Glass from a Liquid by Heating: *in situ* Diffraction Measurements

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Outline

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- **P, S and Se allotropes**
- **P-X Glasses**
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- **Glass From a Liquid by Heating**
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  - *Density evolution*
- **Conclusions**

Introduction

Polyamorphism

- *One substance in two or more different amorphous forms*

  LDA, HDA, VHDA Ice

  O. Mishima, LD Calvert, E. Whalley, Nature (1984)

- *Polyamorphic transition*

  First order transition in liquid P

  Y. Katayama et al., Nature (2000)

Methods

- *High pressure* > 1 GPa

  Density-driven polyamorphism

- *High temperature* > 1000 °C

  Entropy-driven polyamorphism

- *Different allotropic forms of elements*

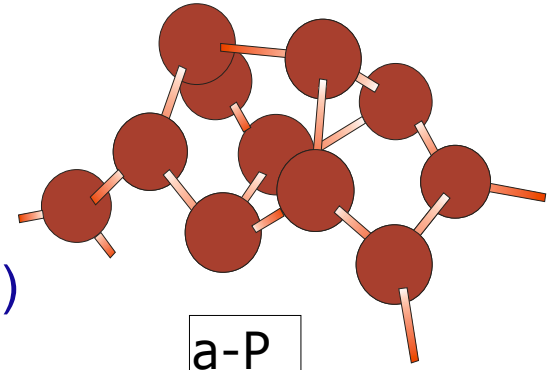
  Chemically-driven polyamorphism

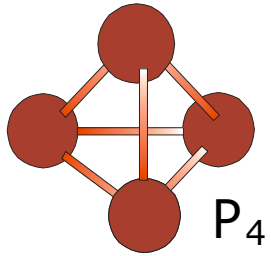
Why P – X (X = S, Se) ?

Different allotropic forms of pure elements

Phosphorus

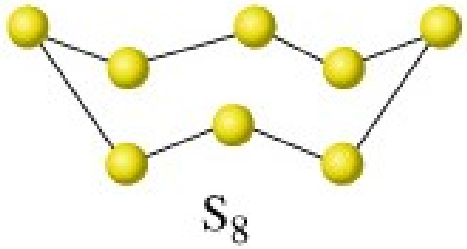
- White P (molecular solid, P_4)
- Red and black P (polymeric forms)

