# Glass in a sustainable future

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*Aalborg University, Denmark*

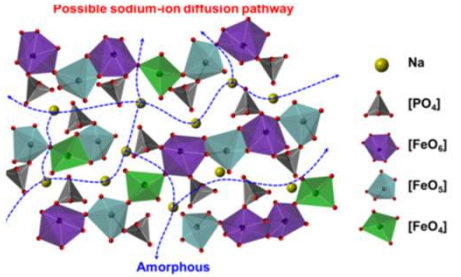
*GLASKONGRESSEN, Hindsgavl slot, November 22, 2022*

# Laboratory for Disordered Materials

**Mission: Understand and develop glass and disordered materials**

AALBORG UNIVERSITY
DENMARK

Started by Yue in 1998; now 26 researchers




## Research groups

### Vittorio Boffa

Associate Professor
*Ultra-Permeable Membranes*
(5 researchers)

**Highlights:**
*J. Membr. Sci. 2014, 2014*
*Carbon 2017, 2018*

E-mail: vb@bio.aau.dk

### Morten M. Smedskjær

Professor
*Oxide Glass Chemistry*
(13 researchers)

**Highlights**:
*Phys. Rev. Lett*. 2010, 2017
*Chem. Mater*. 2009, 2010, 2016, 2017
*ACS Appl. Mater. 2017, Adv. Sci.* 2019
Sci Adv. 2020, ACS Nano 2021

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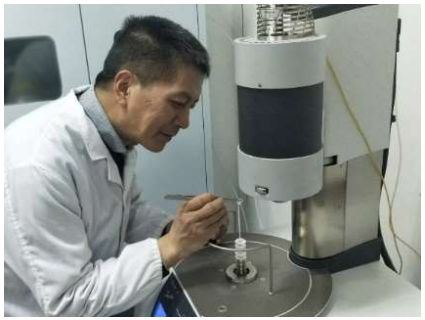

### Yuanzheng Yue

Professor
*Functional Disordered Materials*
(8 researchers)

**Highlights:**
*Nature* 2004, 2005; *JACS* 2010, 2016
*Phys. Rev. Lett*. 2006, 2008, 2010, 2014; *Nat. Commun. 2015, 2018; Adv. Mater*. 2017; *Sci. Adv.* 2018; *Nano Energy* 2018, 2019; *Chem. Rev.* 2019; *Science* 2020, 2022

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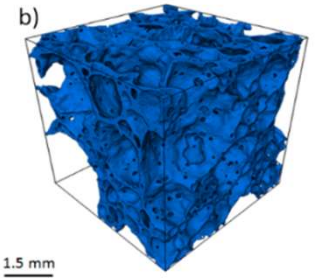
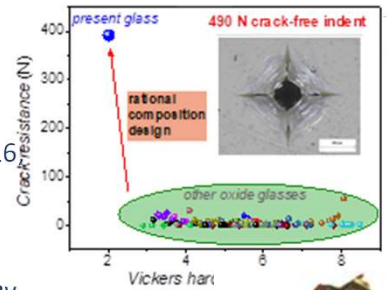
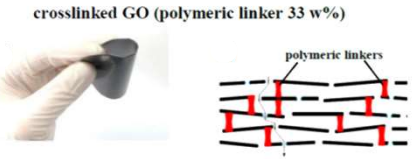
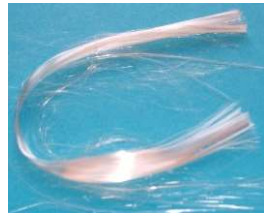
## Our research focuses on:

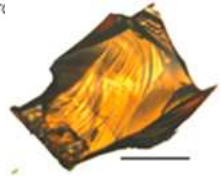
1. Glass for energy storage (Li ion batteries….)
2. Glass for energy saving (stone wool, glass foams)
3. Glass for energy generation (wind energy, solar cells)
4. Glass for reducing $CO_2$ ( in cement production)
5. Bioactive glasses (enzyme immobilization, dental and bone applications)
6. Ultrastrong glasses for display devices and engineering
7. Microstructure modeling and simulation
8. Metal-organic framework glasses
9. Molecular separation membranes
10. Supercooled liquids, glass transition and relaxation

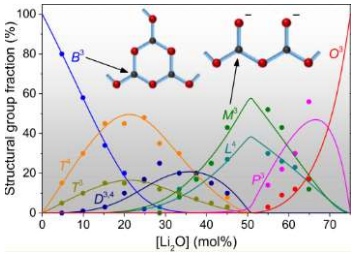


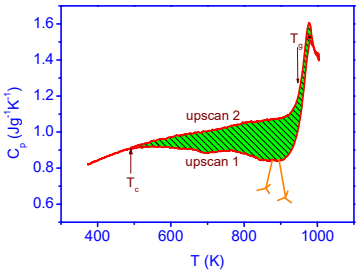







**Another mission: Conduct high quality education**

# Outline

- A brief overview about glass
- Glass’ key role in mitigating climate change
- My group’s glass activities

# Overview about glass

# What is Glass?

*"Glasses are **disordered** materials that lack the periodicity of crystals but behave mechanically like solids"*

- P.G. Debenedetti, F.H. Stillinger

*"Any material that exhibits **glass transition behavior** is a glass"*

- J.E. Shelby

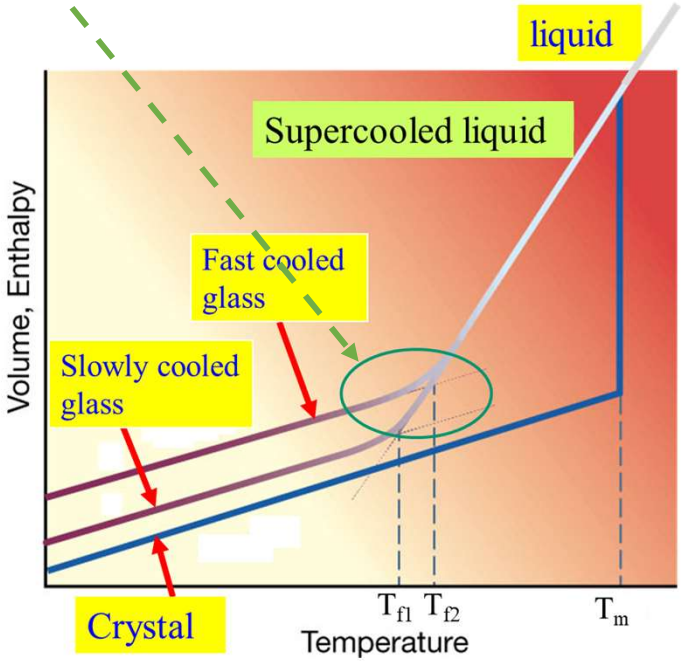
Definition for those who like glass:

*"Glass is frozen beauty."☺*

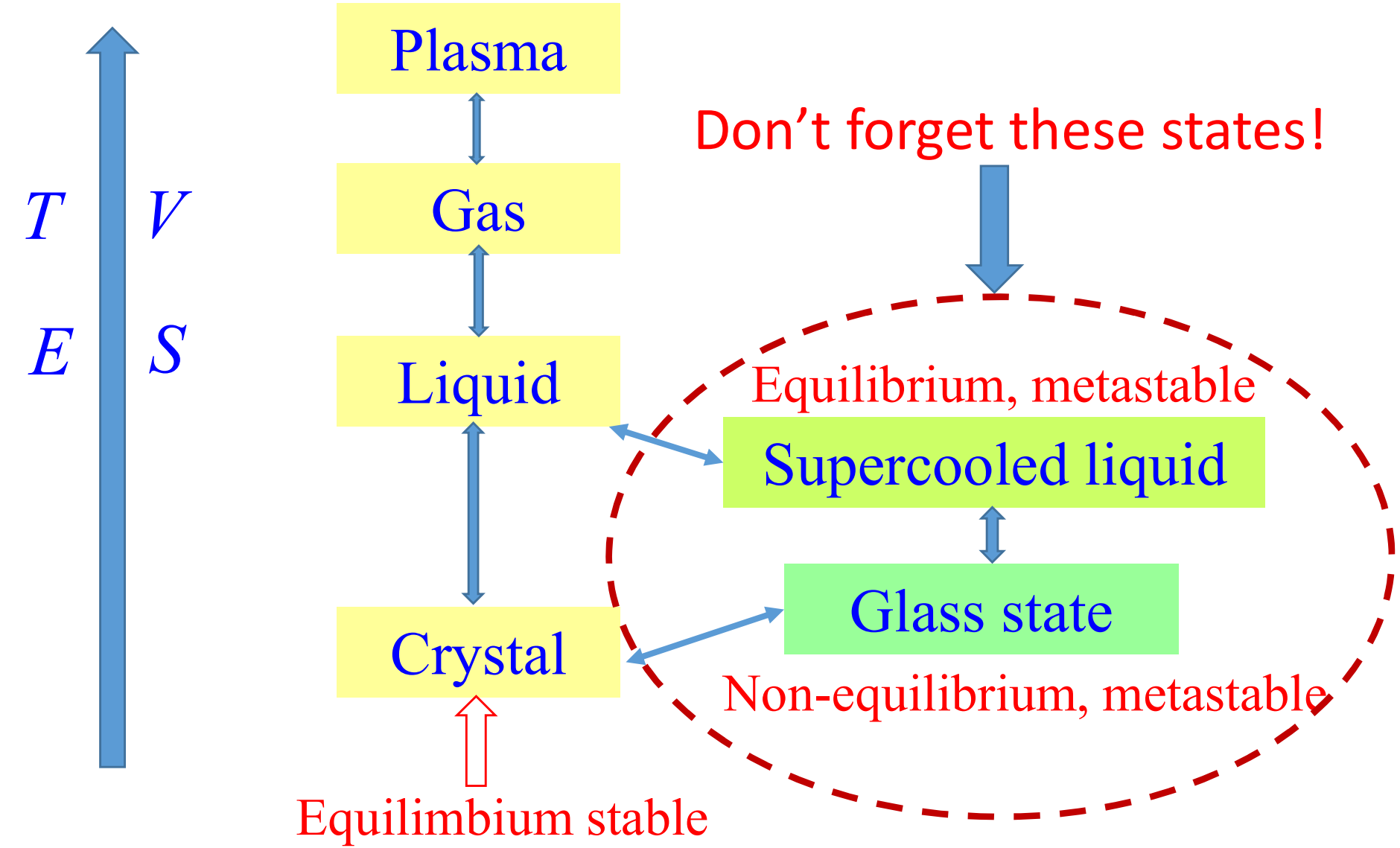
C. A. Angell

*"Glass is a fascinating state of matter."☺*

Y. Z. Yue



# States of Matter



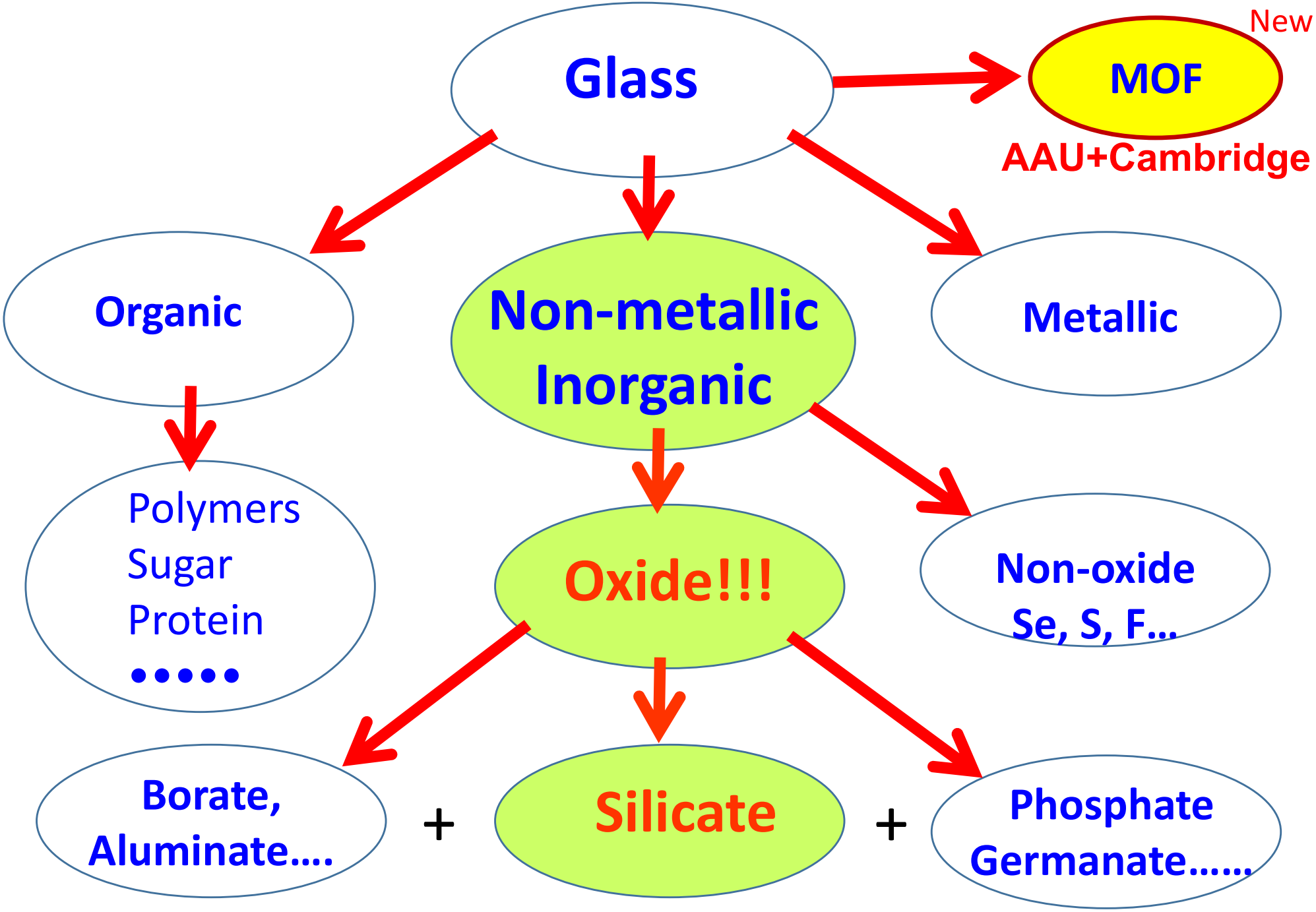
# Glass is witness of

- Civilization of mankind
- Progress of science and technology
- Industrialization
- Development of art
- World trade
- Friendship between different peoples
- ....

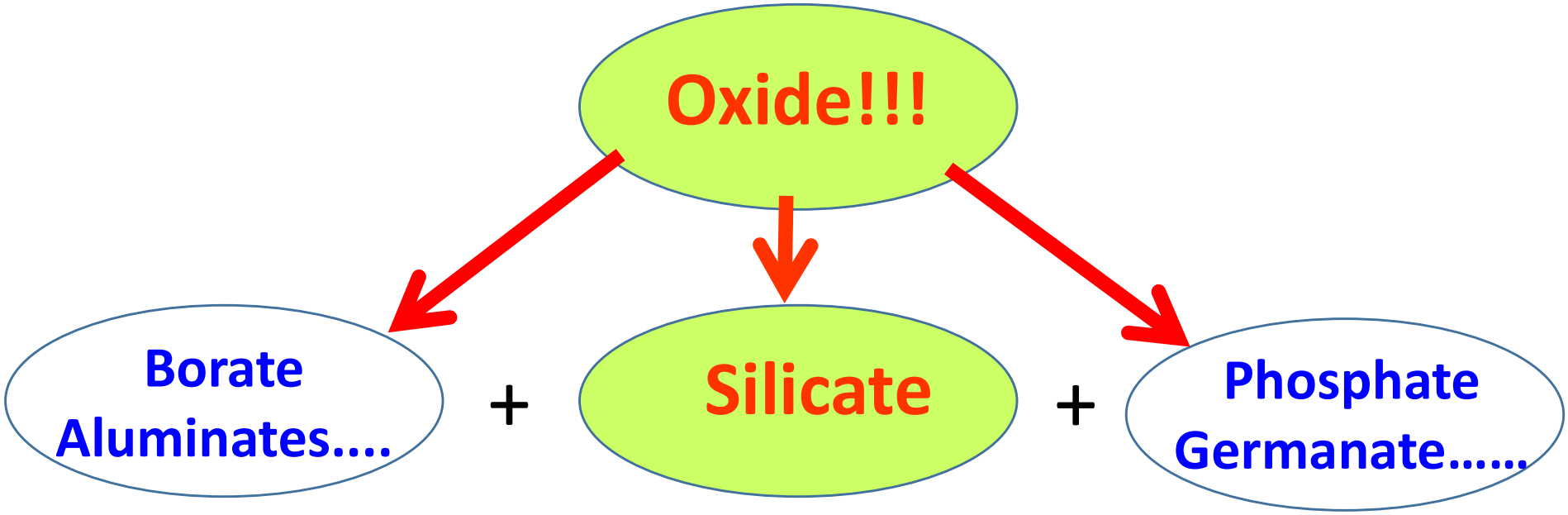
*"Glass...is much more gentile, graceful and noble than any metal, ...it is more delightful, polite and sightly than any other materials at this day known to the world."*

*—Antonio Neri, 1612.*

Today, glass means more…

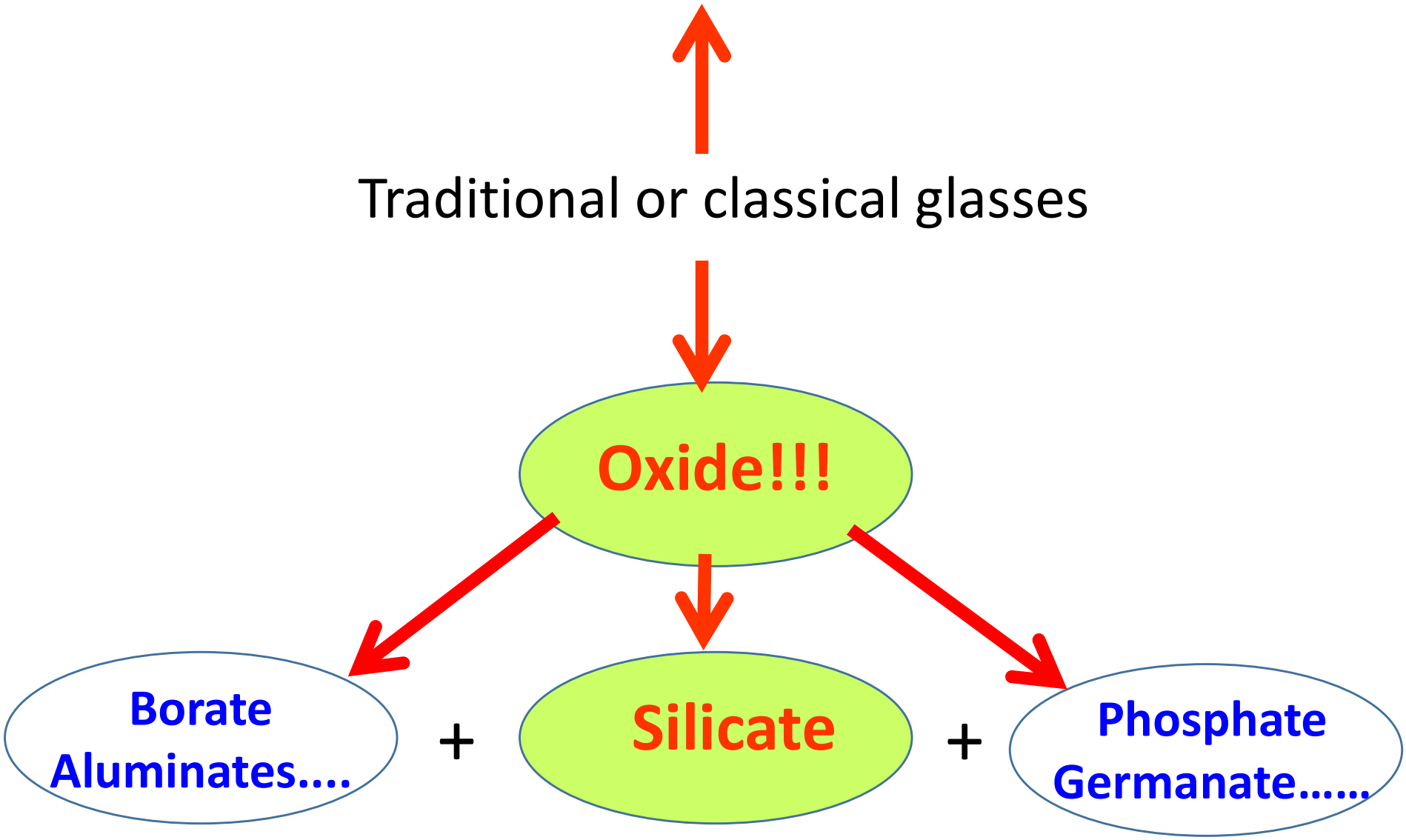



Million kinds of glasses!

