Using mechanochemistry to explore new sodium conducting glasses and glass-ceramics

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Rennes Institute of Chemical Sciences, France

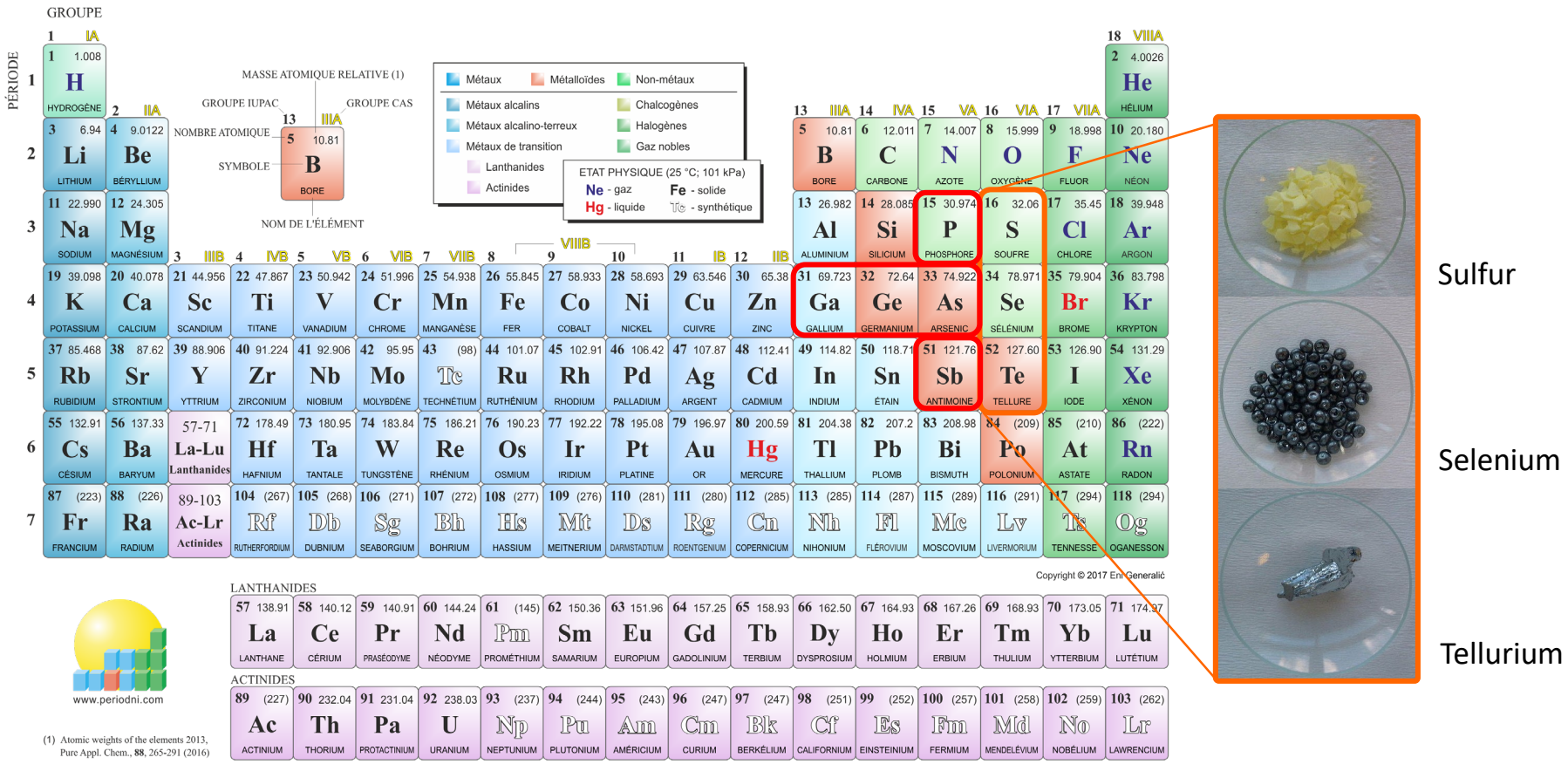
Glasses and ceramics team

New Inorganic Functional Oxides: Synthesis, Characterisation and Simulations

OCTOBER 04, 2023 - OCTOBER 06, 2023

Context – Non-oxide chalcogenide glasses

Compositions



Sulfur

Selenium

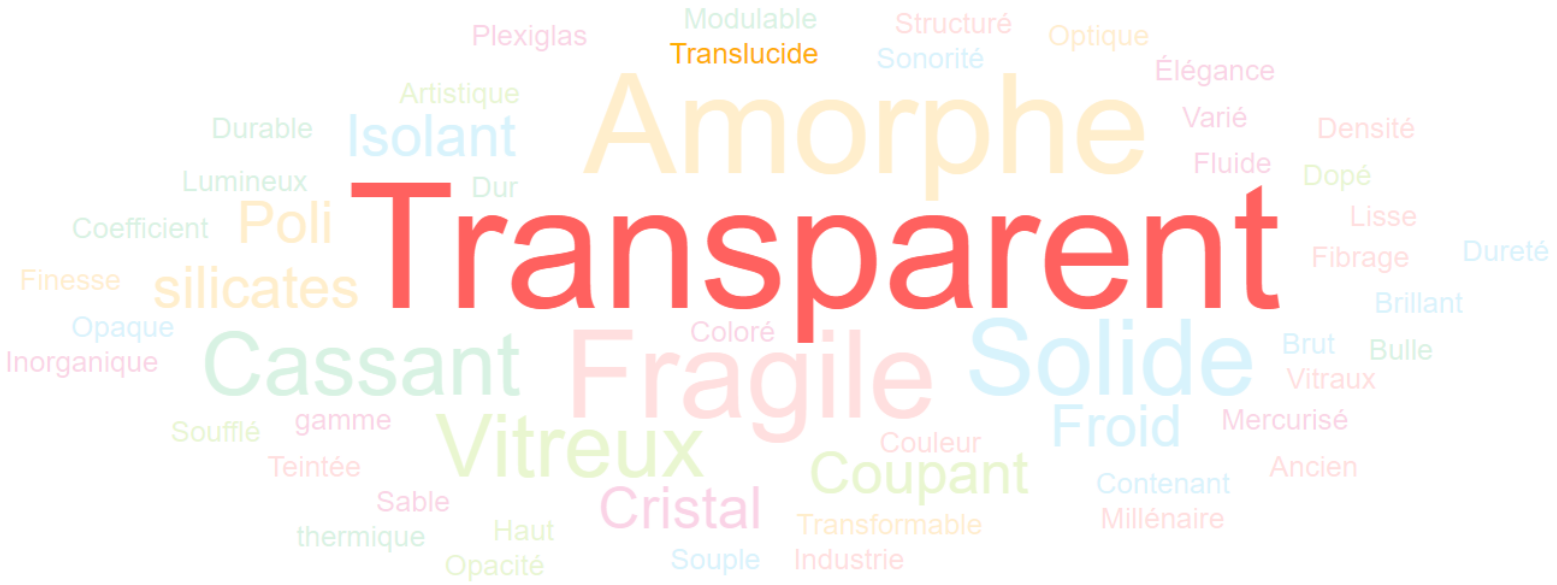
Tellurium

Context – Non-oxide chalcogenide glasses

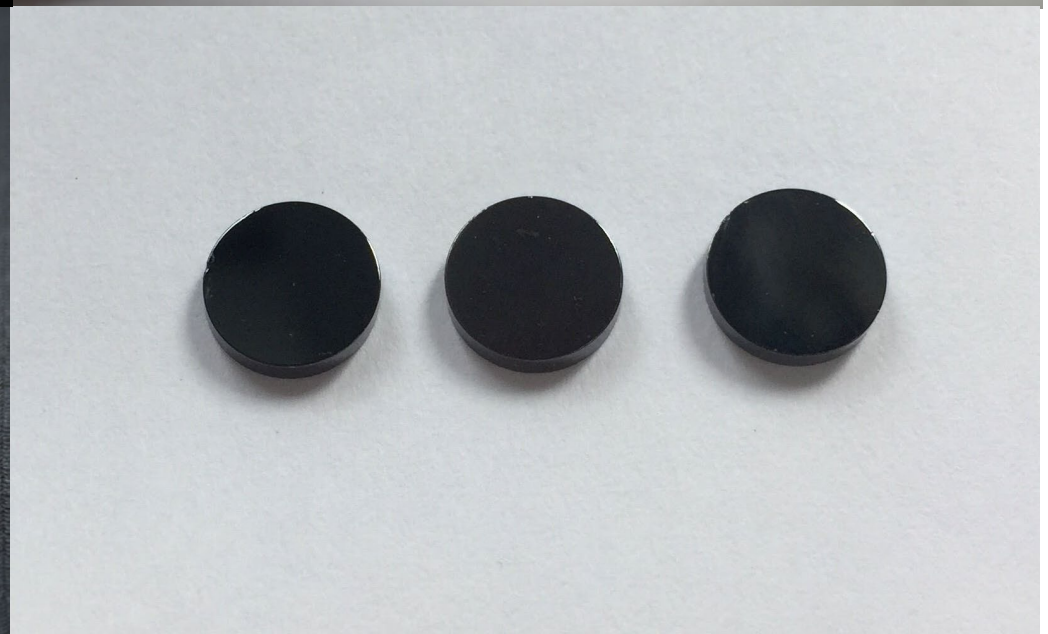
Properties

How would you describe glass (the material) ?

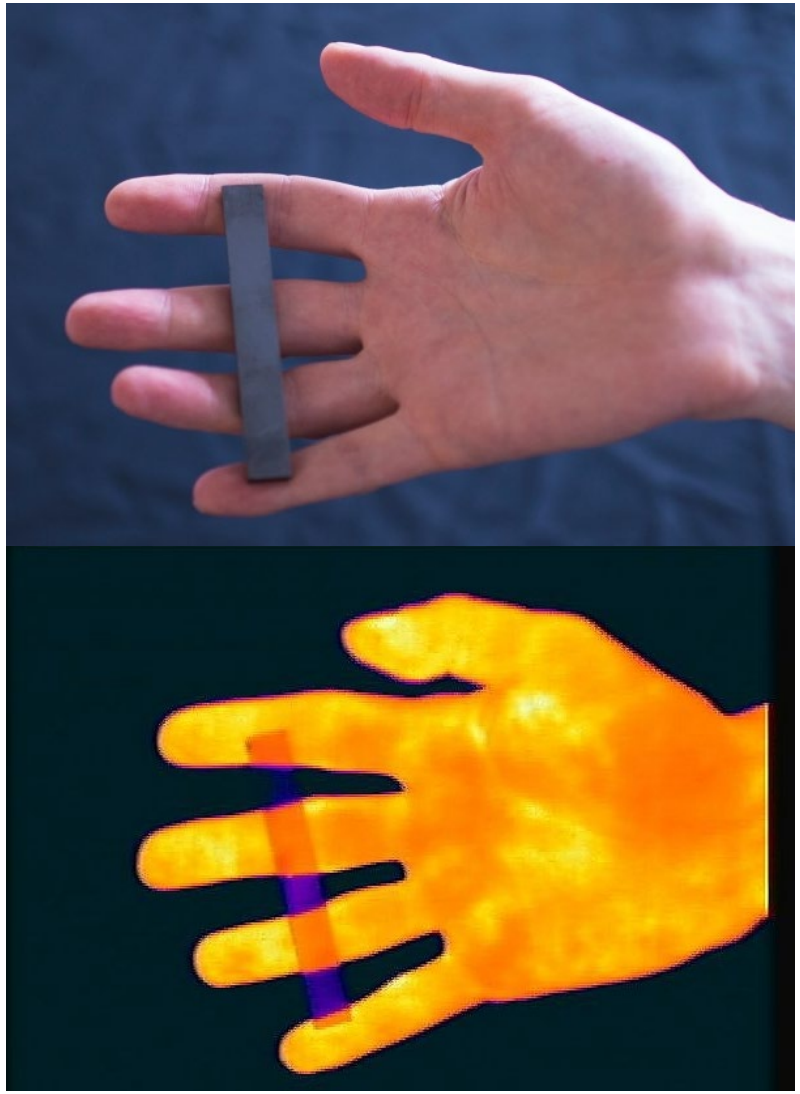
~ 100 answers



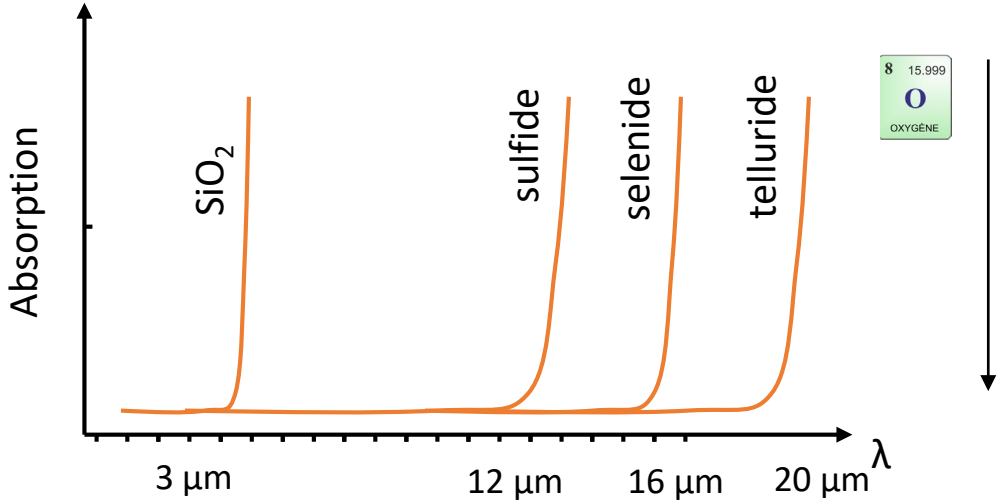
Context – Non-oxide chalcogenide glasses



