comes off. Refractories must be chosen according to the conditions they will face. For example, carbon cannot be used when it will be in contact with oxygen, as it will burn. Acidic refractories cannot be used in a basic environment and basic refractories cannot be used in an acidic environment because they will be

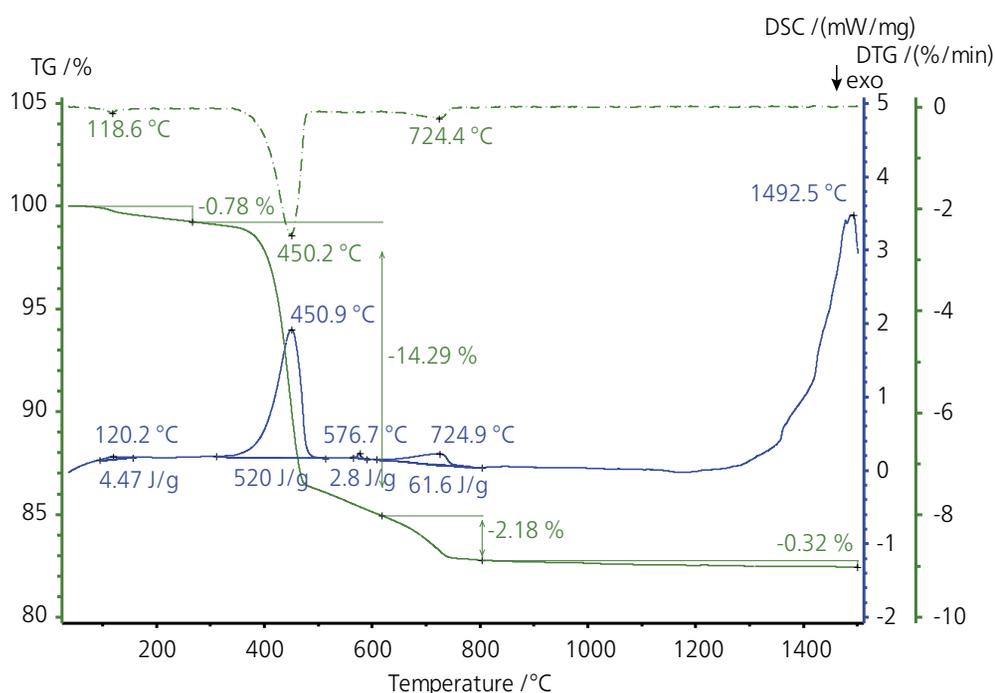
eroded. Zircon, fireclay and silica are acidic, dolomite and magnesite are basic and alumina, chromite, silicon carbide, carbon and mullite are neutral. Nearly all refractory materials must be strong at high temperatures, resistant to thermal shock, chemically inert, and have low thermal conductivities and coefficients of expansion.

Test Results

The temperature-dependent mass change (TG), rate of mass change (DTG) and heat flow rate (DSC) of an oxide refractory were measured. The first mass-loss step is most probably due to the evaporation of humidity while the second and third mass-loss steps are most probably due to the release of bound water and due to the decomposition of carbonate. At highest

temperatures, the sample started evaporating. A melting peak was furthermore detected in the DSC signal at 1493°C. The endothermic DSC peak at 577°C with an enthalpy of 2.8 J/g is due to the structural $\alpha \rightarrow \beta$ phase transformation of a quartz component.

Test Conditions	
Instrument	STA 409
Temperature range	RT ... 1500°C
Heating/cooling	10 K/min
Atmosphere	N ₂ at 70 ml/min
Sample mass	51.53 mg
Crucible	Pt
Sensor	TG-DSC type S



STA measurement on a refractory material with a melting peak above 1490°C

Thermal Conductivity of Inhomogeneous Refractories – LFA Versus TCT

Introduction

Thermophysical properties such as thermal diffusivity, specific heat capacity, and thermal conductivity are crucial parameters for optimizing the production and application of coarse ceramics. For decades, such properties have been determined from stationary methods (e.g., guarded hot plate technique) or standardized transient techniques such as the hot-wire method according to ISO 8894 (see TCT 426 in figure 1). However, these methods are limited to large sample sizes and low thermal conductivities. Moreover, these methods are very time-consuming.

Flash methods are non-contact measurement techniques and can handle high thermal conductivity materials without any difficulties.

Additionally, flash methods are absolute methods for determining thermal diffusivity. Modern instruments (see LFA 427 in figure 2) often also allow the simultaneous measurement of the specific heat capacity of a material so that thermal conductivity can be determined without additional measurements. Since flash methods are limited to homogeneous samples with small dimensions, these methods have not been used for analyzing inhomogeneous coarse ceramics. However, using state-of-the-art highly sensitive systems, testing of larger samples becomes possible now [1]. In addition, the fast testing times of the flash methods allow for measurements of various samples taken from the brick to be tested without further efforts. In the work described herein, the results from laser flash and the hot-wire measurements on a silicon carbide-containing

brick and a magnesia-spinel brick are compared. Measurements were carried out on several small samples of the same material to check the homogeneity of the material and the reproducibility of the methods.

Test Results

Figure 1 depicts the results of thermal conductivity measurements on a magnesia-spinel brick (figure 2) using the LFA 427 and the TCT 426. The dashed line represents the average values (error bar $\pm 10\%$) of combined data from the two different methods. It can clearly be seen that most values of independent LFA and TCT measurements are within the $\pm 10\%$ range from the average. This illustrates the high accuracy of both systems.

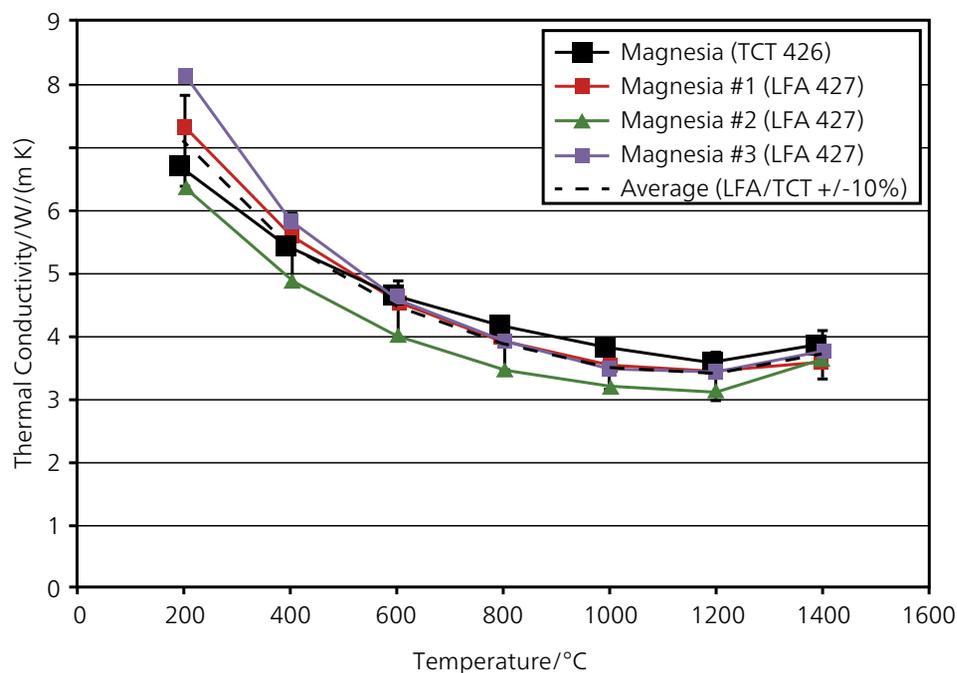


Fig. 1. Thermal conductivity of the magnesia-spinel brick; comparison of LFA and TCT test results; 10% error bar for the average values of all TCT/LFA results.

Refractories

Thermal Conductivity of Inhomogeneous Refractories – LFA Versus TCT ... Continued

Furthermore, the deviation between the different samples shows the possible range of the thermal conductivity due to the inhomogeneity of the

magnesia-spinel brick. A similar comparison of LFA and TCT measurements on silicon carbide-containing brick (figure 4) is shown in figure 3.

Again, the independent measurement values are all within $\pm 10\%$ of the averaged data from the two methods combined.



Fig. 2. Magnesia-spinel brick (85% MgO, and 12% Al₂O₃), measured with the TCT 426 (left) and the LFA 427 (right); the 3 LFA samples were coated with graphite.

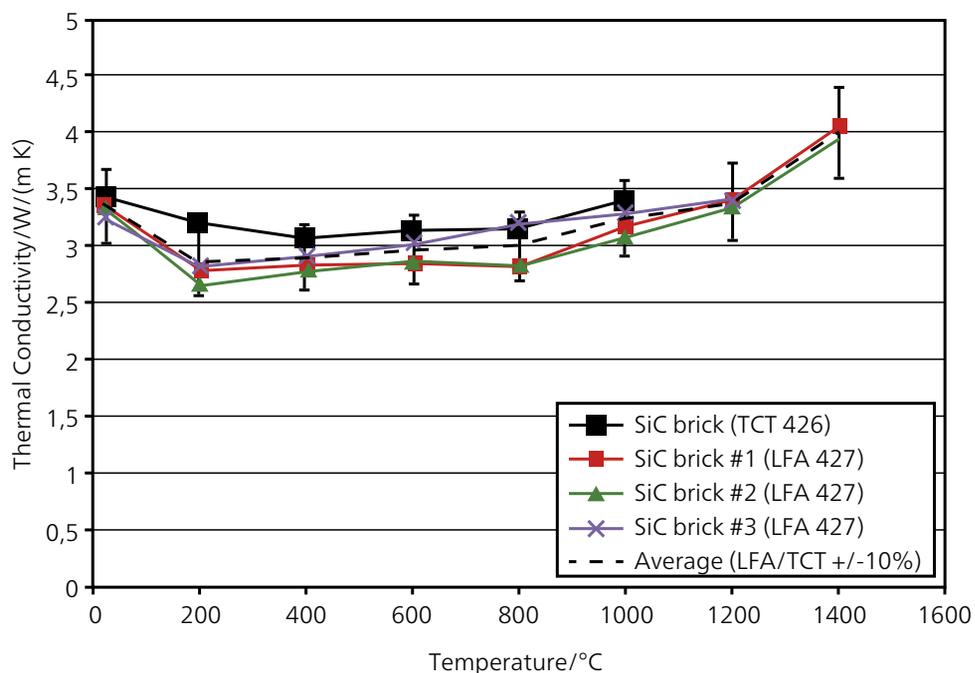


Fig. 3. Thermal conductivity of silicon carbide containing brick; comparison of LFA and TCT results; 10% error bar for the average of all TCT/LFA results

Thermal Conductivity of Inhomogeneous Refractories – LFA Versus TCT ... Continued

Conclusion

The good agreement between the results obtained by the two different methods laser flash and hot wire clearly show that both methods are very suitable for analyzing refractories with a high accuracy. The NETZSCH model LFA 427, however, offers several advantages. Test results can be achieved quickly and with a high

accuracy. The speed of measurement compensates for the small sample dimensions as more samples can be tested with a higher sample throughput. TCT measurements are much more time-consuming due to the huge sample dimension and the long stabilization time. However, the hot-wire method according to ISO 8894 is highly demanded for refractory materials.