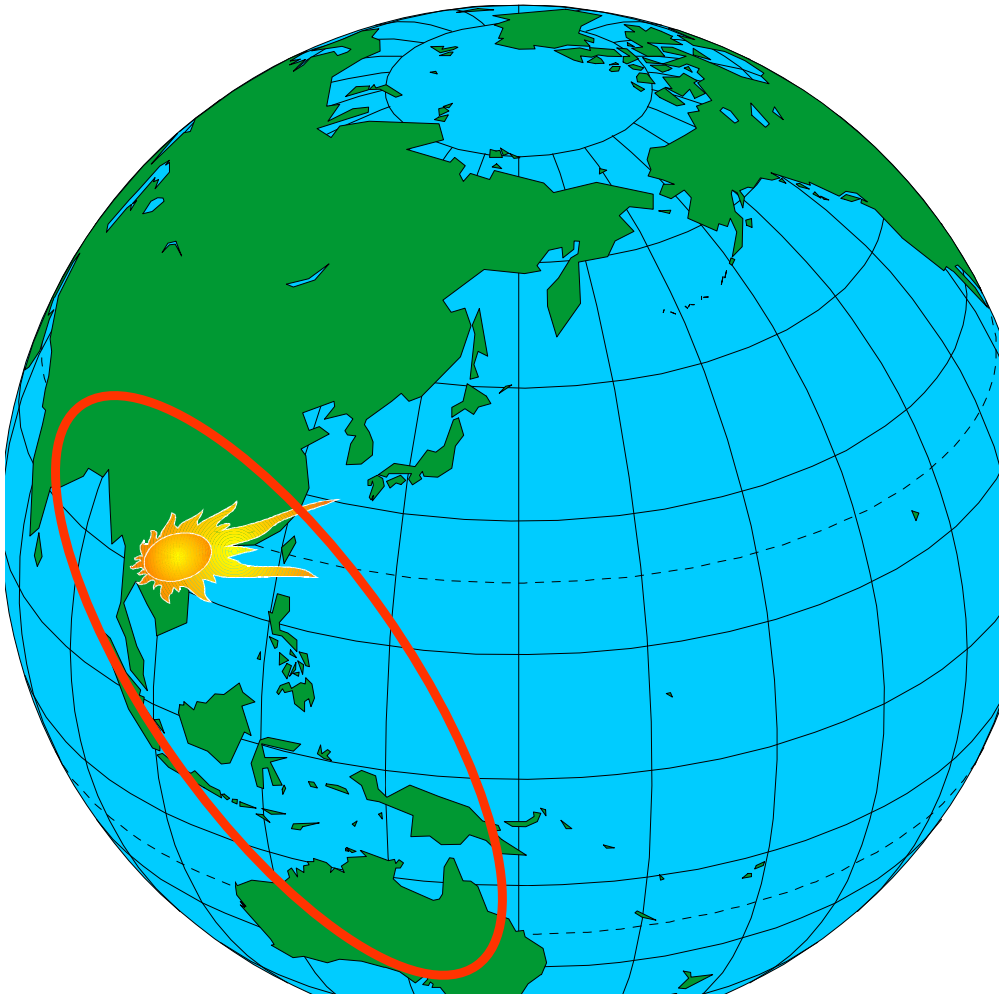



Million kinds of glasses!

# International Year of Glass



# Natural glass



## Austral-asian Tektite Glass

1. Meteorite or comet hits the earth, that leads to
2. high temperatures and enormous pressures.
3. Then the rocks melt.
4. Molten droplets are blasted in and out of the earth's atmosphere
5. The droplets cool quickly to a glassy form and all back to earth.

# Pele's Hair (glass fibers) from Hawaii

**Here we found Pere's hair.**

# Man-made glass
# - Great contribution to civilization

Long Story!

Natural glass

Glass beads
(China)
(7th Cen. BC)

Diatret glass
(Roman)
(1th Cen. AD)

Stain glass
(Jerusalem)
(5th Cen. AD)

Gold ruby
(?????)

Lamp
(19-20
century)

Optical glass
(Jena)
(19th Cen. AD)

Plasma
display

Hubble

How Long?

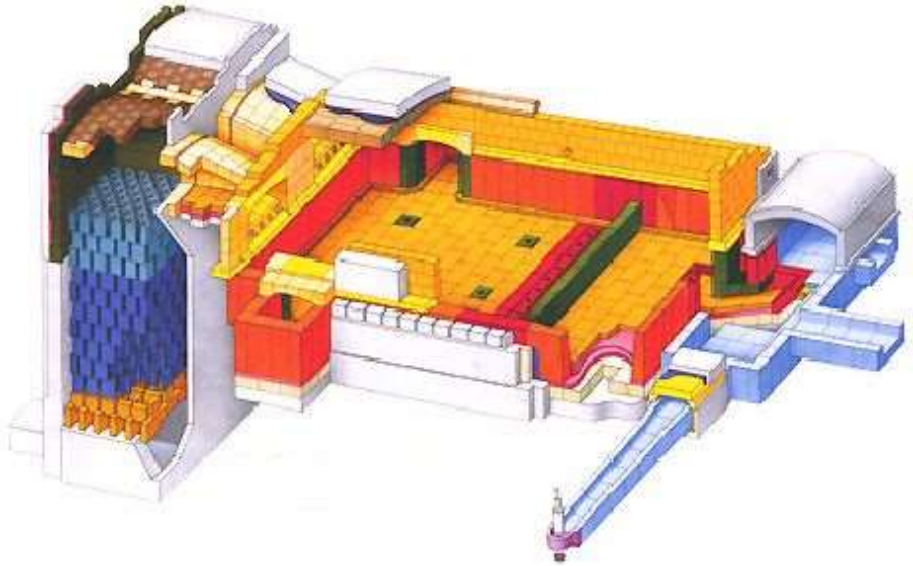
# Advances in melting technology

## Past

Wood-fired melting pot furnace (Roman time)

## Today

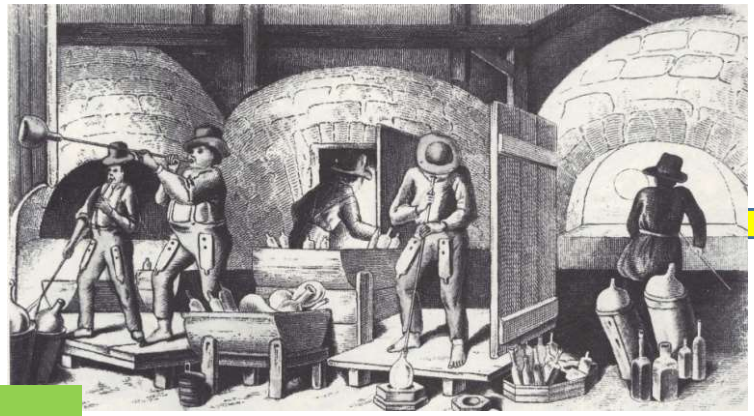
Structure of a continuous tank furnace



Chamber of a tank furnace for melting

# Glass blowing (discovered about 50 BC)
# A major breakthrough of glass technology

Past



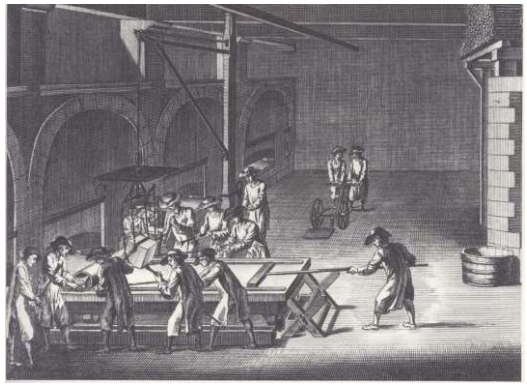
Now

# Development of flat glass forming technology

## Blowing

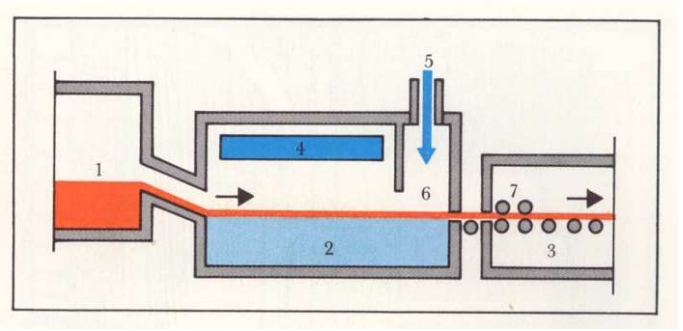
1742

## Pressing



16th century

## Floating



Now

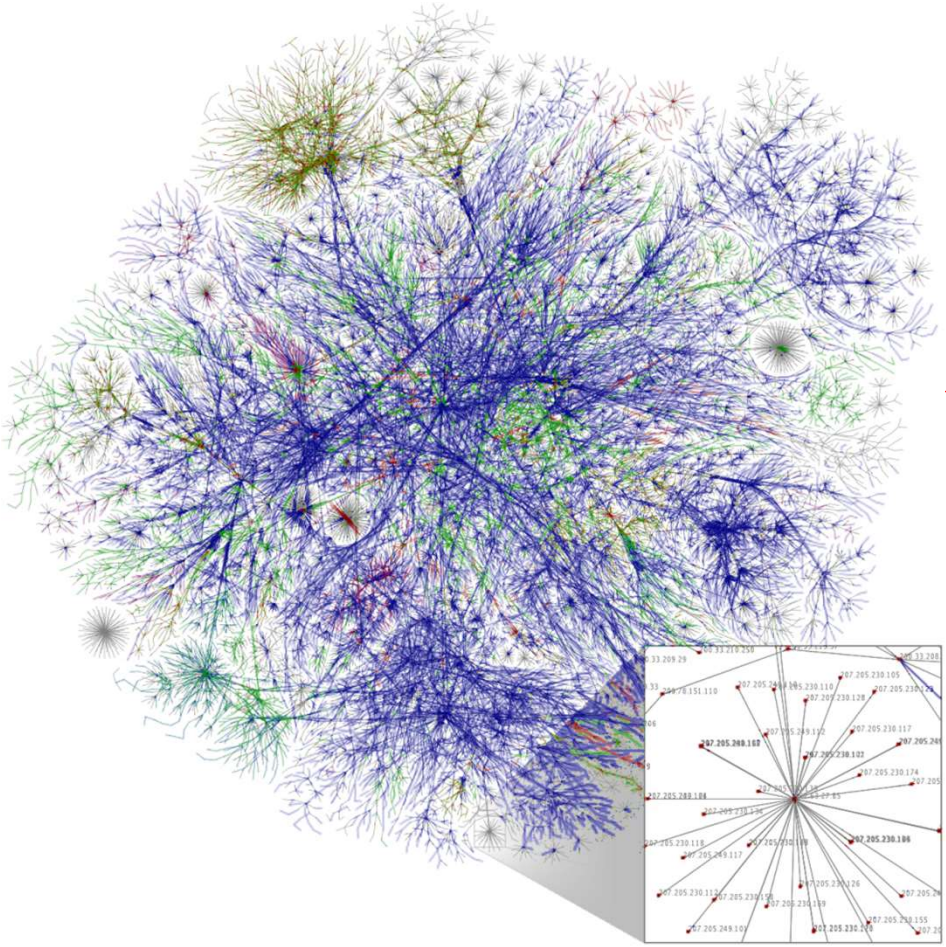
# Science could make glass ultrastrong

A tempered glass that can be bent

- Plastic interlayer (PVB-poly vinyle butyral) is sandwiched with floated/annealed glass.
- Safety glass: Breaking like a spider web.

# Glass and Communication

Internet



Glass

# Glass and modern Life

Fusion draw

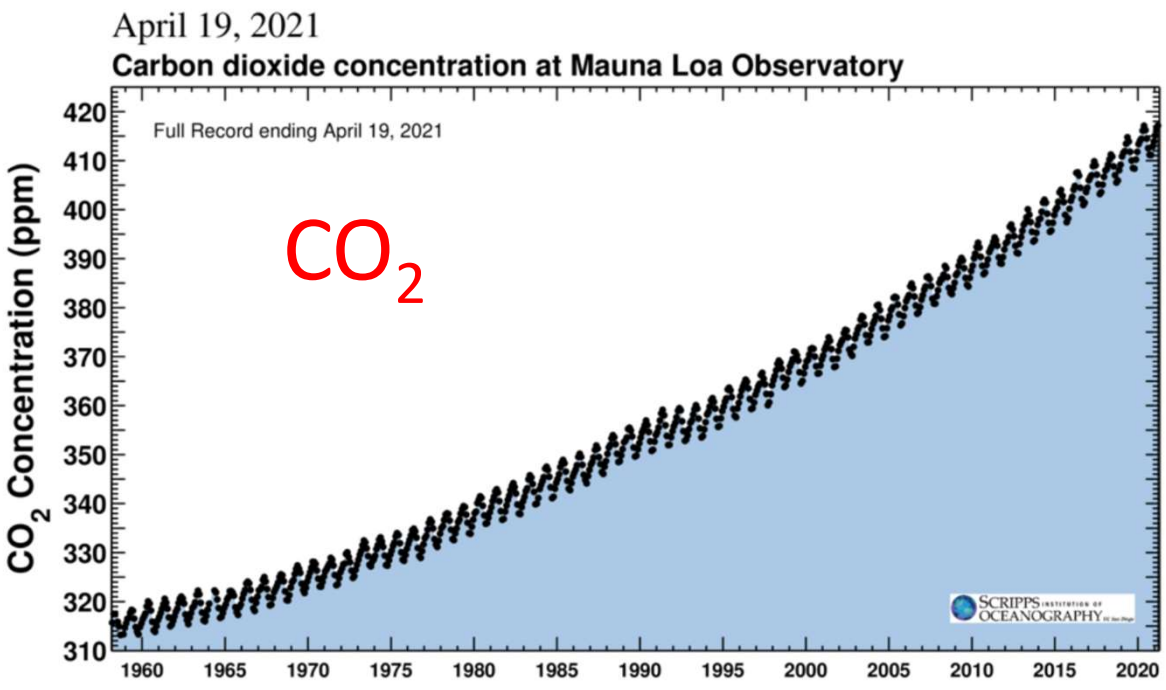
Precision of glass products depends critically on the level of glass science !

Modern Glasses

How does this relate to glass?

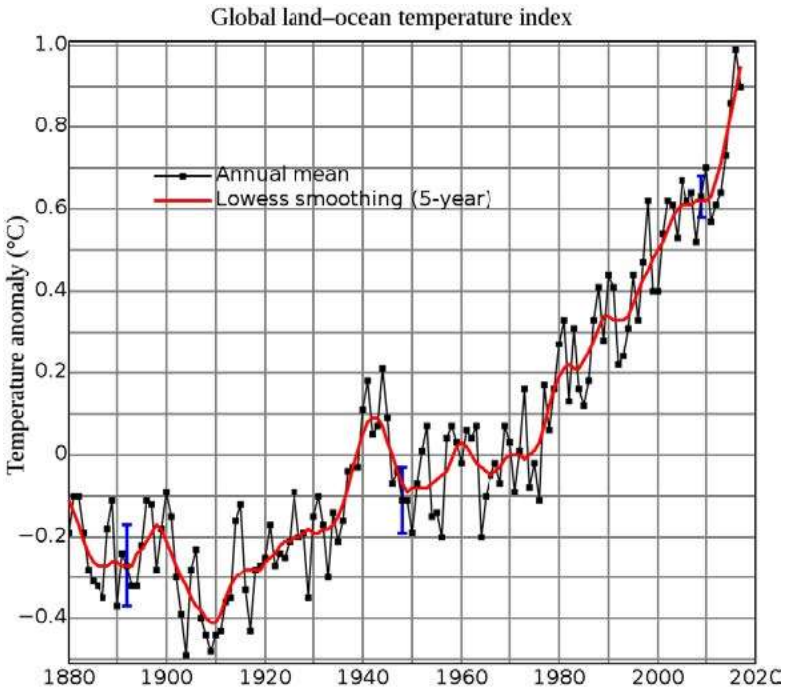
# Glass mitigating climate change

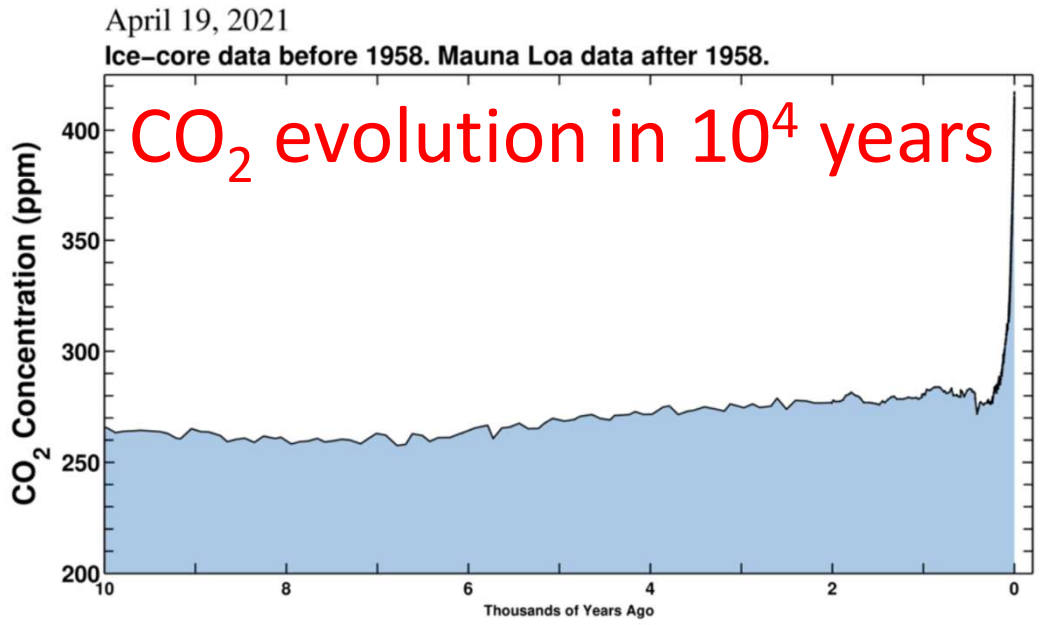
# Climate change is real and man-made!




$CO_2$

Temperature rises!




$CO_2$ evolution in $10^4$ years

*T* increase accelarates!

