ELS
Expert Lab Service

New Optical Thermal Analysis Methods: Absolute, Differential, TGA, Atmosphere

Expert Lab Service is a boutique of ceramic engineering solutions, materials analysis services and **tailor-made laboratory instruments**.

Outline

- Company presentation
- The new **Absolute Optical Platform**
- The new **1700°C MoSi2** furnace for **Vertical Dilatometer** + Microscope
- The new **Differential** Dilatometry and Fleximetry
- Simultaneous **ThermoGravimetry**
- **Controlled Atmosphere**: vacuum and inert
- **Modelling** software

What we do

- **Measurement instruments** for optical thermal analysis: ELS-MDF (microscope, dilatometer, fleximeter)
- **Ceramics Genome:** Ceramic laboratory information management and modeling software
- **Consulting and training**
- **Laboratory tests**

Selected customers

→ CERAMIC TILES MANUFACTURERS

Simpolo Tiles & Bathware

LAMINAM

MARAZZI

→ GLAZE PRODUCERS

vidres

TORRECID

sicer ITALIAN CERAMIC SURFACES

esmalglass·itaca grupo

COLOROBBIA ITALIA

→ RAW MATERIALS SUPPLIERS

SIBELCO

→ TECHNOLOGY SUPPLIERS

SYSTEM Ceramics

SACMI

→ RESEARCH INSTITUTIONS

UNIMORE UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

CGCRI

→ ADVANCED CERAMICS, AEROSPACE

CGW ABRASIVES

+GF+

PRECICAST

Optical Thermal Analysis

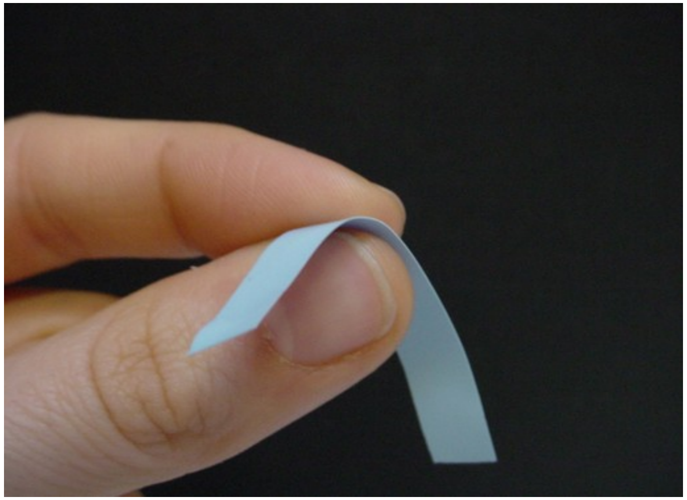
Optical thermal analysis instruments are able to measure thermophysical properties of materials **without any contact between the measurement system and the sample**.

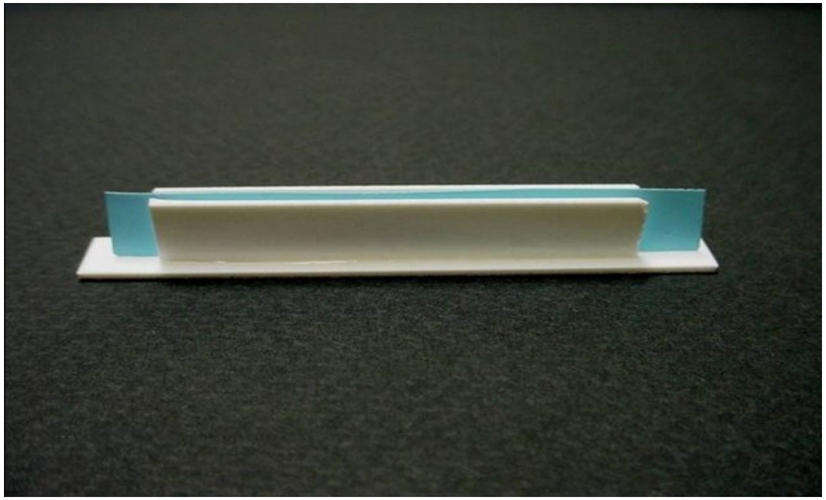
They all work by applying **computer vision techniques** to the sample's image (or some portions of it).

Measurable properties: coefficient of thermal expansion, melting point, elastic tensions, plastic deformation, contact angle, surface tension, viscosity estimation.

Seeing > Touching

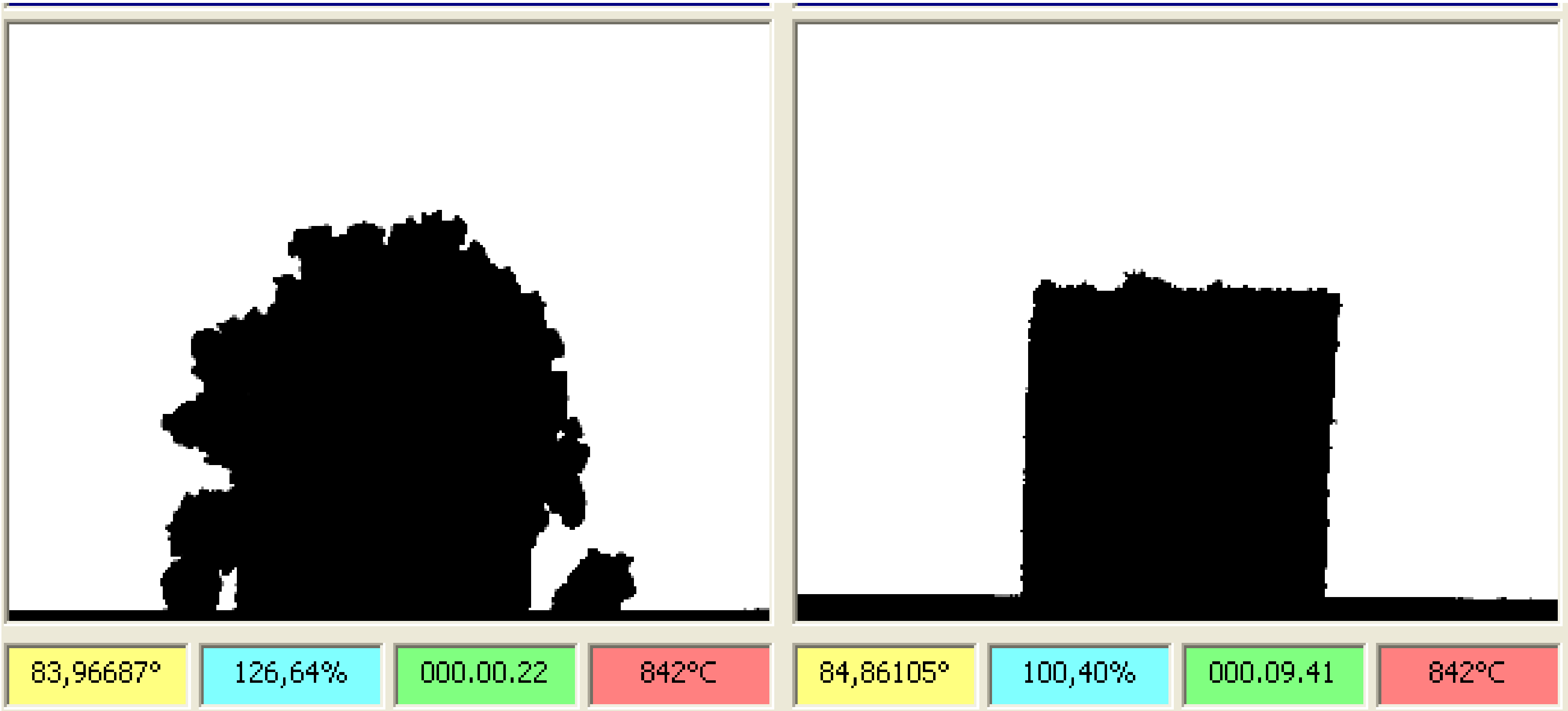
Being contactless, we avoid most of the interference of the instrument on the sample.





Kinetics > Equilibrium

The instrument does not heat up during the measurement. This allows to observe the sample behavior with very fast heating rates.



Materials > Standards

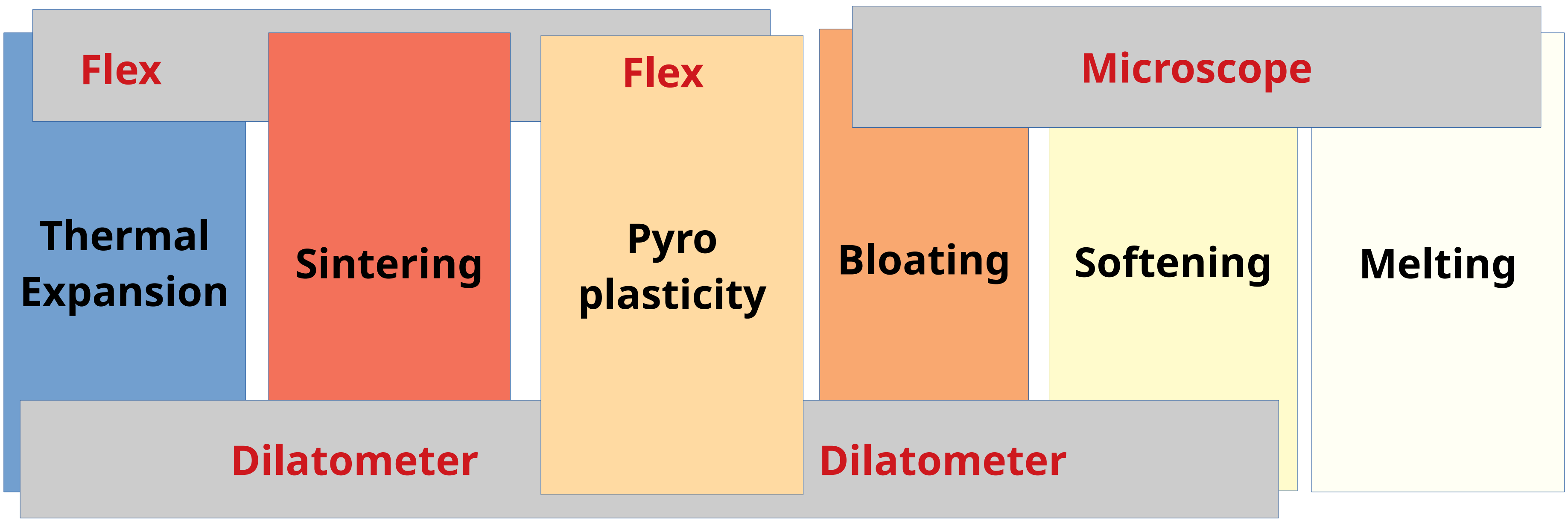
Standards can be to vague to be useful, or of little applicability for your material. We always prioritize materials over standards.