Literature

1] J. Blumm, A. Lindemann: Thermo-physical Properties Characterization of Coarse Ceramics Using the Transient Laser Flash Technique. J.G. Heinrich and Aneziris, Proc 10th ECerS Conf., Göller Verlag, Baden-Baden, 2007, 205-211, ISBN: 3-87264-022.4



Fig. 4. Silicon carbide-containing brick (45% Al_2O_3 , 29% SiO_2 and 25% SiC), measured with the TCT 426 (left) and LFA 427 (right); the 3 LFA samples were coated with graphite

Glass

Soda-Lime Glass

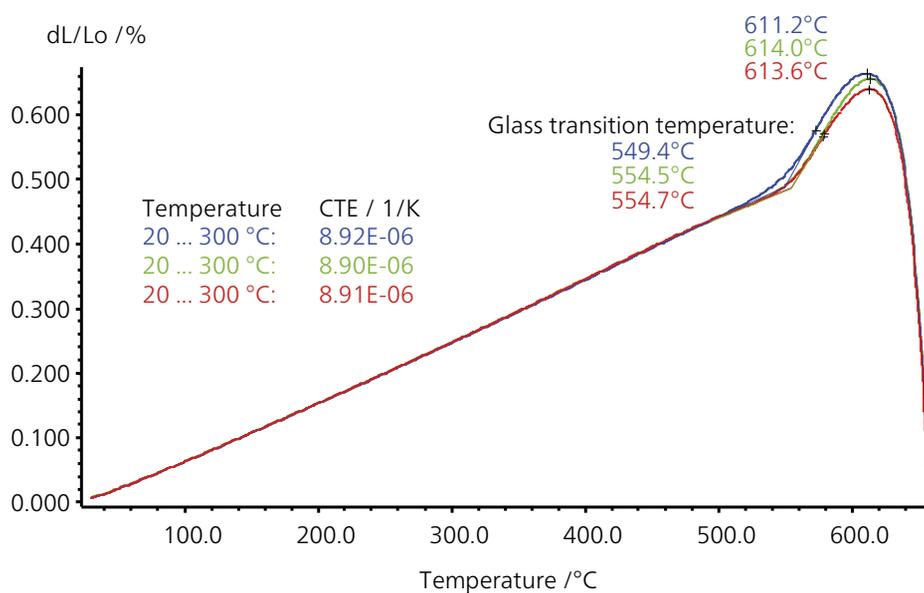
Glass is a uniform amorphous solid material, usually produced when the viscous molten material cools very rapidly to below its glass transition temperature, without sufficient time for a regular crystal lattice to form. The most familiar form of glass is the silica-based material used for windows, containers and decorative objects. In its pure form, glass is a transparent, strong, hardwearing, essentially inert, and biologically inactive material which can be formed with very smooth and impervious surfaces.

Glass is, however, brittle and will break into sharp shards. These properties can be modified or changed with the addition of other compounds or heat treatment. Common glass contains about 70% amorphous silicon dioxide, mixed with other oxides.

Test Results

Presented in the plot are three different measurement results on a soda-lime glass. The samples were taken from the same production line but at different times. It can clearly be seen that the coefficients of thermal expansion are comparable for all three samples. However, sample #3 (blue curve) shows a slightly lower glass transition temperature (549 versus 555°C) and softening point (611 versus 614°C) compared to the other samples. This indicates a slight difference in the composition.

Test Conditions	
Instrument	DIL 402 PC
Temperature range	RT ... 650°C
Heating/cooling	5 K/min
Atmosphere	Air
Sample length	approx. 25 mm
Calibration	with fused silica



Comparison of the expansion behavior of three glass samples taken at different times from the sample production batch



Other Ceramic Materials

TGA Measurements on Calcium Oxalate Monohydrate – Whewellite

Introduction

Oxalates are the salts of the oxalic acid $C_2H_2O_4$ (ethanedicarboxylic acid ($COOH_2$)). The calcium salt of oxalic acid, calcium oxalate, crystallizes in the anhydrous form and as a solvate with one molecule of water per formula, as calcium oxalate monohydrate $CaC_2O_4 \cdot H_2O$.

Occurrence and Application

Although calcium oxalate monohydrate is the salt of an organic acid, it can be found in nature as a primary mineral. Figure 1 shows a Whewellite crystal from the Schlema locality in Germany's Erzgebirge Mountain Range. In addition to Whewellite, weddellite is also known as a second mineral species [1]. Calcium oxalate is also often the main component of kidney stones.

In thermal analysis, calcium oxalate monohydrate is used to check the

functionality of thermobalances. This substance has good storage stability; it is not subject to change over time, nor does it have any tendency to adsorb humidity from the laboratory atmosphere. These features make it an ideal reference substance for use in checking the temperature-base functionality of a thermobalance.

Thermogravimetry

When calcium oxalate monohydrate is heated to $1100^\circ C$, three clearly separated mass-loss steps can be detected by means of the thermobalance. Figure 2 shows a comparison of the thermogravimetric results of two measurements on calcium oxalate monohydrate samples. The relative mass changes of the samples are recorded over the temperature. Presented in figure 3 is the analogous comparison of the two measurements, as a function of temperature, for the first derivative of thermogravimetric results (DTG).

Test Conditions	
Instrument	TG 209 F1 Libra®
Sample	$CaC_2O_4 \cdot H_2O$
Sample weights	8.43 mg (black curve in fig. 2) and 8.67 mg (red curve in fig. 2)
Crucible	Al_2O_3
Atmosphere	Nitrogen
Gas flow rate	40 ml/min
Heating rate	10 K/min (black curve in fig. 2) and 200 K/min (red curve in fig. 2)



Fig. 1. Whewellite crystal from Schlema in Germany's Erzgebirge Mountain Range

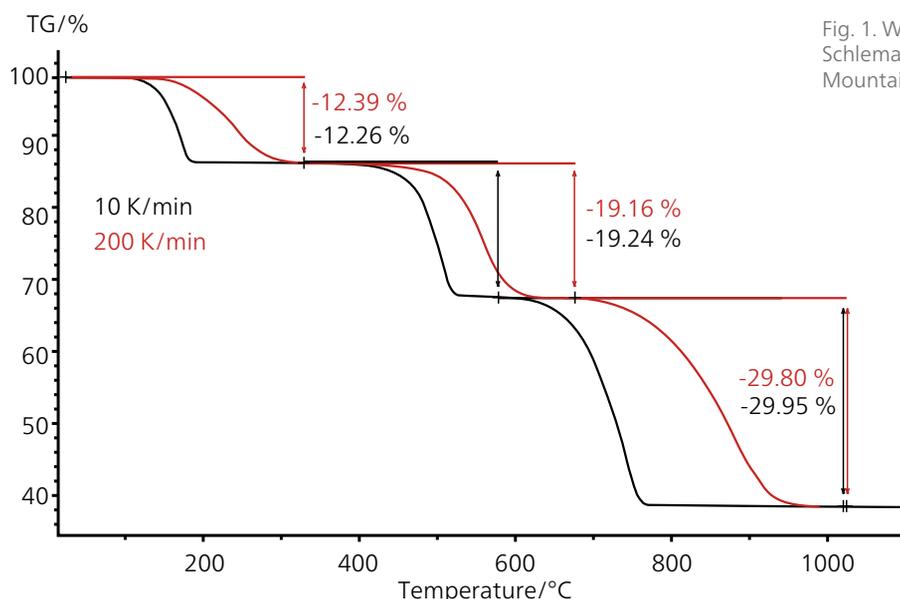


Fig 2. Comparison of the TGA results on calcium oxalate monohydrate for two heating rates: 10 K/min (black) and 200 K/min (red)

TGA Measurements on Calcium Oxalate Monohydrate – Whewellite ... Continued

Under otherwise identical conditions, two different heating rates were selected: 10 K/min (black curve) and 200 K/min (red curve). With the increased heating rate, the temperatures of the mass-loss steps are shifted to higher values and the release rates – the speed of the gas release – are increased approximately tenfold (DTG minima, figure 3). The shift in temperature that takes place upon variation of the heating rate is a well understood occurrence that can be applied toward further evaluation of the kinetic data [2]. Besides the temperature shift, it is also important to note that quantification of the mass-loss steps is independent of the heating rate. The heating rate of 200 K/min thus provides all the same information regarding the thermal degradation of calcium oxalate monohydrate as the more usual heating rate of 10 K/min; no information is lost by accelerating the heating rate. While yielding the same information content, however, the faster heating rate results in tremendous time savings: a measurement at 10 K/min takes almost two hours to cover the temperature range from room temperature to 1100°C, but the same measurement at 200 K/min is completed already in five minutes.

The reaction equations for the thermal degradation reaction of calcium oxalate monohydrate are shown in figure 4. At approximately 170°C, for the measurement at 10 K/min, anhydrous calcium oxalate is formed when water separates from the monohydrate (1). At approximately 500°C, calcium oxalate is transformed into calcium carbonate (CaCO₃), and carbon monoxide (CO) splits off (2).

The subsequent reaction, where the released carbon monoxide is oxidized to carbon dioxide (CO₂) (3), can only occur in an oxygen-

containing purge gas flow (e.g., synthetic air or oxygen). At a temperature of 750°C, calcium carbonate decomposes into calcium oxide with the release of CO₂ (4).

Literature

- [1] <http://www.mineralienatlas.de> und <http://www.wikipedia.de>
- [2] NETZSCH Thermokinetics

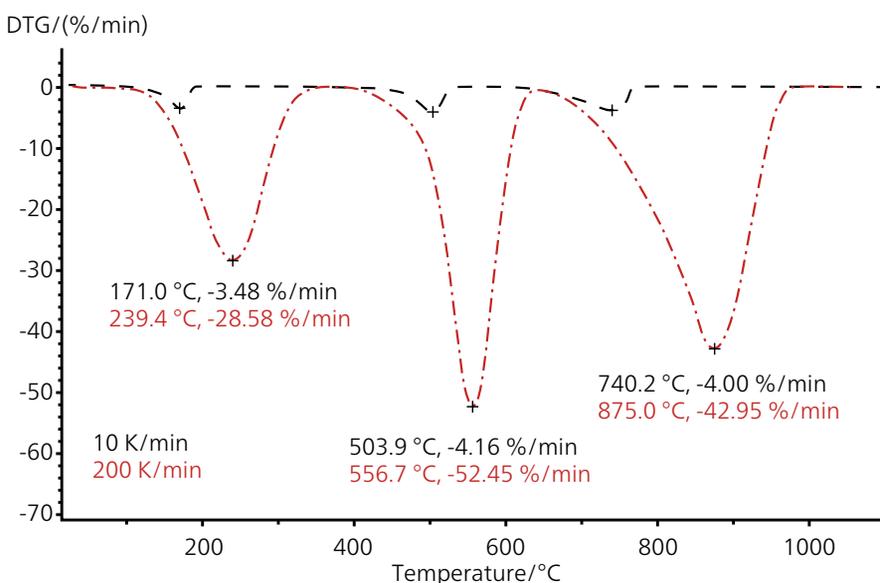


Fig 3. Comparison of the DTG results on calcium oxalate monohydrate for two heating rates: 10 K/min (black) and 200 K/min (red)

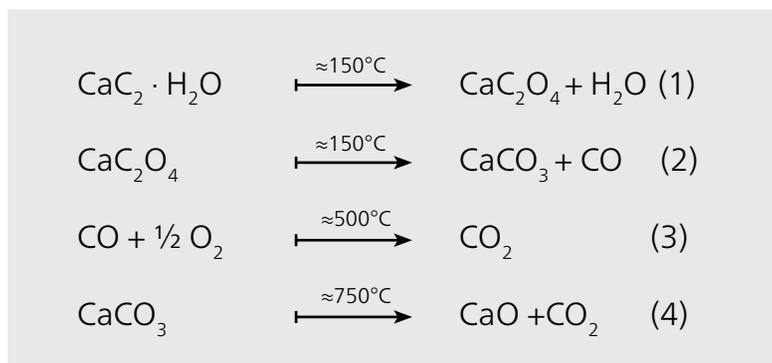


Fig 4. Reaction equations for the thermal degradation reaction of calcium oxalate monohydrate

Other Ceramic Materials

Mica

Origin and Application

Mica schist has been mined ever since prehistoric times. Mica was actually used in window panes prior to the industrial production of glass, since its layered structure allows it to be easily broken into thin sheets. Nowadays, mica is used as a pigment in paints and cosmetics. Due to its good thermal conduction and electrical insulation properties, another important application field for mica is the electronics industry, where it is used as insulating discs for semiconductor components or as a dielectric for very low-loss capacitors [1].

Thermogravimetry

A thermobalance can provide excellent characterization of the thermal

behavior of inorganic substances. It continuously records any change in the sample composition, while the use of a dynamic heating rate (10 K/min in our example) further allows for sample occurrences to be evaluated as a function of temperature. Since the heating rate is a measure of the energy supply to the sample, it allows conclusions to be drawn regarding the required release energy and/or the binding energy of the released substances.