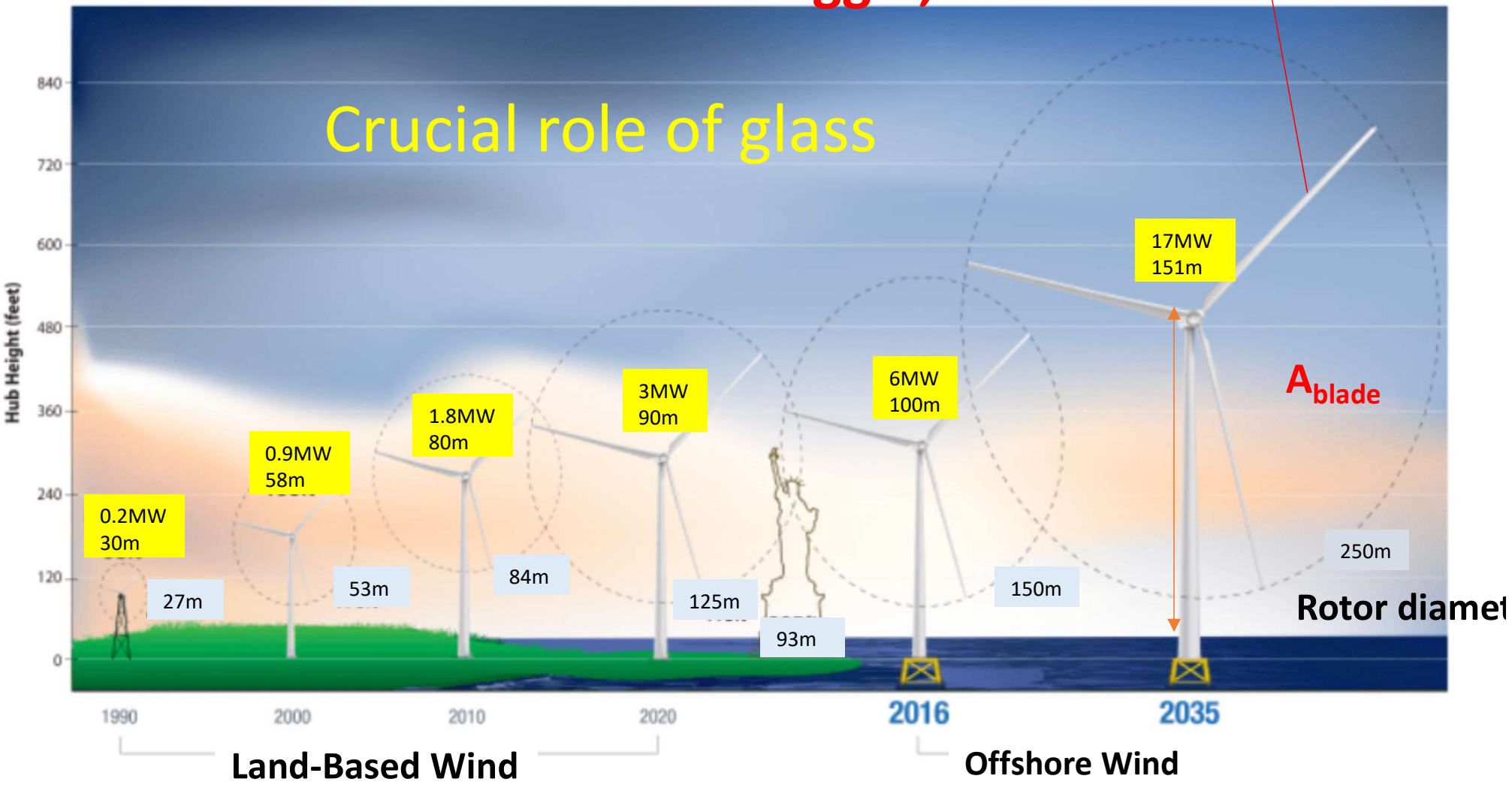
Source: J. Deubener 2021

# Driving Force of Wind Turbine Blade

Glass+Polyester

www.energy.gov; Aug 30, 2021)

## Wind Turbines: the Bigger, the Better




$$P_{avail} = \frac{1}{2} \rho_{air} A_{blade} v_{wind}^{3} C_p$$

where $C_p$ is power coefficient (< 0.59, Betz Limit)



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# Wind Turbines: the Bigger the Better

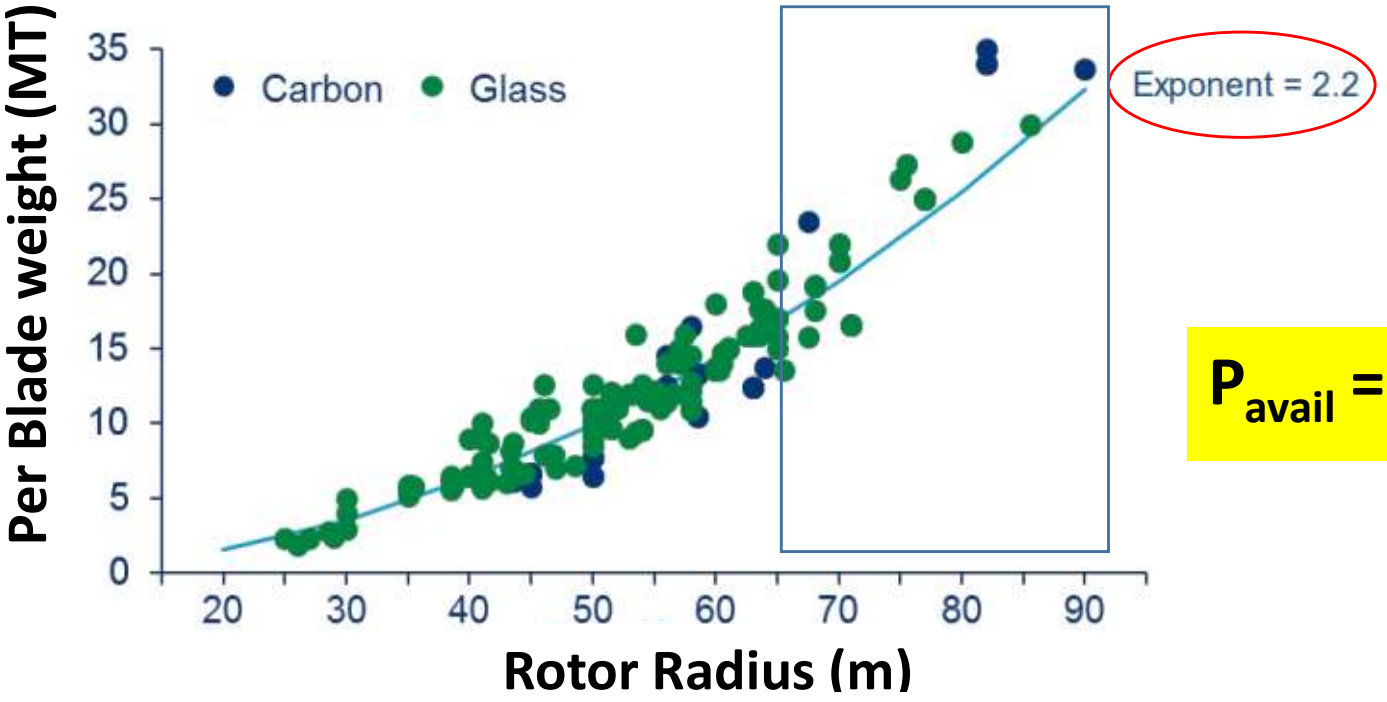
## Onshore Wind

- 65+ meters now standard length for all new designs
- **Enable utilization of "low-wind" areas**
- All E-glass blades pose the "square cube law" challenge

**Lower weight and longer blades now enabled by High Modulus Fiberglass**

https://gwec.net/

**High Modulus Fiberglass**




$$P_{avail} = \frac{1}{2} \rho_{air} A_{blade} v_{wind}^{3} C_p$$

R&D Pathways for Supersized Wind Turbine Blades, Report No. 10080081-HOU-R-01
Lawrence Berkeley National Laboratory (March 7, 2019)

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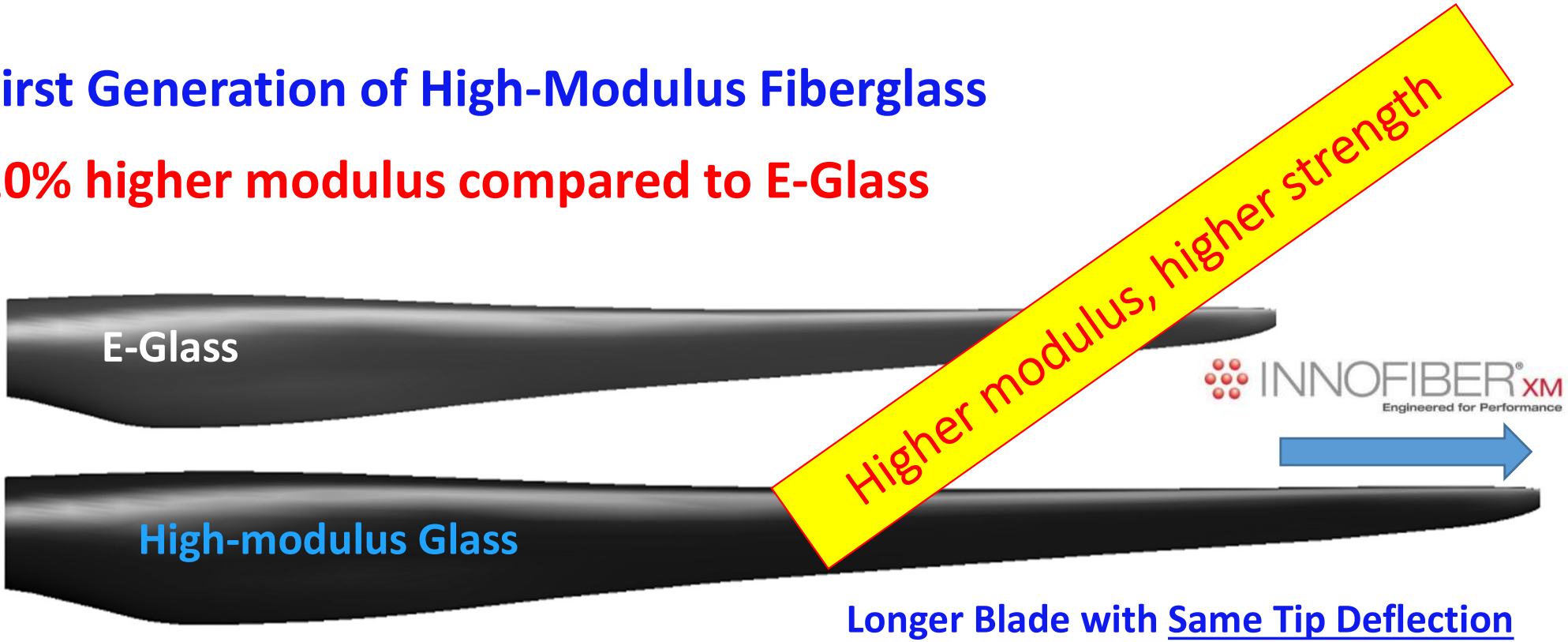
# First Generation of High-Modulus Fiberglass

## 10% higher modulus compared to E-Glass




**Longer Blade with Same Tip Deflection**

| Case Study | Spar Cap Material | Manufacturing Process | Tip Deflection (m) | Blade Length (m) | Energy Output % Increase | Decrease in COE |
|---|---|---|---|---|---|---|
| Baseline Model | UD E-Glass Fabric | Infusion | Same | 33.25 | - | - |
| 1 | UD High-modulus Fabric | Infusion | | 33.88 | 3.80% | 1.8% |
| 2 | UD High-modulus Pultrusion | Pultrusion /Infusion | | 34.5 | 7.70% | 3.57% |

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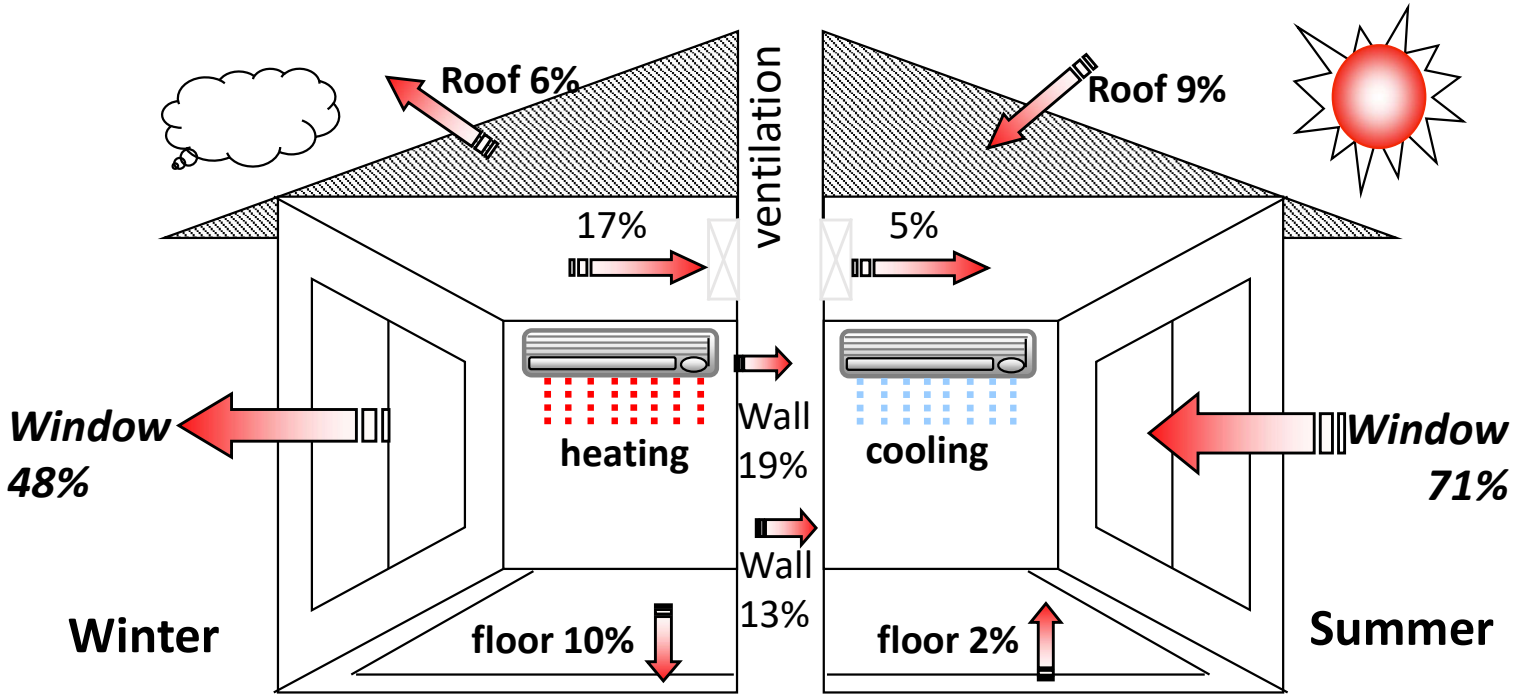
# Energy loss from a Japanese house



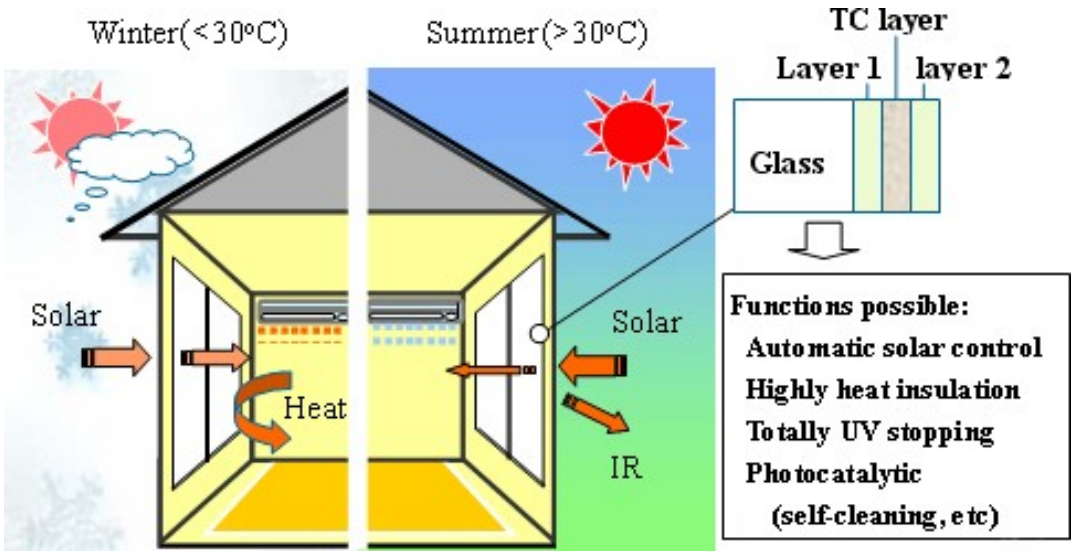

**Winter: 48% due to heating escaping**

**Summer: 71% due to extra solar invasion**

***The window gives the largest heat exchange in a Japanese house model according to simulation***

Source: Ping Jin

# *Smart window is a solution*

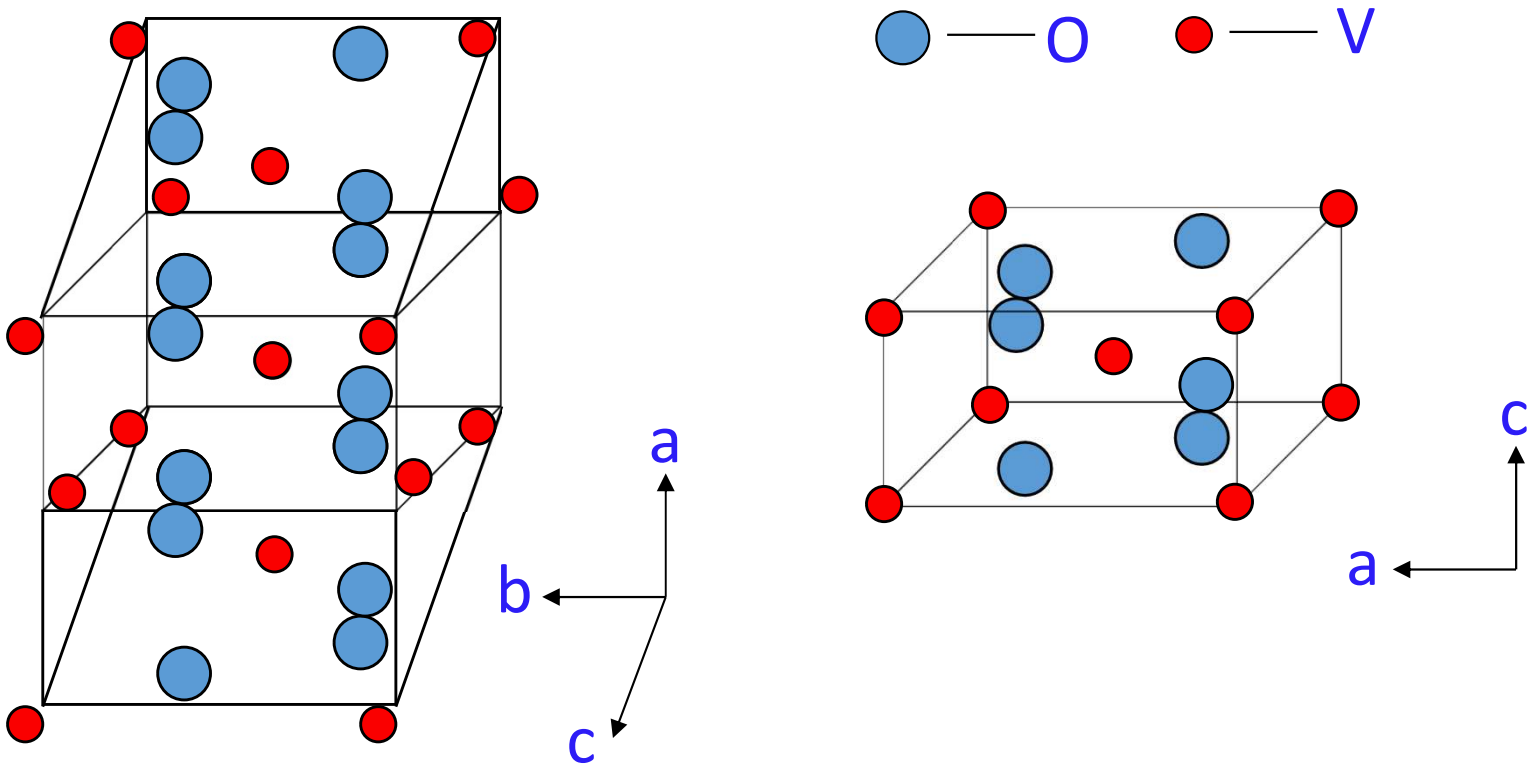



## By Coating

- ***Electrochromic**: effective but structurally complex so expensive;*
- ***Low-E**: effective but optically unchangeable;*
- ***Thermochromic**: simple but with low $T_{vis}$ and low energy efficiency*
- ***Thermotropic**: effective but lose transparency while switching*

