Phosphate solubility and its impacts on the properties of radioactive waste glasses for the Hanford site, US

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ICTP

Joint ICTP-IAEA International School on Nuclear Waste Vitrification

23 - 27 September 2019
Trieste, Italy

Further information:
http://indico.ictp.it/event/8772/
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Contents

The
Hanford
Site

It was established in WW2 for the production of plutonium. Radioactive liquid waste produced from plutonium extraction were stored in underground steel tanks, however, some began to leak.

Clean-up process

The clean-up process at the Hanford site will use a process called vitrifcation (transforming liquid and chemical waste into a non-crystalline amorphous solid) to turn the radioactive liquid waste into a glass [1]. The Hanford waste treatment plant will use a single–stage vitrification process with joule–heated ceramic lined melters. This means that the liquid waste will be mixed with glass forming additives before being added to the melter.

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Sodium Borosilicate Glass

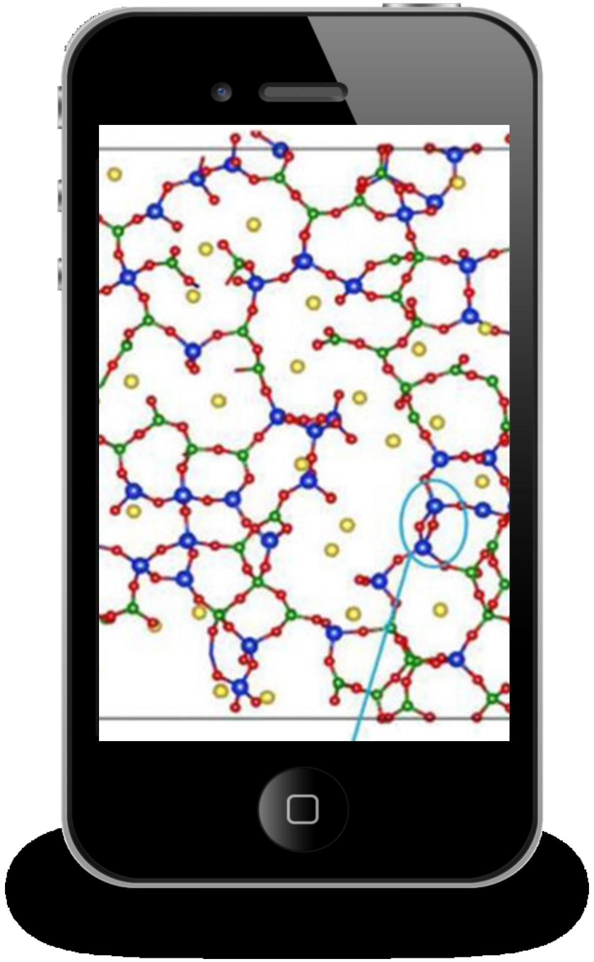
THE DECISION

Borosilicate glass is the main candidate chosen to vitrify the radioactive waste from the Hanford site because it demonstrates excellent chemical durability which is a testament to their potential longevity.

Sodium borosilicate glass contains Na_2O, B_2O_3 and SiO_2.

B_2O_3 and SiO_2 are glass formers and Na_2O is a glass modifier that acts to help reduce the glass formation temperature.

This glass formulation was selected to make understanding the effects of P_2O_5 on the structure and properties of the glass easier to try and understand.



Phosphorus pentoxide (P_2O_5)

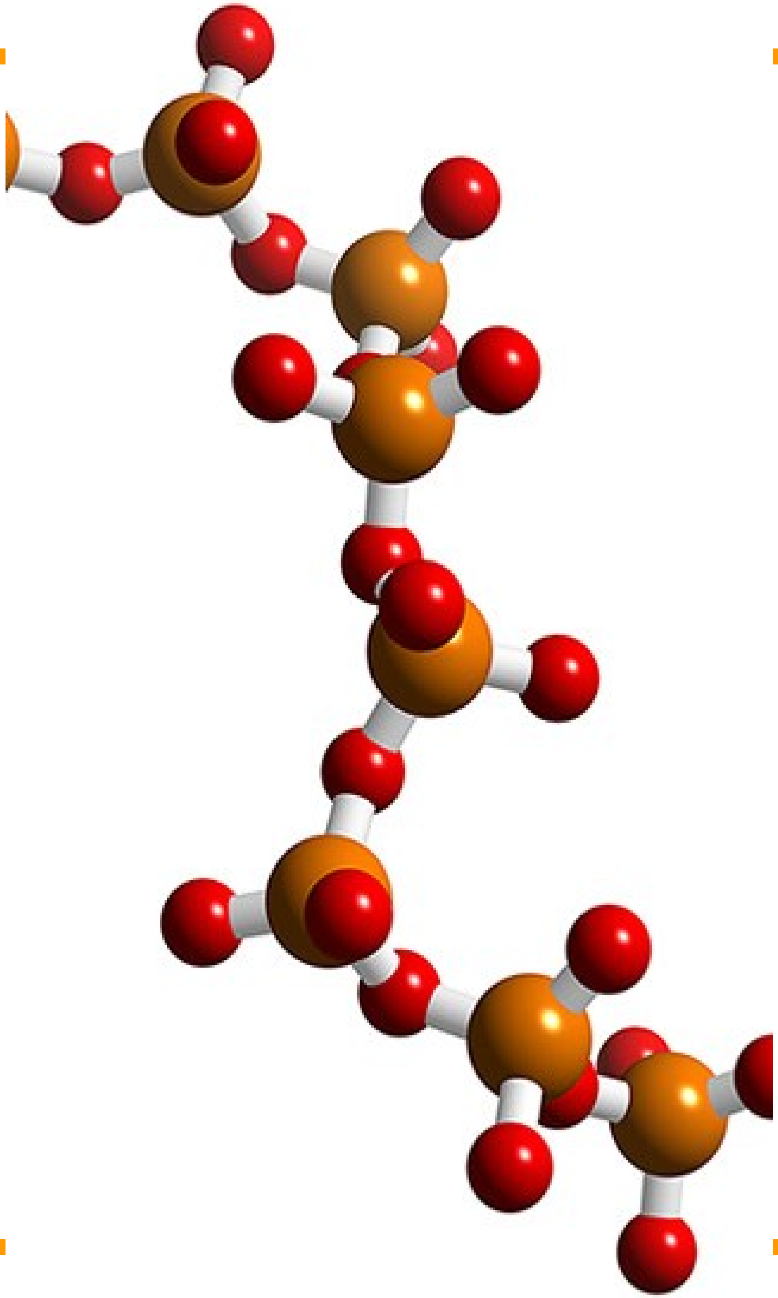


Figure 1 – Phosphorus Pentoxide 3D molecular structure [1]

Phosphorus pentoxide in the Hanford waste originates from the REDOX and Bismuth Phosphate processes [2]. It is poorly soluble in borosilicate glasses with concentrations >4.5 wt% potentially leading to phase separation [3, 4]. In some Hanford waste glasses, P_2O_5 will be present at levels that can impact on melter performance and glass properties, but it may also enhance the solubility of other waste components in the glass.

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Aims of my project

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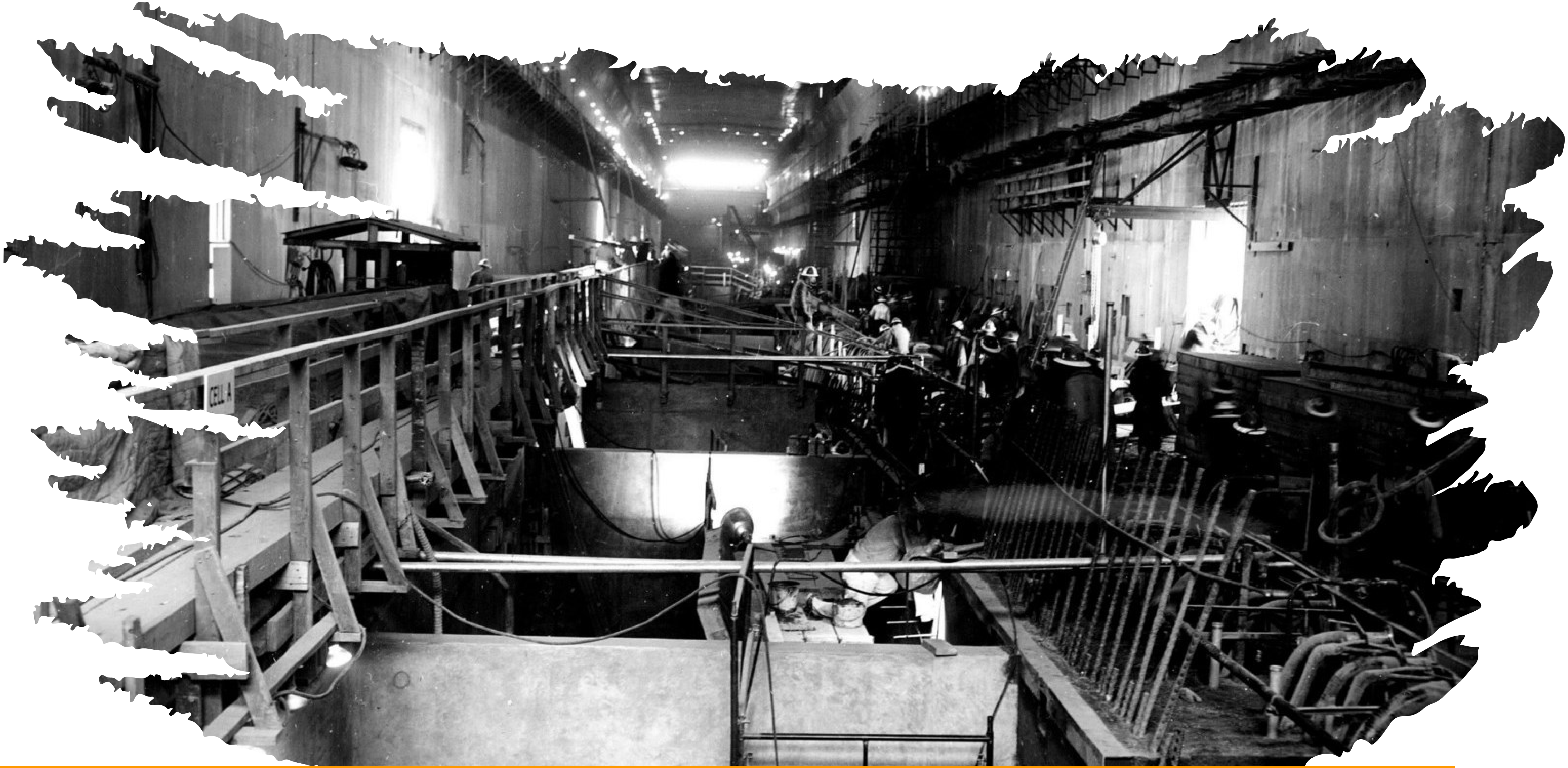
Increase the waste loading of current High Level activity Waste and Low Level activity Waste glasses

Identify and characterise phase separation in glasses

Understand the effects of varying the amount of P_2O_5 on glass properties, composition and structure



Sodium borosilicate glasses doped with phosphorus pentoxide

Methodology – batching, melting, quenching and annealing

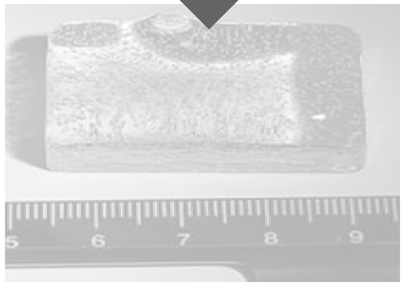
BATCHED

MELTED

SHAPED

ANNEALED

[redacted]



QUENCHED

NBS-xP glasses

Sodium borosilicate glasses doped with phosphorus pentoxide, where x was 0, 1.0, 2.0, 3.0, 4.0, 5.0,5.5 and 6.0 mol%.

Methodology – batching, melting, quenching and annealing

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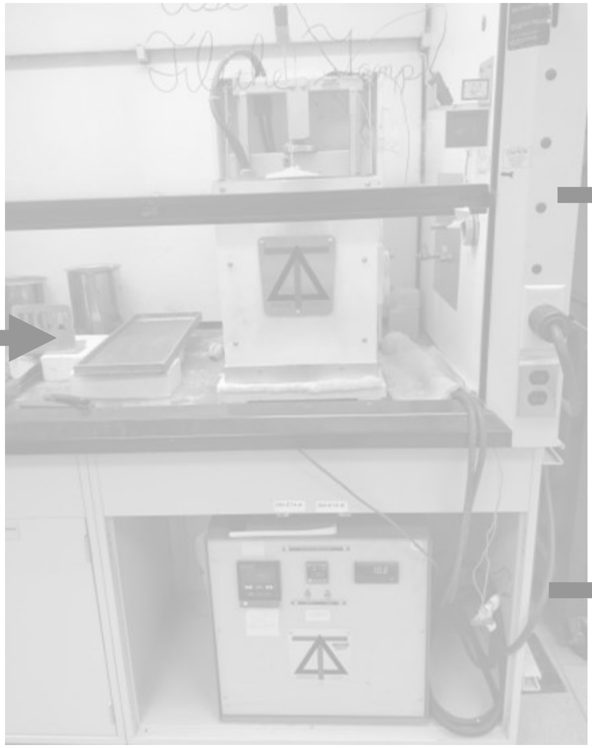

SHAPED

QUENCHED

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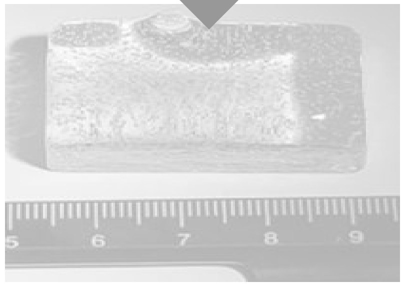

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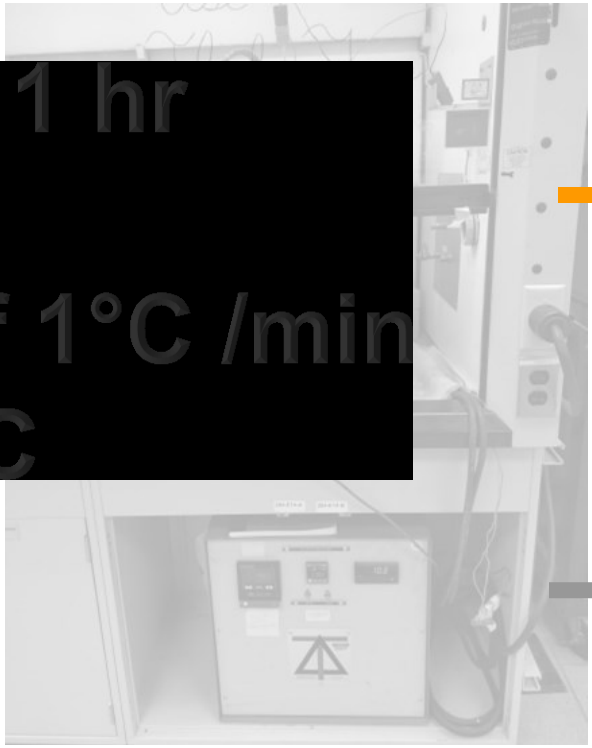

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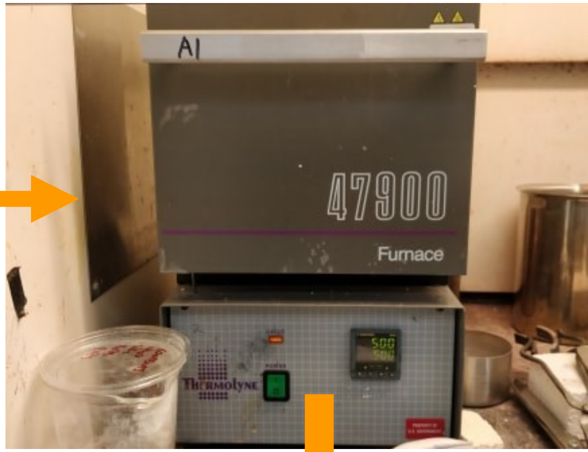
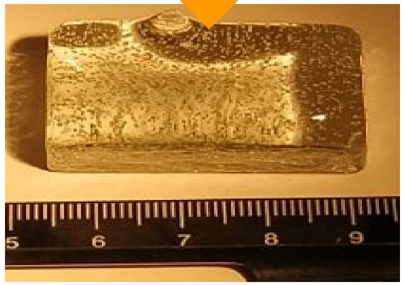
SHAPED

QUENCHED

ANNEALED





NBS-xP glasses

Sodium borosilicate glasses doped with phosphorus pentoxide, where x was 0, 1.0, 2.0, 3.0, 4.0, 5.0,5.5 and 6.0 mol%.

