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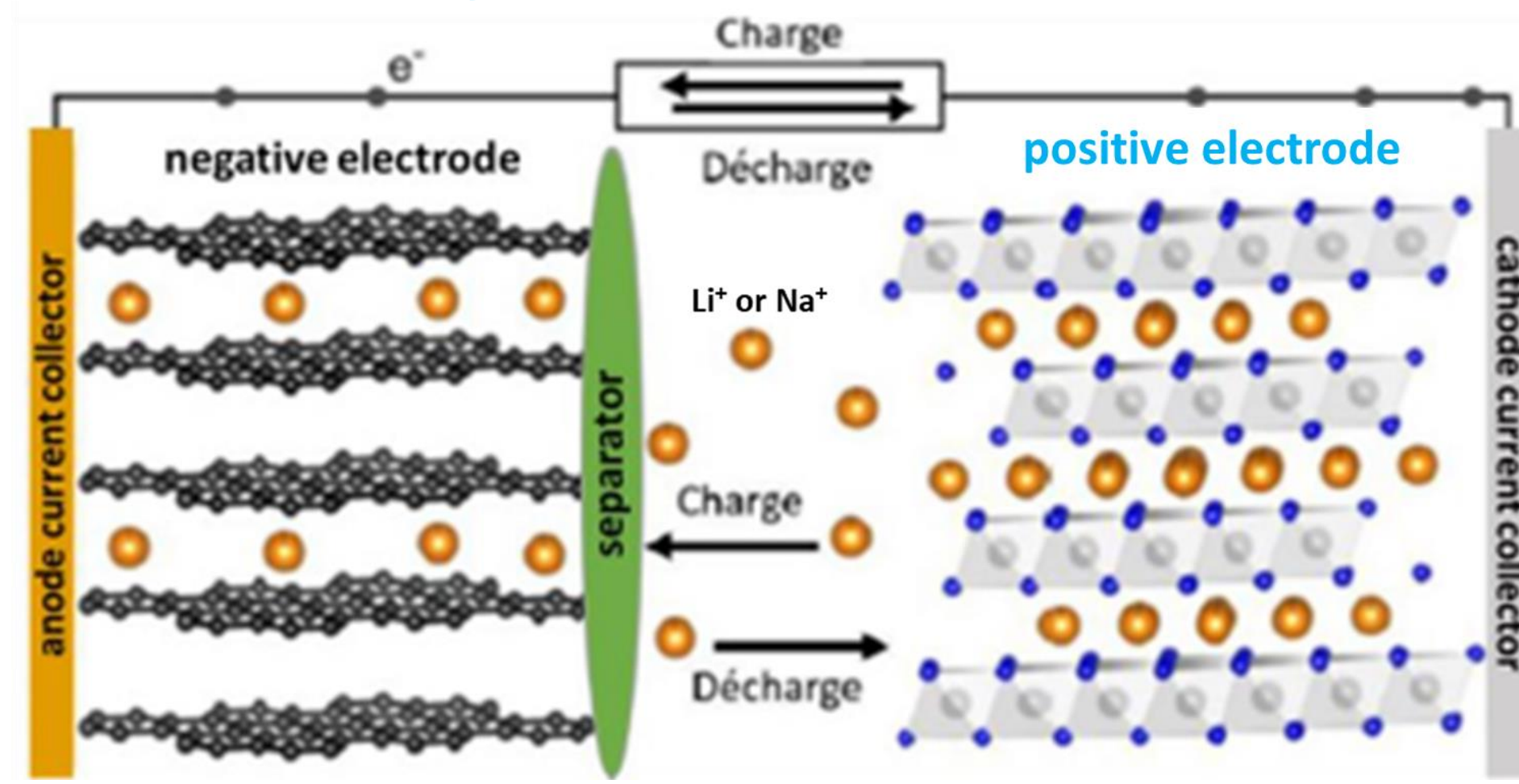
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## Context

- In the frame of CEA Transversal Materials & Processes Competence Programme (PTC), a 2 years (2023-2025) project (22MP07) named **ESTELLA** (Electrodes positives à base de verres pour accumulateurs Li-ion et Na-ion) and aiming at developing new **positive electrode based on oxide glasses** without critical elements (V, Co...)