# *Thermochromic effect is realized by the thermochromic $VO_2$ coating*

## *$VO_2$ crystal with 2 polymorphs:*



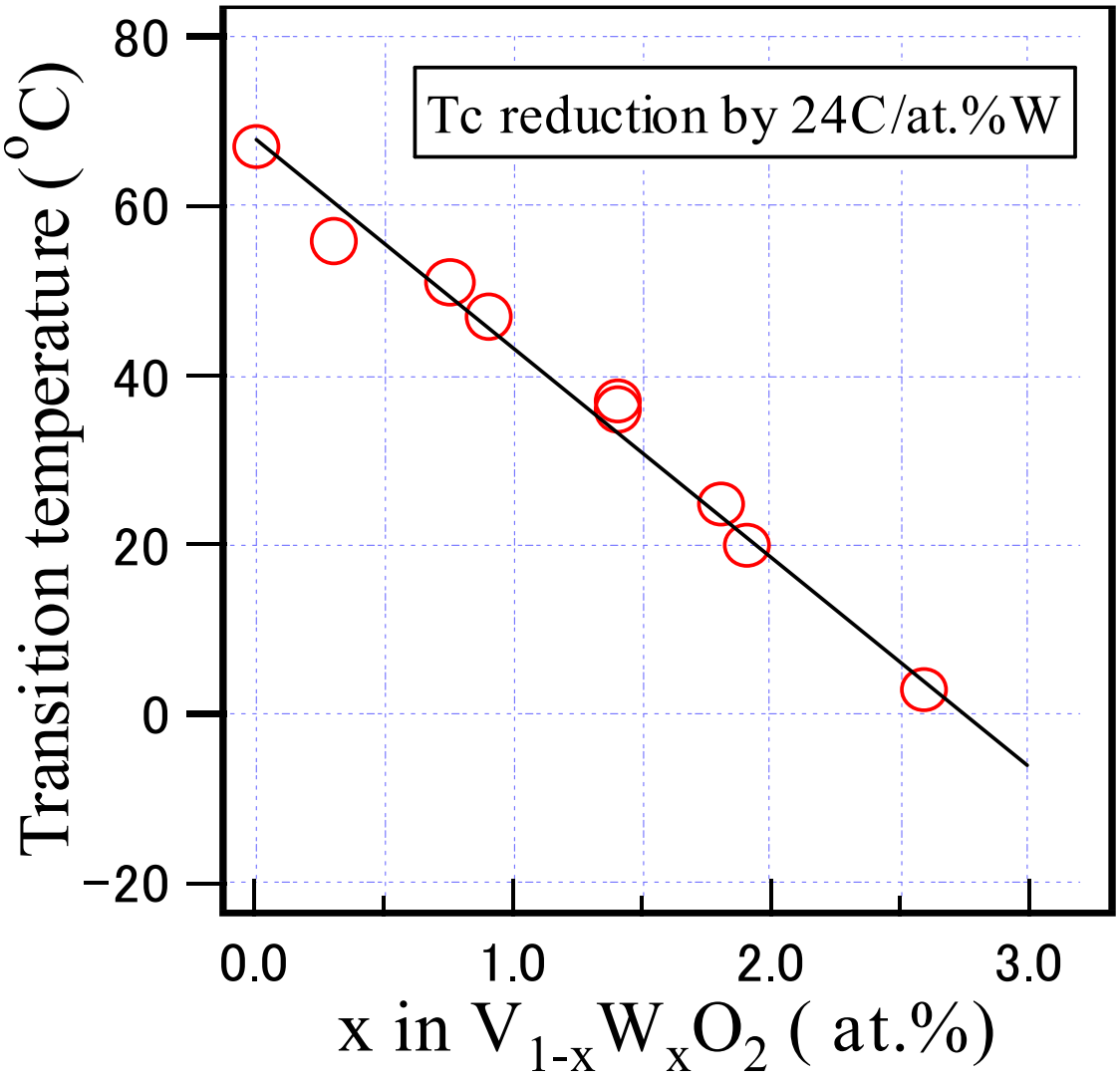

*monoclinic & a semiconductor*
*highly IR transmitting*

340K

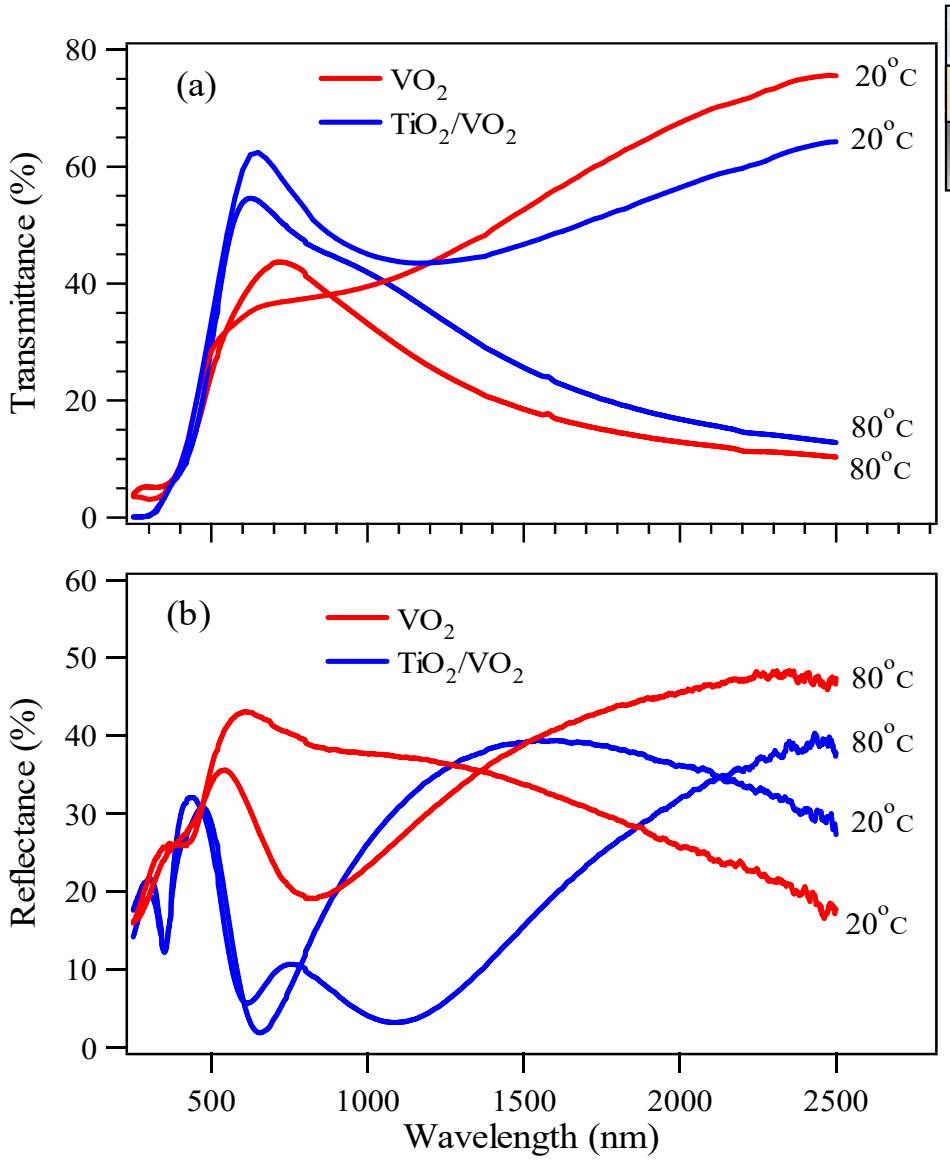
*phase transition*

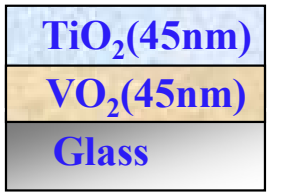
*tetragonal & metallic*
*with high IR reflecting*

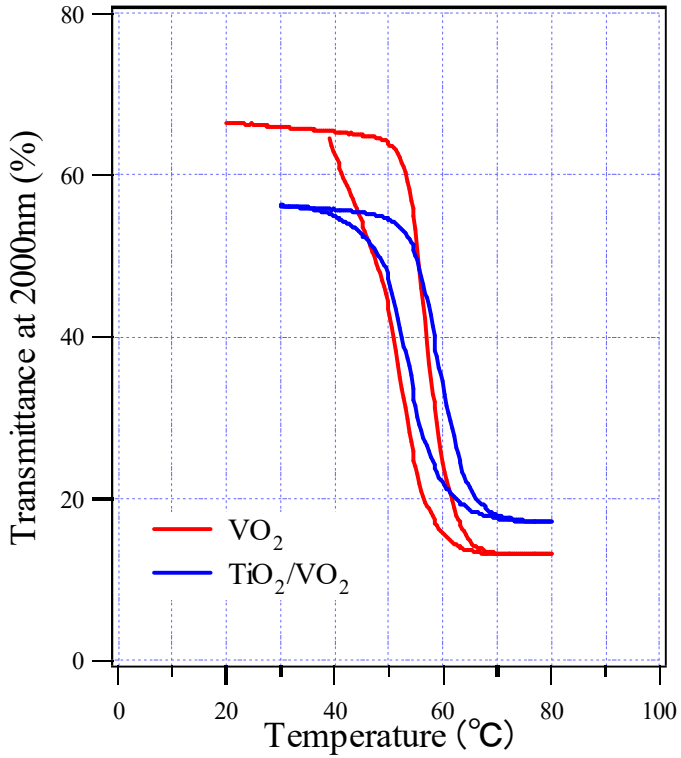
# *Control of switching temperature by metal doping*



# *Optical properties: a single AR structure.*

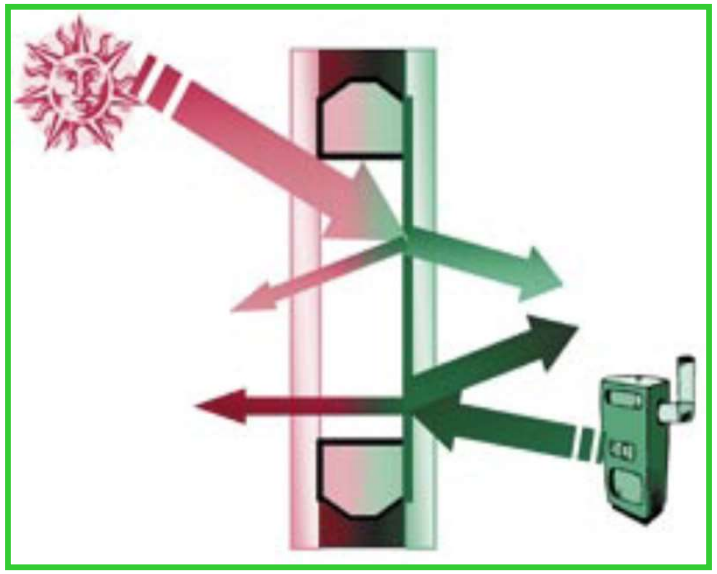


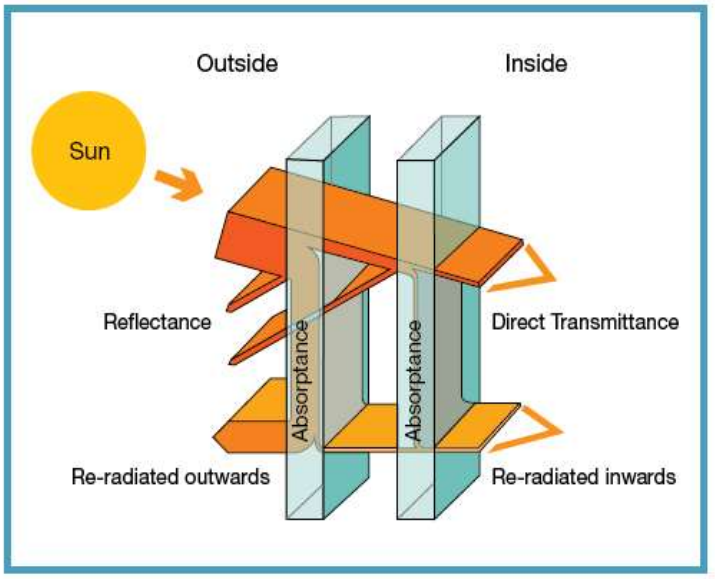



# Advanced glazings

**In cold climates**
**Low-E glass keeps the heat inside.**



**In hot climates**
**Solar Control glass prevents heat from entering**

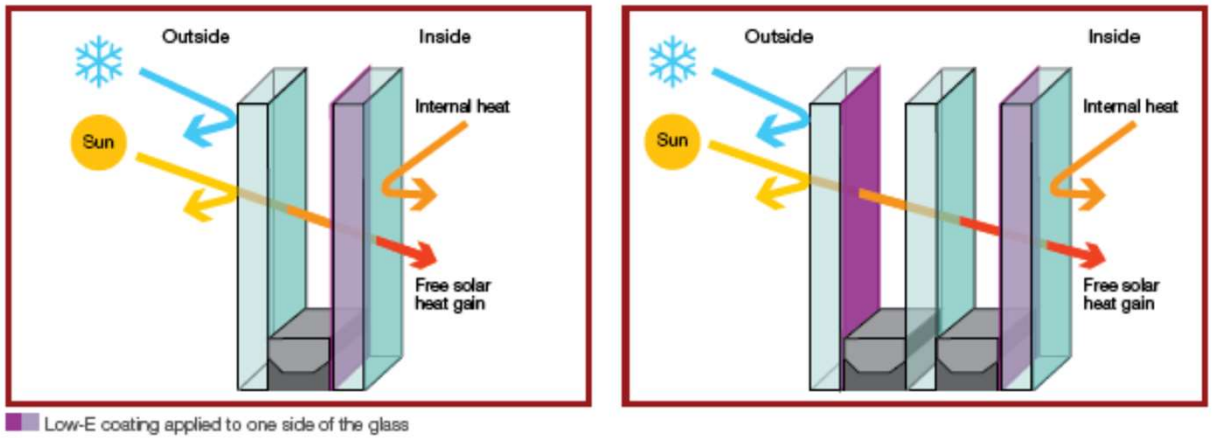



From Alicia Duran

INTERNATIONAL YEAR OF GLASS 2022

# Energy balances in special glazings

## Low-emission glazing (Low-E)



- Manufacturing cost per $m^2$ Low-e double = **25 kg $CO_2$**
- Savings per $m^2$ substitution of simple glazing for Low-E= **91 kg $CO_2$ /year**
- Amortization of emissions = **3.5 months p/single glazing, 10.5 months p/double glazing**
- Potential savings of **96 Mt $CO_2$/year in the EU-27 in 2020** (30% EU target)

http://www.glassforeurope.com/images/cont/166_43490_file.pdf

INTERNATIONAL YEAR OF GLASS 2022

# Our glass activities

# Glass plays a vital role in energy technology!

## My group's activities

Build sustainable society!

Glass ⟷ Energy

Energy → Generation

Energy → Saving

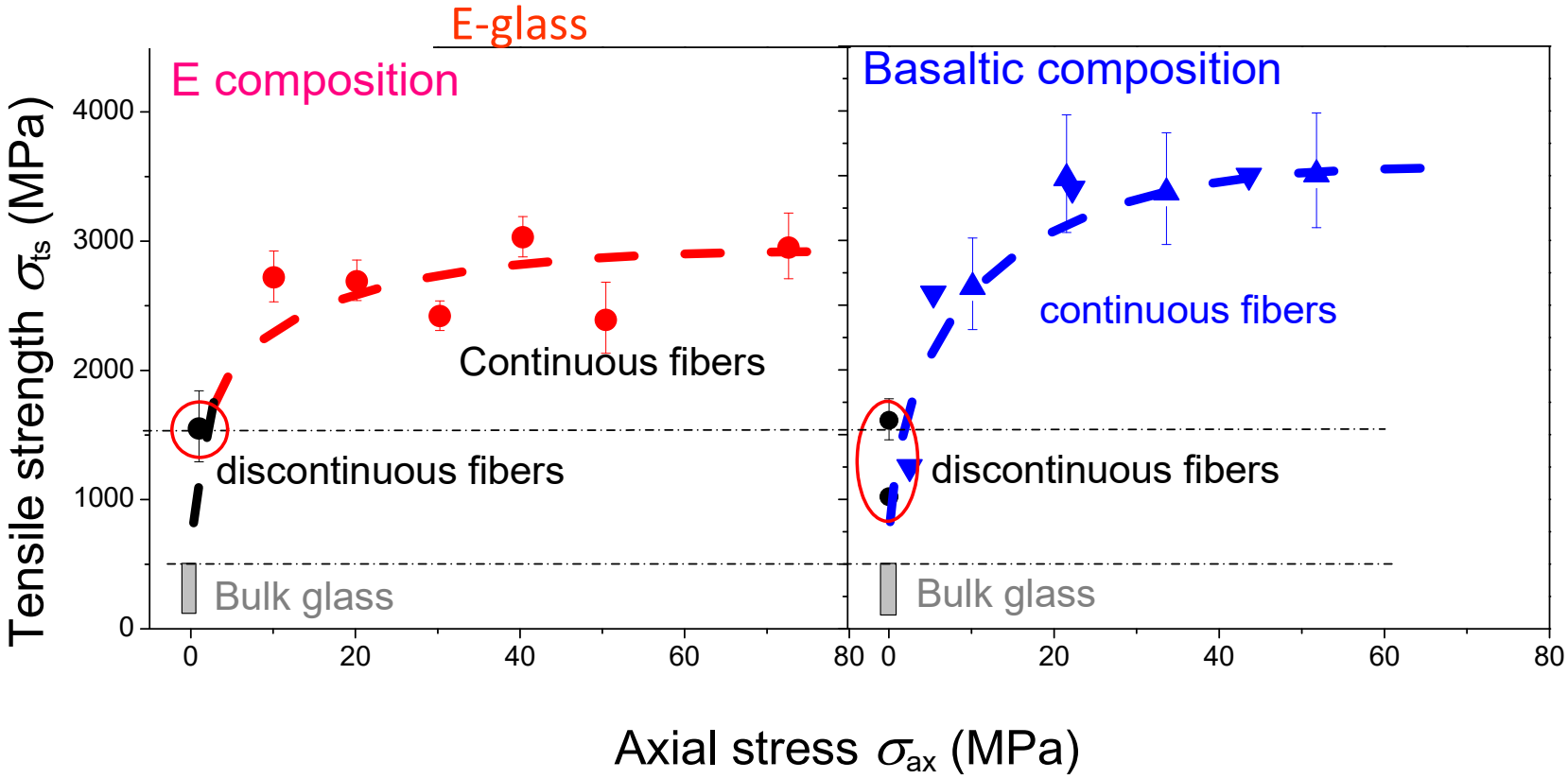
Energy → Storage

Mitigate climate change!

