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Structural design of borosilicate-based nuclear waste glasses

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What is Radioactive Waste?

What is radioactive waste?

According to *International Atomic Energy Agency (IAEA)*, a radioactive waste is defined as a material that contains, or is contaminated with, radionuclides at concentrations or activities greater than clearance levels, and for which no use is foreseen.

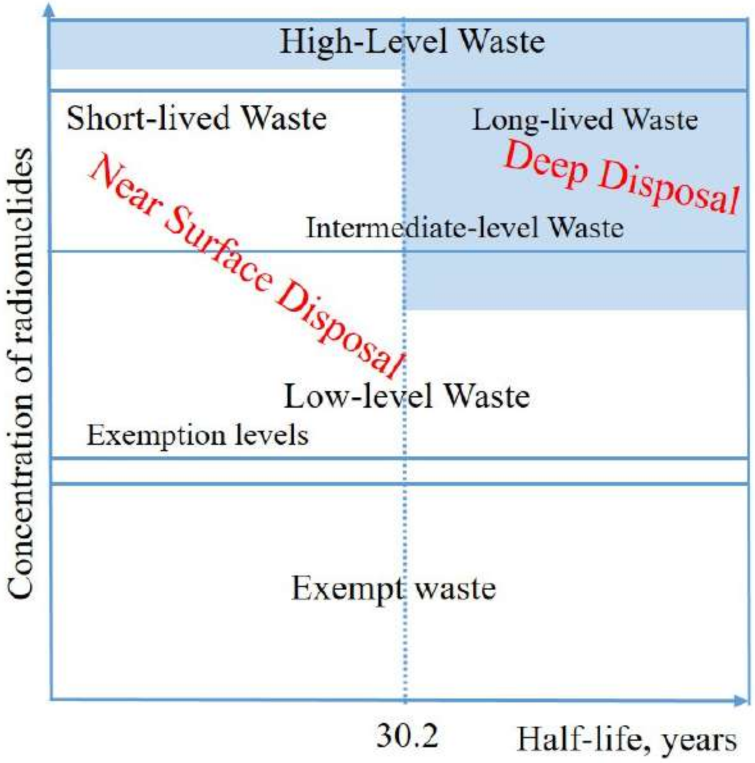
According to IAEA, the global radioactive waste inventory may be classified into *six* different categories based on the radioactivity of its content and half-life ($t_{1/2}$) of its radionuclides.

1. **Exempt waste:** Waste that meets the criteria for clearance or exclusion from regulatory control for radiation protection.

2. **Very short lived waste (VSLW):** Waste that can be stored for decay over a limited period of up to a few years and subsequently cleared from regulatory control. **Example:** radionuclides with very short half-lives often used for research and medical purposes.

3. **Very low level waste (VLLW):** Waste that does not necessarily meet the criteria of exempt waste, but that does not need a high level of containment and isolation, and therefore is suitable for disposal in near surface landfill type facilities with limited regulatory control. **Example:** soil and rubble with low levels of activity concentration.

Ojovan and Lee, An Introduction to Nuclear Waste Immobilization, 2005, Elsevier



Classification of radioactive waste

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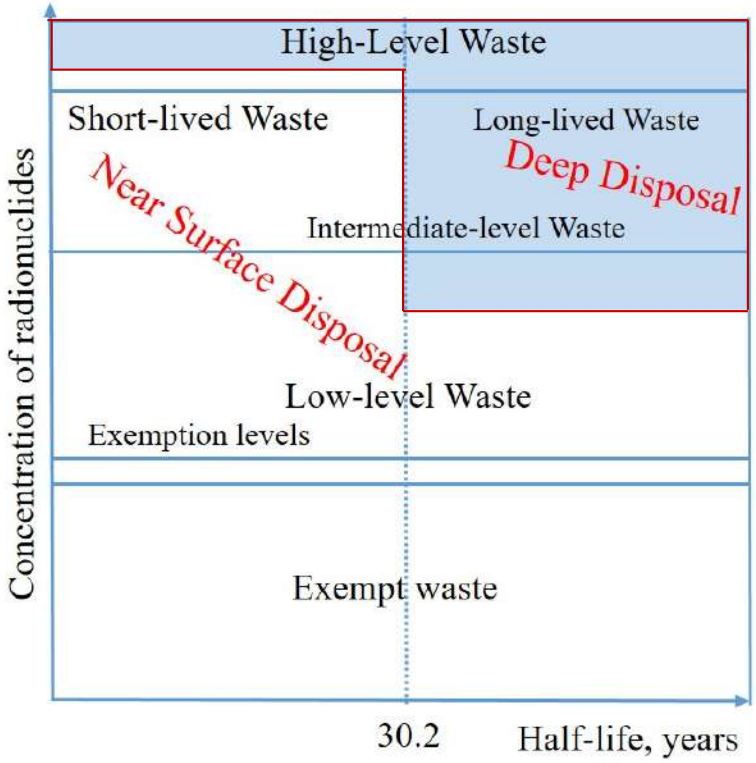
According to IAEA, the global radioactive waste inventory may be classified into *six* different categories based on the radioactivity of its content and half-life ($t_{1/2}$) of its radionuclides.

4. **Low level waste (LLW):** Waste that is above clearance level, but with limited amounts of long lived radionuclides. Such waste requires robust isolation and containment periods of up to few hundred years. They are suitable for disposal in engineered near surface facilities.

5. **Intermediate level waste (ILW):** contains long-lived radionuclides due to which it requires to be disposed at greater depths, or the order of tens of meters – to – few hundred meters.

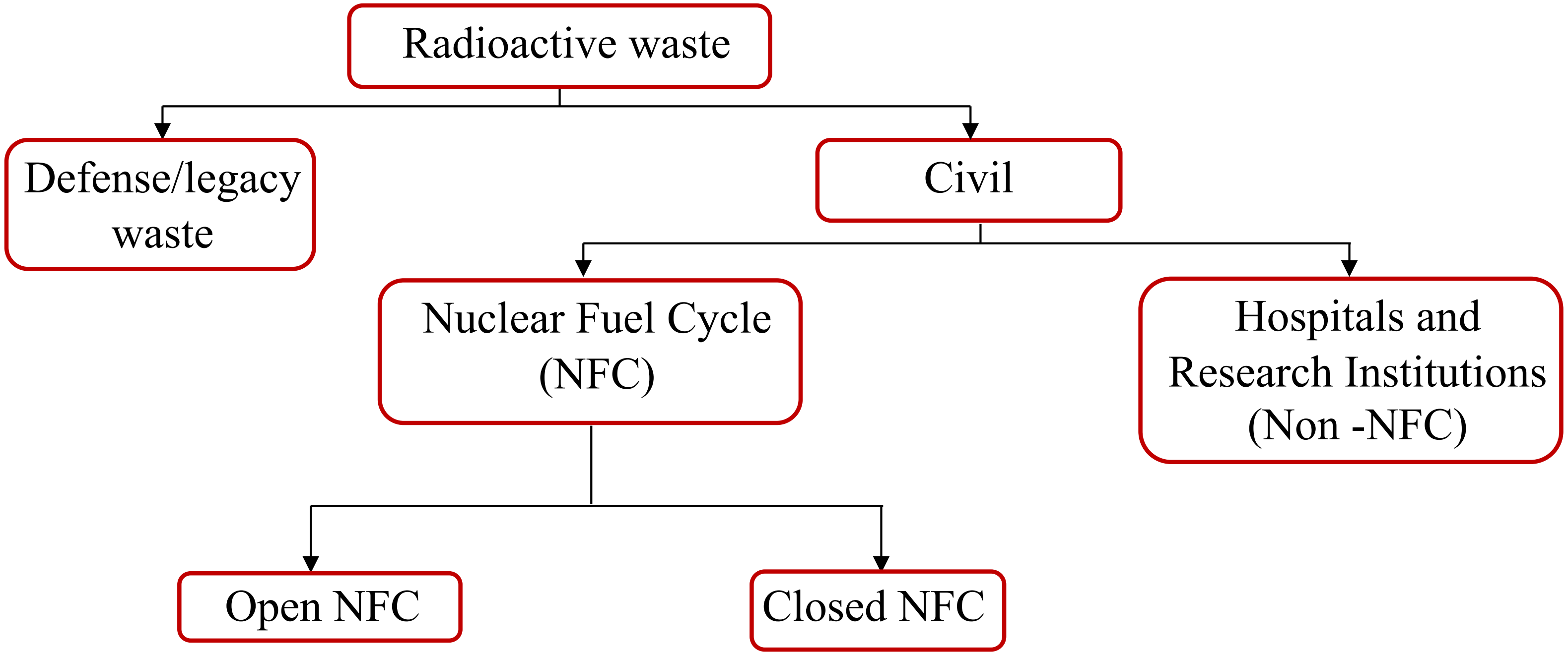
6. **High level waste (HLW):** Waste with large concentration of long-lived radionuclides. Disposal in deep, stable geological repositories usually several hundred meters or more below the surface is the generally recognized option for disposal of HLW.