From ISO 540 on ash fusibility, 1995:
3.1 **deformation temperature** (abbreviation DT):
The temperature at which the *first signs of rounding*, due to melting, of the tip or edges of the test piece occur.

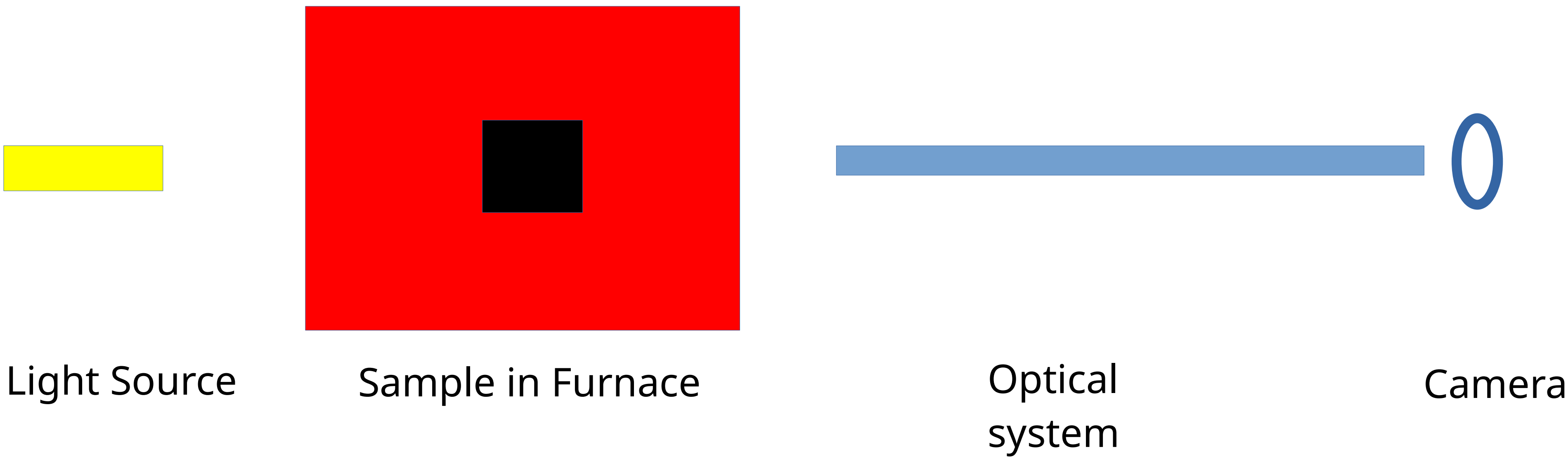
From ASTM E381-19 on CTE with thermomechanical analysis:
6.1.3 Sensing element… **+- 50nm** resulting from changes in length of the specimen.
6.3 Micrometer… with a range up to 10mm to determine specimen dimensions within **+- 25000nm**.

Optical Thermal Analysis for Ceramics

- We measure the deformation that heat and temperature causes in a material, across these behaviours:

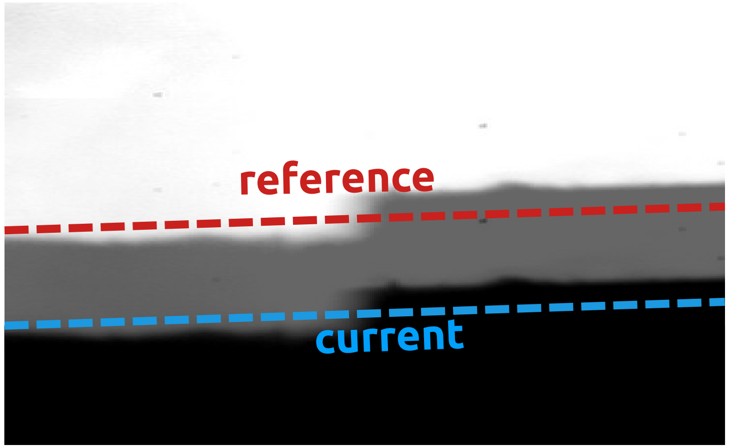


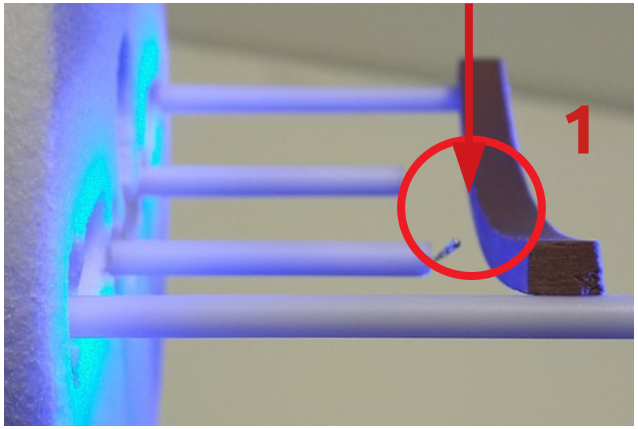
Design of an optical thermal analysis instrument

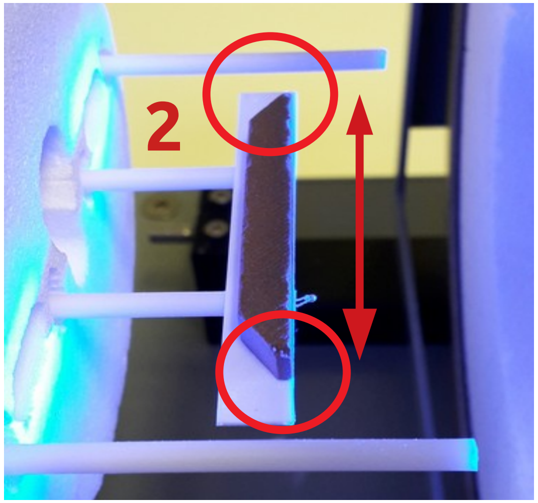


- The optical system brings the *image* of the sample on camera.
- Resolution is limited by the optical system: max ~0.5 microns.
- We can focus a part of the sample and follow its **displacement**, or its entirety to follow its **morphing**.

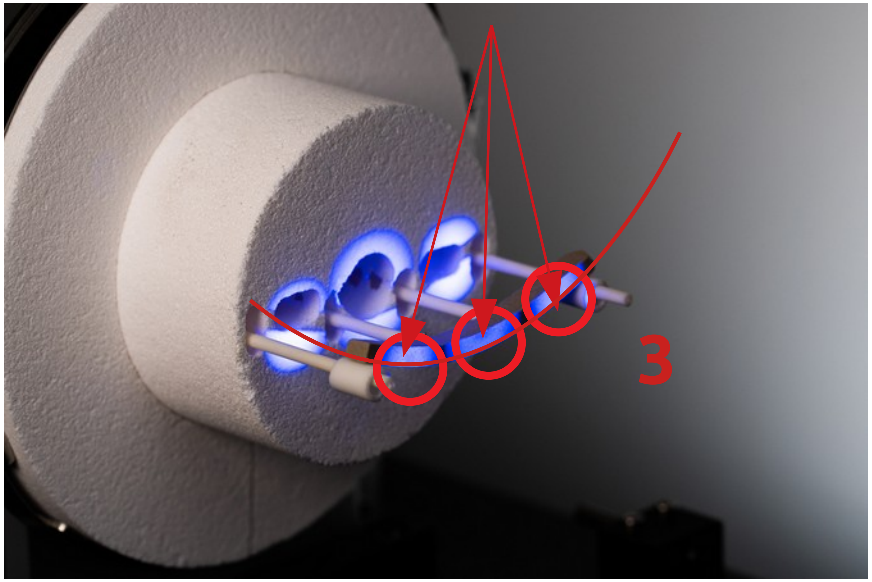
Optical Measurements: Displacements





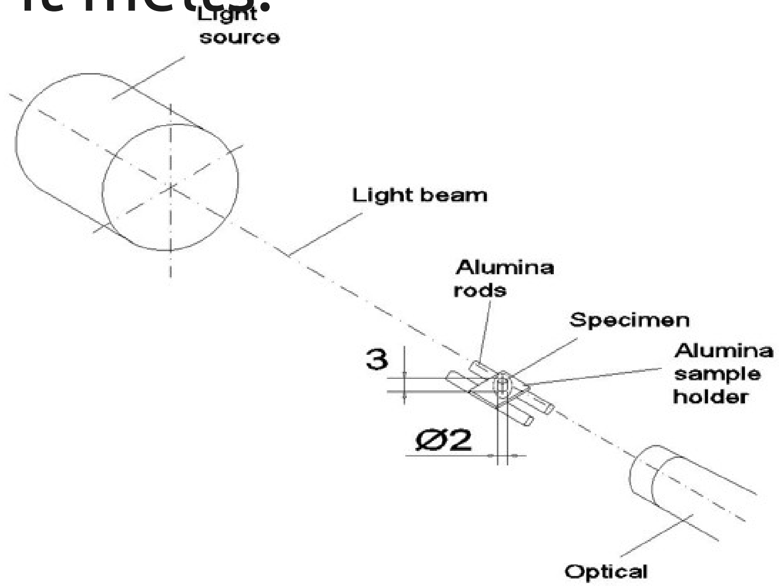


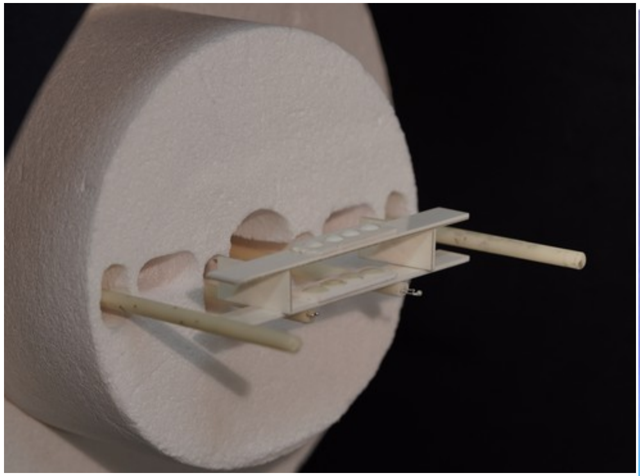
- **Displacement**: maximum zoom (1px=0.4μm) on the smallest possible segment of sample border. We get a (sometimes not so) straight line.
- Position through linear regression + mean line-line distance + statistical filtering
- Delta with initial position = displacement
- **Single point**: **Fleximeter**
- **Two points**: Horizontal/Vertical **Dilatometer**
- **Three points**: **Absolute Fleximeter**