# Glass for energy generation

- Wind power
- Solar cell

# Mechanical performances of glass fibers depends on chemistry and forming condition

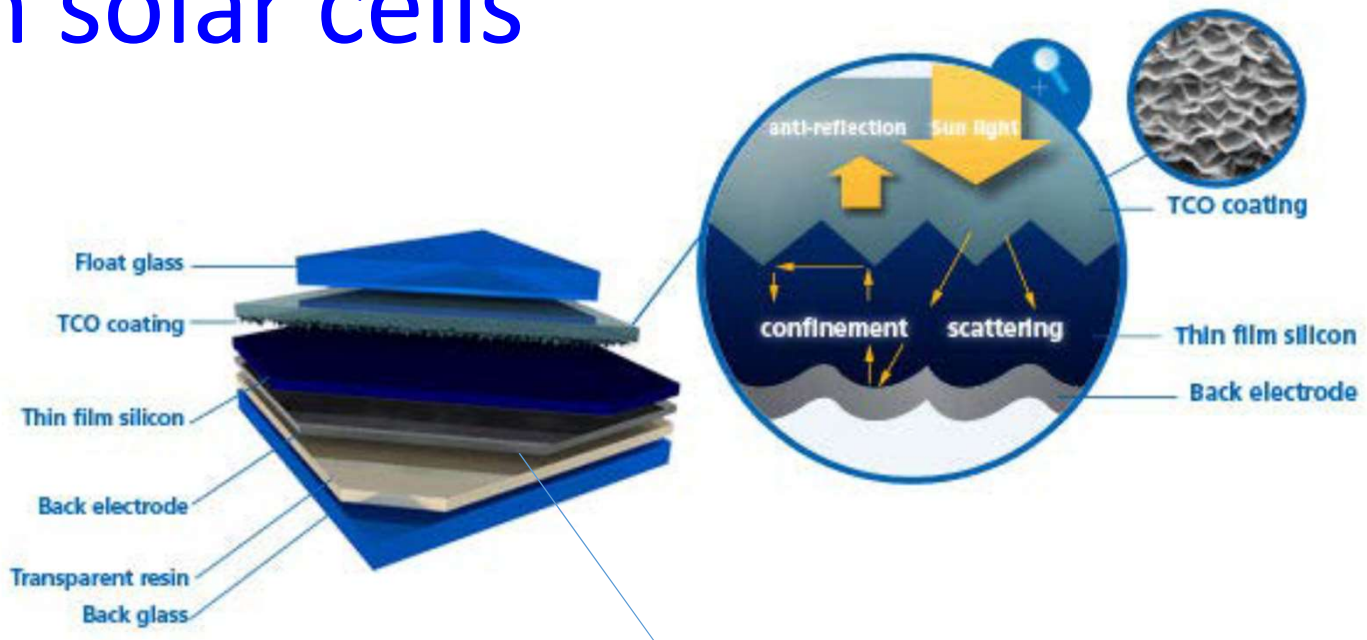



Done by collaboration with Rockwool and PPG

Lund and Yue, *J. Am. Ceram. Soc.* (2010)

New Book: Fiberglass Science and Technology (2021), Li et al

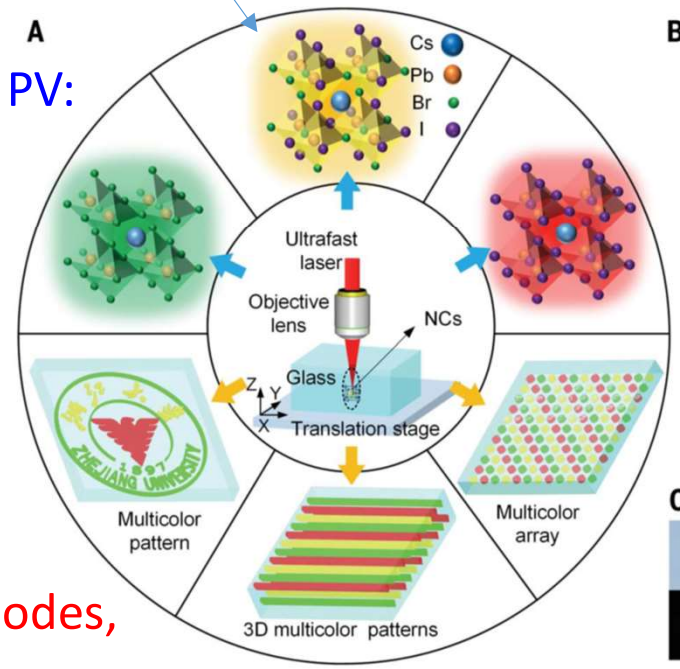
# Glass in solar cells

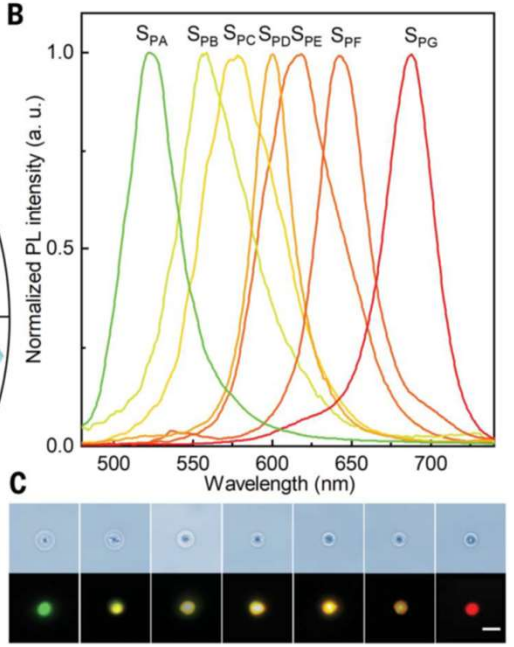



Next generation of semiconductors for PV:
**Perovskite**☺

But its stability is an issue.
Can glass solve this?
Print perovskite into glass by laser.

**Our new work** shows this possibility.
The bandgap can be tuned.
Optical storage, micro–light emitting diodes, and holographic displays…..




Sun et al, *Science* 2022

# Energy saving
## - stone and glass wool

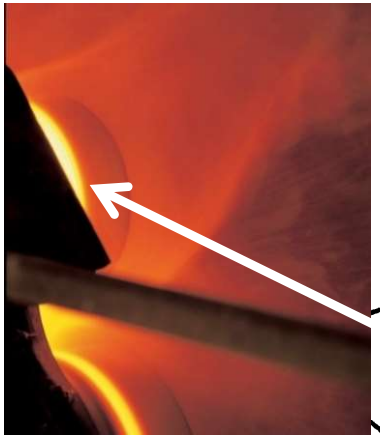
Y. Z. Yue, M. Solvang, “Stone and Glass Wool”, in *Encyclopedia of Glass Science, Technology, History, and Culture*, Volume II, edited by Pascal Richet (2021)
Y. Z. Yue, “Fiber Forming and Its Impact on Mechanical Properties”, in *Fiberglass Science and Technology*, edited by Hong Li (2021)

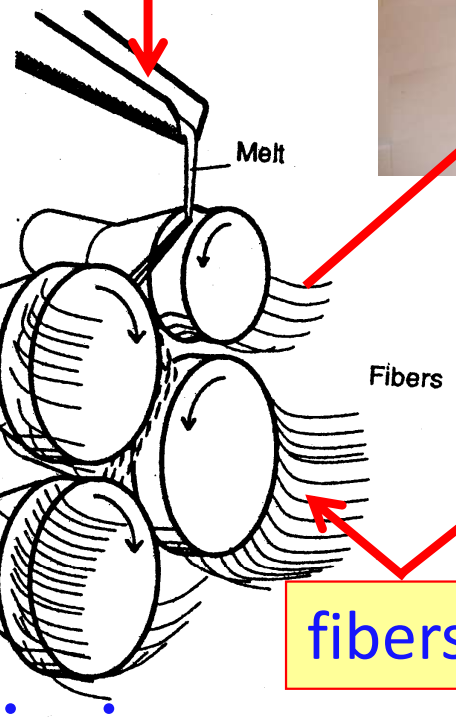
Rockwool project meeting in Helsingør in 2000

# Production of stone wool

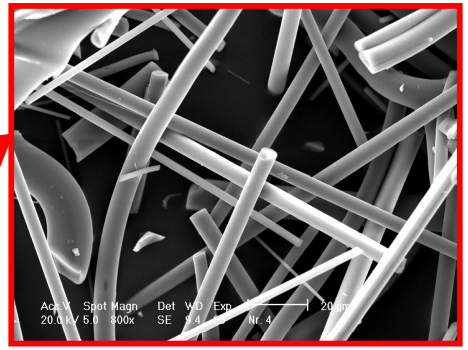
Basalt stone

1500 °C melt

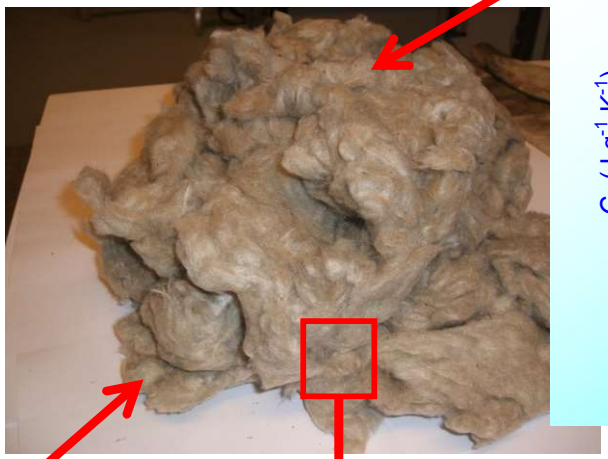




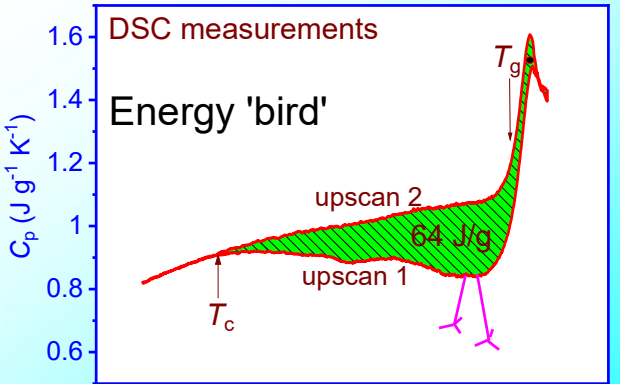

fibers



Cascade spinning process



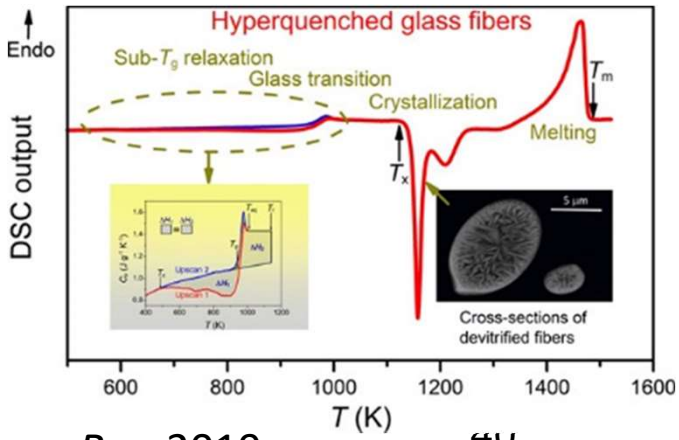
Very glassy!




Yue, Angell, *Nature* 2004

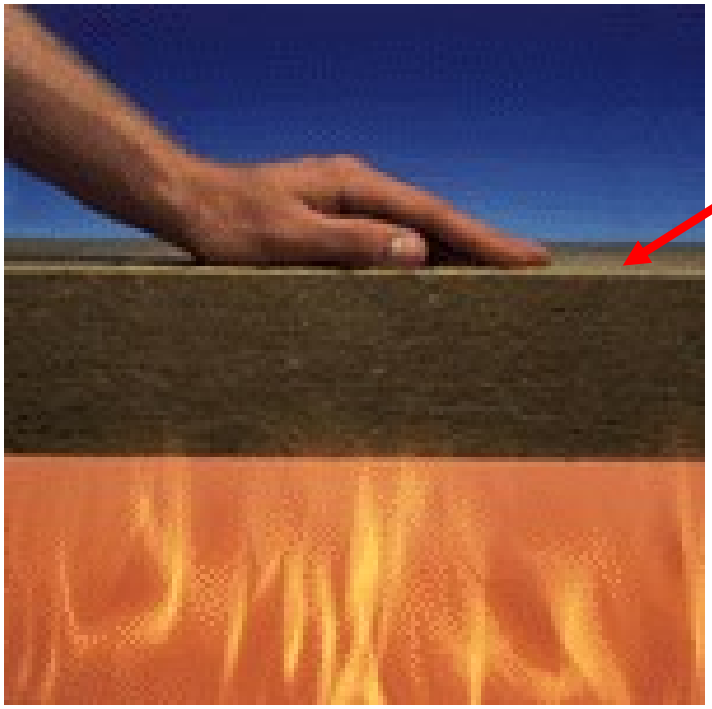
Yue, *J. Non-Cryst. Solids 2022*

Complex!




Zheng et al, *Chem. Rev.* 2019

# An example for collaboration with RI



Now: stand 1000 °C

Wool protects people and environment and save huge energy.

Thermally stable, and also mechanically stable

But how to make stone wool even more stable?

**Goal**: Further enhance the HT stability of wool fibers

# How to do it?

## *Oxidation drives cations to move outward.*

Heat-treatment around $T_g$

↓

Oxidation of $Fe^{2+}$ to $Fe^{3+}$

↓

Inward diffusion of $h^{\bullet}$

↓

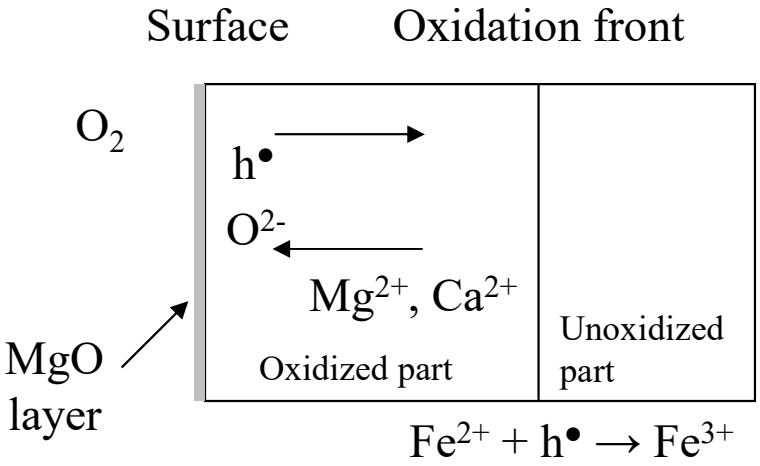
Outward diffusion of $Mg^{2+}$

↓

MgO on surface

↓

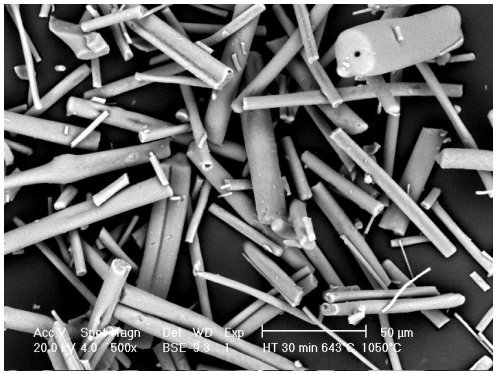
Increases of HT stability

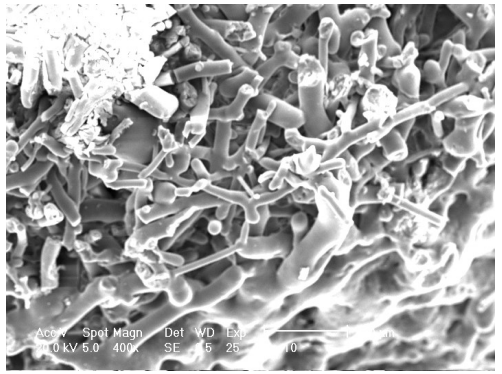



Yue, *et al.*, JACerS (2009)

Treated 600 °C, 0.5 h

Not heat-treated





Then heated to 1050 °C in Ar

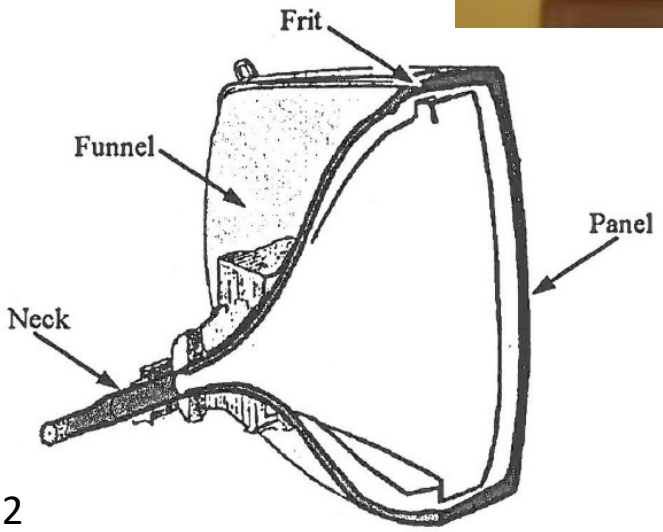
# **Energy saving**

- Glass foams

# Fabricating glass foams from the recycled TV glass

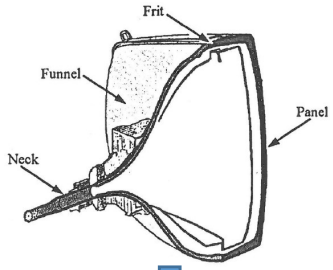
- Waste glass from cathode ray tube (CRT) – panel glass (≈ 66 % of total CRT glass)
  - Non-lead containing
  - Excellent glass stability
  - Low thermal conductivity
- Foaming inducers
  - $Mn_3O_4$ and carbon

$$2Mn_3O_4 + C \rightarrow 6MnO + CO_2$$




| # | Producer | Chemical composition [wt%] | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $Na_2O$ | $K_2O$ | CaO | MgO | SrO | BaO | $ZrO_2$ | SUM |
| 1 | LG Phillips Displays | 60.1 | 2.99 | 0.07 | 8.4 | 6.54 | 0.69 | 0.41 | 8.57 | 8.93 | 2.38 | 99.1 |
| 2 | Philips Displays | 60.0 | 2.63 | 0.05 | 8.0 | 6.55 | 0.69 | 0.33 | 8.47 | 8.69 | 2.38 | 97.8 |

# The procedure of glass foam fabrication in our lab



Glass powder
(CRT panel glass, bottle glass, window glass etc.)

Foaming agent
($Mn_3O_4$+C, $CaCO_3$, $MnO_2$, SiC, etc.)