Ojovan and Lee, An Introduction to Nuclear Waste Immobilization, 2005, Elsevier



Classification of radioactive waste

Source and complexity of radioactive waste



Radioactive waste

Defense/legacy waste

Civil

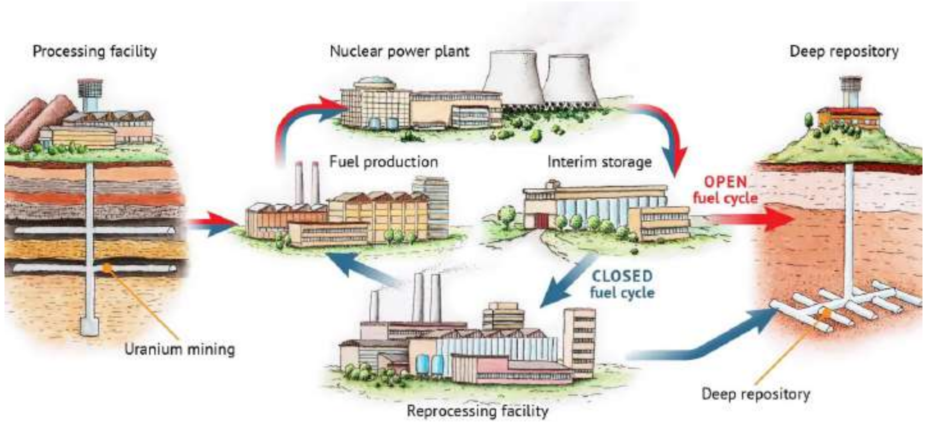
Nuclear Fuel Cycle (NFC)

Hospitals and Research Institutions (Non -NFC)

Open NFC

Closed NFC

- In an open NFC, the spent fuel is disposed of without reprocessing (as HLW). US, Canada, Sweden, and many more countries have adopted open NFC.
- In the closed NFC, spent fuel is reprocessed to extract fissile U and Pu and only the remaining HLW is disposed.
- Worldwide, there are only five commercial reprocessing plants operable: namely in France, UK, Japan, Russia, India.



A schematic representation of open and closed NFCs

Reference: energyencycopedia.com

Radioactive waste classification in USA

While IAEA classifies radioactive waste in six different categories, the radioactive waste in the U.S. has been classified into two categories.

High-level waste

(A) The highly radioactive material resulting from the re-processing of spent nuclear fuel, including liquid waste produced directly in re-processing and any solid material derived from such liquid waste that contains fission products in sufficient concentrations.

(B) Other highly radioactive material that the Nuclear Regulatory Council (NRC) determines by the rule requires permanent isolation.

Proposed shipment of commercial spent nuclear fuel to DOE national laboratories for research and development purposes, DOE/EIS-0203-SA-07 (2015)

Low activity waste

(A) LAW is not same as LLW. While LLW is regulated by Nuclear Regulatory Council (NRC), the LAW is managed under the U.S. DOE's regulatory authority.

(B) LAW is a radioactive material which has been produced during the generation of HLW but has been determined to be non-HLW through a process known as "waste incidental to reprocessing". Since the LAW poses less risk to the health and safety of the people and environment. Therefore, it does not need to be disposed of as HLW.

West Valley Demonstration Project, Waste incidental to reprocessing evaluation for the concentrator feed makeup tank and the melter feed hold tank, 2013, US. DOE.

Glass as a waste form – A historical perspective

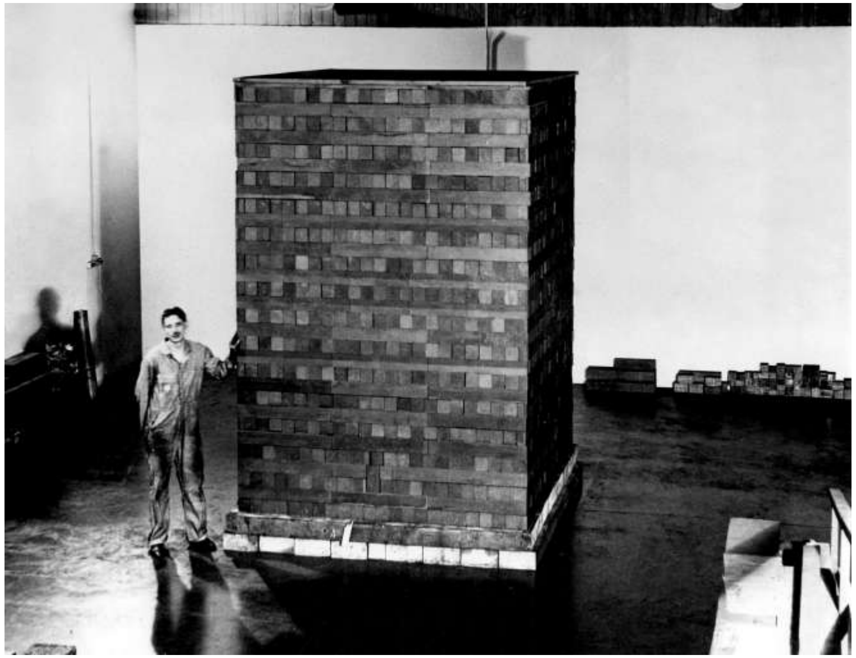
- **1930s:** The first radioactive waste is reported to be produced in Canada and France during the mining of uranium and radium, and use of radium for medical purposes, respectively. Later, uranium was destined for nuclear fuel and military applications. *[nuclearsafety.gc.ca; international.andra.fr]*

- **1940s:** The first self-sustaining nuclear chain reaction took place in Chicago on December 2, 1942, as a part of the *Manhattan Project* resulting in the production of first cupful of HLW. No plans were made for the safe disposal of this new type of waste.

  [Nuclear Free Future Foundation]

- **1950s:** The first research on solidification of fission product solutions began in 1950s in the USA, France, UK and Canada. The only requirement for a waste form was that it be a stable solid.

- **1950s:** The first borosilicate glass formulation was developed between 1956 and 1957 by Goldman et al. at MIT. The researchers examined calcium aluminosilicate porcelain glazes into which they had added B_2O_3 to reduce viscosity and minimize volatilization of radionuclides.



Chicago Pile-1 (CP-1) nuclear reactor
https://ahf.nuclearmuseum.org/ahf/history/chicago-pile-1/

W. Lutze, R.C. Ewing, *Radioactive waste forms for the future.* 1988; M.T. Harrison, Proc. Mater. Sci. 7 (2014) 10; M.I. Goldman et al. *Retention of Fission Products in Ceramic-Glaze-Type Fusions*. in 2nd *UN Int. Conf. on Peaceful Uses of Atomic Energy*. 1958. Geneva: United Nations, New York.

Borosilicate glass as waste form – Global acceptance

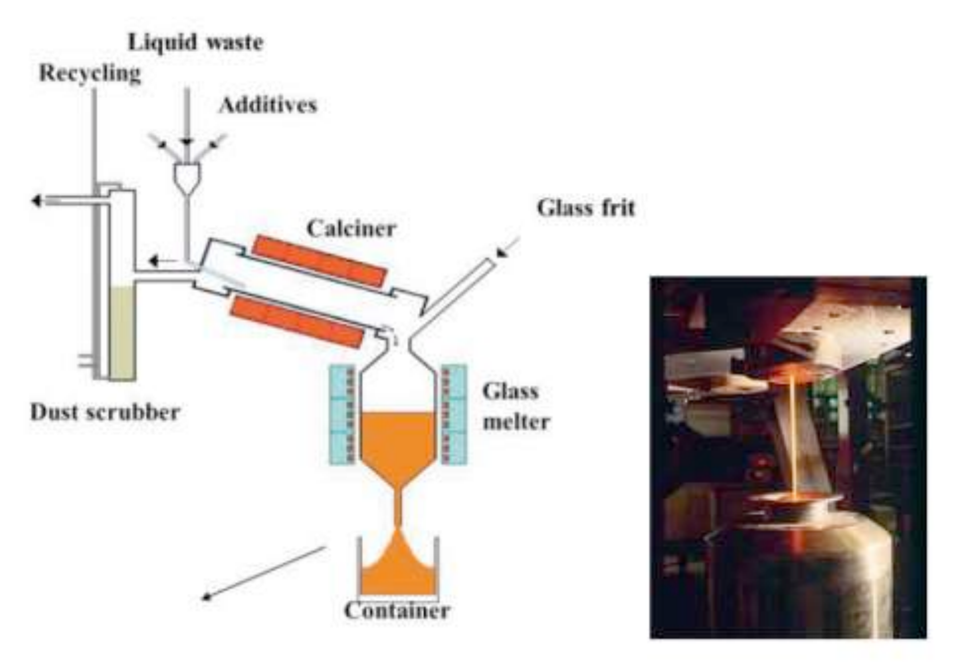
- **1957:** France was the first country to adopt borosilicate glass as a waste form to immobilize their legacy HLW. The first radioactive glass was synthesized at laboratory scale at Saclay (France).

- **By 1968,** the PIVER facility in the Marcoule Pilot Plant was capable of vitrifying up to 200 kg high-activity solutions.