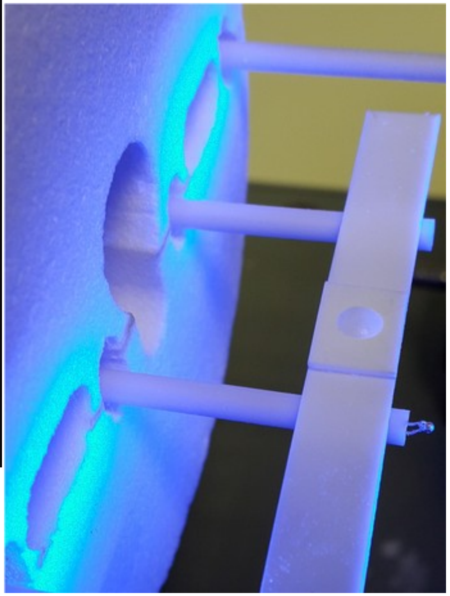


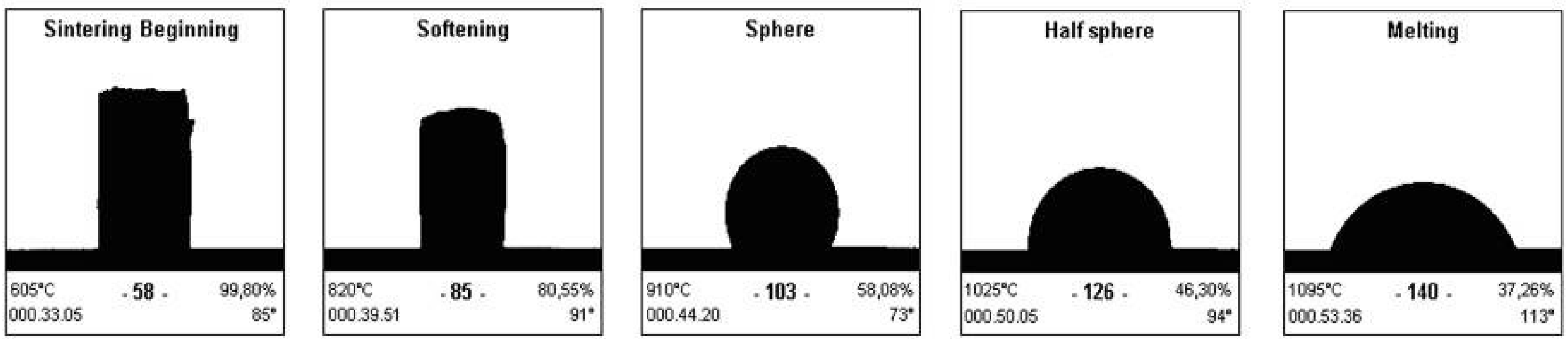
Optical Measurements: Heating Microscope

Follows the change of the entire silhouette of the sample, as it melts.

