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The Glassomer Technology: A Novel Approach to Shaping Mankind's Oldest Material

Why we need 3D Printing to be better than the Romans

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Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT)

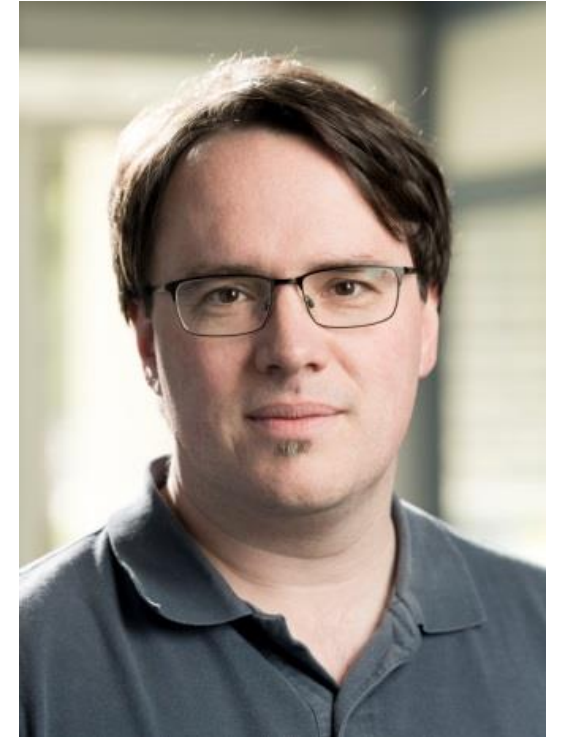


About the speaker

Prof. Dr.-Ing. habil. Bastian E. Rapp

- 2005, mechanical engineering
2005 Applied Cultural Sciences
University of Karlsruhe
- 2008, PhD in Microfluidics and Biosensors
University of Karlsruhe
- 2017, Habilitation on fluid mechanics and microfluidics
Karlsruhe Institute of Technology (KIT)
- 2018, Full Professor Process Technology, IMTEK, University of Freiburg
- 2018, Founding CEO and current CTO of Glassomer GmbH
- several industry/academic awards (selection): *Edison Award*, *Südwestmetallpreis*
- only supervisor to have two PhD students win the *Deutscher Studienpreis*

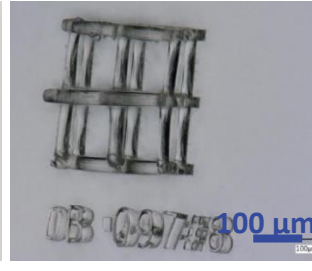
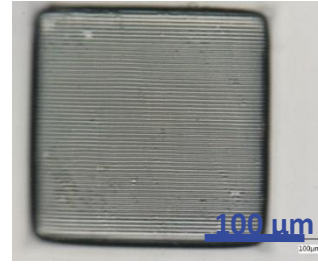
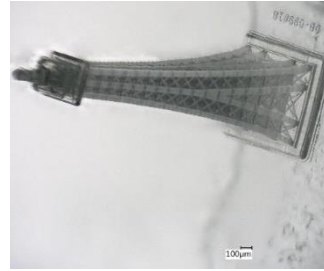
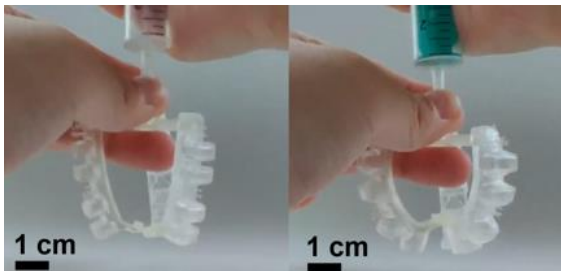
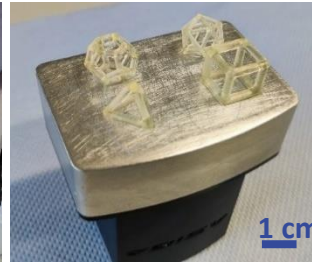
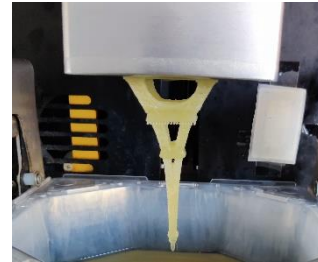
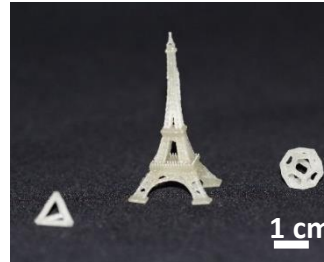
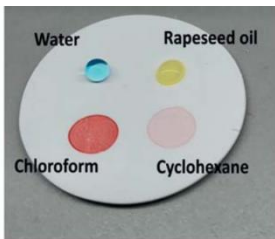
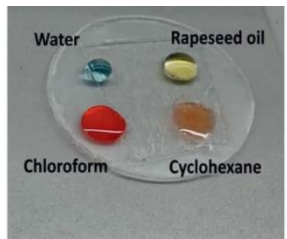
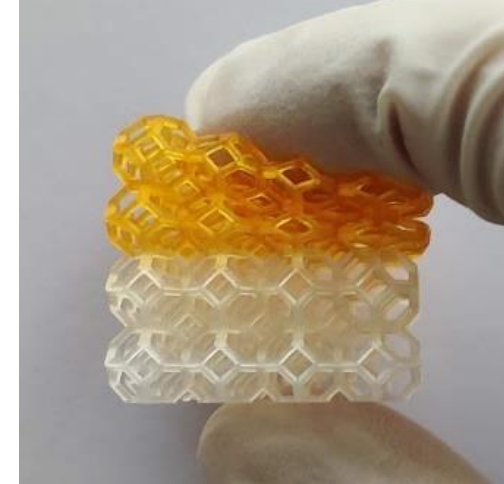
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Laboratory of Process Technology
Department of Microsystem Technology (IMTEK)
University of Freiburg