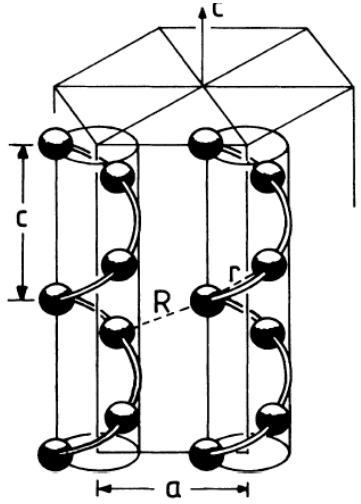




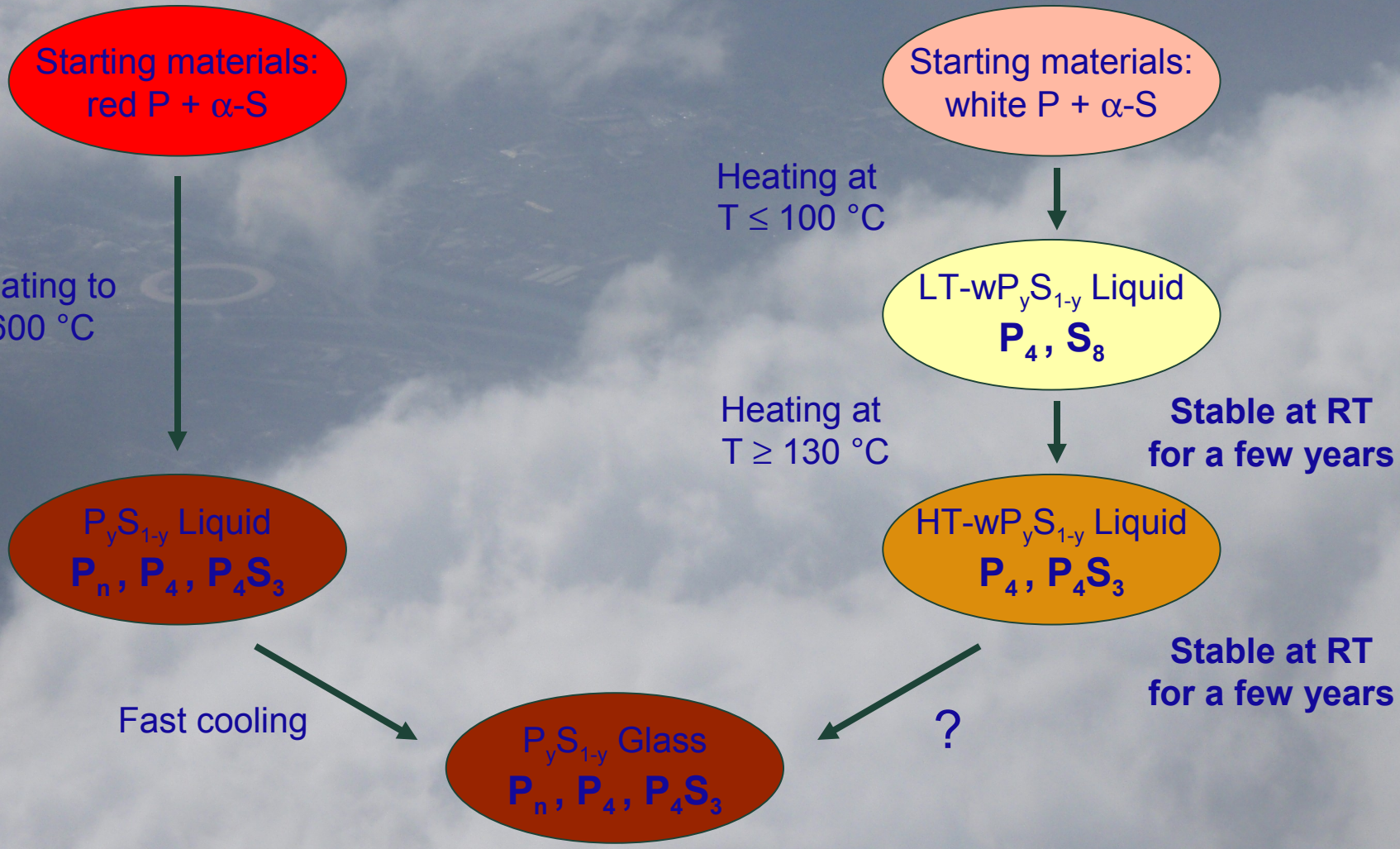
Sulphur or selenium

- Rings (α-S_8, α-Se_8, etc.)
- Chains (μ-S, trigonal Se, etc.)