Methodology – characterisation techniques

XRD

- Bruker D8 Advance
- CuKα radiation, scan rate of 2θ with step size 0.015° and a scan step size of 177 sec. Samples were measured between 5° and 70°.

SEM / EDS

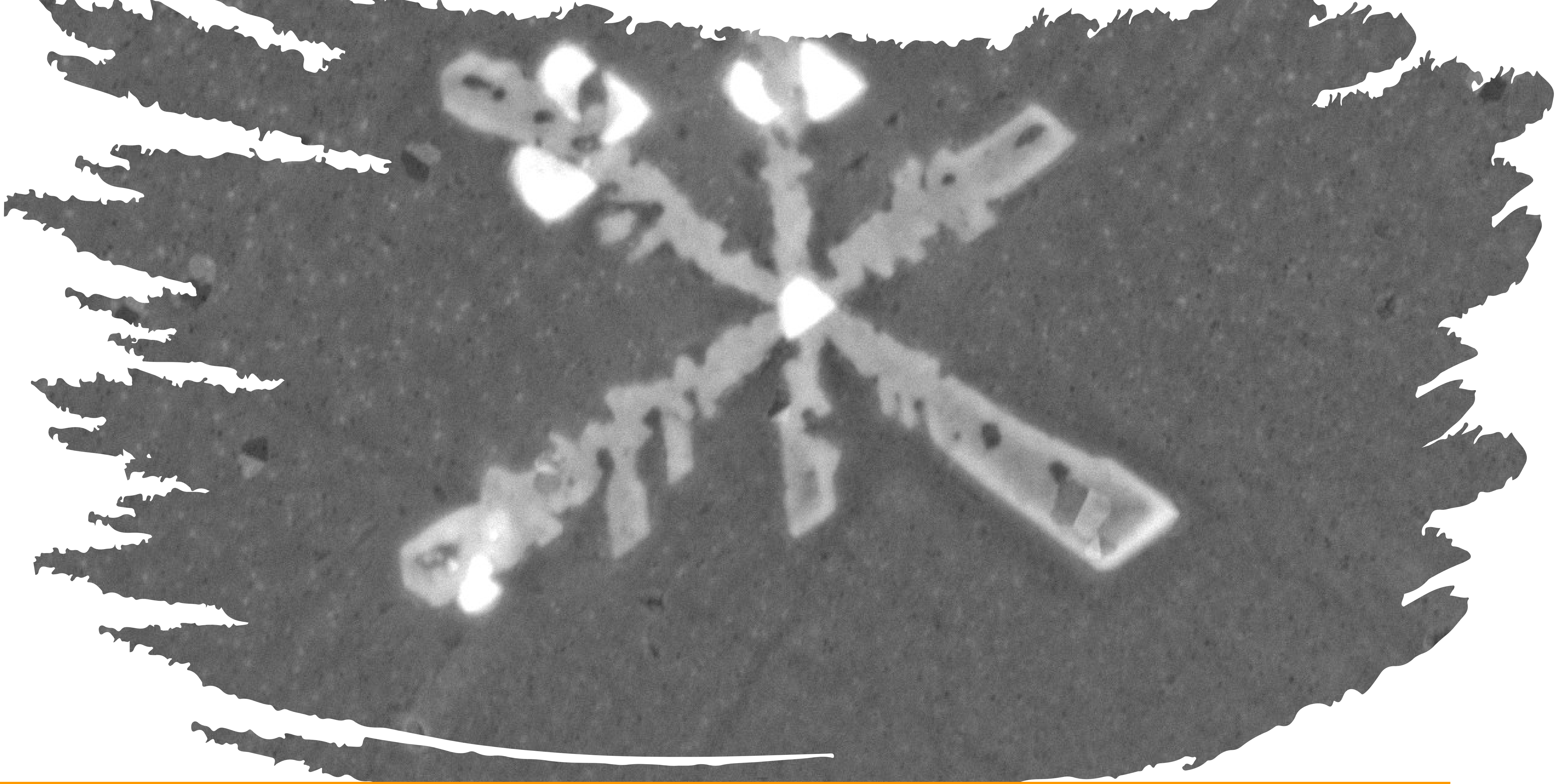
- JOEL JSM-7001F field mission SEM
- JOEL PC – SEM v.2.1.0.9 software for analysis

Optical

- Canon EOS Rebel T5 Camera
- Keyence VHX-2000
  - Magnification of 20x, 30x and 50x

DTA

- SDT Q600 V20.9 build 20
- Used to determine the T_g
- Heated up to 625°C (5 step program)



RESULTS

Results – The NBS-xP samples

Sample	Batched composition (mol%)			
	SiO_2	B_2O_3	P_2O_5	Na_2O
NBSP0	55.81	16.28	0.00	27.91
NBSP1.0	55.26	16.12	1.00	27.63
NBSP2.0	54.70	15.95	2.00	27.35
NBSP3.0	54.14	15.79	3.00	27.07
NBSP4.0	53.58	15.63	4.00	26.79
NBSP5.0	53.02	15.47	5.00	26.51
NBSP5.5	52.74	15.38	5.50	26.37
NBSP6.0	52.47	15.30	6.00	26.23

Table 1 – Compositions of NBSP samples

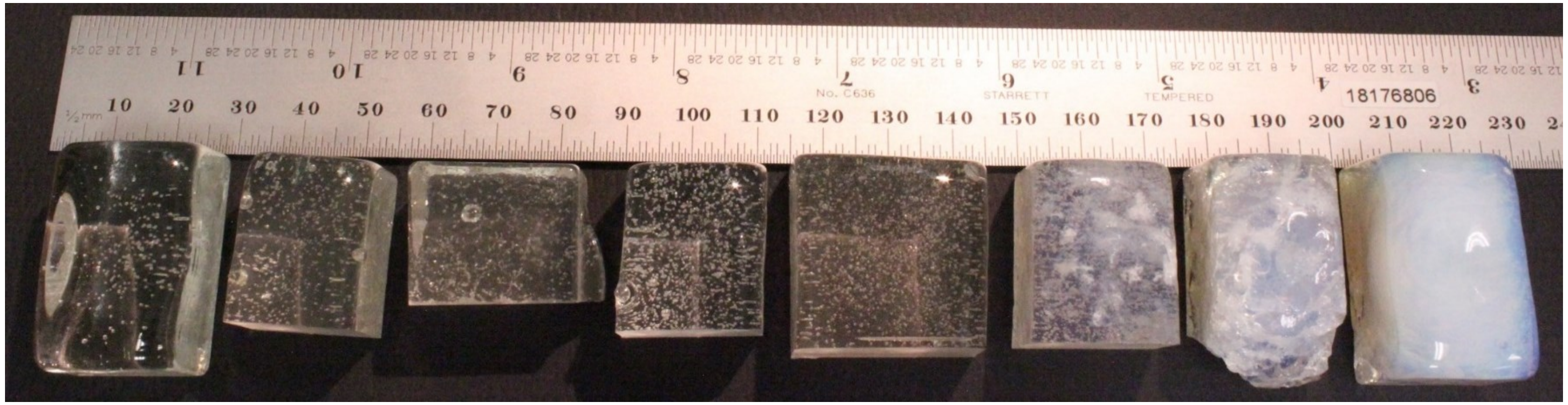


Figure 2 – NBSP samples (left to right) 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 5.5 and 6.0 mol% P_2O_5

Figure 3 – NBSP5.0

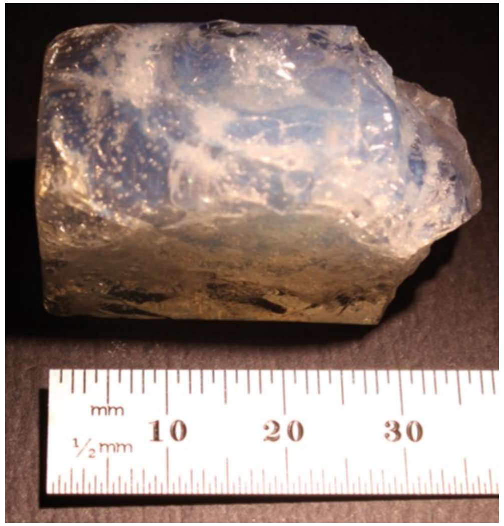


Figure 4 – NBSP5.5

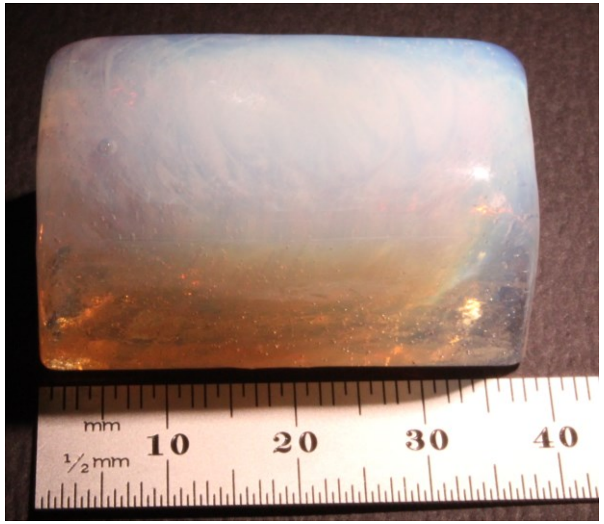
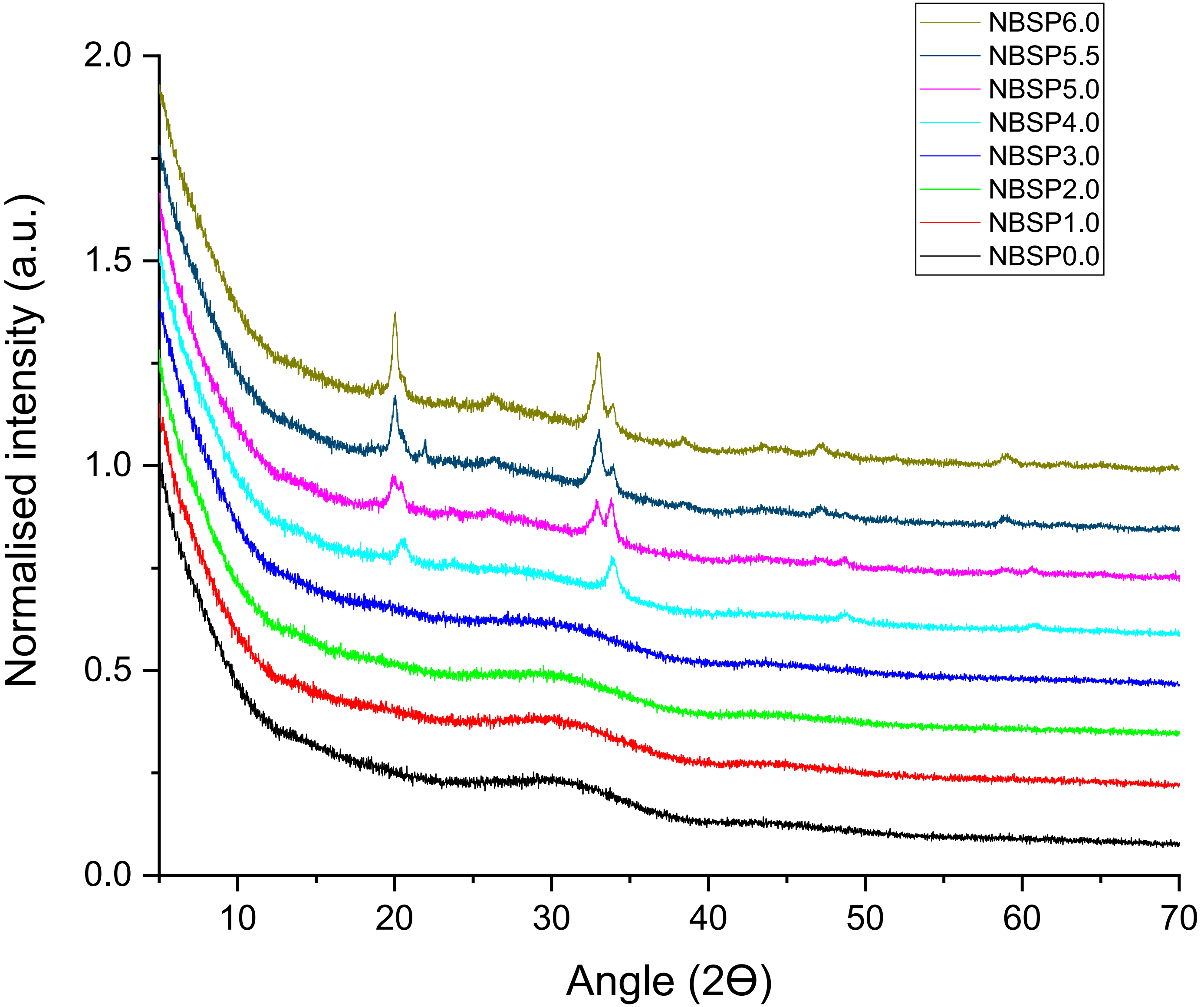


Figure 5 – NBSP6.0

Terminology

Opalescence: phase separation appears as a milky white and/or blue colour in a translucent glass

XRD analysis – NBSP0.0 – 3.0



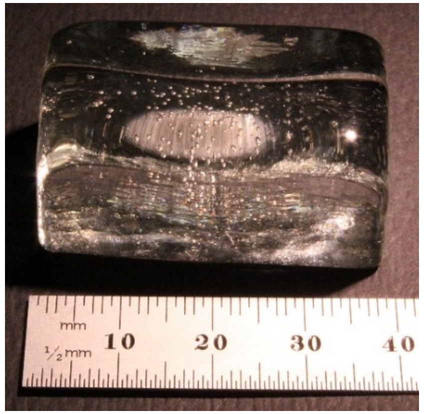


Figure 6 – NBSP0.0 (black)

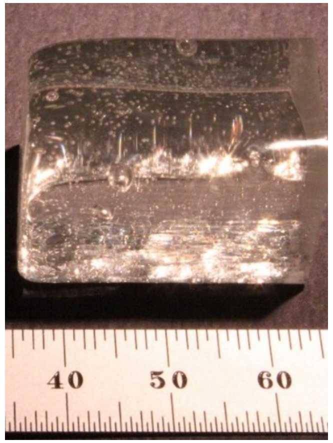


Figure 7 – NBSP1.0 (red)

Figure 8 – NBSP2.0 (green)