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About my group, about myself

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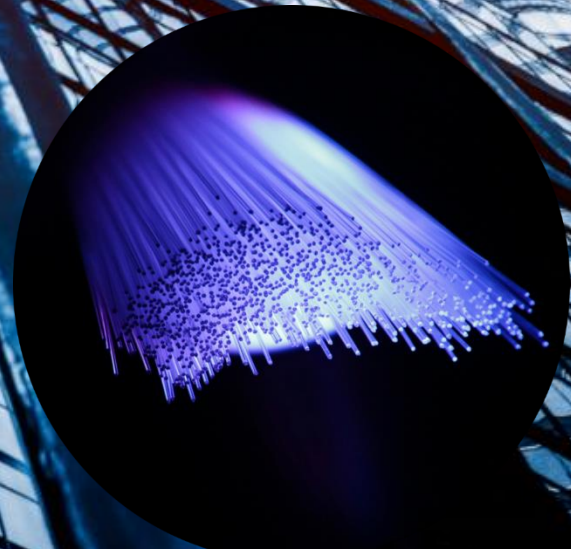


- interdisciplinary group: chemists, engineers, biologist and physicists
- focus on microsystem engineering, material design as well as process, instrumentation and application development
- several academic and industrial awards
- publishes in the most important international journals including *Advanced Materials*, *Lab-on-a-Chip*, *Angewandte Chemie* and *Nature* as well as *Science*

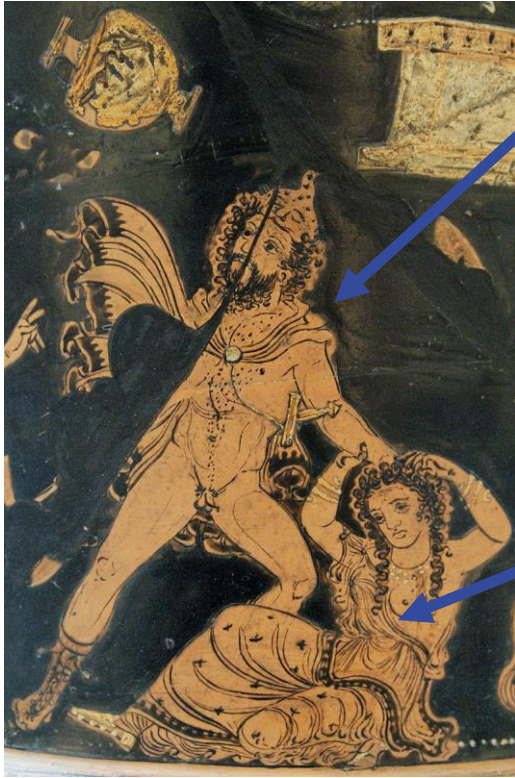
Glass – a fascinating material

Glass has shaped the history of mankind for more than

5000 years



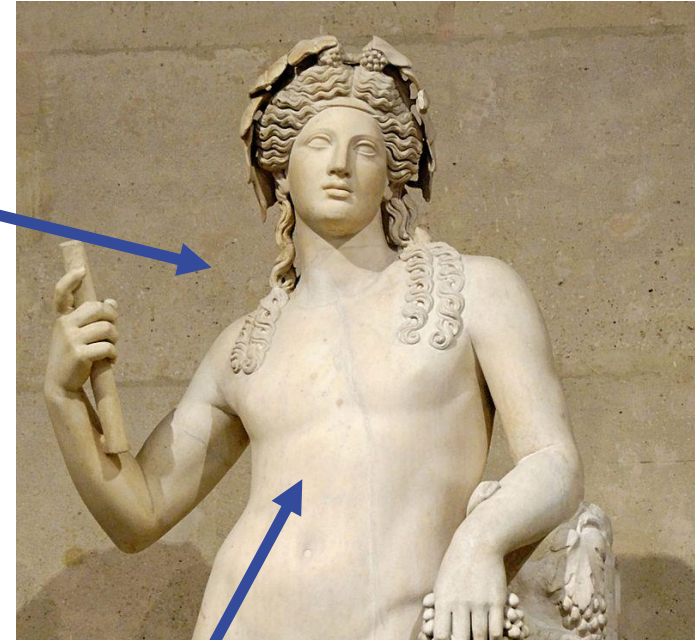
Once upon a time in Greece (like a long (mythical) time ago)



Lycurgus of Thrace (king of Edoni)

banned the cult of **Dionysus**
(the god of wine-making,
aka **Bacchus**)

and imprisoned his followers
including **Ambrosia**



which enraged **Dionysus** who transformed
Ambrosia into a **vine**

which restrained and mocked and then
ultimately killed **Lycurgus**



Source: British Museum, Wikimedia, 04/2023

The Romans – a tale of ...



great conquerors



impressive architecture



the first Autobahn



Formula 1



important contributions to science
(slaying Archimedes come to mind)



But some very impressive craftsmanship
The Lycurgus Cup

- green color: reflecting light → silver nanoparticles
- red color: transmitting light → gold nanoparticles

**(proudly created by stirring glass with a dirty spoon
– quite literally)**

Discover the Lycurgus Cup

Did you know the Romans (sort of) invented nanotechnology?



Though it measures just 15.9cm by 13.2cm, the Lycurgus Cup has been described as the most spectacular glass of its period. Housed in the British Museum, the beautiful piece is one of the most interesting surviving objects from the Roman Era.





Glass Manufacturing Lacks Innovation



Melting / Glass blowing

- ☹ high temperatures ($>1000\text{ }^{\circ}\text{C}$)
- ☹ dangerous

Grinding

- ☹ only simple geometries
- ☹ wastes material

Etching

- ☹ only simple geometries
- ☹ very dangerous chemicals (HF)

A lot has happened in the 21st century: **the polymer revolution**

- Injection molding et al. → fast and scalable
- 3D Printing → versatile and intricate

Conventional Glass making

Melting

requires

7.7 GJ/ton

Refining

requires

3.7 GJ/ton

Shaping

requires

5.6 GJ/ton



Toothpaste to the rescue!