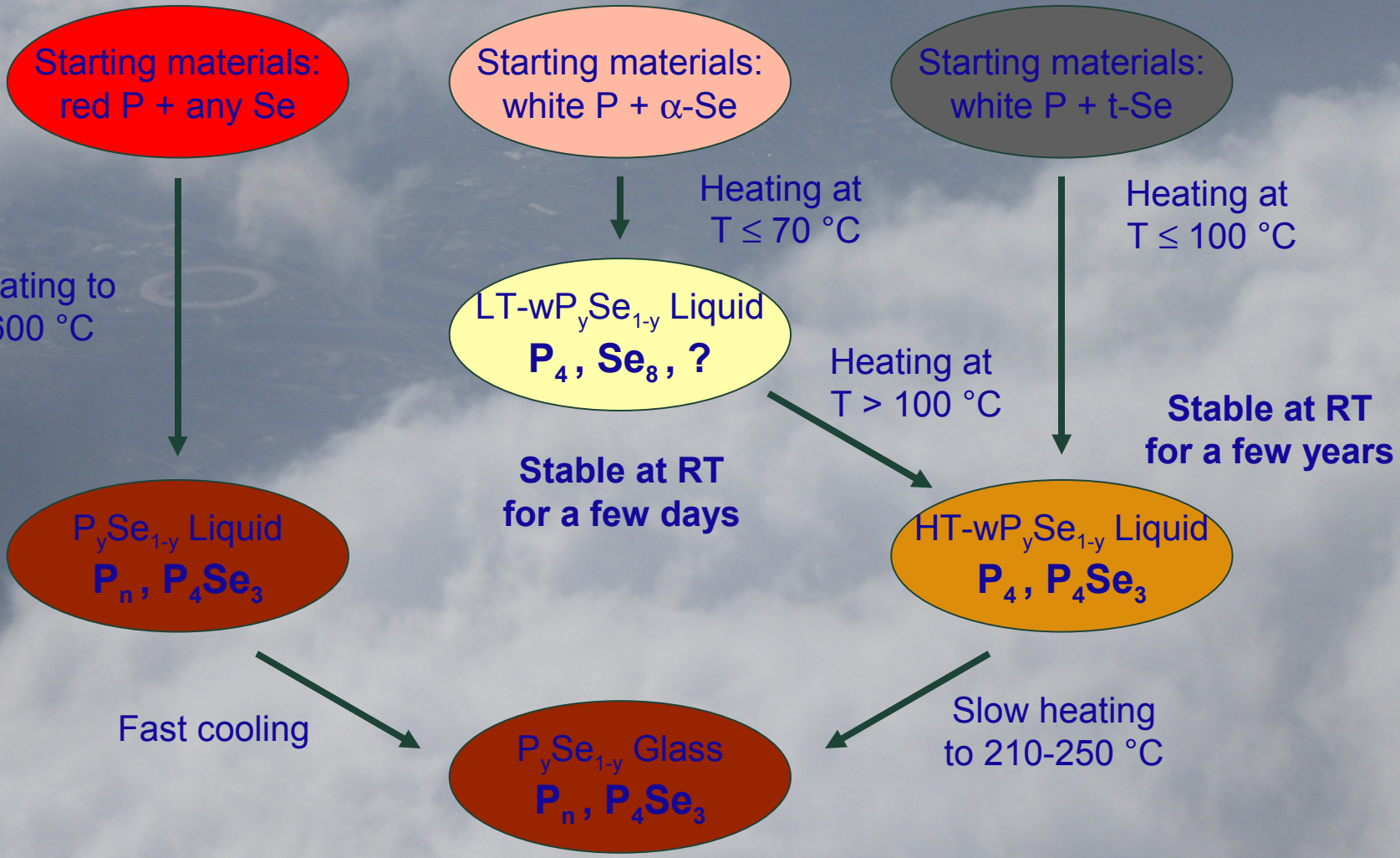




P-S polyamorphic liquids and glasses



P-Se polyamorphic liquids and glasses



Glass from a liquid by heating

Experimental details

- ***In situ* Diffraction:**

  Energy = 100 keV, 2D-Frelon CCD at 400 mm,

  Q-range 0.3-12 $Å^{-1}$