## Why glass instead of crystal?

- Higher theoretical specific capacities than for the best crystalline materials (above 300mAh/g) [1]
- Flexibility of the network could incorporate more Li incorporation than crystalline one
- Easy to synthesize



## Objectives

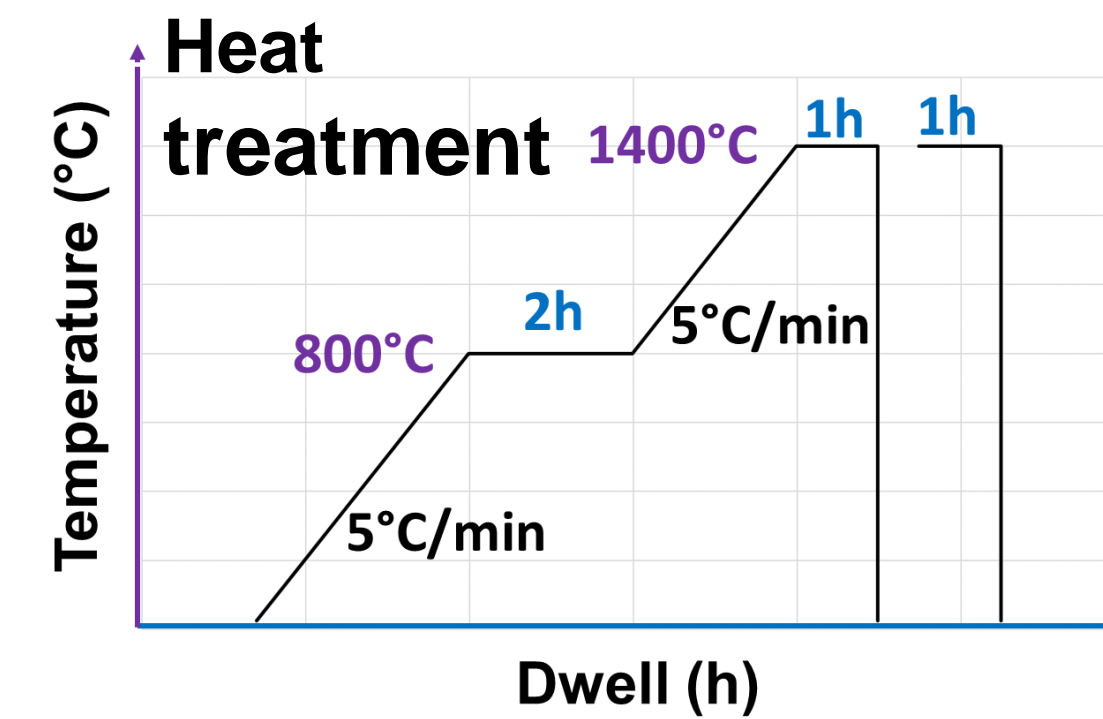
- Identify vanadium-free glass systems materials with **high specific capacity** and **high operating voltage** resulting in energy densities close to 1000 Wh.kg<sup>-1</sup> at the active material level
- Highlight** the glass physicochemical properties that have a first-order influence on the electrochemical performance
- Identify chemical compositions that are performant in terms of electrochemical performance for replacing lithium (expensive and not very abundant) with other alkali metals such as Na

## Glass synthesis

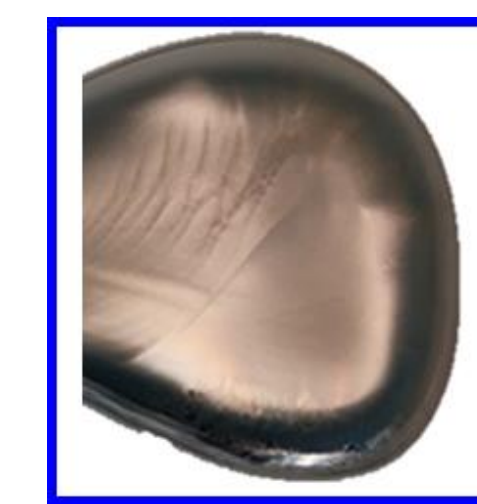
Alkali Oxide + Glass Forming Oxide + Transition Metal Oxide