Test Results

The example presented here with a mica sample shows three well separated mass loss steps; one at 357°C, another at 657°C and the third at 1092°C. The good separation of these mass-loss steps allows for easy

Test Conditions	
Instrument	TG 209 F1 <i>Libra</i>
Temperature range	RT ... 1100°C
Heating/cooling	10 K/min
Atmosphere	Nitrogen
Sample mass	5.102 mg
Crucible	Al ₂ O ₃
Gas flow rate	40 ml/min



Fig 1. Mica

Mica ... Continued

quantification of the amounts of gas evolved from the samples via step evaluation at the various temperatures. The relative mass changes amount to 0.26%, 1.00% and 3.71%. The release temperature is an indicator of the strength of the adsorption or bond: the higher its value, the stronger the adsorption of the gas to the crystal surface or the bond to the crystal structure prior to release. In contrast with "flash pyrolysis" – where the sample is heated to the maximum temperature within a few seconds and all gases are thus released very abruptly – thermogravimetry's very variable heating rates and combination of dynamic and isothermal segments allow for the gaseous decomposition products to be released as a function of temperature and therefore in a stepwise fashion. Our example with

mica additionally shows that a heating treatment of the sample to 1100°C at 10 K/min was not sufficient to allow for conclusion of the full decomposition reaction, and thus of course was not sufficient for its quantification either. In fact, a subsequent isothermal phase of 30 minutes was necessary to totally complete the reaction. Such flexibility in temperature control not only facilitates quantification, but additionally allows for identification of the gases evolved from the sample during the thermogravimetric process. Well suited for this is a technique called "coupling", where thermoanalytical measuring instruments are coupled to instruments for spectroscopic methods such as mass spectrometry or FT-IR spectroscopy.

Literature

- [1] <http://www.mineralienatlas.de> and <http://www.wikipedia.de>
- [2] Rex W. Grimshaw "The Chemistry and Physics of Clays and Allied Ceramic Materials", John Wiley & Sons, New York, 19.

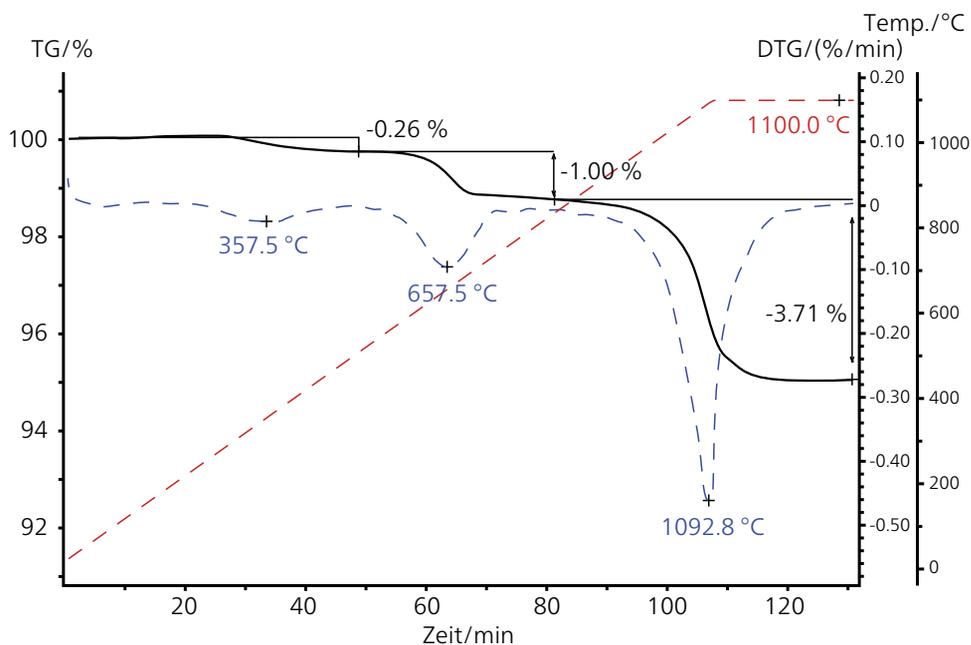


Fig 2. Test results on mica, obtained with the TG 209 **F1** Libra

Other Ceramic Materials

Ceramic Mass (Bentonite)

Bentonite is a clay consisting mainly of montmorillonite and stands out due to its absorbent capabilities. Some of the main uses are as a binder, purifier, absorbent and as a groundwater barrier.

Test Conditions Results

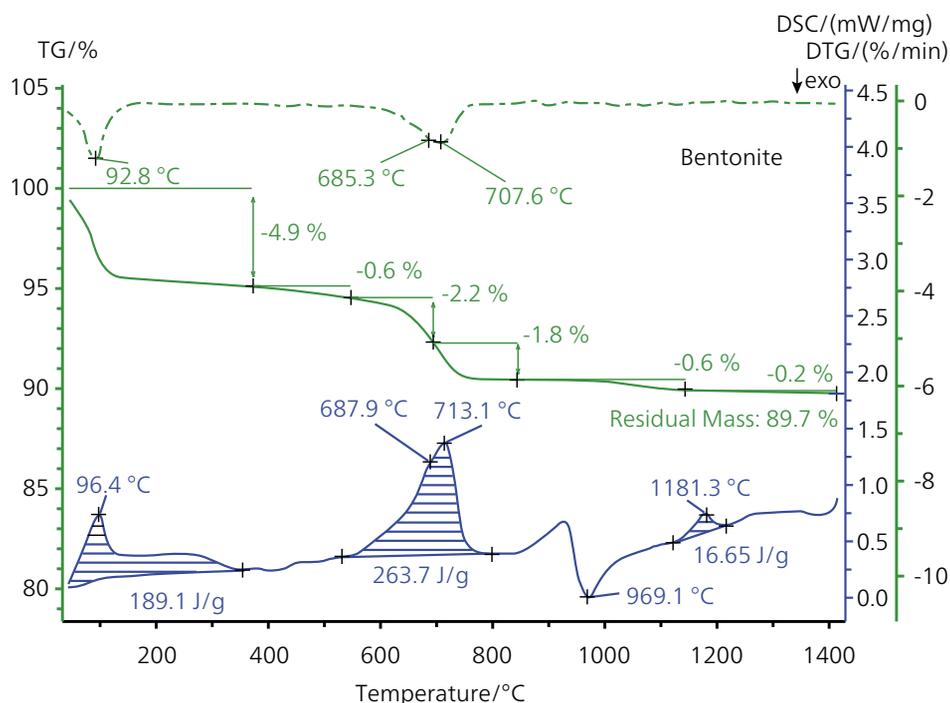
This plot exhibits the TGA (green), DTG (green dotted) and DSC (blue) curves of a 19.7 mg bentonite sample. The 1st mass-loss step (DSC peak temperature 96°C) is due to the release of water followed by a small mass-loss step of 0.6%. This is most likely due to the release of SO₂ indicating a pyrite contamination. Above 600°C, water is

released from the bentonite structure (DTG peaks at 685°C and 708°C). The exothermic DSC peak at 969°C represents the phase transition of this clay mineral. The endothermic DSC peak at 1181°C is most likely due to partial melting or a further SO₂ release.

Conclusion

Complex thermal behavior can be investigated with the STA 449 **F5 Jupiter**®. In case of inhomogeneous mixtures, crucibles with high volumes are available which allow for an increased sample mass of several grams.

Test Conditions	
Instrument	STA 449 F5 Jupiter
Temperature range	RT ... 1400°C
Heating/cooling	10 K/min
Atmosphere	Nitrogen
Sample mass	19.7 mg
Crucible	Pt
Sensor	TG-DSC type S



Complex thermal behavior of bentonite in Pt crucibles at a heating rate of 10 K/min in a nitrogen atmosphere (70 ml/min)

Titanium Dioxide

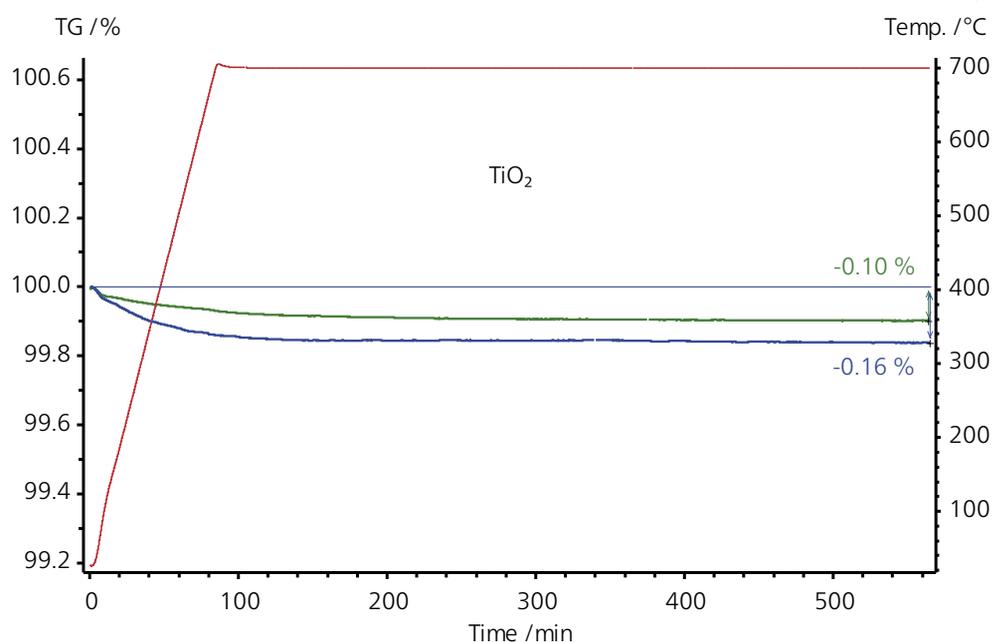
Titanium dioxide is the most widely used white pigment because of its brightness and very high refractive index. When deposited as a thin film, its refractive index and color make it an excellent reflective optical coating for dielectric mirrors. TiO_2 is also an effective opacifier in powder form, where it is employed as a pigment to provide whiteness and opacity to products such as paints, coatings, plastics, papers, inks, foods, and most toothpaste. In cosmetic and skin care products, titanium dioxide is used both as a pigment and thickener, and in almost every sun block with a physical blocker, titanium dioxide is found both because of its refractive index and its resistance to discoloration under ultraviolet light. This advantage enhances its stability and ability to protect the skin from ultraviolet light.

Test Results

The TiO_2 samples were relatively pure as can be concluded from the detection of the small mass loss of both samples. The difference in the mass loss of the samples is most probably due to differences in surface water and/or titanium hydroxides. It can also be gathered from the TG curves that the drying process at 700°C takes about 3 hours.

Test Conditions

Instrument	STA 449 Jupiter®
Temperature range	RT ... 700°C
Heating/cooling	8 K/min
Atmosphere	$\text{N}_2/\text{H}_2(95:5)$ at 60 ml/min
Sample mass	200 mg
Crucible	Alumina
Sensor	TG type S



Thermal stability of two titanium oxide samples, demonstrated by TGA measurements at 700°C

TECHNICAL CERAMICS



Glass

Pyrex® 7740

Pyrex® is a borosilicate glass material first developed by Corning. It is used in a variety of applications including glassware for laboratory use. It is stable within a wide temperature range (temperature limit: 490°C – for extreme service¹) and has high resistance to strong acids, bases, and other corrosive substances. Because it has a very low thermal expansion, Pyrex glassware can be made with thick walls, giving it greater mechanical strength and making it an ideal choice for laboratory use.

Dilatometry and thermomechanical analysis are ideal methods to measure the thermal expansion of Pyrex and other low-expansion glasses or ceramics.

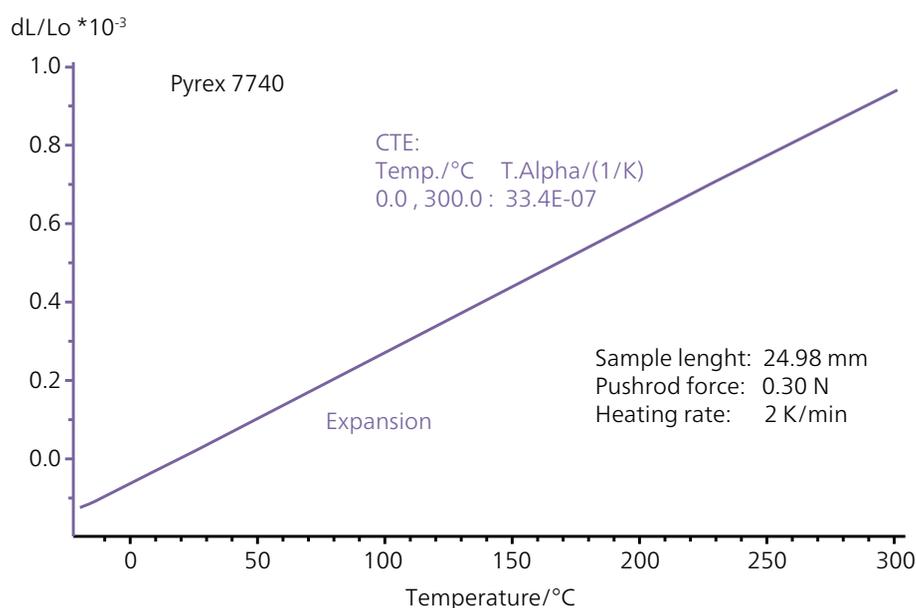
Test Results

The expansion curve of the Pyrex® glass shows an almost perfect linear behavior up to 300°C. The average value of the coefficient of thermal expansion (technical alpha value, CTE) between 0°C and 300°C was determined to be $33.4 \cdot 10^{-7} \text{ 1/K}$. The deviation from literature data (CTE: $32.5 \cdot 10^{-7} \text{ 1/K}^{1,2}$) is just $0.9 \cdot 10^{-7} \text{ 1/K}$. This clearly demonstrates the ability of the TMA 402 **F1 Hyperion** for being applied also to low-expansion materials.