- **Diffraction:**

  Energy = 100 keV, 2D-Frelon CCD at 400 mm and 181 mm,

  Q-range 0.3-25 $Å^{-1}$

- **Transmission:**

  2 diodes => $I_1/I_0 \sim T$

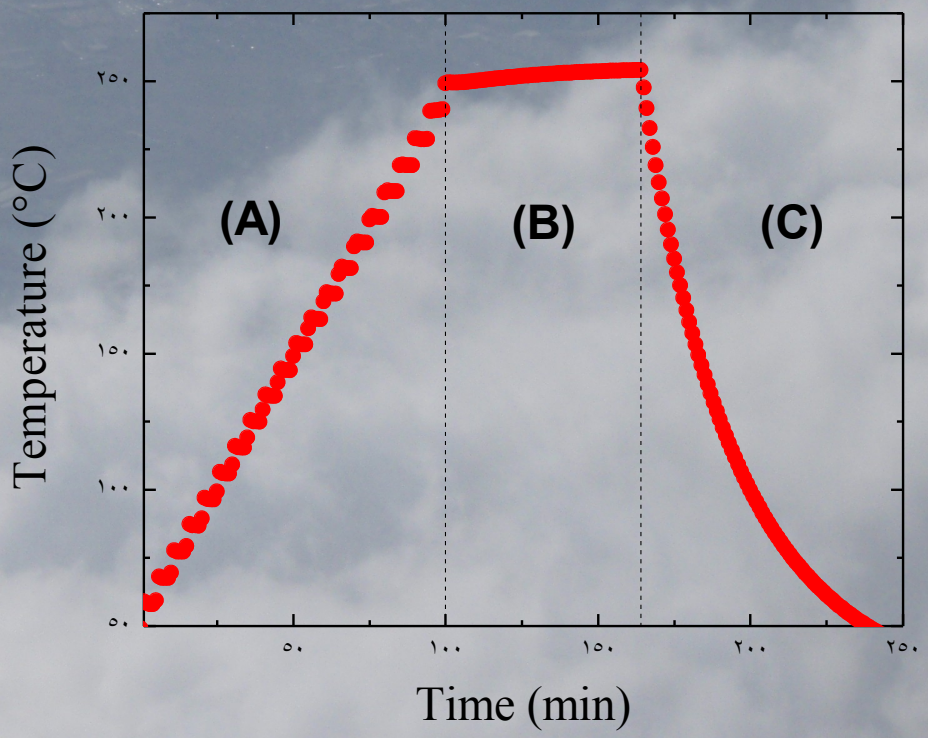
Temperature profile

A. Heating the liquid

C. Transformation