Sample name	Nominal composition							
	Na <sub>2</sub> O		SiO <sub>2</sub>		Mn <sup>(II)</sup> O		Mn <sup>(IV)</sup> O <sub>2</sub>	
	wt.%	mol%	wt.%	mol%	wt.%	mol%	wt.%	mol%
Si <sub>4</sub> Na <sub>2</sub> Mn(II)	27.7	25.8	56.0	58.1	18.3	16.1	-	-
Si <sub>4</sub> Na <sub>2</sub> Mn(IV)	16.2	17.1	60.4	65.4	-	-	23.4	17.5

Precursor powders mixing in Pt crucibles

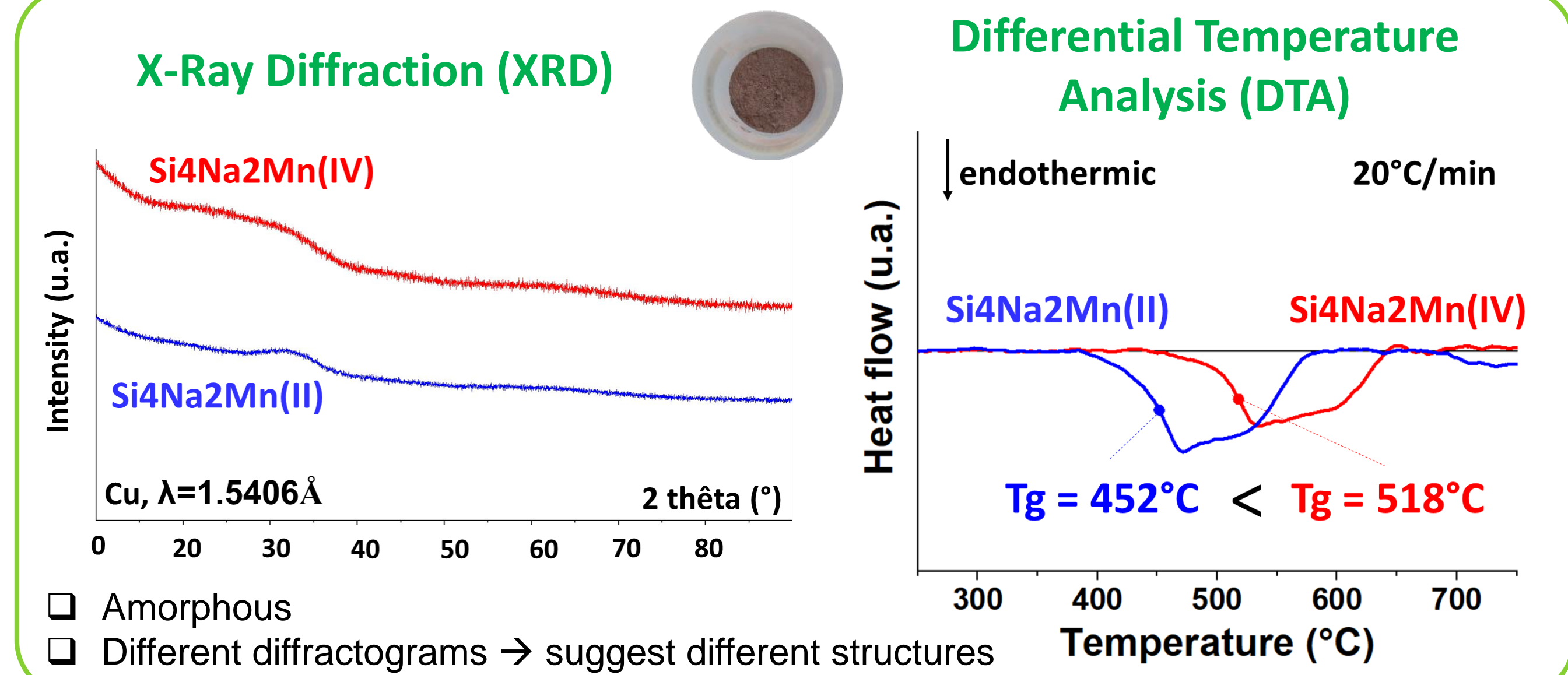
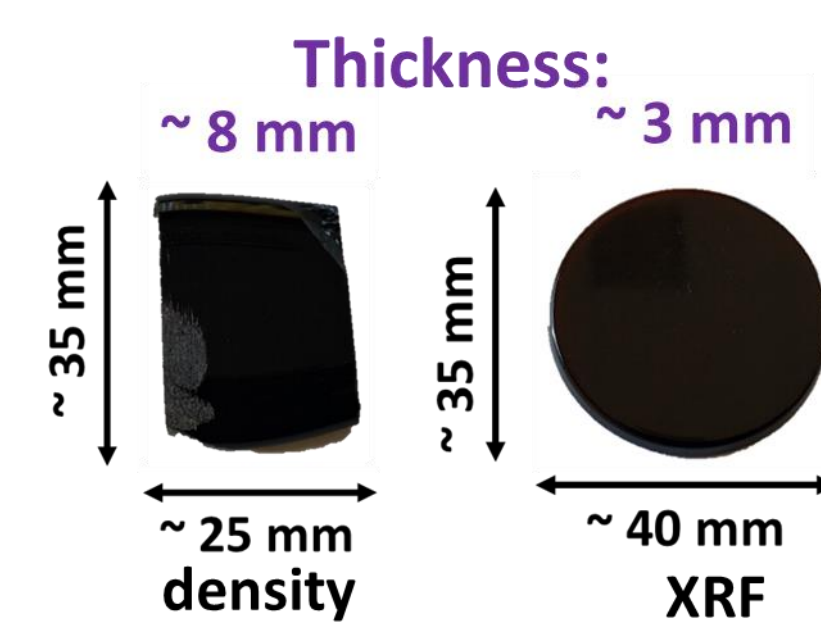