- **1960s:** The UK selects borosilicate glass and focuses on the development of a single-stage ‘in-can’ batch process based on induction heating, i.e., FINGAL (Fixation in Glass of Active Liquors).

- **1981:** The United States selects two waste forms as potential candidates for the immobilization of their legacy HLW.
  1. Borosilicate glass – as the reference waste form
  2. Synroc – as an alternative waste form

- Today, majority of the nuclear nations around the world have accepted borosilicate glass matrix as a host for the immobilization of their defense and civil HLW.

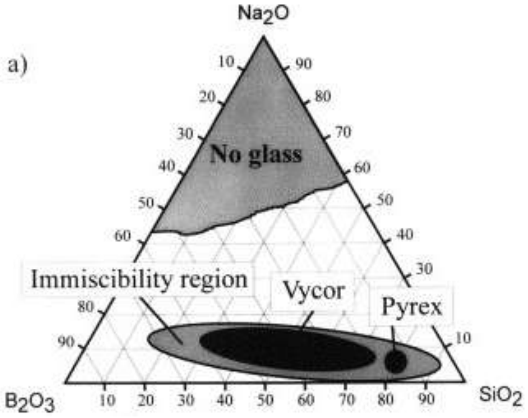


Two step calciner/hot crucible French vitrification process. FP solution is continuously introduced in a calciner, and the glass is melted in a metallic furnace by induction.

- Vernaz and Brueziere, *Proc. Mater. Sci.* 7 (2014) 3.
- W. Lutze, R.C. Ewing, *Radioactive waste forms for the future.* 1988.
- M.T. Harrison, *Proc. Mater. Sci.* 7 (2014) 10.
- C.P. Kaushik, *Proc. Mater. Sci.* 7 (2014) 16
- Lu et al., *Radiation Protection* 40 (2020) 67 (in Chinese).
- Li et al., *Atomic Energy Sci. Technol.* 54 (2020) 126 (in Chinese).

Why borosilicate glass?

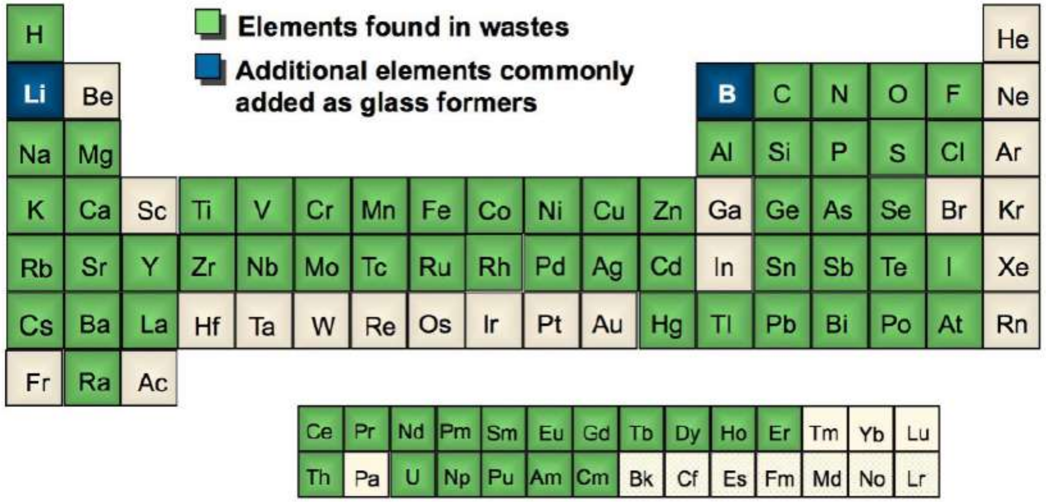
- Amorphous nature and flexible structure
- Large glass forming region.



- Glasses can be processed at temperatures ≤ 1200˚C.

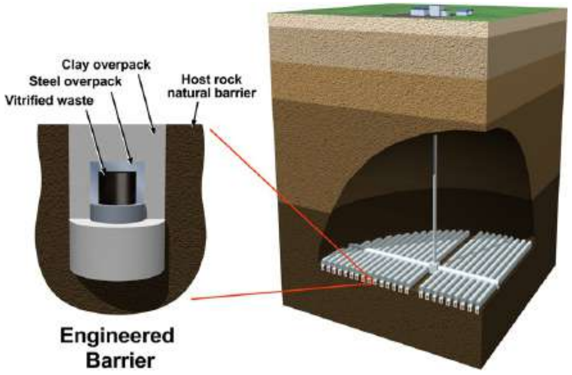
View inside JHCM plenum

Smith et al., Application of Joule Heated Ceramic Melter (JHCM) Technology for Stabilization of Radioactive Waste in the United States, 2015.



Typical chemistry of radioactive waste stored in underground steel tanks at Hanford site in Washington State. 56 million gallons (2.1 × 10^8 liters) of radioactive waste will be immobilized into borosilicate glass.

- Long-term chemical durability when stored in geological repository.



Thorpe et al., *npj Mater. Degrad.* 5 (2021) Article 61

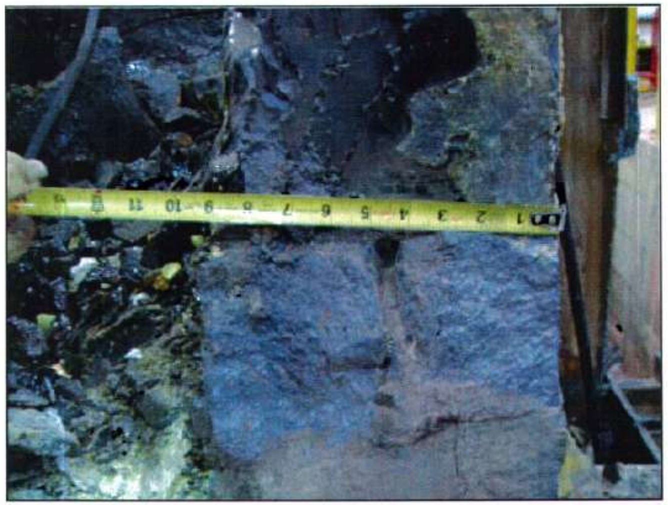
- Solubility of radionuclides in borosilicate glass
  - Sulfur solubility
  - Molybdenum solubility
- Suppression of crystallization
  - Nepheline crystallization

Why is sulfur a problem for nuclear waste vitrification?

Sulfate loading – A Challenge for waste vitrification

- Hanford LAW has high concentration of SO_4^{2-}. HLW also contains SO_4^{2-}.
- SO_4^{2-} is also present in the nuclear waste of France, UK, Japan, China and India.
- SO_4^{2-} has low solubility (<1 wt.%) in borosilicate glasses.
- Exceeding the SO_3 solubility in glass results in the formation of yellow colored "*gall*" salt phase – rich in SO_4^{2-}, Cr, Tc – floating on the melt.
- Conductive and corrosive – Detrimental for the life and safe operation of the melter.

Inside view of DM3300 melter after its lid was removed. SO_4^{2-} rich yellow salt can be seen sticking to the refractory walls.



Approximately 10 cm (4 inches) of loss of K-3 refractory at the melt line.

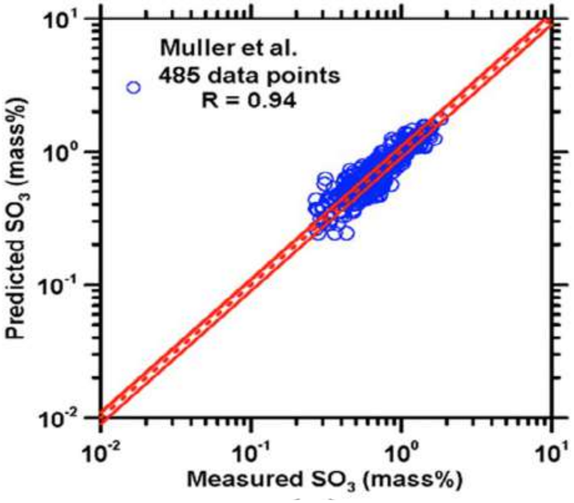
Goel et al., *J. Phys. Chem. C* 126 (2022) 655;
Jin et al., *Int. Mater. Rev.* 68 (2023) 1135

Sulfate loading – A challenge for waste vitrification

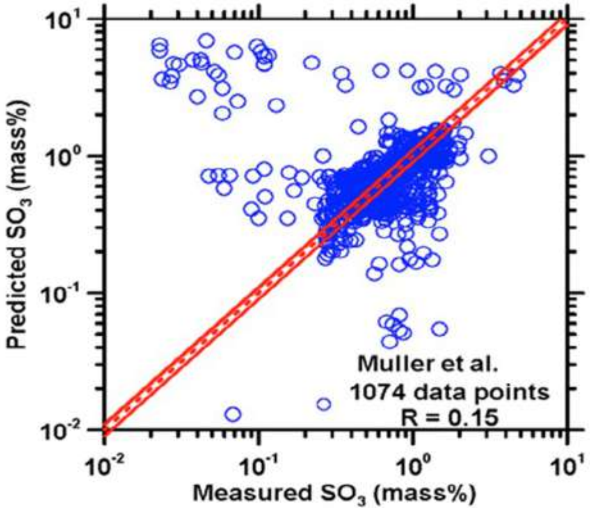
Aim: To design glass compositions with enhanced sulfur loading.

$$W_{SO_3}^{Pred} = \sum_{i=1}^{18} s_i n_i + selected\left\{\sum_{i<}^{q-1}\sum_{j}^{q} s_{ij} n_i n_j\right\}$$

Empirical model to predict sulfate solubility in LAW glasses



Sulfate loading predictive ability of the model comprising data of 485 LAW glasses.