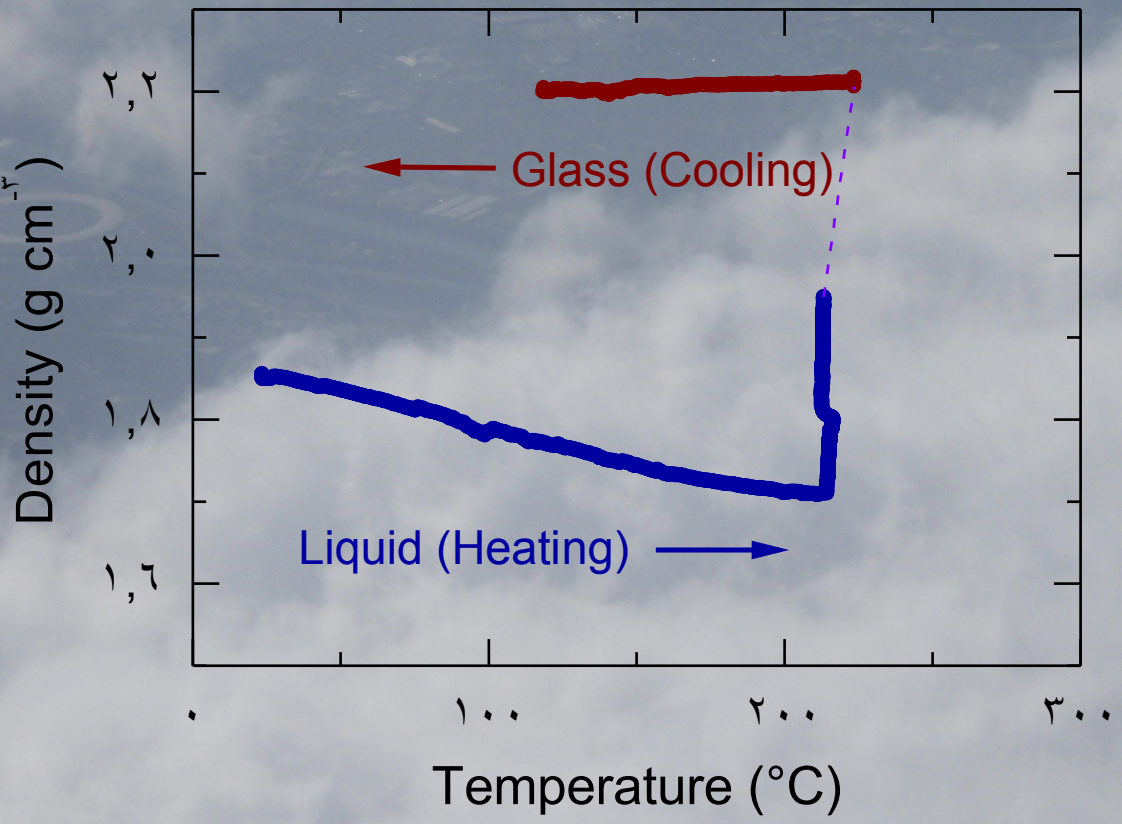
E. Cooling the glass

Total time ~4 hours

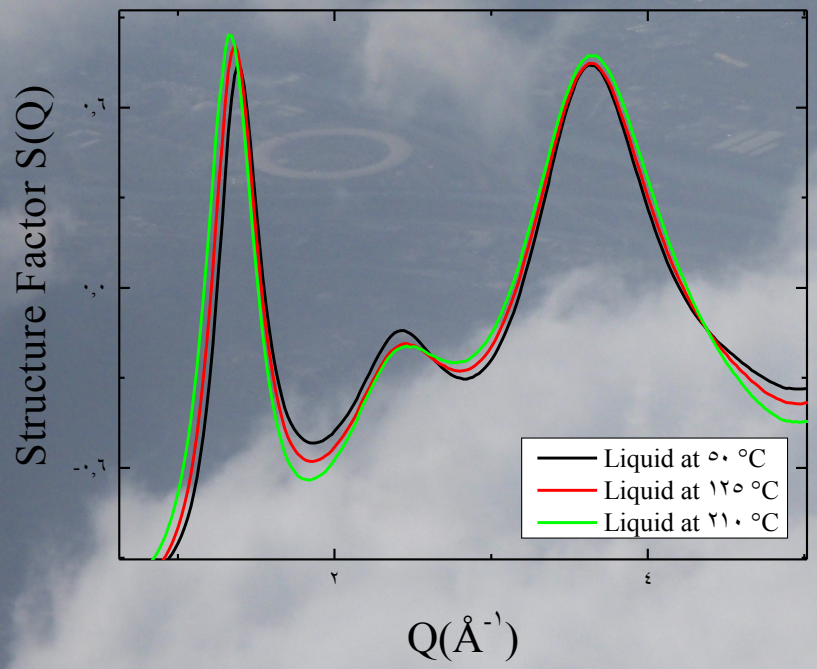


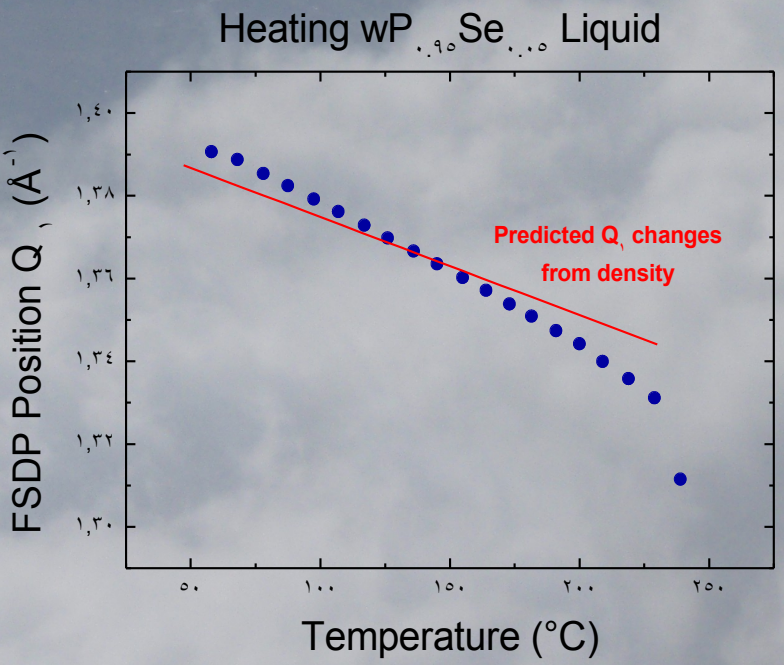
Results

Density as a function of temperature

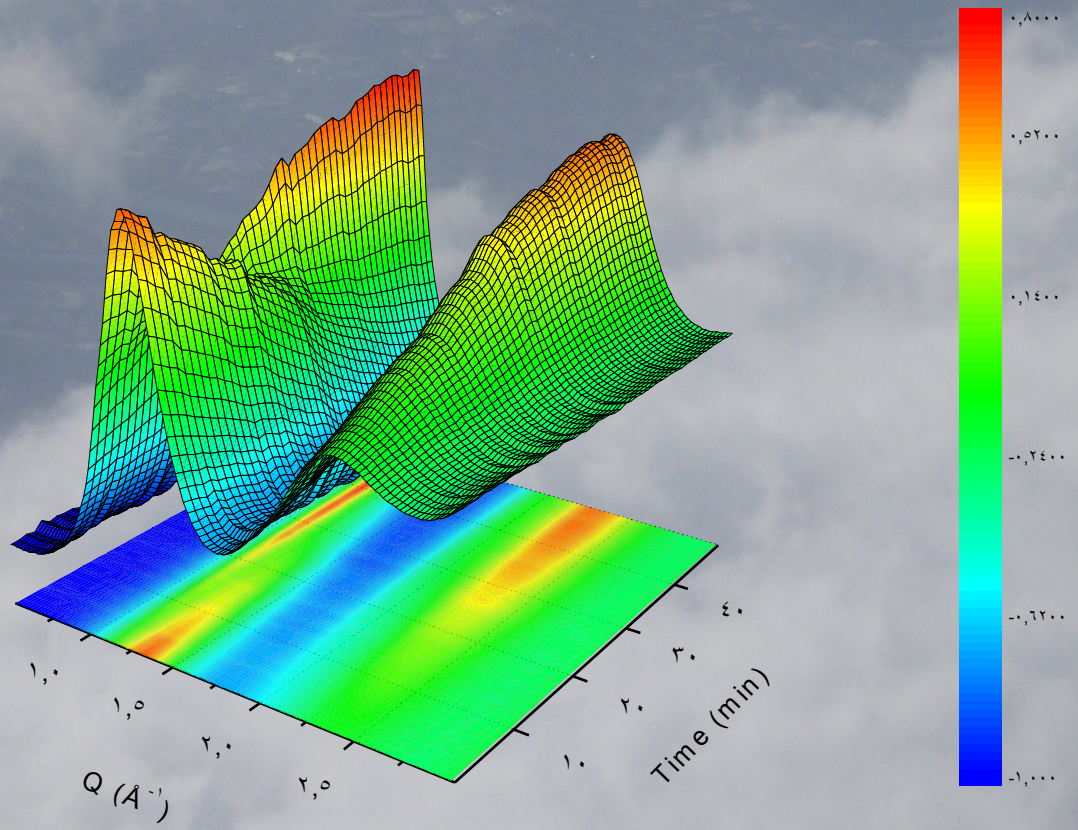


FSDP: heating the liquid