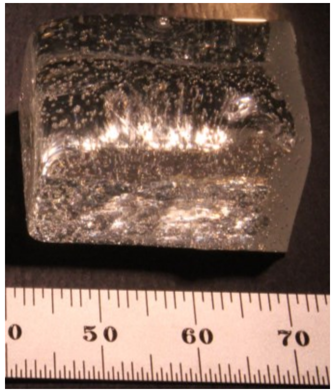
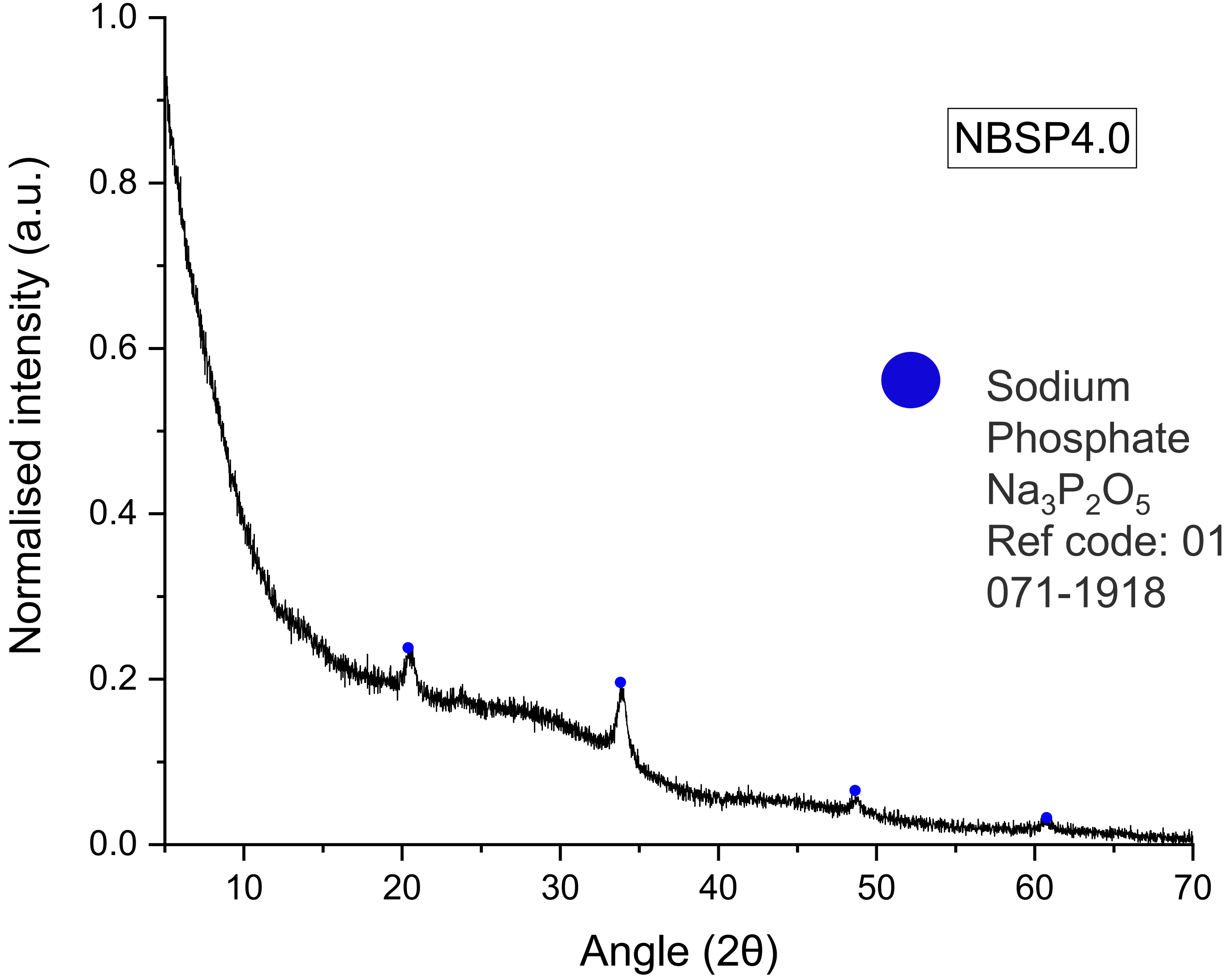


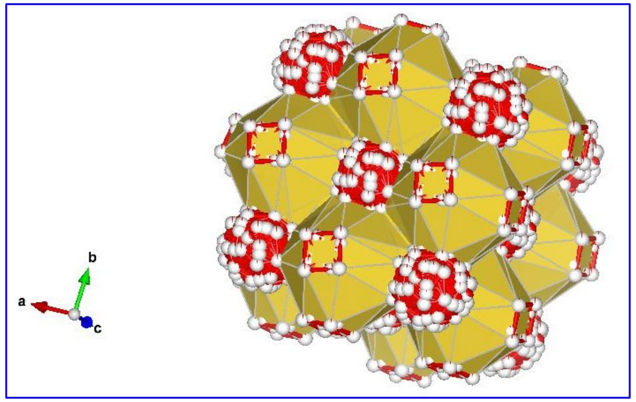
Figure 9 – NBSP3.0 (blue)

XRD analysis – NBSP4.0

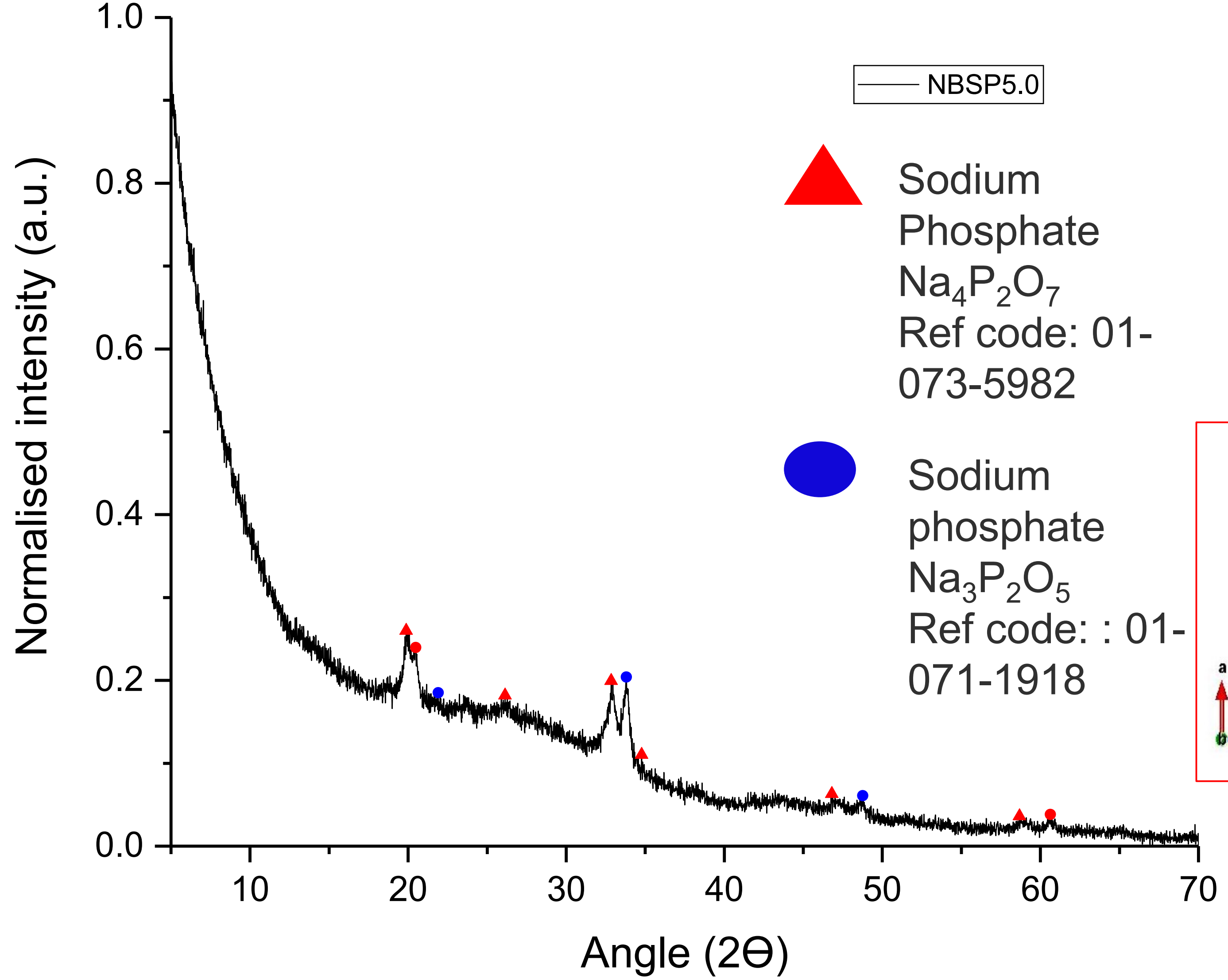


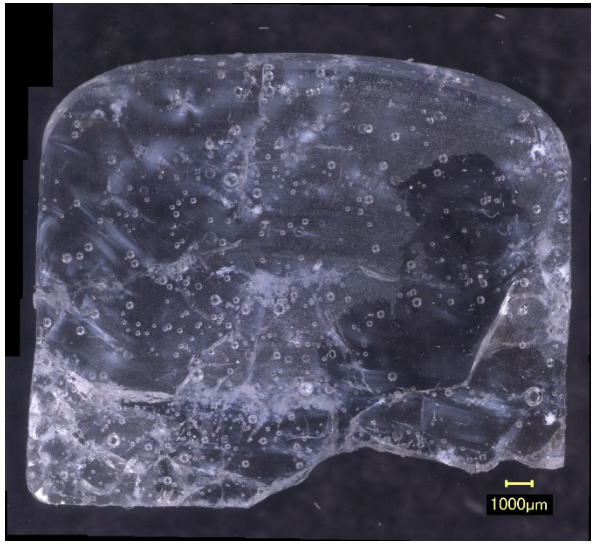
Sodium Phosphate $Na_3P_2O_5$ Ref code: 01-071-1918