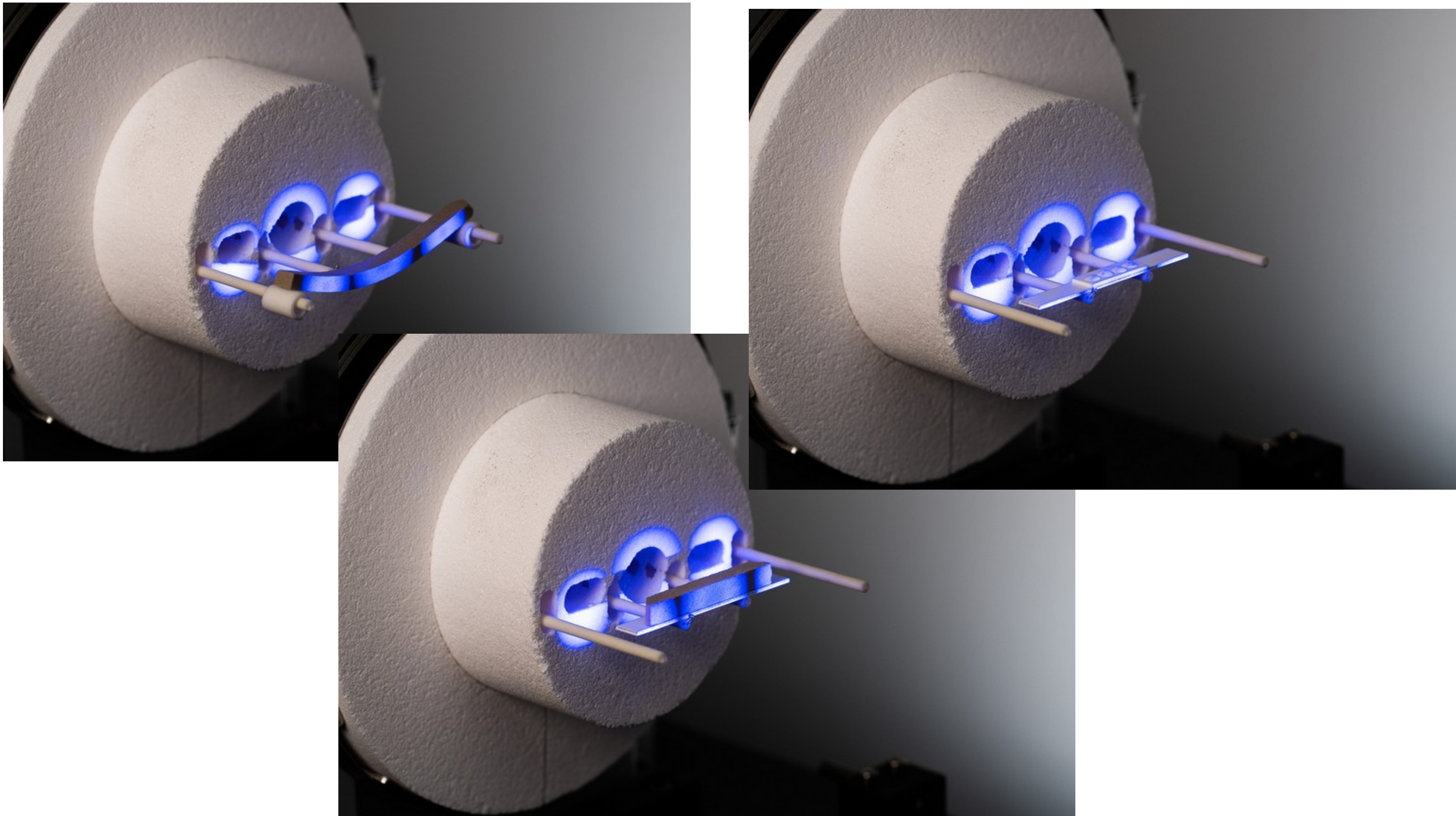






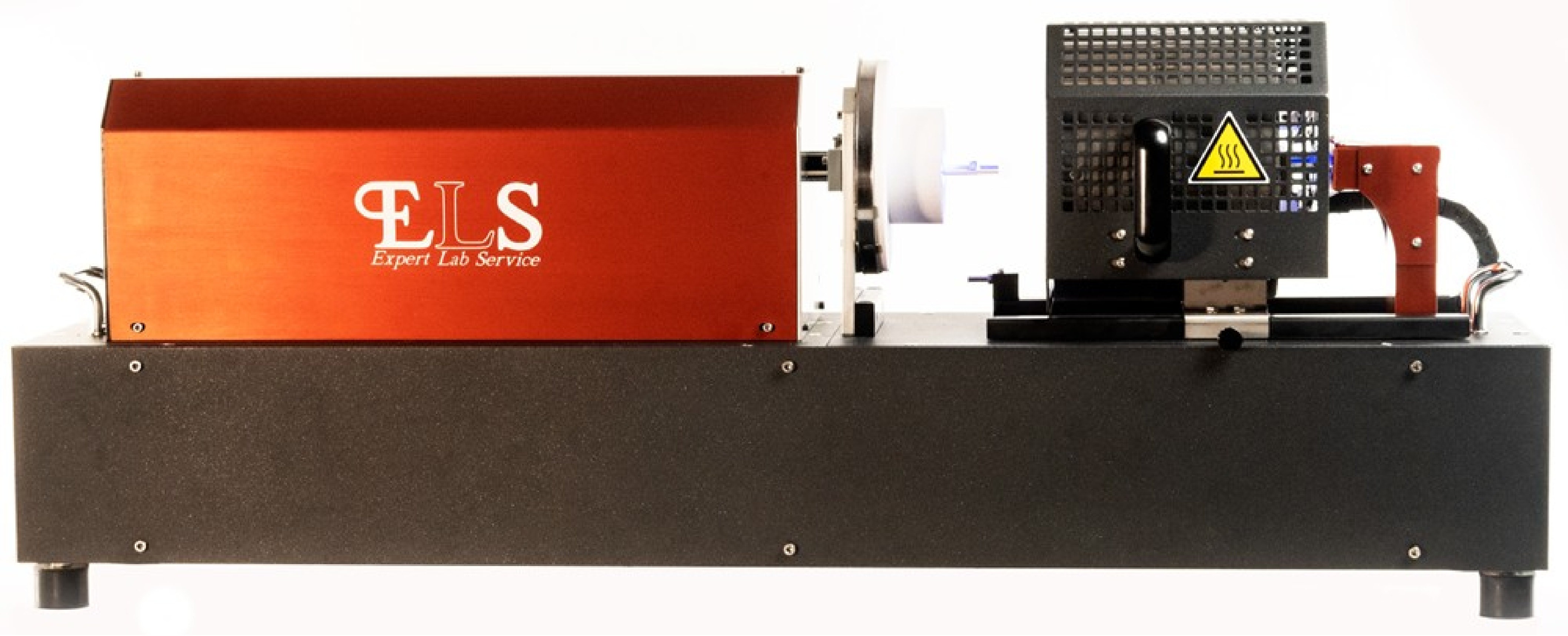


Microscope, Dilatometer, Fleximeter

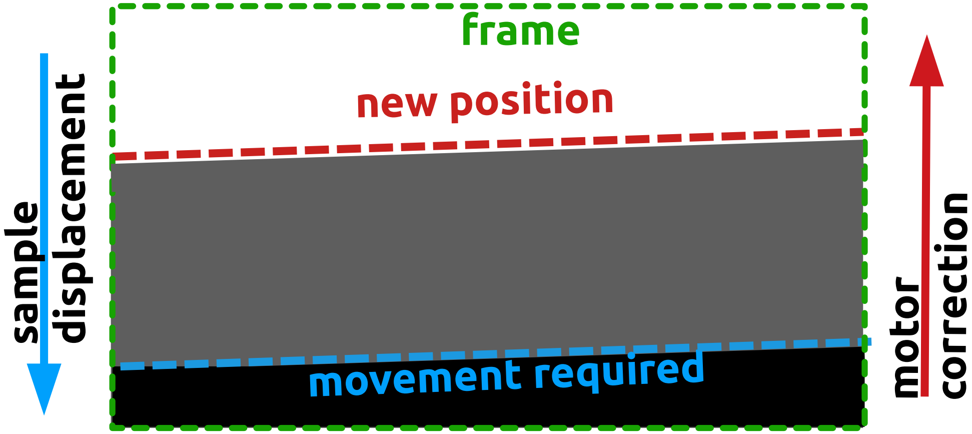


ELS-MDF

The all-in-one optical thermal analyzer

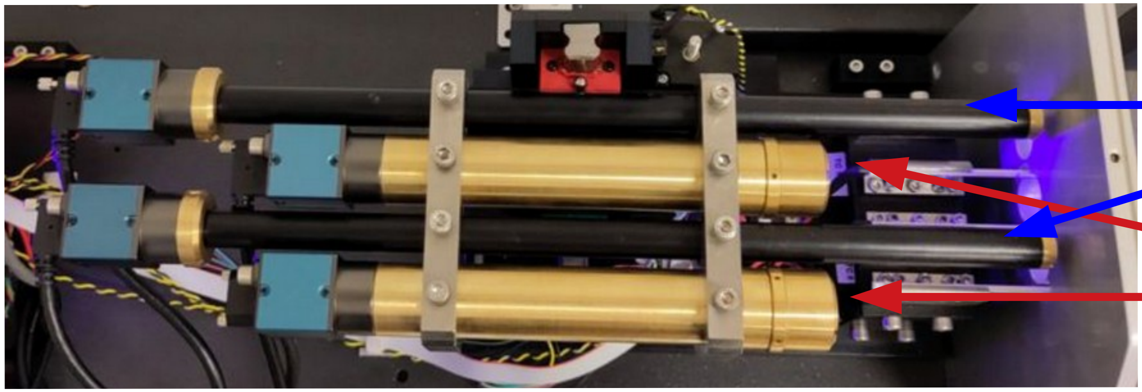


State of the Art: Motorized Optics



- Full HD cameras (1280x920 px) magnified to 0.5um/px are able to follow 640um, or **1.3%** of expansion/sintering over 50mm.
- When the sample is going to exit this window, a motor moves the camera, takes a new zero and restarts the measurement.
- Drawbacks:
  - Each movement causes 0.5um of error.
  - The dynamics occurring during the intervention time is lost
  - The initial length must be measured with an external micrometer, usually having 20 times less resolution than the instrument itself (10um against 0.5um!)

Next Iteration: Absolute Optical Platform

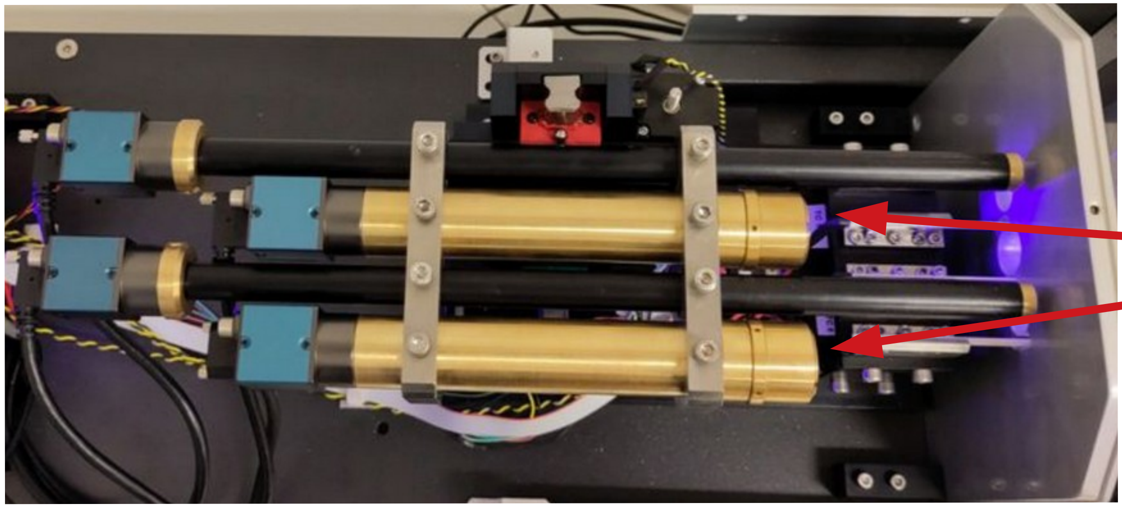


High Precision Optics (HPO)

High Range Optics (HRO)

- The **Absolute Optical Platform** features a total of **60Mpx** of sensors and a massively parallel computer vision software to simultaneously decompose and analyze multiple huge frames.
- The entire measurement is executed **without any camera movement**.
- The position of the optics relative to each other is fixed in a robust **Invar** assembly, **immune to thermal expansion**.
- The field of view is big enough to make possible, for the first time in a commercial instrument, **Differential Optical Measurements.**
- **Initial dimension measurement** is possible.
- **No complex alignments. Easier maintenance. Self-installation.**
- The entire optical bench can translate XY in order to execute **8 functions**

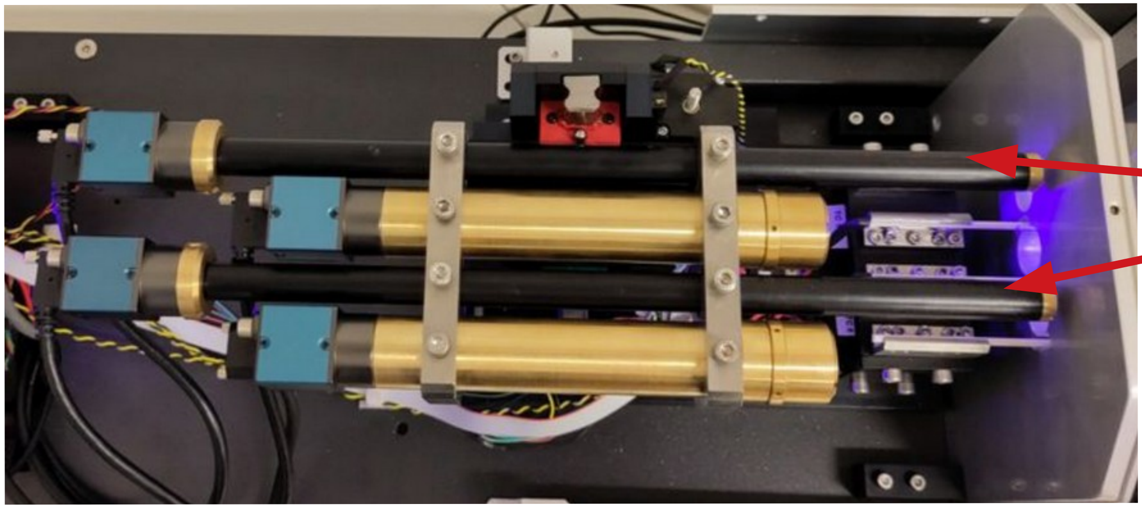
Absolute Optical Platform: High Range



High Range Optics

- Two **high range optics** (HRO) for:
  - HRO **Horizontal Dilatometer**, to follow **sintering** up to **35%** with 3.4um resolution over 50mm (70ppm).
  - HRO **Fleximeter**, for **pyroplasticity**, up to 6mm.
  - **Heating Microscope** up to 3 samples (variants up to 4 and 8), up to 10x10mm
  - HRO **Differential Horizontal Dilatometer**, to load non-sticky samples (see later).

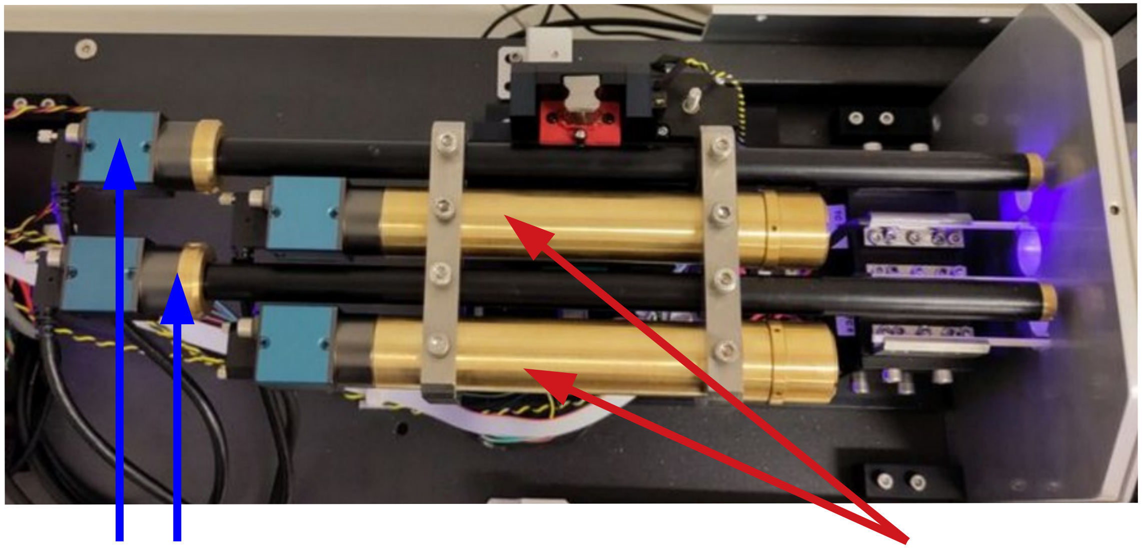
Absolute Optical Platform: High Precision



High Precision optics

- Two **high precision optics** (HPO) for:
  - HPO **Dilatometer** to follow **CTE** up to **4%** with 0.5um of resolution over 50mm (10ppm).
  - HPO **Absolute Fleximeter**: One HP optic in the middle and two HR at the sides, to execute the circular approximation and the Absolute Fleximeter function.
  - HPO **Differential Fleximeter**: by framing both a non-bending reference and the sample.
  - **HP Microscope** samples of less than 1x1mm.