Context – Non-oxide chalcogenide glasses



⇒ transparent in the infrared



Optical devices – Lens – infrared imaging

Sensors – Thin films – detection of pollutants in water

Fiber optics – Battery diagnostics

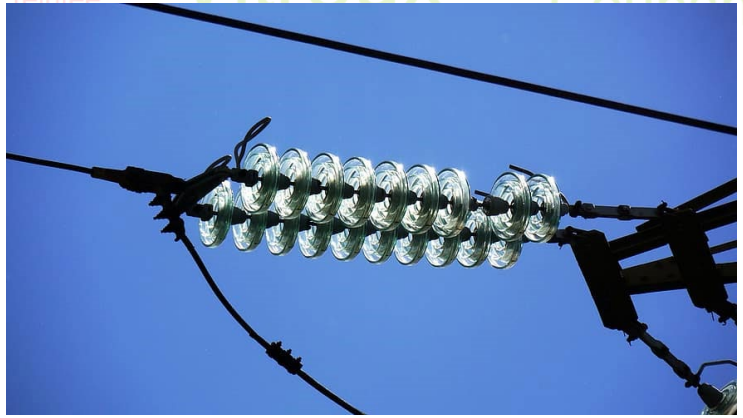
Context – Non-oxide chalcogenide glasses

Properties

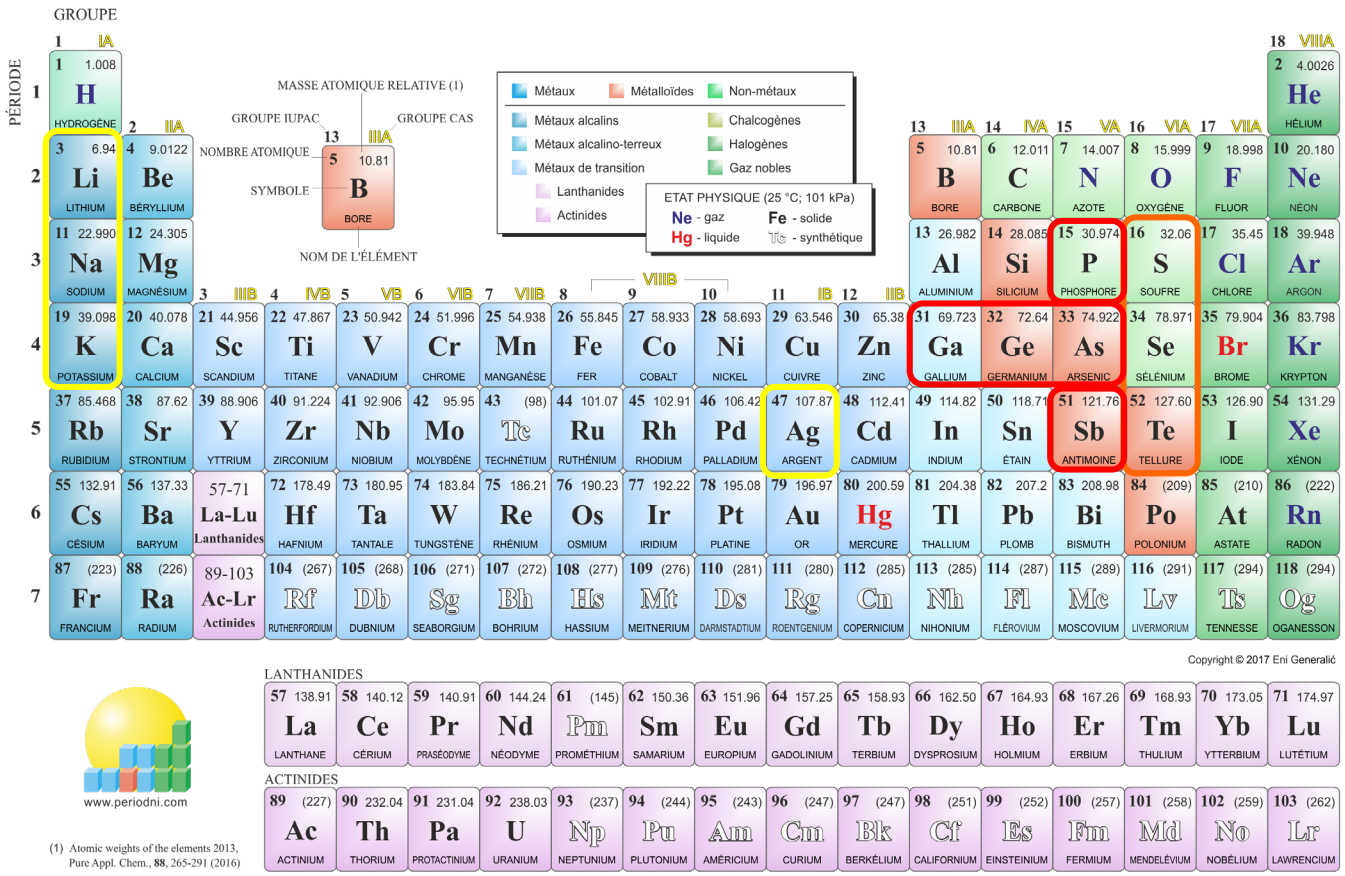
How would you describe glass (the material) ?

Plexiglas Modulable Translucide Structuré Sonorité Optique Élégance Artistique Durable Isolant Amorphe Varié Densité Fluide Dopé Lumineux Dur Coefficient Poli Transparent Lisse Fibrage Dureté Finesse silicates Brillant Opaque Coloré Inorganique Cassant Fragile Solide Brut Bulle Vitraux Soufflé gamme Froid Mercurisé Vitreux Couleur Teintée Courant Ancien

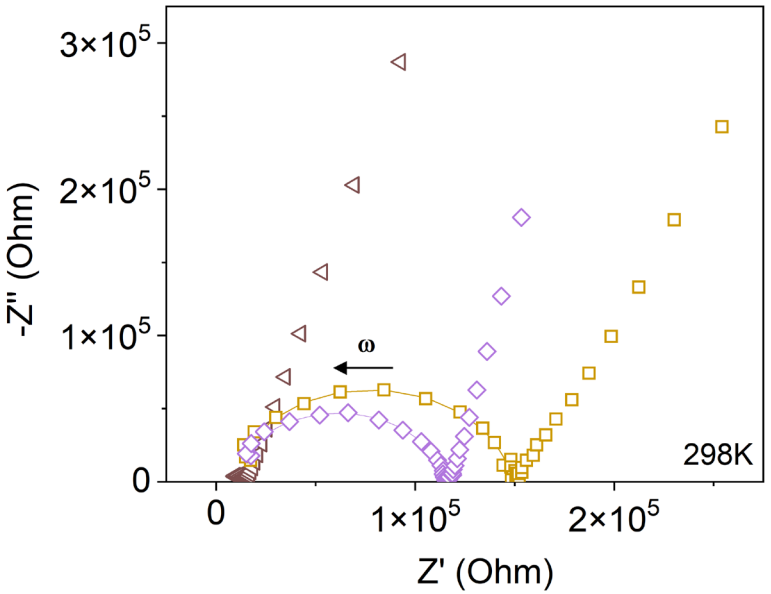
Insulating



Context – Non-oxide chalcogenide glasses



Impedance spectroscopy



⇒ ionic conductivity

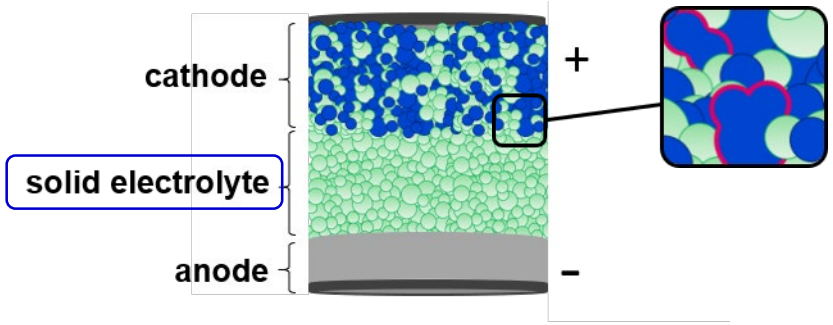
⇒ solid state electrolyte in all solid state batteries

Context – Ion conducting materials for solid-state electrolytes

Conventional Li-, Na- ion batteries ⇒ Liquid electrolyte

⚠ **Flammability and limited electrochemical stability**

All solid-state batteries:



Li or Na conducting materials:

⇒ high ionic conductivity

⇒ stability toward the electrodes

⇒ high electrochemical stability window

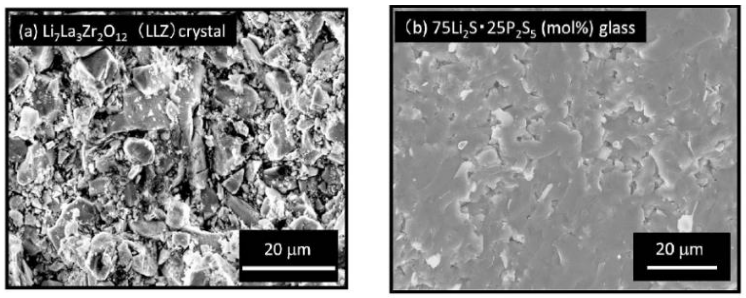
⇒ high ductility

Sulfide glasses

Context – Ion conducting materials for solid-state electrolytes

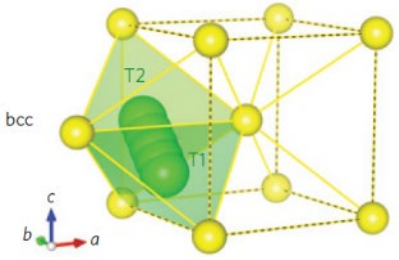
Why sulfide glasses?

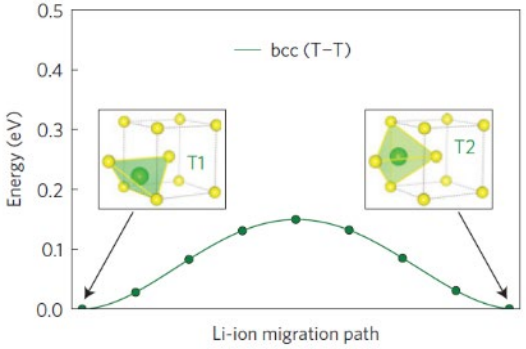
- Mechanical properties



Sakuda et al, *Sci. Rep.* **2013**, 3, 2261

- High conductivity over a wide range of compositions vs crystalline materials



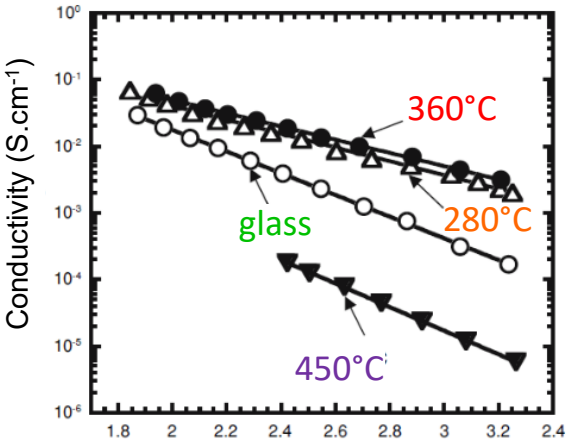


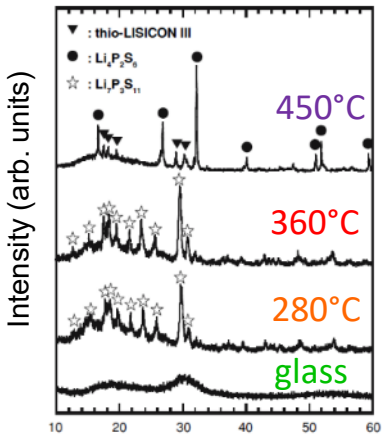
Wang et al., *Nat. Mater.* **2015**, *14*, 1026

- Glass-ceramics

Precursors for new metastable phases with higher ionic conductivities

ex : $Li_7P_3S_{11}$ (70 Li_2S – 30 P_2S_5)





Hayashi, J Mater Sci, **2008,** 43, 1885

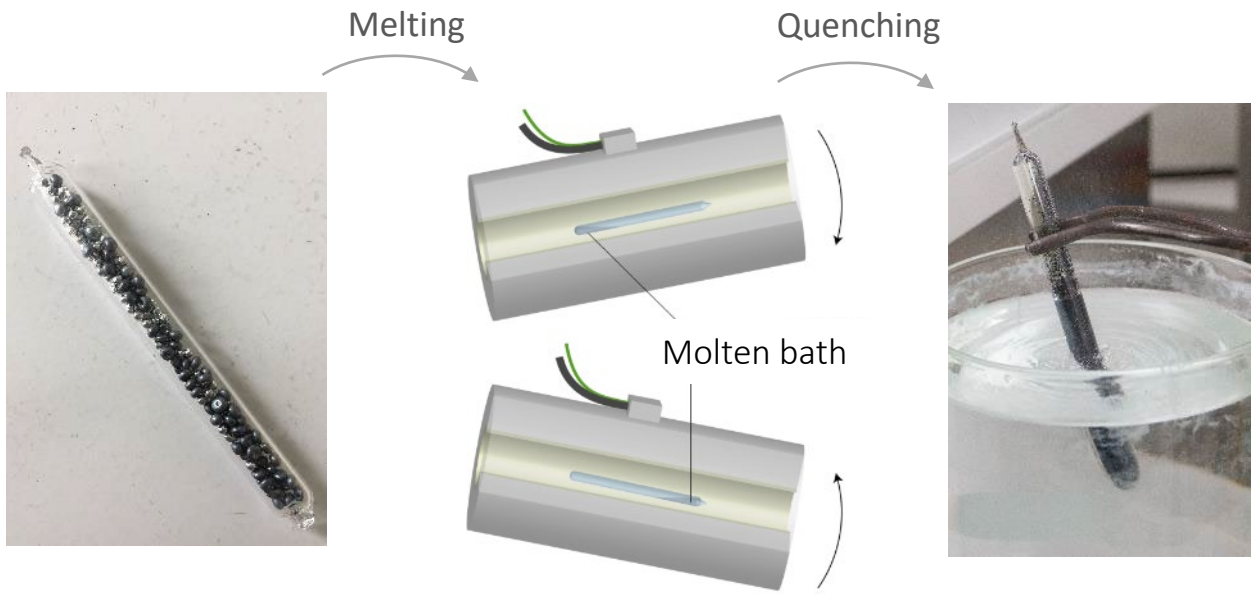
Glass: 10^{-4} S.cm^{-1} at room temperature