INGREDIENTS/SKŁADNIKI/COCTAB/INCI: AQUA, PARAFFINUM LIQUIDUM, CERA MICROCRISTALLINA, GLYCERIN, SORBITAN SESQUIOLEATE, OENOTHERA BIENNIS OIL, MAGNESIUM SULFATE, PARFUM, PANTHENOL, **SILICA**, DIMETHYL SILYLATE, CALCIUM PCA, PHENOXYETHANOL, IMIDAZOLIDINYL UREA, METHYLPARABEN, ETHYLPARABEN, PROPYLENE GLYCOL, PEG-8, TOCOPHEROL, ASCORBYL PALMITATE, ASCORBIC ACID, CITRIC ACID, BENZYL SALICYLATE, CITRONELLOL, HEXYL CINNAMAL, BUTYLPHENYL METHYLPROPIONAL, LIMONENE, LINALOOL, ALPHA-ISOMETHYL IONONE, GERANIOL.

TESTOWANY DERMATOLOGICZNIE - DERMATOLOGICALLY TESTED

Najlepiej użyć przed końcem: data i nr serii na opakowaniu
/Best used before the end of: date and batch No. on the packaging
/Годен до: дата и номер партии на упаковке

50 ml/мл
1,7 fl. oz.



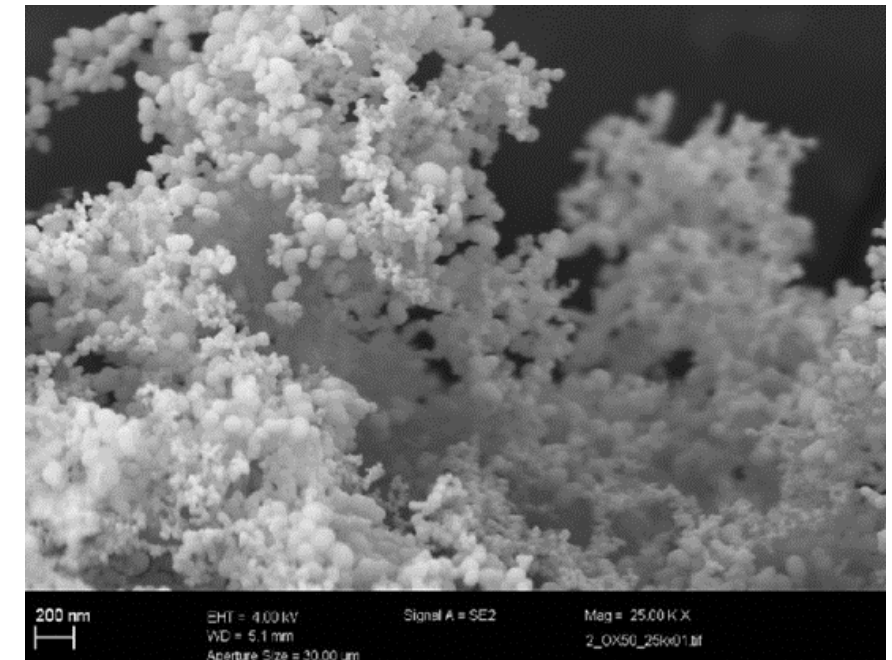
Q CENTRUM PORAD
0801 888 988

Miraculum S.A.
Al. Jerozolimskie 184 B,
02-486 Warszawa,
ul. Prof. M. Bobrzyńskiego 14,
30-348 Kraków, Made in Poland,
www.miraculum.pl



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- silica (nanoparticles) are a common admixture used in cremes and lotions
- they are cheap and readily available
- and essentially glass in its smallest form



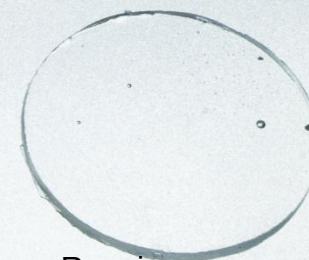
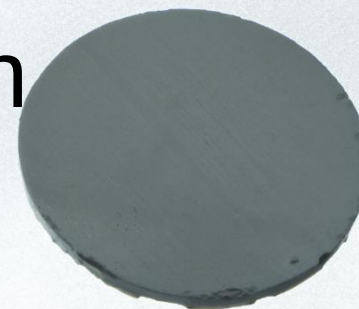
Source: Amazon, Heraeus