Absolute Optical Platform: 9 functions



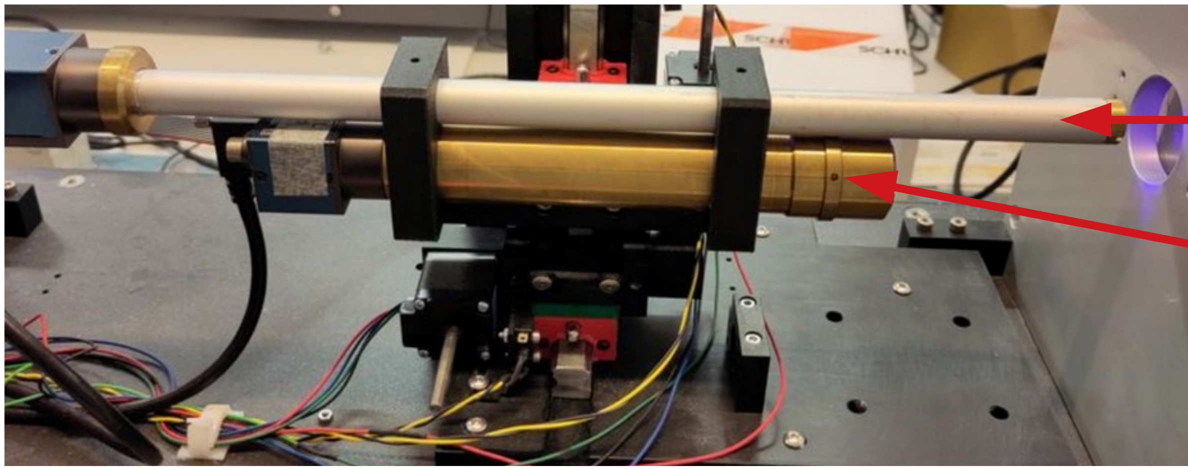
High Precision Optical (HPO):

1) Horizontal Dilatometer (CTE, 10ppm res)
2) Differential Horizontal Dilatometer (non-sticky)
3) Differential Fleximeter (<150um tensions)
4) Absolute Fleximeter (>150um tensions)
5) Microscope (max 1.5mm height)

High Range Optical (HRO):

6) Dilatometer (for sintering, 70ppm res)
7) Differential Dilatometer (or double sample)
8) Fleximeter (for pyroplasticity)
9) Microscope (x3, x4, x8, max 10mm height)

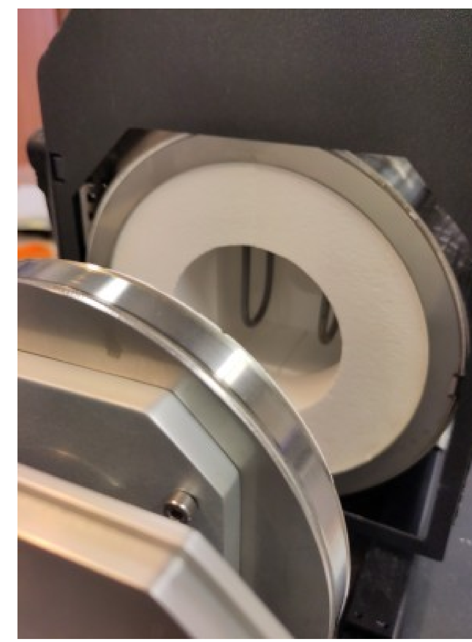
Absolute Optical Platform: Vertical 1700°C



High Precision Optics (HPO)

High Range Optics (HRO)

- MoSi2 are less fragile, less expensive and easier to replace than Pt/Rh elements
- **Heating Microscope**:
  - The vertical design of the furnace allow to run sintering tests while framing the entire sample (15mm of height)
  - A dedicated, microscope-only design can host x8 samples
- **Differential Vertical Dilatometer:**
  - 15mm sample, 0.5um resolution, for accurate CTE

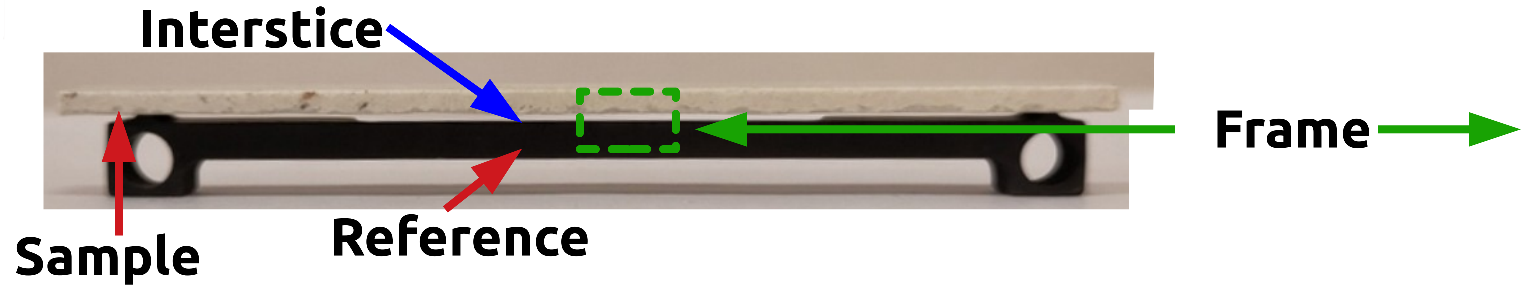


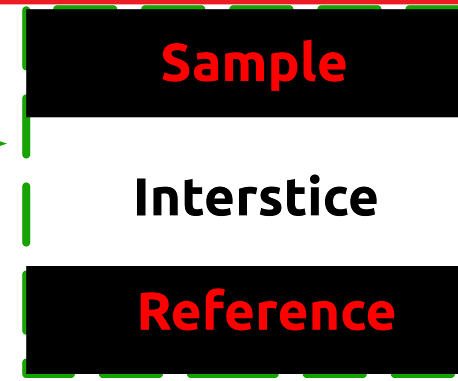
MoSi2 Furnace

The Optical Differential Concept

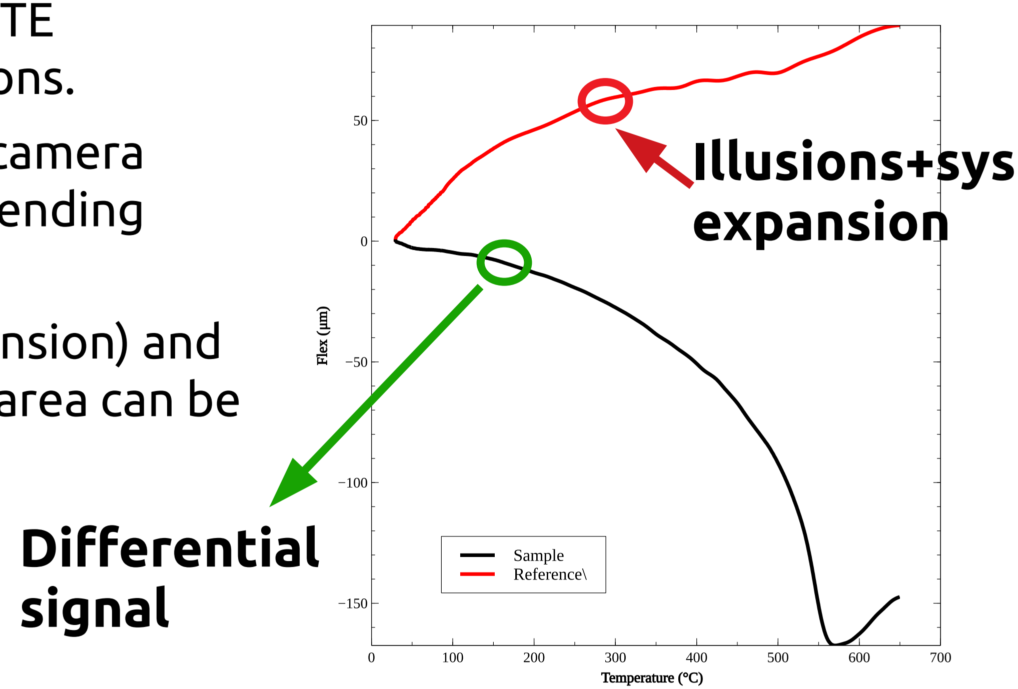
- Even optical instruments cannot be immune to **thermal anisotropies** affecting the sample, the furnace and the thermocouple. Fast heating rates, possible because of the cold measurement system, exacerbate this issue - especially at lower temperature (<400°C).
- In the **vertical** dilatometer configuration, moreover, temperature gradients in air moving parallel to the measurement direction can cause **optical illusions and aberrations**.
- Thanks to the new high resolution sensor, **both the sample and a calibration reference can be framed** simultaneously.
- 3 variants:
  - **Differential Fleximeter**: a non-bending reference and the sample are stacked one above the other, with a tiny space between them where the sample can bend. **One camera** frames the reference and the sample at the same time.
  - **Differential Vertical Dilatometer**: sample and reference stand close to each other. Their tips, separated by a tiny space, are framed by the **same camera**.
  - **Differential Horizontal Dilatometer**: sample sits above the reference (which can be an alumina plate). Two cameras frame the interface point between sample and reference.

The Optical Differential Fleximeter

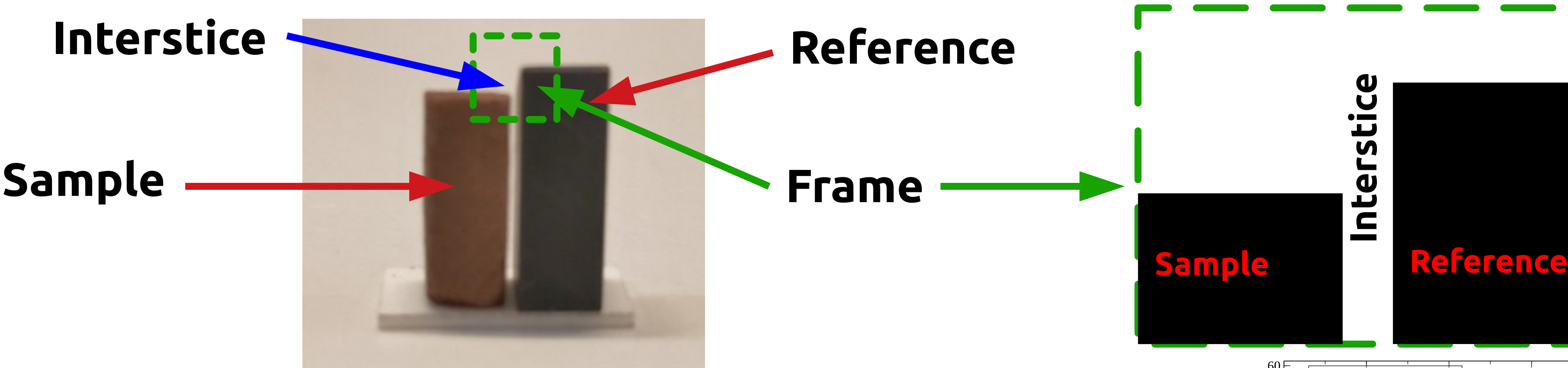


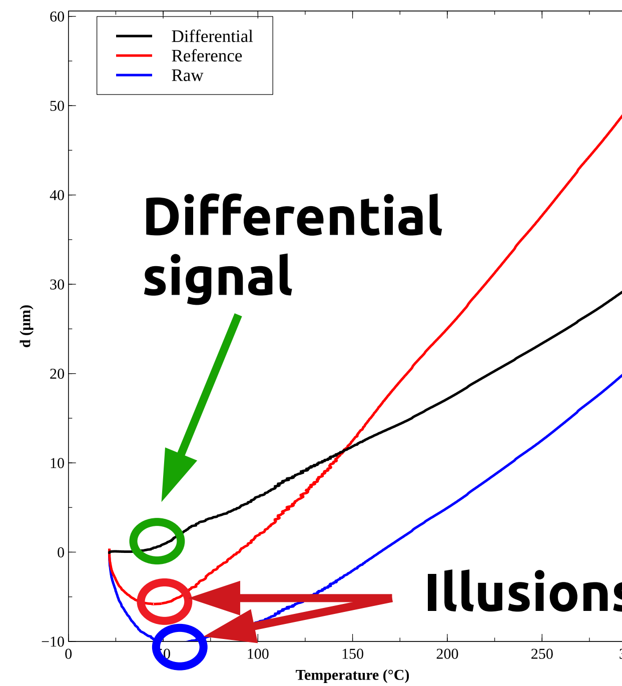


- Even though these effects are negligible for traditional ceramics, they become significant for low-CTE advanced ceramics and aerospace applications.
- The Differential Fleximeter uses a high res camera **simultaneously** frame the **Sample**, a non-bending **Reference** and the **Interstice** between.
- Both the **system's deformation** (rod's expansion) and any **thermo-optical illusions** affecting the area can be measured and **canceled in real time**.