Sulfate loading predictive ability of the model comprising data of 1074 LAW + HLW glasses.

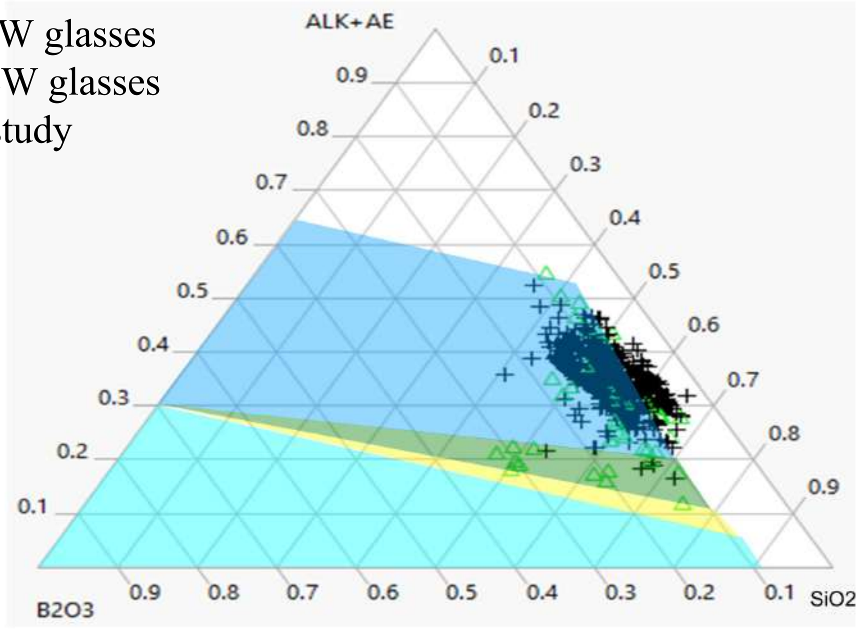
Goel et al., ACS Appl. Mater. Interfaces. 13 (2021) 45

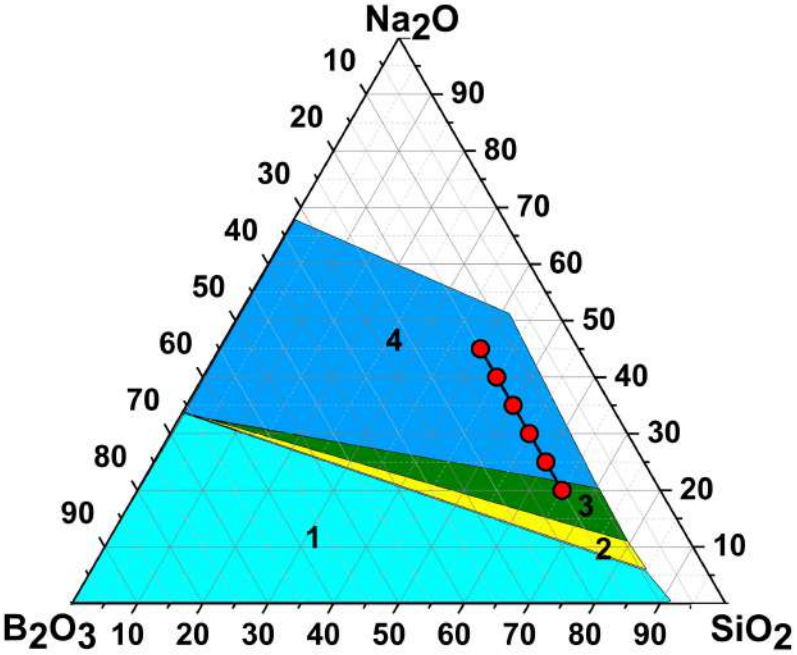
Two options

1. Expand the compositional regions and synthesize 100s – 1000s glasses to collect more experimental data and improve the empirical models.
2. ✓ Understand the chemo-structural drivers controlling the sulfate loading in glasses and develop non-empirical/semi-empirical models powered by experimental data, MD simulations and theory-guided machine learning.

Structural design of borosilicate-based nuclear waste glasses

Black: LAW glasses
Green: HLW glasses
Red: Our study



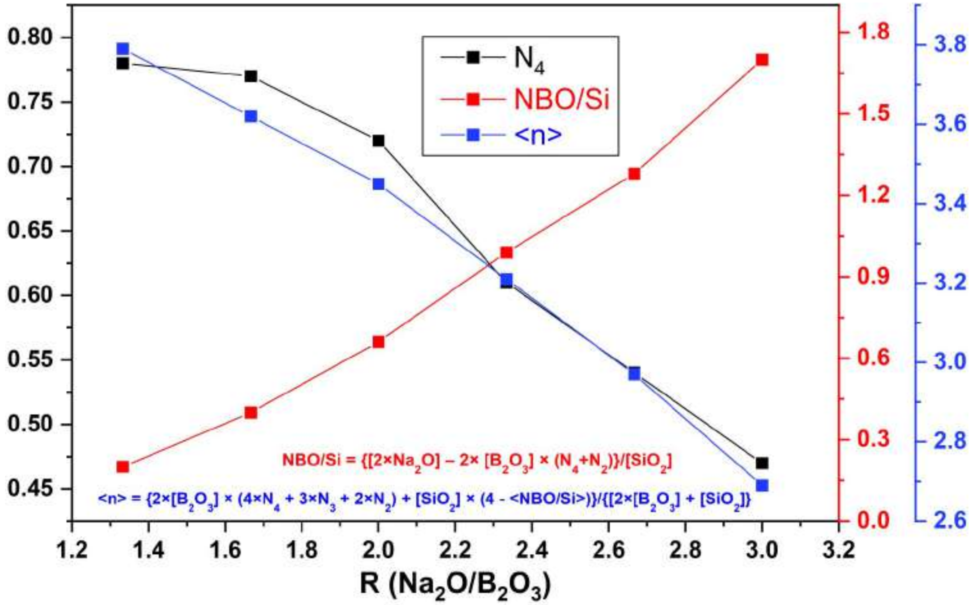


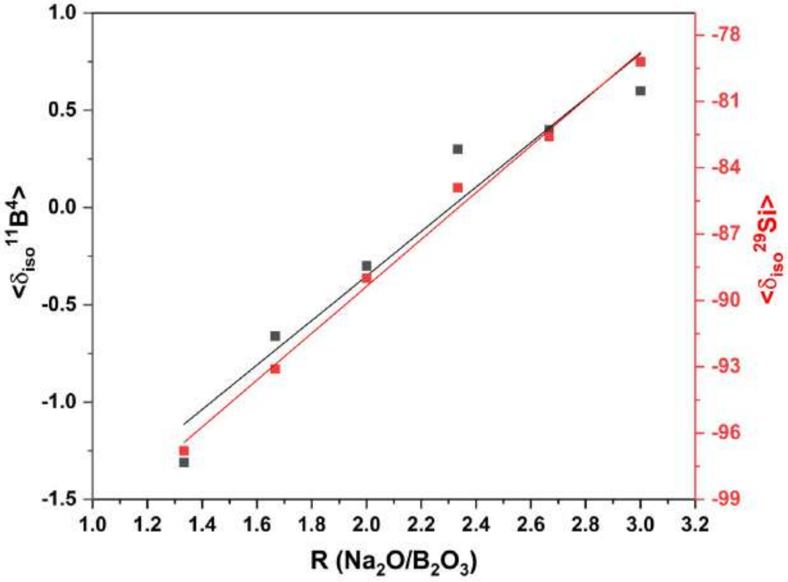
- ➢ Collected the compositional data of >1000 nuclear waste glasses and normalized them to Na_2O – B_2O_3 – SiO_2 and A_2O+AeO – B_2O_3 – SiO_2 ternary systems.

- ➢ Majority of the nuclear waste glasses traversed along high-K (SiO_2/B_2O_3) regions of Dell-Yun-Bray ternary with varying Na_2O/SiO_2 ratio and B_2O_3 being 10 – 20 mol.%.

- ➢ The structure of a series of glasses in the system (20 + x) Na_2O – 15 B_2O_3 – (65 - x) SiO_2 (x = 0 – 25 mol.%) was studied using ^{11}B, ^{23}Na and ^{29}Si MAS NMR spectroscopy and Raman spectroscopy.