A new approach: The Glassomer Technology

Material Production

requires

2.9 GJ/ton



Requires

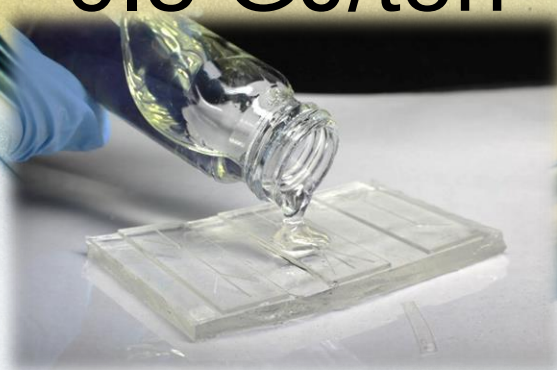
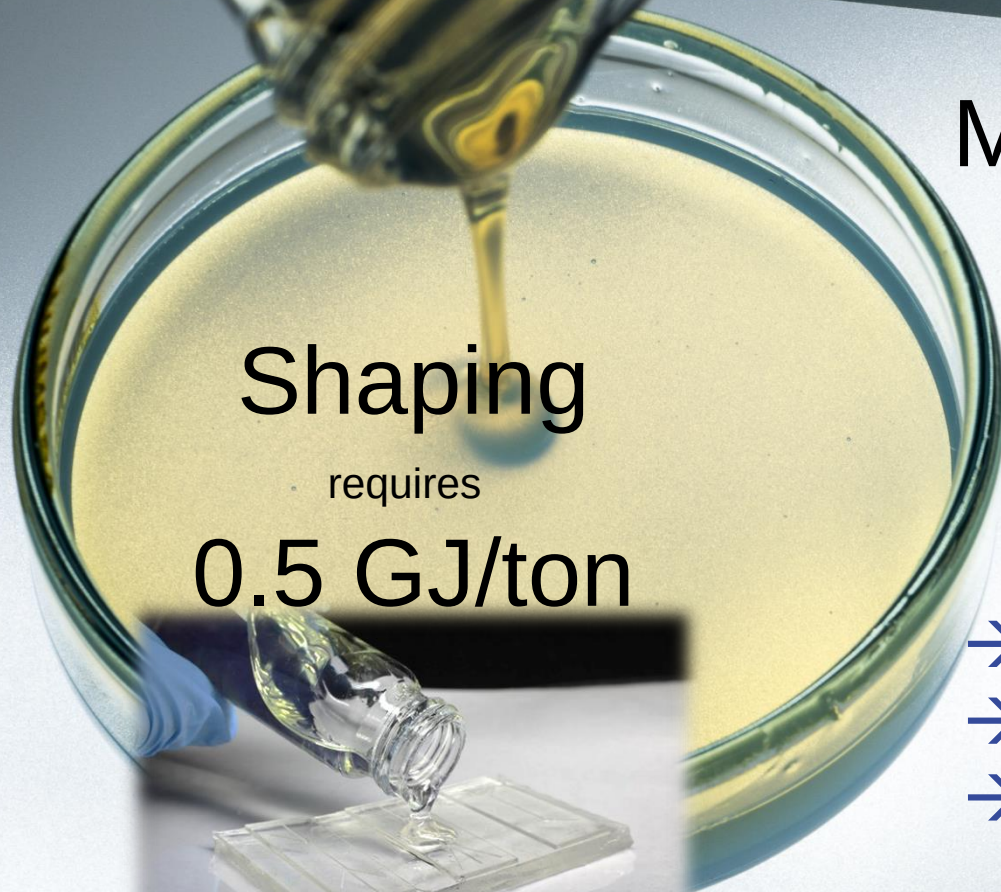
No Refining



Shaping

requires

0.5 GJ/ton



- 80 % less energy required
- Almost unlimited designs
- Highest purity

Glassomer materials behave and look like polymers.

When you put them in an oven, this happens:



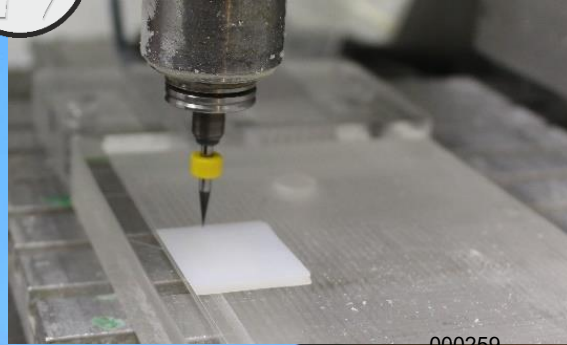
The polymer is converted to glass!



Injection Molding



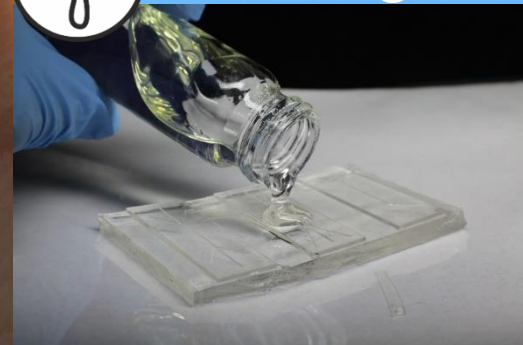
CNC Machining



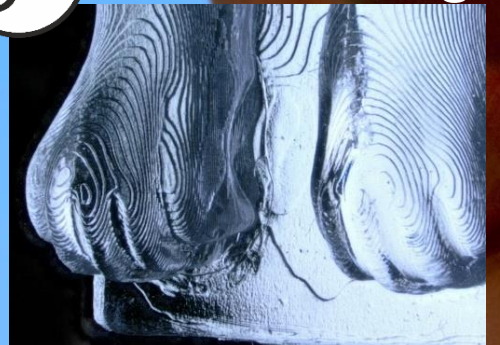
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Casting