Melted and rapidly quenched on stainless plate in air



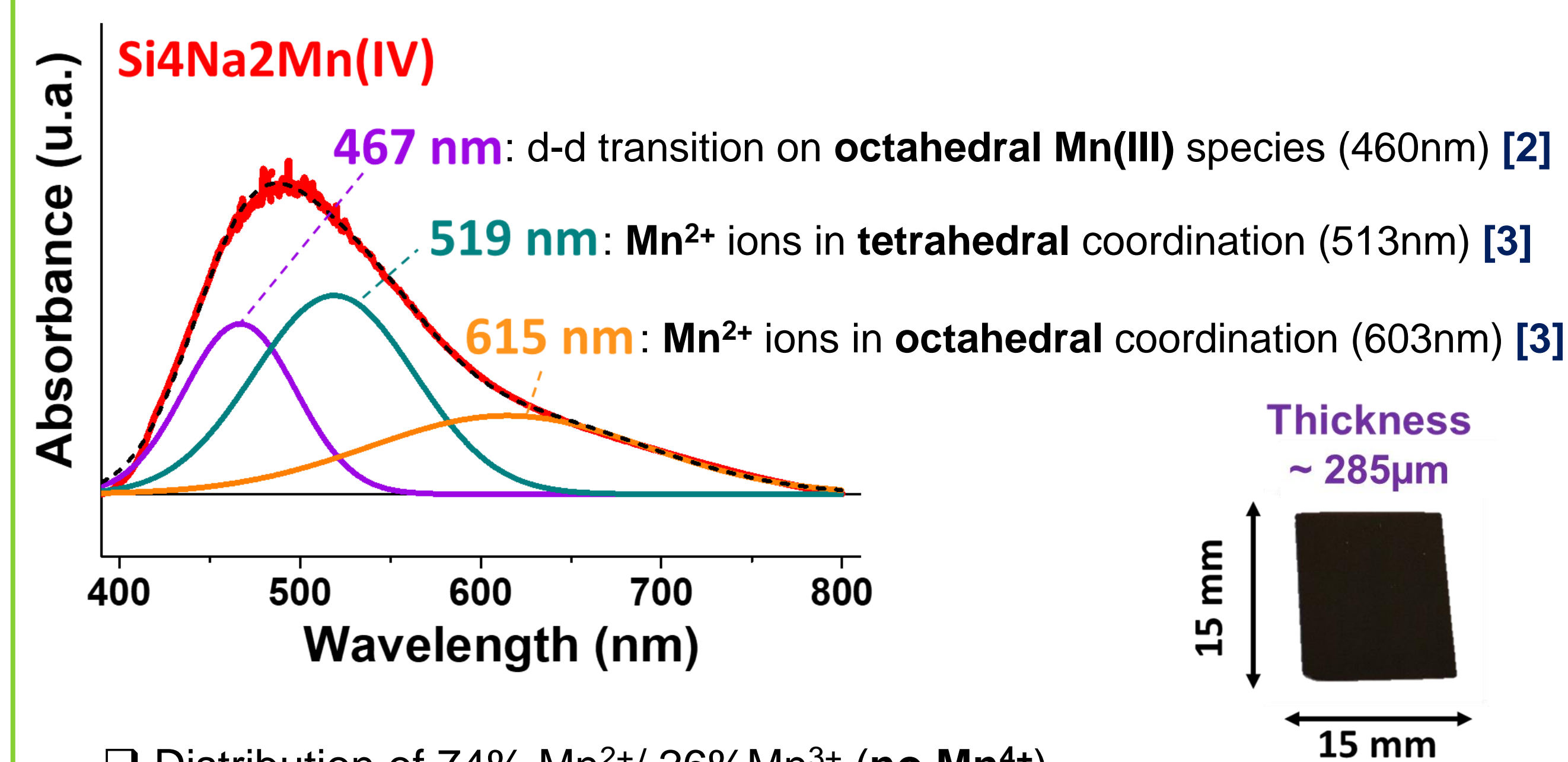
## Experimental results

	Si/Na		Si/Mn		Density d	Reduced density (mol/cm <sup>3</sup> )
	Nominal	XRF	Nominal	XRF		
	Si <sub>4</sub> Na <sub>2</sub> Mn(II)	1.1	1.1 +/- 0.1	3.6		
Si <sub>4</sub> Na <sub>2</sub> Mn(IV)	1.9	1.9 +/- 0.1	3.7	3.9 +/- 0.2	2.706 +/- 0.001	0.42

\* d/M<sub>mol</sub>: Number of moles of material by cm<sup>3</sup> XRF: X-Ray Fluorescence

