Materials Based Issues Within Vitrification Furnaces

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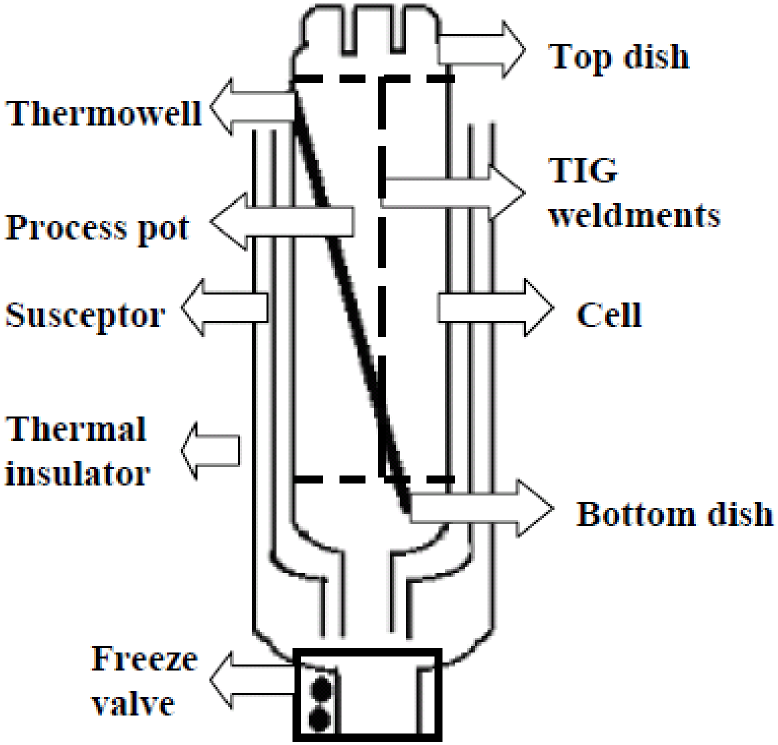
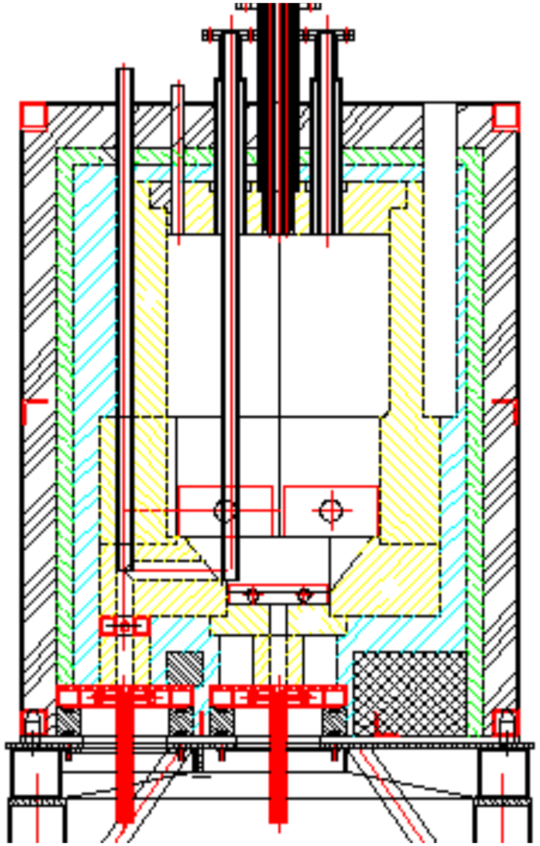
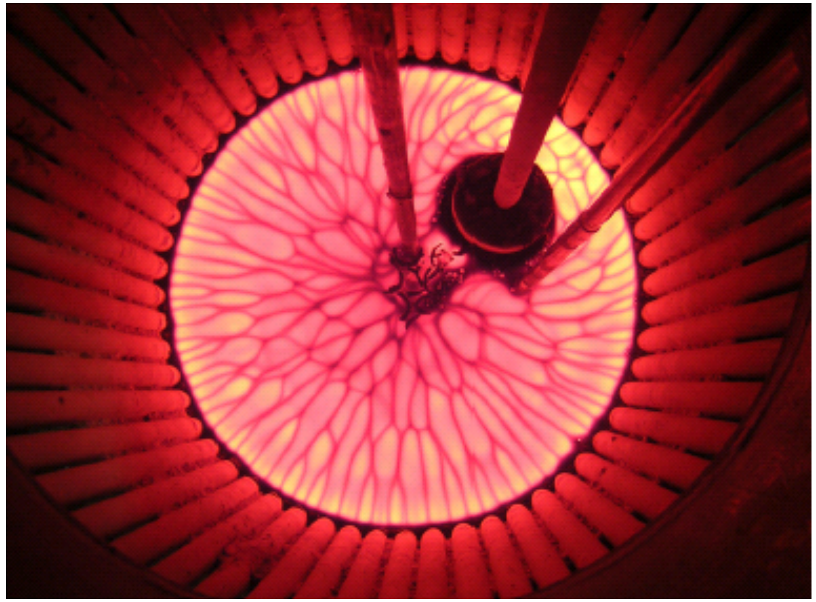
Achievements: 3. Indigenous development of vitrification technology







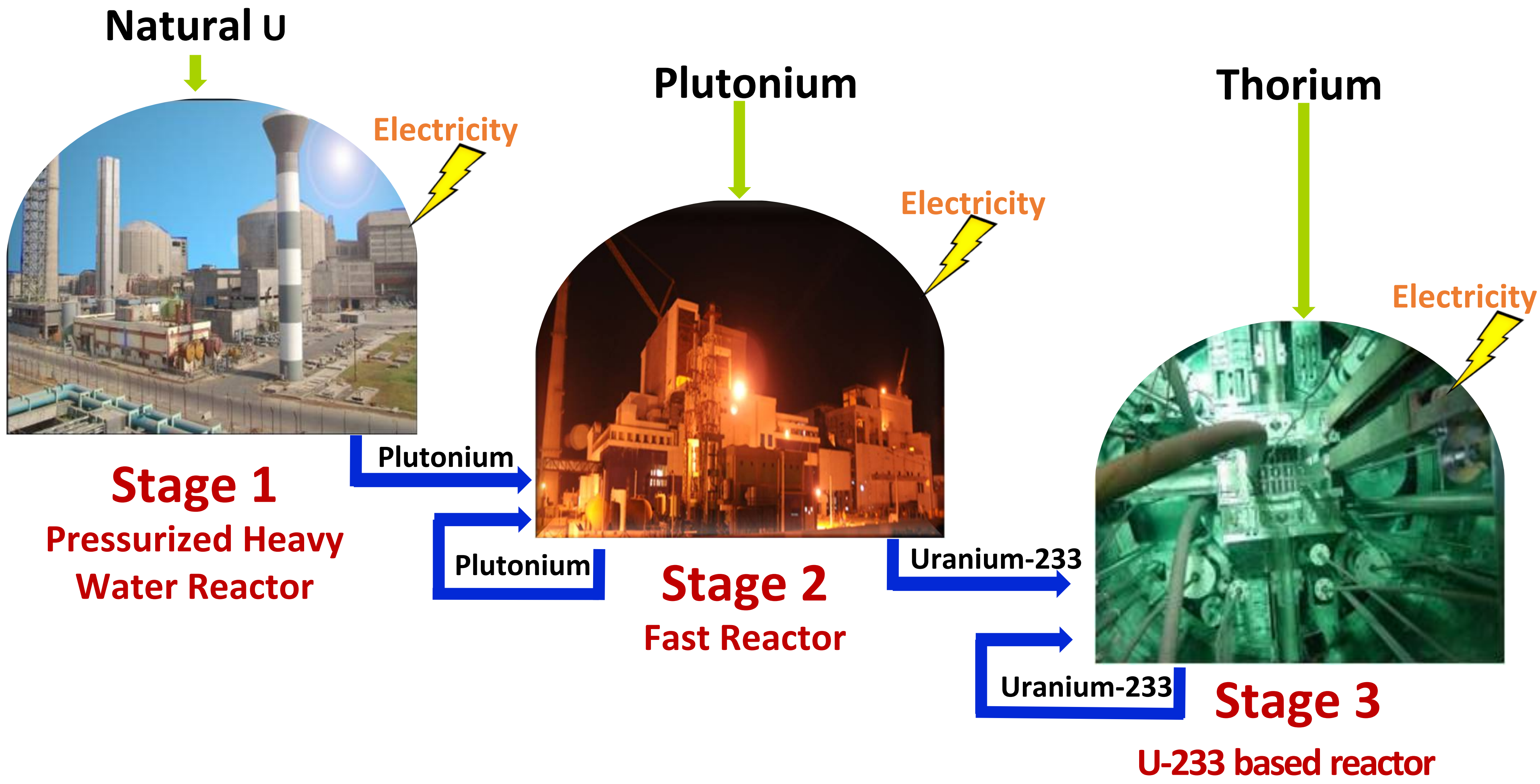
Metallic melter pot	Ceramic melter pot	Cold crucible
Proven technology	Proven technology	Demonstration stage
Induction heating	Joule heating	Induction heating
1000°C max.	1050°C max.	1500°C max.
Borosilicate glass	Borosilicate glass	Aluminosilicate glass

The Issues

Immobilization of Nuclear Wastes

Their interactions with Vitrification furnaces

Three Stages of Indian Nuclear Power Program

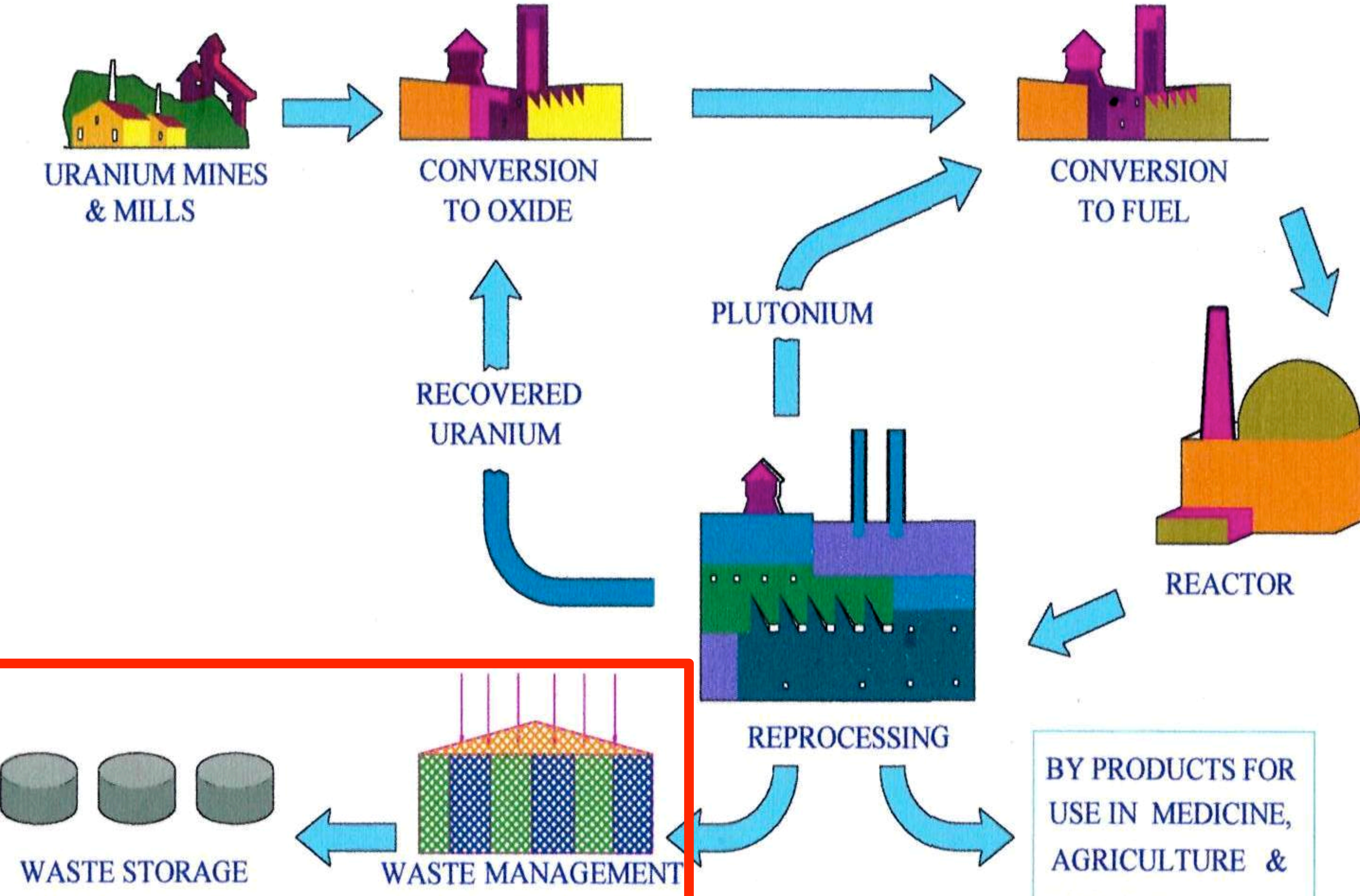


Operational: 22;

Total: 6780 MW;

Target: 20480 MW

Closed nuclear fuel cycle



Inert Host Matrix = Wasteform

Sodium borosilicate glass is not an universal host matrix for nuclear wastes!

We also need

ALTERNATIVE WASTEFORMS!

(Non Conventional Sodium Borosilicate glass matrix)

Wasteform Selection Criteria

Homogeneous Microstructure

Solubility limit, waste loading, uncontrolled crystallization

Chemical durability

Leaching

Available Technology

Processing temperature

Nuclear waste vitrification - The Background

HLW: conc. Acidic soln. containing 30-40 elements

+ NaOH (to reduce the corrosiveness of HLW)

Initial Proposal: Synthesis Nepheline syenite glass

Challenges: high temperature (~1400^{o}C) operation

Solution: replace Al_2O_3 by B_2O_3

Processing temp. reduced from ~1400^{o}C to ~950^{o}C

ALTERNATIVE WASTEFORMS

Example 1: Sulphate containing waste

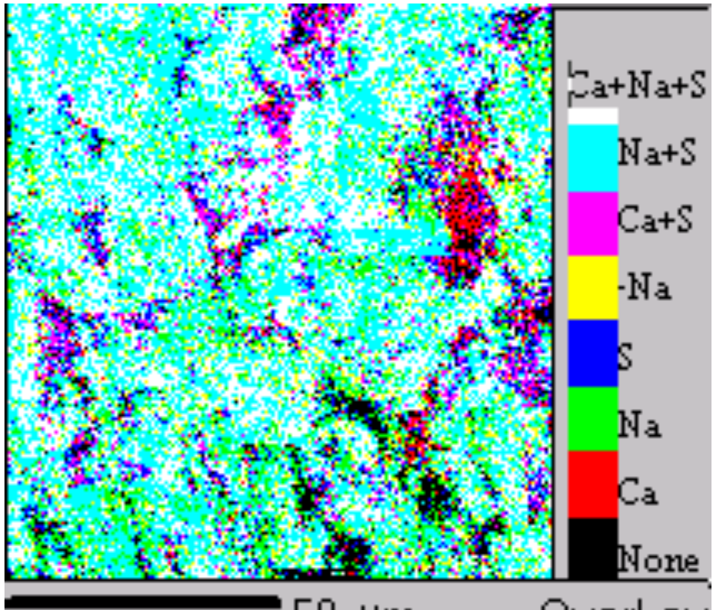
Usage:

Legacy waste Immobilization

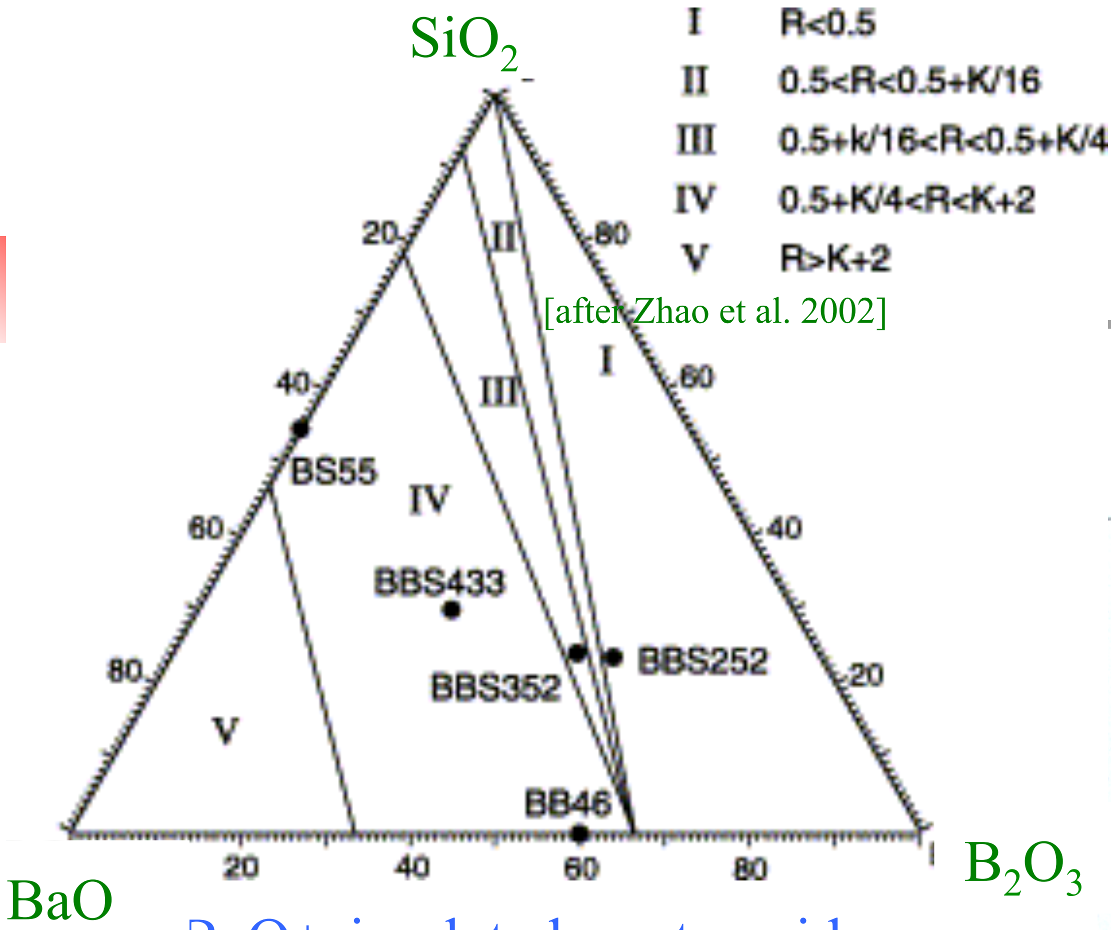
Challenge:

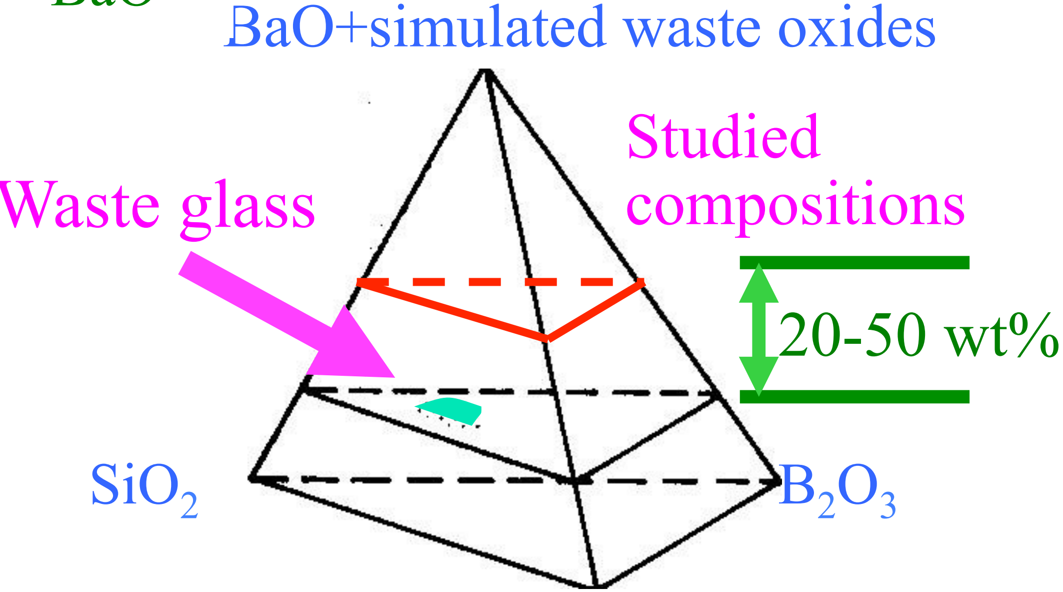
Sulphate – Silicate immiscibility

Partitioning of Cs and Sr in water soluble Yellow phase.