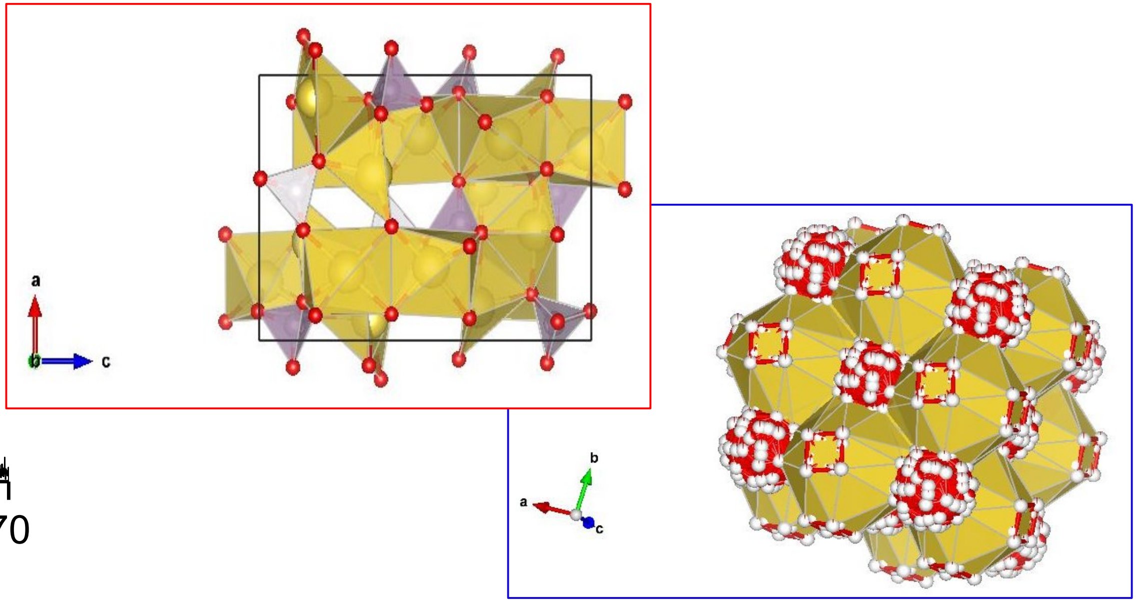
Figure 10 – NBSP4.0



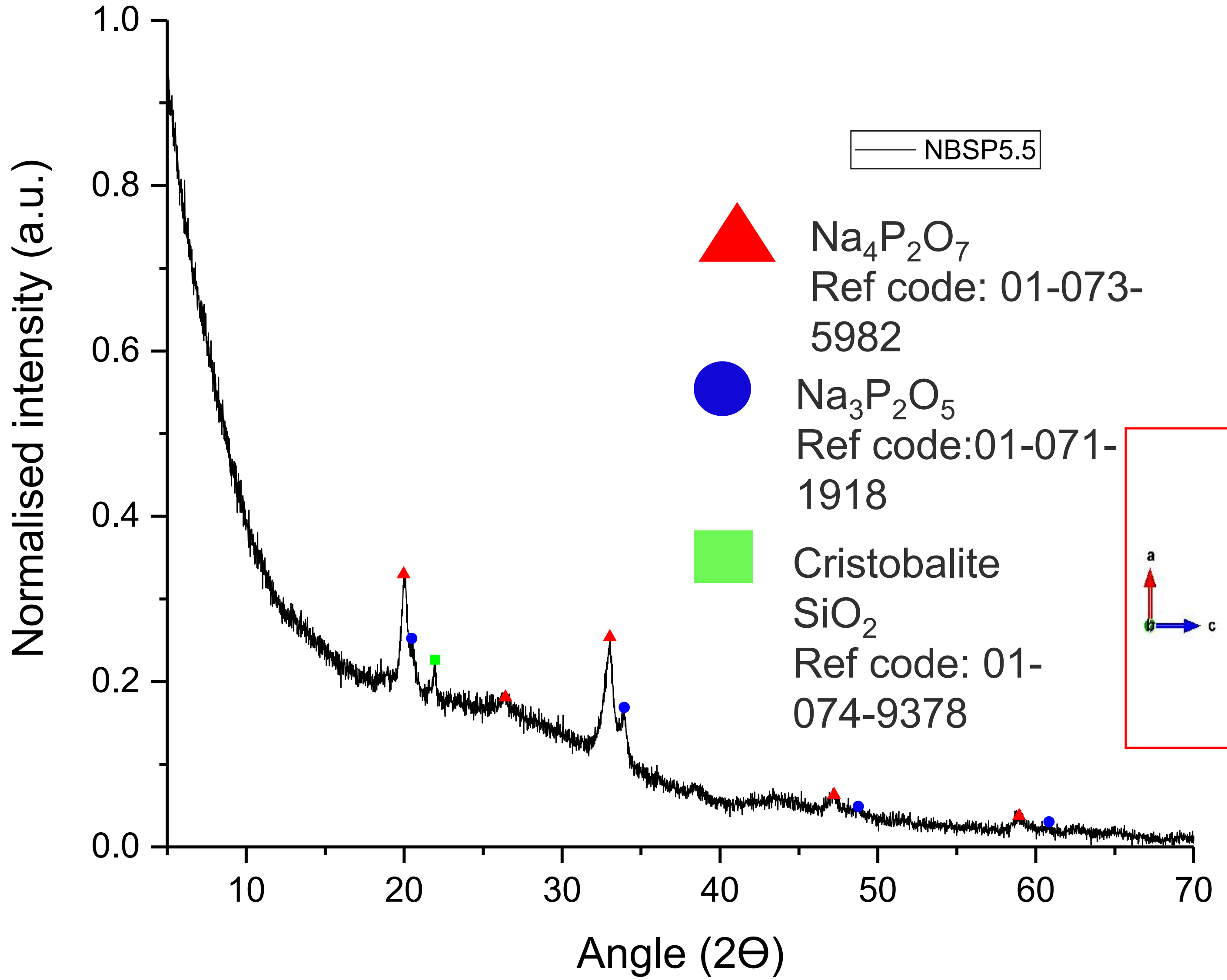
XRD analysis – NBSP5.0

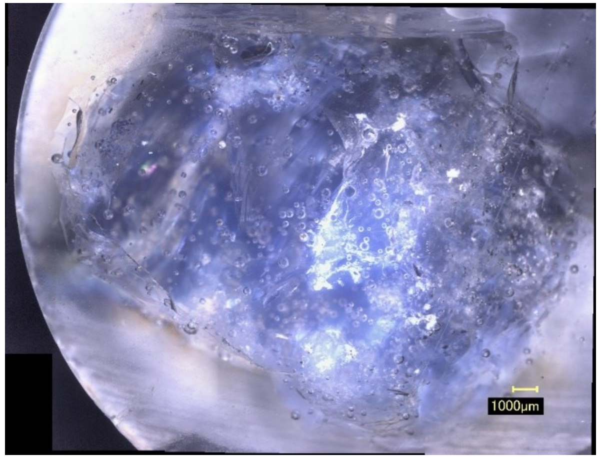


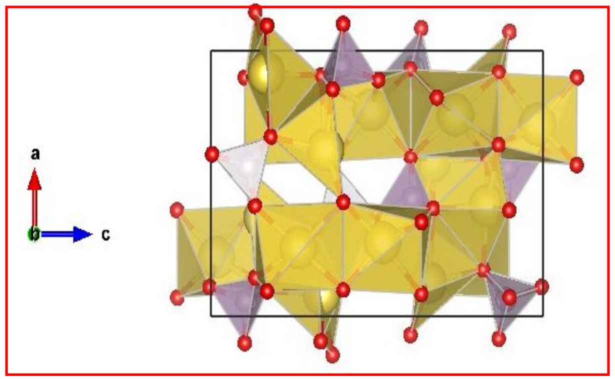


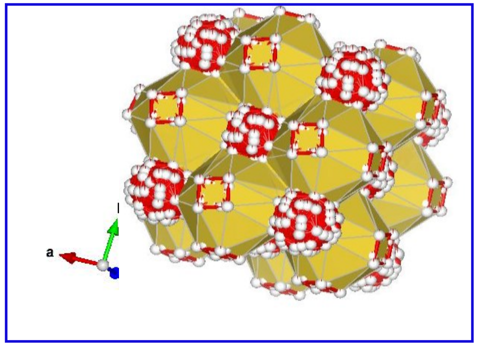


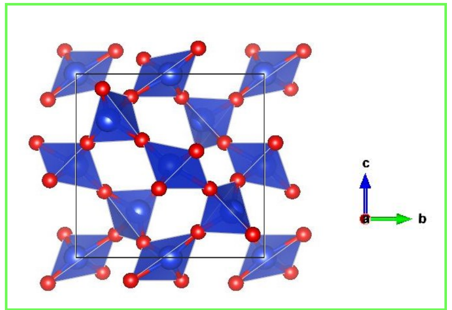
XRD analysis – NBSP5.5



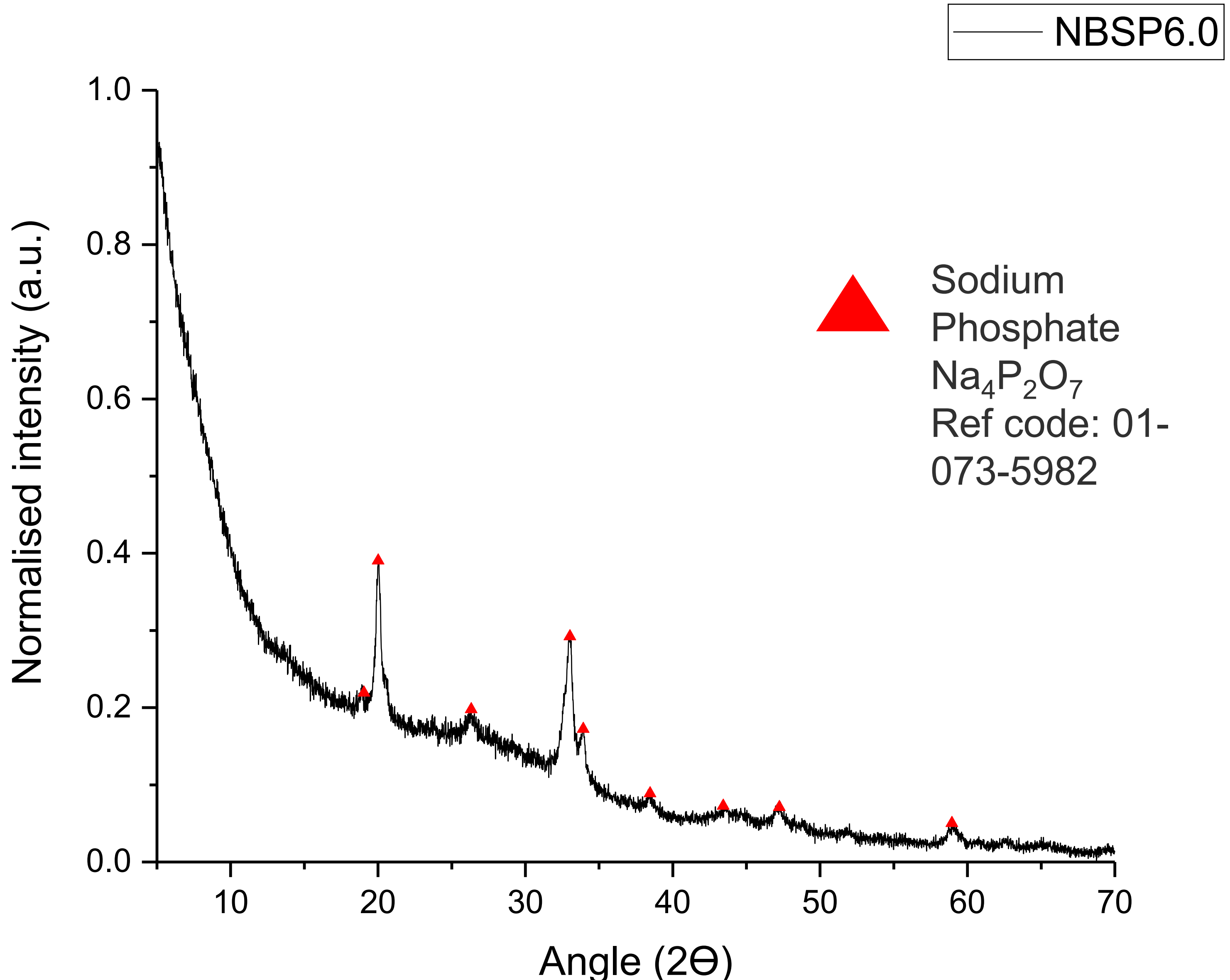


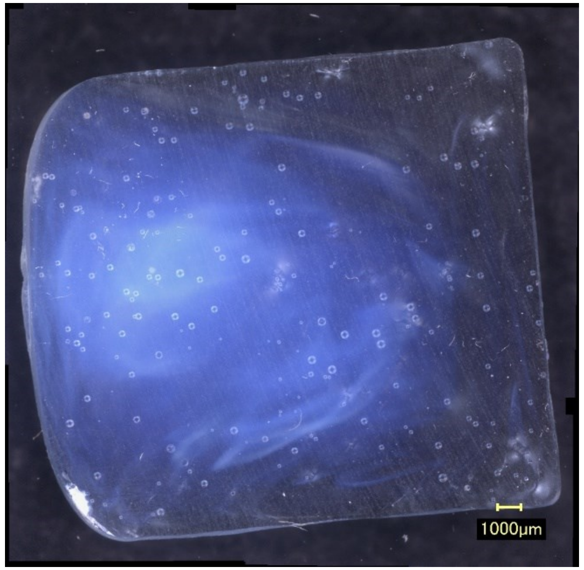


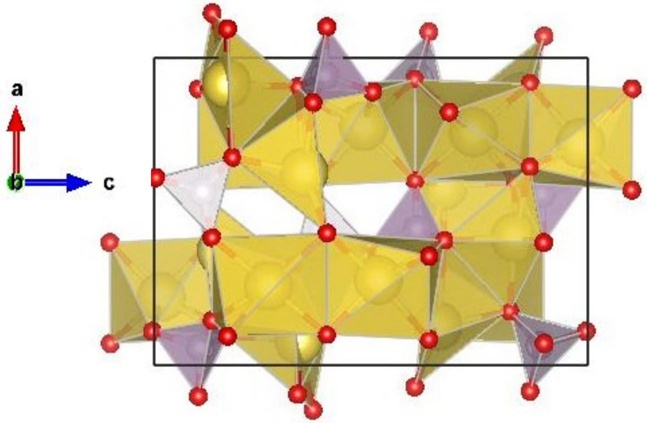




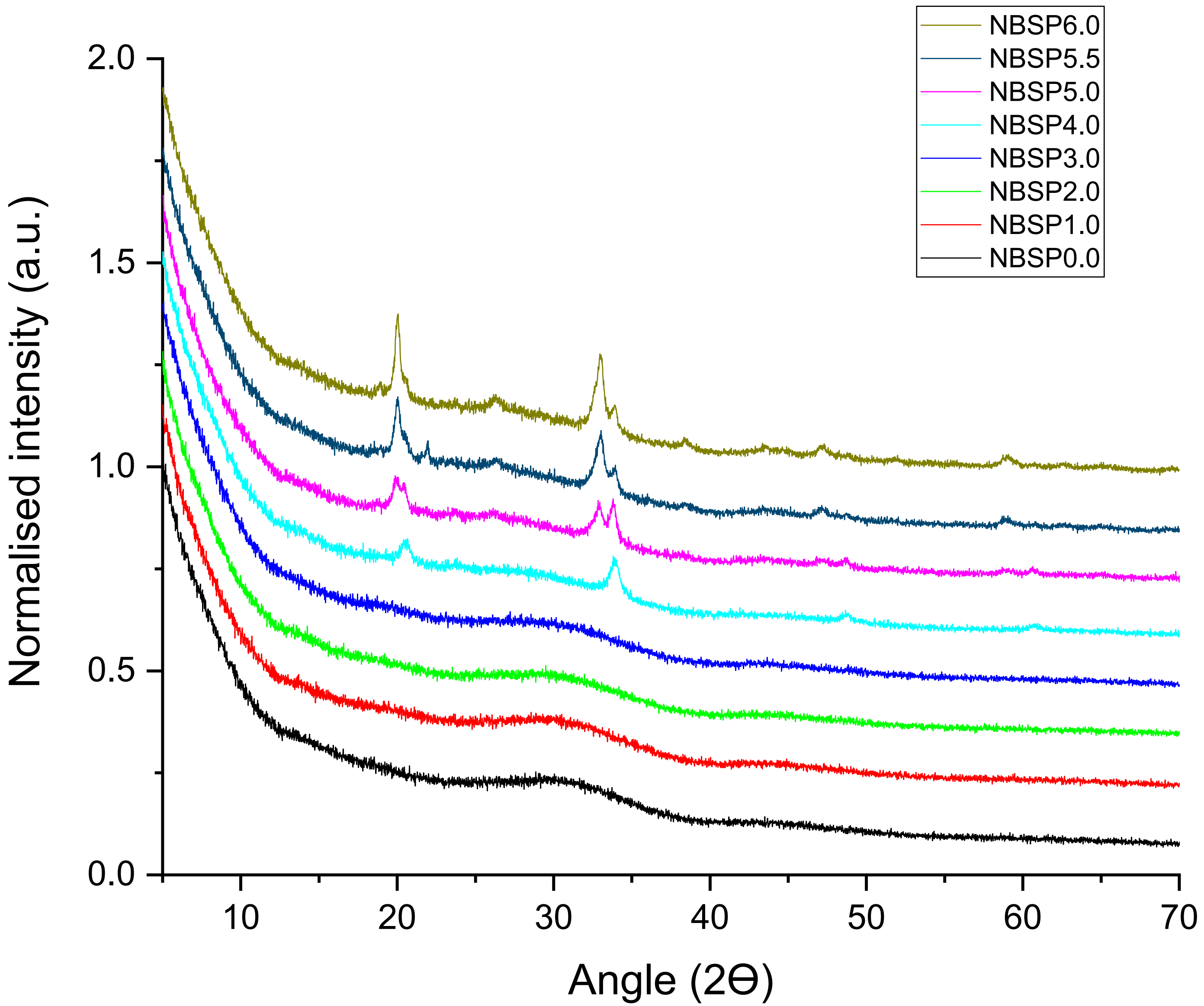
XRD analysis – NBSP6.0





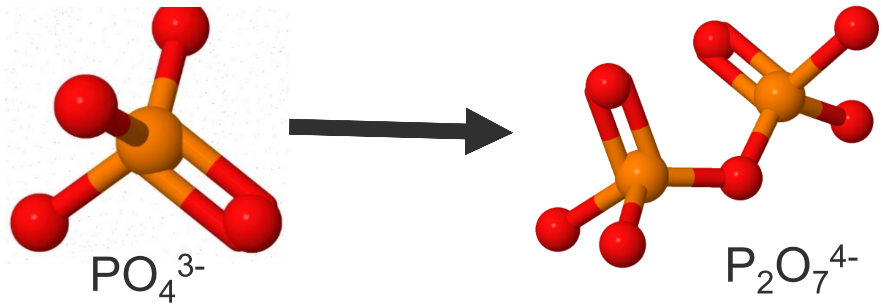


XRD analysis – Discussion



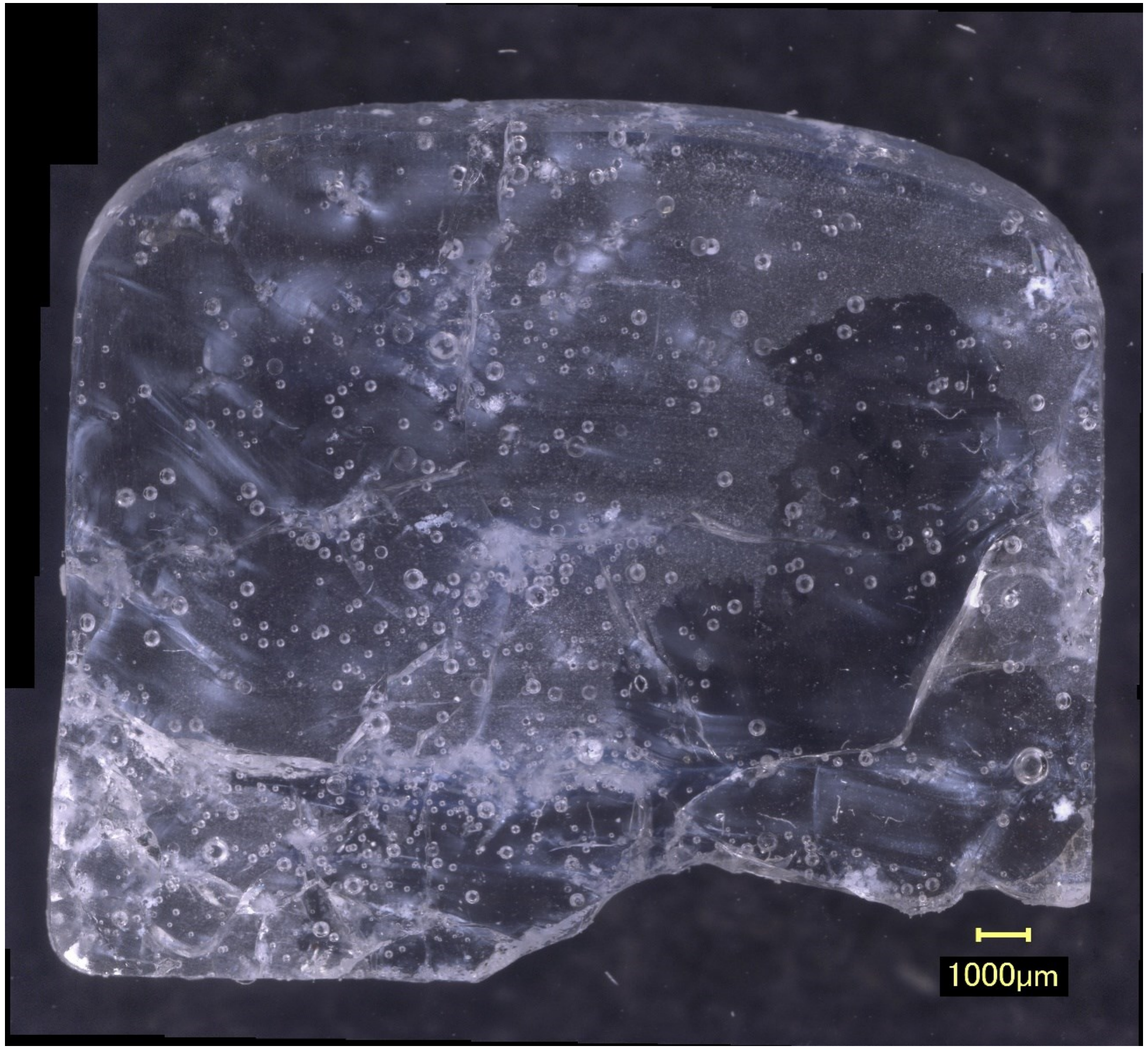
As the phosphate content increased the glasses became increasingly more crystalline, with a shift in the type of phosphate species present.