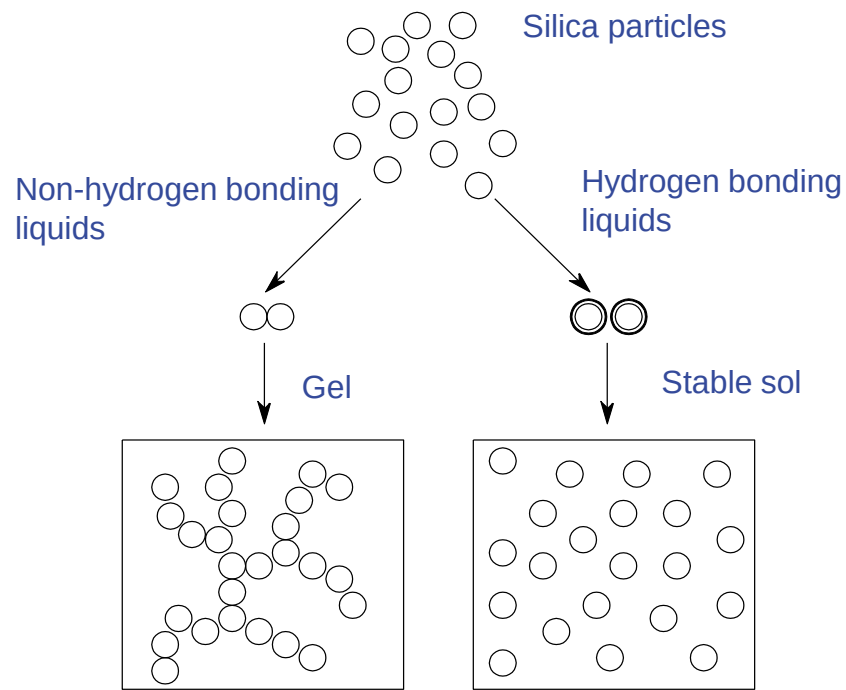


3D Printing

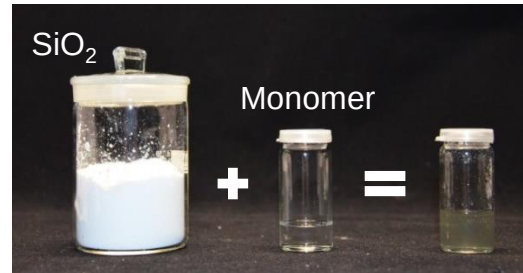
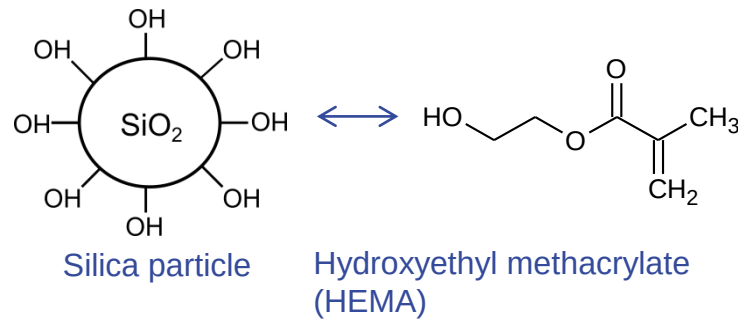


Glassomer® Technology: The silica in toothpaste

- Requirement for high quality glasses: high powder content
- Liquids, pastes or solid Glassomer® materials



Adapted from: Raghaven *et al.*, *Langmuir* **2000**



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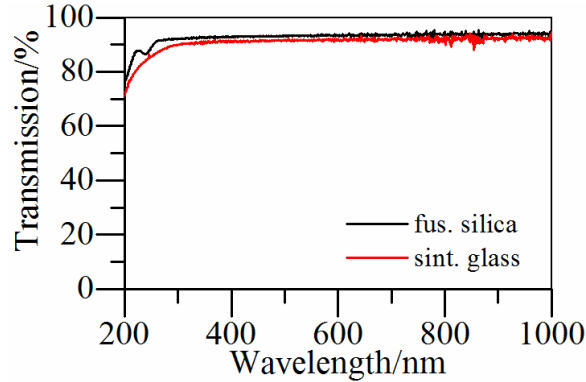


Kotz *et al.*, *Adv Mat* **2015**

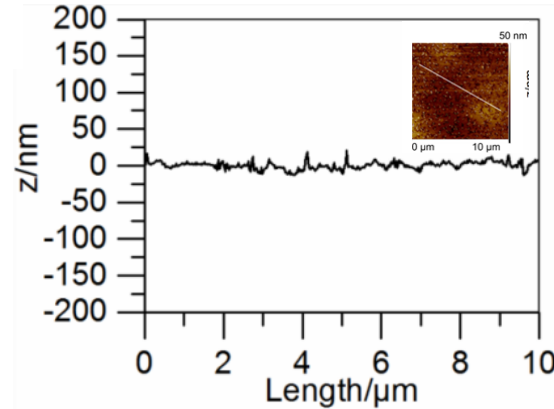
Glassomer® glass = Fused Silica



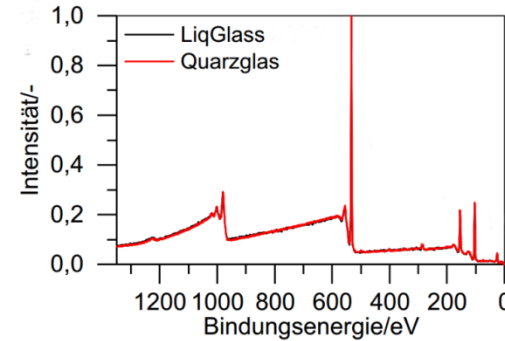
High Transparency



Low Surface Roughness



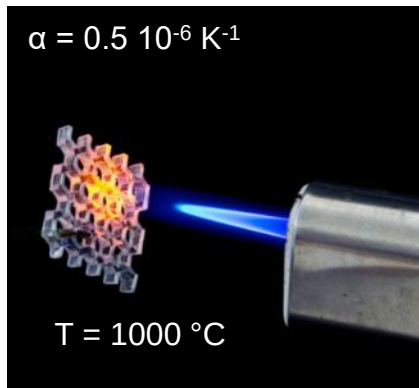
XPS



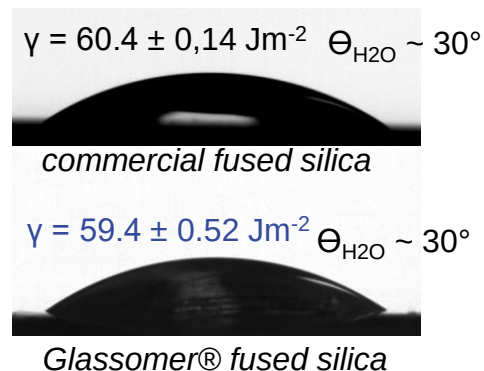
Hardness (Vickers)

Glassomer: 980 HV
Comm. fused silica: 800 HV

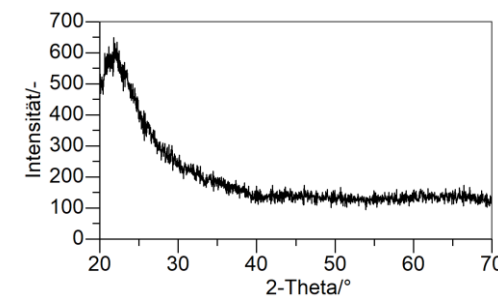
Thermal Resistance



Surface Properties



XRD



Bending strength

Glassomer: 115 MPa
Comm. fused silica: 100 MPa

Kotz et al., Nature 2017

“One of the most important innovations in the field of glass processing of the last 400 years”

NYPTUN
Laboro

World Premiere
Injection molding of glass
Check out our newest technology in

Science



Glassomer Technology published in Science

Our worldwide unique technology of glass making is published in Science - check out how glasses will be made in the future!