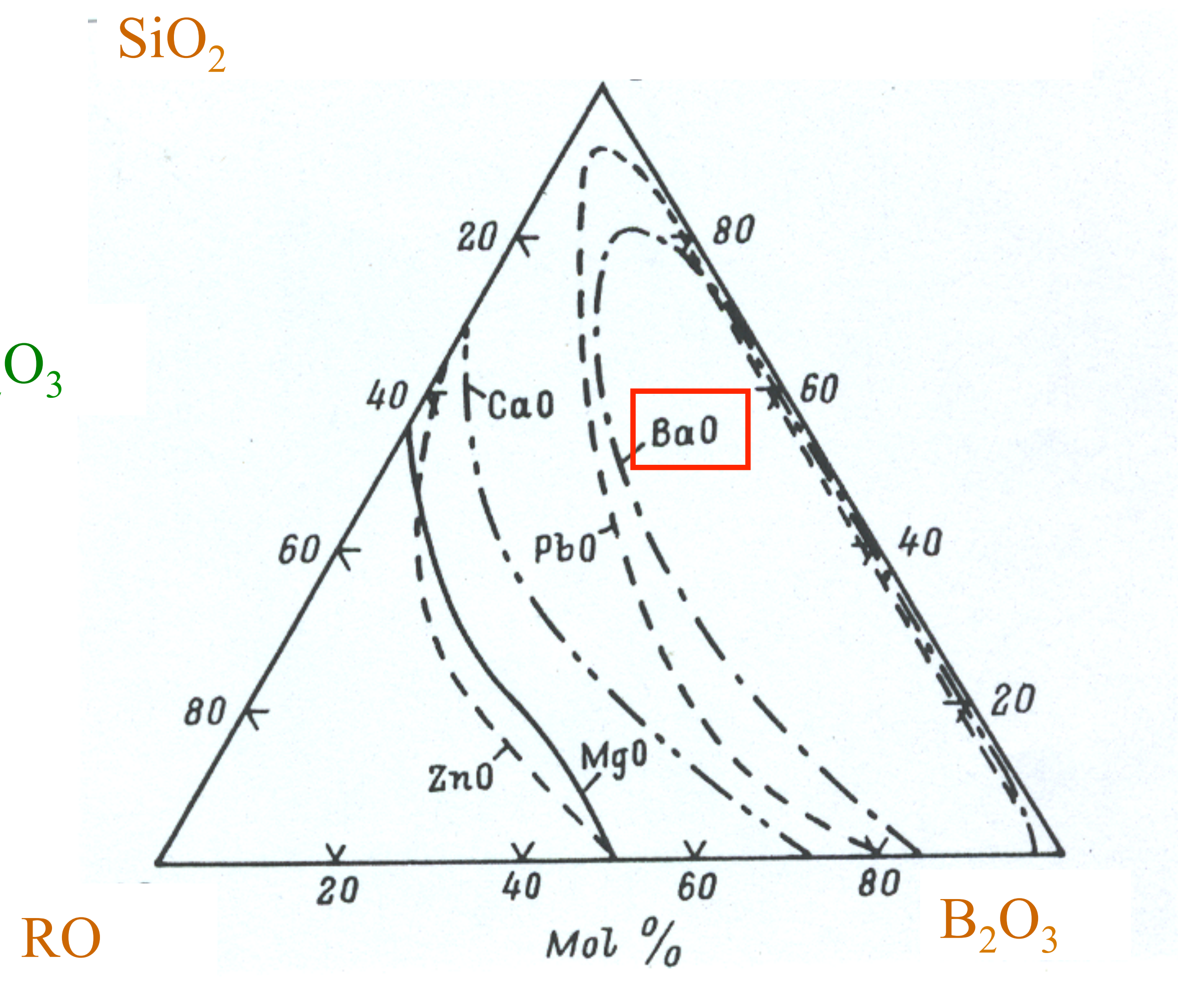
Barium Borosilicate matrix



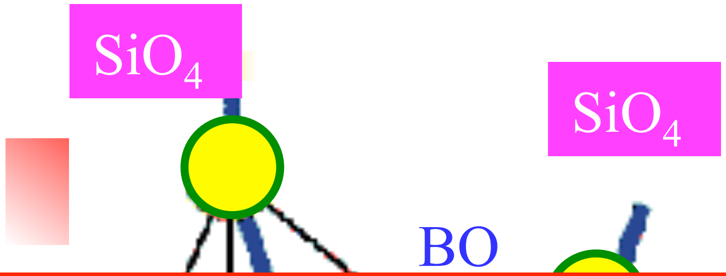


Clues

- barite ($BaSO_4$) is one of the leach resistant phase
- barite is thermally more stable than many of the others and have been reported from granulite facies rocks
- Ba and S have been reported from natural glass



Why sulfate is not retained in borosilicate matrix?



Bond valence theory

Bond valence: measure of chemical bond strength

= valence/coordination number.

SO_4 bond valence = 6/4 = 1.5 valance unit

Valance sum rule:

Observations:

(i) Ba^{2+} can polymerize sulfate network with silicate network most effectively,

(ii) At 1000°C, barite is the most stable phase among the sulfates.

1 + 1.5 > 2; impossible

$CaSO_4$	1400	0.20	-950.74
$SrSO_4$	1600	0.013	-973.69
$BaSO_4$	**1580**	**0.0002**	**-976.29**

Possible options

Mineral/Ceramic	Elements from waste	Radiation durability (dpa)	Typical NR (g/cm^2 day)	Structure
Monazite: $(Ce, La, Nd, Th)PO_4$	Ln, An	>10	10^{-7}	Monoclinic, *P21/n*
Zircon: $ZrSiO_4$	Ln, An, Nb, Ta, Hf	0.3–0.4	4×10^{-7}	Tetragonal *I4/amd*
Zirconolite: $CaZrTi_2O_7$	Ln, An, Nb, Sc, Y, Hf	0.2–0.3	4.5×10^{-6}	Monoclinic
Pyrochlore: AB_2X_7Y (A = Ca, Na, REE, An, Zr, Ti; B = Ti, Zr, Th, U, Nb, Ta, Sn, Al, Fe; X = O, F; Y = O, OH, F)	Na, Y, Ln, An, Ti, Nb, Ta, W, Cl, I	0.3–0.4	1.5×10^{-6}	Cubic, *Fd3m*
Zirconia: ZrO_2	Zr, Ln, An	>10		Several polymorphs; the mineral form is baddeleyite, monoclinic *P2/c*
Garnet: $A^{VIII}_3 B^{VI}_2 [SiO_4]_3$	Cr, Mn, Fe, Co, Ni	0.2		Cubic, *Ia3d*
Hollandite: AB_8O_{16} (A = Na, K, Rb, Cs, Sr, Ba, Pb; B = Co, Ni, Fe, Cr, Si, Ti, Mn)	Na, K, Rb, Cs, Sr, Ba, Ra, Ti, Cr, Mn, Fe, Co, Ni, Mo, Pb, Bi, Ag		10^{-6}	Monoclinic, *I4/m*
Perovskite: ABO_3 $CaTiO_3$	Nb, Fe, Ta, Ln, An, Na, Sr, Y	0.4–1	2.5×10^{-8}	Cubic, *Im3*
Apatite: $Me_{10}(XO_4)_6Y_2$	Na, Sr, Ln, An, S, I, Y, Mn	0.24	2×10^{-7}	
Britholite: $Ca_2Ln_8(SiO_4)_6O_2$		0.3–0.4	2.5×10^{-6}	
Murataite: $(Y,Na)_6(Zn,Fe)_5Ti_{12}O_{29}(O,F)_{10}F_4$	Na, Ca, Al, Ti, Mn, Fe, Ni, Ln, Ce, Nd, An	0.2	10^{-9}	Cubic, $F\bar{4}3m$
NZP: $NaZr_2(PO_4)_3$	Na, K, Rb, Cs, Sr, Ln, An, Fe			
TiC-Al_2O_3 composite	^{14}C		10^{-6}	Cubic, *Fm3m* Rhombohedral, $R\bar{3}c$

ALTERNATIVE WASTEFORMS

Example 2: Sr loaded glass pencils

Usage:

Radioisotope Thermoelectric Generator (RTG)
Bone Cancer Treatment

Challenge:

High heat generation due to radioactive decay of Sr-90.

Anorthite Feldspar ($CaAl_2Si_2O_8$)

~1000 ppm Sr in

$(Ca_{1-x}Zr_{1-x}Nd_{2x}Ti_2O_7)$

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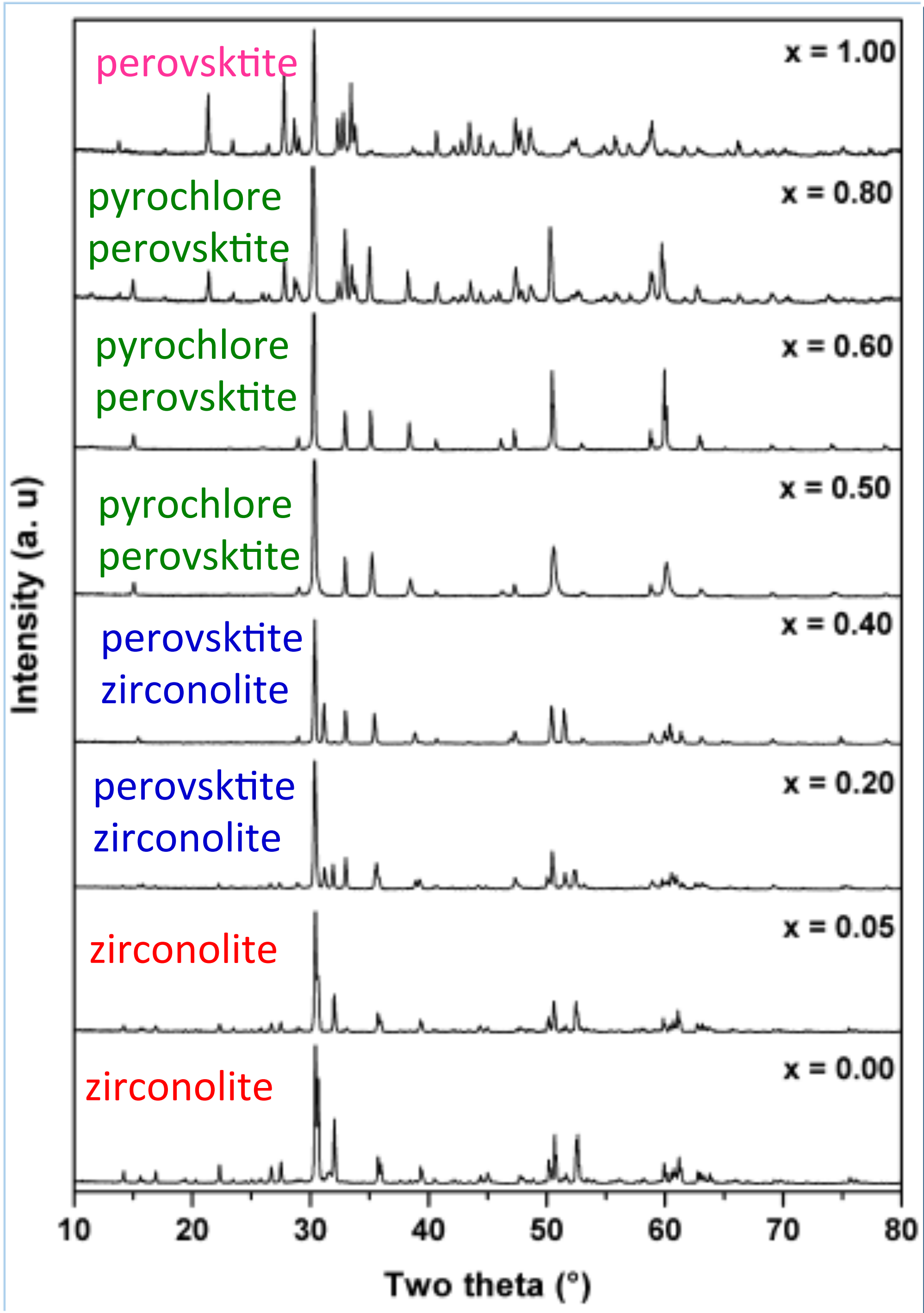
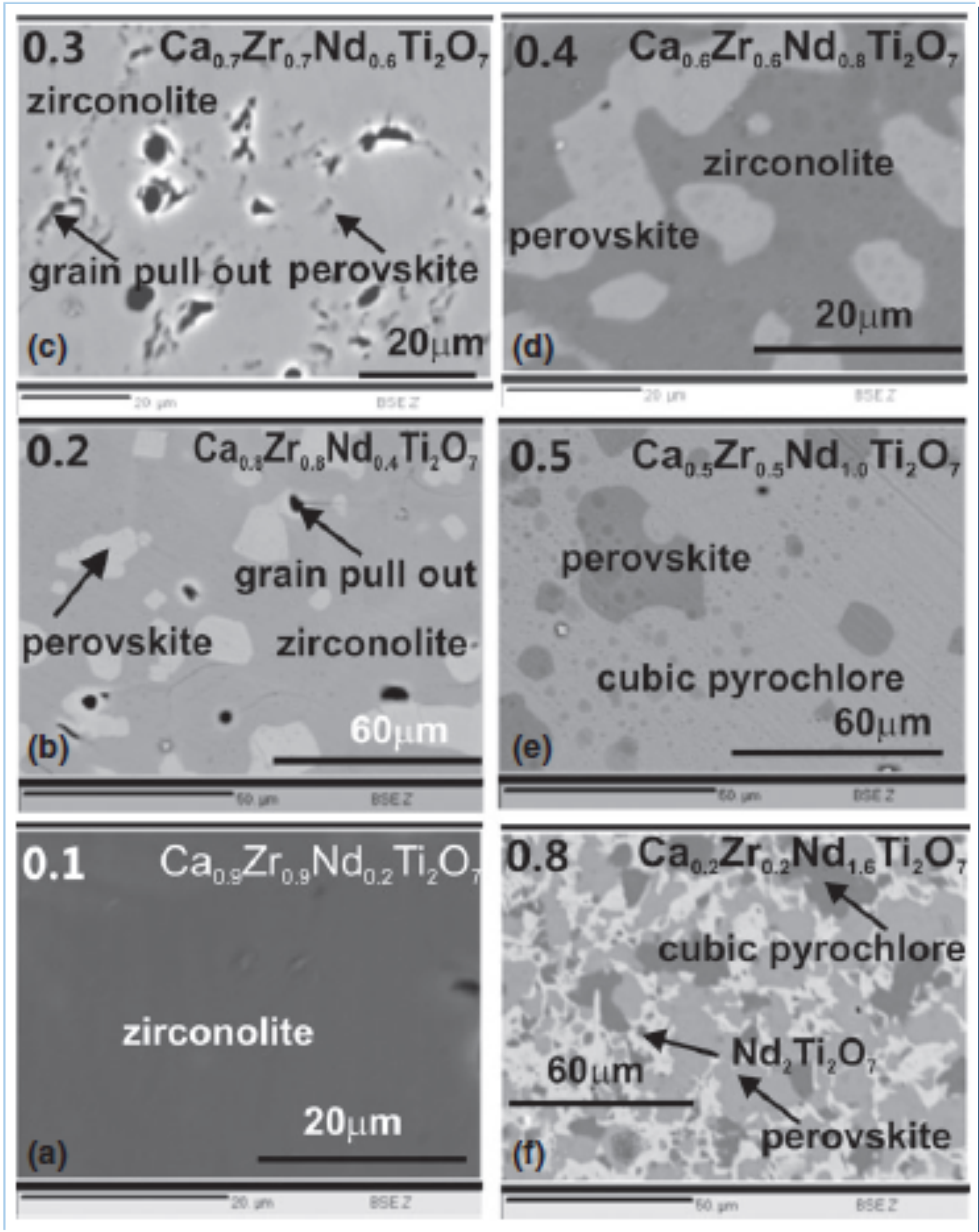
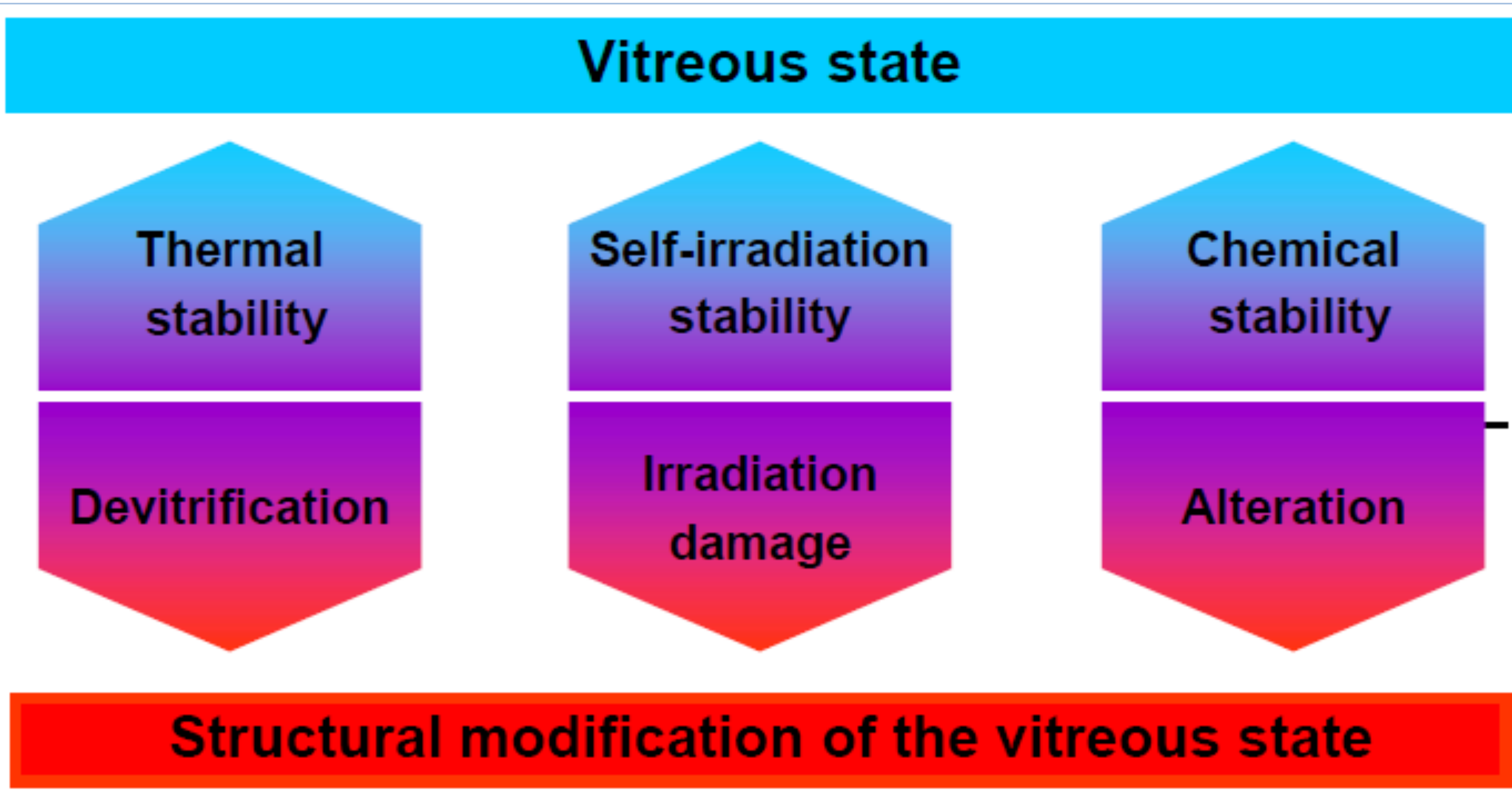
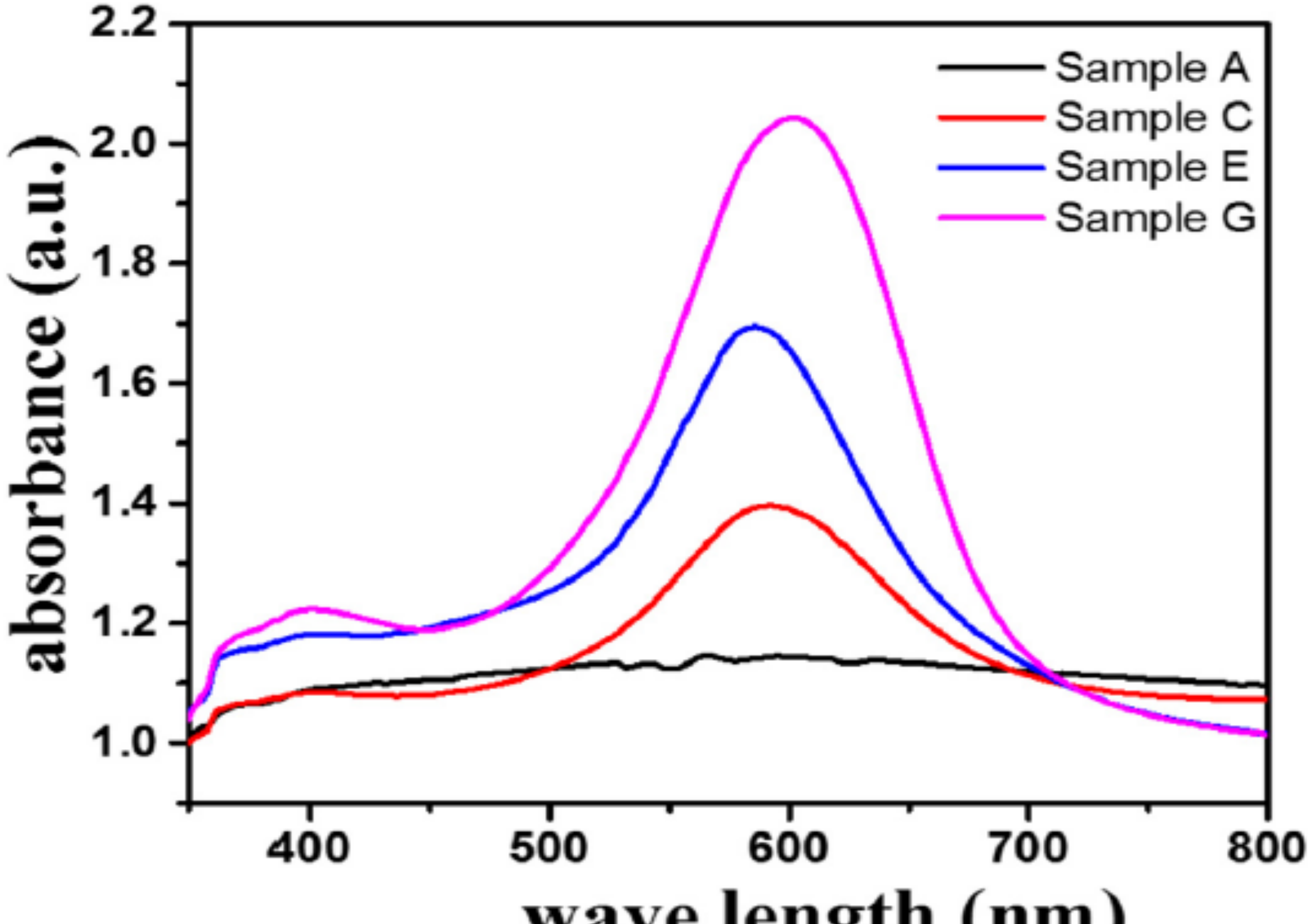