Structure of borosilicate-based nuclear waste glasses





- Increasing Na_2O/SiO_2 (and resulting increase in R = Na_2O/B_2O_3) results in a **(1)** gradual replacement of BO_4 units by BO_3 and BO_2O^- units; **(2)** linear increase in the average number of NBOs per Si unit; **(3)** decrease in the average network connectivity, <*n*>, in the glass structure.
- The average chemical shift of ^{29}Si MAS NMR spectra, $<\delta_{iso}{}^{29}Si>$ is directly proportional to Na_2O/SiO_2 and reflects an increasing fraction of Si^3 (and some Si^2 in glasses containing ≥35 mol% Na_2O) units in the glass structure.
- An increase in $<\delta_{iso}{}^{11}B^4>$ with increasing R may be attributed to the increasing connectivity between $BO_{4/2} – SiO_{3/2}O^-$ and $BO_{4/2} – BO_{2/2}O^-$ units.

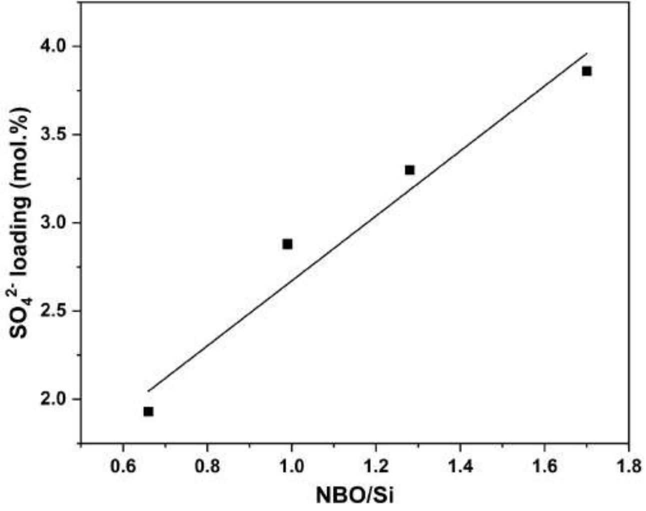
Goel et al., *J. Phys. Chem. C* 126 (2022) 655

Why is it that most nuclear waste glasses have been designed along Na_2O-SiO_2 join in Na_2O-B_2O_3-SiO_2 ternary?

- **High waste loading:** Na^+ has the highest concentration in Hanford waste followed by Al^{3+} and Fe^{2+}/Fe^{3+}.

- **Lower processing temperatures:** Na_2O acts as flux, thus lowering the melting temperature of the waste feed.

- **High sulfur solubility**: Sulfate solubility increases with increase in the fraction of NBOs in the glass structure.

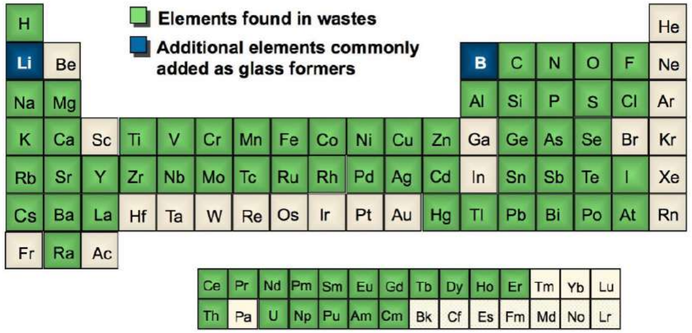


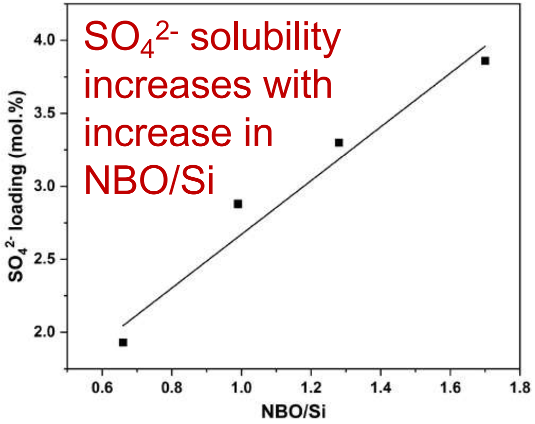
- SO_4^{2-} needs Na^+ for charge-compensation.
- SO_4^{2-} steals Na^+ associated with NBOs, thus repolymerizing the network.

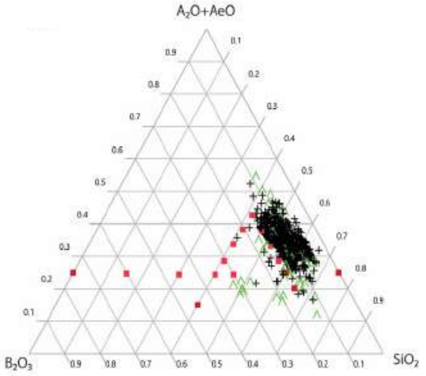
Goel et al., *J. Phys. Chem. C* 126 (2022) 655

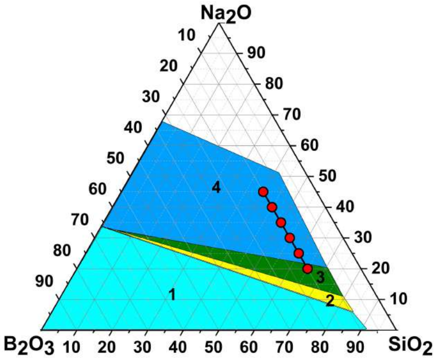
Structural dependence of sulfur solubility in borosilicate glasses

Too Simplified!




SO$_4^{2-}$ solubility increases with increase in NBO/Si

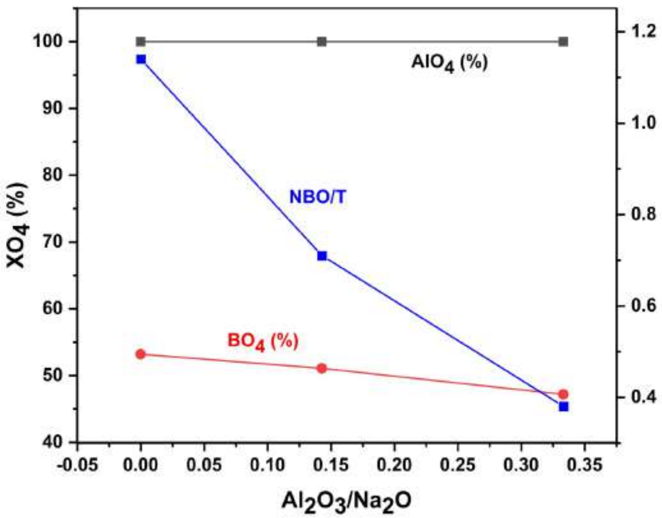


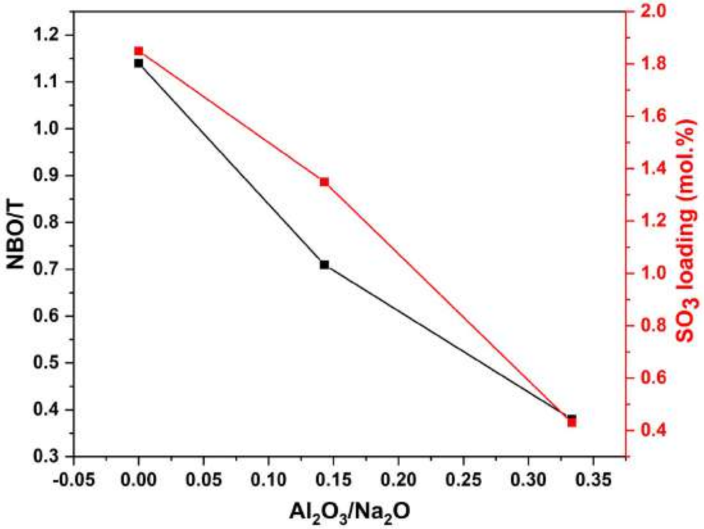


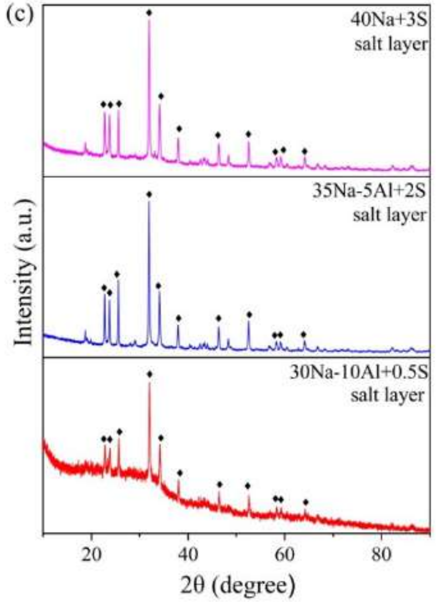
- ➢ Nuclear waste glasses are compositionally complex
- ➢ High Ionic field strength cations (e.g., Li$^+$, Ca^{2+})
- ➢ Al_2O_3 – 2nd largest concentration in the Hanford waste
- ➢ Fe_2O_3 – 3rd largest in the Hanford waste
- ➢ Other elements

Impact of Al_2O_3 on sulfur solubility

(40-*x*) Na_2O–*x* Al_2O_3–10 B_2O_3–50 SiO_2 (*x* = 0, 5 and 10 mol.%)