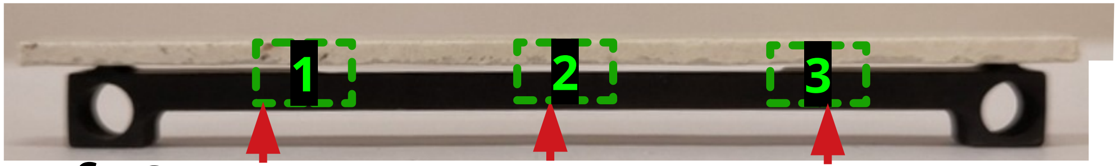
The Optical Differential Vertical Dilatometer





- Traditionally, Optical Vertical Dilatometer reads a bad signal at lowT, showing an ***apparent shrinking.*** Caused by difference in air motion between the top and the bottom of the sample.
- The situation was better with small furnaces (impractical with MoSi2). Was used only for **sintering** studies.
- The **Differential** technique **measures the illusion on the reference** and subtracts it from the sample.
- Leading to **good CTE** measurements in Vertical mode even at low T.

The case for Absolute+Differential Fleximeter



Left Camera **Center cam** **Right cam**

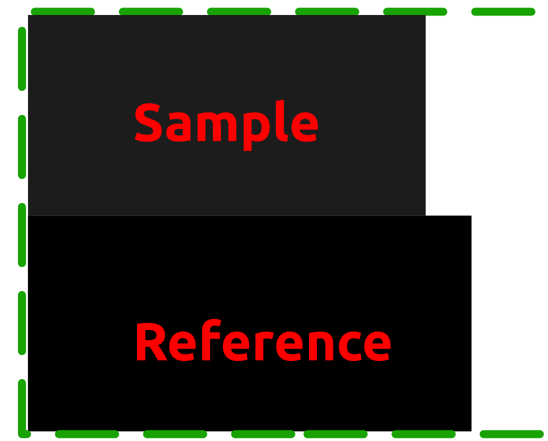
- Measuring in three-points gives an additional information about the material: is it bending like an **elastic** or a **plastic** material?
- Elastic bending follows **Timoshenko beam theory**. The material curves along a **circular** profile with a curvature radius depending on elastic moduli and CTE mismatch. Even a uniform a material will bend elastically if its modulus drops with rising T.
- **Pyroplastic** bending follows the parabolic profile of bending moments.
- Absolute+Differential can measure:
  - The relative modulus change in the elastic phase
  - The exact onset of the transition elastic→plastic

$$r=\frac{L}{6}\frac{3(1+m)^2+(1+mn)\left(m^2+\frac{1}{mn}\right)}{(\alpha_2-\alpha_1)\,\Delta T\,(1+m)^2}$$

m = thickness ratio, L_1/L_2
L = total thickness, L_1+L_2
n = moduli ratio, E_1/E_2
α = coefficients of thermal expansion
ΔT = temperature delta, causing expansion of each layer
r = curvature radius, produced by the differing expansion

Optical Differential Horizontal Dilatometer

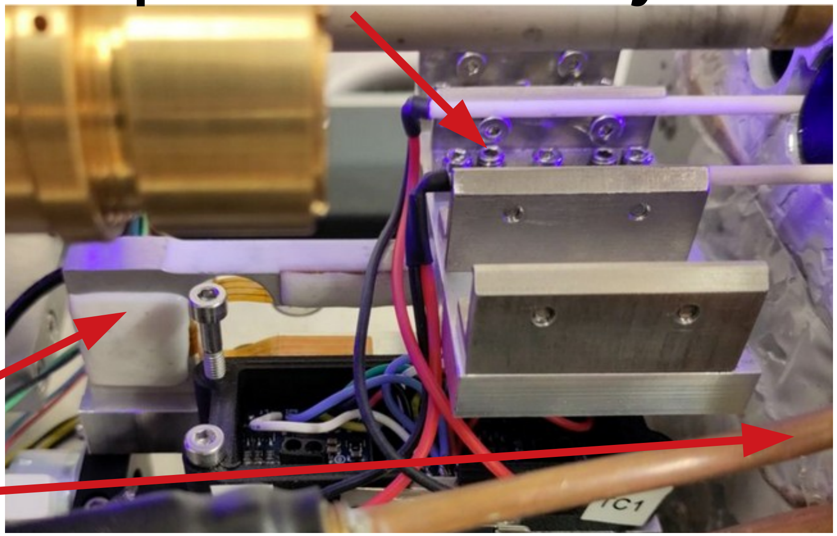
- The Horizontal Dilatometer already provides optimal results.
- In presence of **strong T transients**, the T **gradients** in the sample and with the thermocouple can produce a low-T expansion *delay*.



- The **Differential Horizontal Dilatometer** techniques allows to cancel the temperature effect. The reference sample has a large contact surface with the sample, lower thermal mass (thin plate) and can also have higher thermal diffusivity (in case of metal plate).
- This function can also measure two independent samples without any differential calculation. Doubles the productivity.
- Caveat: sample must be not stick with reference or with the second sample during the measurement!

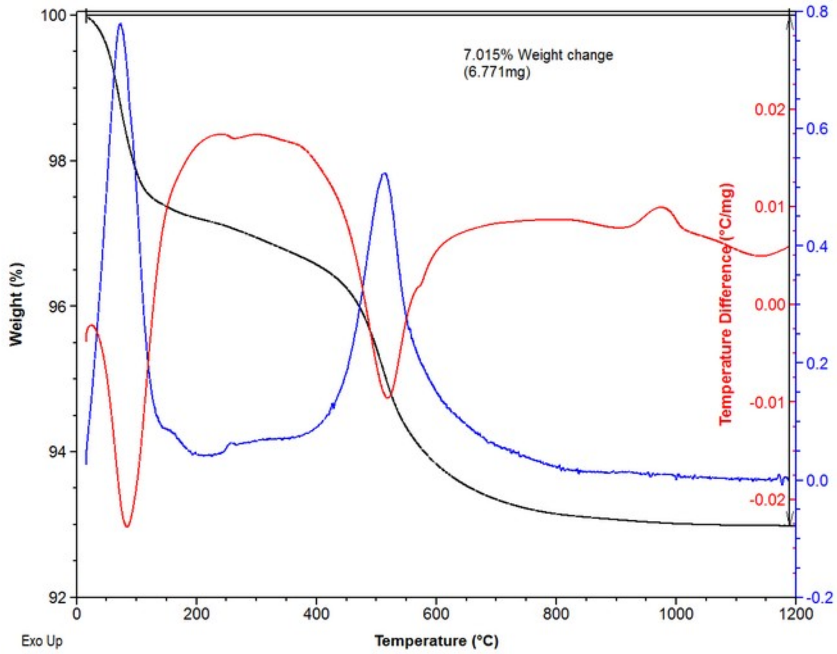
Simultaneous Thermogravimetry: Dil-TGA, Flex-TGA

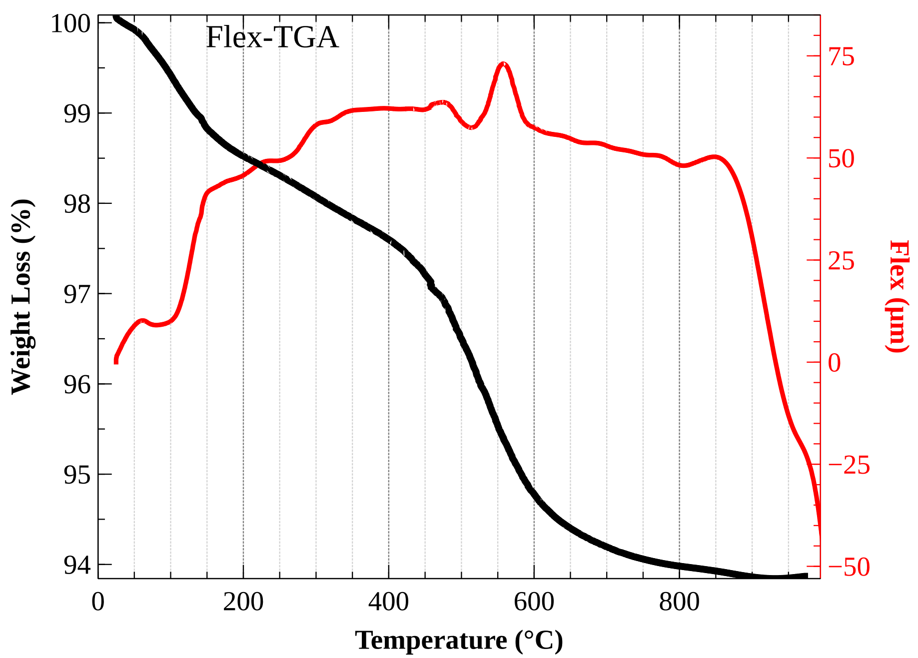
- Combined techniques offer the obvious advantage of **saving time**, as two or more properties are measured during the same test run.
- The most interesting point is **commensurability**:
  - Typical TGA setup analyzes **few mg** of material in a **tiny and slow furnace**
  - While the results can be extremely accurate, they might be not much **representative of what happens** in a **bigger** sample at **faster** rates (eg: rate of gas exchange)
- As dilatometry was traditionally a contact measurement, **no simultaneous TGA was conceivable!**
- Simultaneous TGA allows to measure weight change on the **same sample**, in the **same furnace**, with the **same thermal cycle** and at the **same time** as the dilatometric or fleximetry signal. **Commensurable**!
- We mounted the entire sample holder assembly on different types of load cells (here *one* of the iterations).