Tracking pandemic virus threats in Thailand's bats p. 234 | A subset of killer T cells help restrain human immune responses pp. 243 & 265 | Aerosols can focus incident light internally p. 293

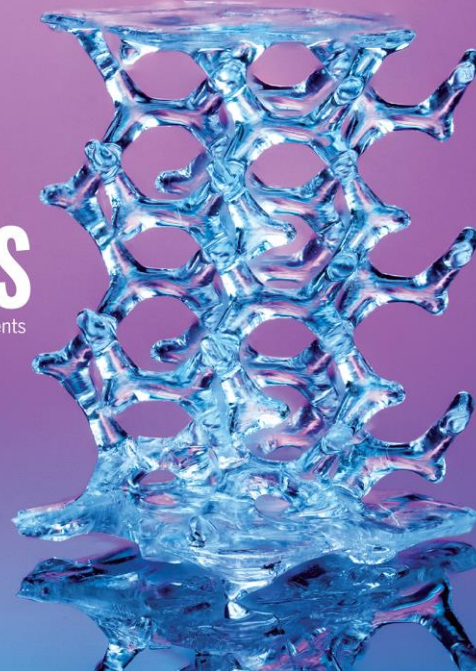
Science

\$15
15 APRIL 2022
science.org

AAAS

PRINTED
GLASS

Microscale components
made using axial
lithography p. 308



Our first paper in **nature**



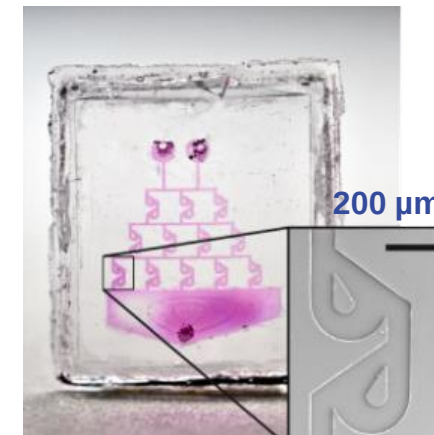
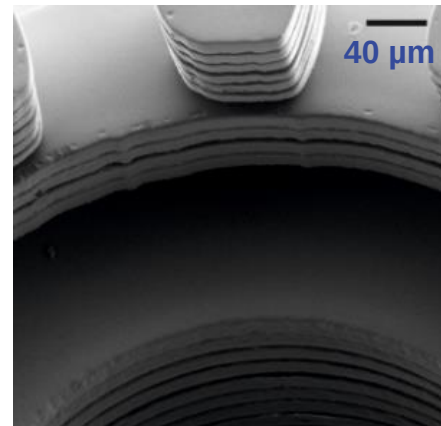
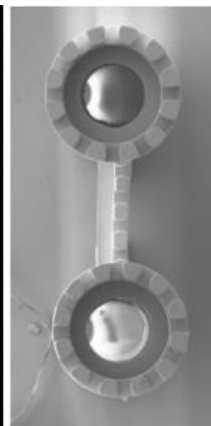
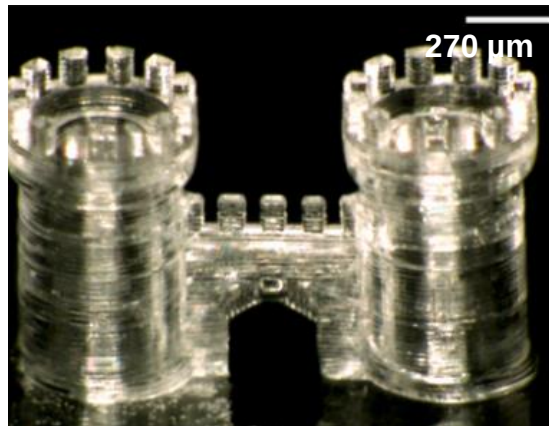
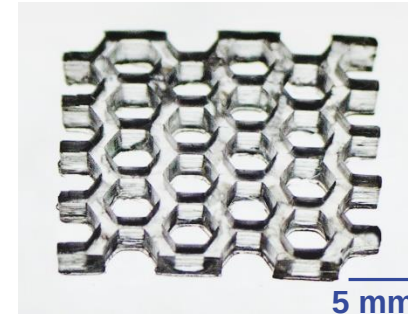
Our first Nature paper!
Three-dimensional printing of transparent fused silica glass

Glassomer® 3D Printing

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- Structure glass by using
 - liquid Glassomer®
 - off-the-shelf 3D printers
 - high resolution microstereolithography