¹Corning data sheet: Properties of PYREX®, PYREXPLUS® and Low Actinic PYREX® Code 740 Glasses

² www.valleydesign.com/pyrex.htm

Test Conditions	
Instrument	TMA 402 <i>Hyperion</i>
Temperature range	-20 °C ... 300°C
Heating/cooling	2°C/min
Atmosphere	Helium, 20 ml/min
Sample length	24.98 mm
Sample holder	Fused silica
Measurement mode	Expansion



Thermal expansion measurement on Pyrex® glass

CRT Panel Glass

Nowadays, high-quality precision glass is used for the aerospace, optical, electronic and various other commercial industries. Due to the fact that CRT monitors held a host of advantages over LCDs (e.g., color rendering, contrast ratios, color depths, multisync) improvement of the CRT technique is guaranteed. Modern monitors are flat. As the thermal stress for flat screen CRTs is larger than for curved screen CRTs, a special tempered glass is needed to withstand it. In addition numerical simulations are necessary to optimize the product and the manufacturing process.

For this, knowledge of the thermo-physical properties of the panel glass is necessary. The thermal diffusivity was measured using the LFA 427 from room temperature up to 1600°C. For the range above the softening point, a special sample holder of platinum for slags and pastes was used. A graphite

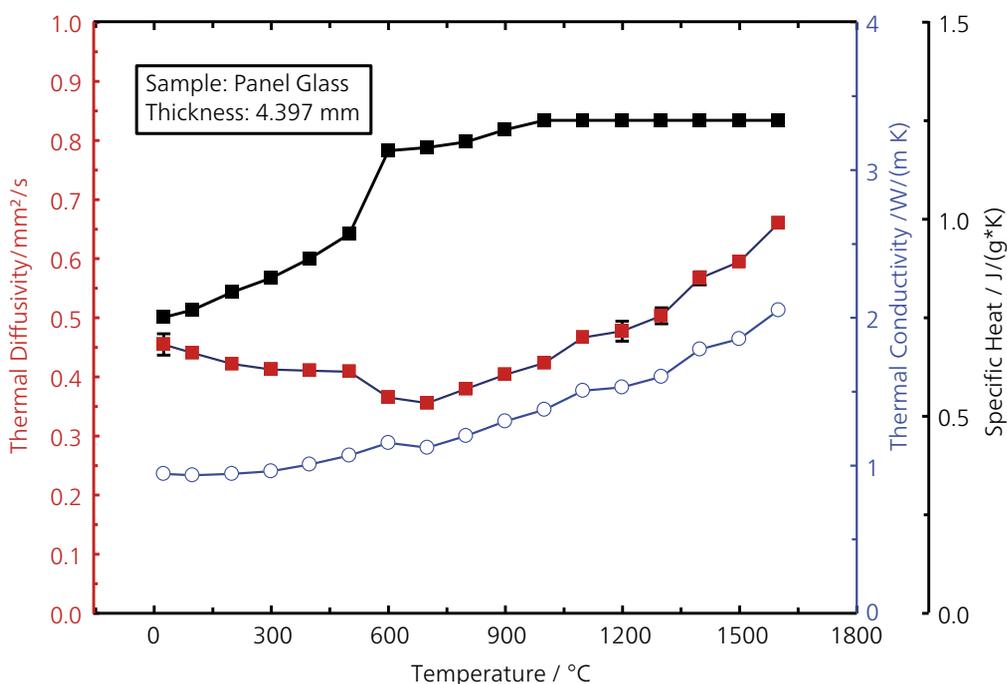
coating was necessary to realize a homogeneous energy entry on the front side and a homogeneous back side of the glass sample. A radiation model was used to consider the radiation heat transfer within the glass sample.

Test Results

The specific heat capacity and thermal diffusivity show a step above 500°C. The thermal conductivity increased continuously. This is typical for a glass transition and shows the good agreement between the measurements with two different devices (LFA and DSC). The example clearly demonstrates that the LFA 427 can analyze samples with undefined dimensions (above the softening point) and samples with a high degree of transparency at high temperatures without any problems.

Test Conditions

Instrument	LFA 427
Temperature range	RT ... 1600°C
Sample holder	12.7 diameter / Pt slag
Sample thickness	4.397 / 0.5 mm
Sample surface preparation	Graphite
c_p from DSC standard	Sapphire



LFA measurement on CRT panel glass using the slag sample holder

Glass

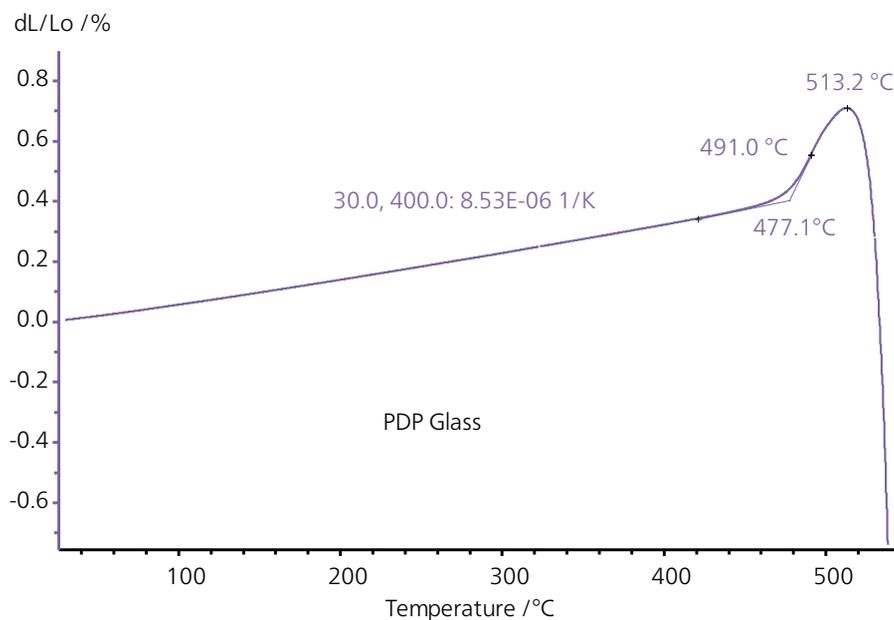
Glass for Plasma Display Panel

PDP (Plasma Display Panel) are bright, have a wide color gamut, and can be produced in fairly large sizes, up to 260 cm (102 inches) diagonally. They have a very high "dark-room" contrast, creating the "perfect black" desirable for watching movies. The display panel is only 6 cm (2 ½ inches) thick, while the total thickness, including electronics, is less than 10 cm (4 inches). The used glass material has to fulfill certain optical, mechanical and electrical specifications. Dilatometry is a very versatile tool for the characterization of glass material and can also be used for the quality control of the raw glass.

Test Results

The thermal expansion (technical alpha value) between 30 and 400°C was determined to $8.53 \cdot 10^{-6}$ 1/K. The dilatometric softening point was detected at 513°C with an inflection point at 491°C and an extrapolated onset at 477°C (glass transition temperature). These values are suitable for quality control purposes of the glass composition. With the automatic softening point detection of the NETZSCH dilatometer software, heating of the furnace can be stopped at a given shrinkage. This prevents the sample holder from sticking to the "molten" glass.

Test Conditions	
Instrument	DIL 402
Temperature range	RT ... 600°C
Heating/cooling	5 K/min
Atmosphere	Air, static
Sample length	25 mm
Sample carrier	Alumina



Dilatometer measurement on a glass for plasma display panel



Structural Ceramics

Yttrium Stabilized Zirconia

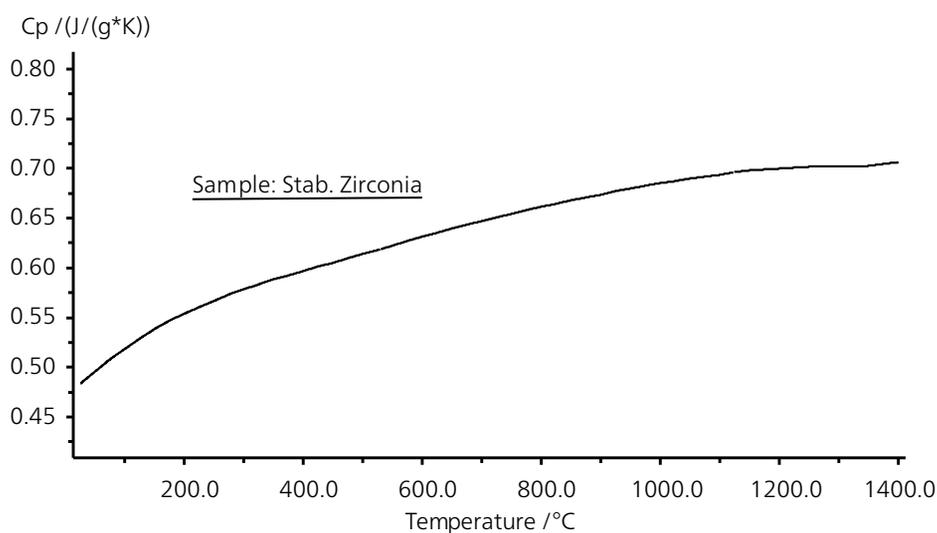
Zirconium dioxide, better known as zirconia (ZrO_2), exists as a monoclinic, tetragonal and cubic crystal modification. The most familiar and commonly used modification is the cubic form, which occurs for pure zirconia only at temperatures above 2950 K. In order to stabilize the cubic form also at room temperature, other oxides are added as stabilizers. Zirconia has some special properties such as high bending and tensile strength, high abrasion and corrosion resistance, low thermal conductivity and a thermal expansion similar to cast iron. It can therefore be used as thermal barrier coatings for gas turbine blades. Another material-specific property of zirconia is the ability to conduct oxygen ions at elevated temperatures. This phenomenon can, for example, be utilized for measurement of oxygen partial pressures or for the preparation

of solid oxide high-temperature fuel cells.

Test Results

Presented in the figure is the specific heat capacity of an yttria stabilized zirconia sample between room temperature and 1400°C. Starting at approximately 0.48 J/(g·K) at room temperature, the specific heat capacity increases over the entire temperature range. At high temperatures, nearly no temperature dependence was obtained, which is in agreement with the well-known Debye theory. It can clearly be seen that no phase transition is visible in the temperature range between 1100 and 1300°C. This proves that the sample measured here was fully stabilized. No monoclinic form was in the sample at room temperature.