Thermogravimetry

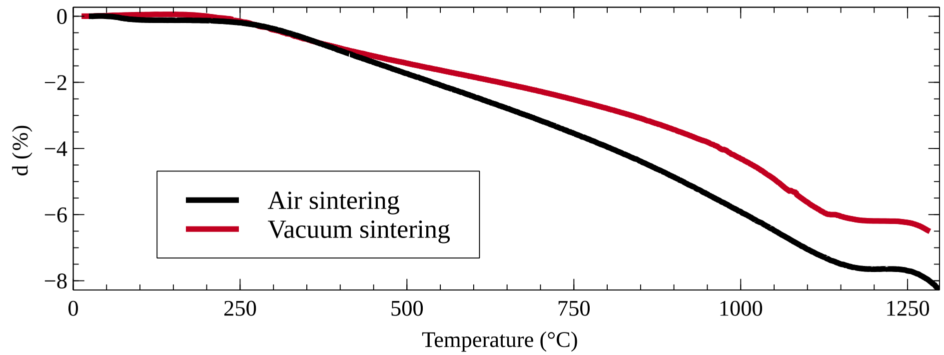
- We are testing load cells in the range 1-10mg. No ambition to compete with dedicated TGA: we aim at industrial ceramics, weight losses in the order of 2-5%. Aim at 0.1% resolution.
- Even with 10mg resolution, overall results over a typical 3gr sample are comparable with TA Instrument's QSeries DSC-TGA.
- Not aiming at measuring during Microscope analysis. Samples are too small.
- Delivery expected in Q2 2024.

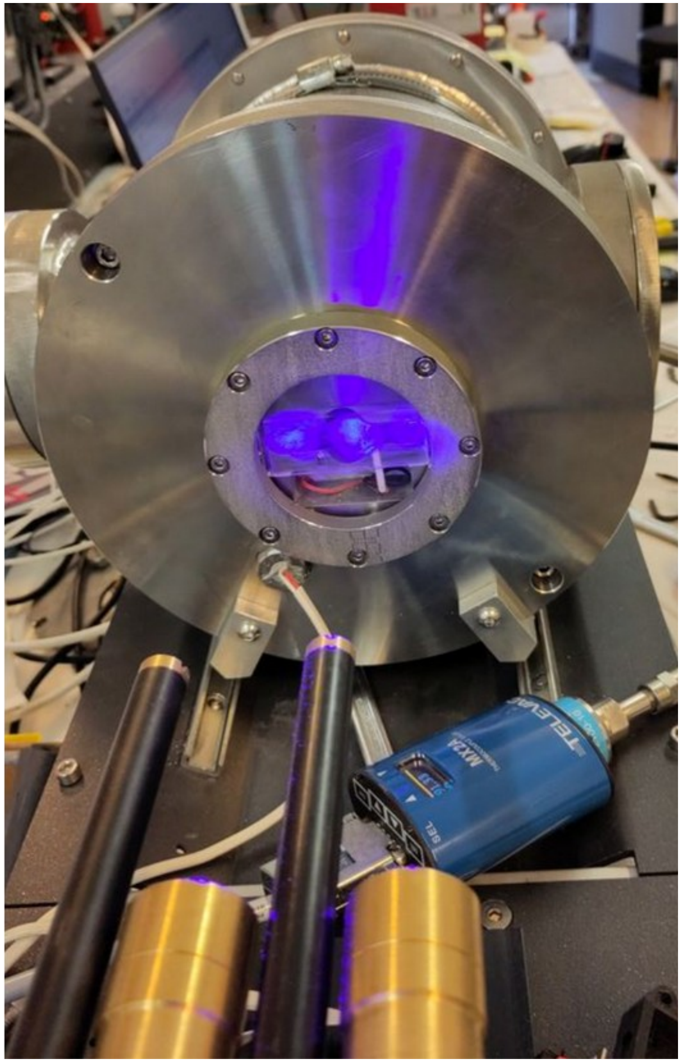




Controlled Atmosphere and Vacuum

- The entire furnace, sample holders, heating elements contacts and thermocouple is enclosed in a vacuum chamber. Mild vacuum down to 5mBar.
- Mounting our standard platinum heating elements. Tested up to 1300°C in vacuum on spacecraft thermal shields.
- By purging with inert gas and then filling slightly above atmospheric pressure, ensures absence of O2.
- Tested over 3D additive manufacturing metal alloys without signs of oxidation
- Delivery expected in Q4 2024.





Ceramics Genome: *bring ceramics alive!*

- Ceramic modeling software: from the composition of raw materials and minerals to the laboratory measurements.
- A **vertical solution specialized** in ceramics laboratory information management. Entirely web based.
- Launched for beta testing in 2022, we are now customizing the user experience.
- Two main components: Composition and **Measurements**.
- The Measurements components creates web Reports easy to **search and view**.
- Our target is to provide **standardized** plotting and calculation tools covering **most ceramists' needs** in a **simplified** package.

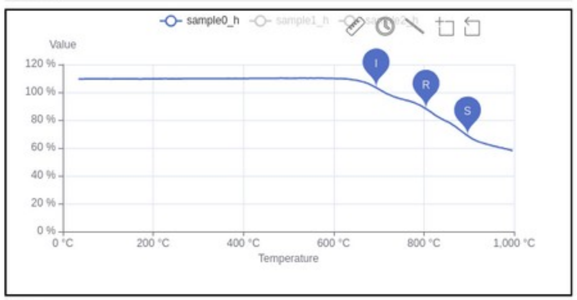
Date	O...	Name	T...	Duration	°C	°C/min
9/20/2023, 8:15:39 AM		Au granitico 20230920		78.84	1082.49	50.00
9/19/2023, 4:31:00 PM		ag granitico		25.54	979.59	50.00
6/30/2023, 11:59:52 AM		oro platino 1450		28.44	1401.48	50.00
6/30/2023, 11:59:52 AM		Alloy Au Pd 1450		28.44	1401.48	50.00
6/30/2023, 10:34:14 AM		Alloy Au Pd		53.57	1401.39	50.00
6/30/2023, 8:07:25 AM		Alloy Au Pd		142.56	742.51	5.00
6/29/2023, 1:54:50 PM		Alloy Au Pd		72.43	1398.74	50.00
5/23/2023, 7:46:48 AM		Indium 20230523 -20 80 - 1 200		83.73	160.86	20.00
5/22/2023, 8:15:25 AM		Indium 20230522 -20 80 - 1 200		83.70	160.69	20.00
5/19/2023, 7:49:36 AM		Indium 20230519 -20 80 - 1 200		86.20	163.26	20.00
5/18/2023, 1:39:29 PM		Indium 20230518 -20 80 - 1 200 ii		97.55	174.67	20.00
5/18/2023, 1:39:29 PM		Indium 20230518 -20 80 - 1 200 ii		97.55	174.67	20.00
5/18/2023, 10:45:03 AM		Indium 20230518 -20 80 - 1 200		104.87	181.90	20.00
5/18/2023, 10:45:03 AM		Indium 20230518 -20 80 - 1 200		104.87	181.90	20.00
5/18/2023, 8:01:15 AM		Indium 20230518		38.82	216.49	5.00
5/17/2023, 2:15:28 PM		Saccarin dried 20230517 stasi iii		40.77	249.50	20.00
5/17/2023, 11:12:23 AM		Saccarin dried 20230517 stasi ii		40.77	249.55	20.00
5/17/2023, 8:28:04 AM		Saccarin dried 20230517 stasi		40.84	249.38	20.00
5/16/2023, 4:27:10 PM		Saccarin dried 20230516 stasi ii		40.67	249.54	20.00
5/16/2023, 2:49:58 PM		Saccarin dried 20230516 stasi		40.60	249.49	20.00
60		60		65.26		26.63

Download table | Load all

delta t vetro finestra, HSM

Main | Logging | File | Bill | Sample0 | Sample1 | Sample2 | Admin

Name	basso sx
Sintering	693.67 °C (3956 s)
Softening	804.36 °C (4621 s)
Sphere	896.42 °C (5173 s)
Half Sphere	--- °C (--- s)
Melting	--- °C (--- s)