- Amorphous
- Different diffractograms → suggest different structures

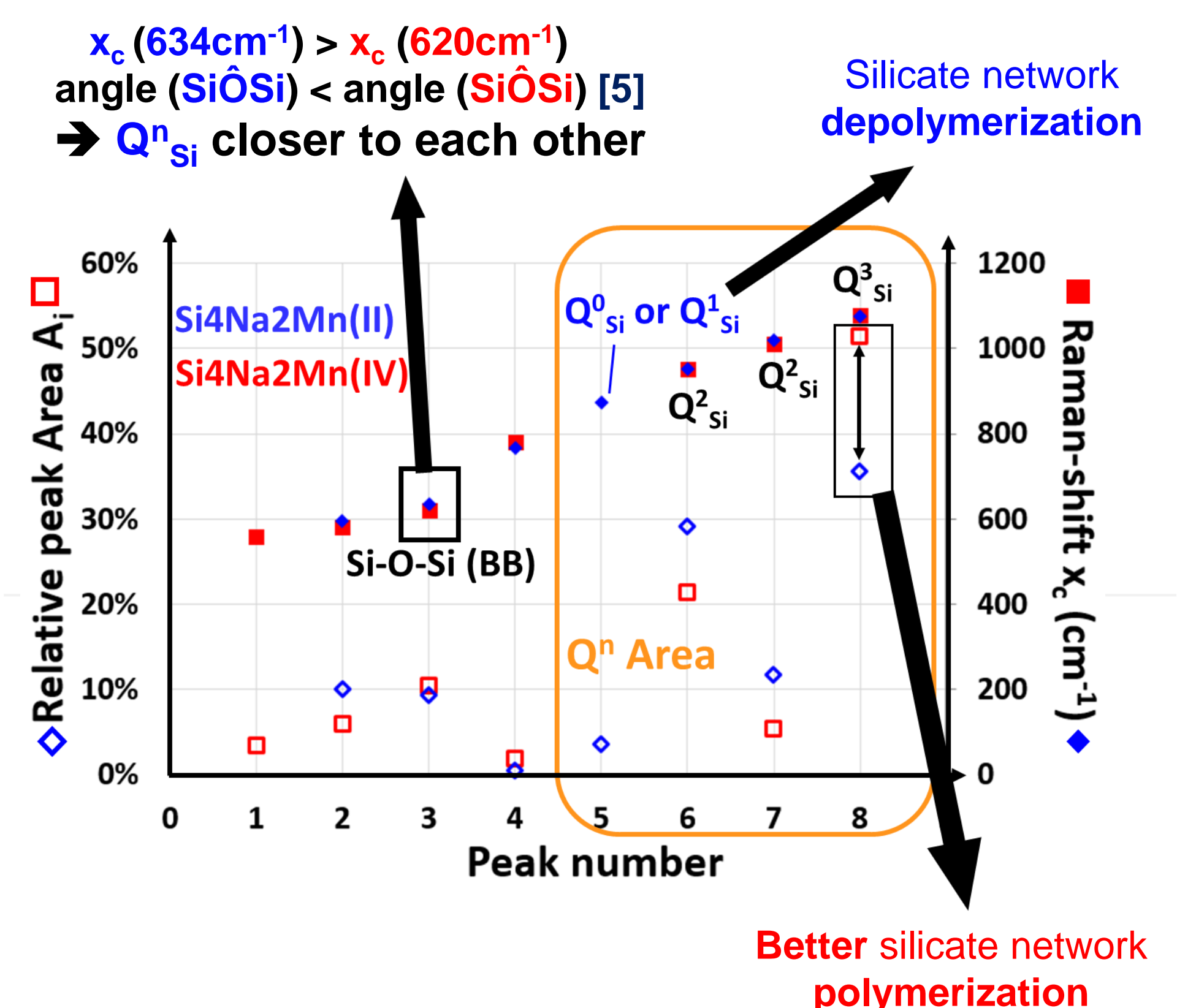