$Li_7P_3S_{11}$: 4 x 10^{-3} S.cm^{-1} at room temperature

Properties can be modified by the synthesis method

Context – Synthesis routes for sulfide glasses

Melt-quenching method



⇒ sulfur vapors

⇒ reactivity of Li or Na with silica

⇒ high temperature

Mechanochemistry

© Emmanuel PERRIN / CNRS Images

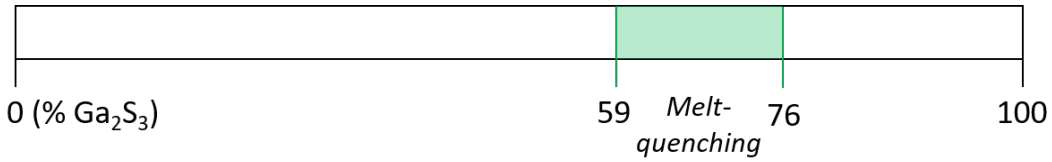
⇒ room temperature

⇒ large quantity of material

Context – System studied

Na_2S-Ga_2S_3

Barnier et al., *Solid State Ionics* **1990**, *44*, 81



crystallization

Glass-ceramics

Is it possible to enlarge the amorphous domain using mechanochemistry?

Conductivity properties?

New phases?

Properties?

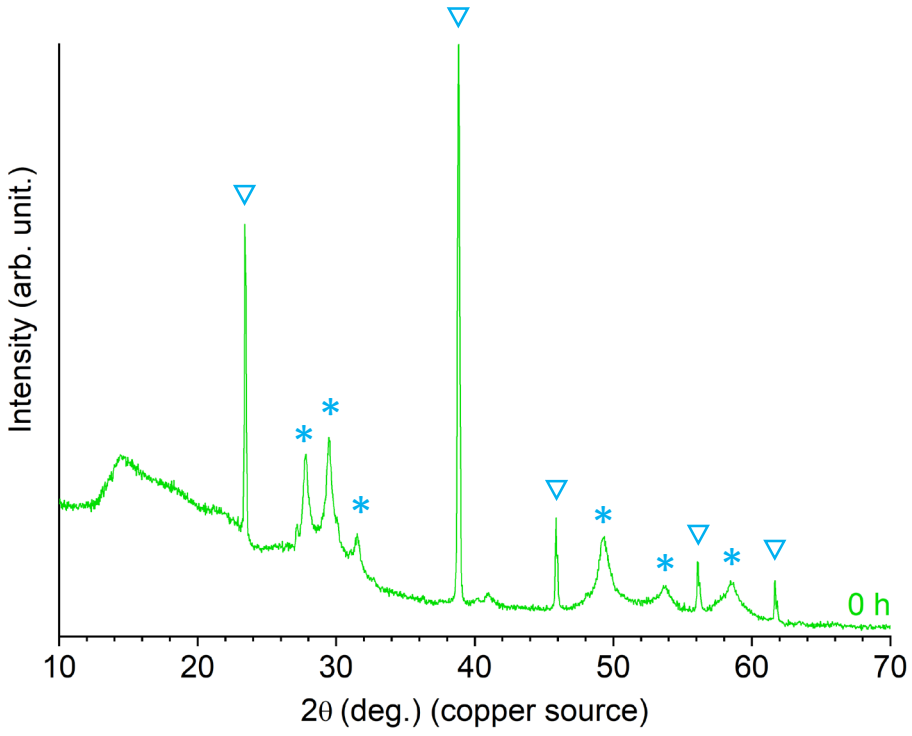
Glasses obtained by mechanochemistry

x Na_2S – (100-x) Ga_2S_3

- ▽ Na_2S + * Ga_2S_3 milled in ZrO_2 vessels with ZrO_2 balls

X-ray diffraction

ex: 50 Na_2S – 50 Ga_2S_3



Dénoue et al. *Mater. Res. Bull.* **2021**, *142*, 111423

Verger et al. *Inorg. Chem.* **2022**, *61*, 18476

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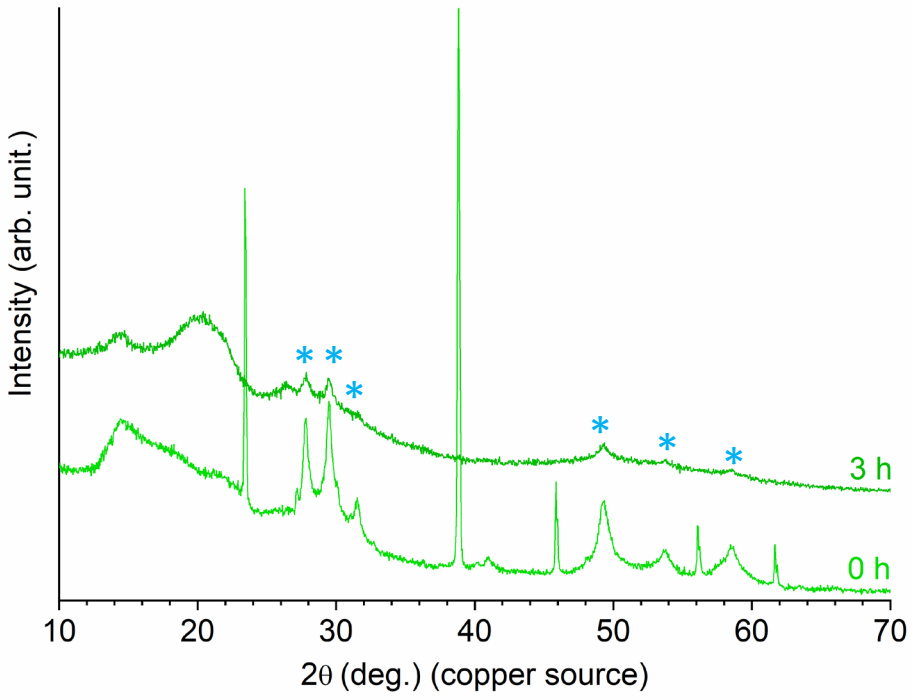

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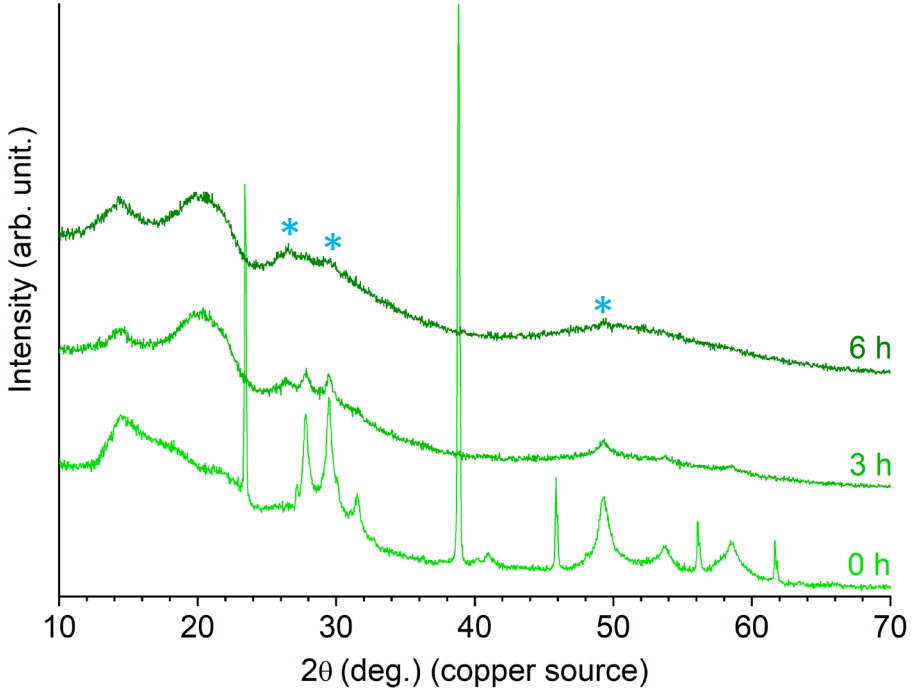

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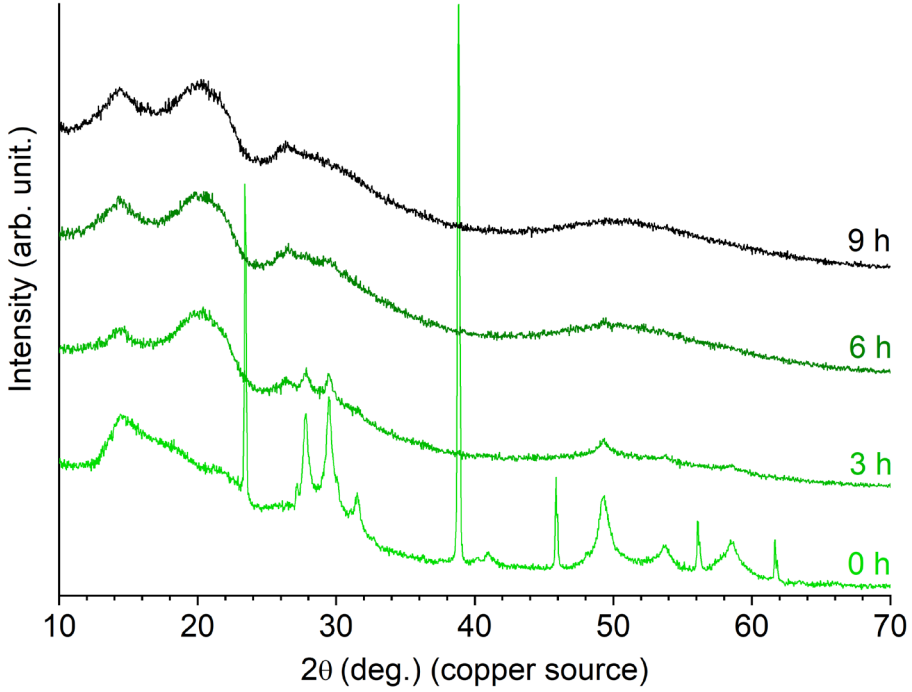
x Na_2S – (100-x) Ga_2S_3

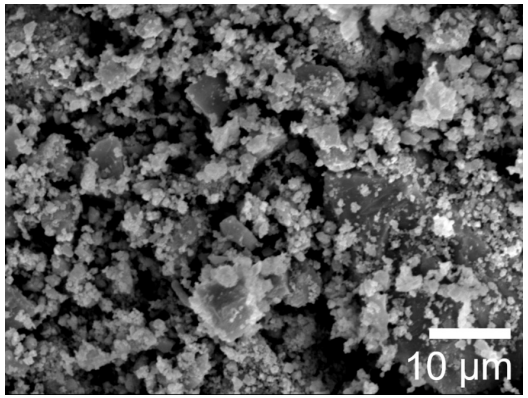
- ▽ Na_2S + ∗ Ga_2S_3 milled in ZrO_2 vessels with ZrO_2 balls ⇒ Amorphous powder for $20 \leq x \leq 80$

PhD K. Dénoue

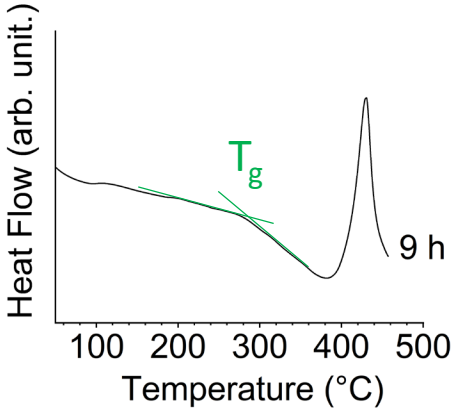
X-ray diffraction

ex: 50 Na_2S – 50 Ga_2S_3





Differential scanning calorimetry



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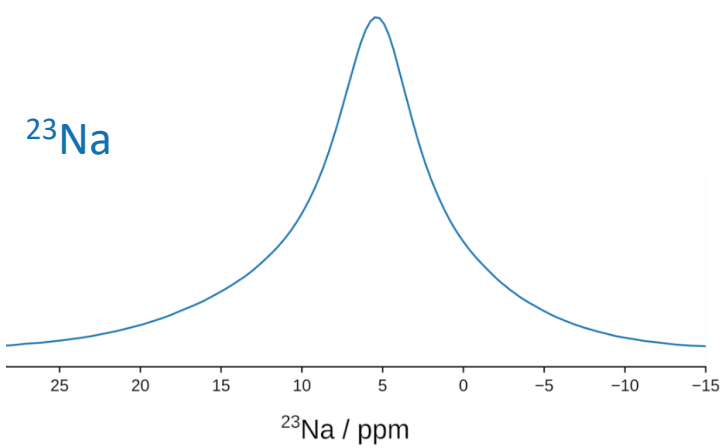
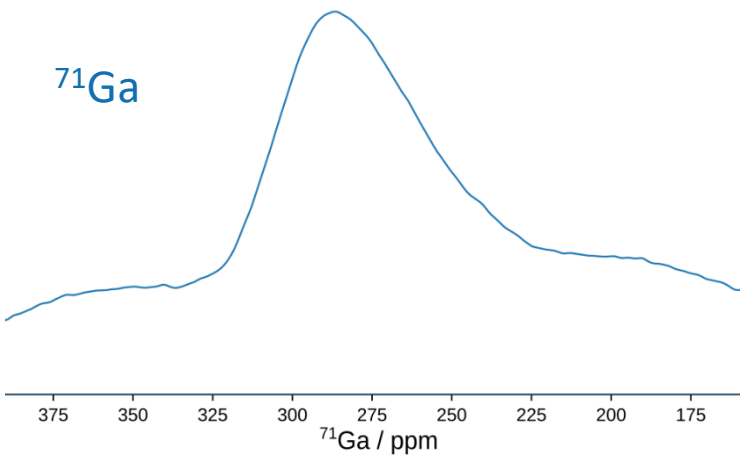
⇒ Amorphous powder for $20 \leq x \leq 80$

NMR spectroscopy

ex: 50 Na_2S – 50 Ga_2S_3





⇒ Broad signal typical of amorphous material

⇒ Local Structure ?