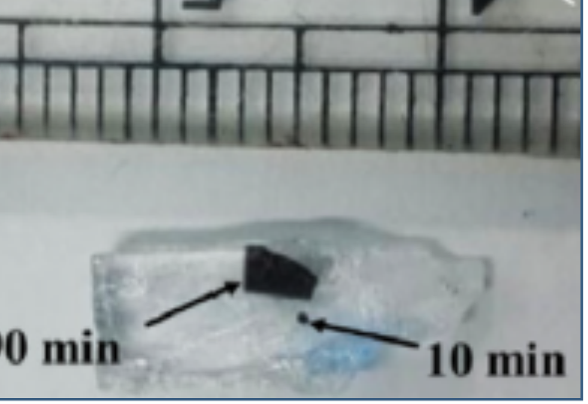


Long term performance assessments



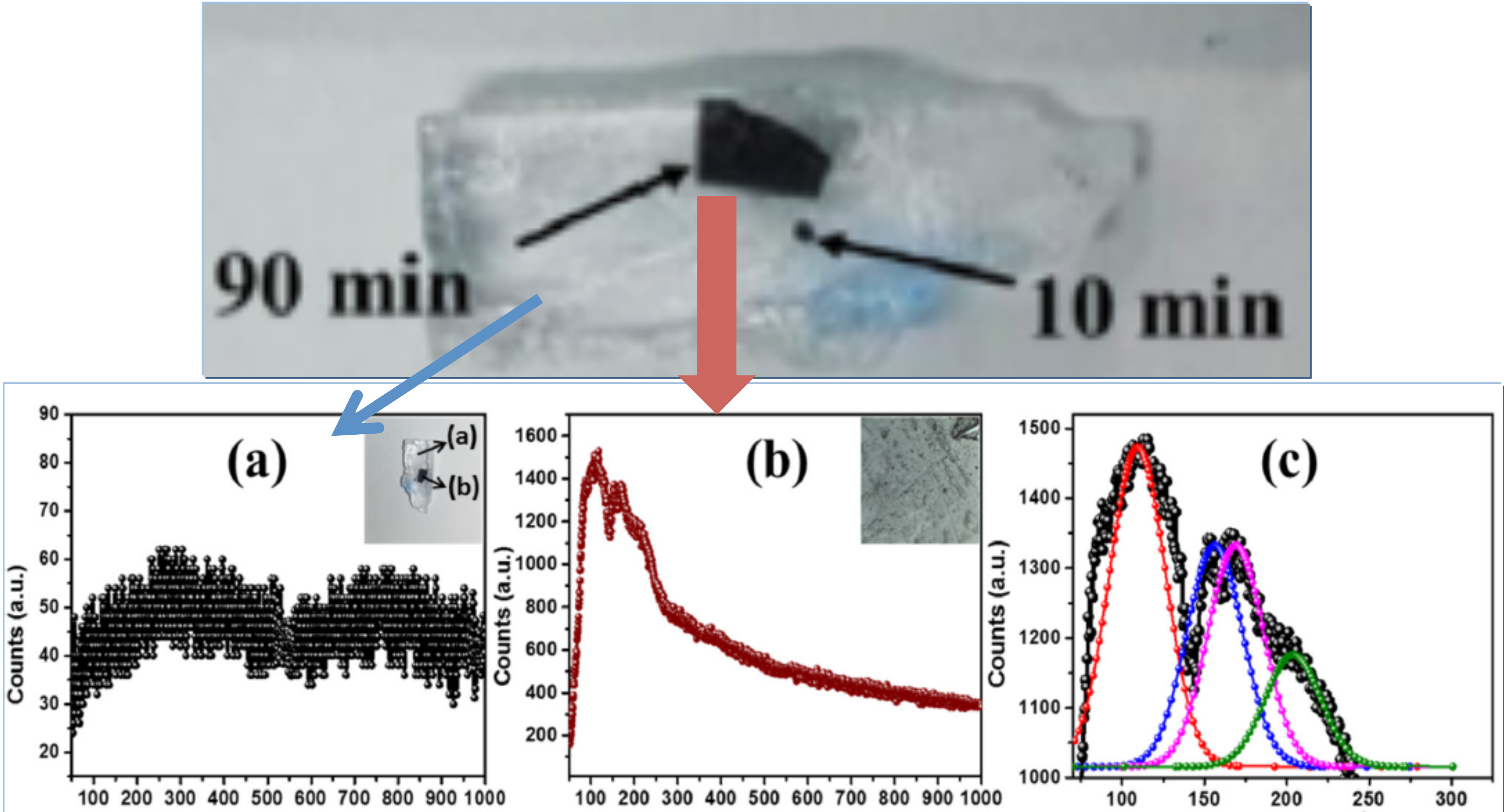
Ion Beam Analysis

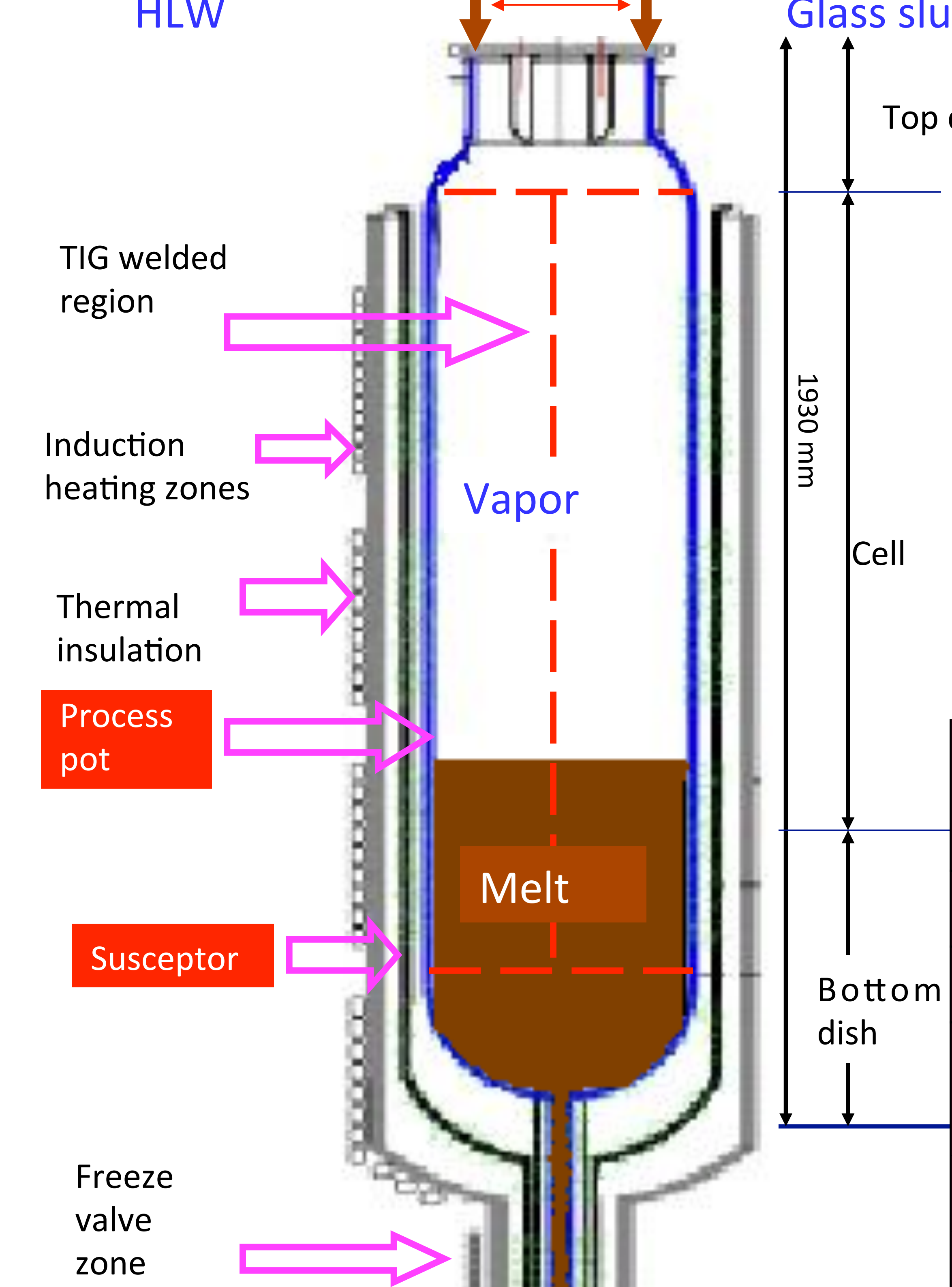

absorbance (a.u.)
wave length (nm)
Sample A
Sample C
Sample E
Sample G
2.2
2.0
1.8
1.6
1.4
1.2
1.0
400
500
600
700
800



irradiation by ~20 μm width proton beam

beam fluence of 6.75×10^{17} protons/cm^2





Metallic melter pot

Operation parameters:

Susceptor (induction heating): ~1050^{0}C

Process pot (radiation heating):~1000^{0}C

Melting pt. SUPERNI 690: ~1345^{0}C

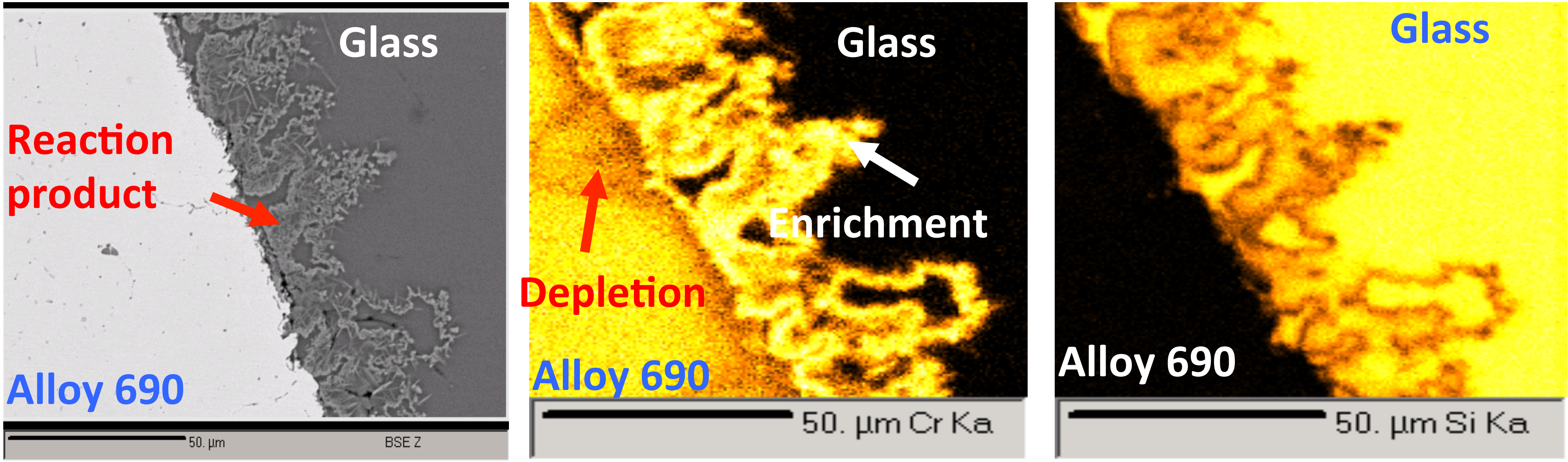
Dead wt.: ~200 kg

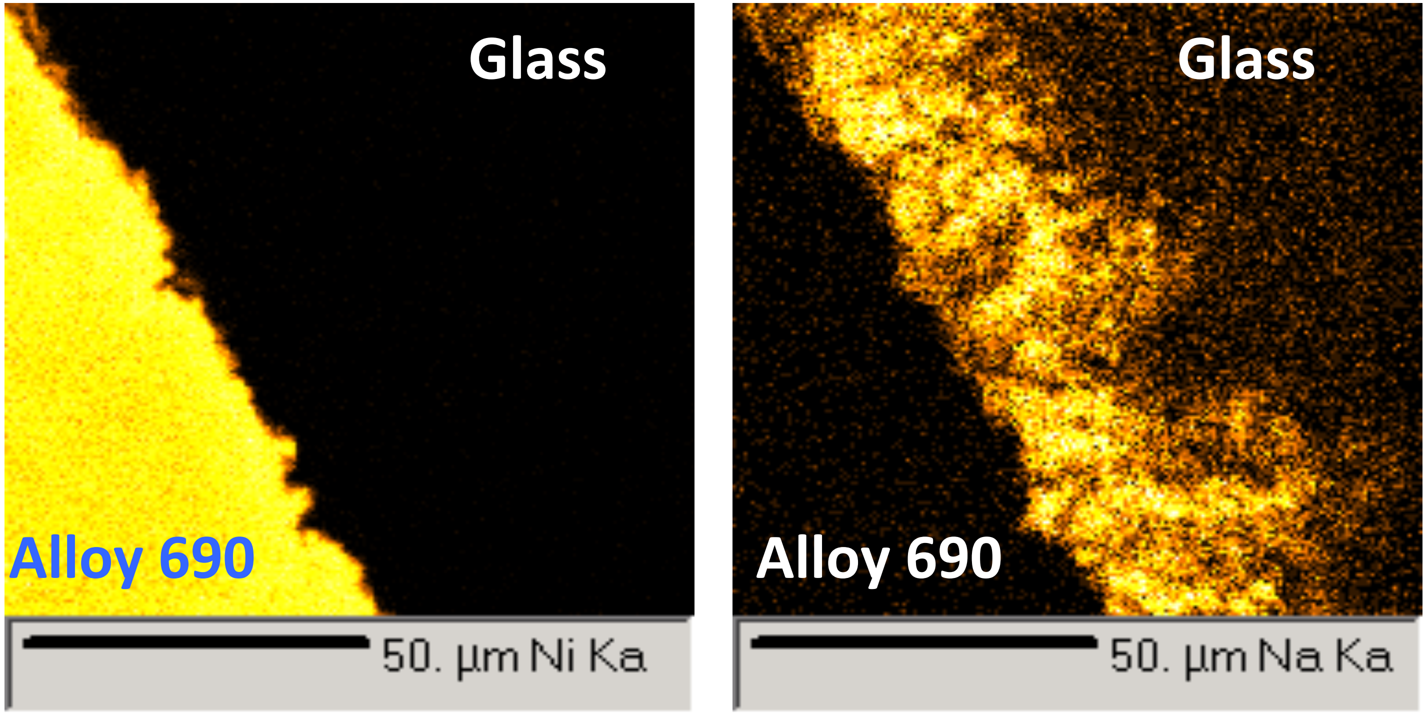
Glass poured in canister: 90 kg

Activity immobilized: 1700 Ci

Stage/process	Pot temperature (^{o}C)
Feeding	100-105
Evaporation	105 – 120
Calcination	300 – 700
Fusion & melt formation	700 - 850
Soaking	900 - 950
Pouring	950 - 1000