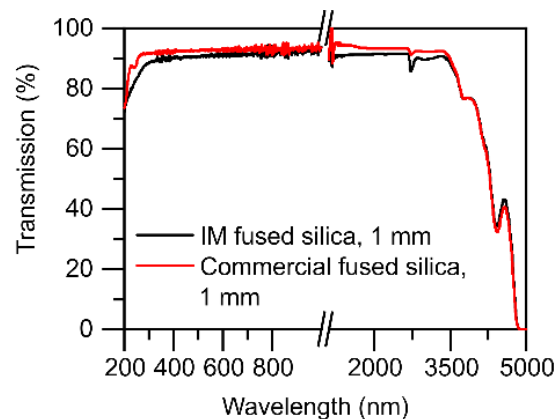
Kotz *et al.*, Nature 2017



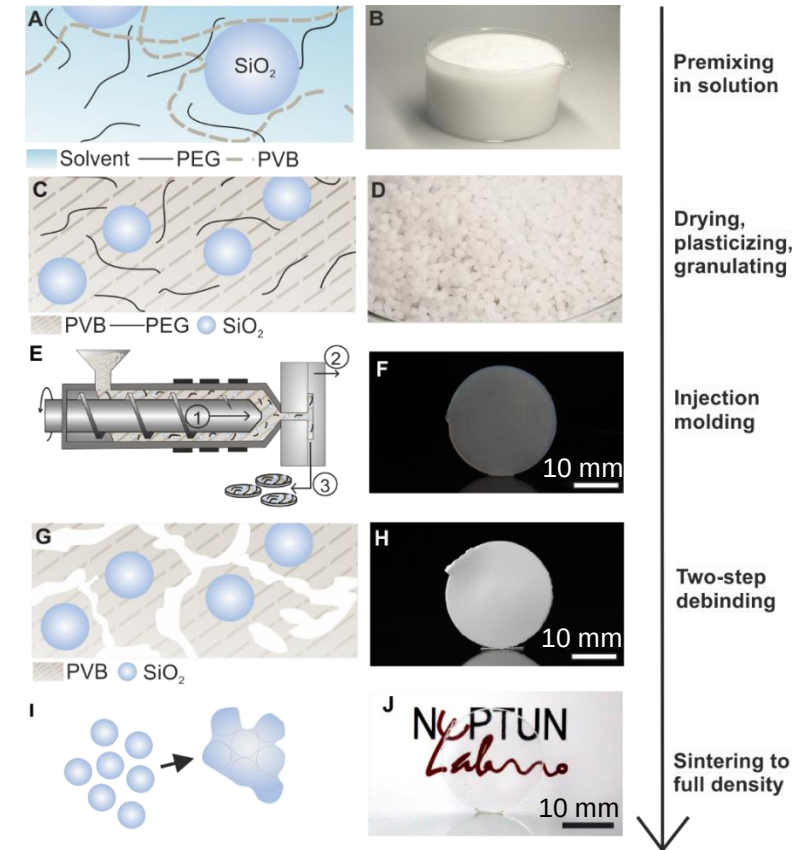
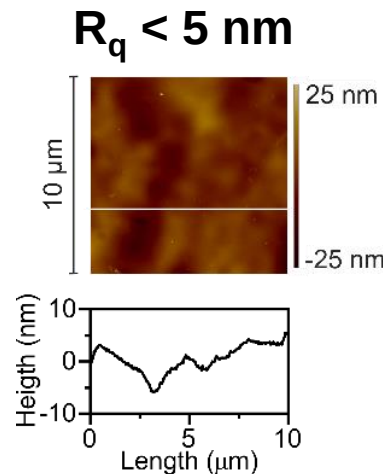
What about injection molding?

Powder injection molding

- Thermoplastic silica nanocomposites
 - Thermoplastic binder
 - Premixing step to avoid abrasion
- Processing temperature $\sim 130^\circ\text{C}$
- High-quality fused silica glass