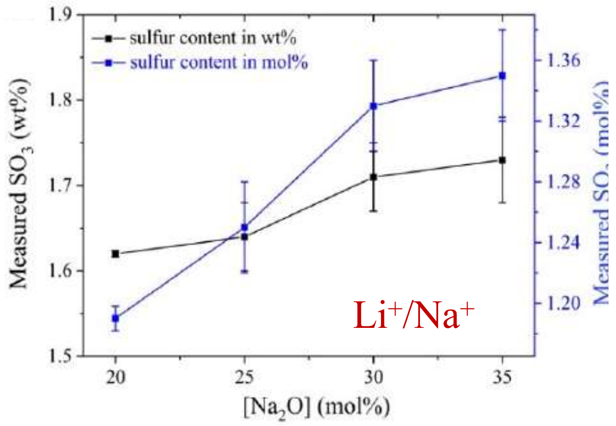


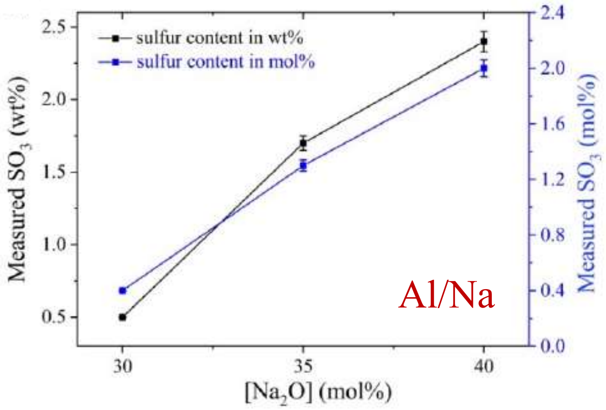
- ➢ ^{27}Al MAS NMR spectroscopy shows Al in 4-coordination, while the ^{11}B MAS NMR shows a decrease in N_4 from 53% to 47% with increase in Al/Na ratio.
- ➢ The NBO/T decreases from 1.14 to 0.38 with increase in Al/Na ratio, thus, suggesting an increased polymerization in the glass structure.
- ➢ SO_3 solubility decreases linearly with decrease in NBO/T.
- ➢ Excess SO_3 crystallizes as Na_2SO_4 and appears as white layer on the glass surface.

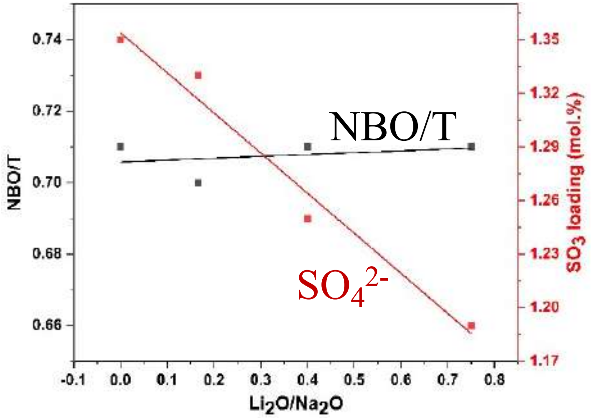
Goel et al., *J. Am. Ceram. Soc.* 104 (2021) 5030

Impact of Li^+/Na^+ on sulfur solubility

$(35-y)\ Na_2O–yLi_2O–5Al_2O_3–10B_2O_3–50SiO_2$ (y = 0, 5, 10 and 15 mol.%)







- ➢ SO_3 solubility decreases with increase in Li^+/Na^+ ratio.
- ➢ The decrease in sulfur solubility is minimal when compared to the impact of Al/Na ratio.
- ➢ Sulfur solubility is decreasing despite minimal change in NBO/T.

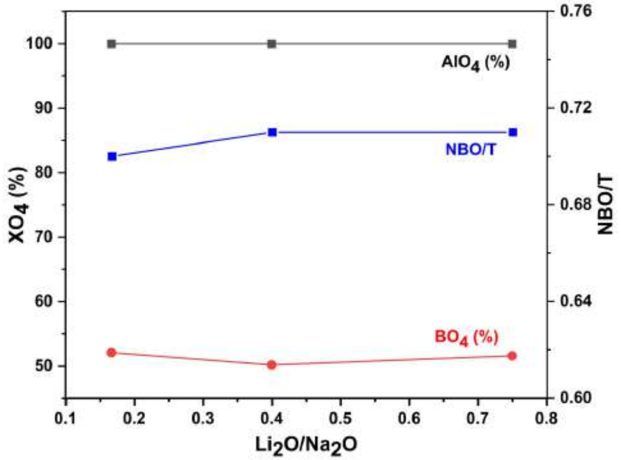
1. Why is there a decrease in SO_3 solubility with changing Li^+/Na^+ when both are alkali cations and there is no change in NBO/T?
2. Why is the decrease so subtle compared to that observed with changing Al_2O_3/Na_2O ratio?
3. Is there a preference (Li^+ or Na^+) for charge compensating SO_4^{2-}?

Goel et al., *J. Am. Ceram. Soc.* 104 (2021) 5030

Impact of Li^+/Na^+ on sulfur solubility

(35-*y*) Na_2O–*y*Li_2O–5Al_2O_3–10B_2O_3–50SiO_2 (y = 0, 5, 10 and 15 mol.%)

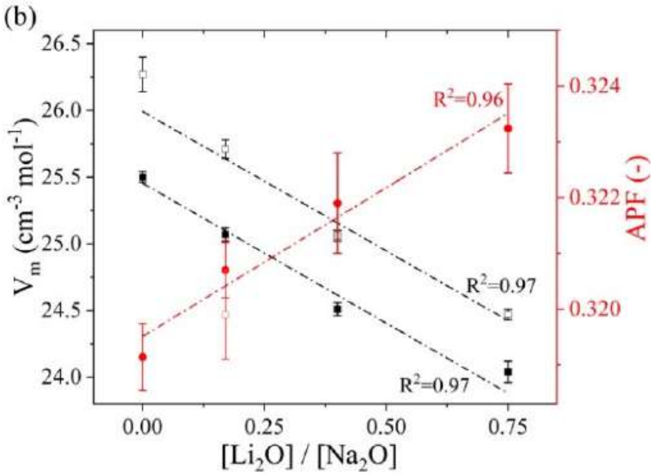
- Aluminum is 4-coordinated and there is negligible change (±1.5%) in N_4 fraction with changing Li^+/Na^+ ratio.
- The NBO/T remains unchanged, i.e., 0.70 – 0.71.



If the degree of polymerization remains unchanged, what is leading to a decrease in SO_3 solubility with increasing Li^+/Na^+ in glasses?

Reason 1: Densification of glass network

- Increased compactness in the glass structure, shown by the increasing atomic packing factor, leads to smaller interstices in the glass network for sulfate units to be accommodated.
- The structural densification is due to the higher cation field strength and smaller size of Li^+ in comparison to Na^+, which results in formation of smaller voids (compared to Na^+) due to the smaller Si−O−T (T=Al & Si) bond angle, and efficient filling up of the voids.



Goel et al., *J. Am. Ceram. Soc.* 104 (2021) 5030

Impact of Li^+/Na^+ on sulfur solubility

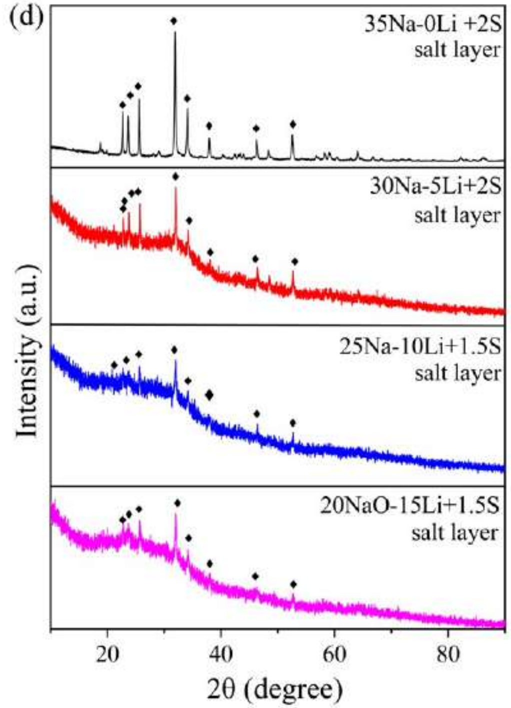
(35-*y*) Na_2O–*y*Li_2O–5Al_2O_3–10B_2O_3–50SiO_2 (y = 0, 5, 10 and 15 mol.%)

Reason 2: Depletion of Na^+ from the alkali inventory

- Exceeding the sulfur solubility in Li/Na borosilicate glasses results in the formation of white salt layer on the surface of glasses.