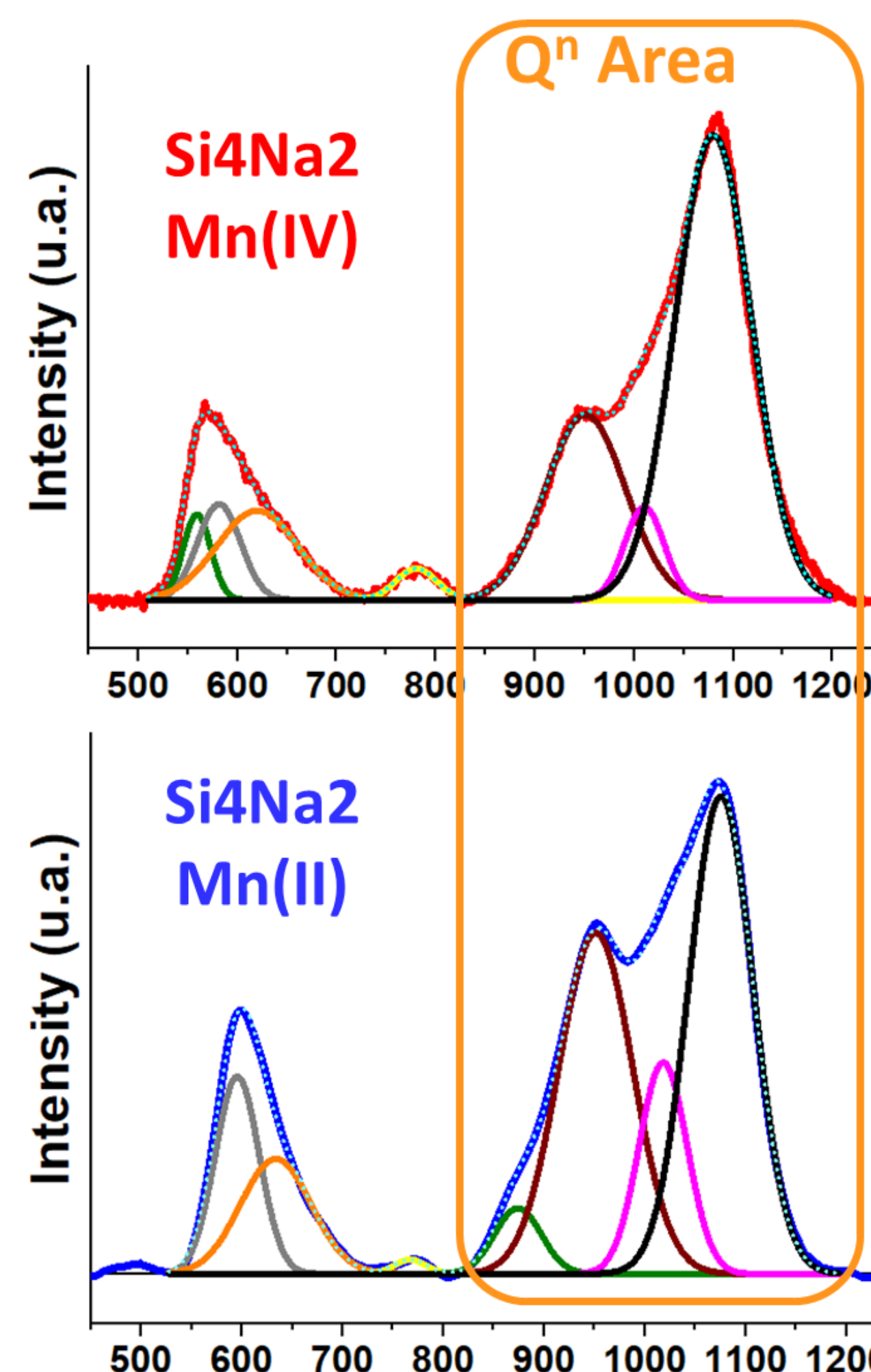
## UV-visible Spectroscopy