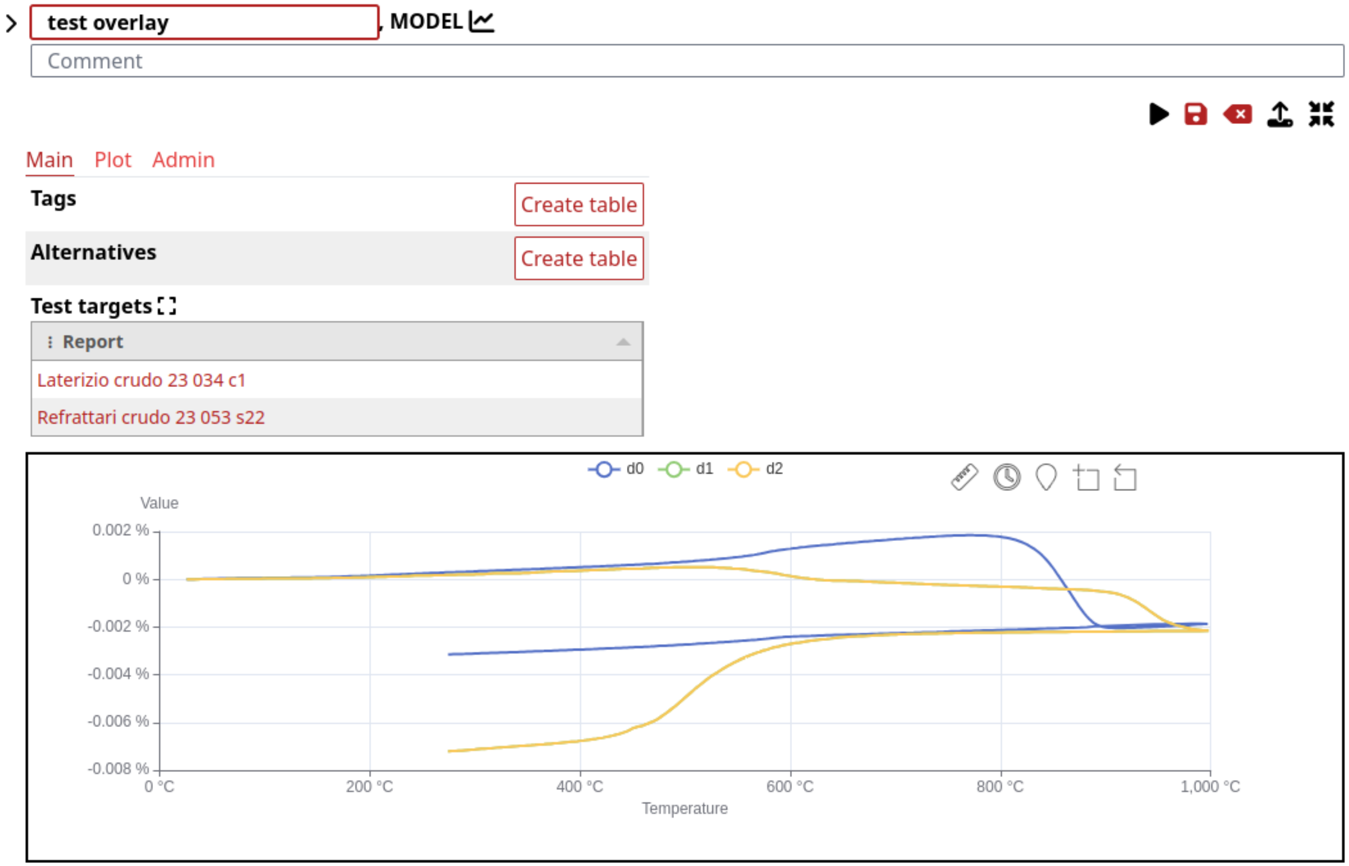
I: Sintering
R: Softening
S: Sphere

Shapes Images

Show

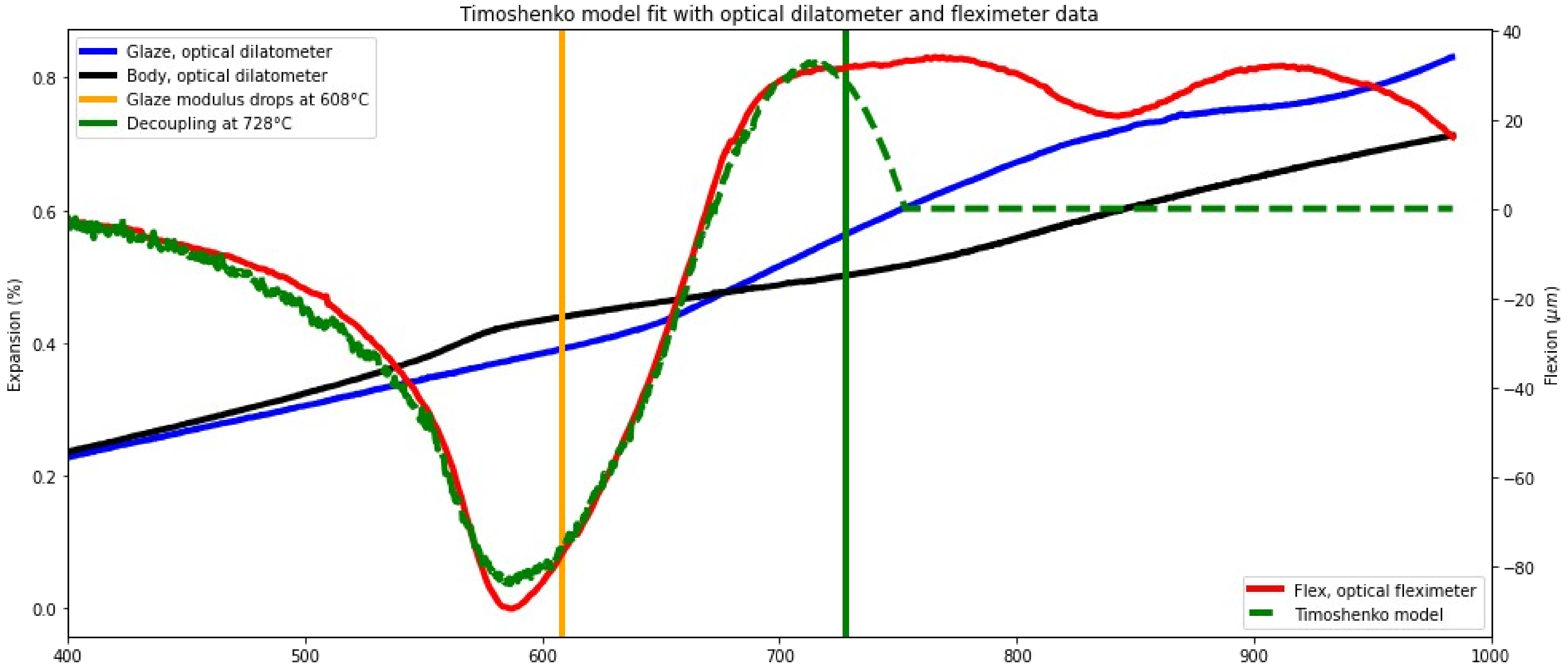
Ceramics Genome: Overlay curves

- Select any number of tests to create an overlay document that can be saved.
- Each curve can show characteristic points if found during the test.



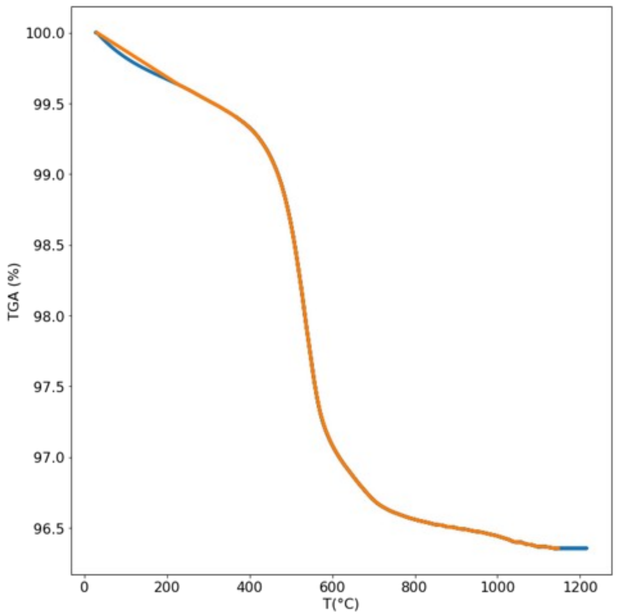
Ceramics Genome: Coupling temperature

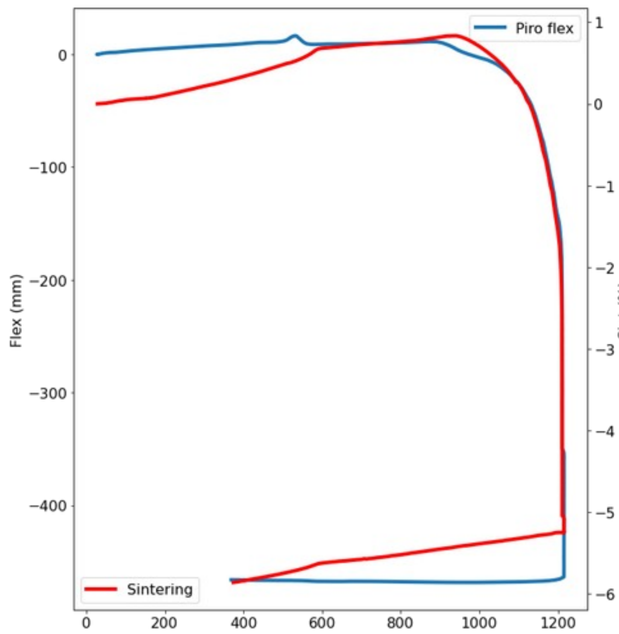
- Detect the coupling temperature from body and glaze dilatometric curves and the product fleximeter curve.
- Models the theoretical Timoshenko curvature from the dilatometer tests and detects the point at which the real fleximeter departs from the prediction as the coupling T.

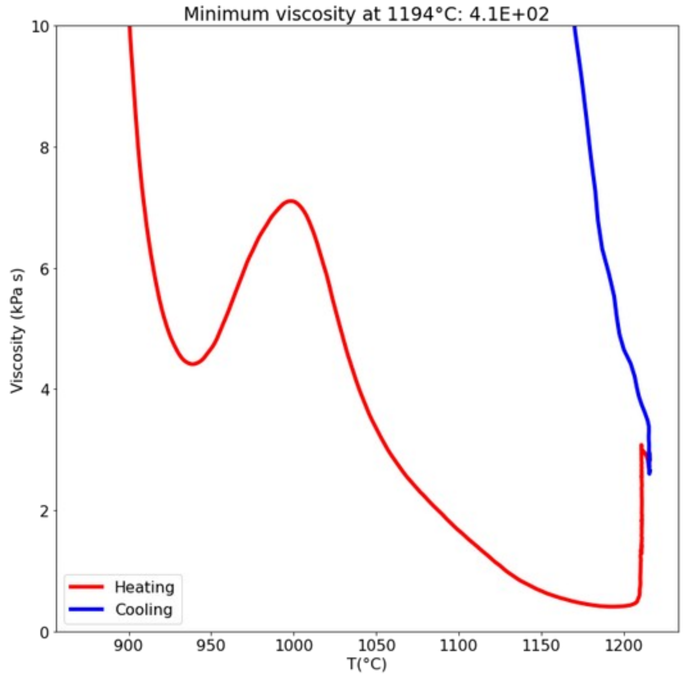


Ceramics Genome: Viscosity

- Based on the equations from Adcock, Drummond, McDowall (1959)
- Measurement Inputs: Flex, to calculate the speed of deformation; Dilatometer, to correct the volume of the sample; TGA, to correct the density. Can use Flex-TGA and Dil-TGA signals.
- Needs initial density and sample's geometry if not saved by the operator in the test file.





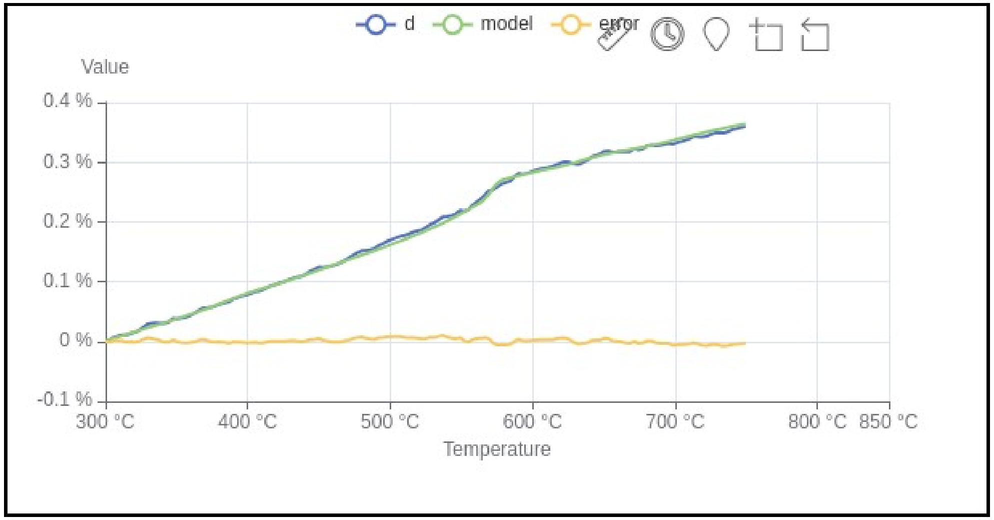


Ceramics Genome: Quartz estimation

- Estimate the volumetric quartz content based on the shape of the quartz transition.
- Select the curve, input bulk density if known, play.
- Outputs the estimated volume and weight, and the model plot showing the discrepancy between the predicted curve and the real one.

Main Plot Data Output Admin

Success	×
Message	---
Quartz Volume	11.09 %
Quartz Weight	12.56 %
Finest quartz fraction	---
Intermediate quartz fraction	---
Rough quartz fracion	---



Thank you

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