Verger et al. *Inorg. Chem.* **2022**, *61*, 18476

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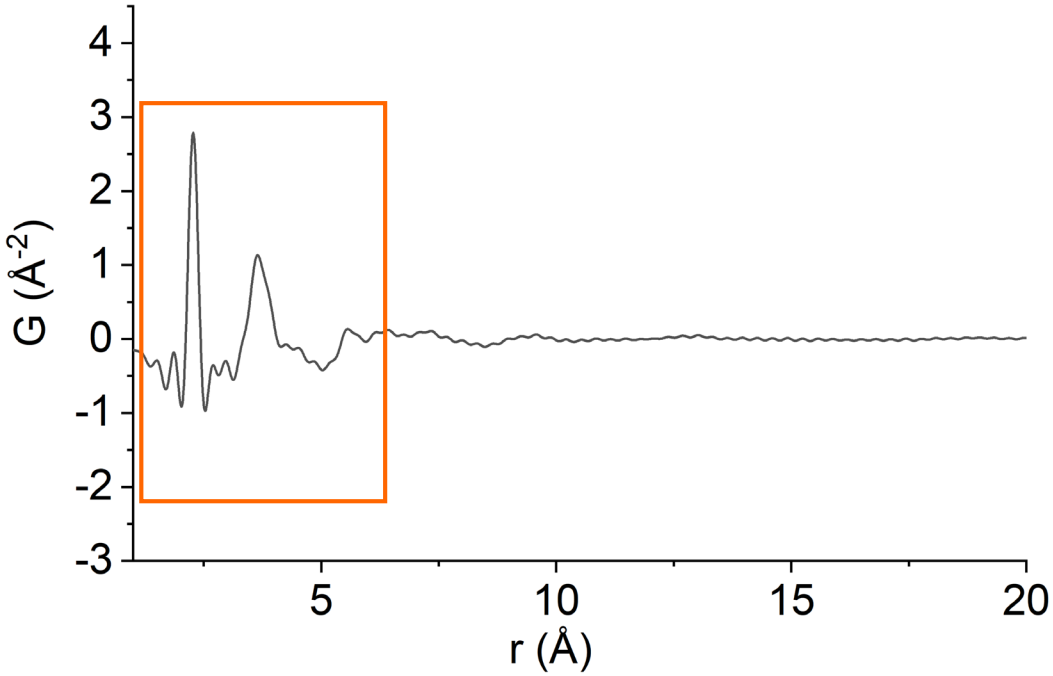
Pair-distribution function analysis (PDF)

diamond I15-1 beamline

ex: 50 Na_2S – 50 Ga_2S_3



Verger et al. *Inorg. Chem.* **2022**, *61*, 18476

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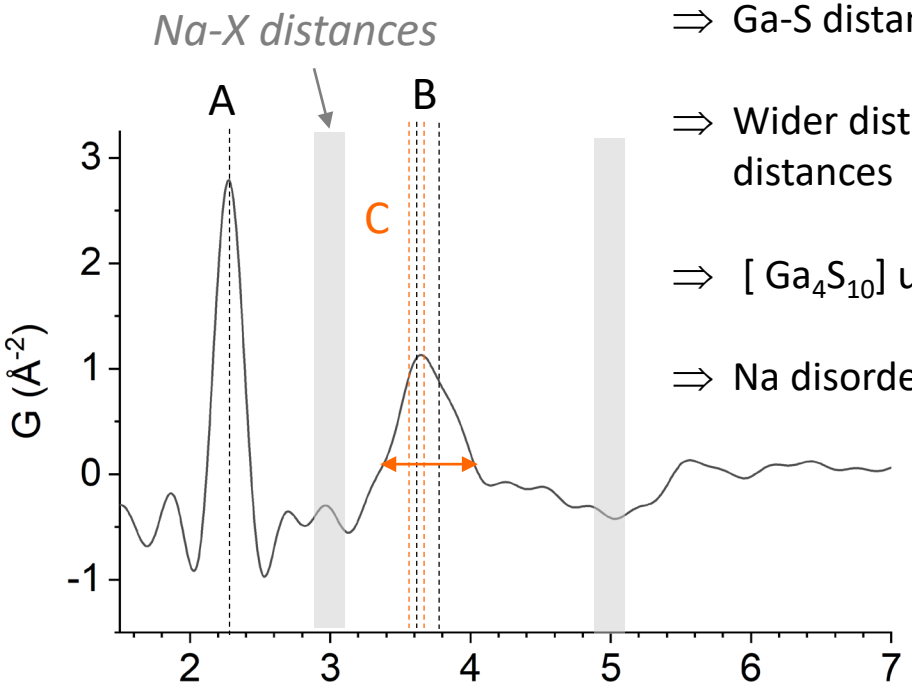
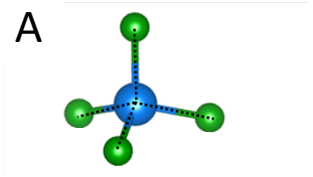


⇒ Ga-S distances detected

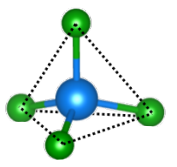
⇒ Wider distribution of Ga-Ga and S-S distances

⇒ [Ga_4S_{10}] unit distorded

⇒ Na disorder

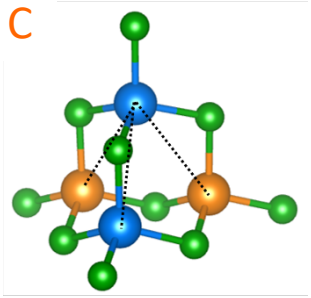


2.26 – 2.27 Å



3.61 – 3.76 Å

[GaS_4] tetrahedron



3.58 – 3.64 Å

[Ga_4S_{10}] unit

S
Ga 1
Ga 2

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Glasses obtained by mechanochemistry

x Na_2S – (100-x) Ga_2S_3

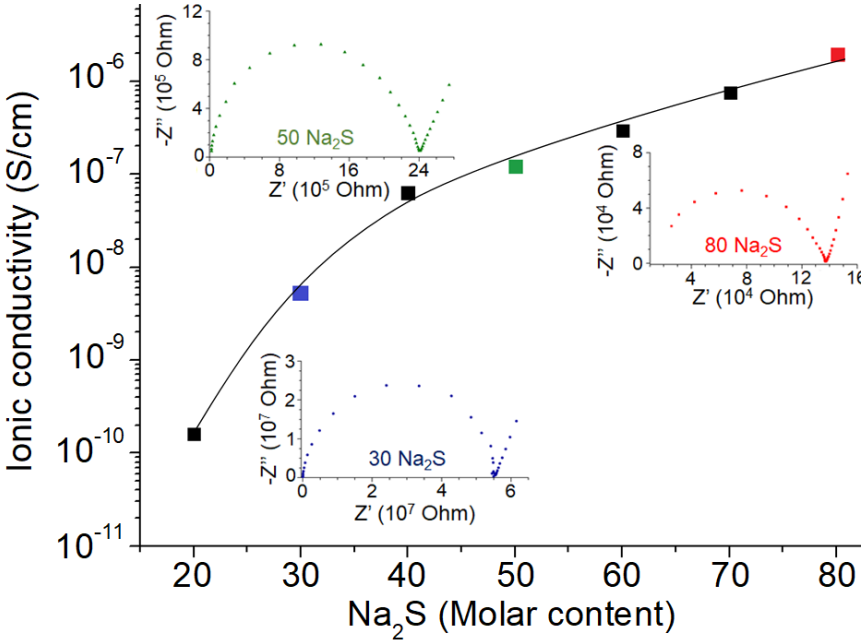
- Na_2S + Ga_2S_3 milled in ZrO_2 vessels with ZrO_2 balls ⇒ Amorphous powder for $20 \leq x \leq 80$

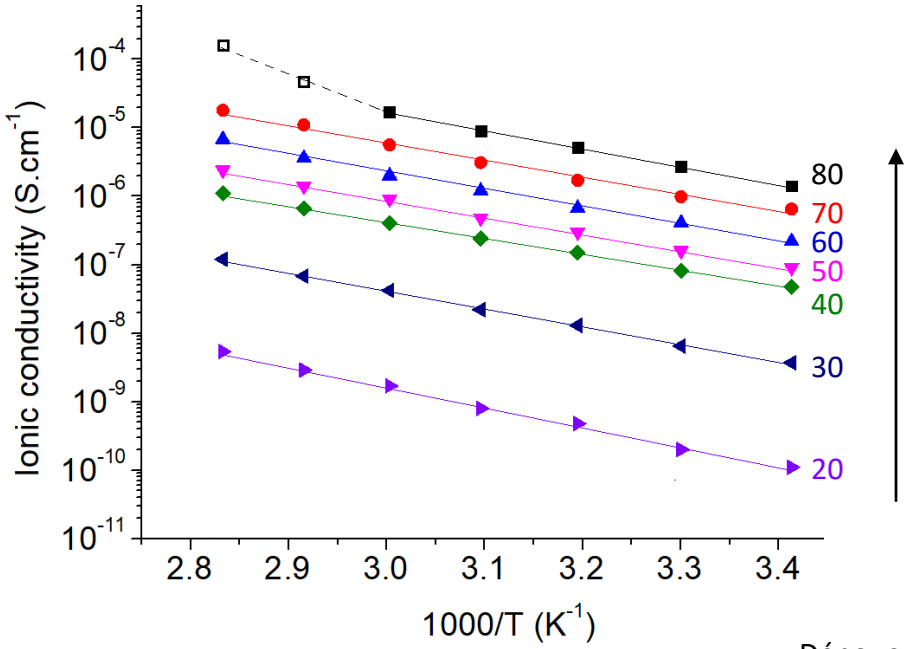
- Powders cold-pressed ⇒ highest conductivity for 80 Na_2S – 20 Ga_2S_3 : $\sigma = 2 \times 10^{-6}$ S.cm^{-1} at 25°C

  ⇒ how to increase the σ ?

  ⇒ aliovalent substitution with Ge

Impedance Spectroscopy





$$\sigma = \frac{\sigma_0}{T} \times \exp\left(-\frac{E_a}{k_b T}\right)$$

% Na ↗

Dénoue et al., *Mater. Res. Bull.* **2021**, *142*, 111423

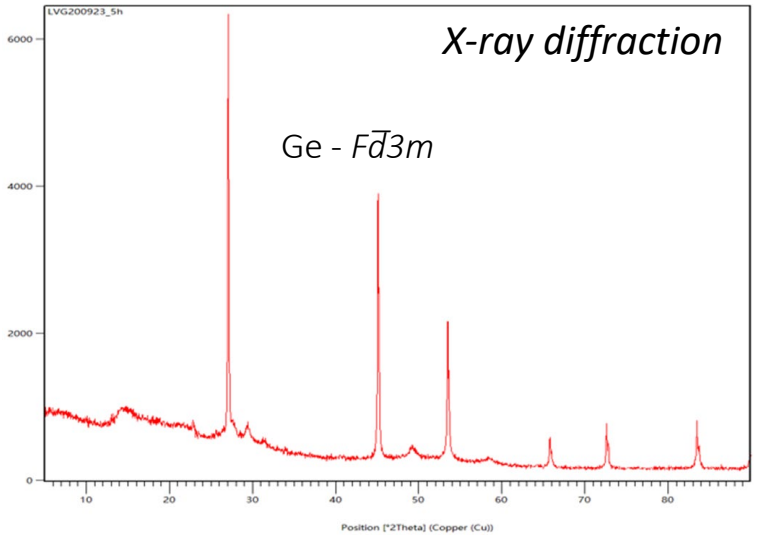
Glasses obtained by mechanochemistry

$x\ Na_2S – (100\text{-}x)\ [0.5\ Ga_2S_3\text{-}0.5\ GeS_2]$

- Difficulty of reactivity/amorphization with Ge using mechanochemistry

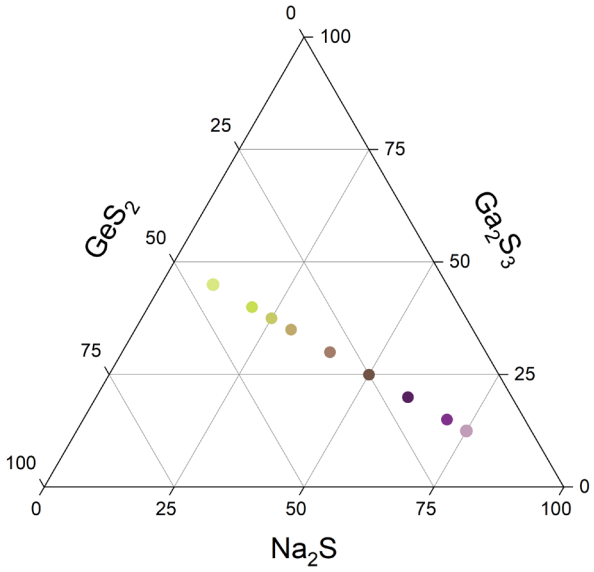
⇒ Glass [0.9 GeS_2 – 0.1 Ga_2S_3] is synthesized by melt quenching