- Distribution of 74% Mn<sup>2+</sup>/ 26%Mn<sup>3+</sup> (no Mn<sup>4+</sup>)

- Tetrahedral structure of Mn<sup>2+</sup>** (44%) suggests that some of the Mn is involved in establishing the glass network

## Raman Spectroscopy

Experimental conditions: laser 532nm, 1800gr/mm, 4.6mW, 10 x 60s acquisition time  
N.B.: Deconvolution spectra after subtracting baseline to raw data and normalized intensity at max

Harmonic oscillator analogy

$$x_c(\text{cm}^{-1}) \equiv \sqrt{\frac{\text{bond strength}}{\text{reduced mass}}}$$

$$\text{Spectral Weight SW}(\text{cm}^{-1}) = \frac{\sum_{i=0}^n A_i(Q^i)x_c(Q^i)}{\sum_{i=0}^n A_i(Q^i)}$$

$$\text{SW}(\text{Si}_4\text{Na}_2\text{Mn(IV)}) = 1040 \text{ cm}^{-1} > \text{SW}(\text{Si}_4\text{Na}_2\text{Mn(II)}) = 1013 \text{ cm}^{-1}$$

It suggests that more energy is needed to modify the Q<sup>n</sup> atomic network for Si<sub>4</sub>Na<sub>2</sub>Mn(IV)

Peak	Peak Raman-shift x <sub>c</sub> (cm <sup>-1</sup> )		Possible vibration modes (from literature)
	Si <sub>4</sub> Na <sub>2</sub> Mn(II)	Si <sub>4</sub> Na <sub>2</sub> Mn(IV)	
1	-	559	550, 540: Si-O-Si bridging O bending mode [4] [5]
2	596	581	600: Defect band D2 (O breathing in 3-membered rings of SiO <sub>4/2</sub> ) [4] 580: Si-O rocking mode in Q <sup>4</sup> [5]
3	634	620	660: Si-O-Si bending mode [7]
4	767	780	700-850: Si-O-Si symmetric stretching mode [5]
5	874	-	900: Si-O <sup>-</sup> in Q <sup>1</sup> [5]
6	951	950	850: Si-O <sup>-</sup> in Q <sup>0</sup> [5]
7	1018	1010	950-1000: Si-O <sup>-</sup> in Q <sup>2</sup> [4] [5] [6]
8	1075	1079	850-880: Si-O <sup>-</sup> in Q <sup>0</sup> [6] 1050-1100: Si-O <sup>-</sup> in Q <sup>3</sup> [4]

## Conclusions

- Raman Spectroscopy to better understand T<sub>g</sub> values:
  - Depolymerizing of the glass network (peak 5).
  - Less energy may be needed to modify Si<sub>4</sub>Na<sub>2</sub>Mn(II) atomic structure (Spectral Weight). These suggest that the atomic structure of the Si<sub>4</sub>Na<sub>2</sub>Mn(II) is easier to modify than Si<sub>4</sub>Na<sub>2</sub>Mn(IV) and so, its T<sub>g</sub> is less high:
    - In agreement with T<sub>g</sub> measured by ATD.
- Raman Spectroscopy and reduced density:
  - The structure of Si<sub>4</sub>Na<sub>2</sub>Mn(II) would be more packed than Si<sub>4</sub>Na<sub>2</sub>Mn(IV) one (angles SiOSi).
  - In agreement with the reduced density computed (higher for Si<sub>4</sub>Na<sub>2</sub>Mn(II)).
- UV-vis Spectroscopy characterization and oxidation states
  - At high elaboration temperature (1400-1550°C), Mn<sup>4+</sup> can be reduced to Mn<sup>3+</sup> and Mn<sup>2+</sup> [8].
  - In agreement with the UV-visible characterization for Si<sub>4</sub>Na<sub>2</sub>Mn(IV) (no Mn<sup>4+</sup>).

## Perspectives

- Evaluating the free volume of these materials from density measurements and UV-vis characterization
- Testing these two materials electrochemically to better understand the role of the structure properties on battery performances
- Elaborating and characterizing new chemical systems, changing the nature and proportion of the three elements classes, to better understand the importance of different material parameters (oxidation state, Q<sup>n</sup>, polyhedra centered on metal transition, T<sub>g</sub>, density, ...)

## Acknowledgements

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## References

- [1] Afyon, S., et al., *Sci. Rep.* **4**, 7113 (2015)  
 [2] Senanon, W., et al., *J.NonCrys.Sol.* **552**, 120445 (2021)  
 [3] Wen, H., et al., *J.Lum.* **213**, 263-272 (2019)  
 [4] Limbach, R., et al., *J.NonCrys.Sol.* **471**, 6-18 (2017)  
 [5] Yadav, A.K., et al., *RSC Adv.* **5** **83**, 68583-67609 (2015)  
 [6] Park, J. H., et al., *J.NonCrys.Sol.* **358** **23**, 3096-3102 (2012)  
 [7] Basha, S. J., et al., *Opt.Mat.:X*, **1**, 100024 (2019)  
 [8] Petersen, R. R., et al., *J.NonCrys.Sol.* **475**, 74-82 (2015)