Test Conditions	
Instrument	DSC 404 Pegasus®
Temperature range	RT ... 1400°C
Heating/cooling	20 K/min
Atmosphere	Argon at 50 ml/min
Sample mass	82.04 mg
Crucible	Pt with lid
Sensor	DSC type S



DSC measurement on stabilized zirconia (ZrO_2)

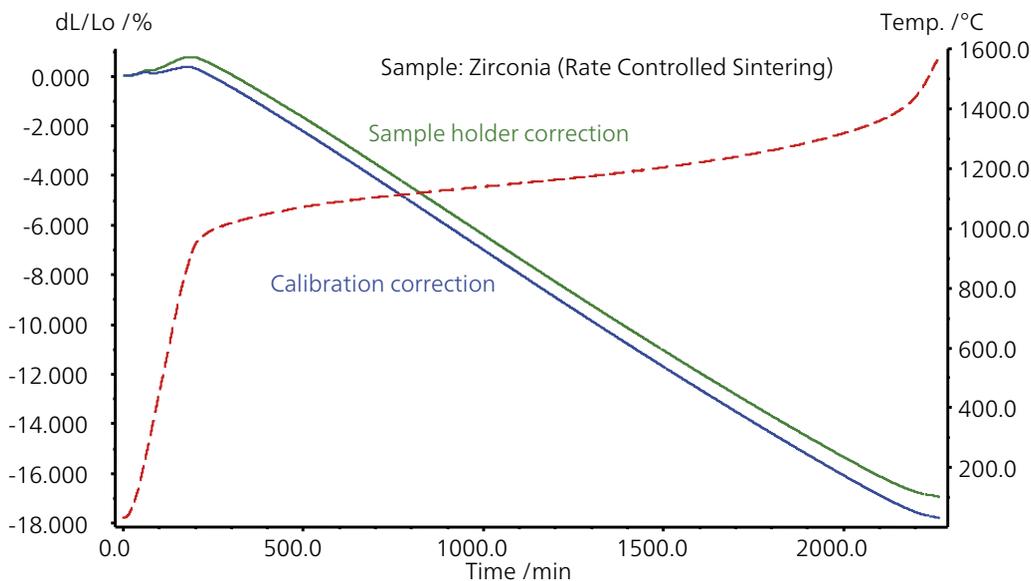
Zirconia – Correction for RCS Measurements

The thermal expansion of zirconia was measured using the NETZSCH model pushrod dilatometer 402. Using the double sample dilatometer, it is possible to measure the sample and standard parallelly. Hence, the sample and standard go through exactly the same temperature program. This is an advantage especially for Rate Controlled Sintering where the course of the temperature raise is not completely predictable. Zirconia was measured with the DIL 402 CD+RCS software extension employing a constant shrinkage rate of 0.01%/min.

Test Results

In the figure, it is shown that at the beginning with a temperature of 1000°C, the heating rate is reduced in order to keep the rate of shrinkage at a level which can be specified in the test program, in this case 0.01%/min. The green curve shows the thermal expansion in consideration of a sample holder correction for which literature values for the sample holder material was used. Much more accurate and less time-consuming is the correction with a standard which is parallelly measured ("calibration correction", blue curve).

Test Conditions	
Instrument	DIL 402
Temperature range	RT ... 1600°C
Heating/cooling	0 ... 10 K/min
Atmosphere	Air
Sample length	10.13 mg
Sample holder	Alumina
Sample material:	Alumina



Dilatometer measurement on zirconia – Correction for RCS Measurements

Structural Ceramics

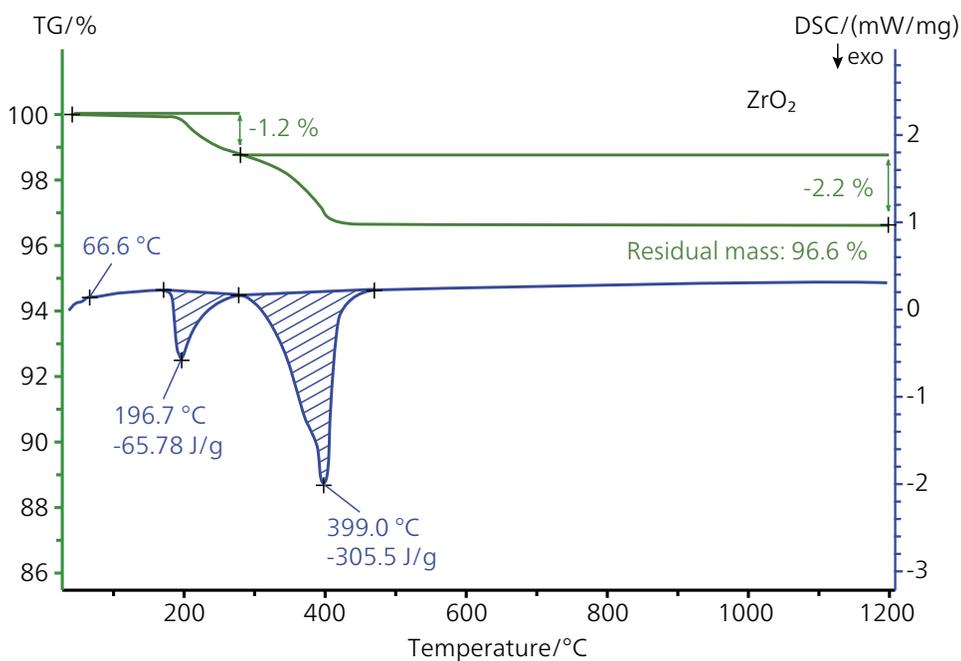
Stabilized Zirconia

Zirconium dioxide (ZrO_2) is one of the most frequently studied ceramic materials. Upon heating, zirconia undergoes disruptive phase changes. By adding small percentages of yttria, these phase changes are eliminated, and the resulting material has superior thermal, mechanical and electrical properties.

Test Results

This STA measurement between room temperature and 1200°C exhibits two small losses up to 450°C (3.4% in total; green TGA curve) which correspond very well with the two exothermic peaks at 197°C and 399°C in the DSC curve (blue). These effects (mass loss up to 500°C, exothermic peaks with high enthalpies) can be typically observed during the binder burnout of ceramic materials. The small endothermic DSC peak at around 67°C is caused by the melting of the binder.

Test Conditions	
Instrument	STA 449 F5 Jupiter®
Temperature range	RT ... 1200°C
Heating/cooling	10 K/min
Atmosphere	Synthetic air
Sample mass	26.2 mg
Crucible	Pt
Sensor	TGA-DSC type S



STA measurement of zirconium dioxide (26.2 mg) in platinum crucibles at a heating rate of 10 K/min

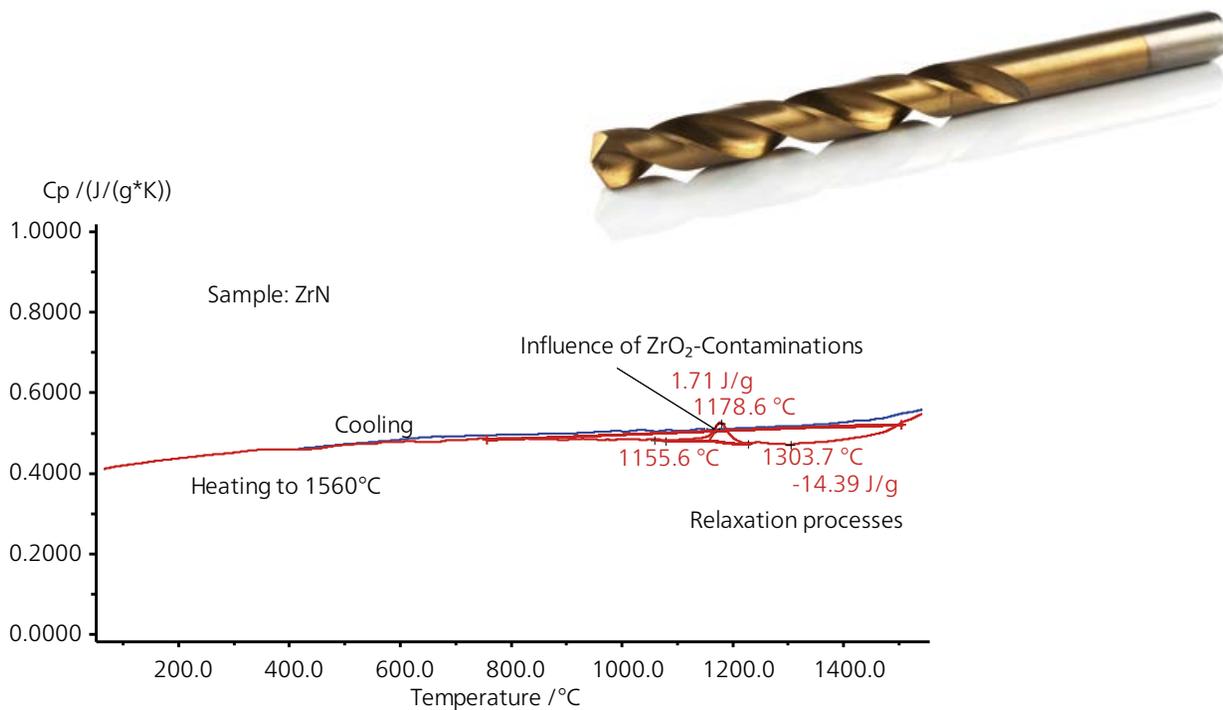
Zirconium Nitride

Zirconium nitride is a hard refractory ceramic with a high melting point (2960°C) and high density (7.09 g/cm³). It has been used recently as an alternative to titanium nitride for coating drill bits. Both coatings are supposed to keep the bit sharper and cooler during cutting. Due to the high temperature stability and the stability against nuclear radiation, it is one of the materials considered for nuclear applications. It can, for example, be used as a matrix material in the production of nuclear fuel systems. One of the advantages of the material is that it has a low ability to absorb source neutrons, which are driving the spallation process. For safety process control, however, the thermophysical properties must be known.

Test Results

The specific heat flow increases from slightly above 0.4 J/(g·K) at room temperature to 0.55 J/(g·K) at 1500°C. The slight change in specific heat capacity indicates that the Debye-temperature is on a low level for this nitride ceramic. During heating, a slight decrease in specific heat capacity was observed above 900°C. This effect is caused by relaxation processes in the non-stoichiometric sample material. During cooling, a continuous decrease with a decreasing temperature was measured. Starting at 1156°C (extrapolated onset), a small endothermic peak overlaps the specific heat. This peak is caused by a phase change in the zirconium oxide, occurring inside the sample as a contamination.

Test Conditions	
Instrument	DC 404 Pegasus®
Temperature range	RT ... 1560°C
Heating/cooling	20 K/min
Atmosphere	Argon at 50 ml/min
Sample mass	191 mg
Crucible	Pt with lid
Sensor	DSC type S



DSC measurement on zirconium nitride from room temperature to 1560°C in argon

Structural Ceramics

Zirconium Silicate

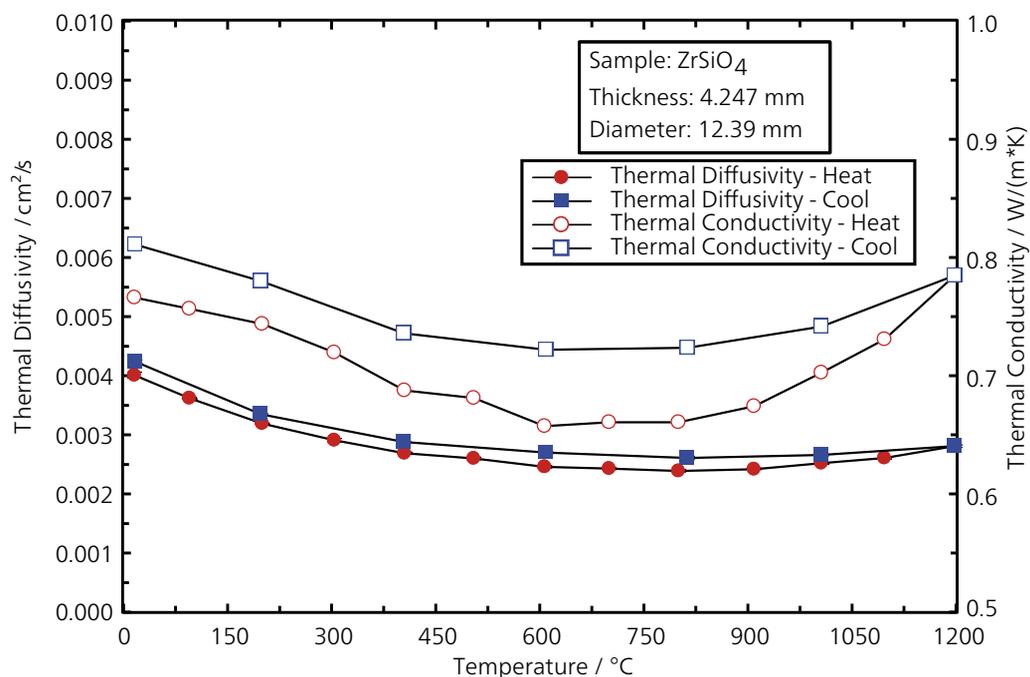
Zirconium silicate is a mineral belonging to the group of nesosilicates. Its chemical formula is $ZrSiO_4$. The crystal structure of zirconium silicate is tetragonal crystal class. The natural color of zirconium silicates varies between colorless, yellow-golden, red, brown or green. Colorless specimens that show gem quality are a popular substitute for diamond; these specimens are also known as "Matura diamond" (but note that cubic zirconia is a completely different synthetic mineral with a different chemical composition). Commercially, zirconium silicates are mined for the metal zirconium which is used for abrasive and insulating purposes. It is the source of zirconium oxide, one of the most refractory materials known. Crucibles of ZrO_2 are used to fuse platinum at temperatures in excess of 1755°C. Zirconium metal is used in nuclear

reactors due to its neutron absorption properties.