⇒ Na_2S + Ga_2S_3 + [0.9 GeS_2 – 0.1 Ga_2S_3] milled in ZrO_2 vessels with ZrO_2 balls



⇒ Amorphous powders for $10 \leq x \leq 75$

PhD J. Zhang



Zhang et al., *Under review*

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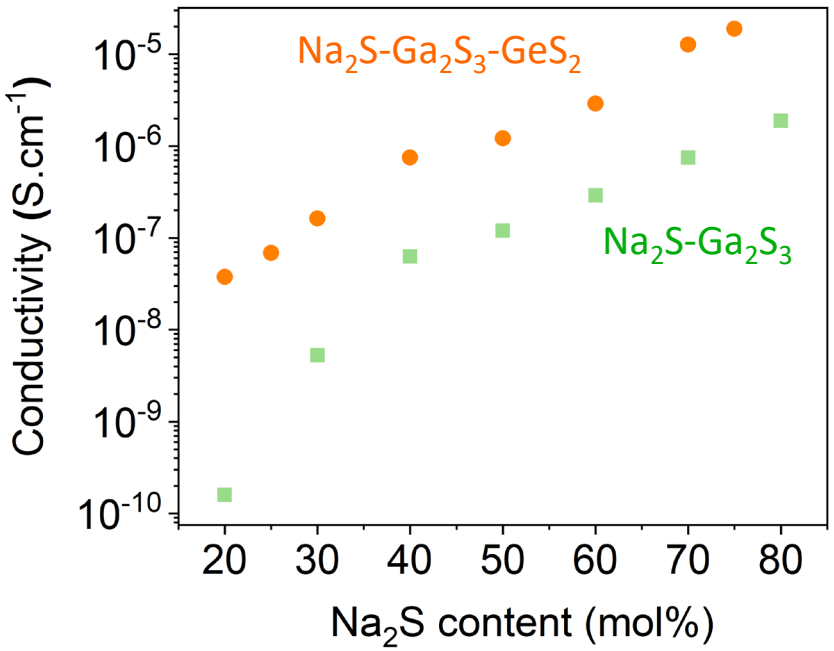
Impedance Spectroscopy



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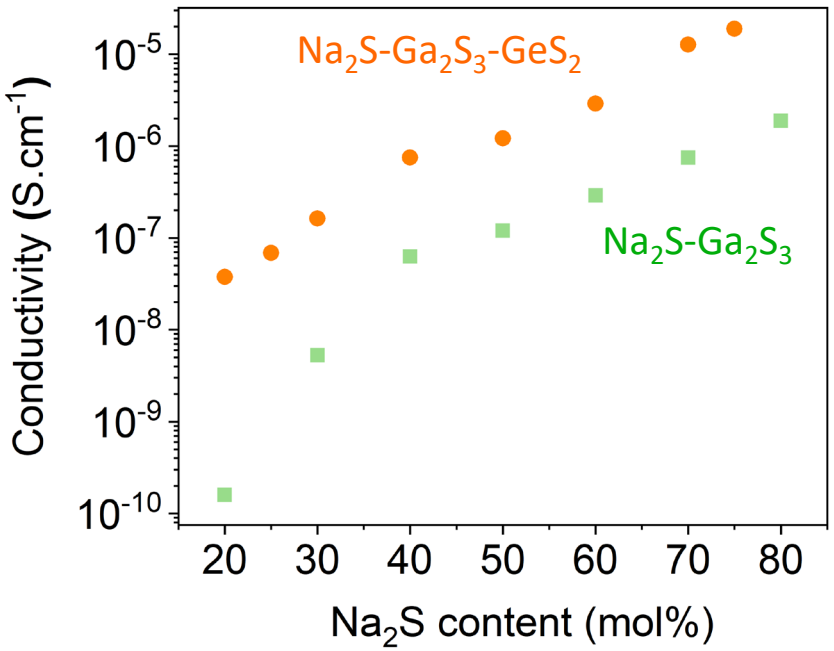
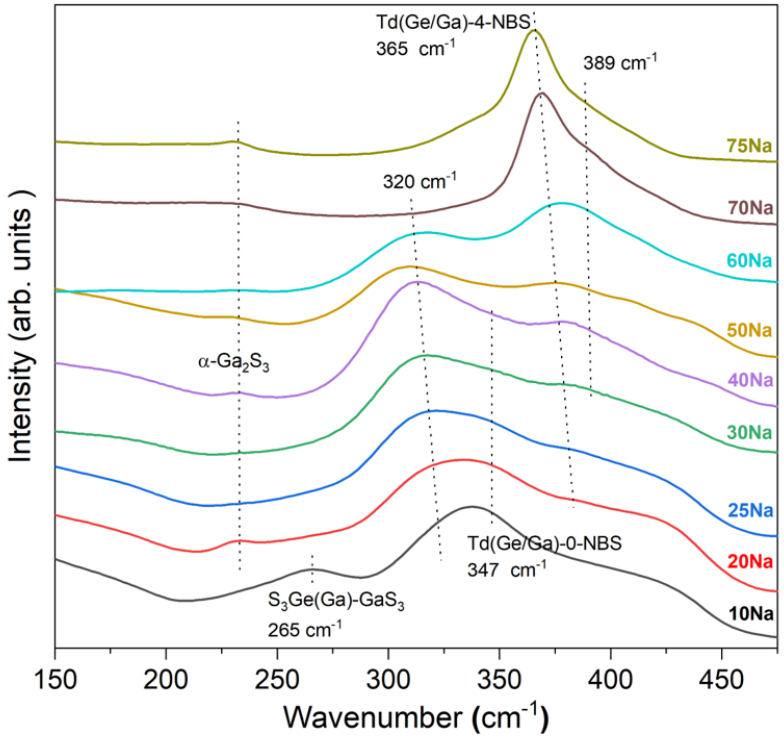
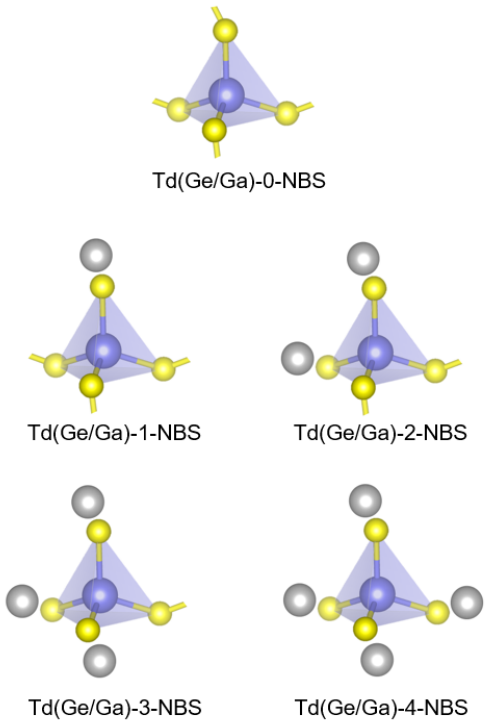


Raman spectroscopy





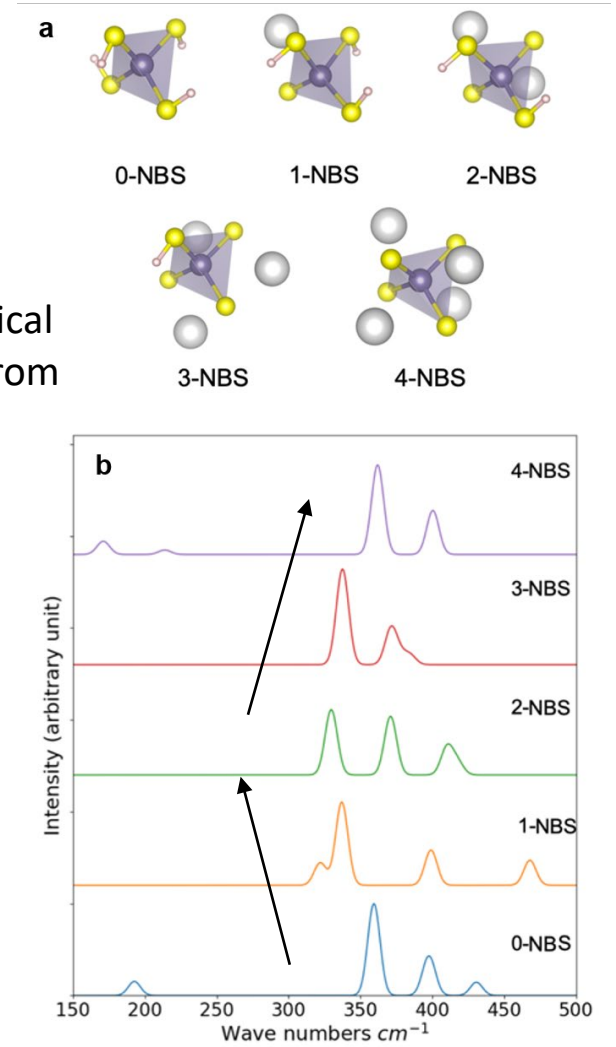
Zhang et al., *Under review*

Glasses obtained by mechanochemistry

$x\ Na_2S – (100-x)\ [0.5\ Ga_2S_3\text{-}0.5\ GeS_2]$

DFT calculations

Inorganic theoretical chemistry team from ISCR



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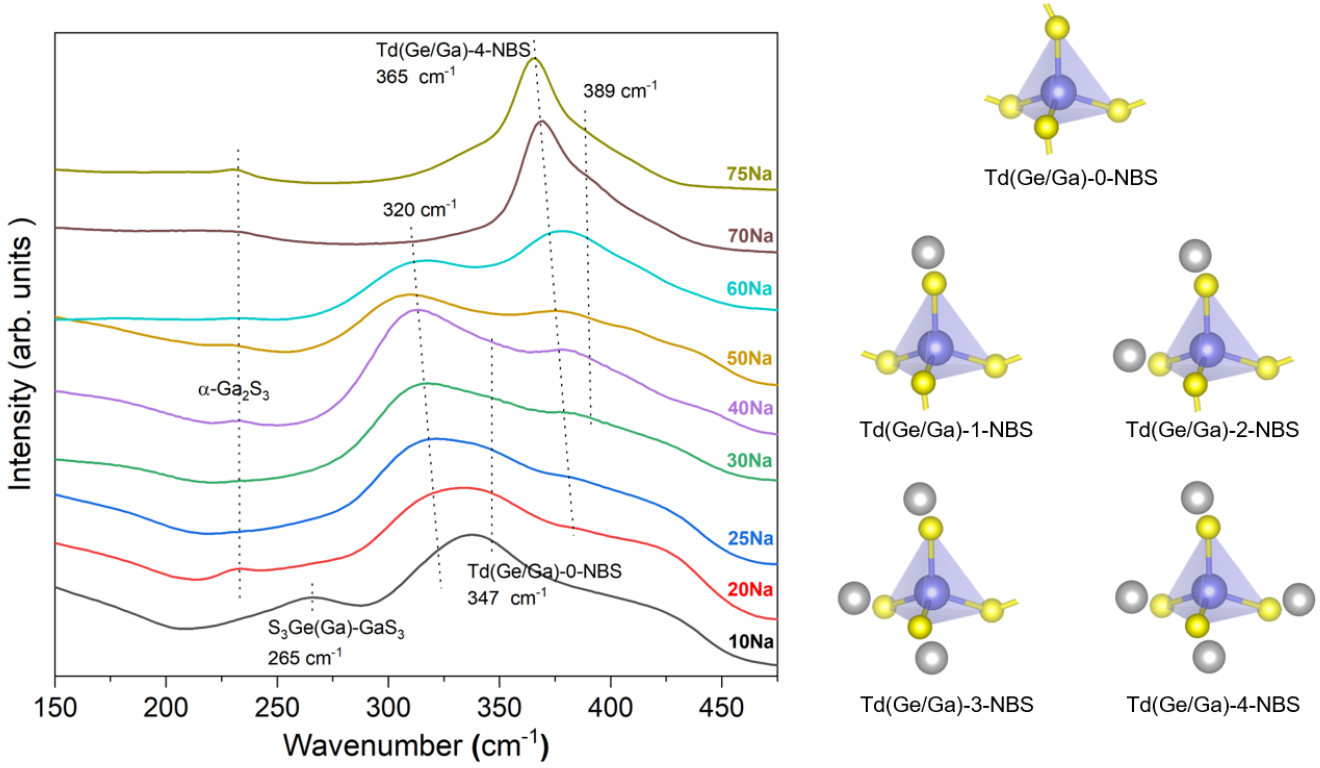


Zhang et al., *Under review*

Glasses obtained by mechanochemistry

$x\ Na_2S – (100\text{-}x)\ Ga_2S_3$

⇒ Amorphous powder for $20 \leq x \leq 80$

⇒ highest conductivity for $80\ Na_2S – 20\ Ga_2S_3$:

$\sigma = 2 \times 10^{-6}\ S.cm^{-1}$ at 25°C

⇒ not suitable for solid state electrolytes

$x\ Na_2S – (100\text{-}x)\ [0.5\ Ga_2S_3\text{-}0.5\ GeS_2]$

⇒ Amorphous powder for $10 \leq x \leq 75$

⇒ highest conductivity for $75\ Na_2S – 25\ [0.5\ Ga_2S_3\text{-}0.5\ GeS_2]$:

$\sigma = 1.8 \times 10^{-5}\ S.cm^{-1}$ at 25°C

Precursors for new crystalline phases ?