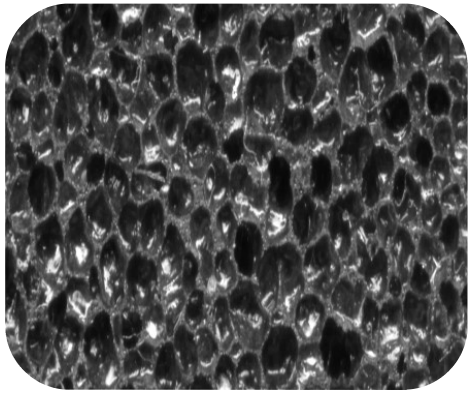
Mixing

Powder mixture

Uniaxial compression

Powder pellet

Heating

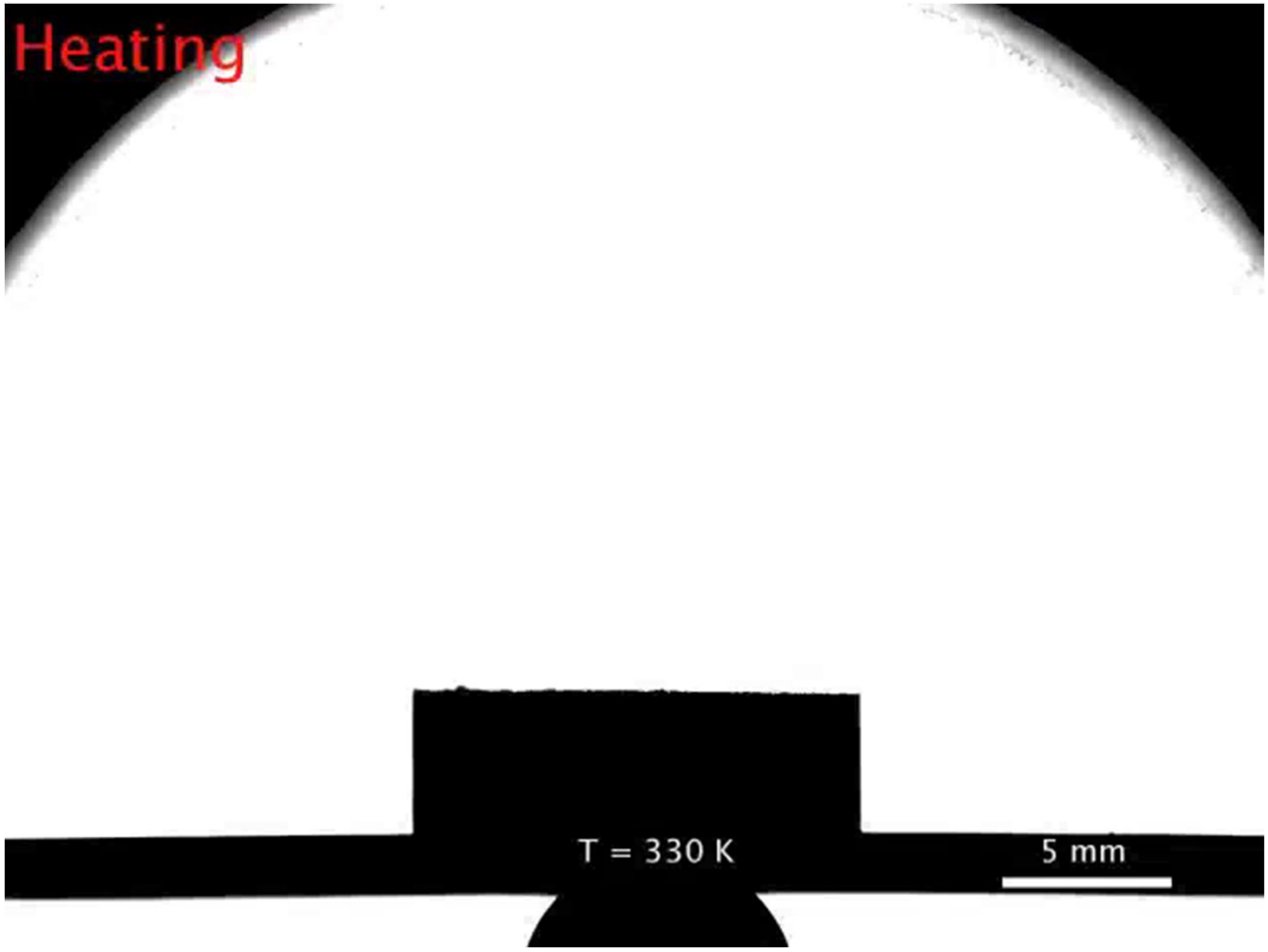


Porous melt

Cooling

Glass foam

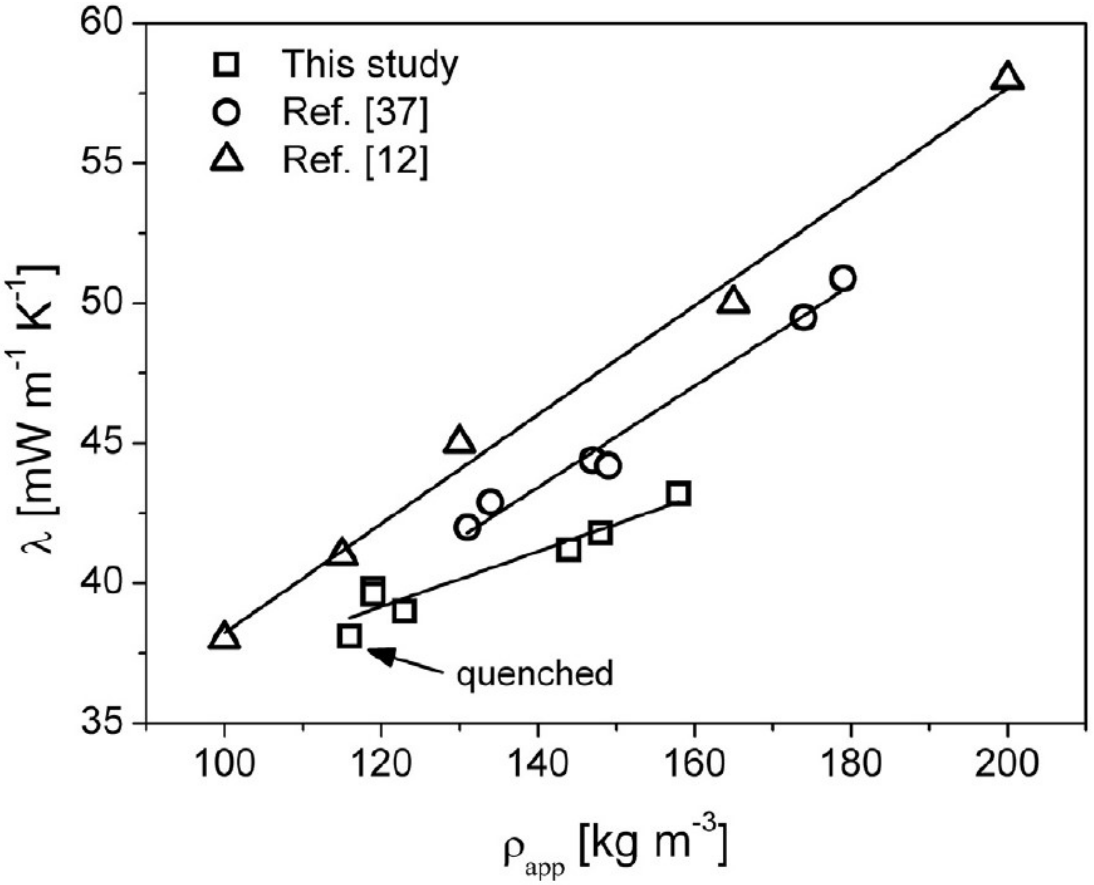
Sligtly reducing atmosphere




Petersen, König, Yue, *Int. J. Appl. Glass Sci.* (2016)

# Impact of density/porosity on thermal conductivity

- Thermal conductivity decreases with increasing porosity.
- This is because gas has lower thermal conductivity than solid.



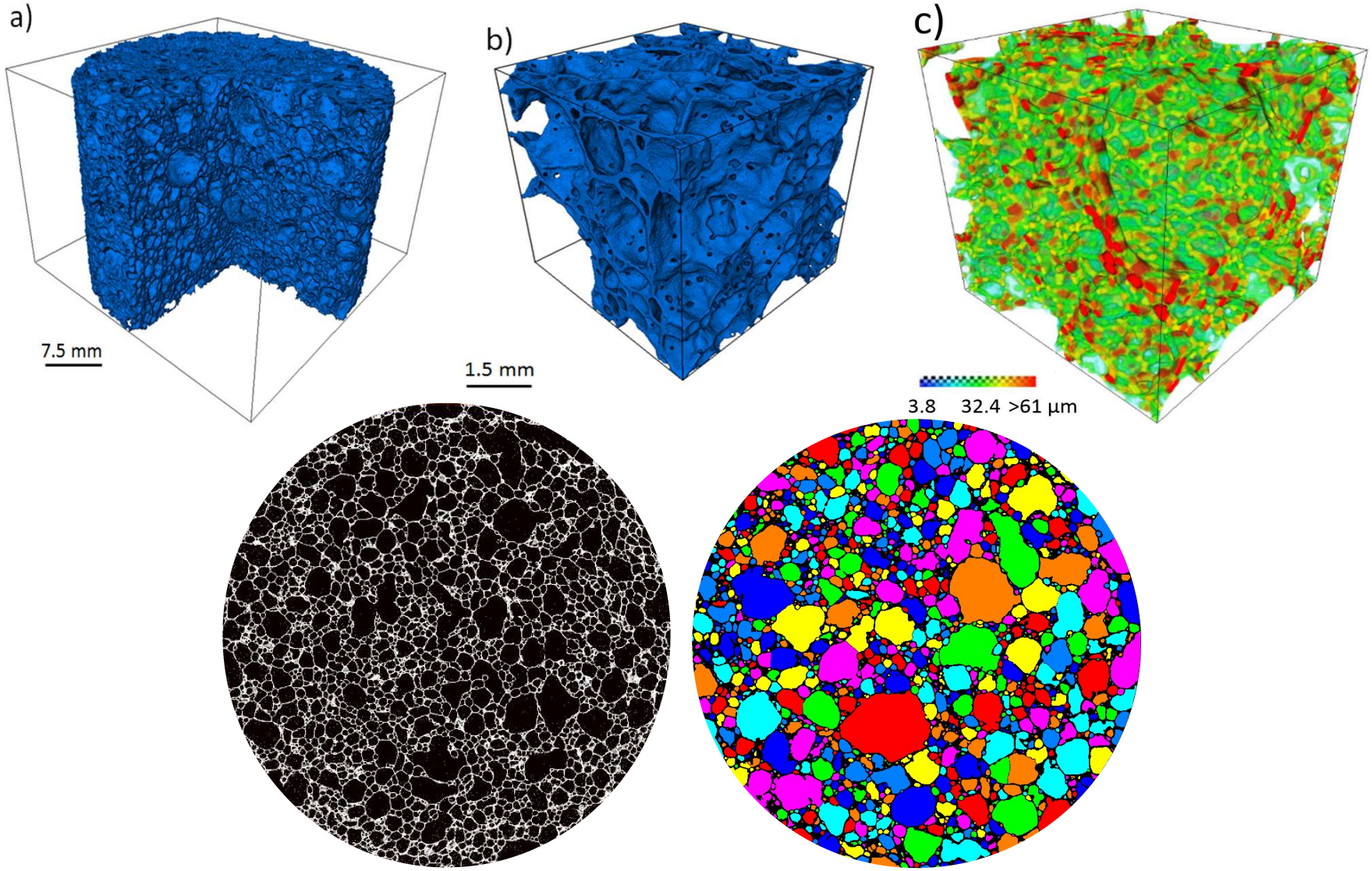

König et al., J. Non-Cryst. Solids (2016)

The challenging question:

How can we reach the lower thermal conductivity?

Many factors play roles.

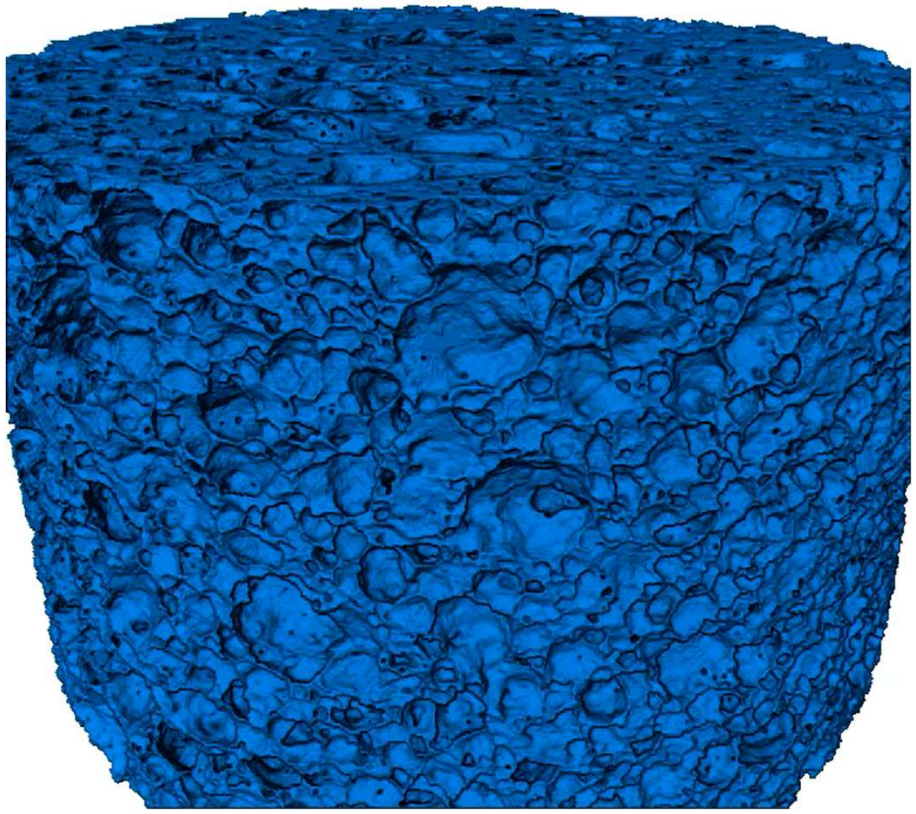
# 3D pore structure (obtained by X-ray tomography)



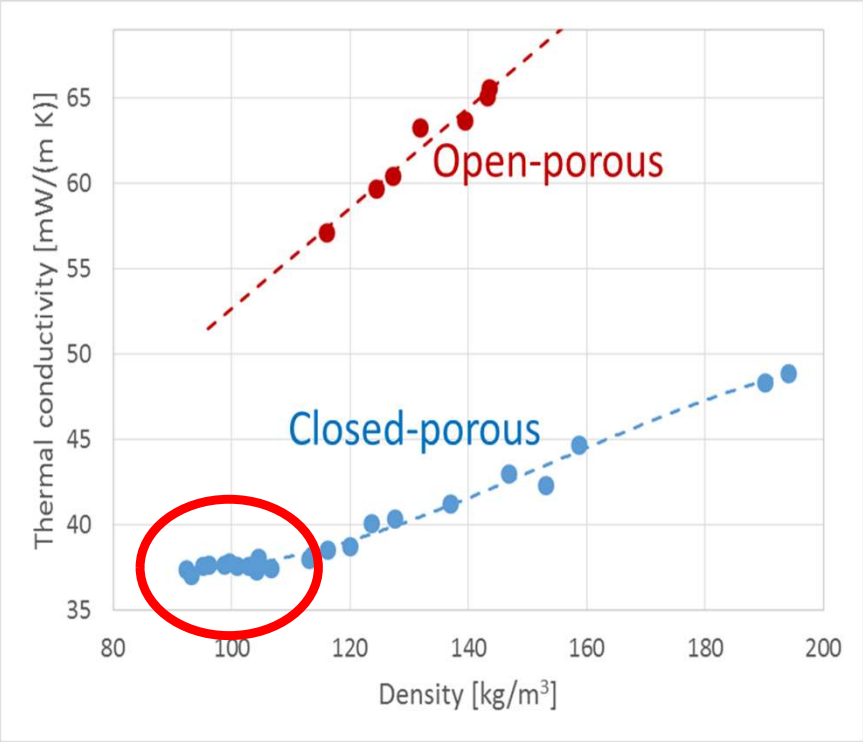

Østergaard, et al., *Mater. Lett*. 2019, *Acta Mater*. 2020

# 3D pore structure

- Obtained by X-ray tomography (XMT)
- Reflect the full pore shape and size
- Provide guidance for the manufacturing of glass foams.
- Determine λ of glass foams using image-based modelling
- Predict the porosity dependence of λ.



# The thermal conductivity of our glass foams is much lower than that of commercial ones.




Measured using HFM @ 10°C middle temperature

König et al, 25th ICG, Boston, June 12, 2019

Model house

# Energy storage

## - Glass batteries

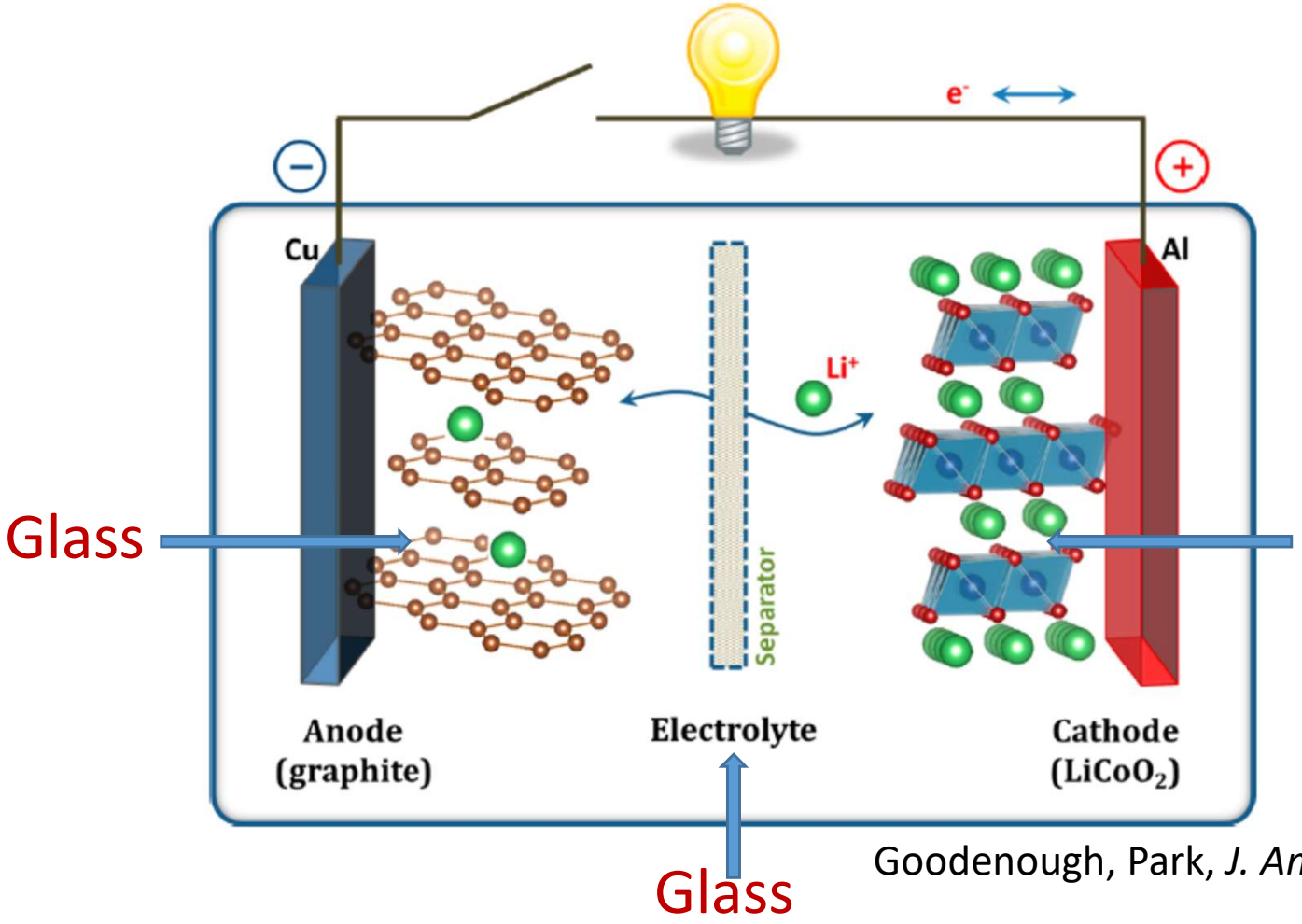
towards

high energy density

High power density

# Lithium/Sodium Ion Batteries

## My dream: All-glass batteries



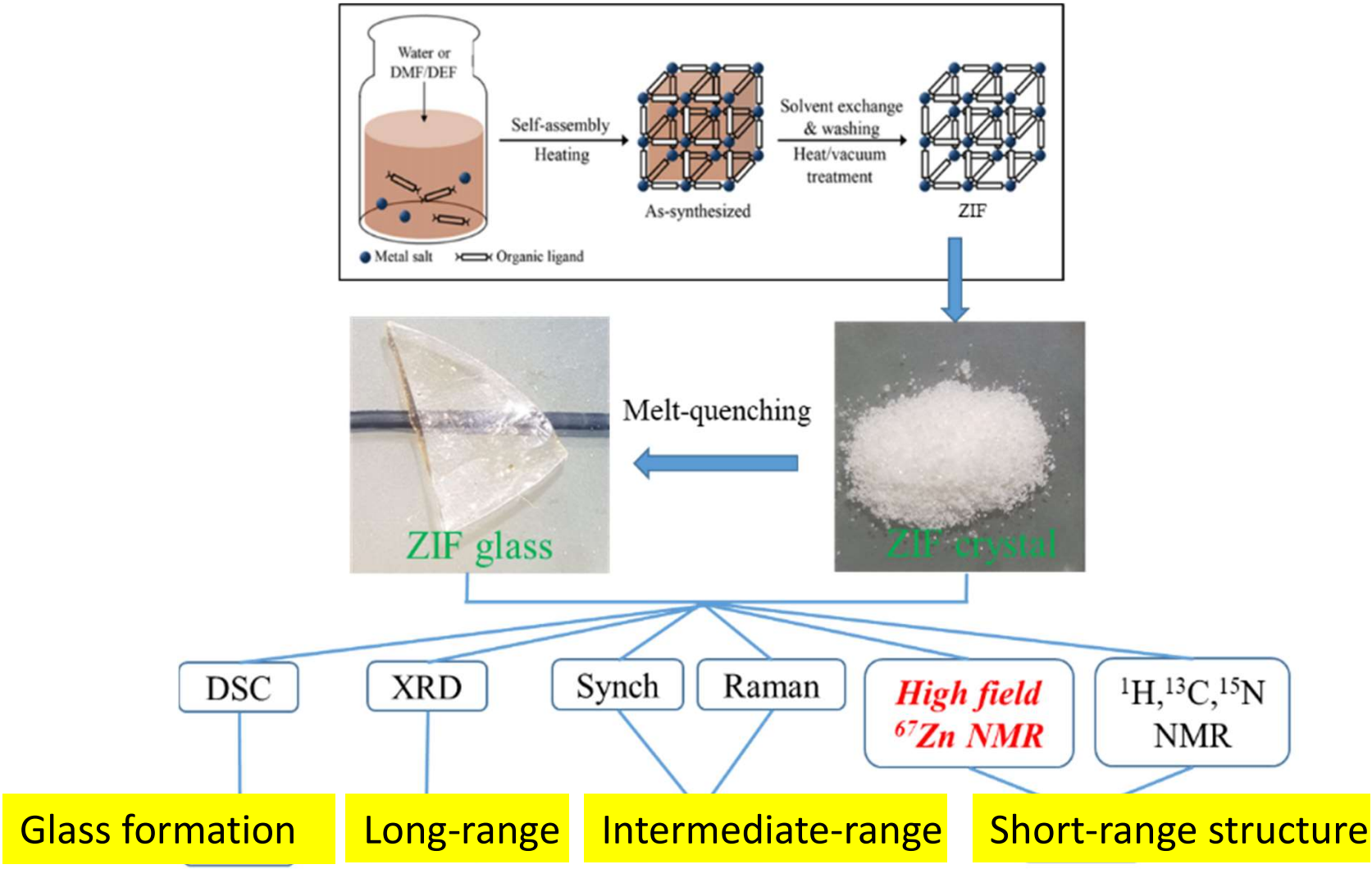

Goodenough, Park, *J. Am. Chem. Soc*. 2013

We are making progress in this direction:

*Energy Environ. Sci.* 2014, *Nano Energy* 1998, 1999, 1999, 1999, 2020, 2021, *Adv. Mater.* 2022

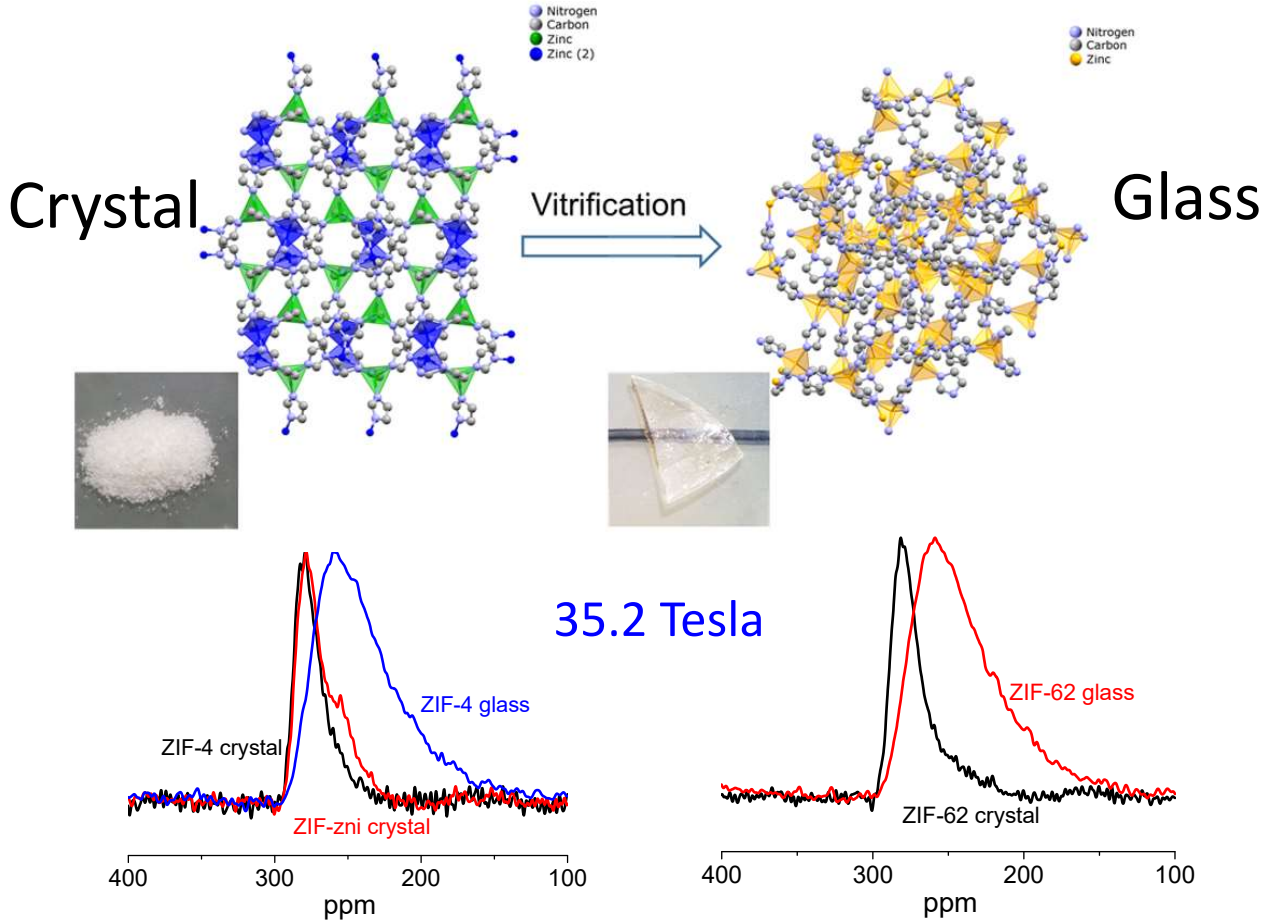
# A recent advance:
# Metal-Organic Framework (MOF)
# GLASS ANODE

# Experimental approach of MOF glass research




- Synthesis of ZIF crystals
- Melting and quenching towards glass
- Observation of phase-transitions and glass transition
- Determination of structure and phases

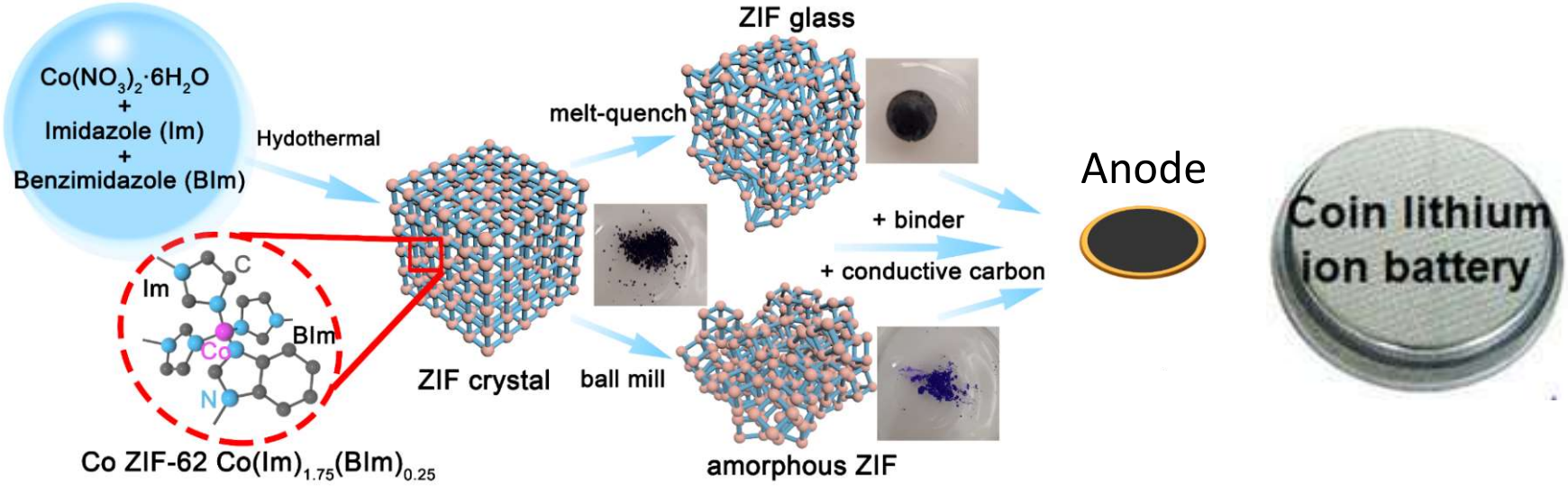
# $^{67}$Zn MAS NMR spectra reveal a high degree of short-range order in ZIF glasses!




The difference in the spectra between ZIF glass and crystal implies a high degree of short-range disorder in ZIF glass

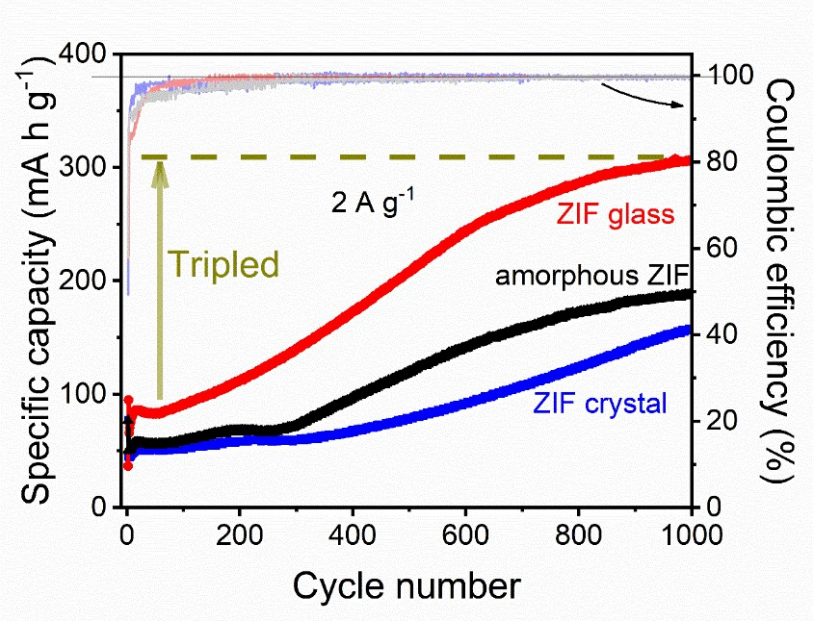
R.S.K. Madsen, A. Qiao, J. Sen, I. Hung, K.Z. Chen, Z.H. Gan, S. Sen*, Y.Z. Yue*, *Science* 367 (2020) 1473–1476

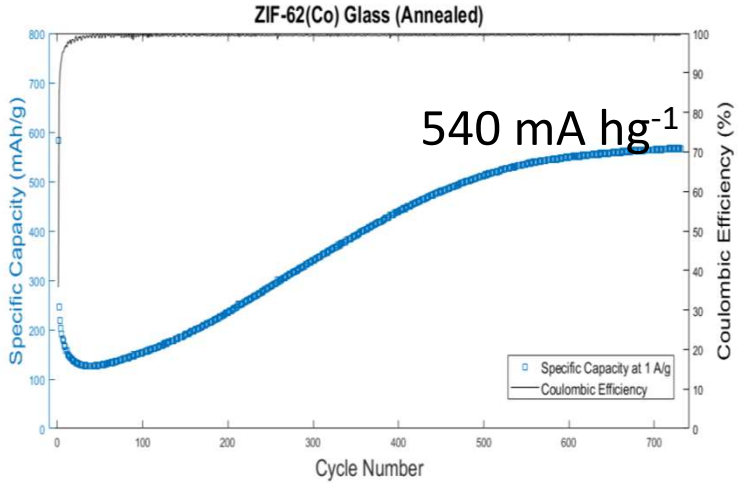
# The first MOF glass anode - ZIF-62 (cobalt) for LIBs




**Surprising observations:**

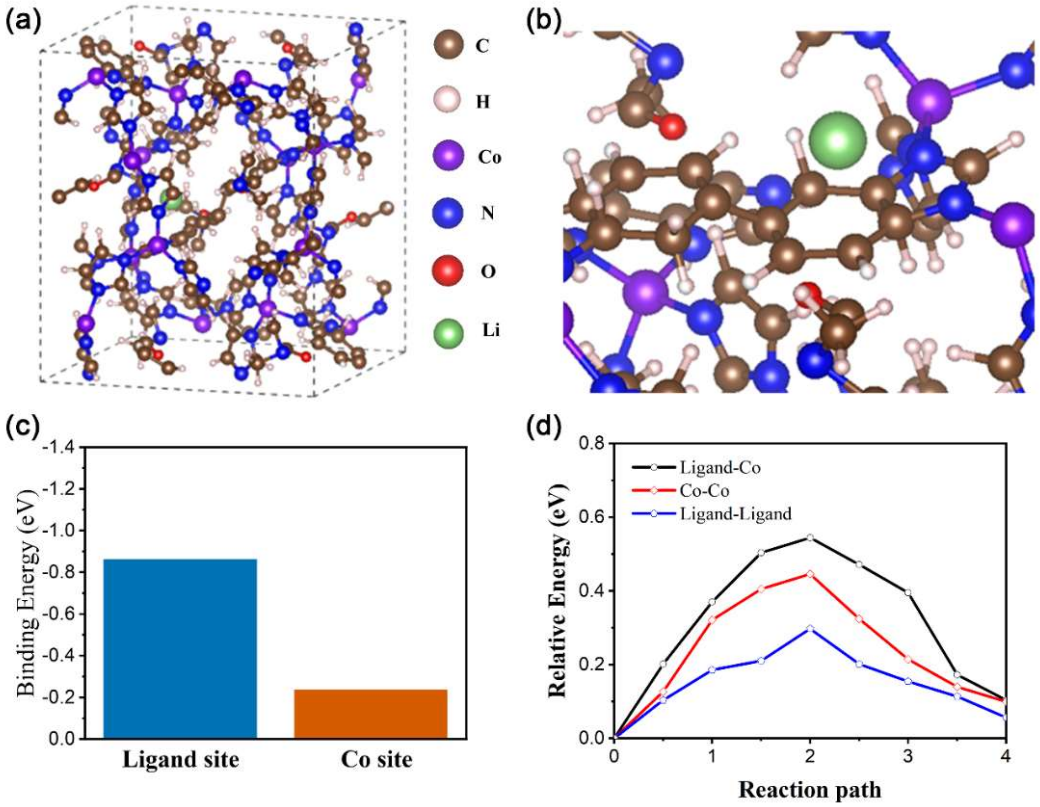
**Cycling induced a 3- to 5-fold increase in capacity☺**



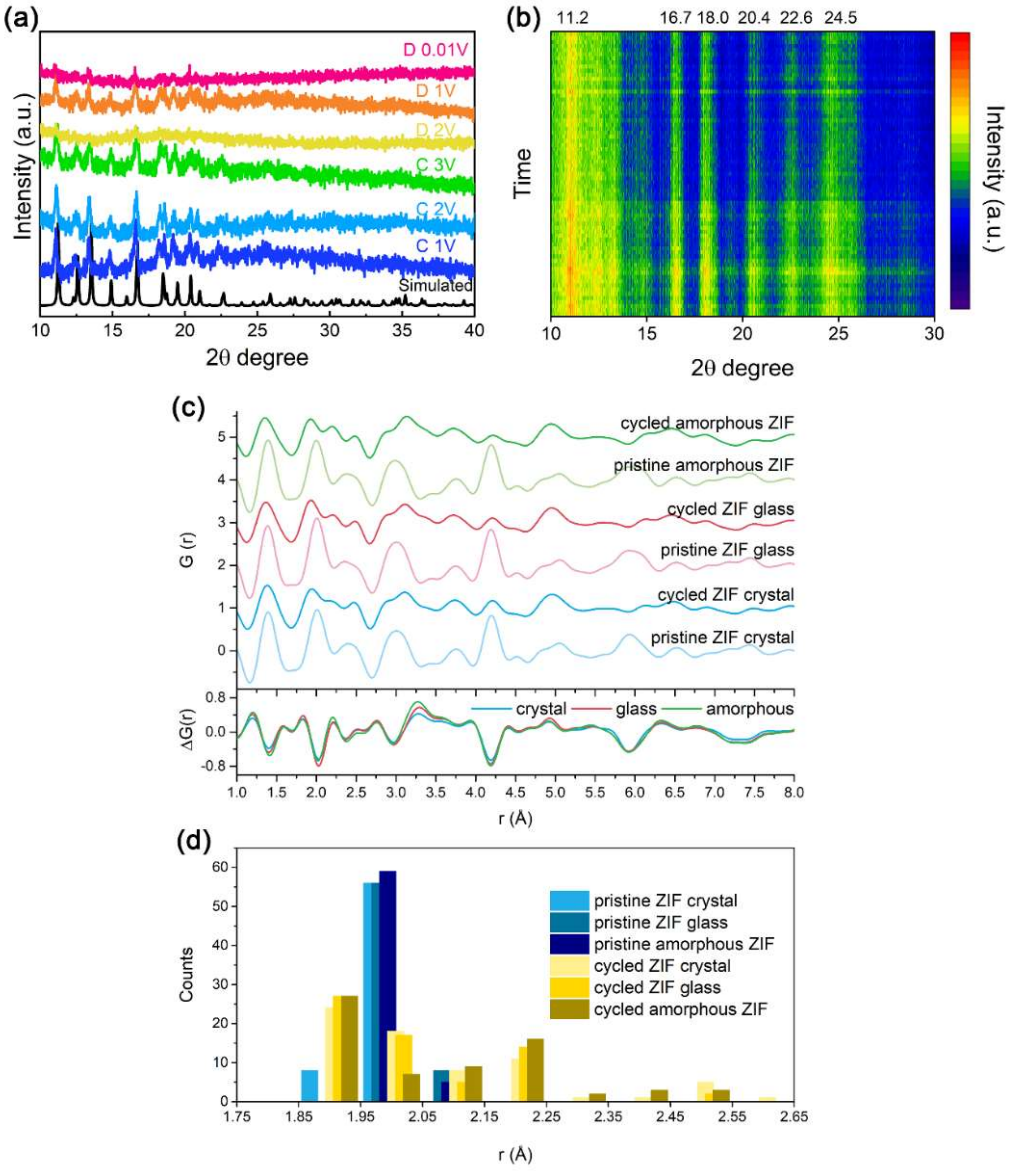




After sub-$T_g$ annealing (unpublished)