Test Results

The LFA measurement was carried out during heating and cooling. It can be seen that there are significant differences between the heating and cooling results. The thermal diffusivity versus temperature decreases up to 800°C. Then a slight increase was obtained (most probably due to the increase of radiative heat transfer). The thermal conductivity follows more or less the behavior of the thermal diffusivity. It can be seen that there are irreversible changes during heating and cooling. Due to structural changes and annealing of defects in the structure, the thermal diffusivity and conductivity are higher during the cooling run.

Test Conditions	
Instrument	LFA 427
Temperature range	RT ... 1200°C
Atmosphere	Ar at 60 ml/min
Sample holder	Standard 12.7 mm
Sensor	InSb



LFA measurement on zirconium silicate during heating and cooling

Silicon Carbide Honeycomb Structure

In the last few years, the environmental protection has become increasingly important. For this, permanent improvement of exhaust systems of Diesel engines is, for example, necessary. Presented here is an example for measurements on a part from particulate filter with a honeycomb structure. Due to the high thermal loads of this parts under operating conditions, knowledge of the thermal conductivity is important, e.g., for the generation process of the filter system. For LFA measurements, a homogeneous sample surface is necessary. For the in-plane measurements, the honeycomb structure was closed using a special SiC paste (square sample). Concerning the heat transfer during the measurement, no significant influence of additional SiC material

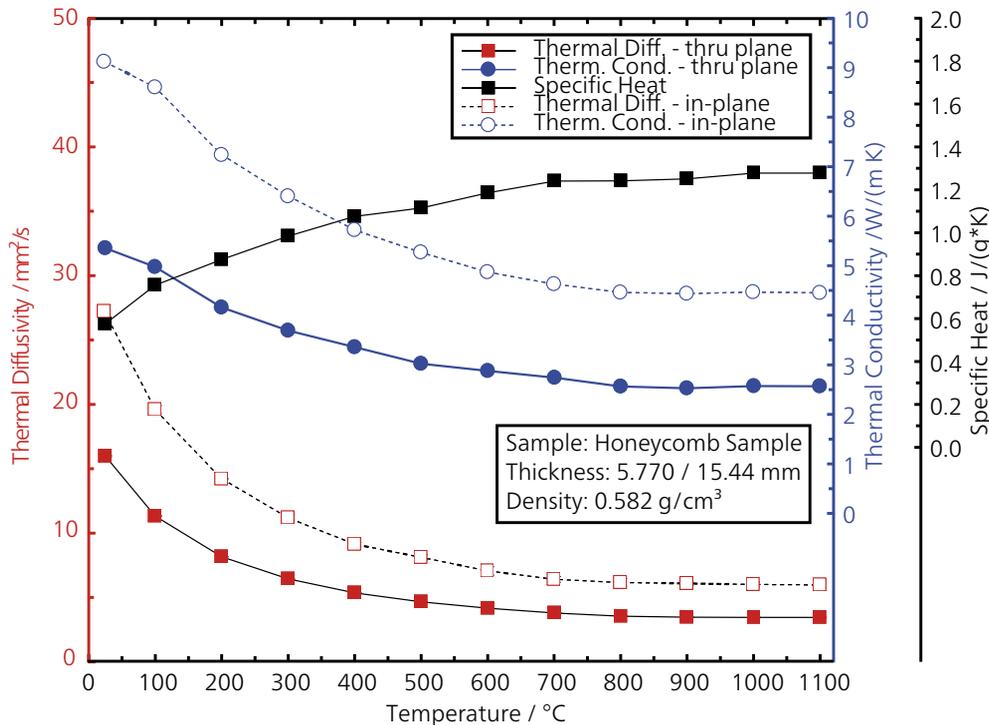
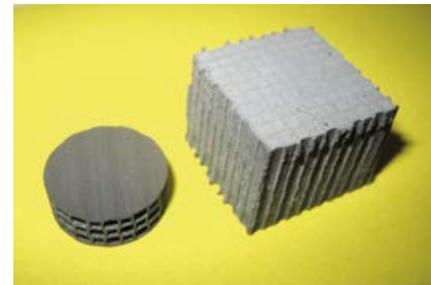
would be expected because only the free space within the surface structure is filled.

Test Results

The results show significant differences for the thermal diffusivity and thermal conductivity dependent on the measurement direction. The specific heat capacity was measured using a round sample (through plane, without SiC paste). The specific heat capacity increases over the entire temperature range as expected from the Debye theory and the values are typical for SiC ceramics. The example clearly demonstrates that the LFA 457 can analyze inhomogeneous materials (honeycomb structures) without any problems.

Test Conditions

Instrument	LFA 457 <i>MicroFlash</i>
Temperature range	RT ... 1000°C
Sample holder	12.7 mm diameter
Sample thickness	5.77 / 15.44 mm
Sample surface preparation	SiC / Graphite
c_p from LFA standard	Alumina



LFA Measurements on SiC honeycomb structure

Structural Ceramics

Silicon Carbide

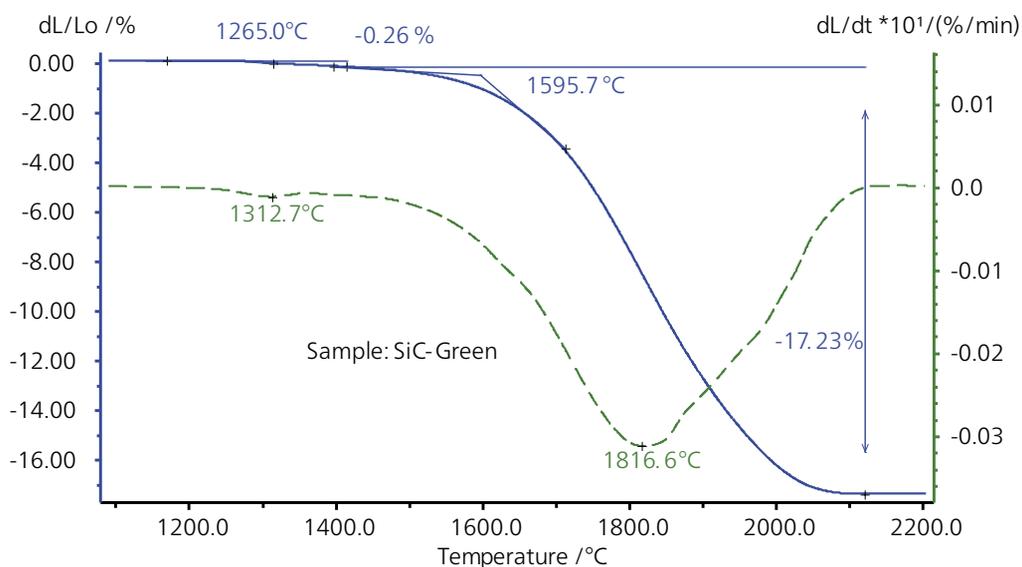
Silicon carbide (SiC) is a ceramic compound of silicon and carbon. Mostly silicon carbide is man-made for use as an abrasive (when it is often known by the trademark carborundum), or more recently, as a semiconductor and moissanite gemstones. Alpha silicon carbide (α -SiC) is most common, and is formed at temperatures higher than 2000 °C. Alpha SiC has the typical hexagonal crystal structure. Beta modification (β -SiC), with a face-centered cubic crystal structure, is formed at temperatures below 2000 °C, but has relatively few commercial uses. Silicon carbide has a specific gravity of 3.2 g/cm³, and its high melting point (approximately 2700 °C) makes silicon carbide useful for bearings and furnace parts. It is also chemically highly inert. SiC also has a very low thermal expansion coefficient

and no phase transitions that would cause discontinuities in thermal expansion.

Test Results

Presented in the figure are the measurement results (thermal expansion) on a silicon carbide green body (SiC powder mixed with a sintering aid) between 1000°C and 2200°C. Two sintering steps can be seen in the measurement curve. The first one (maximum shrinkage rate at 1313°C) is due to the reduction of the sintering aids: The second one (maximum shrinkage rate at 1817°C) is due to the shrinkage/densification of the green body. The example shows that sintering can be measured even at temperatures around and above 2000°C with a DIL 402.

Test Conditions	
Instrument	DIL 402
Temperature range	1000 ... 2200°C
Heating/cooling	5 K/min
Atmosphere	Helium
Sample length	18.66 mm
Calibration	with Poco graphite



Dilatometer measurement on silicon carbide in the temperature range from 1000°C to 2200°C in helium

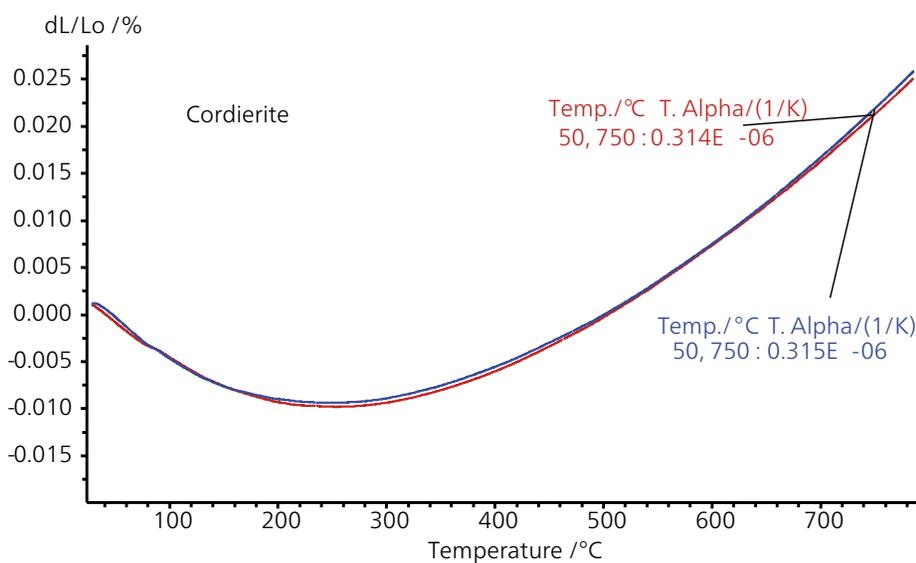
Cordierite

The thermal expansion of two cordierite samples was measured using a pushrod double dilatometer 402. Cordierite is a magnesium iron aluminium cyclosilicate. Iron is almost always present and a solid solution exists between Mg-rich cordierite and Fe-rich sekaninaite with a series formula: $(\text{Mg,Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18}$ to $(\text{Fe,Mg})_2\text{Al}_4\text{Si}_5\text{O}_{18}$. A high temperature polymorph exists, indialite, which is isostructural with beryl and has a random distribution of Al in the $(\text{AlSi})_6\text{O}_{18}$ rings. One of the key features of cordierite ceramics is a low coefficient of thermal expansion. This is one of the reasons why cordierite ceramic is commonly used in catalytic converters in the automotive industry.

Test Results

The thermal expansion of two cordierite samples was simultaneously measured with the DIL 402 CD. The two curves are nearly identical representing the very good uniformity of the material. Typical for cordierite ceramics, the material shows a shrinkage up to 250°C. Then, the material expands. The CTE between 50°C and 750°C was approx. $0.315 \cdot 10^{-6} \text{ 1/K}$.