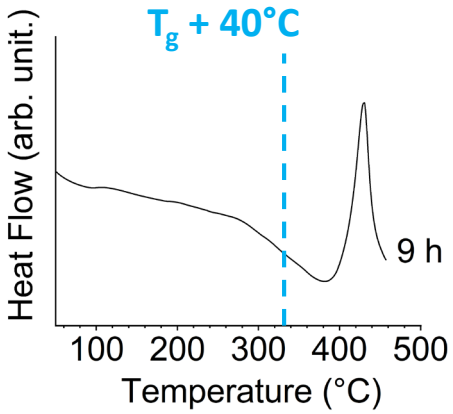
⇒ crystallization tests

Glass-ceramic in the Na_2S-Ga_2S_3 system

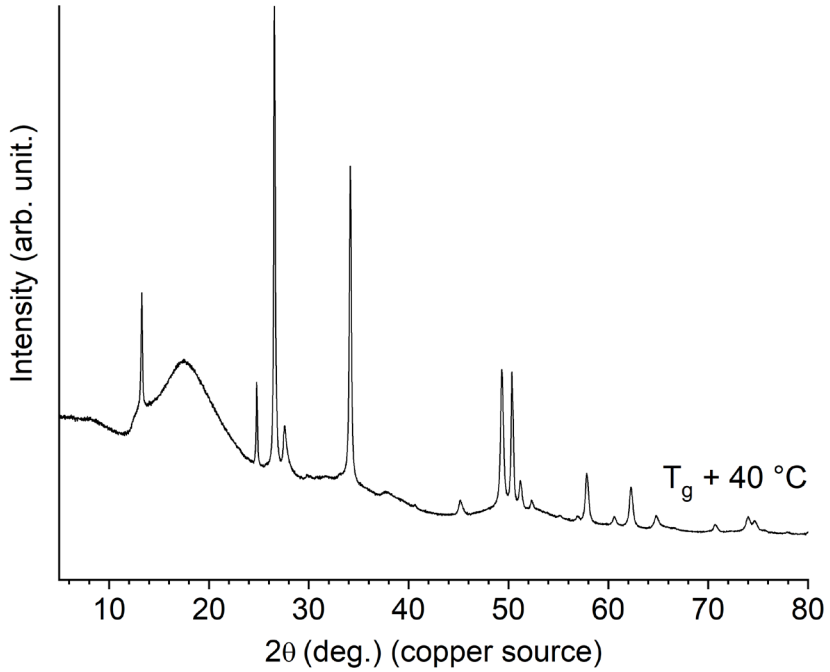
$x\ Na_2S – (100\text{-}x)\ Ga_2S_3$

Glass
$x = 50$ $NaGaS_2$ —*Annealing above T_g*→ Glass-ceramic

T_g + 40°C	24 h	335 °C



X-ray diffraction



CHEMISTRY OF MATERIALS **2020**, *32*, 5589

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⇒ Flux crystal growth in silica tube at 650-750 °C

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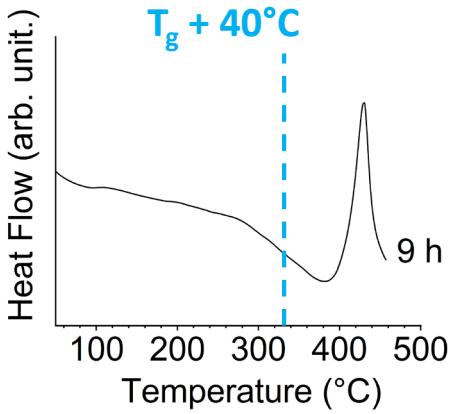
T_g + 40°C	24 h	335 °C



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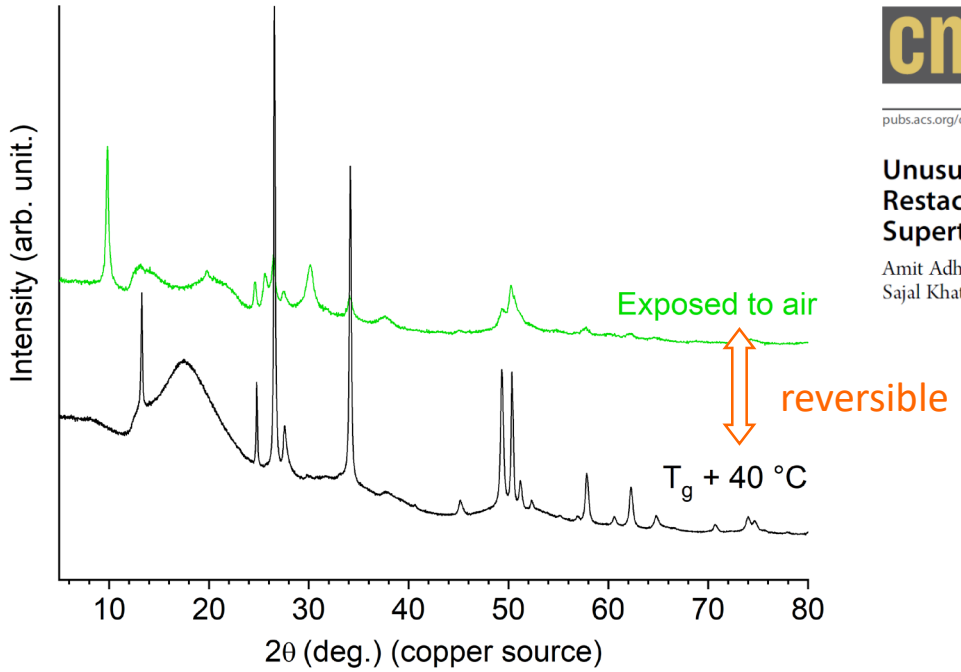

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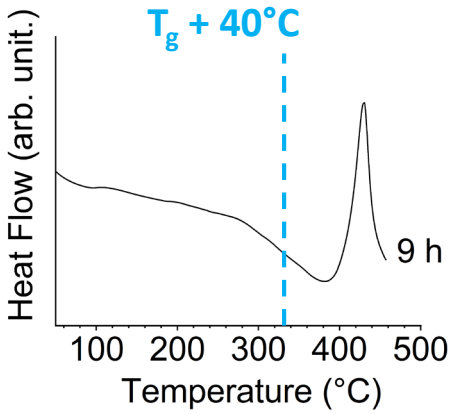

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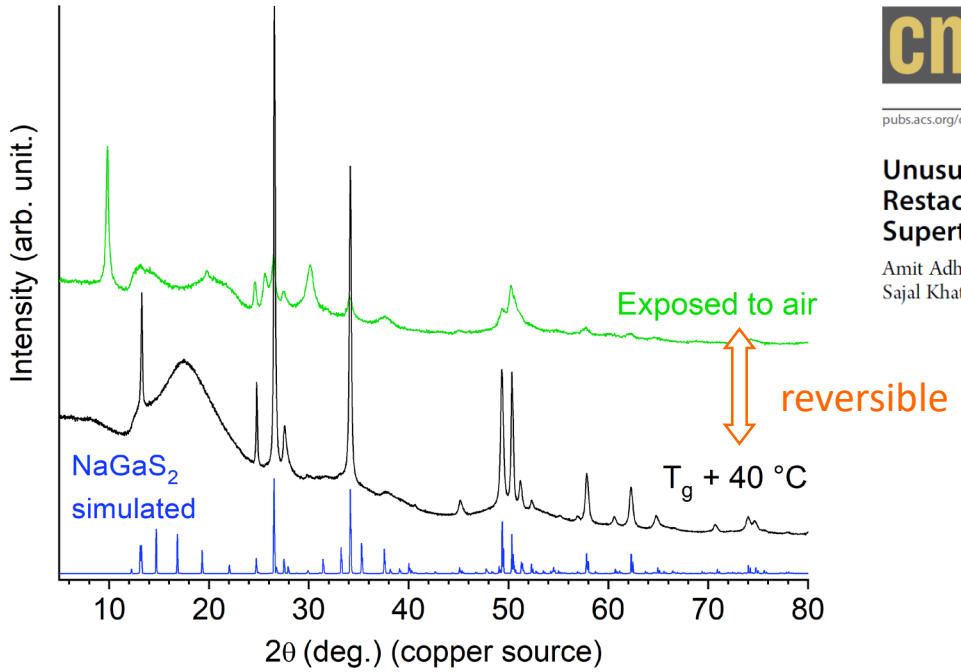

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⇒ Flux crystal growth in silica tube at 650-750 °C

⇒ Structure solved

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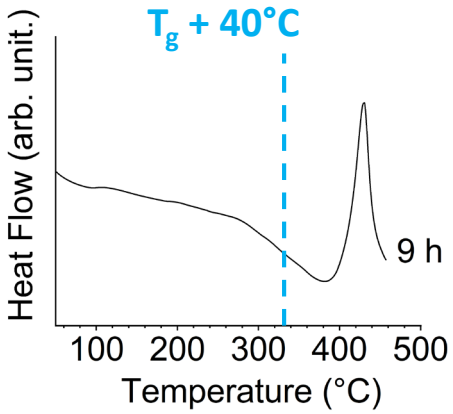

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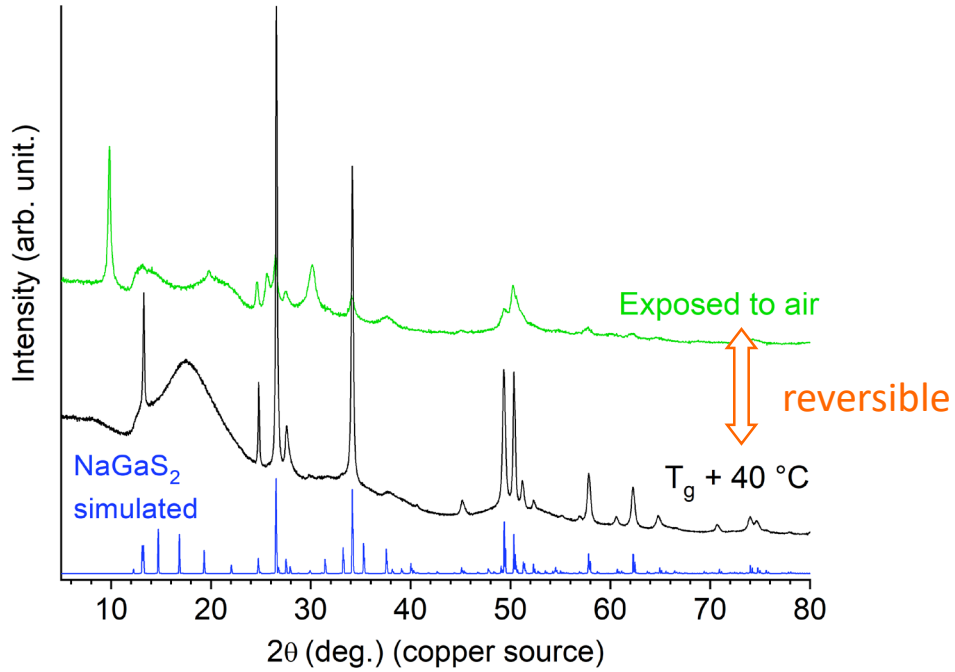
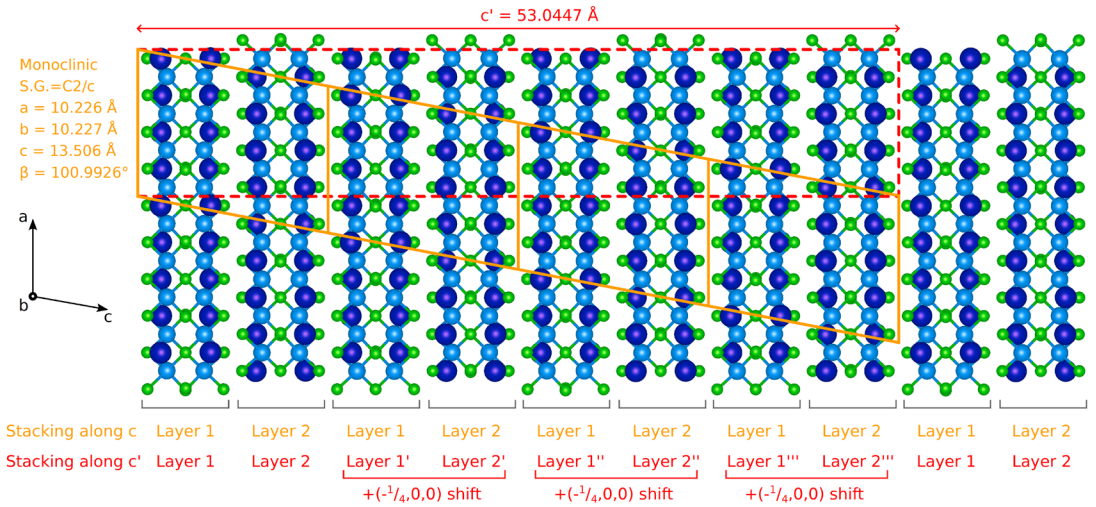