# Explore the structural origin of the capacity enhancement

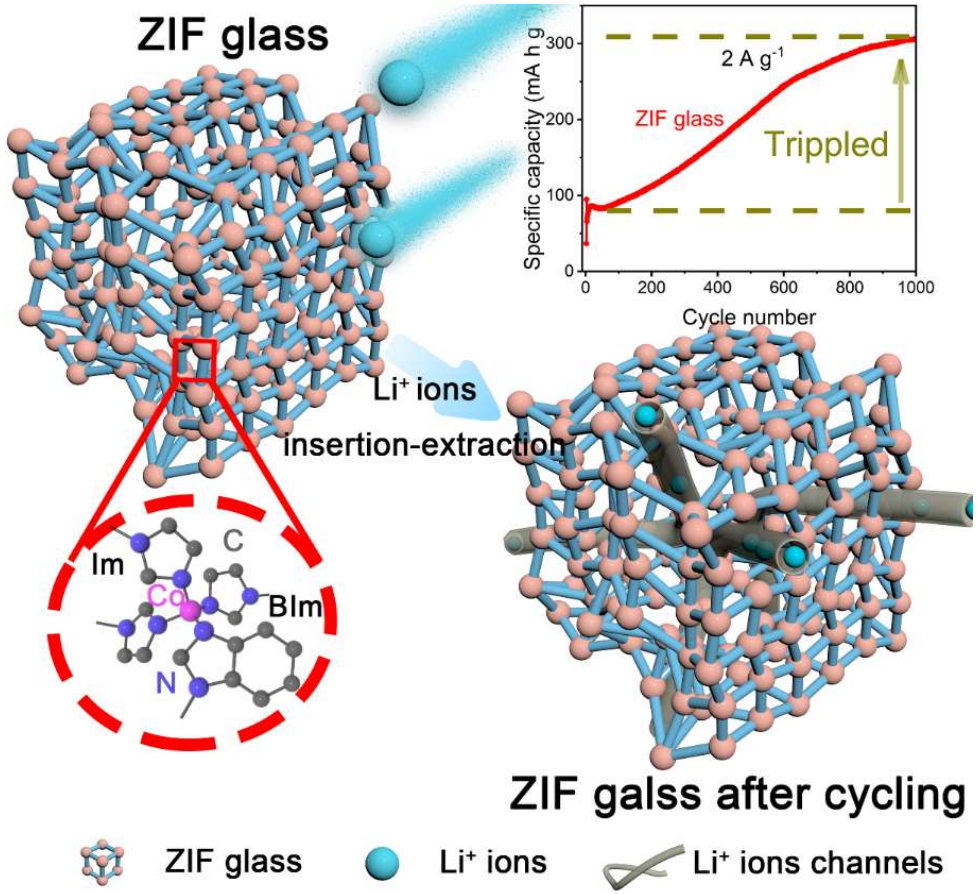



DFT calculation of binding sites, binding energy, and reaction path for $Li^+$ ions




Ex and in situ XRD patterns and PDF analysis of ZIF anodes before and after 1000 charge-discharge cycles

# Origin of the remarkable enhancement of ZIF glass anode induced by discharging/charging cycles




Compared to ZIF crystal, ZIF glass has

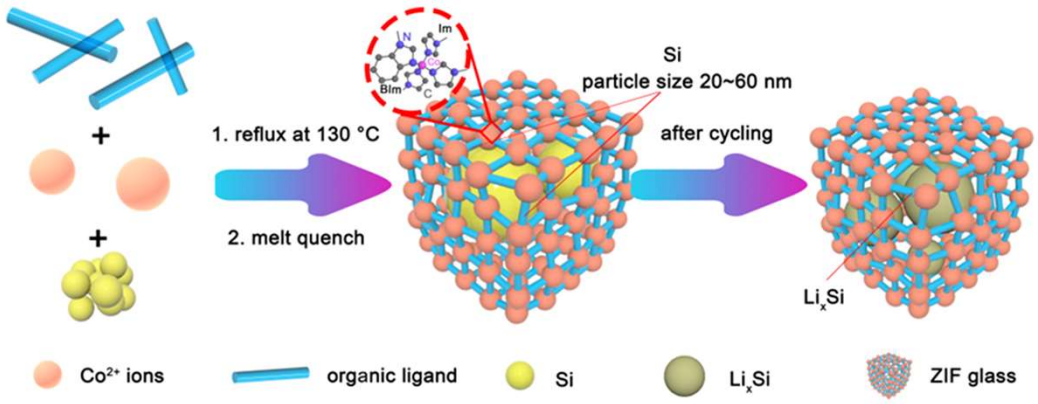
- Higher potential energy
- Frustrated structural network
- Weaker coordination bonds
- Disorder in all length scales

Upon cycling:

- Impact of Li on the coordination bonds gives more voids and channels for Li-transfer.
- Structure network is liberated and becomes more stable.
- Linkers are intact.

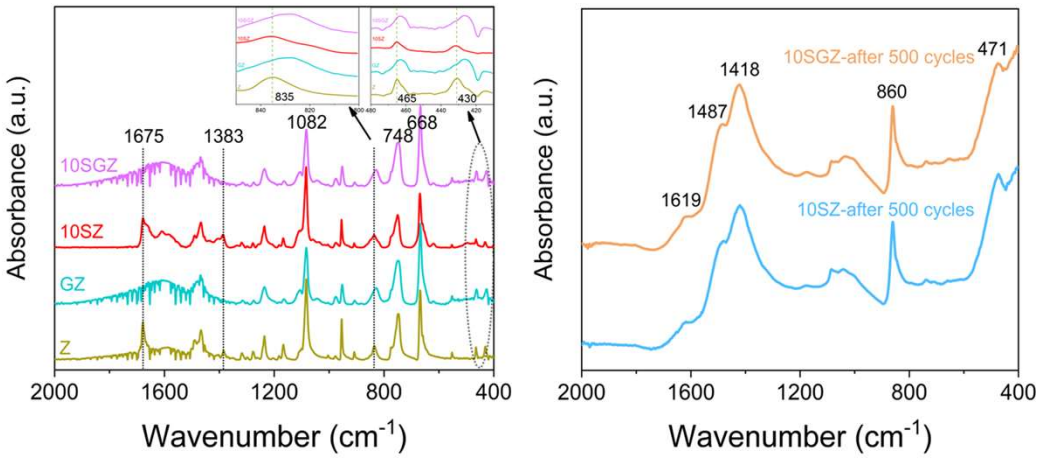
C.W. Gao, Z.J. Jiang, S.B. Qi, P.X. Wang, L.R. Jensen, M. Johansen, C.K. Christensen, Y.F. Zhang, D.B. Ravnsbæk, Y.Z. Yue
*Advanced Materials* 34 (2022) 2110048

# Si@MOF-glass composite-based anode

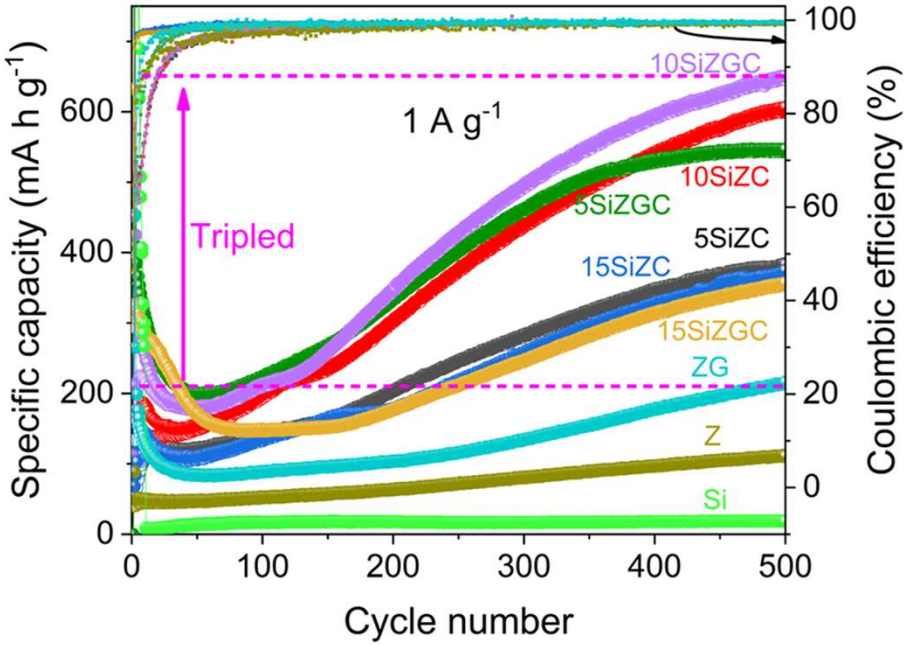



- Si@MOF-glass composite was prepared by combining reflux and melt-quenching methods.
- Si@MOF-glass composite-based anode gives a synergistic effect on lithium storage.

FTIR




- Co-N and aromatic ring is weaker in glass.
- Bonds are broken upon cycling.
- Raman and XPS confirmed the FTIR results.




**Yan, Gao**, Qi, Jiang, Jensen, Zhan, Zhang, Yue
*Nano Energy* 103 (2022) 107779

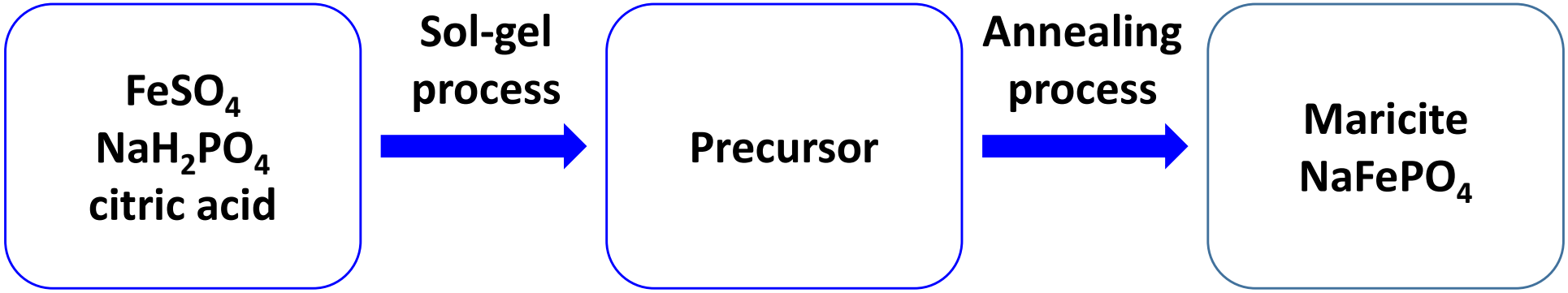
# Amorphous $NaFePO_4$ solid for NIBs

# $NaFePO_4$ crystal (Maricite)

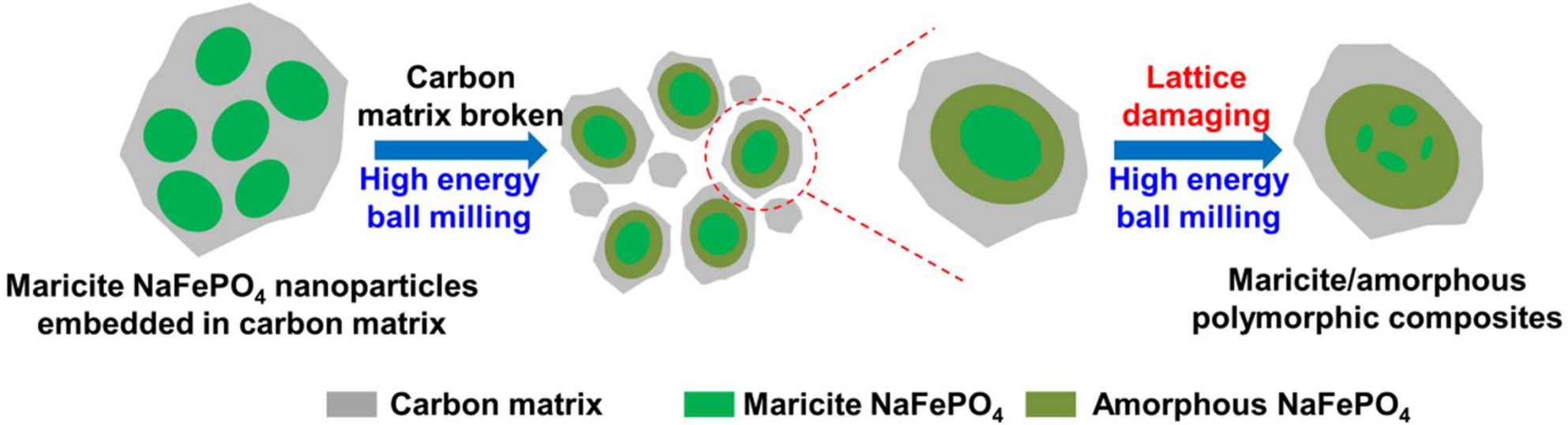
- Maricite could be a potential cathode material. for Na ion batteries (NiBs)
- But it is electrochemically not active
- Can we make it disordered and thereby electrochemically active?
- We chose the high-energy ball-milling to make it amorphized or disordered.

# Fabrication of the Amorphous maricite $NaFePO_4$

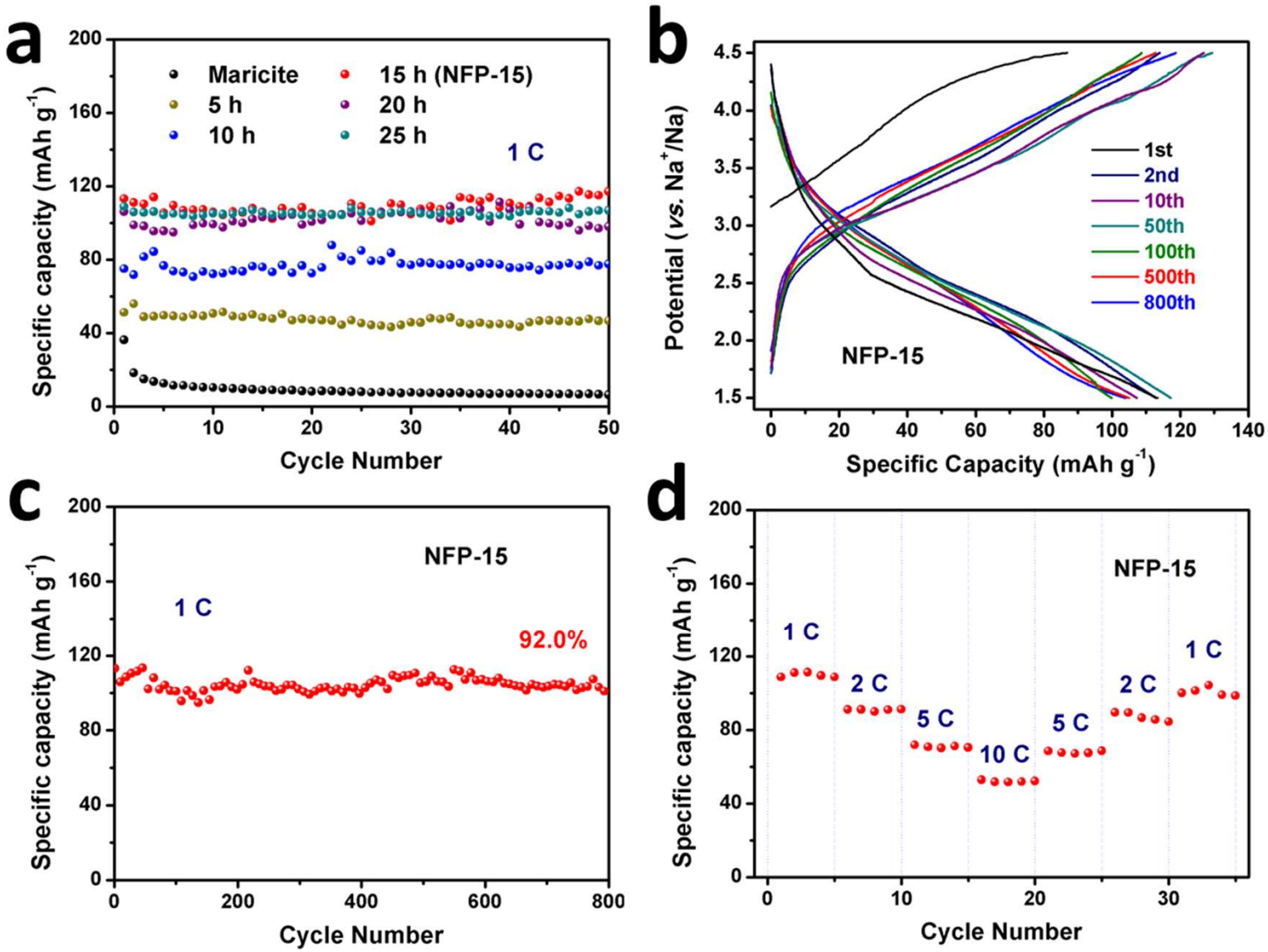
## 1. The synthesis of maricite $NaFePO_4$




## 2. Amorphosizing $NaFePO_4$ by ball milling



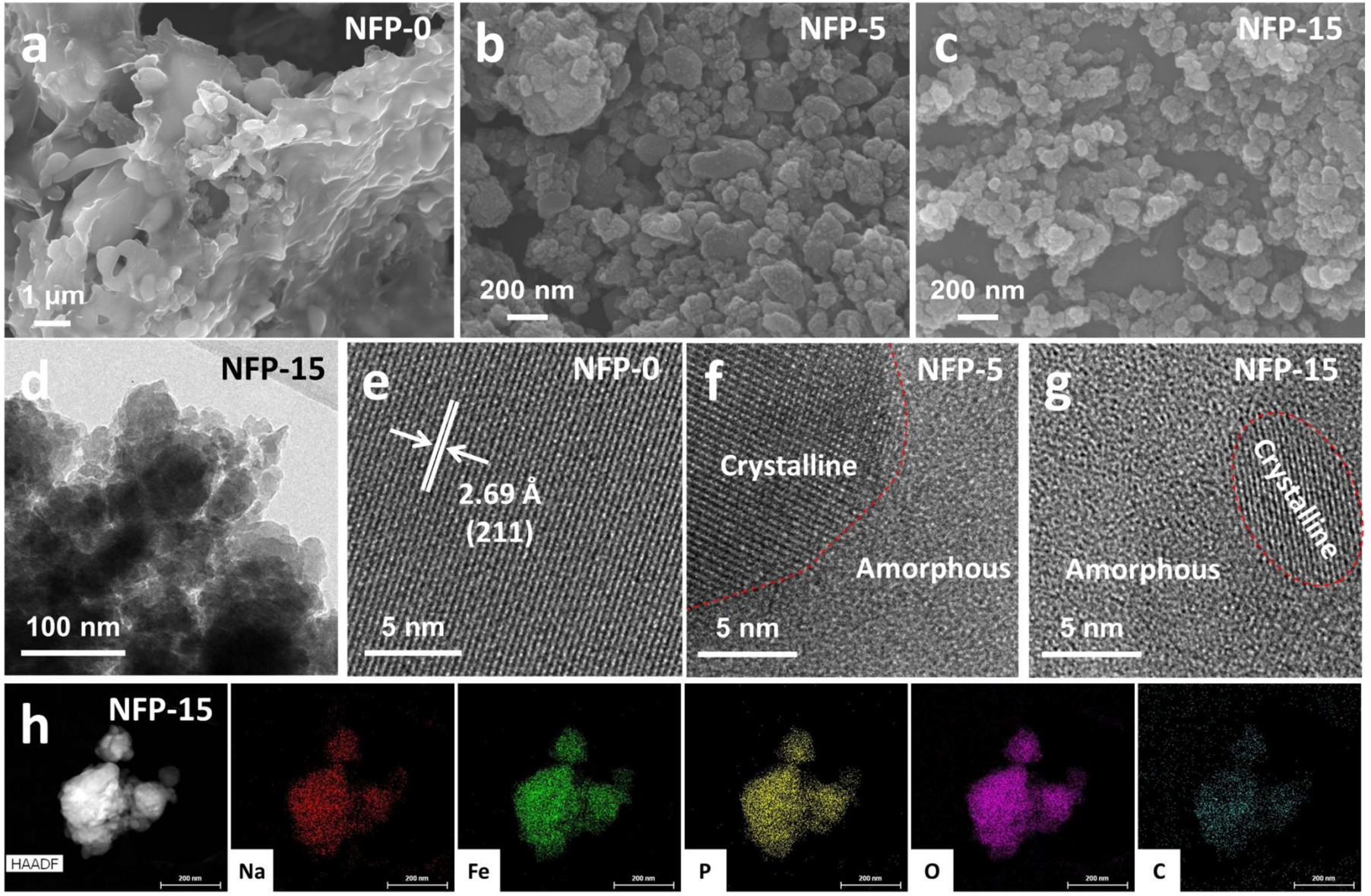
# Enhancing sodium Storage Performance by disordering




**The polymorphic composites exhibit enhanced capacity by 15 hrs ball milling.**

Xiong, et al., *Nano Energy* 2019

# Material Characterizations




**Upon high energy ball-milling, the particle size decreases and the amorphous content increases.**

# Concluding remarks

Glass has a bright future and continues to contribute to a green transition and hence to a sustainable society☺

Thank all my group members, co-authors and collaborators

Thank you for your attention!