Test Conditions	
Instruments	DIL 402 CD
Temperature range	RT ... 800°C
Heating/cooling	10 K/min
Atmosphere	Air
Sample length	25.9 mm
Sample holder	Quartz glass



Measurement on cordierite from RT to 800°C using a pushrod double dilatometer model

Bioceramics

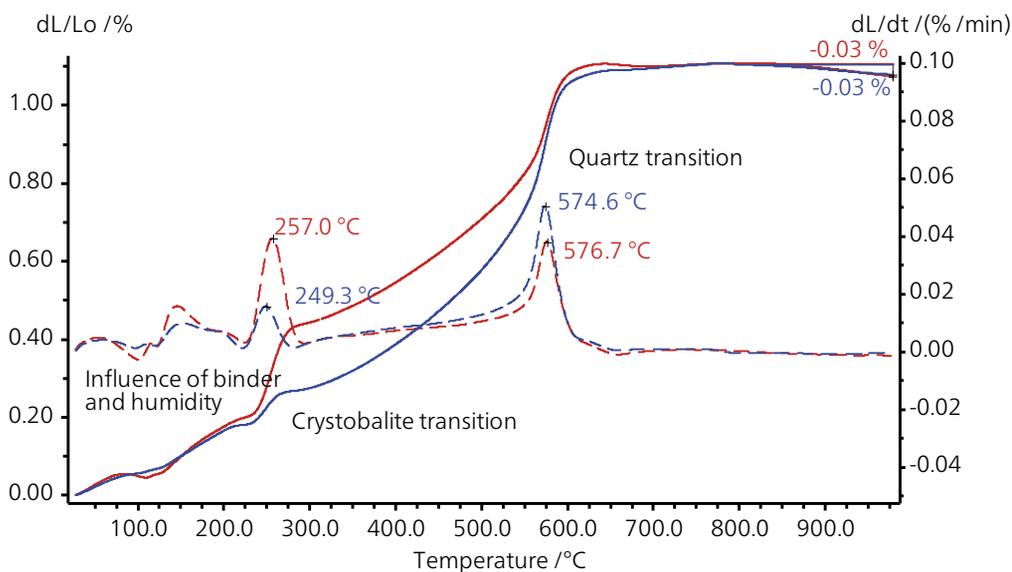
Mold Material for Casting of Dental Alloys

Casting of precious metals for dental applications is a growing area in the medical field. More and more people prefer metal inserts in their teeth as they are more robust and biocompatible and yield a long lifetime. However, the costs for such precious metal alloys are high and the production process is critical. In case of expansion mismatches between the mold material (generally a mixture of different silica modifications) and the metal, the shape of the dental implant can no longer be accurately controlled. Thermal expansion measurements on the mold material are therefore crucial to achieve a good casting product.

Test Results

Presented in the figure are two thermal expansion measurements on different types of casting materials. The difference in the expansion behaviour between 200°C and 600°C can clearly be seen. The reason for the difference in the expansion behavior can be explained by the composition of the samples. Sample 1 (blue curve) has a lower cristobalite and a higher quartz content. Sample 2 (red curve) has a higher cristobalite (higher expansion step between 200°C and 300°C) and a lower quartz content. The difference in the structural composition can simply be analyzed by means of a dilatometer test.

Test Conditions	
Instrument	DIL 402 PC
Temperature range	RT ... 1000°C
Heating/cooling	5 K/min
Atmosphere	Air, static
Sample length	approx 25 mm
Calibration	with alumina



Differences in thermal expansion of two different types of casting materials by means of the DIL 402 PC



Tribological Ceramics

Tungsten Carbide

Tungsten carbide, WC or W_2C , is a chemical compound containing tungsten and carbon, similar to titanium carbide. Its extreme hardness makes it useful in the manufacture of cutting tools, abrasives and bearings, as a cheaper alternative to diamond. Tungsten carbide is also used as a scratch-resistant material for jewelry including watch bands and wedding rings.

Carbide cutting surfaces are often useful when machining tough materials, such as carbon steel or stainless steel, as well as in situations where other tools would wear away, such as high-quantity production runs. Sometimes, carbide will leave a better finish on the part, and allow faster machining. Carbide tools can also withstand higher temperatures than standard high-speed steel tools. Generally, tungsten carbide parts are

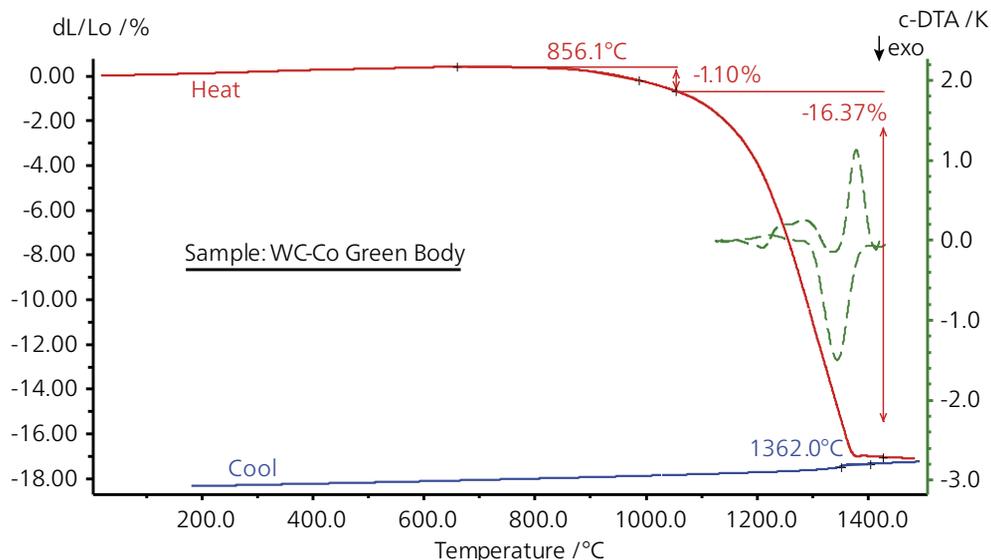
sintered from the powder at elevated temperatures. To reduce the sintering temperatures cobalt is generally added as a sintering aid.

Test Results

Presented in the plot are the measurement results (thermal expansion) for a tungsten carbide green body up to 1500°C. As can be seen, sintering (starting at 856°C) occurred in two steps (1.10 and 16.37%). Slightly above 1350°C, sintering stopped rapidly. This effect is caused by melting of an eutectic formed by tungsten, carbon and the sintering aid (cobalt). The melting process is indicated by an endothermic peak in the *c-DTA* analysis. During cooling, the eutectic solidifies at 1362°C (step in the thermal expansion, exothermic peak in the corresponding

c-DTA curve). The example shows that sintering of such hard metals can easily be analyzed with a pushrod dilatometer including *c-DTA* analysis.

Test Conditions	
Instrument	DIL 402 C
Temperature range	RT ... 1500°C
Heating/cooling	10 K/min
Atmosphere	Helium
Sample length	23.75 mm
Calibration	With alumina



Dilatometer results on a tungsten carbide green body to 1500°C

Silicon Nitride

The temperature program during the firing process of a ceramic green body, most of all during the binder burnout and sintering phase, has paramount influence on the later product quality. By modifying the temperature program of a dilatometer measurement, it is possible to optimize the properties of sintering products; e.g., densification and grain size distribution.

Figure A shows the length change (sintering) between 1050°C and 1850°C under the influence of different heating rates. As the heating rate increases, sintering is shifted to higher temperatures. For the kinetic analysis, a 4-step model was employed. Based on this model, a non-linear regression was carried out adjusting the different reaction parameters, such as pre-exponential factors and activation energies (solid lines; measurement data is depicted in points).

It becomes possible to calculate the sintering process for different temperature profiles or for constant shrinkage rates. Figure B depicts the temperature profile for rate controlled sintering (RCS) at a constant length change rate of 0.087%/min.

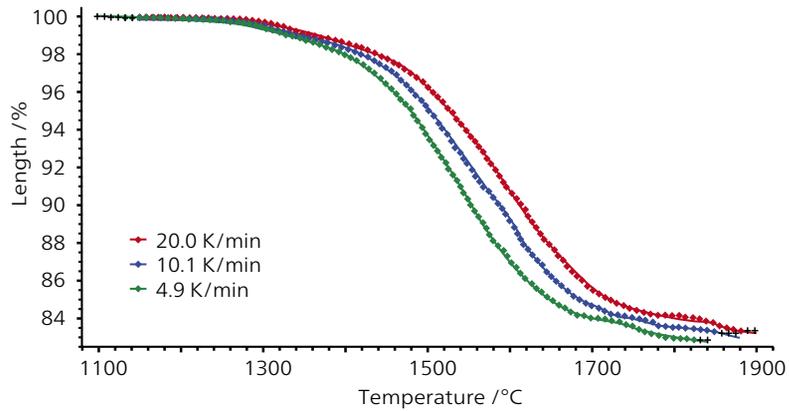


Figure A: Dilatometer measurements on Si_3N_4 powder containing 5 m% of Y_2O_3 and 5 m% of Al_2O_3 as sintering additives.

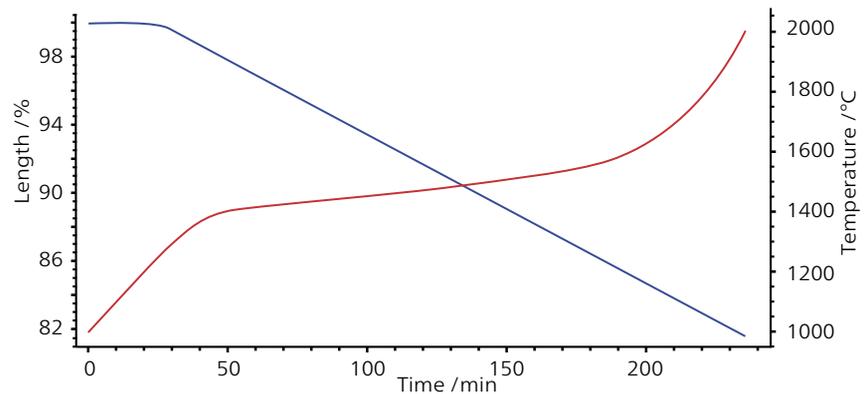


Figure B: Predicted temperature profile for RCS at a constant length change of 0.087%/min

Test Conditions	
Instrument	DIL 402 C
Temperature range	RT ... 2000°C
Heating/cooling	5, 10, 20 K/min
Constant length for RCS	0.087 %/min
Atmosphere	Nitrogen
Sample length	15 mm (approx.)
Calibration	With graphite

Tuning the Quality of High-Tech Ceramics

Electroceramics

Manganese Dioxide

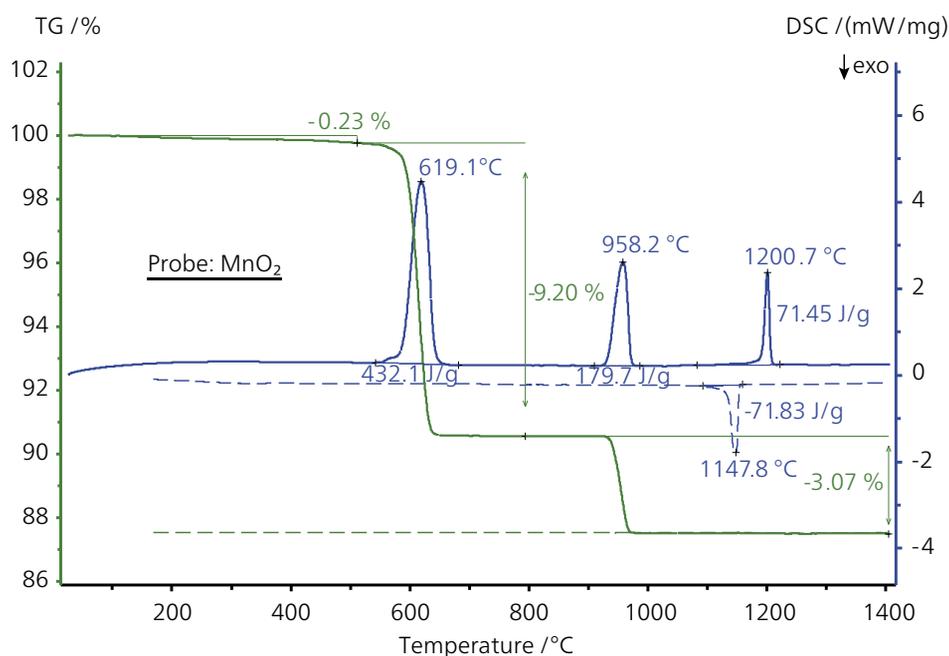
Manganese dioxide (MnO_2) is a blackish or brown solid occurring naturally as the mineral pyrolusite which is the main ore of manganese. The main use of MnO_2 is for cathode materials in dry-cell batteries, such as the alkaline battery and the zinc carbon battery. Manganese dioxide is also used as an oxidant in organic synthesis: For example, allylic alcohols can be oxidized to the corresponding aldehydes. It can also be used as a catalyst, for instance, in the preparation of oxygen from potassium chlorate.