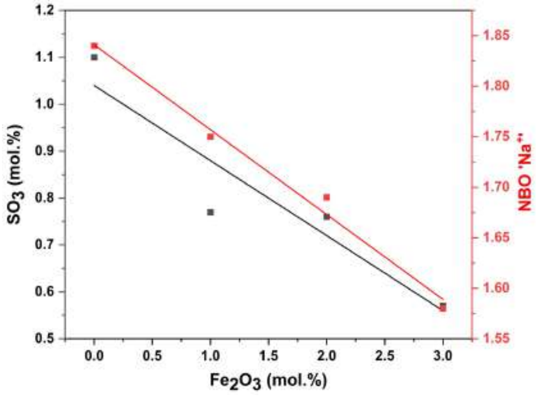
- XRD reveals this layer to be Na_2SO_4. The result are intriguing as no Li_2SO_4 formation can be observed.

- This suggests that SO_4^{2-} tends to be preferentially charge compensated by Na^+ over Li^+ probably because it is easier for SO_4^{2-} to break the Na^+---NBO linkage (20 kCal/mole) compared to Li^+---NBO linkage (36 kCal/mole).



To summarize:

1. The degree of network polymerization has a significant impact on sulfur solubility in borosilicate glasses compared to the ionic field strength of a non-framework cation.
2. High ionic field strength cations lower the solubility of sulfur in borosilicate glasses.
3. The decrease in SO_4^{2-} solubility in glasses as a function of Fe_2O_3 can also be explained based on the decreasing polymerization in the glass network.



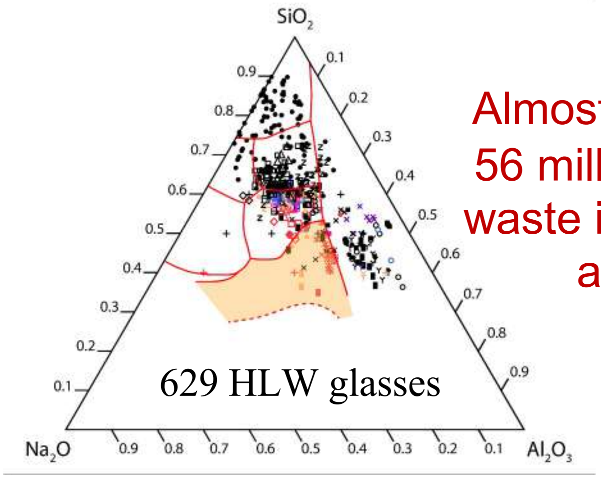
Goel et al., *J. Am. Ceram. Soc.* 104 (2021) 5030; Goel. et al. *J. Phys. Chem. C* (2024) Submitted.

Nepheline crystallization in HLW glasses

Nuclear waste vitrification in the United States

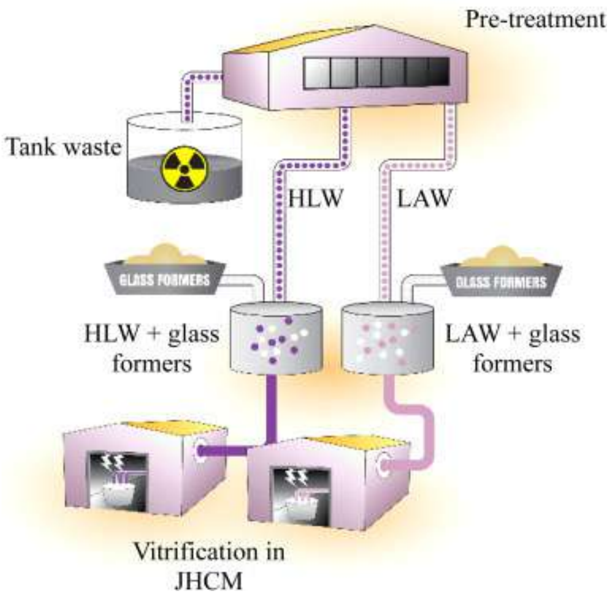
~56 million gallons of high-level radioactive waste is stored in underground steel tanks at Hanford site in Washington state.

Underground waste tanks at Hanford site (before they were buried)



Almost half of the 56 million gallons waste is rich in Na and Al.

	Al-Limited	Al & Na-Limited
Al_2O_3	52.95	45.13
B_2O_3	0.42	0.77
BaO	0.12	0.06
Bi_2O_3	2.53	2.45
CaO	2.38	1.53
CdO	0.05	0.02
Ce_2O_3	0.00	0.00
Cl	0.00	0.00
Cr_2O_3	1.15	1.50
Cs_2O	0.50	0.50
F	1.47	0.48
Fe_2O_3	13.03	5.95
HfO_2	0.00	0.00
K_2O	0.31	1.40
La_2O_3	0.00	0.00
Li_2O	0.38	0.16
MgO	0.26	0.46
MnO	0.00	0.00
Na_2O	7.91	26.88
Nd_2O_3	0.00	0.00
NiO	0.88	0.21
P_2O_5	2.32	4.27
PbO	0.90	0.19
Re_2O_7	0.00	0.00
RuO_2	0.10	0.10
SiO_2	10.81	6.48
SnO_2	0.00	0.00
SO_3	0.44	0.46
TiO_2	0.02	0.36
ZnO	0.18	0.38
ZrO_2	0.87	0.26

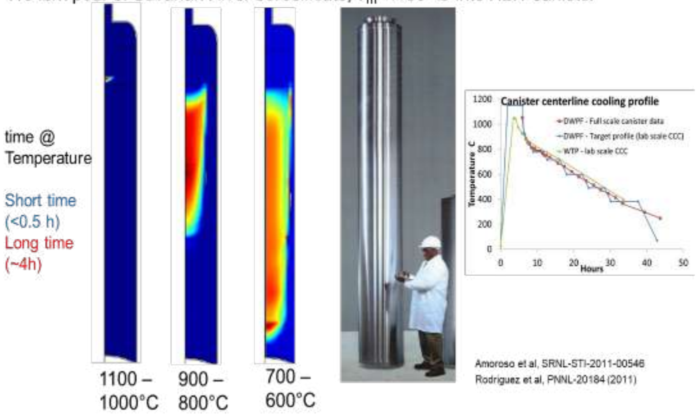


HLW is mixed with SiO_2, H_3BO_3, Na_2O (for Al-limited) Li_2O, CaO, etc., and melted at 1150 ˚C in a JHCM to vitrify it into borosilicate glass.

Nuclear waste vitrification in the United States

Video for representational purpose only

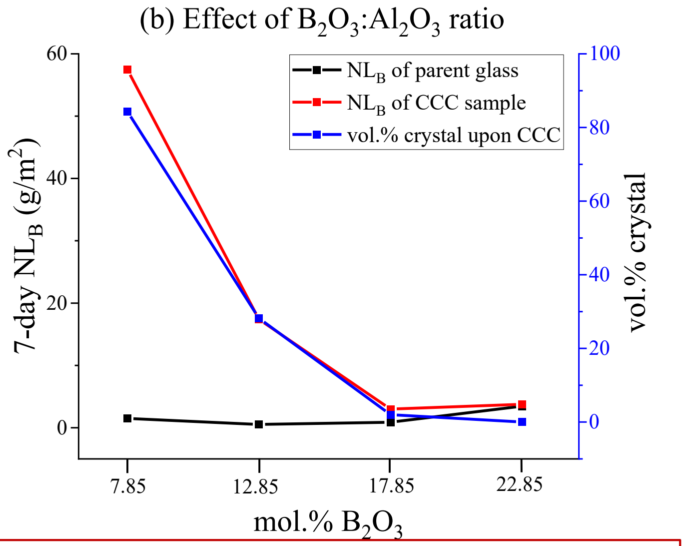
119 lb/h pour of Savanah River borosilicate, T_m=1150 °C into HLW canister



Amoroso et al, SRNL-STI-2011-00546
Rodriguez et al, PNNL-20184 (2011)

Due to poor dissipation of heat from the glass melt inside the steel canister, the glass tends to crystallize into nepheline ($NaAlSiO_4$).

The crystallization of nepheline ($Na_2O•Al_2O_3•2SiO_2$) results in removal of 3 moles of network formers (1 Al_2O_3 + 2 SiO_2) per mole of Na_2O. This impacts the chemical durability of the final waste form.



Normalized loss of boron from glasses as a function of B_2O_3 content and nepheline crystallization.

The impact of nepheline crystallization in glasses on their chemical durability is more severe than increasing the B_2O_3 content.

Predictive modeling to control of nepheline crystallization

Several empirical models have been proposed in last 20 years to design compositions with minimal tendency towards nepheline crystallization.

1. Nepheline Discriminator (ND) model
2. Optical Basicity (OB) Model
3. Machine learning based models
4. Submixture model

All the models are data intensive, statistical and have been designed with one aim, i.e., to predict Go vs. No-Go

Rationale for choosing empirical models over physics/QSPR-based models

1. **Complex:** Functional glasses have significant compositional complexity. Experimentally, it is difficult to decipher the role of every constituent in the glass structure and its impact on crystallization.
2. **Expensive:** Modeling crystallization is a tedious process because of the longer time and length scales associated with the glass than liquids.
3. **Experimental Validation:** The models still need experimental validation.

Problems with empirical models

1. **Conservative:** They can only make predictions in the given compositional domain.
2. **Outliers:** There are always some compositions where the predictions do not match with the experimental results.
3. **No explanation:** These models do not provide scientific explanation for the observed trends.