Mader, Science, 2021

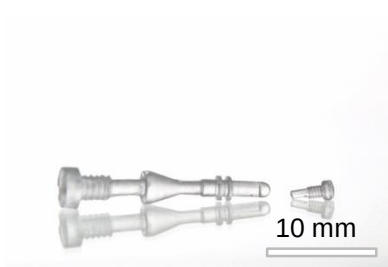


Mader, Science, 2021

Injection molding of fused silica glass

High-throughput, fully automated injection molding

Complex shapes



Mader, Science, 2021

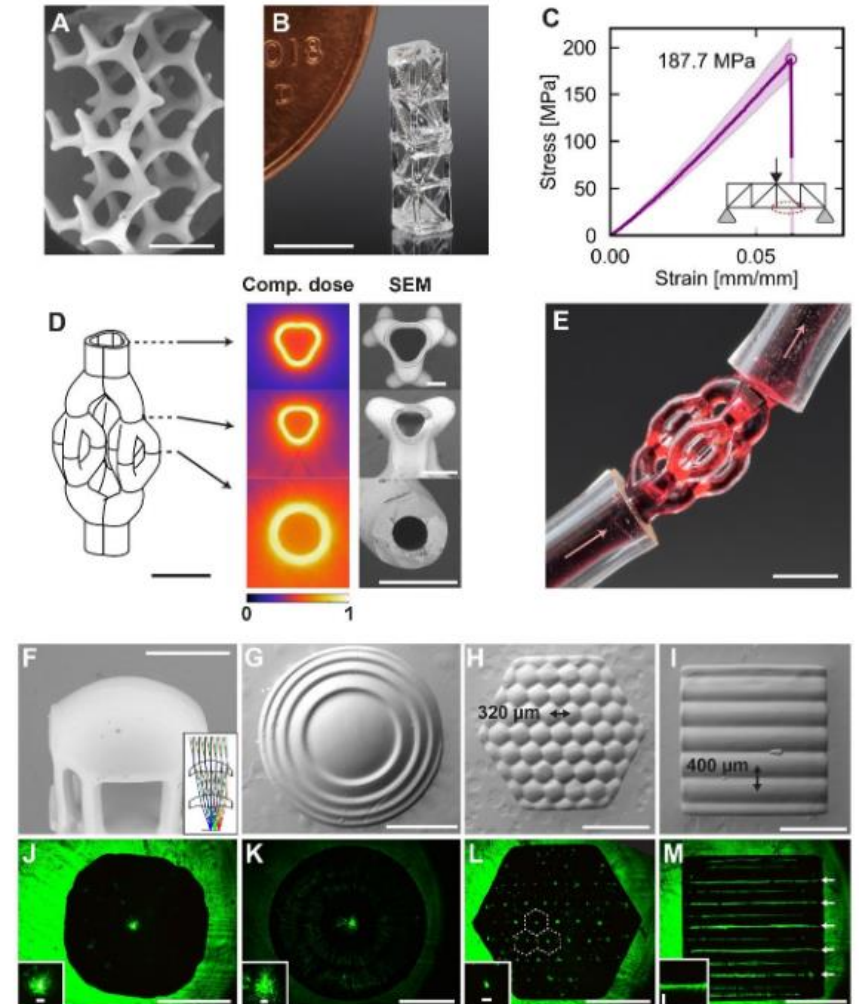
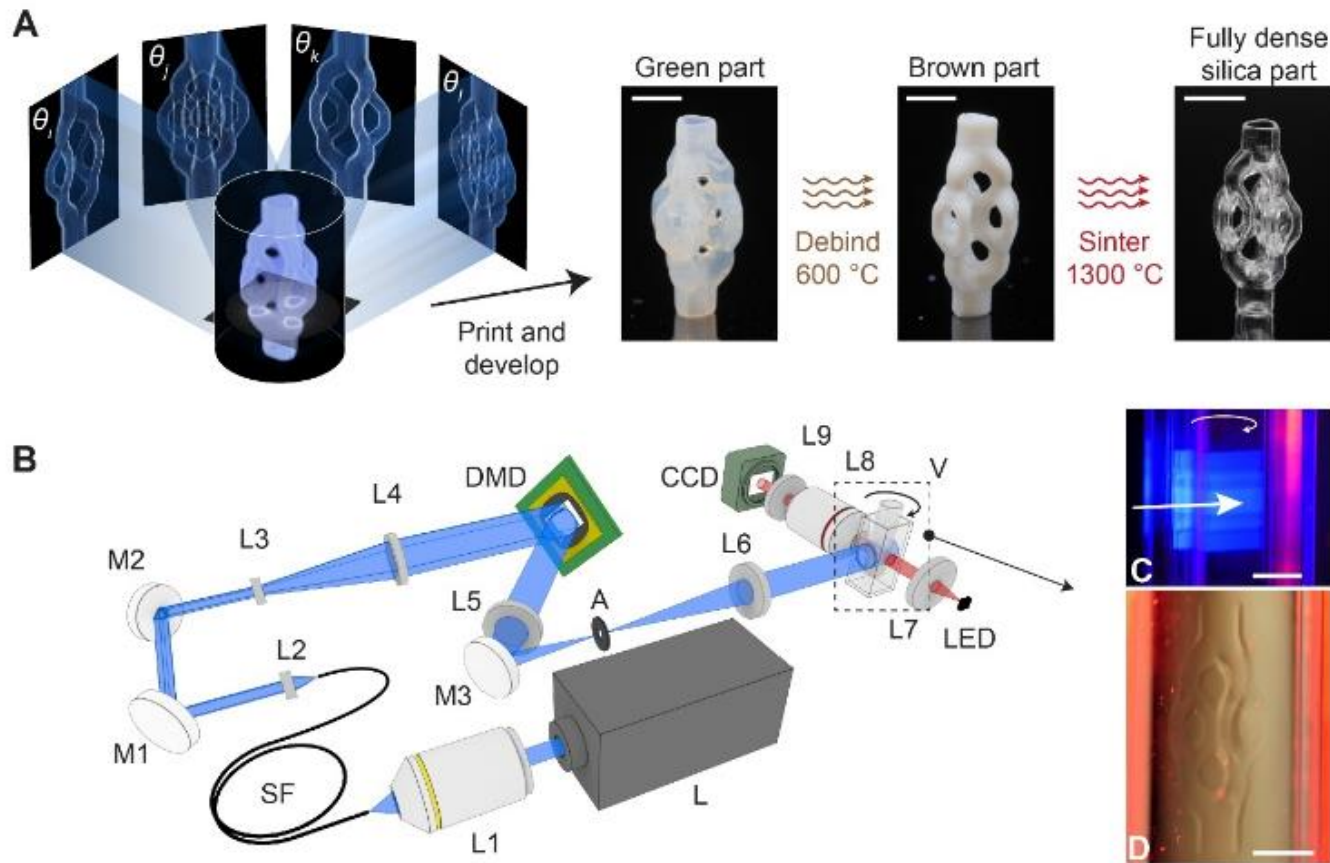


Optics



Glassomer meets CAL

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Toombs *et al.*, Science, 2022

Revisiting history: The Lycurgus Cup in the 21st century



Roman glass cup from 4th century AD

- green color: reflecting light → silver nanoparticles
- red color: transmitting light → gold nanoparticles

Essentially

- Roman Nanotechnology
- still very challenging to create with today's technology

Approach

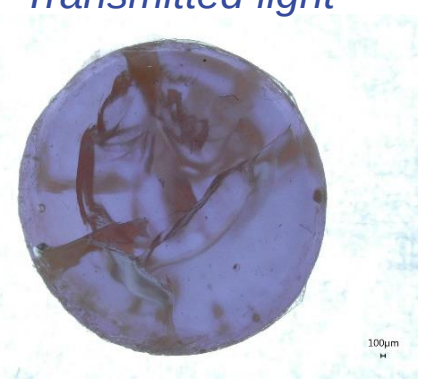
- synthesis nanoparticles (stabilized, monodisperse → tricky but possible)
- mixed into a Glassomer slurry
- cure, debind and sinter such that the nanoparticles do not diffuse
- try to 3D print



Reflected light



Transmitted light



It works!
(although the color is still slightly off)

Acknowledgements

Thank you for
your attention!

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Lab

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All former members of the group.

All current and former students, Hiwis and interns,

All our collaborators from academia and industry.



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