Microstructure of the glass/alloy 690 interface





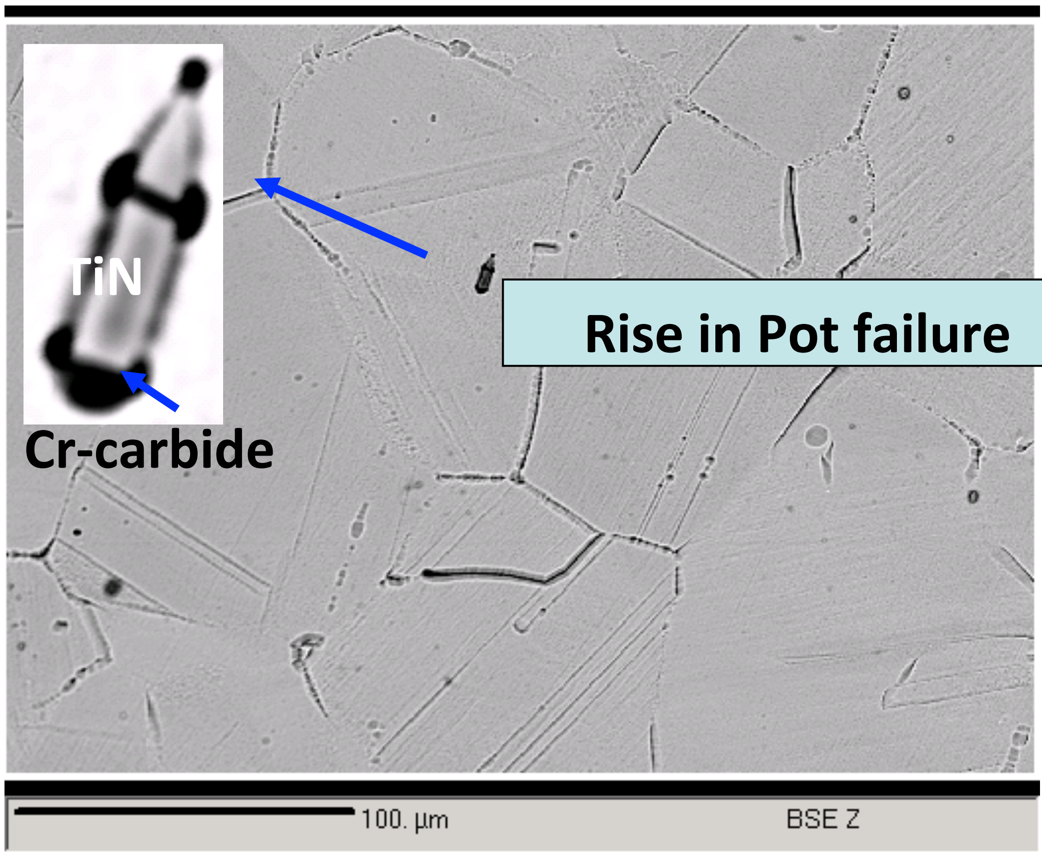
Points to ponder

- Depletion of Cr in alloy
- Depletion of Si in glass
- Enrichment of Yellow phase constituents

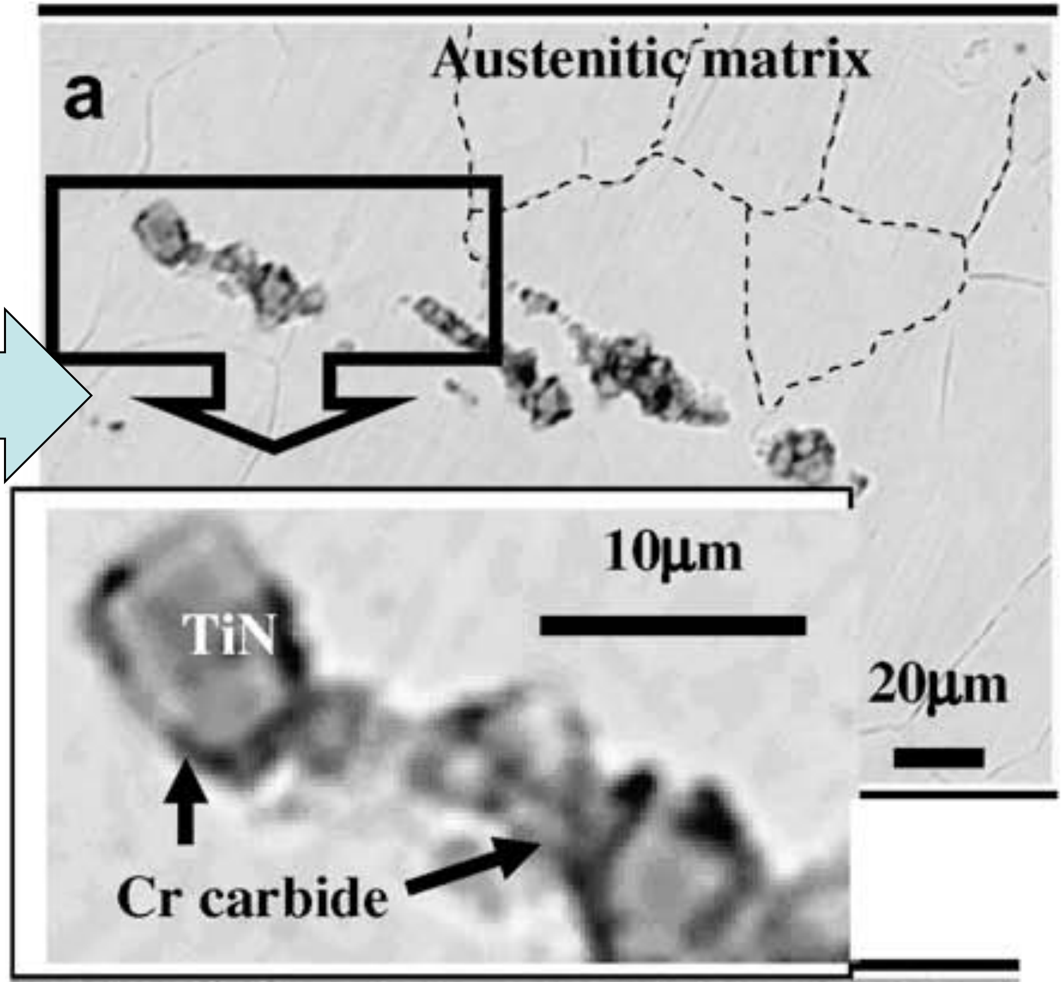
48 hours, 950^{0}C, SUPERNI 690 & BBS

Microstructure – pot failure correlation

Composition	Ni	Cr	Fe	Mn	Al	Si
As received material	60.72	28.79	9.78	0.16	0.12	0.41
172.80 ks	66.74	21.63	10.83	0.00	0.24	0.66
345.60 ks	73.48	15.00	11.02	0.00	0.19	0.33
518.40 ks	75.28	14.11	10.22	0.00	0.05	0.39
691.20 ks	75.51	13.68	10.27	0.06	0.07	0.41



Rise in Pot failure



Feasible solutions

(i) Development of diffusion barrier coatings

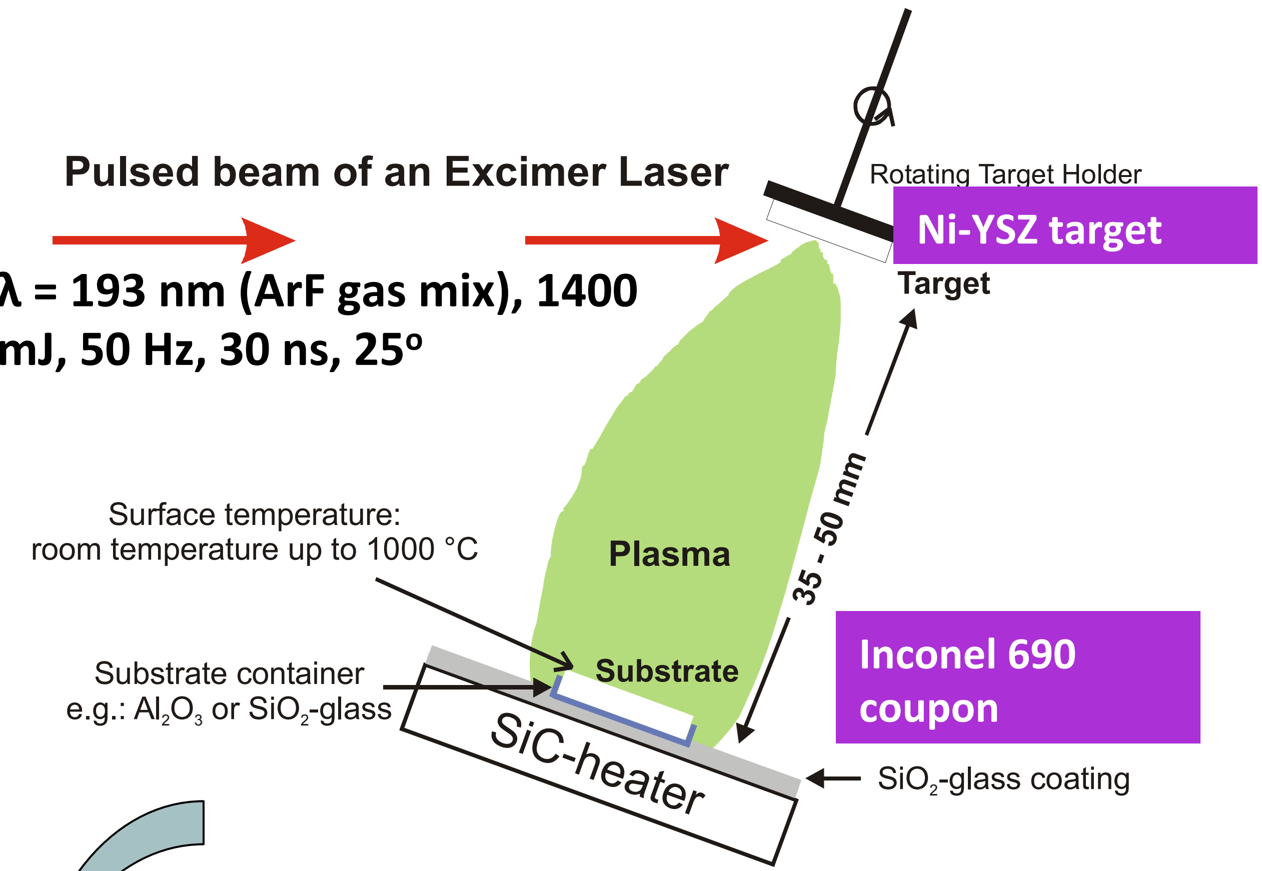
(ii) Development of an alternative alloy with higher corrosion resistance

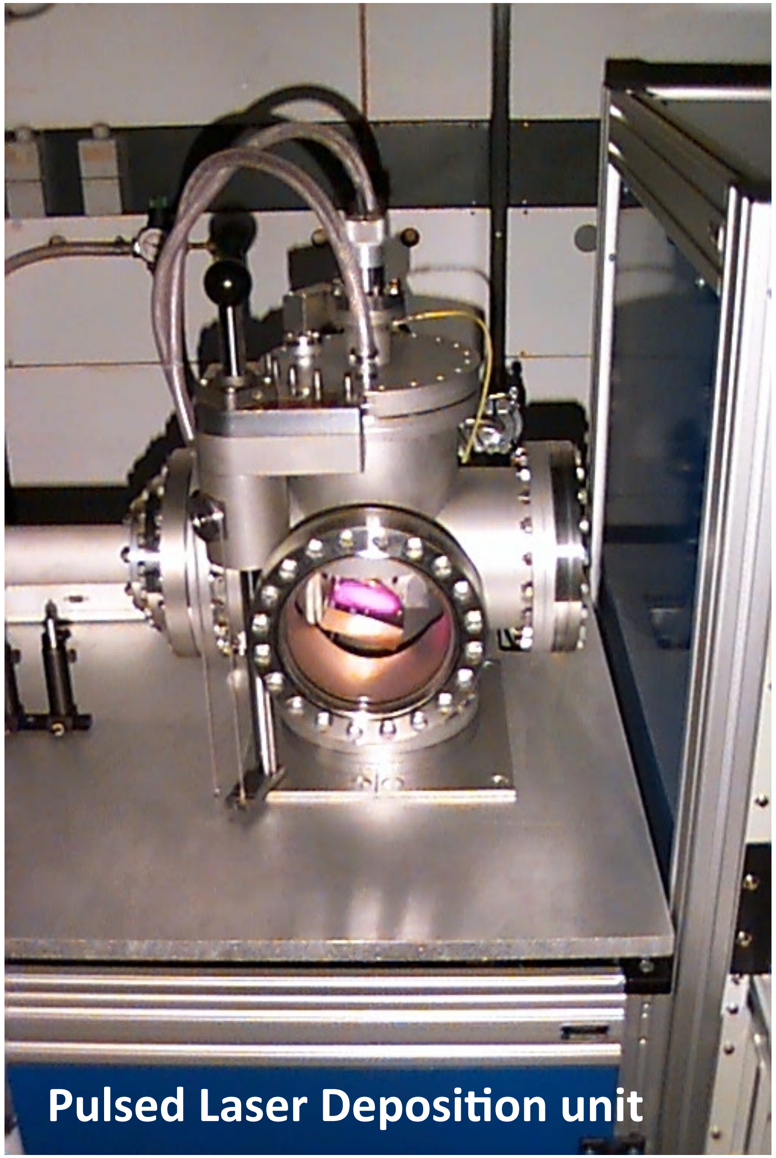
Alloy 693 (Alloy 690 + 2.5wt% Al_2O_3)

(iii) Improve the glass compositions

Diffusion barrier coating on Inconel 690

Schematic illustration of a PLD-system



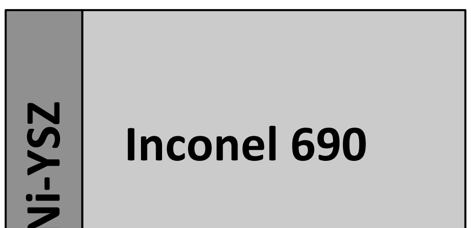


The whole setup is positioned in a UHV-chamber.
The ablation process can operate at a controlled
O_2- or N_2-gas atmosphere

=> stoichiometric transfer from the target to the substrate!