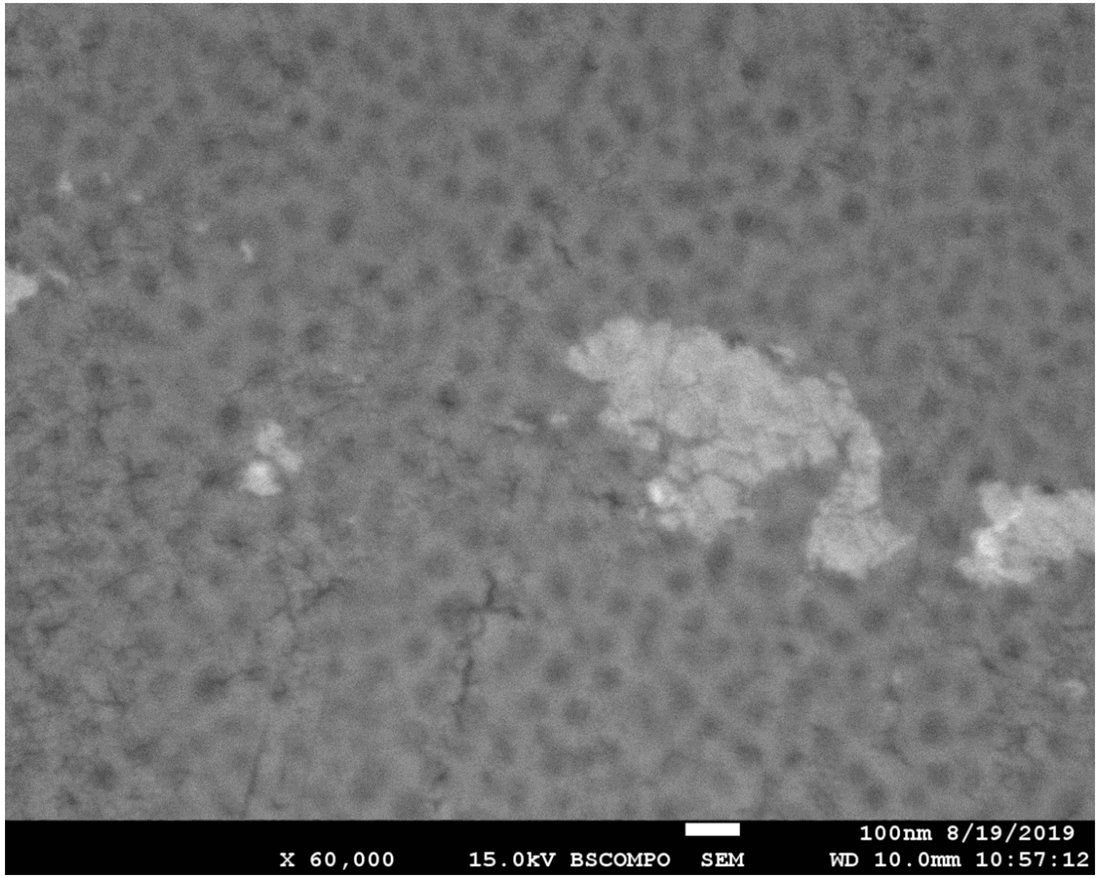
The ratio between PO_4^{3-} and $P_2O_7^{4-}$ anions changes in favour of the pyrophosphate cations ($P_2O_7^{4-}$) as the P_2O_5 content increases.



This increase in $P_2O_7^{4-}$ anions means that more sodium ions are needed to charge compensate the phosphorus and are scavenged from the silicon network, resulting in its repolymerisation [5, 6].

SEM – NBSP5.0, Site 1

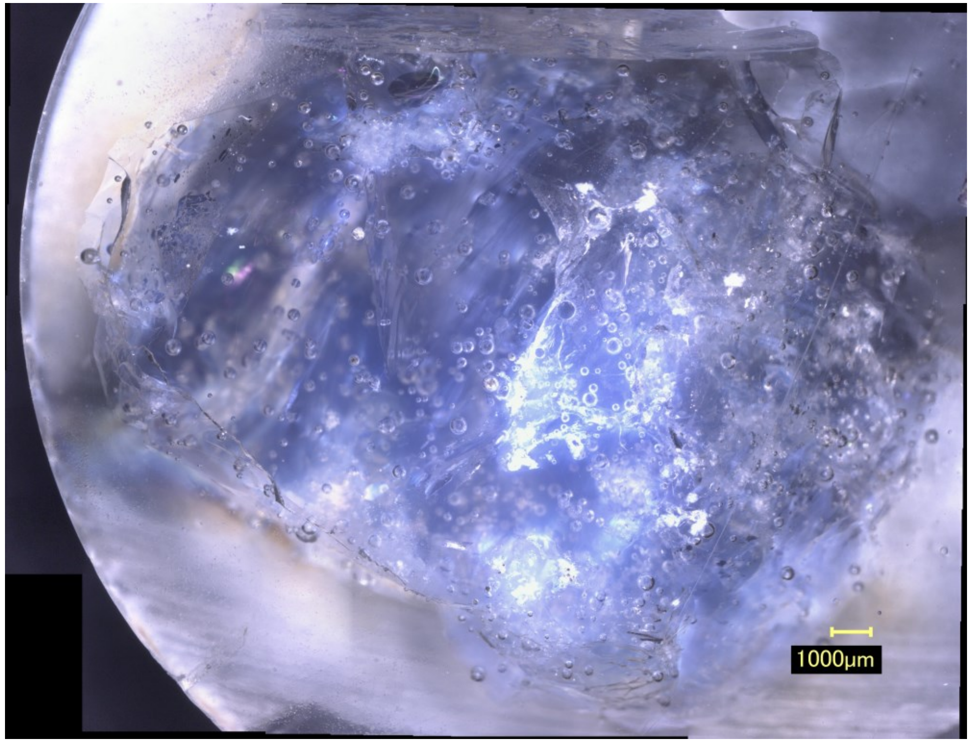


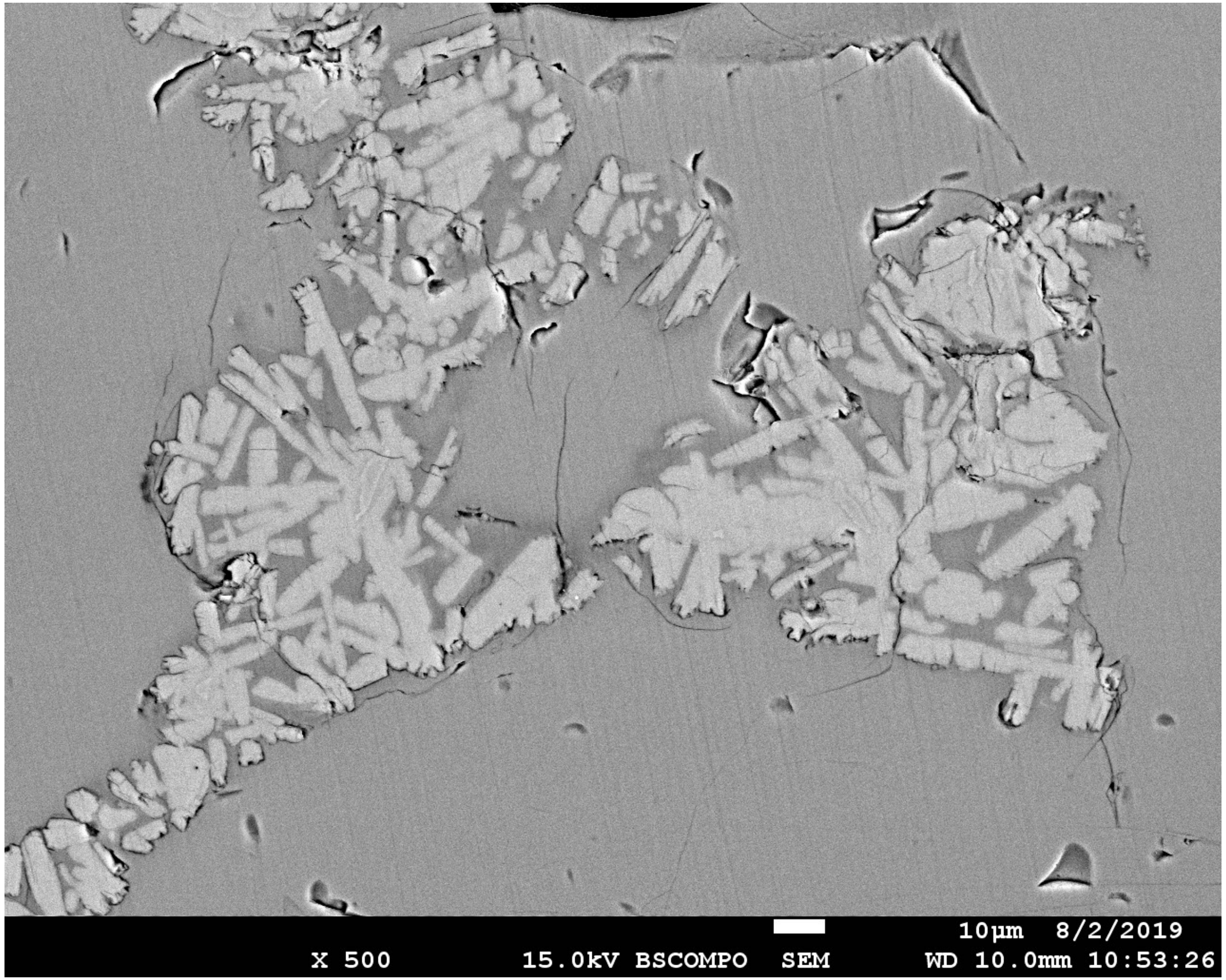


Phase separation

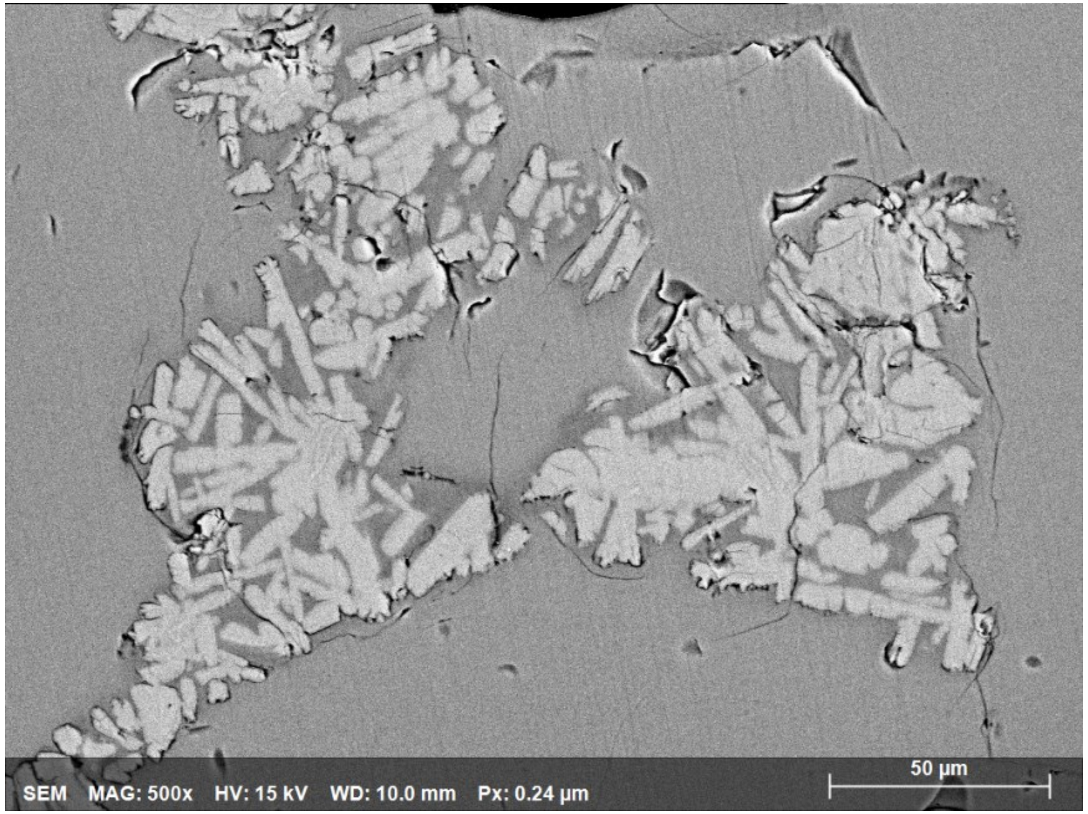
Phase separation occurs by either two mechanisms: spinodal decomposition or nucleation and growth.