Test Results

The STA measurement shows mass-loss steps at approx. 600°C and 950°C which are due to the reduction of

MnO_2 into Mn_2O_3 and finally into Mn_3O_4 . The values of 9.20% and 3.07% match exactly with the stoichiometrical values thus reflecting the high accuracy of the balance system. Endothermic DSC peaks with enthalpies of 432 J/g and 180 J/g were detected during the reduction steps. The endothermic DSC peak at 1200°C is due to a reversible structural transformation which was observed at 1148°C upon cooling (dashed lines).

Test Conditions	
Instrument	STA 449 F1 Jupiter®
Temperature range	RT ... 1400°C
Heating/cooling	20 K/min
Atmosphere	Synthetic air at 70 ml/min
Sample mass	32.14 mg
Crucible	Pt
Sensor	TG-DSC type S



STA measurements on Manganese Dioxide (MnO_2) in the temperature range from RT to 1400°C

Barium Zirconate

Introduction

BaZrO₃ crystallizes in the ideal cubic perovskite structure. The melting point of BaZrO₃ is higher than 2500°C. It is interesting as crucible material for crystallization of the high-temperature superconductor material group of the Y-Ba-Cu-oxides due to its chemical stability.

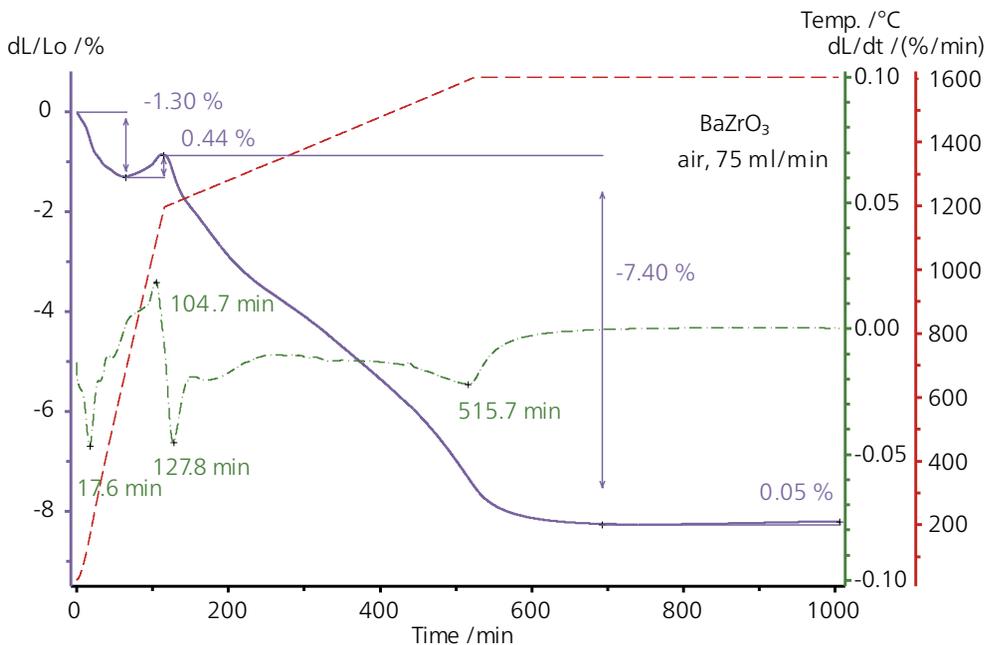
Test Results

A pressed powder pellet of BaZrO₃ was measured with the high-temperature dilatometer 402 C in air at a special

temperature program. After the binder burnout during heating to 1000°C, sintering of the sample started and was not finished after the 2nd heating ramp at 1 K/min to 1590°C. During the isothermal segment, the sample length further decreased during 3.5 hours. Then, an expansion occurred most probably due to grain growth. The grain growth might reduce the density of the sample again and the isothermal segment had then to be stopped. With the dilatometer results, the sintering behavior can be studied and helps optimize the properties of the fired ceramic.

Test Conditions

Instrument	DIL 402 C
Temperature range	RT ... 1590°C
Atmosphere	Air at 50 ml/min
Sample length	3 mm
Sample carrier	Alumina



Dilatometer measurements on a pressed powder pellet of barium zirconate in air

Electroceramics

Yttrium Barium Copper Oxide – Superconductor

Yttrium barium copper oxide is a so-called high-temperature ceramic superconductor. The phenomenon of superconductivity was discovered by H. Kammerling-Onnes in 1911. Until 1986, superconductivity of metals was restricted to temperatures of the order of liquid helium temperature. The discovery of superconductivity in certain oxides at temperatures above 35 K (so-called high-temperature superconductivity) by Bednorz and Müller launched a flurry of research into these superconducting materials. YBCO was the first material to become superconducting above 77 K, the boiling point of liquid nitrogen, which was a break through in the refrigerant used to cool the material to below the critical temperature. The superconducting

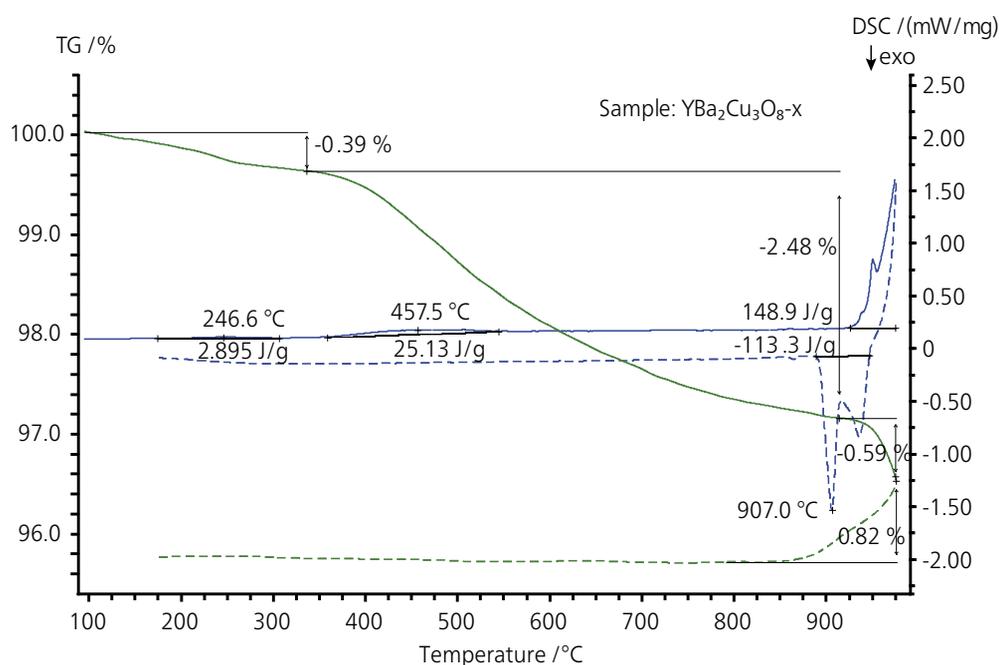
properties of YBCO depend strongly on its oxygen content as well as on its microstructure – properties which both can be strongly affected by thermal treatment. Prominent applications of high-temperature superconductors are, for example, superconducting magnets, wires, current limiters and so-called Josephson-junctions.

Test Results

The temperature-dependent mass change (TG) and heat-flow rate (DSC) of an YBCO sample were simultaneously measured. The full lines refer to heating, the dashed lines to cooling. Upon heating, three mass-loss steps were observed which are due to the release of humidity at low

temperatures and due to reduction of the sample at higher temperatures. In general, simultaneous thermal analyzers are ideal tools for the preparation and characterization of ceramics such as high-temperature superconductors.

Test Conditions	
Instrument	STA 449 Jupiter®
Temperature range	RT ... 1000°C
Heating/cooling	10 K/min
Atmosphere	Argon at 70 ml/min
Sample mass	22 mg
Crucible	Pt
Sensor	TG-DSC type S



Temperature-dependent mass change and heat-flow rate of yttrium barium copper oxide (YBCO)

Titanium Dioxide – Varistor

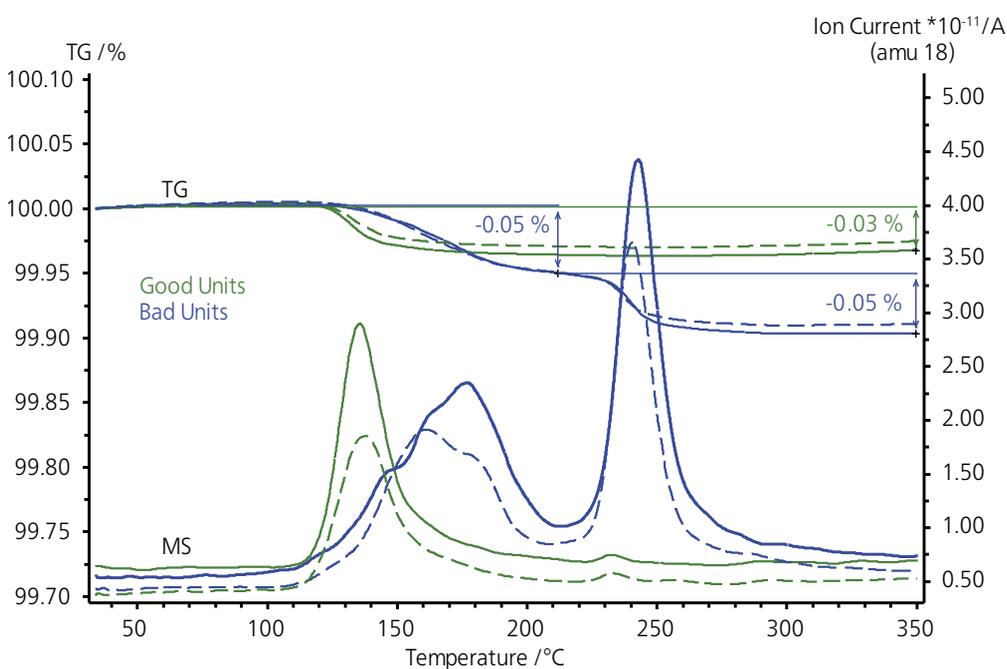
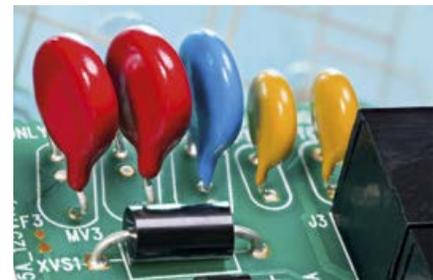
Passive electronic components do not require a source of energy to perform their intended function in an electronic circuit. Examples of passive components include resistors, capacitors, inductors, diodes, varistors, etc. A varistor is equivalent to a combination of back-to-back diode pairs which lead to a voltage dependent resistor (VDR). These electronic components are soldered onto circuit boards using SMD technology (surface mounted devices) or through-hole technology. Thermal analysis – in particular thermogravimetry (TG) – allows for characterization and thus for quality control of such electronic components. Simultaneous mass spectroscopy enables furthermore identification of the evolved gases from the sample – another valuable source of information even for the development and production of electronic parts.

Test Results

By means of simultaneous thermogravimetry (TG) and mass spectroscopy (MS), good and bad varistor parts could be distinguished. Reproducibility tests were also carried out (dashed lines). The bad parts showed two mass loss steps of 0.05% whereas the good parts showed only one mass loss step of 0.03%. As can be seen from the mass spectrometer curves, the origin of the mass-loss steps is due to the release of water with mass number 18. In the bad varistor parts, a larger amount of humidity is even captured up to ~250°C which is critical for automatic soldering onto the circuit board.

Test Conditions

Instrument	STA 449 Jupiter®- QMS 403 Aëolos®
Temperature range	RT ... 350°C
Heating/cooling	10 K/min
Atmosphere	Helium at 70 ml/min
Sample mass	approx. 900 mg
Crucible	Al ₂ O ₃
Sensor	TG-DSC type S



STA-MS Measurements on a good and bad varistor parts

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