homogeneous thickness ~ 5 mm², roughness < 1 nm

Thin film coating



100-200 nm

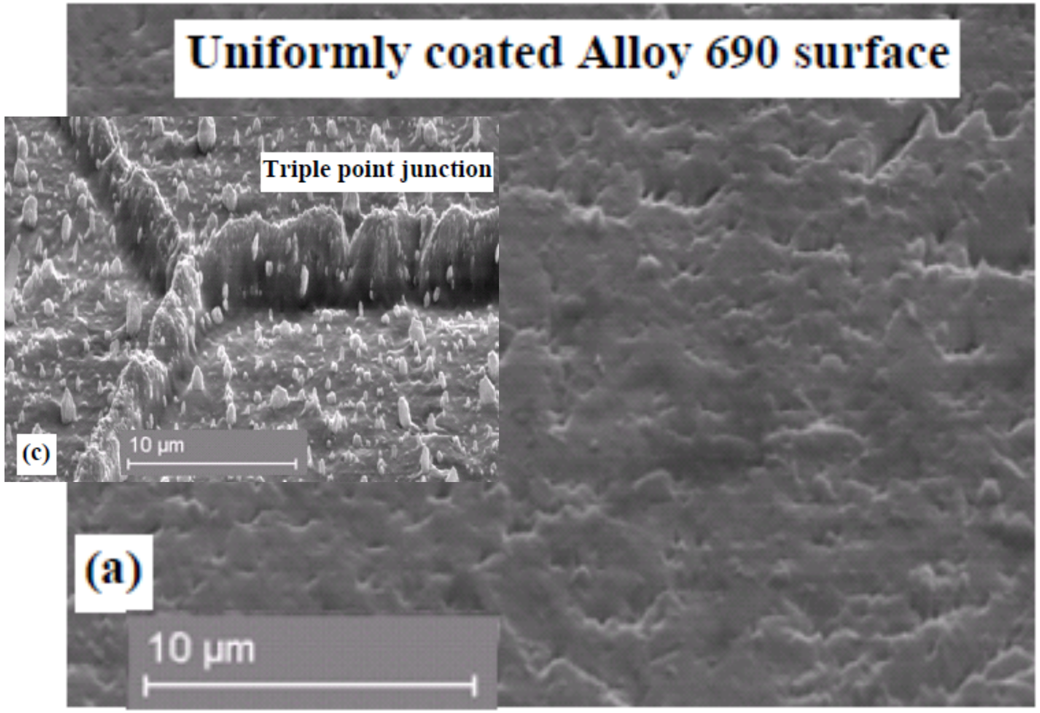
Diffusion annealing

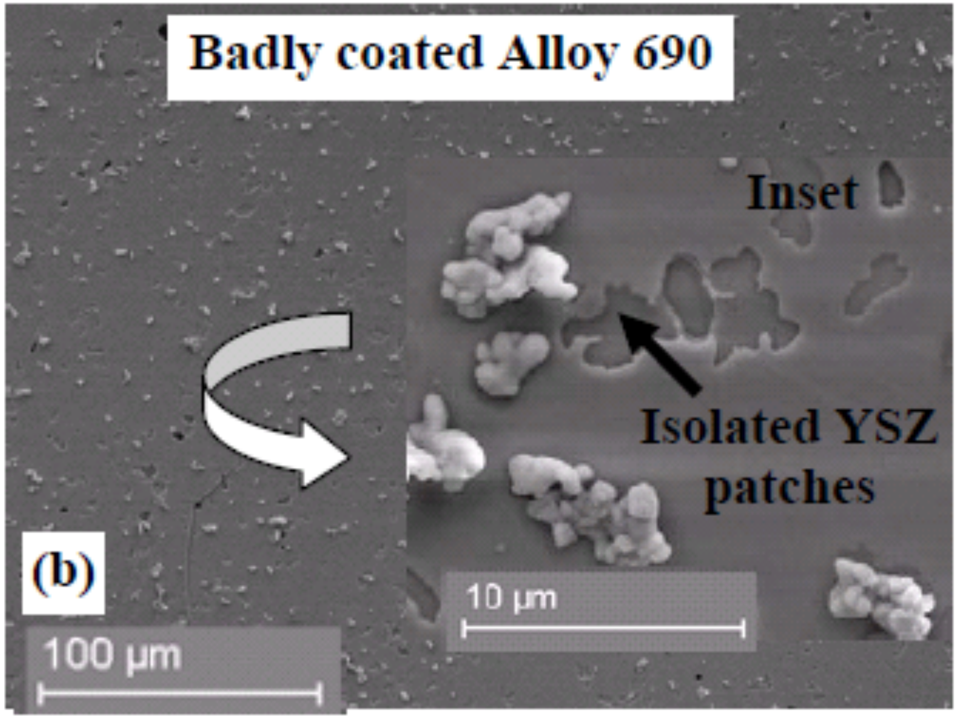
Ni-NiO buffer, 800°C, 30 min; stress relax., good adhesion

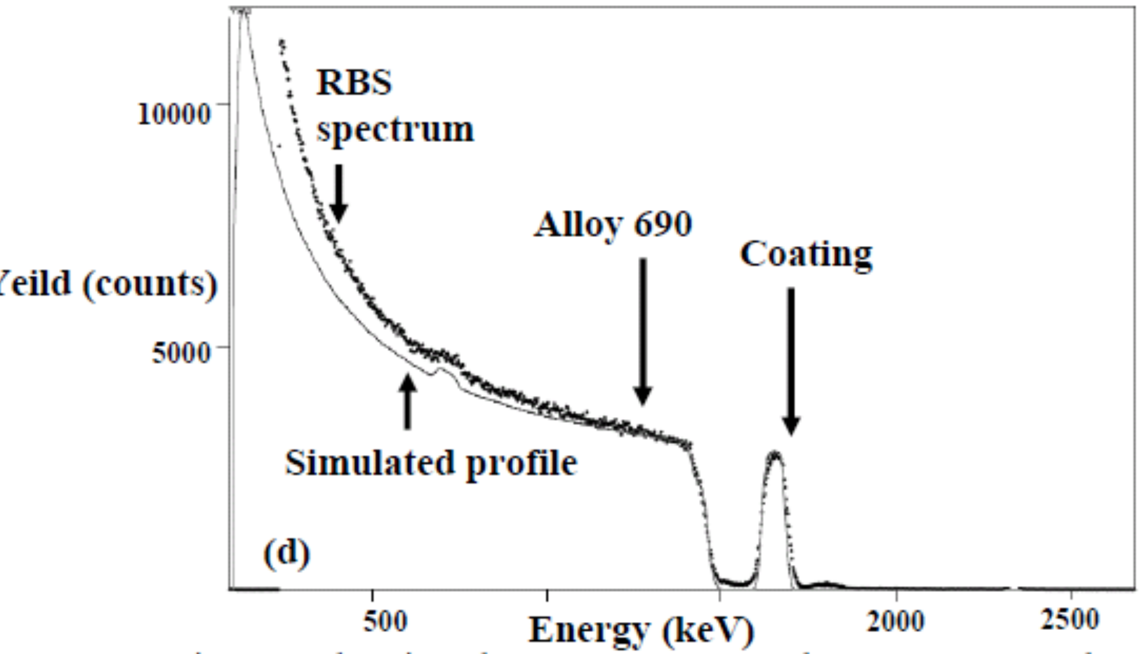
Diffusion profile analysis

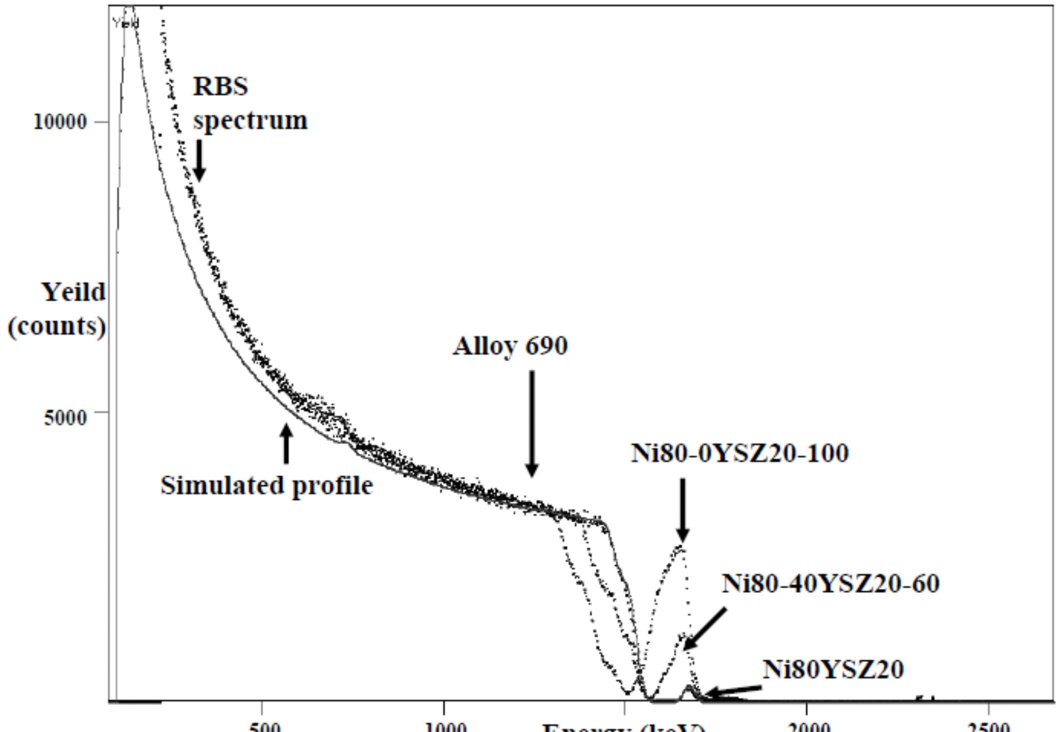
Rutherford Backscattering Spectroscopy: depth<500 nm, 2MeV ^4He, 0.5 mm ϕ, Si

Composite coating: Ni-YSZ

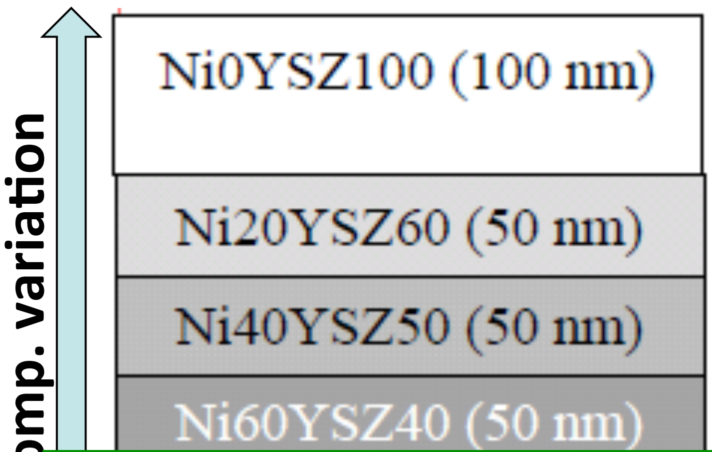


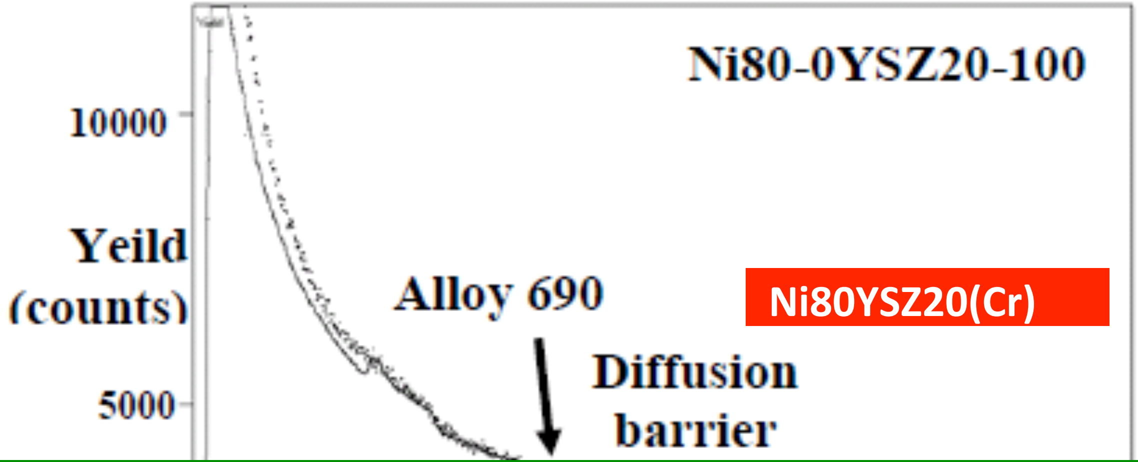




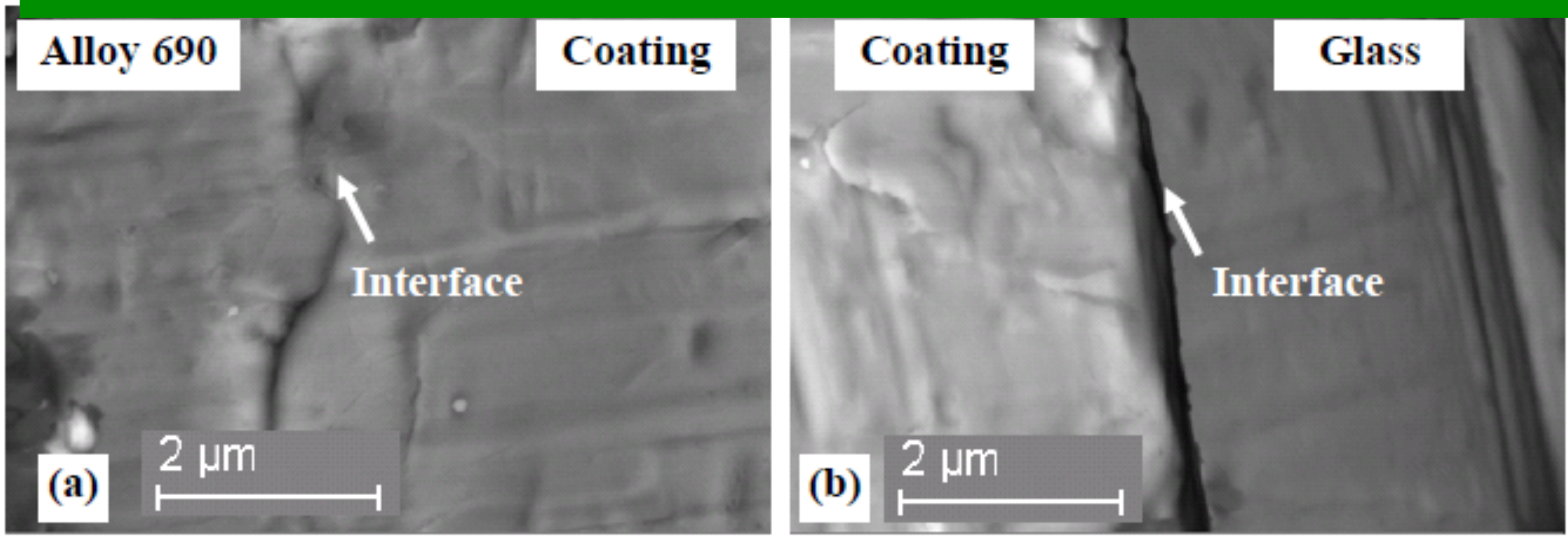


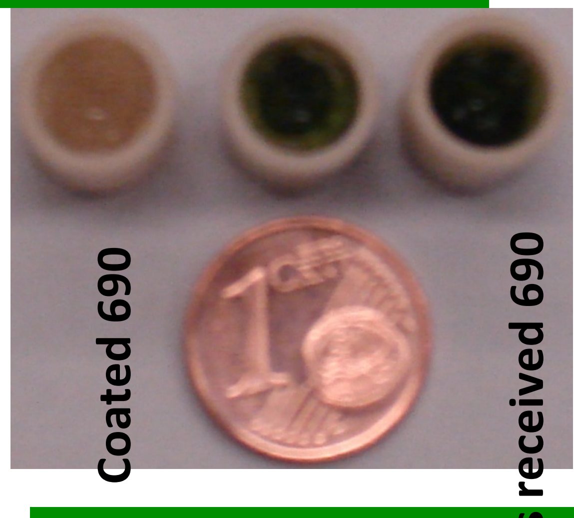
Composite coating: Ni-YSZ





Metallurgical challenge: Capabilities to coat large scale job specimens is yet to be achieved.



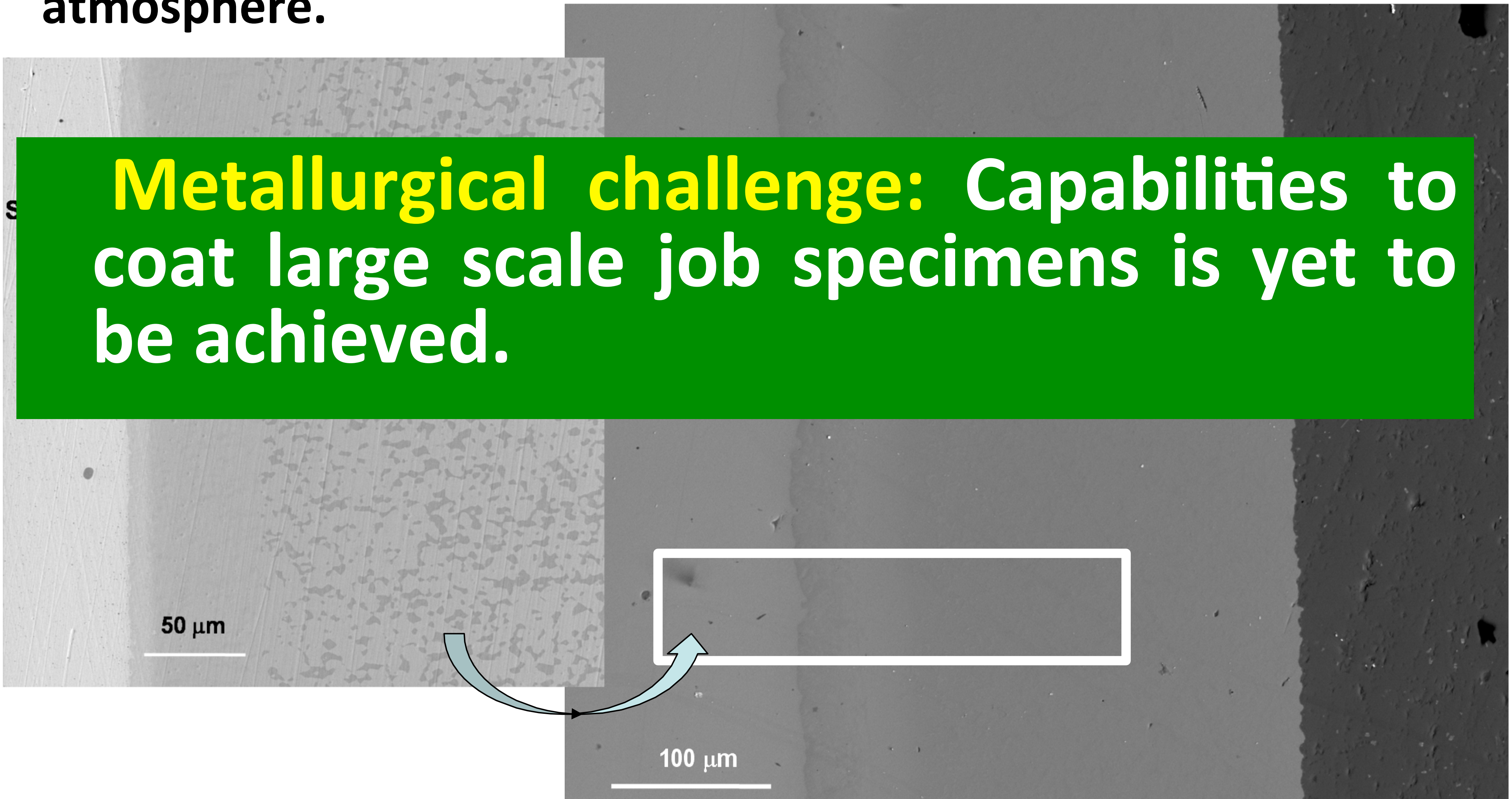


1000ºC, 1-6 hr

Intermetallic coating: Ni aluminide

Pack aluminization process: 15mm x 10mmx 5mm Alloy 690 coupons were embedded in pack mixture (Al powder, Al_2O_3 powder, NH_4Cl) and annealed at 1273K for 10 hours in Ar atmosphere.