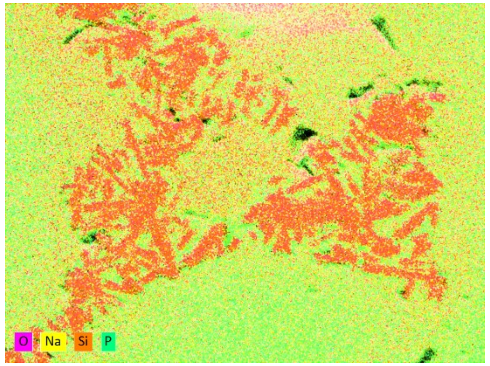
SEM – NBSP5.5, Site 1

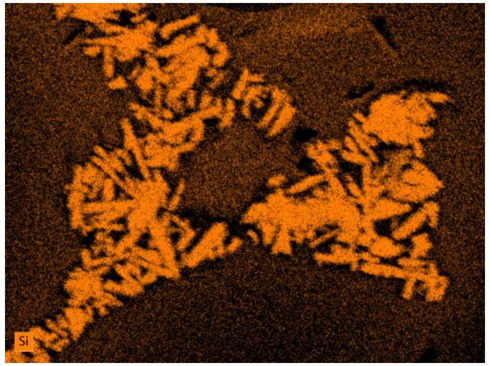


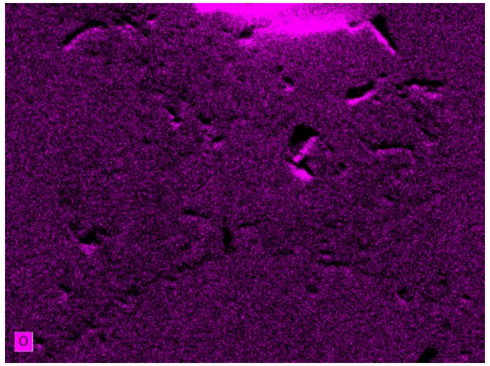


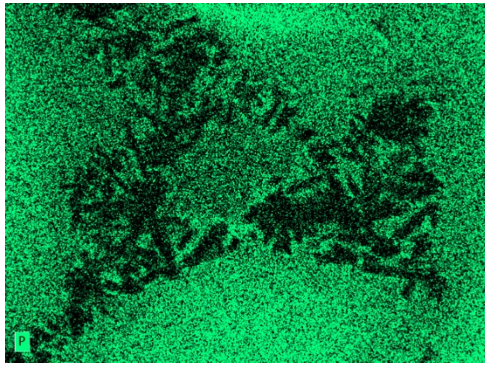
EDS – NBSP5.5, Site 1

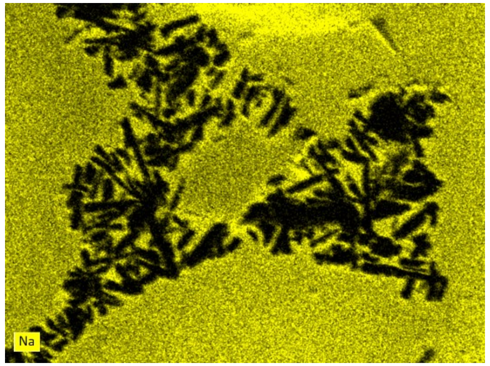


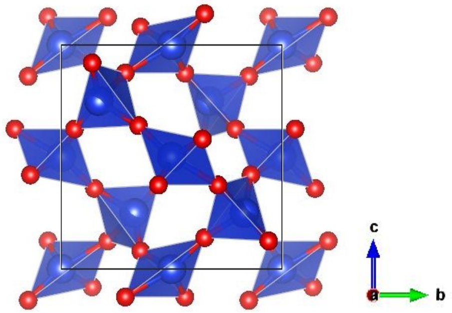








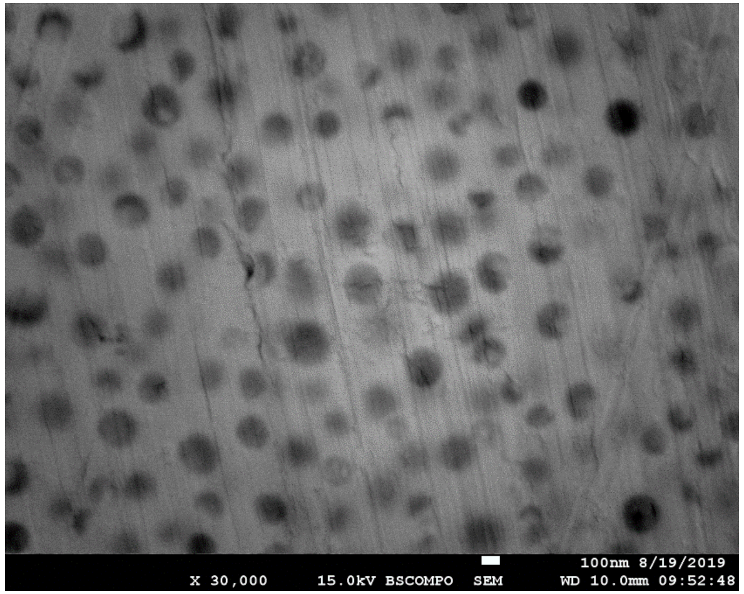


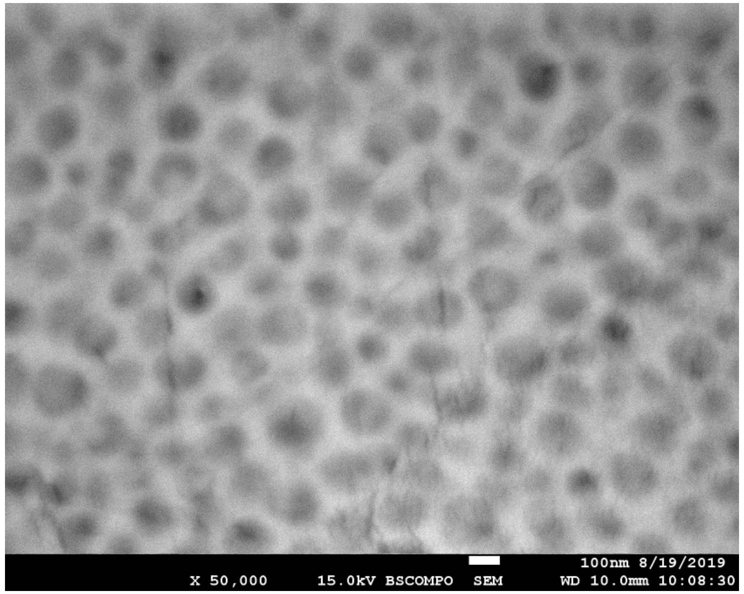


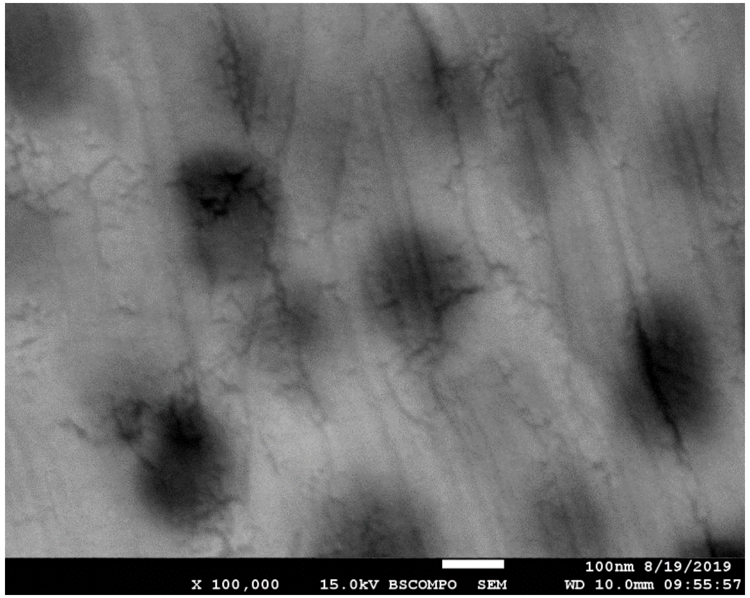
Cristobalite

EDS – NBSP5.5, Site 2

Increased magnification, x30k, x50k and x100k

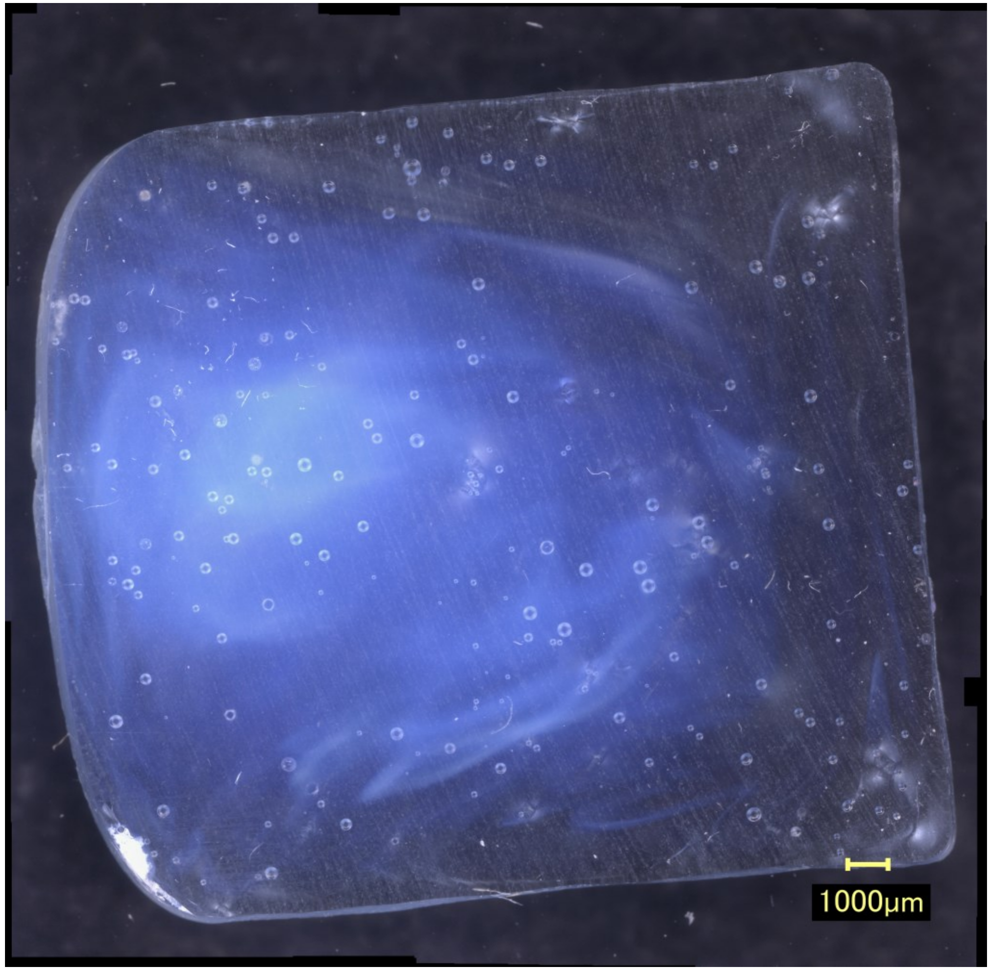


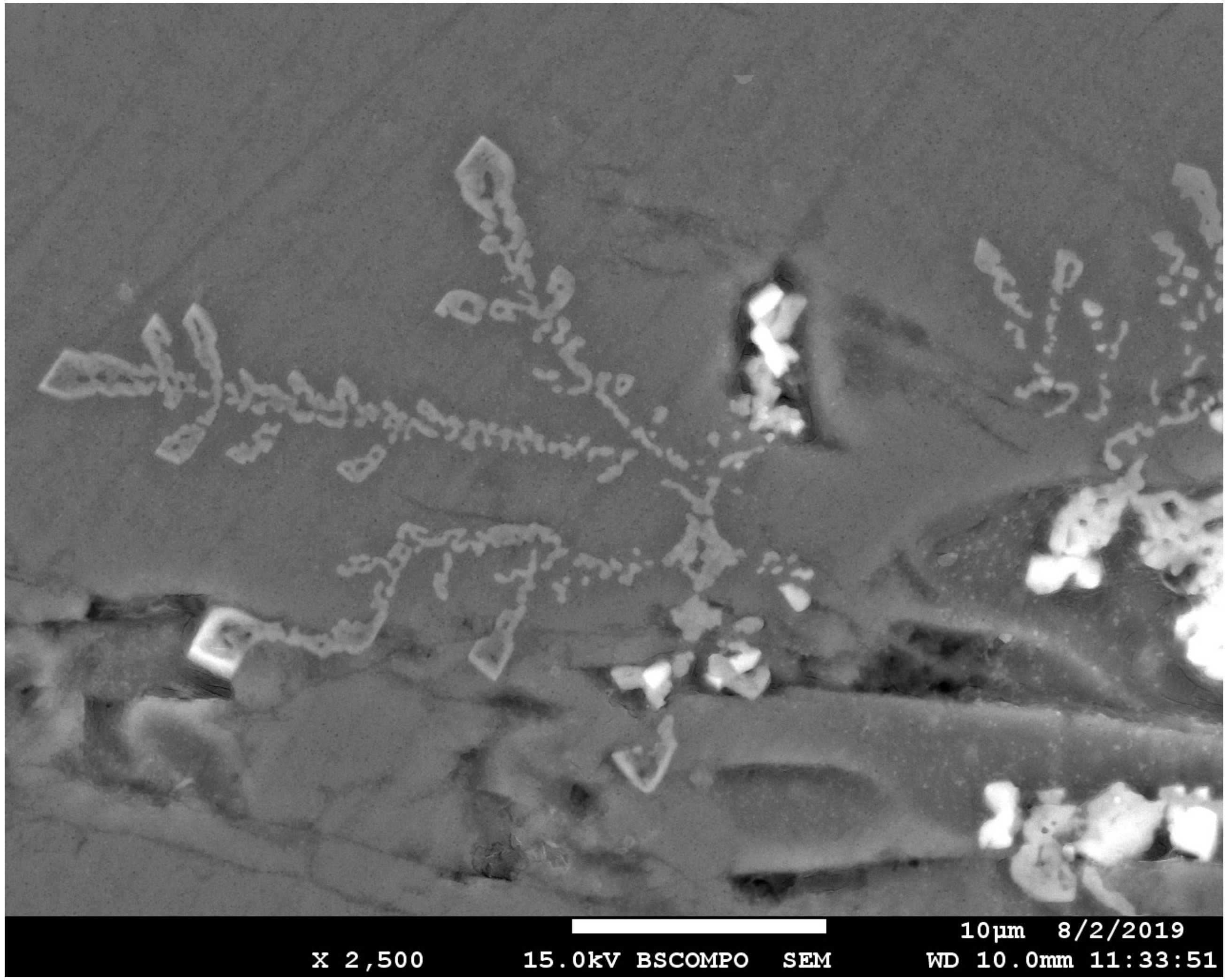




Phase separation

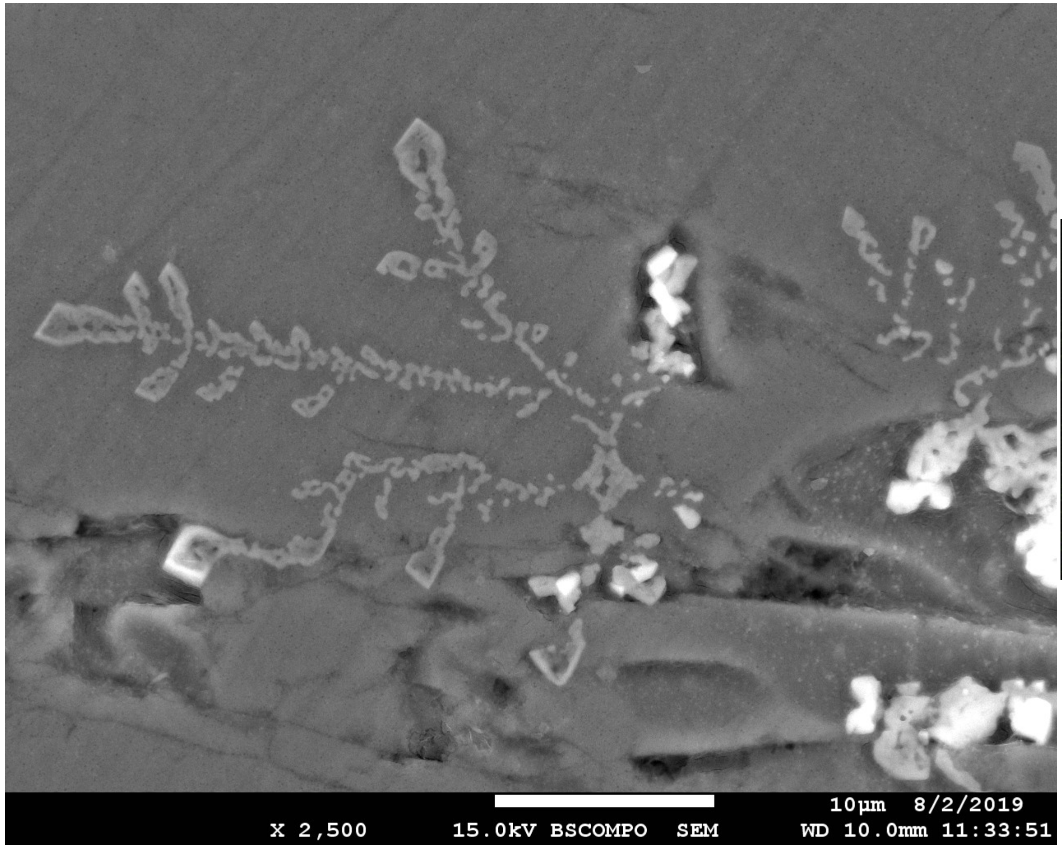
SEM – NBSP6.0, Site 1