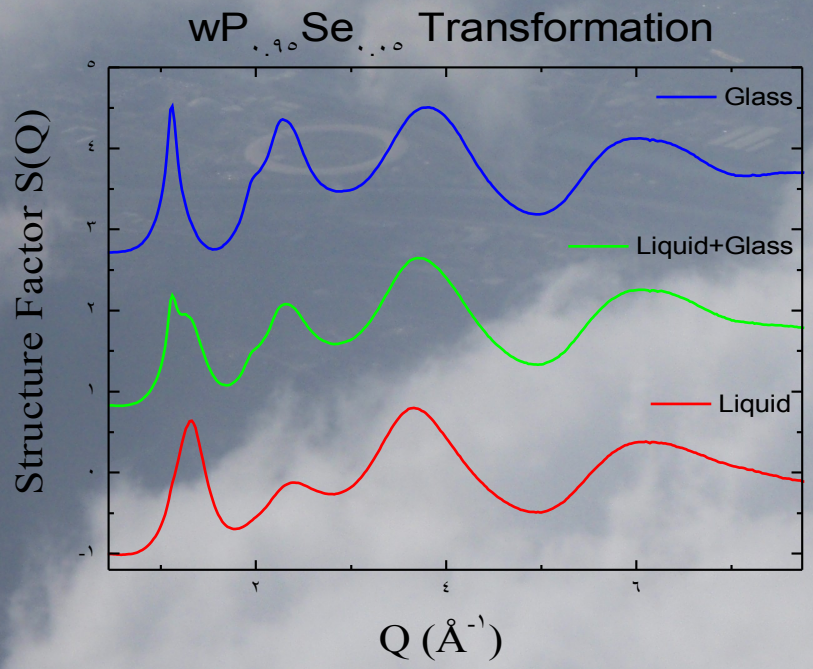


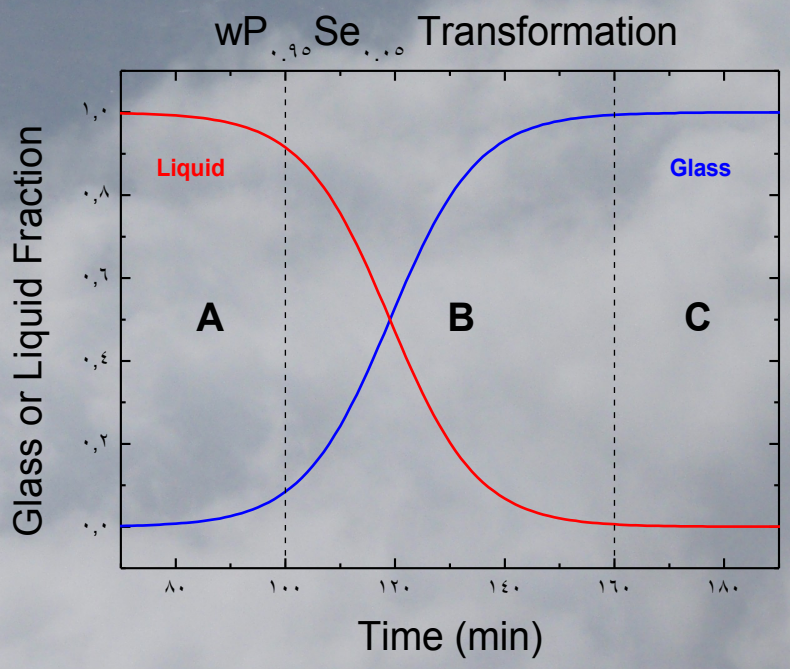


FSDP: transformation



FSDP: transformation





Conclusions

- Using different allotropic forms of P, S or Se in the synthesis, drastically different P-X (X = S, Se) polyamorphic liquids and glasses have been obtained.

- A glass of the same composition and having very similar properties and structure can be produced both by
  - rapid quenching of the melt or
  - slow heating of a different liquid polymorph

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