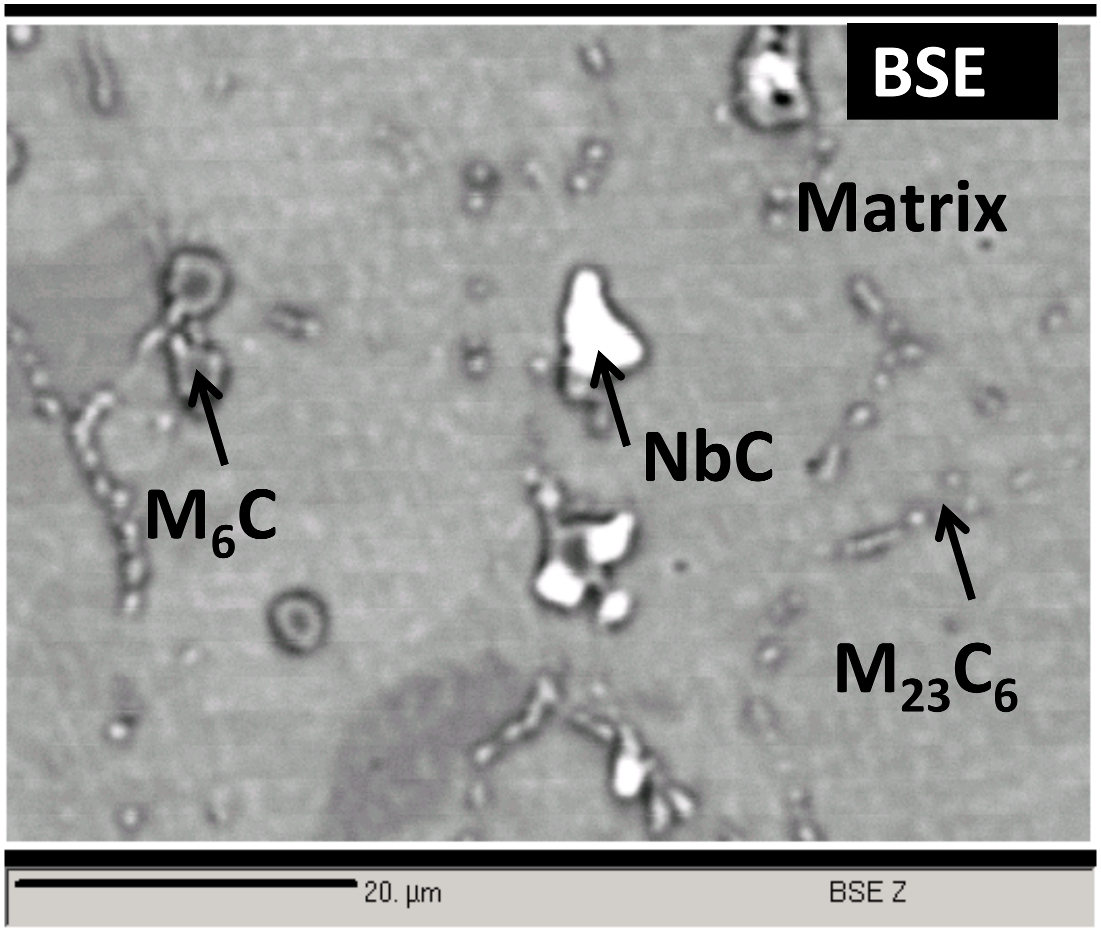
Metallurgical challenge: Capabilities to coat large scale job specimens is yet to be achieved.

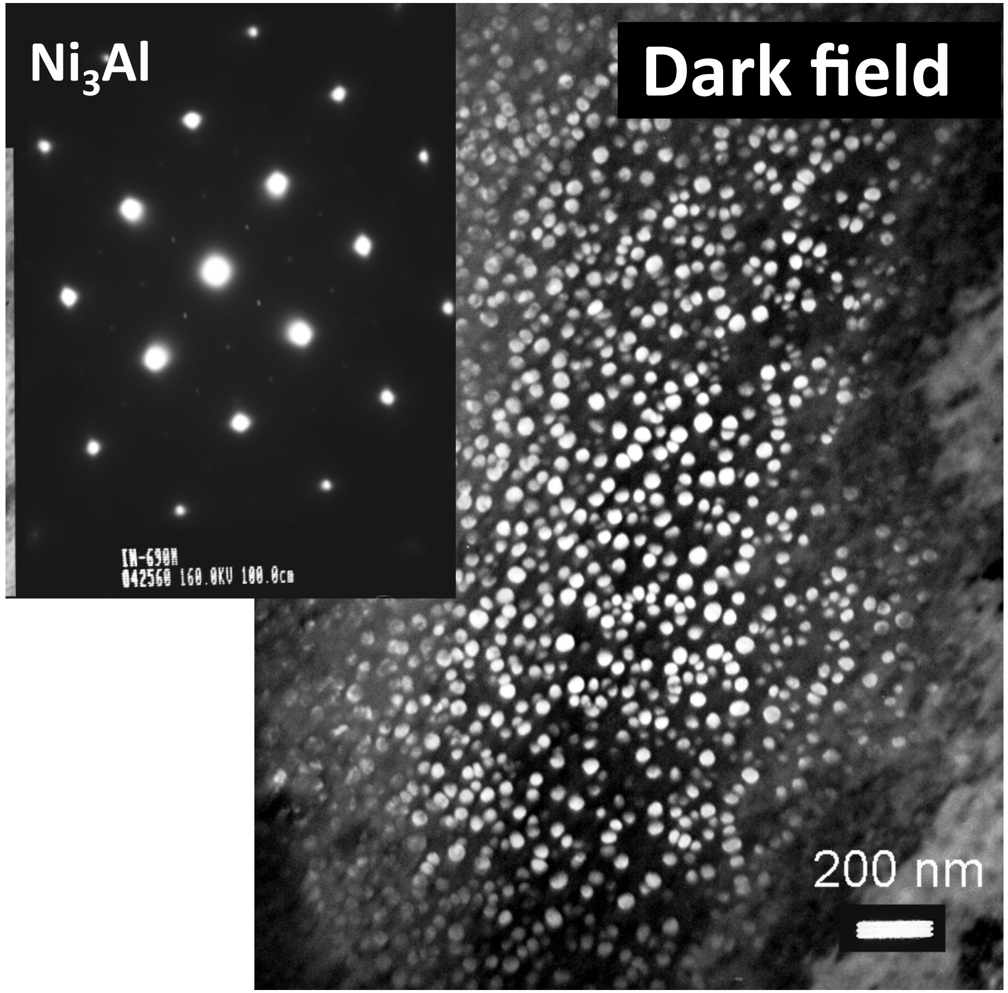


Alternative Alloy: Alloy 693

Element (wt %)	Cr	Fe	Al	Cu	Si	Mn	S	C	Nb	Ti	N	Ni
SUPERNI 690	27.0-31.0	7.0-11.0	**0.50** max	0.50 max	0.5 max	0.5 max	0.01 max	0.05 max	-			Bal.
SUPERNI 690M (G3327) (minimum)	27.0	2.5	2.5	-	-	-	-	-	0.5	-	-	Bal.
(maximum)	31.0	6.0	**4.0**	0.5	0.5	1.0	0.01	0.15	2.5	1.0	-	Bal.
(product)	29.32	3.96	3.19	<0.02	0.04	0.09	<0.002	0.097	1.86	0.42	130 ppm	Bal.
XRF analyses	29.63	3.08	3.68	-	-	0.29	-	-	2.65	0.34	-	Bal.

Alloy 693: Microstructure

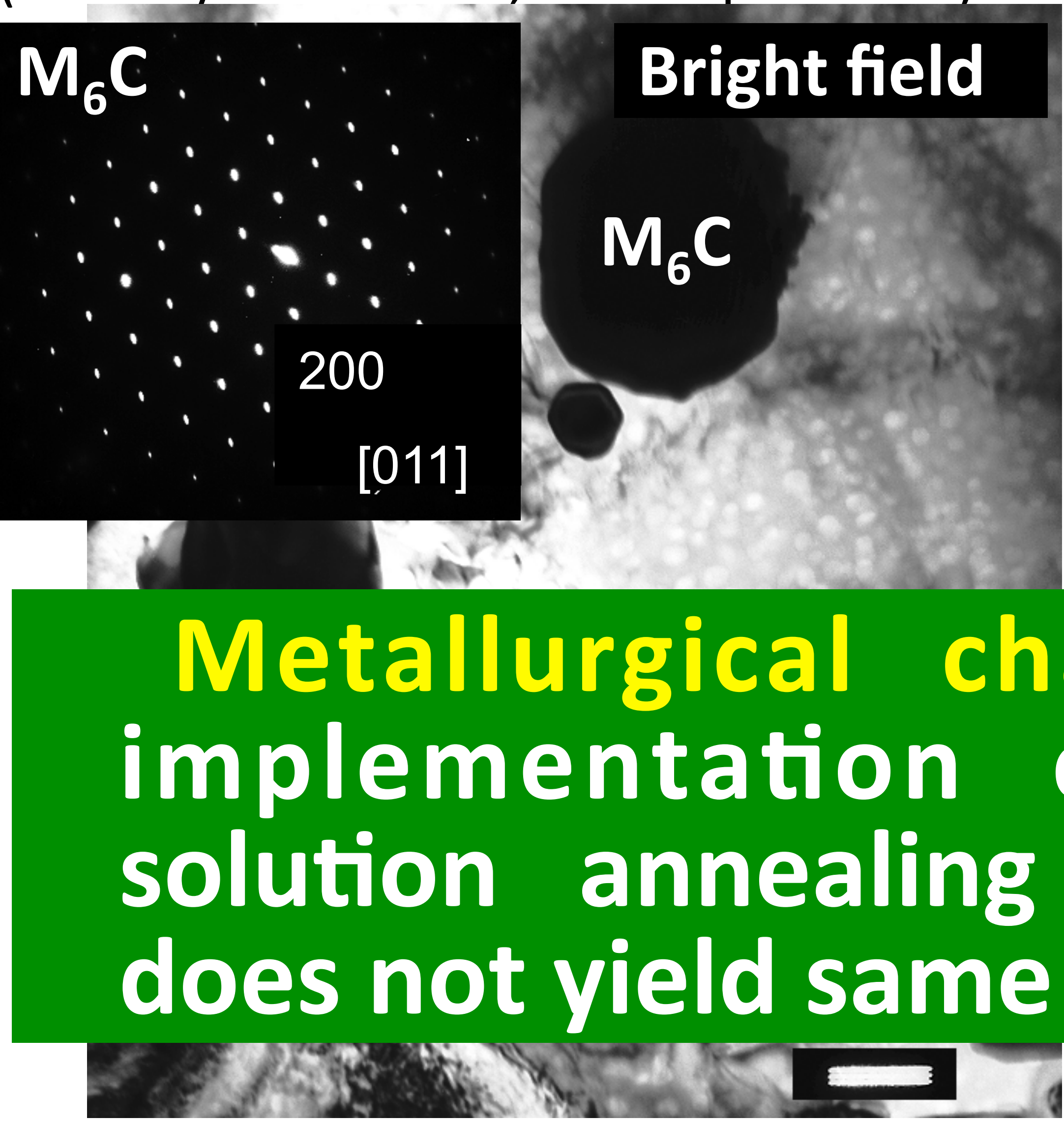




Distribution of intragranular M_6C and NbC, and intergranular $M_{23}C_6$ type precipitates within matrix.

Uniform distribution of fine ordered Ni_3Al type precipitates within austenitic matrix of as-received SUPERNI 690M sample. Inset shows SAD pattern of Ni_3Al type phase (faint spots) along with the austenite matrix

(1100^{0}C/30 minutes, water quenched)



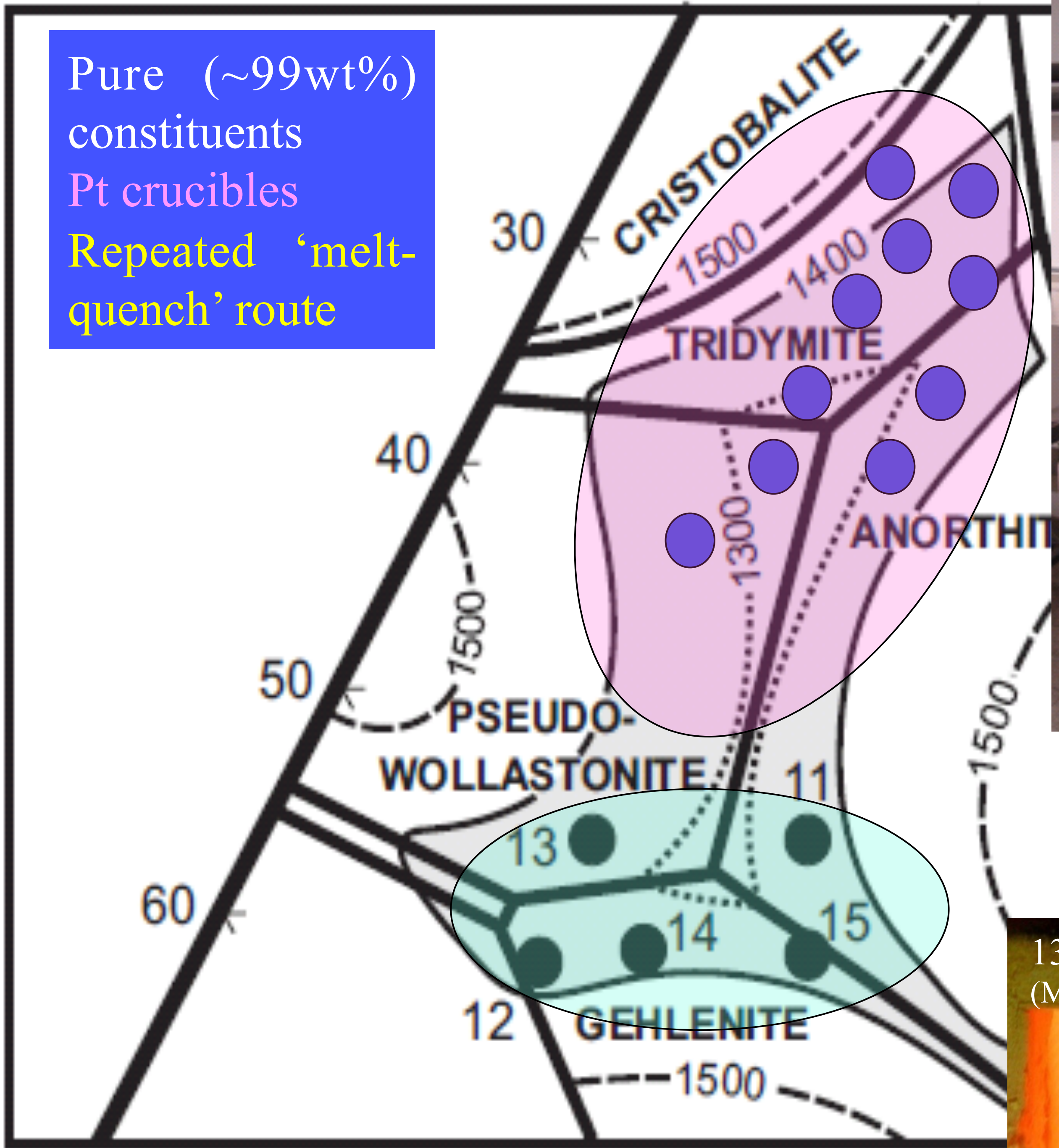
Metallurgical challenge: Plant scale implementation of laboratory scale solution annealing treatment procedure does not yield same result.

Distributions of M_6C and fine grained ordered Ni_3Al type precipitates within austenitic matrix.

Cleaner matrix with some M_6C type precipitates and planar arrangement of dislocations. Inset shows SAD pattern of austenite matrix (fcc).

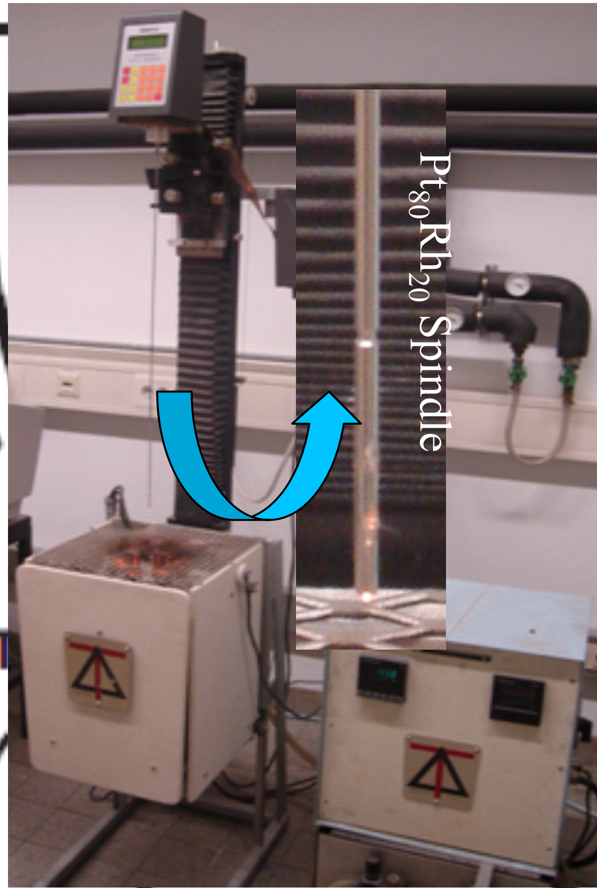
Experimental design & strategy: II. Preparation of glasses

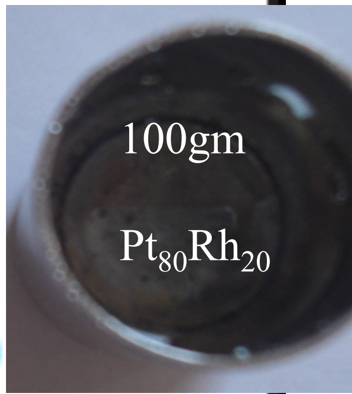
Pure (~99wt%) constituents
Pt crucibles
Repeated 'melt-quench' route



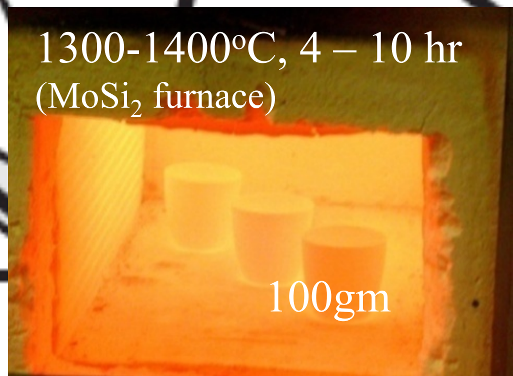
650°C, 10-14 days

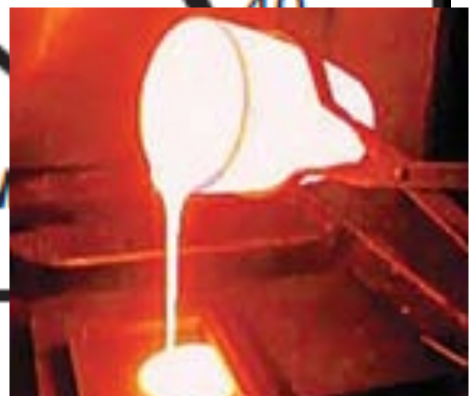
SiC -vertical furnace
Spindle 10-100 rpm
$Pt_{90}Rh_{10}$ thermocoupl