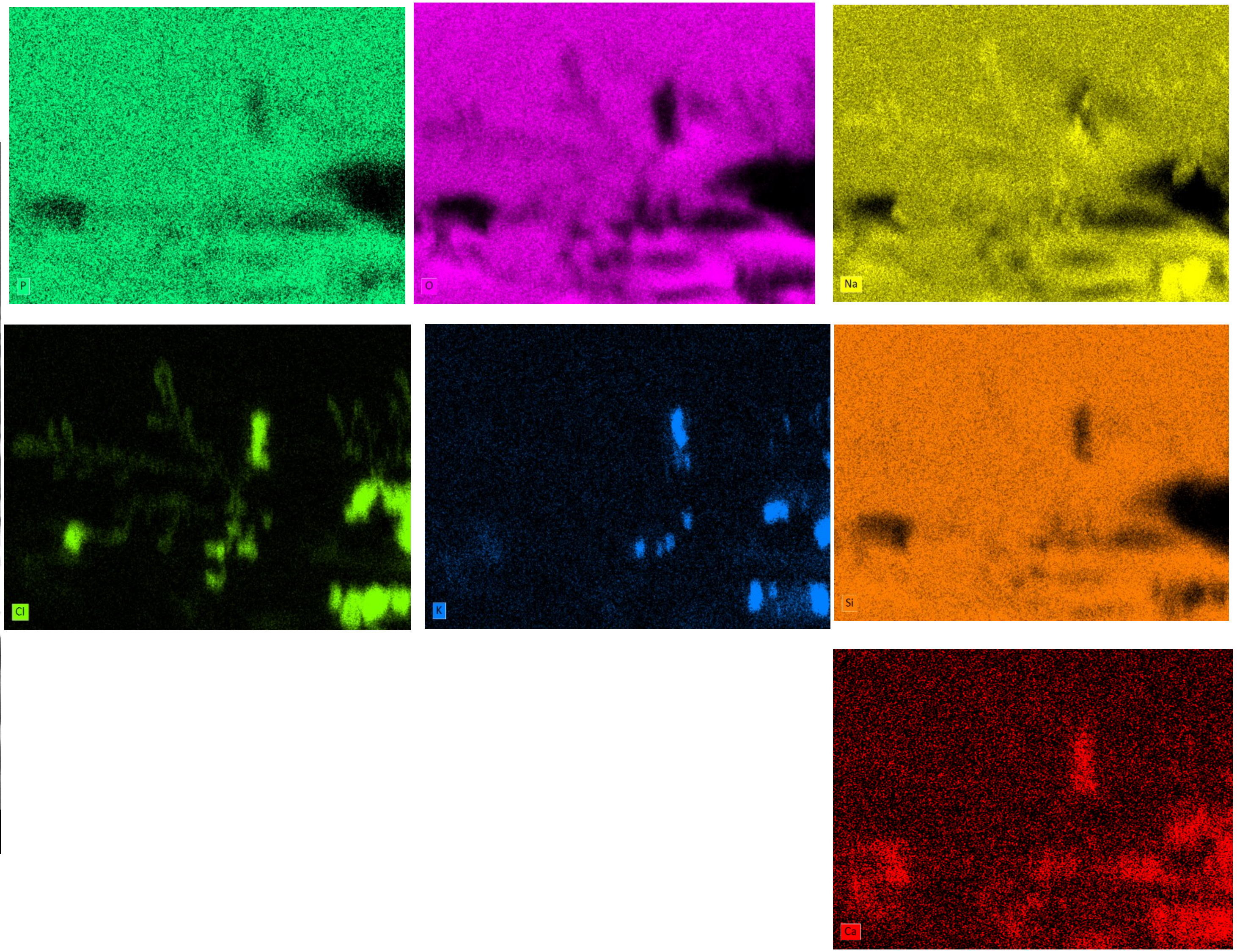




EDS – NBSP6.0, Site 1

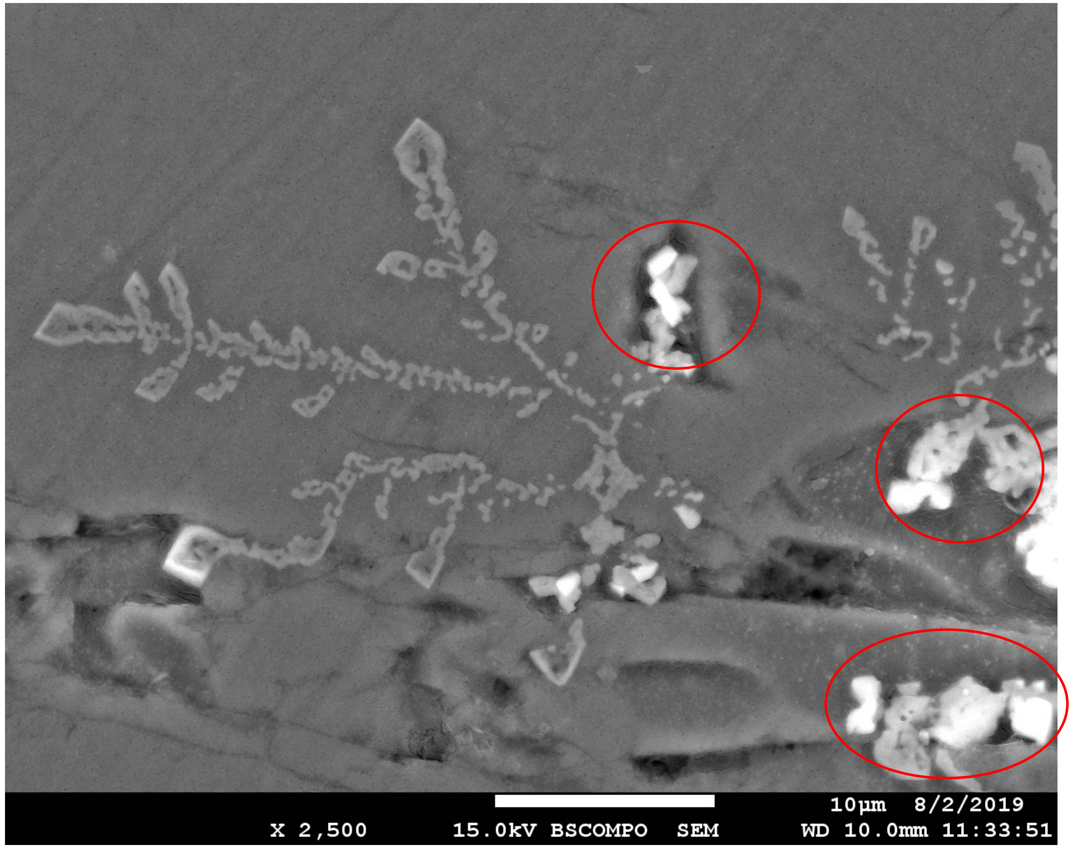
Sodium phosphate (Na_4PO_7) crystals

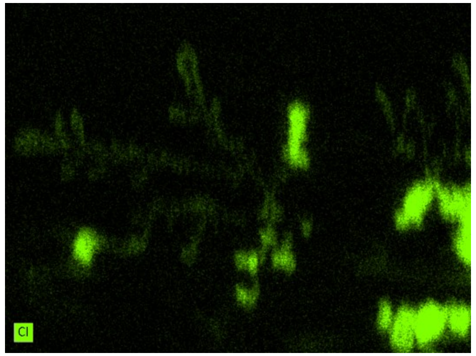


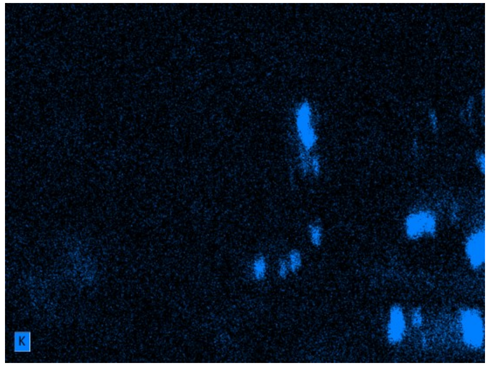


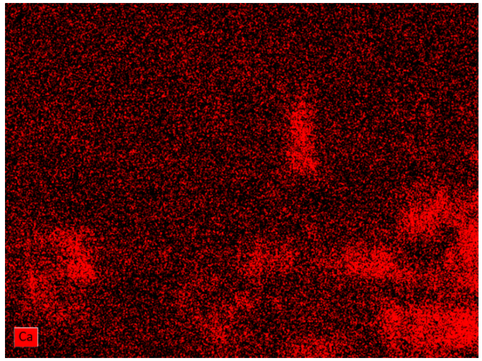
EDS – NBSP6.0, Site 1

Potassium, chlorine and calcium contamination



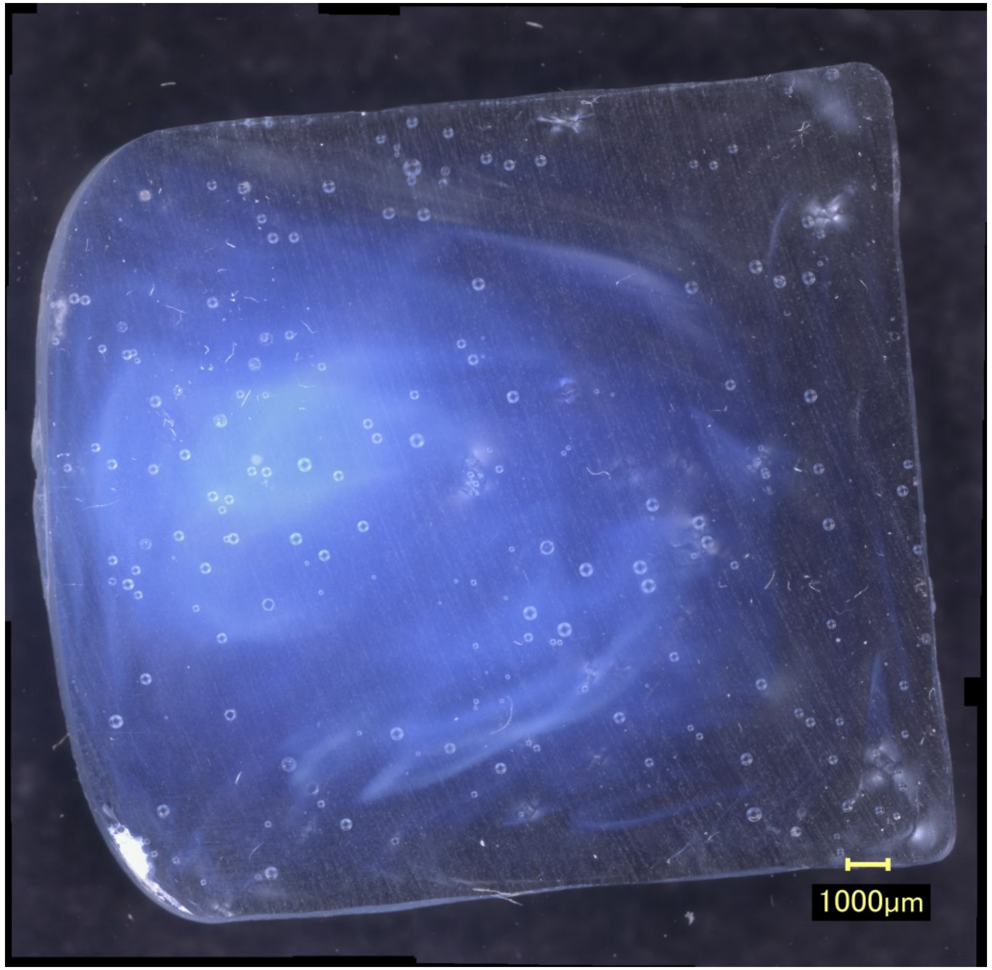


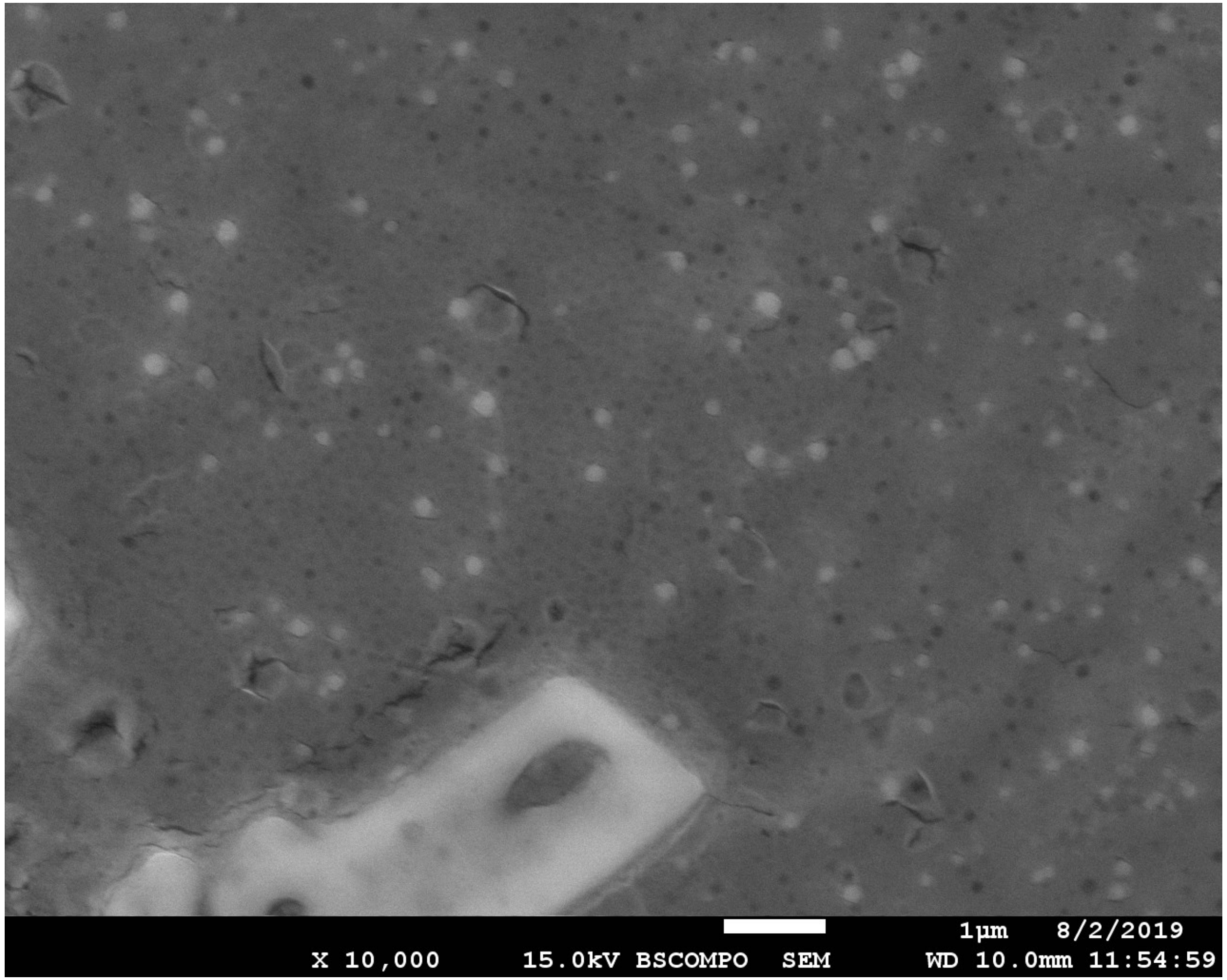




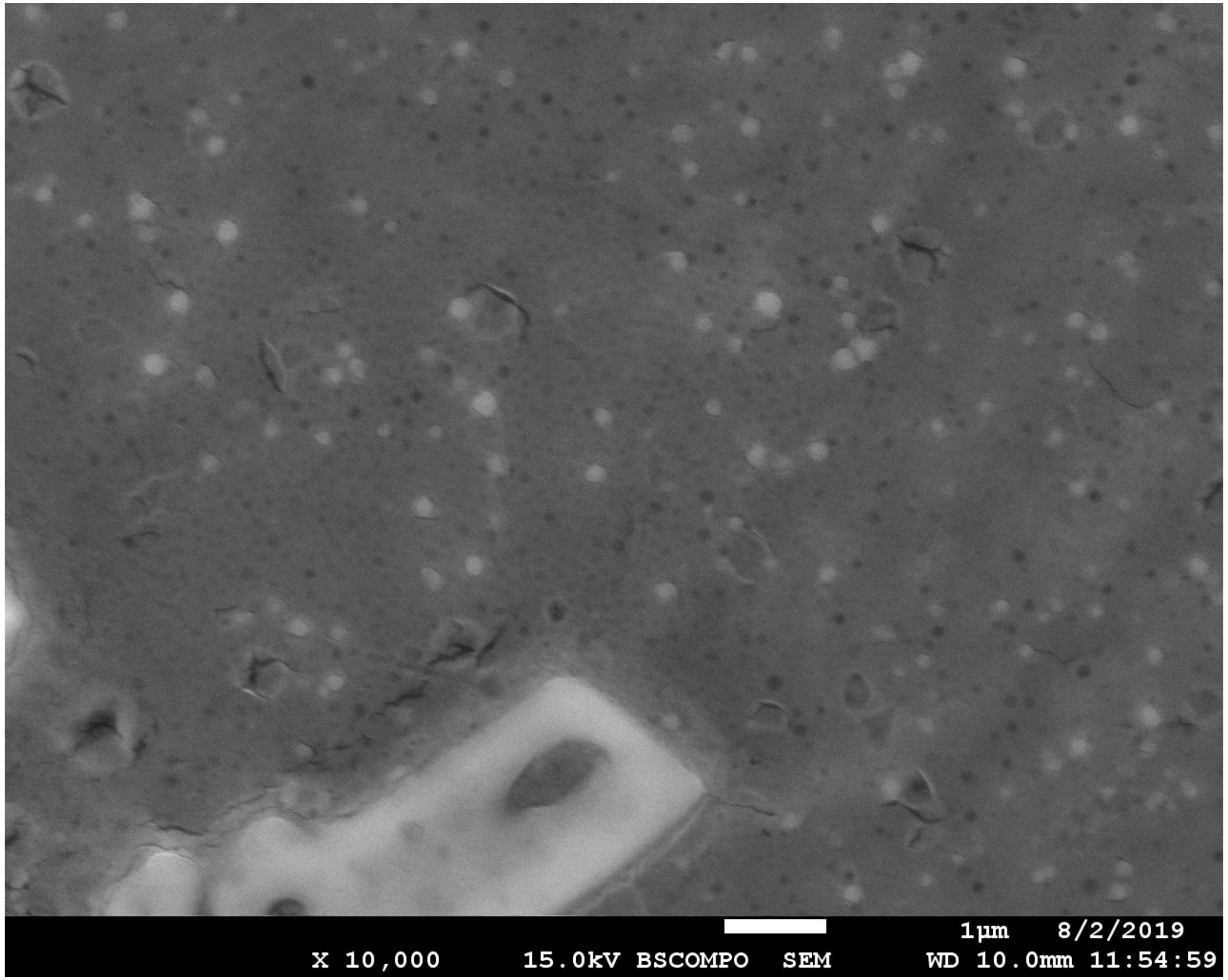
The contaminants may have come from the batching process or when the raw powder was milled with an agate mill. The lab where this glass was made uses calcium carbonate, potassium chloride, potassium carbonate, potassium nitrate and sodium chloride.