⇒ Layered structure

⇒ Stacking faults



Ga
Na
S

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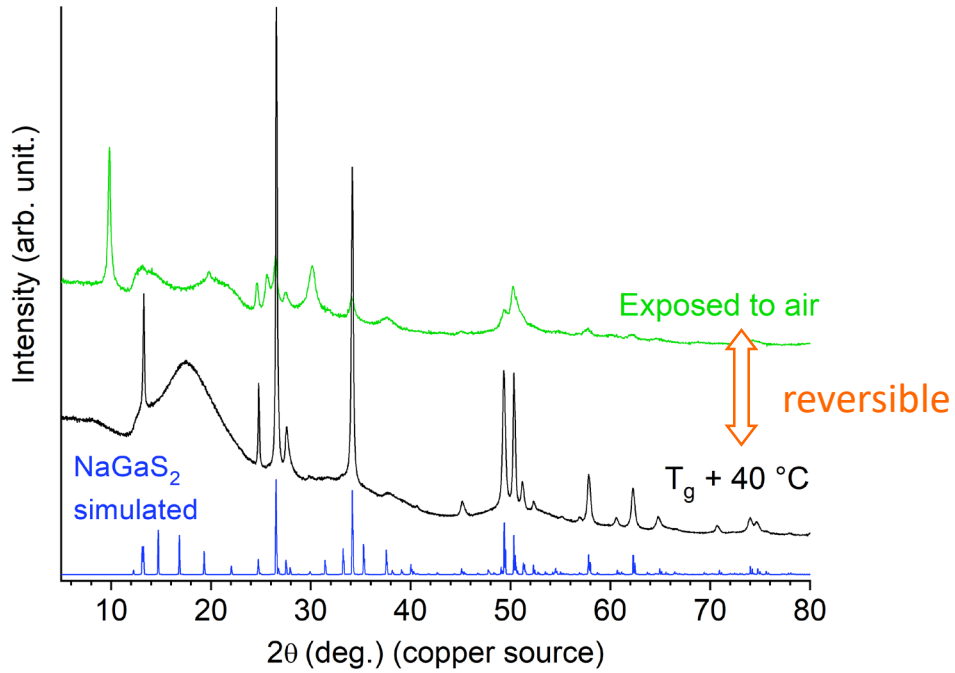

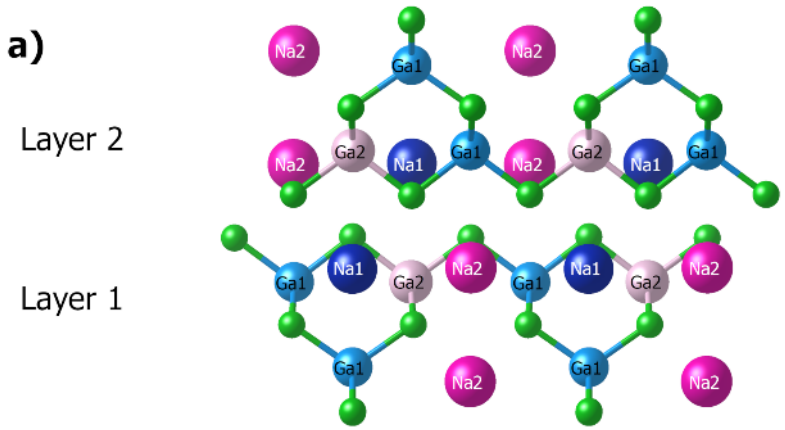

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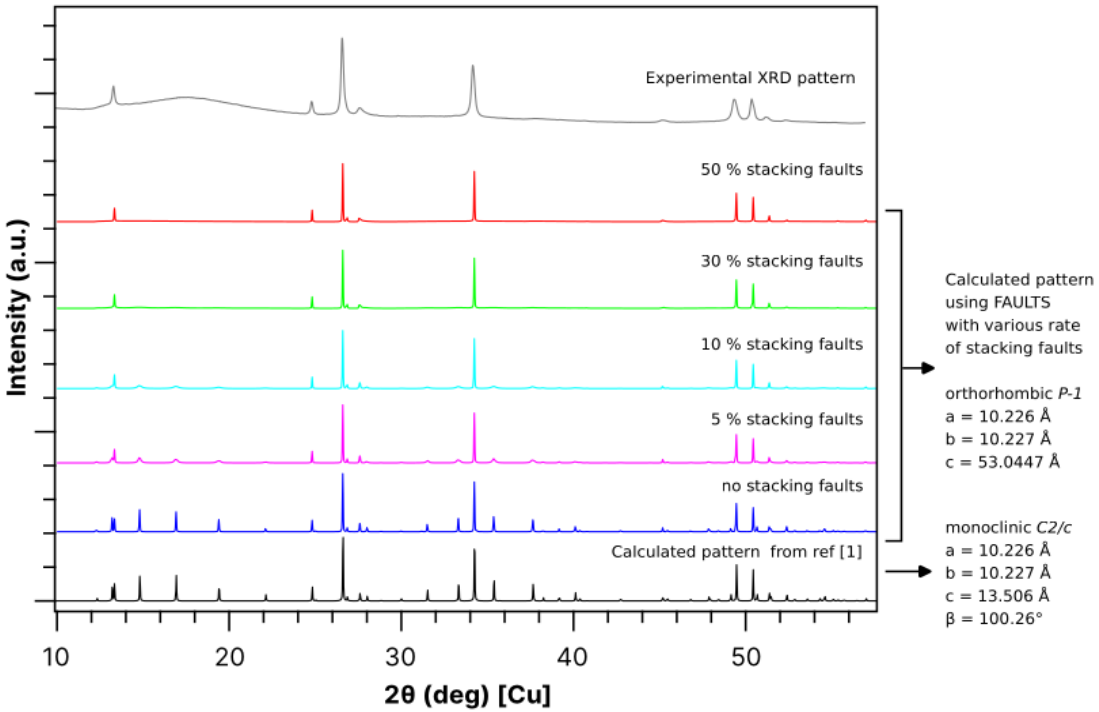
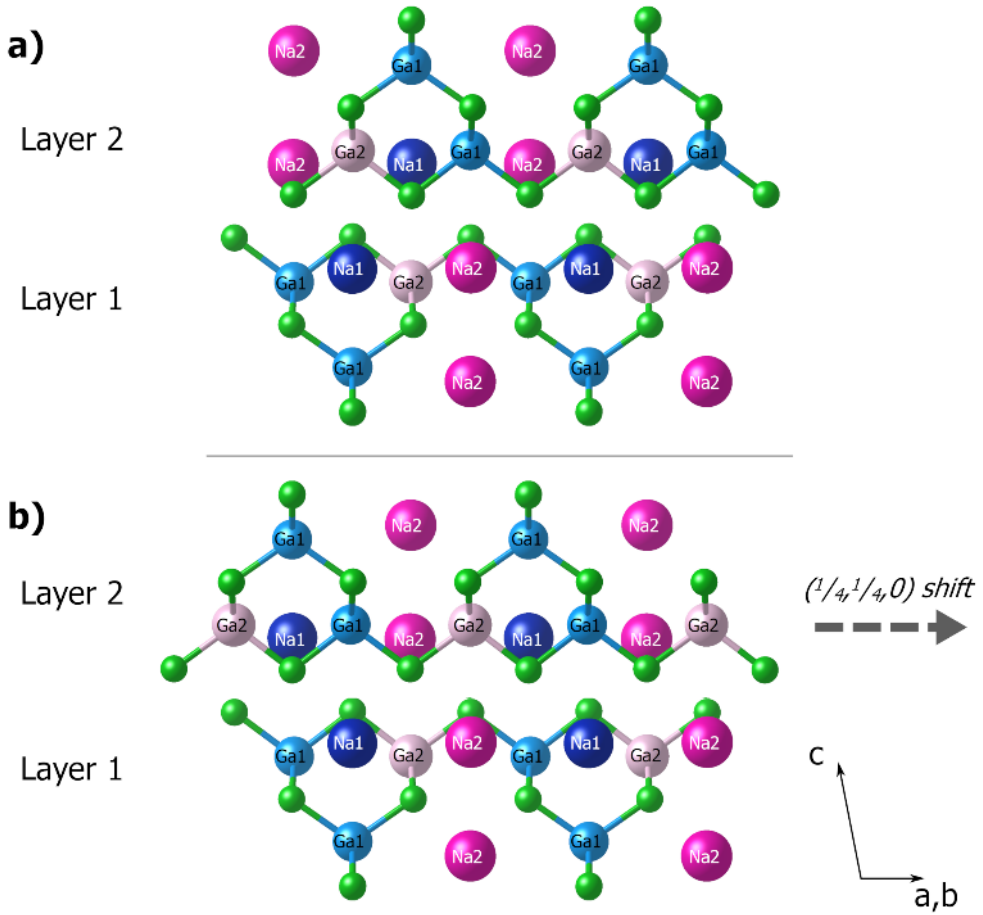
Simulation with FAULTS





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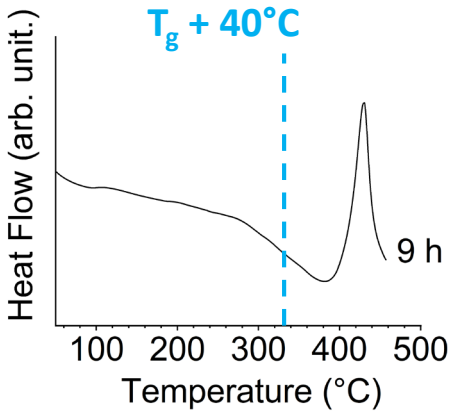
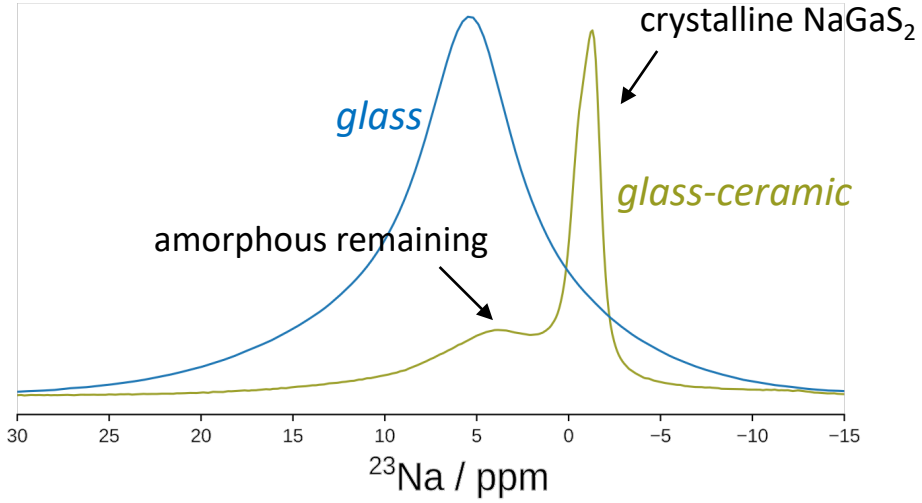


⇒ Quantification of amorphous phase remaining ✗ XRD ✓ NMR



T_g + 40 °C 24h → crystalline $NaGaS_2$: 47.5 %

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Glass-ceramic in the Na_2S-Ga_2S_3 system

x Na_2S – (100-x) Ga_2S_3

Glass
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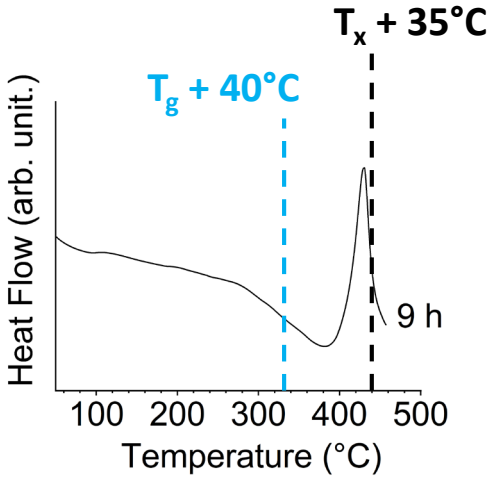
T_g + 40°C	24 h	335 °C
T_x + 35 °C	**1.5 h**	**440 °C**



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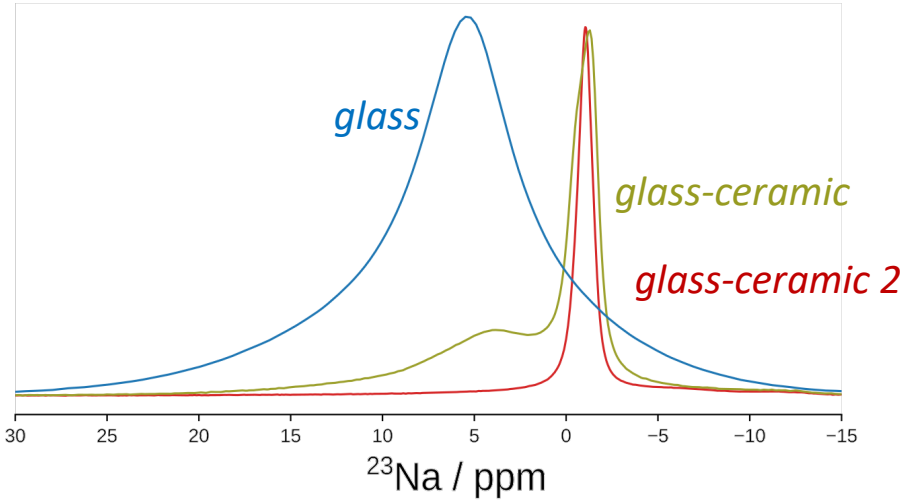

T_g + 40 °C 24 h ⟶ crystalline $NaGaS_2$: 47.5 %

T_x + 35 °C 1.5 h ⟶ crystalline $NaGaS_2$: 83.8 %

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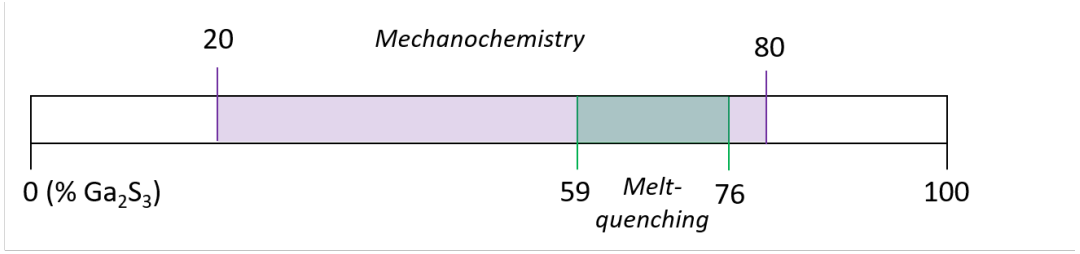
Conclusion and perspectives