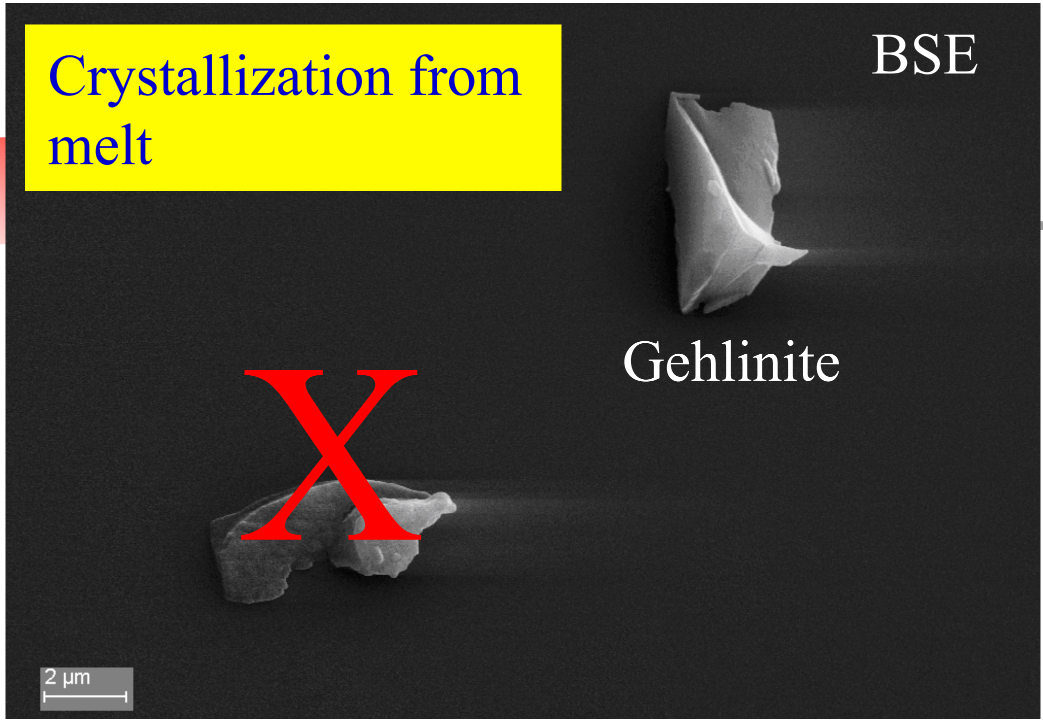


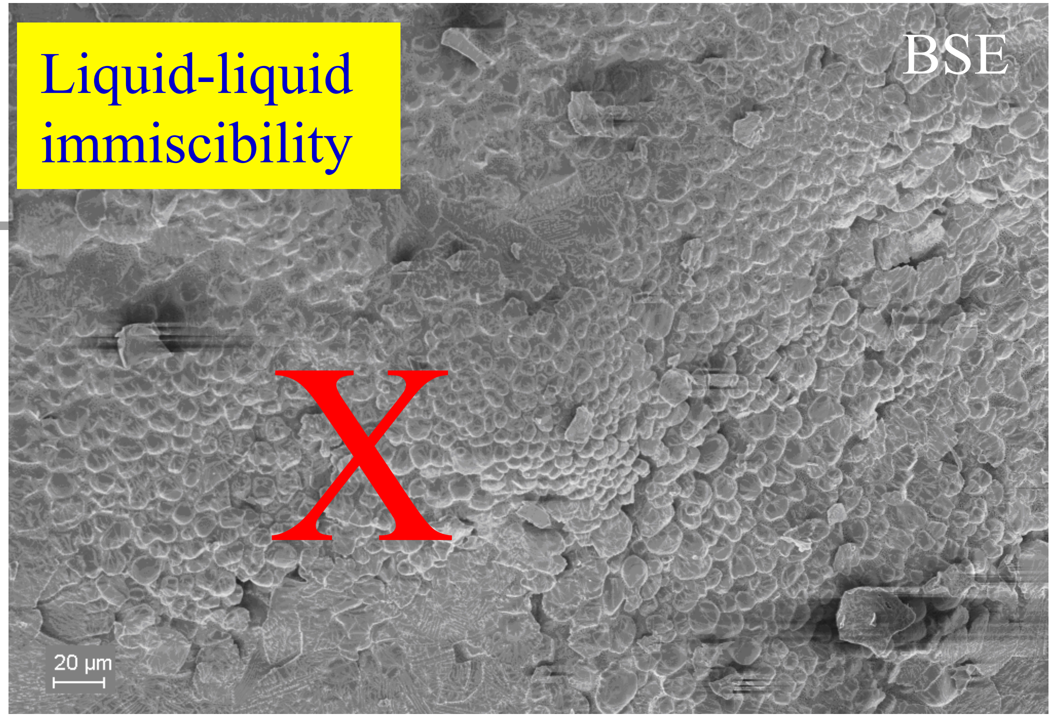
1300-1400°C, 4 – 10 hr
($MoSi_2$ furnace)

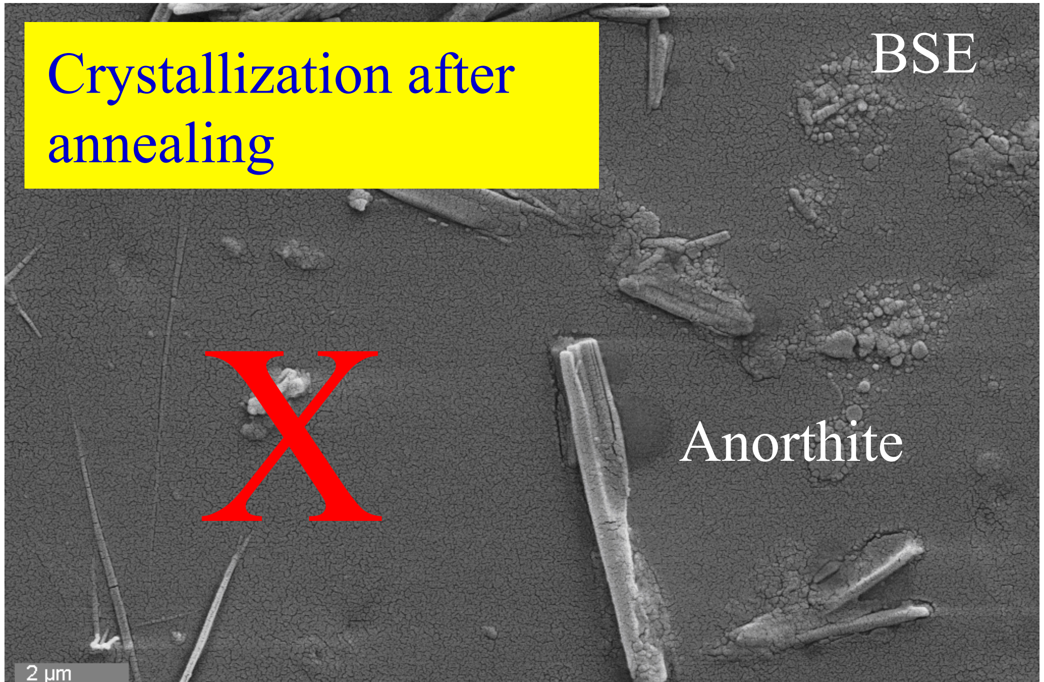


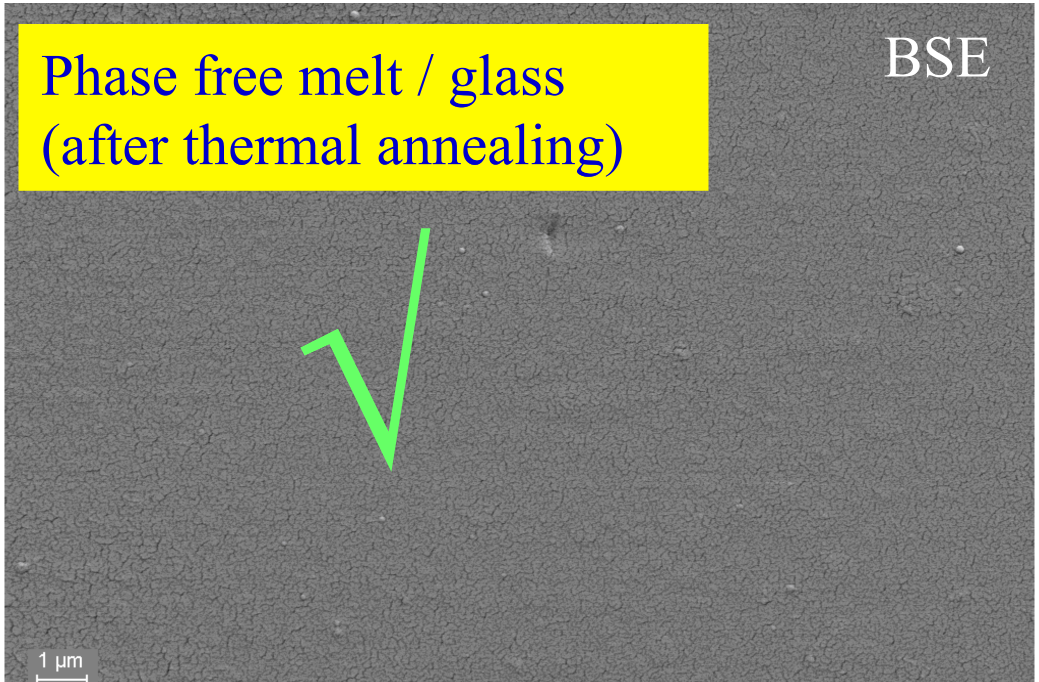


Selection of suitable glass sample(s)









Structural analyses:

Nuclear Magnetic Resonance (NMR) – ^{29}Si, ^{11}B, ^{27}Al

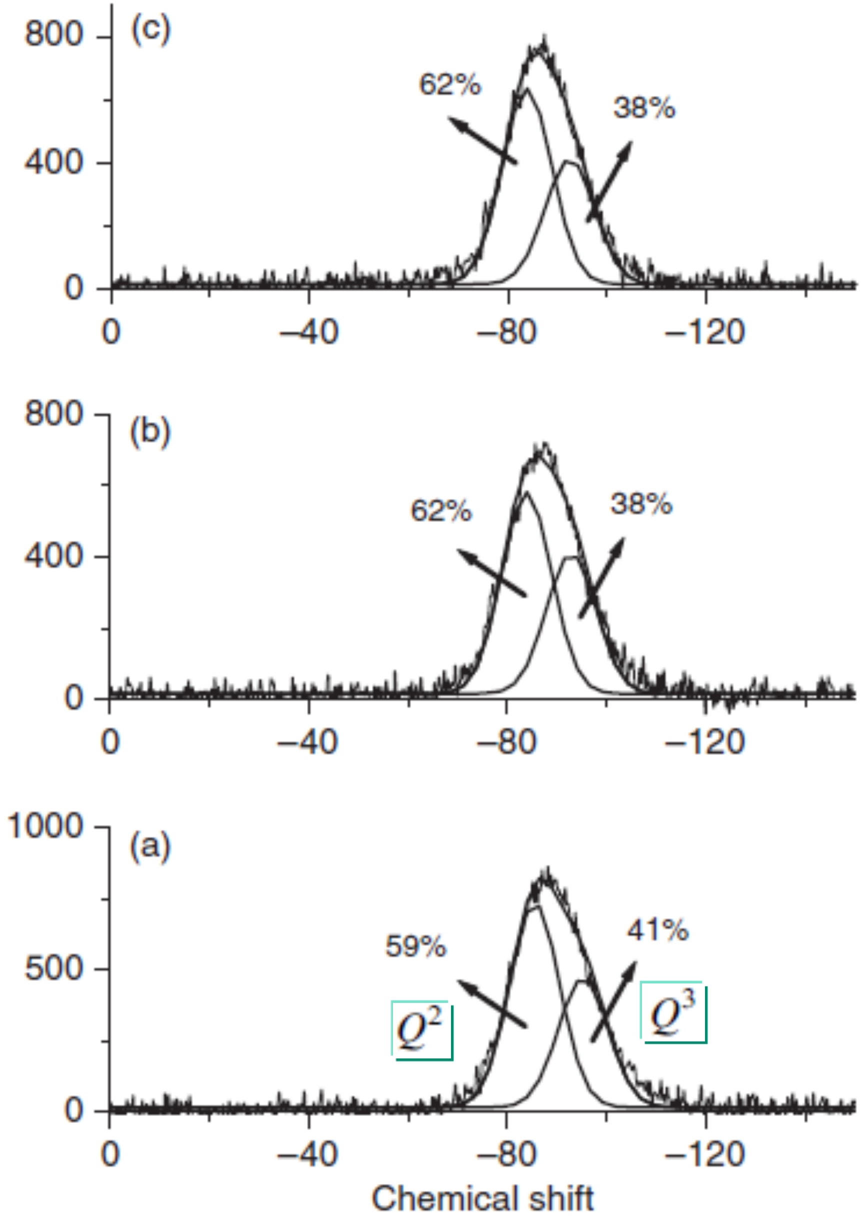


Fig. 5. ^{29}Si MAS NMR patterns for sodium barium borosilicate base glass samples loaded with (a) 0 mol% SO_4^{2-}, (b) 2 mol% SO_4^{2-}, and

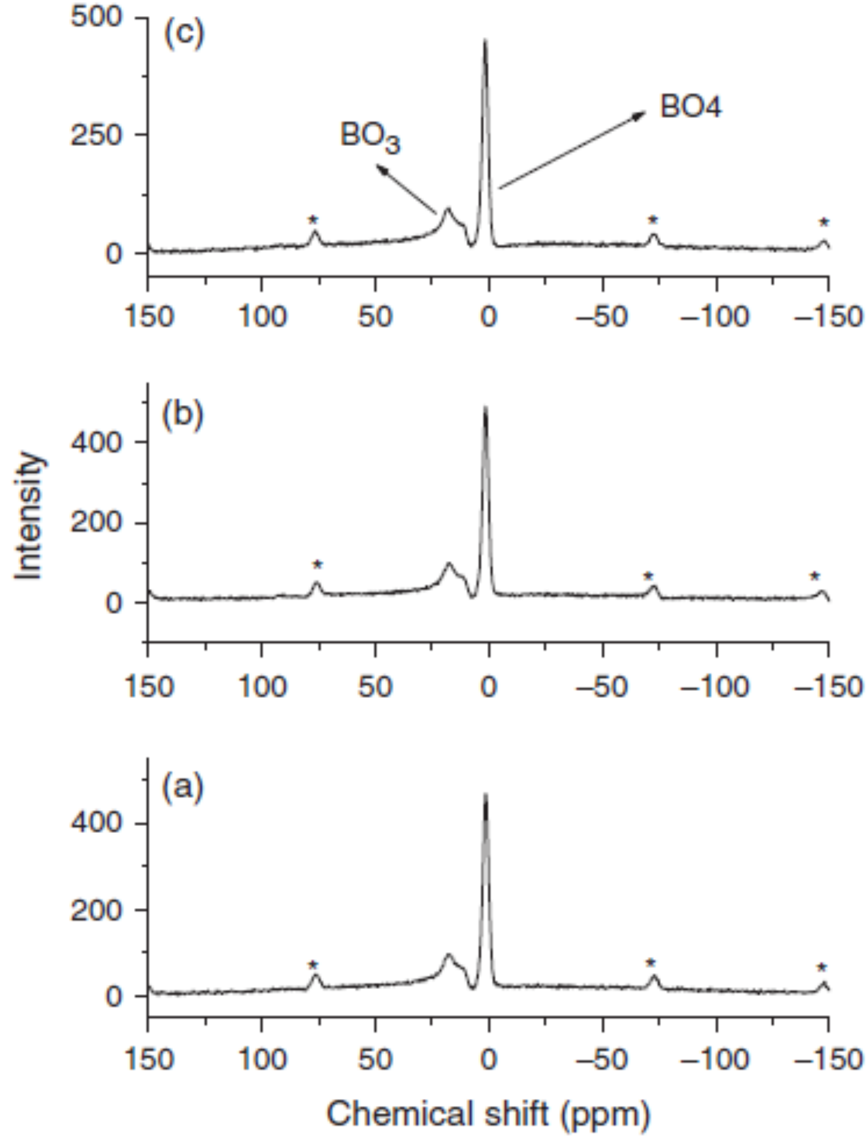
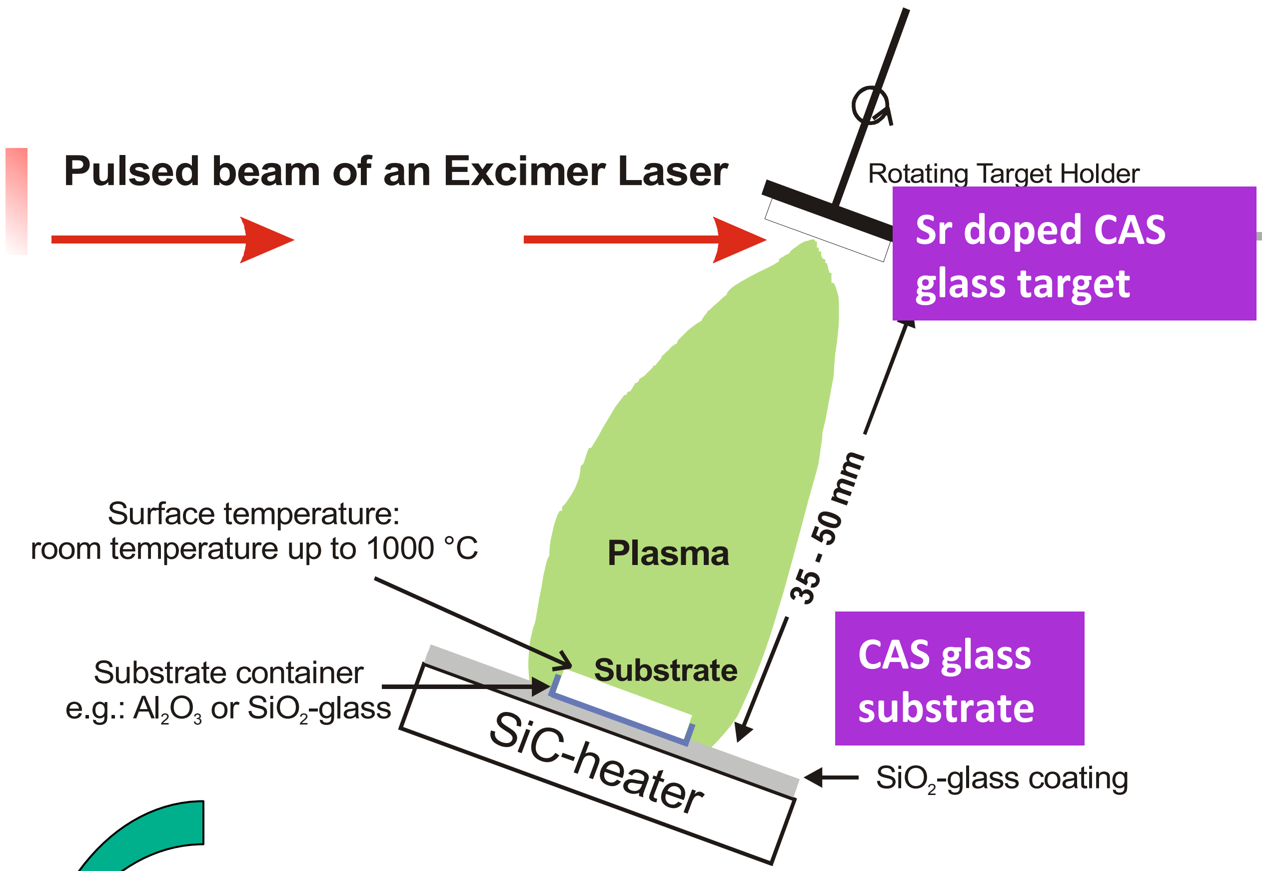
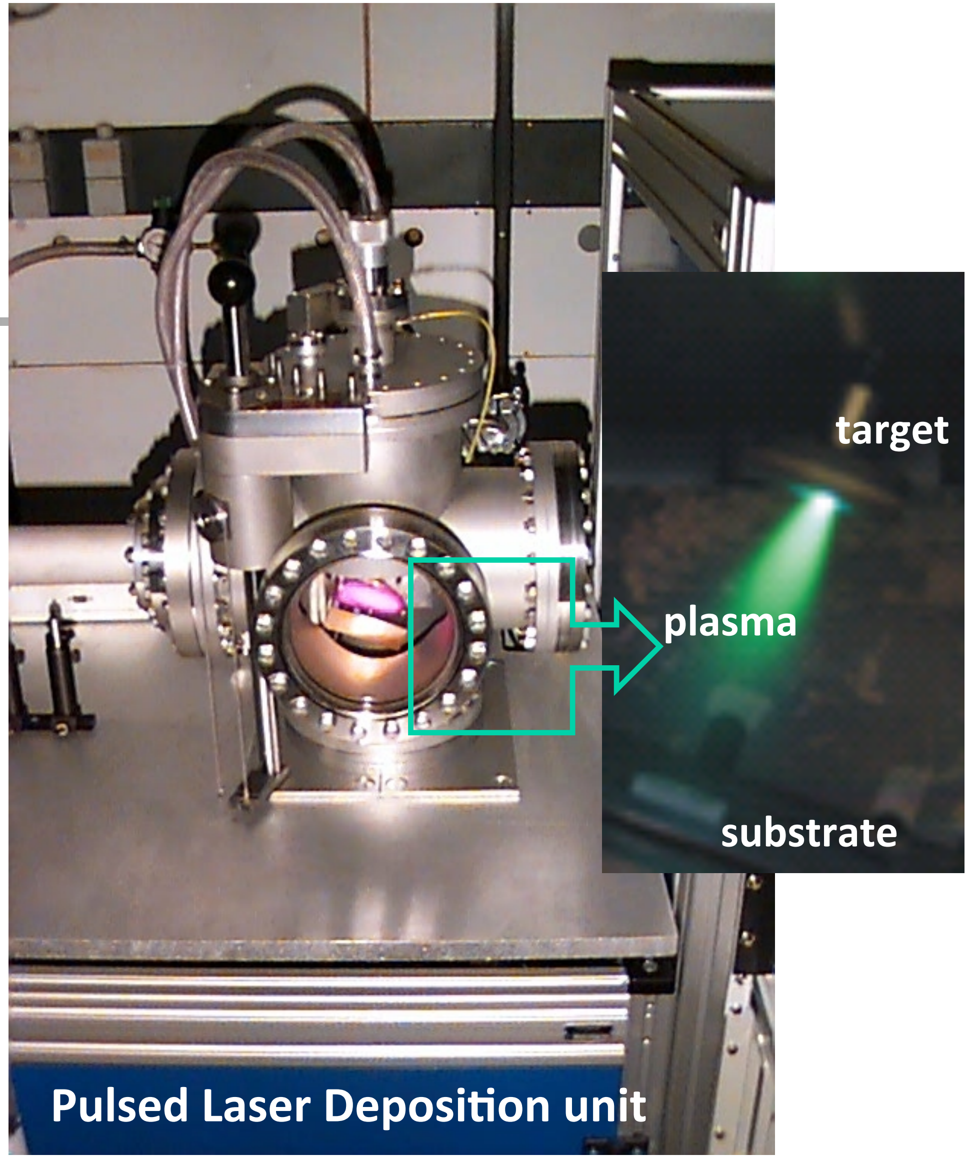