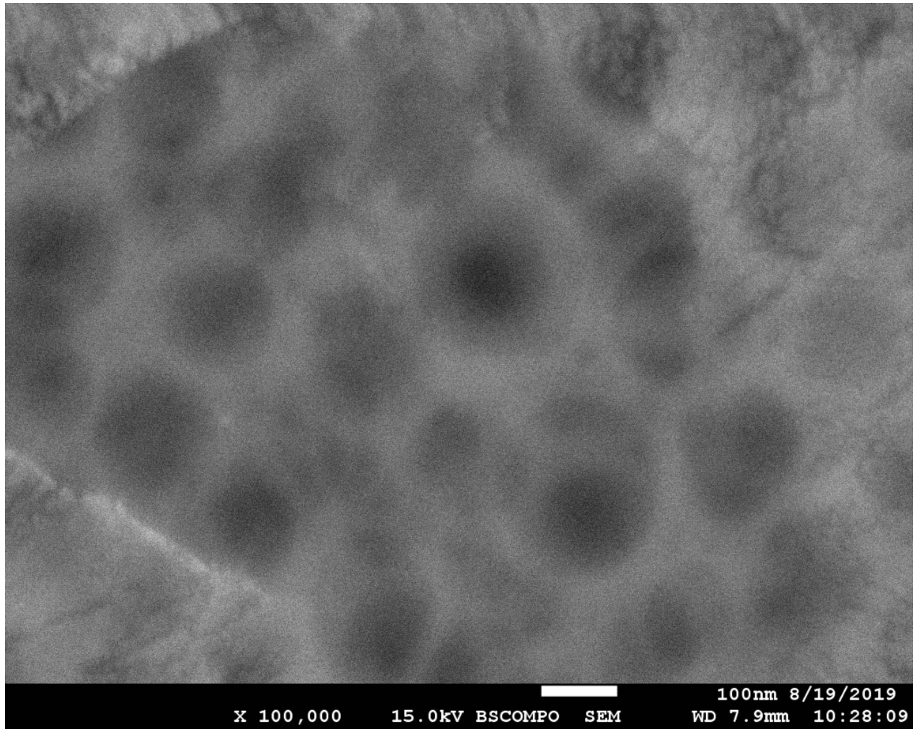
SEM – NBSP6.0, Site 2





SEM – NBSP6.0, Site 2 and 3





Phase separation

DTA – Glass transition temperature (T_g)

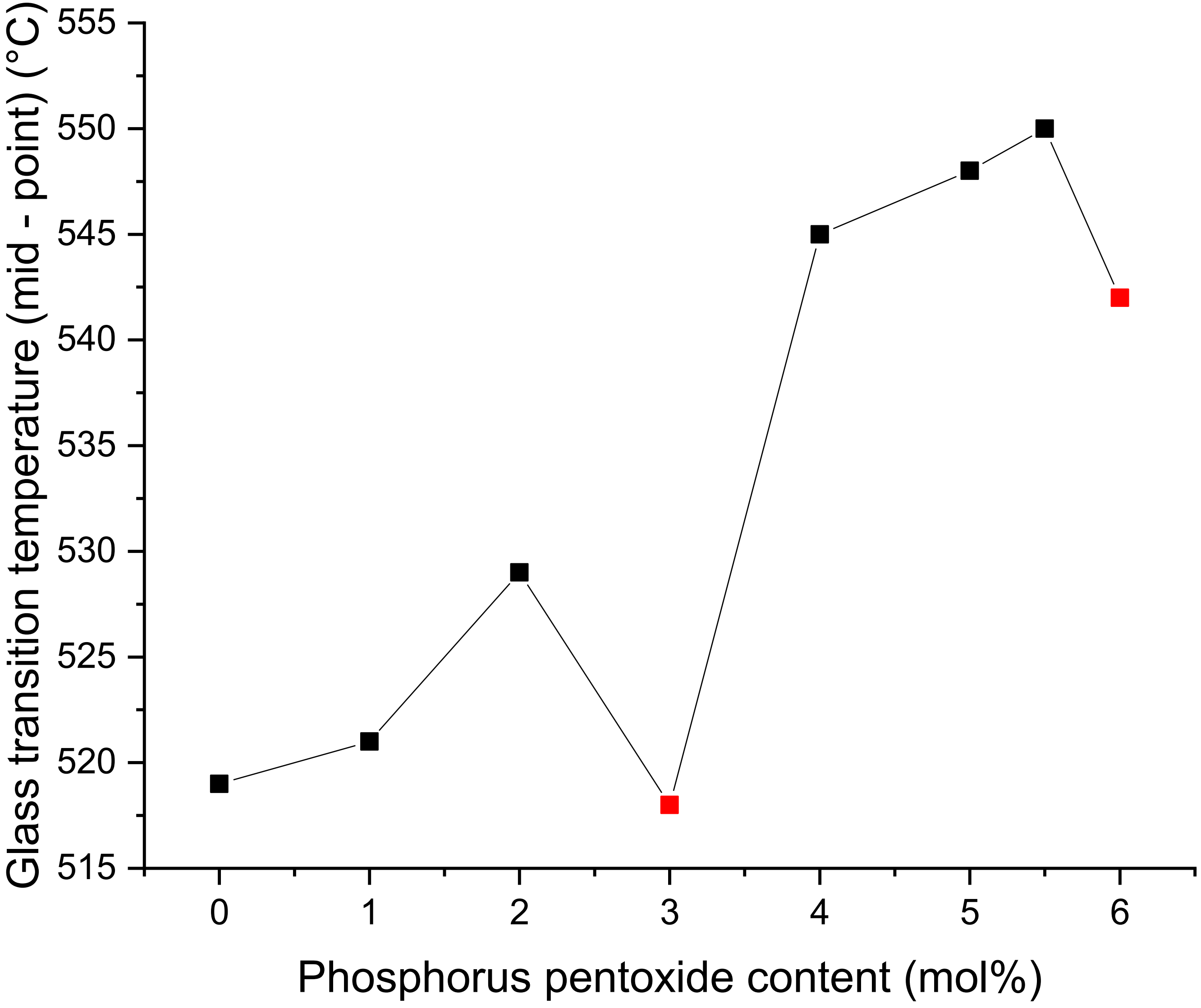


Figure 11: A graph showing how T_g is affected when the P_2O_5 content is changed.

Average mid-point T_g values were plotted

Sample ID	Average T_g ± 1.0 (°C)
NBSP0.0	519
NBSP1.0	521
NBSP2.0	529
NBSP3.0*	518
NBSP4.0	545
NBSP5.0	548
NBSP5.5	550
NBSP6.0^	542

Table 2 – T_g temperatures of NBSP samples collected from DTA

*The sample had DTA conducted more than once on a sample from the same batch and from a different batch.

^ The sample had DTA conducted more than once on a sample from the same batch

DTA – Glass transition temperature (T_g)

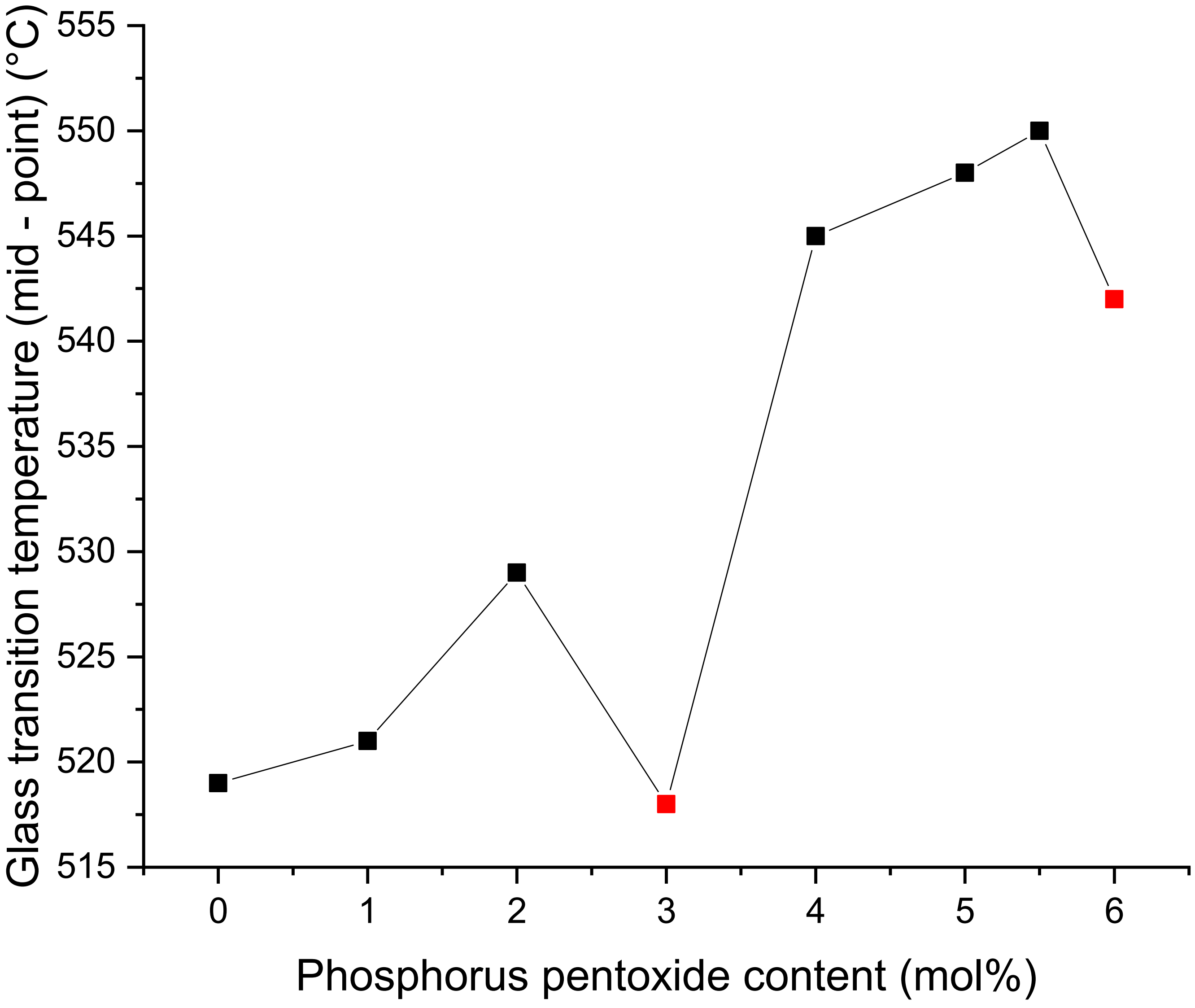


Figure 11: A graph showing how T_g is affected when the P_2O_5 content is changed.

Why is their a reduction in T_g at 3.0 mol% and 6.0 mol% P_2O_5?

- It suggests that the silicate network is becoming depolymerised, meaning there is an increase in the non-bridging oxygens (NBO's).
- P_2O_5 may be promoting the formation of P-O-B species leading to a less connected network and, therefore, a decrease in T_g [5].
- The P-O-B species may be forming because there is not enough Na^+ ions to charge compensate the less polymerised phosphate units [5].
- ^{31}P-NMR and ^{11}B-NMR would need to be used to investigate the structure and species of the glasses.

Conclusions

NBSP1.0, 2.0 and 3.0 were measured to be X-ray amorphous, with crystallinity beginning to occur in NBSP4.0.

Macro scale phase separation is visible in the samples as **opalescence**, as seen in samples NBSP5.0, 5.5 and 6.0.

Increasing the P_2O_5 content has lead to the **phase separation** of the glasses and the following crystalline phases to be present: cristobalite and sodium phosphate ($Na_3P_2O_5$ and $Na_4P_2O_7$).

NBSP5.0, 5.5 and 6.0 may have the same mechanism by which phase separation occurs or not, it is unclear without further analysis.

The ratio between $Na_3P_2O_5$ and $Na_4P_2O_7$ changes in favour of the $Na_4P_2O_7$ as the P_2O_5 content increases, as shown by XRD.

T_g of the glass samples can be effected either way: it can increase or decrease.

- Increase = depolymerisation of the glass network
- Decrease = repolymerisation of the glass network
- Change in viscosity

Future Work

What will I do to characterise these particular glasses further?

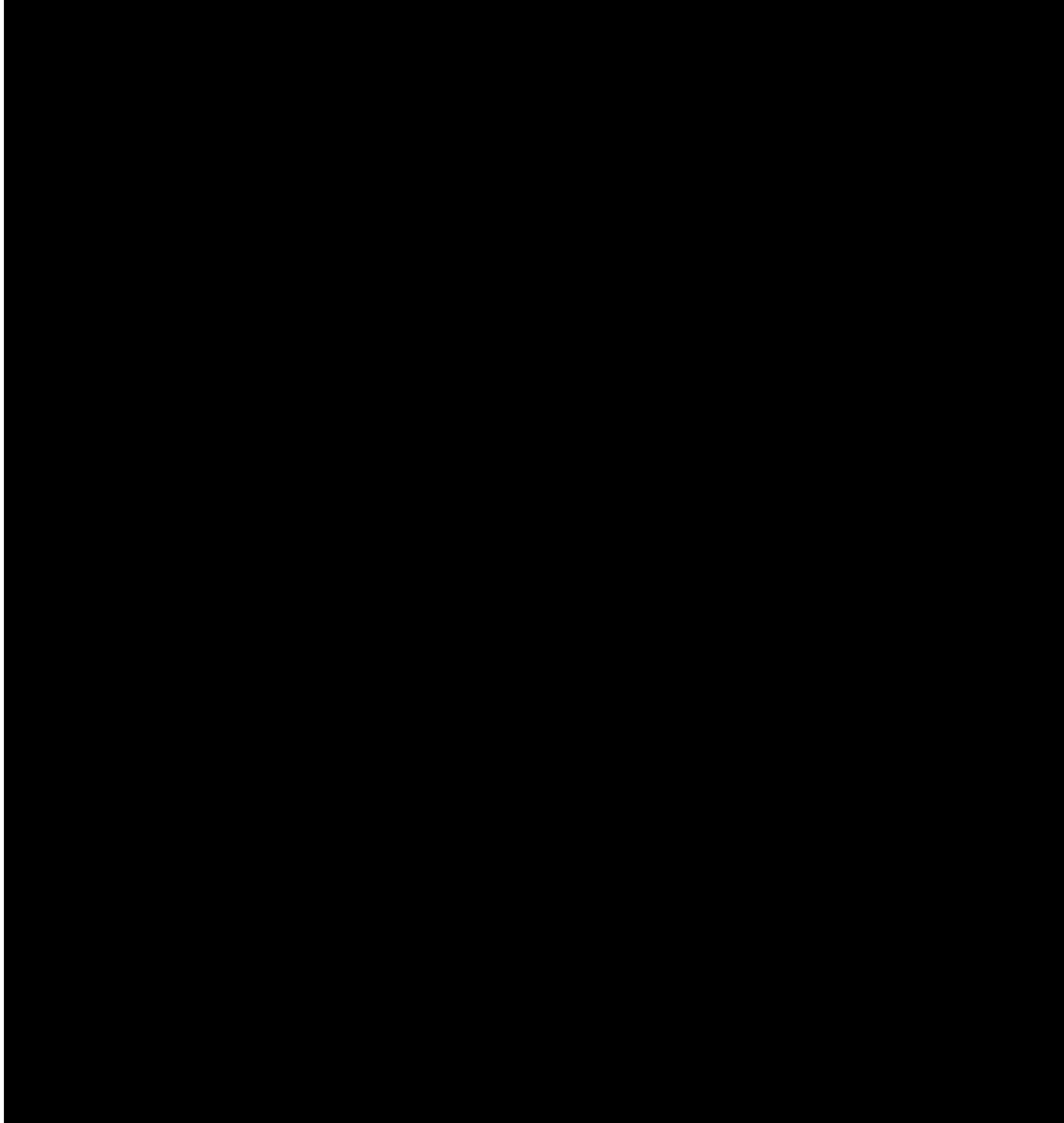
Raman Spectroscopy

NMR spectroscopy

X-Ray Fluorescence

Viscosity

PCT – Method B



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