Chalcogenide glasses:

- optical properties (transparency in the IR)
- electric conductivity properties

Na_2S-Ga_2S_3

Na_2S-Ga_2S_3-GeS_2



⇒ Amorphous domain enlarged by mechanochemistry, Na- and Ga-rich composition

⇒ Study the conductivity properties as a function of Na content

⇒ Conductivity increases of one order of magnitude with substitution with Ge

Conclusion and perspectives

50 Na_2S . 50 Ga_2S_3 ($NaGaS_2$)

crystallization

Na_2S-Ga_2S_3

$NaGaS_2$ crystallized:
$\sigma = 2.88 \times 10^{-7}$ S cm^{-1} at RT

Glass-ceramics

Not suitable for solid state electrolyte… but :

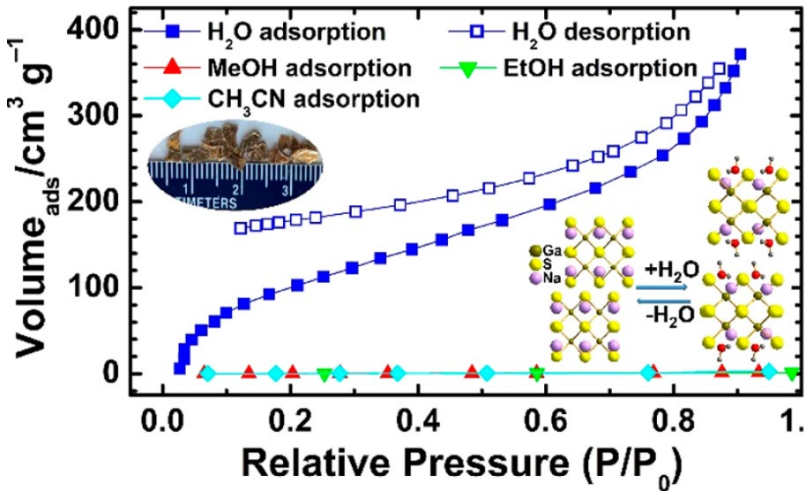
⇒ New synthesis route for $NaGaS_2$:

- no silica tube, no solvent
- temperature lowered of 50 %
- large quantity of material
- particule size : 30 nm

⇒ Selective water adsorption

⇒ Ion exchange properties

⇒ Exfoliation: towards new 2D functionals materials ?



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Acknowledgments

Glasses and Ceramics Research team

Inorganic theoretical chemistry team (Eric Furet, Xavier Rocquefelte)

Mathieu Allix, Cécile Genevois, Sandra Ory

Daniel Irving

Glass and energy materials group
Prof. Steve W. Martin, Jacob Wheaton

Thank you for your attention

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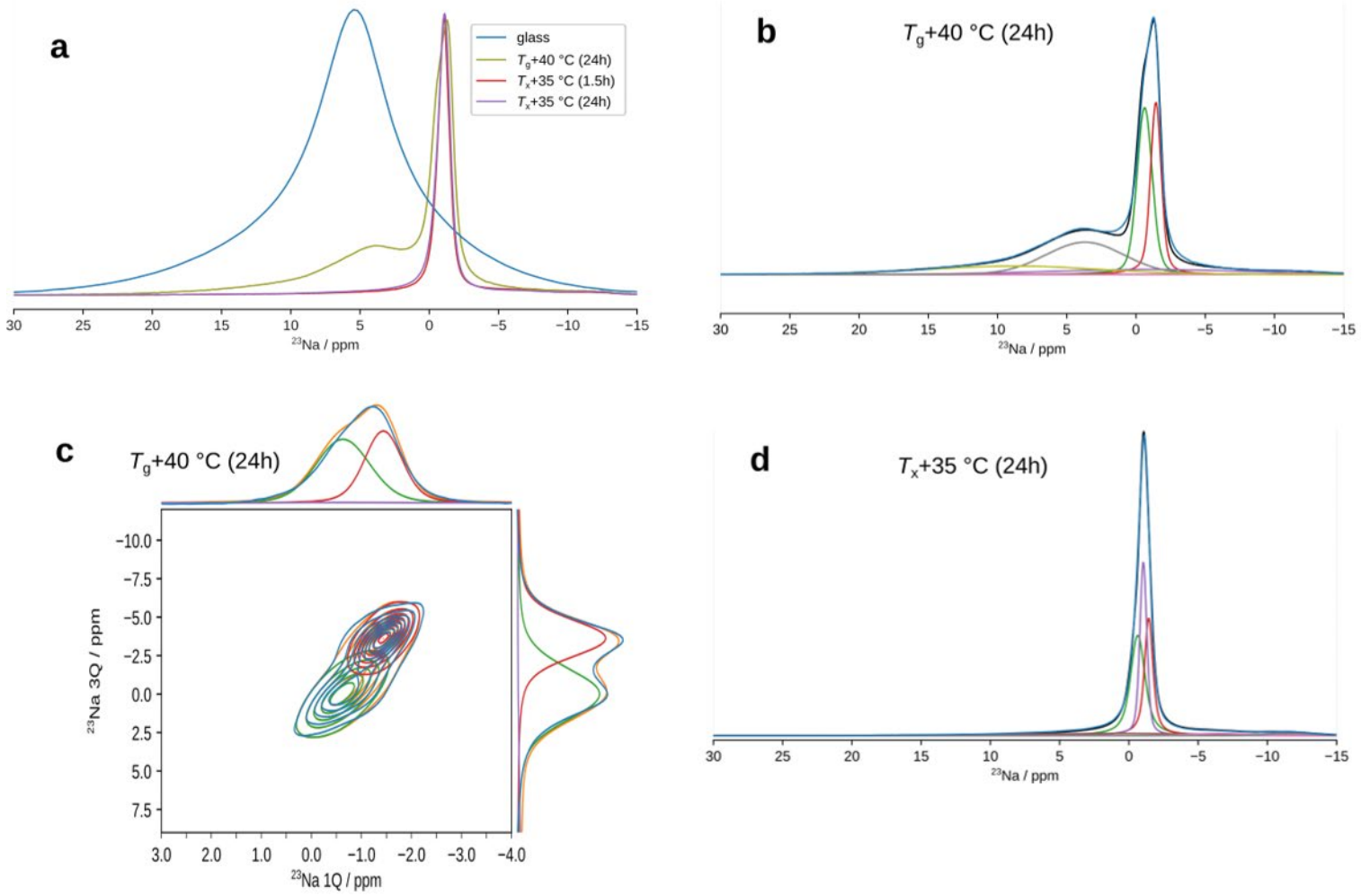
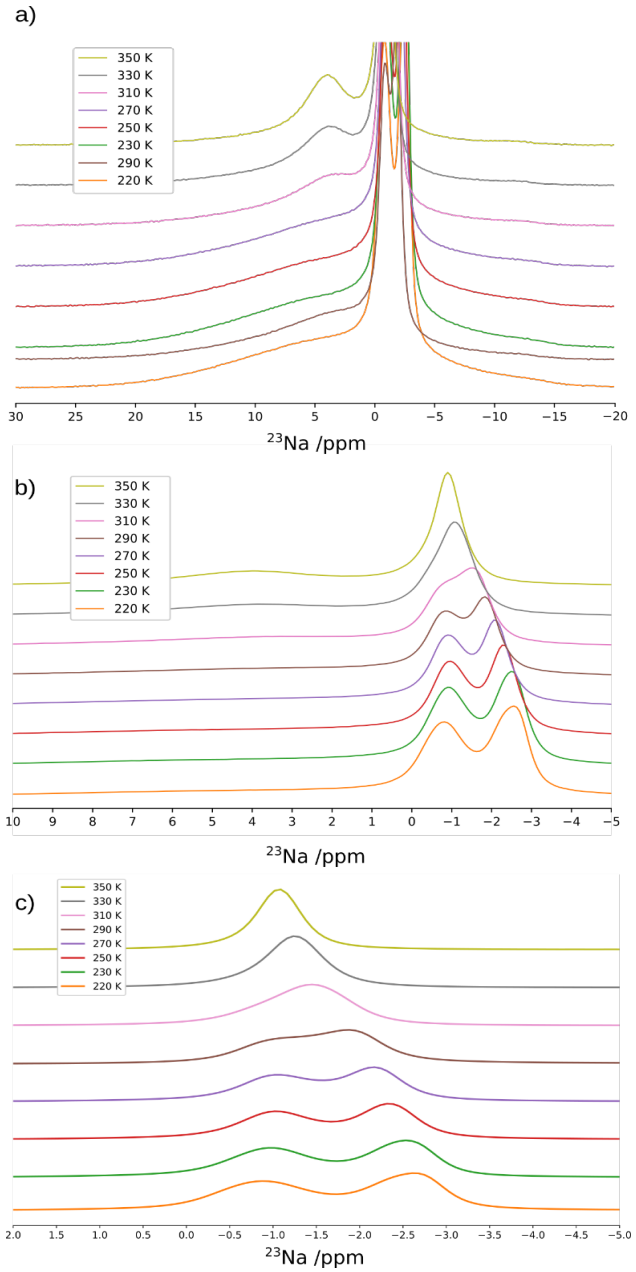
Rennes Institute of Chemical Sciences, France

Glasses and ceramics team

New Inorganic Functional Oxides: Synthesis, Characterisation and Simulations

OCTOBER 04, 2023 - OCTOBER 06, 2023


a
glass
T_g+40 °C (24h)
T_x+35 °C (1.5h)
T_x+35 °C (24h)
^{23}Na / ppm
b
T_g+40 °C (24h)
^{23}Na / ppm
c
T_g+40 °C (24h)
^{23}Na 3Q / ppm
^{23}Na 1Q / ppm
d
T_x+35 °C (24h)
^{23}Na / ppm


a)
350 K
330 K
310 K
270 K
250 K
230 K
290 K
220 K
^{23}Na /ppm
b)
350 K
330 K
310 K
290 K
270 K
250 K
230 K
220 K
^{23}Na /ppm
c)
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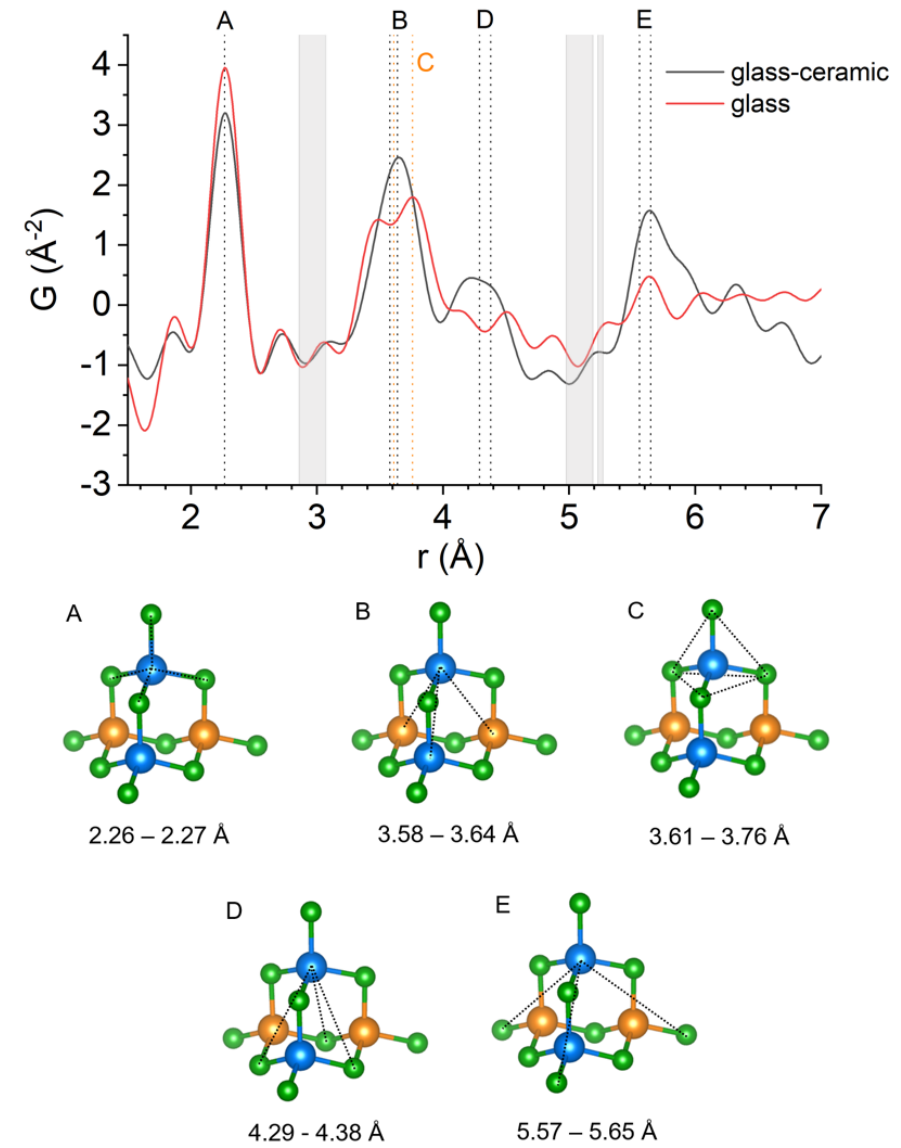
330 K
310 K
290 K
270 K
250 K
230 K
220 K
^{23}Na /ppm


A
B
C
D
E
glass-ceramic
glass
G (Å^{-2})
r (Å)
2.26 – 2.27 Å
3.58 – 3.64 Å
3.61 – 3.76 Å
4.29 - 4.38 Å
5.57 – 5.65 Å