Fig. 6. ^{11}B MAS NMR patterns for sodium barium borosilicate base glass samples loaded with (a) 0 mol% SO_4^{2-}, (b) 2 mol% SO_4^{2-}, and

Diffusion study using Pulsed Laser Deposition technique

Schematic illustration of a PLD-system

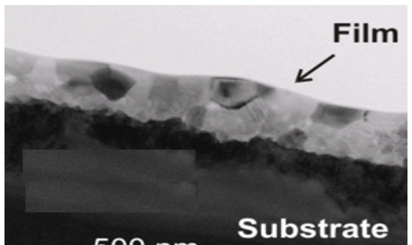




The whole setup is positioned in a UHV-chamber. The ablation process can operate at a controlled O_2- or N_2-gas atmosphere

=> stoichiometric transfer from the target to the substrate!

Thin film coating



Diffusion annealing

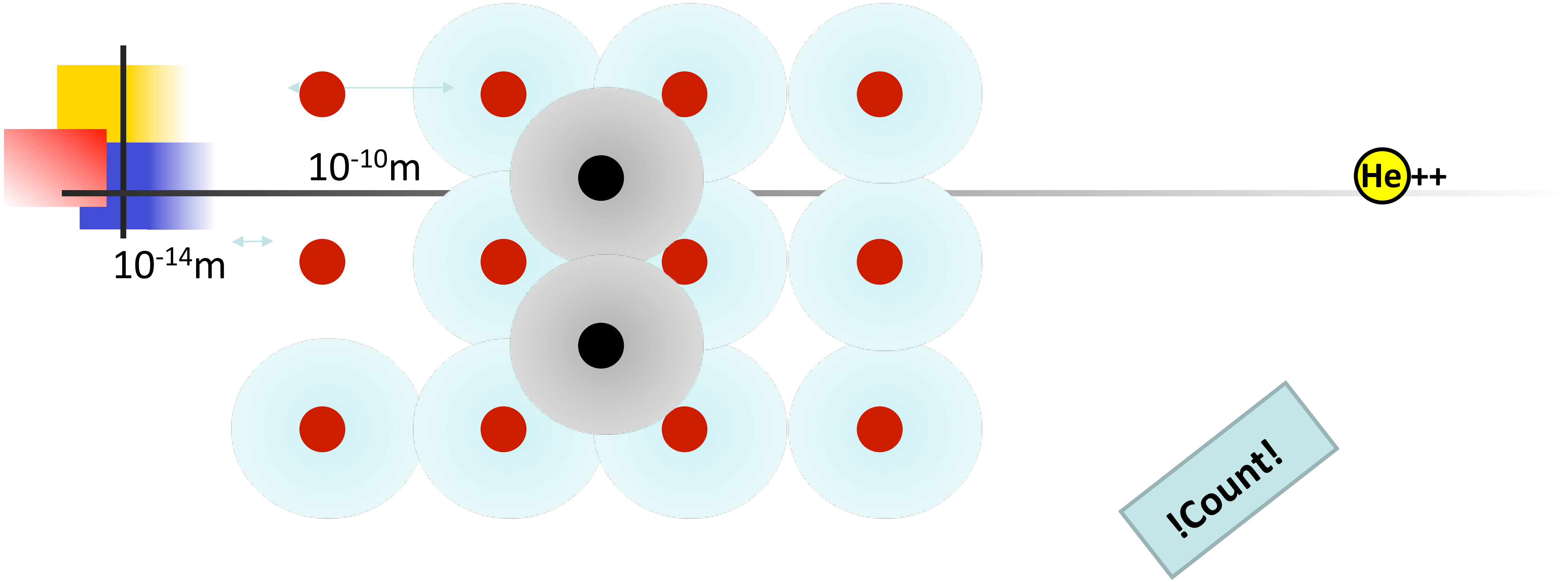
600-900°C (T_g 975°C)

30 mins-10days

Diffusion profile analysis

Rutherford Back-scattering Spectroscopy

Rutherford Back-Scattering Spectroscopy: Basics



Suitable for short elemental depth profiling (diffusion profiles upto several tens of nm) appropriate to characterize small diffusivities typical of any cations within ordered/disordered aluminosilicate network.

Non-destructive technique; determines absolute concentrations without any standard.

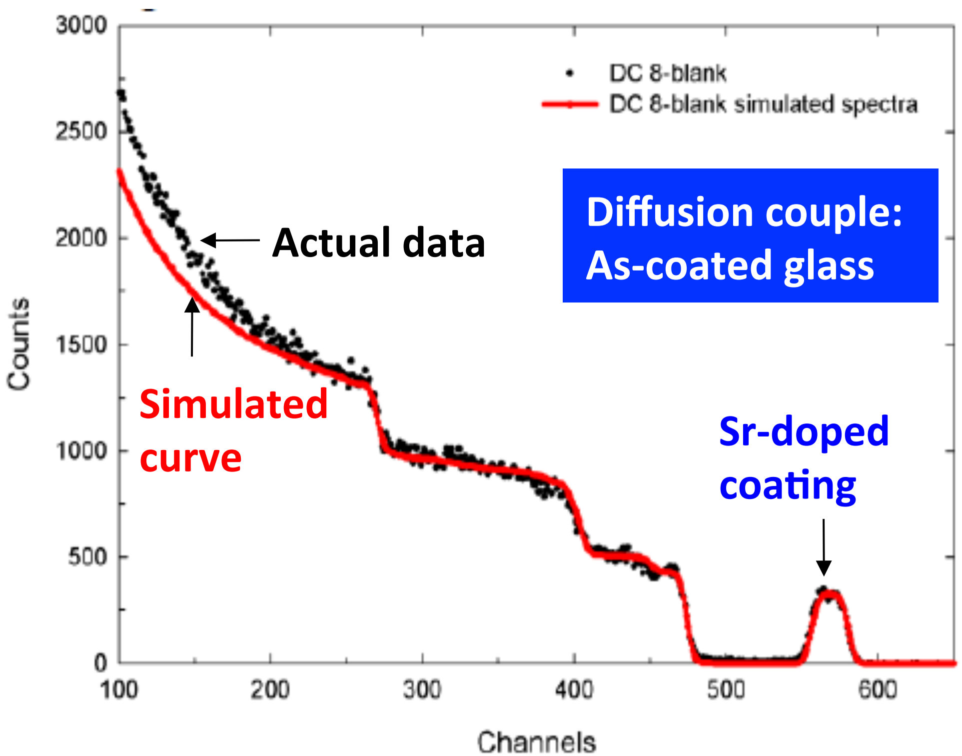
The energy after scattering is determined by:

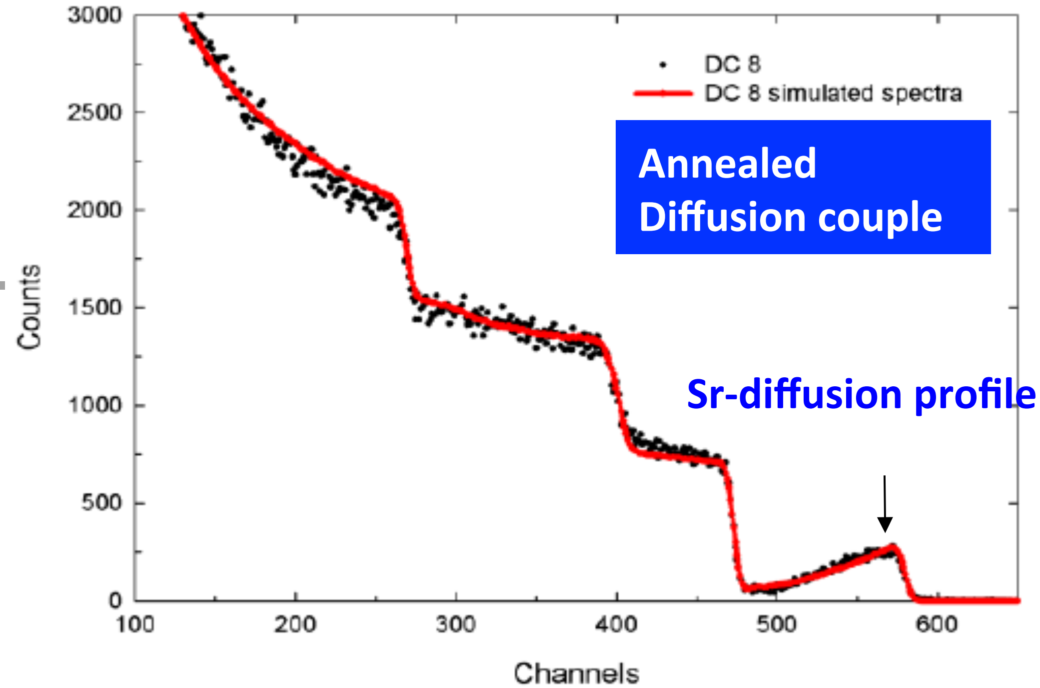
1. by the masses of the particle and target atom, 2. stopping

$$\frac{d\sigma}{d\Omega} \propto \left[\frac{Z_{Ion} Z_{Probe}}{E_{Ion}} \right]^2$$

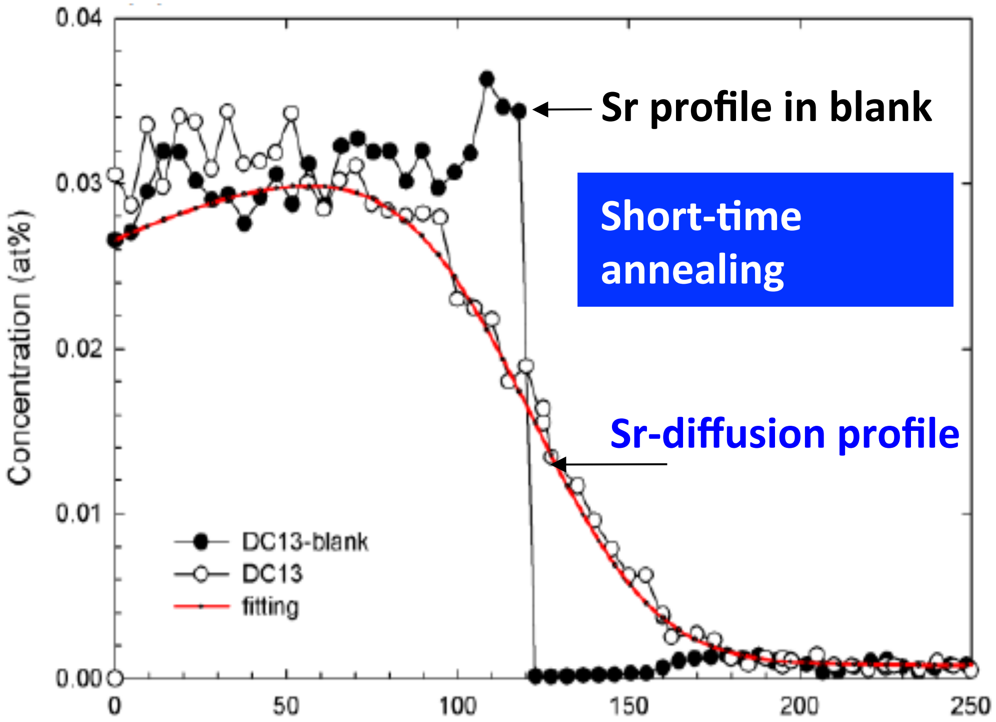
$$k = \left[\frac{\sqrt{M_{Probe}^2 - M_{Ion}^2 (\sin\theta)^2} + M_{Ion} \cos(\theta)}{M_{Ion} + M_{Probe}} \right]^2$$

Sr-diffusivity within calcium aluminosilicate glass

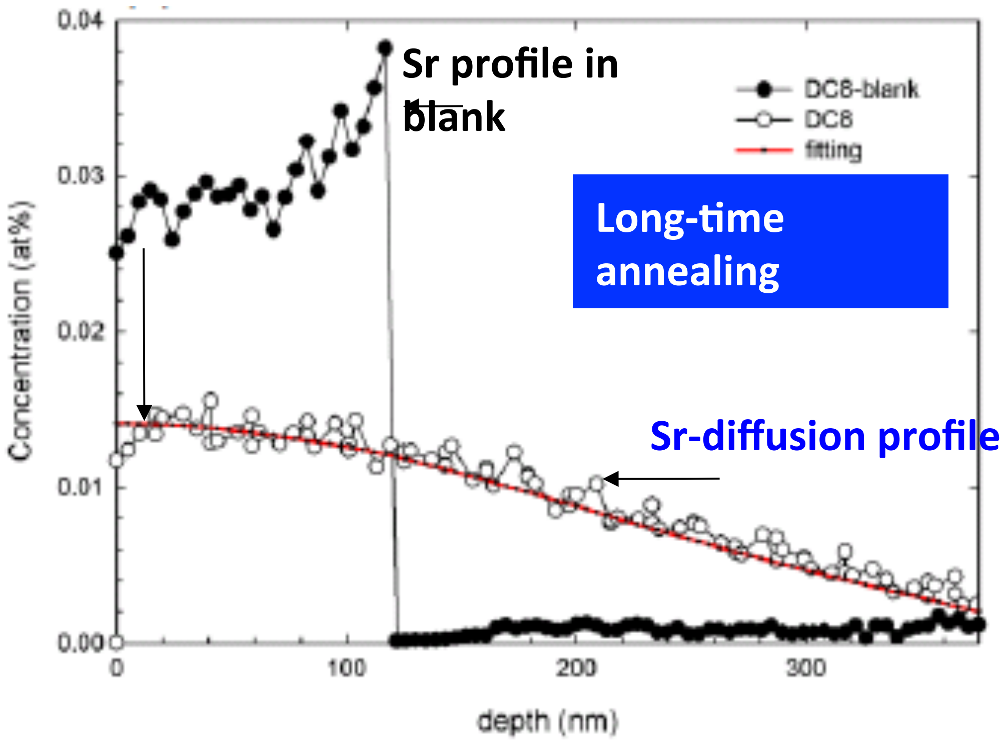




log D



:AS11



Concluding Remarks

Nuclear Energy is an inevitable option for 'domestic energy mix' is going to be there for most of the IAEA Member countries. With more innovative nucler fuel designs and upgradation of reprocessing technologies coming in the challenges of nucler waste immobilisation is going to be more tough.

Basic Principles of Natural Sciences and Physical Sciences should be blended extensively used for addressing materials based challenges in nuclear waste immobilization.

However, for faster implementation of the program active participations from members of IAEA community is highly encouraged.