Quantitative Structure – Property Relationships (QSPR) based Predictive Models

Goal 1: Elucidate the chemo-structural descriptors controlling the crystallization of nepheline in multicomponent glasses.
Challenge: Functional glasses, for example, nuclear waste glasses, are compositionally complex – 20-30 oxides.

$Na_2O – Al_2O_3 – B_2O_3 – SiO_2$

$Na_2O – Al_2O_3 – Fe_2O_3 – SiO_2$

$Na_2O – Al_2O_3 – P_2O_5 – SiO_2$

$Na_2O – CaO/Li_2O – Al_2O_3 – SiO_2$

$Na_2O – CaO/Li_2O – Al_2O_3 – B_2O_3 – SiO_2$

$Na_2O – Al_2O_3 – Fe_2O_3 – B_2O_3 – SiO_2$

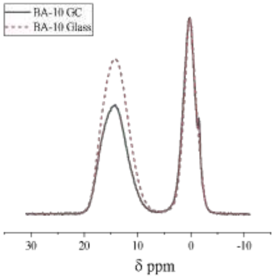
$Na_2O – Al_2O_3 – P_2O_5 – B_2O_3 – SiO_2$

$Na_2O – Fe_2O_3 – Al_2O_3 – B_2O_3 – P_2O_5 – SiO_2$

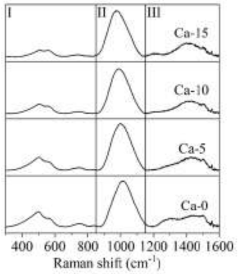
$Na_2O – CaO/Li_2O – Al_2O_3 – B_2O_3 – P_2O_5 – SiO_2$

$Na_2O – CaO/Li_2O – Fe_2O_3 – Al_2O_3 – B_2O_3 – P_2O_5 – SiO_2$

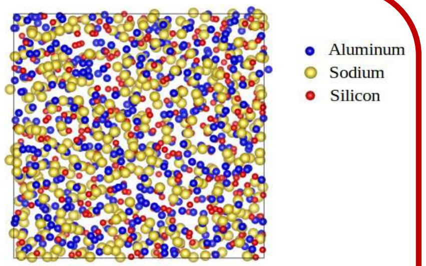
Melt-quench



1D and 2D NMR



Raman

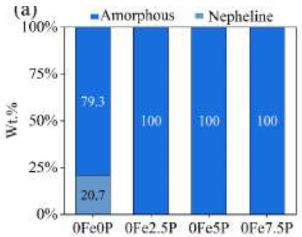


MD simulations

Glass Synthesis

Structure

CCC test



XRD

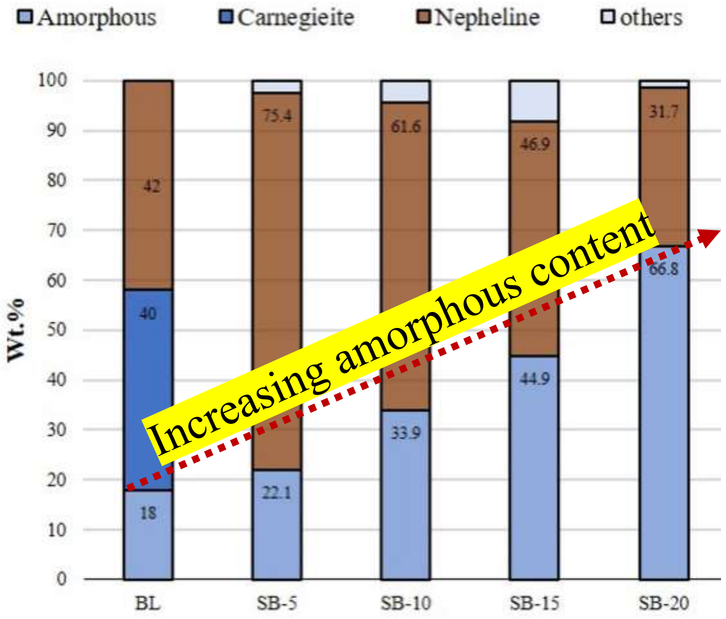
Crystallization

RUTGERS

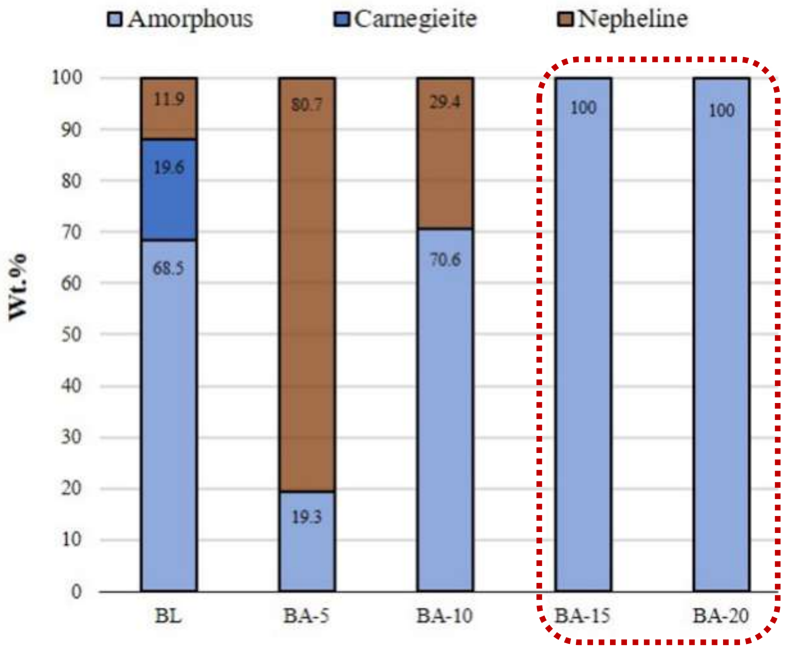
Crystallization in $NaAlSiO_4 - B_2O_3$ glass system

Does B_2O_3 suppress nepheline crystallization?

$25Na_2O–25Al_2O_3–xB_2O_3–(50\text{-}x)\ SiO_2$
$x = 0 – 20$ mol.%



$25Na_2O–(25\text{-}x)Al_2O_3–xB_2O_3–50\ SiO_2$
$x = 0 – 20$ mol.%



B_2O_3 is not highly effective in suppressing nepheline crystallization when substituted for SiO_2 but completely suppresses nepheline crystallization when substituted for Al_2O_3.

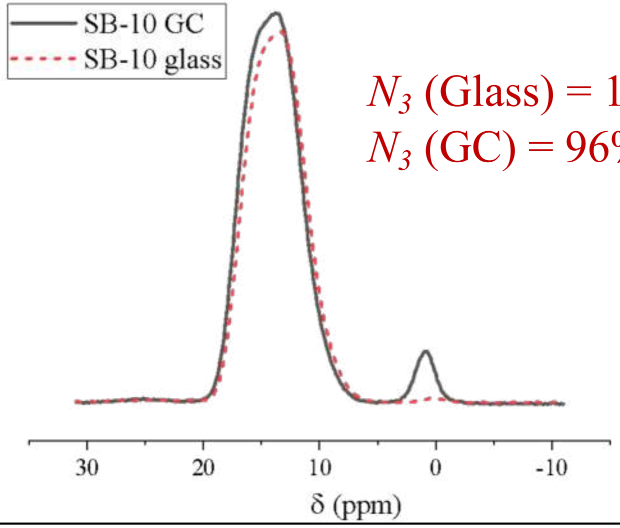
Why is that?

Crystallization in $NaAlSiO_4$ – B_2O_3 glass system

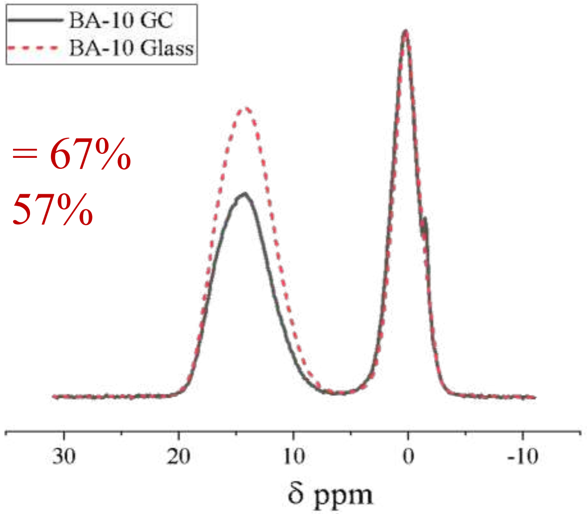
Structural investigation of glasses and glass-ceramics by MAS NMR spectroscopy

$25Na_2O–25Al_2O_3–xB_2O_3–(50-x) SiO_2$
$x = 0 – 20$ mol.%

$25Na_2O–(25-x)Al_2O_3–xB_2O_3–50 SiO_2$
$x = 0 – 20$ mol.%



N_3 (Glass) = 100%
N_3 (GC) = 96%



N_3 (Glass) = 67%
N_3 (GC) = 57%

^{11}B MAS-NMR of glasses and glass-ceramics

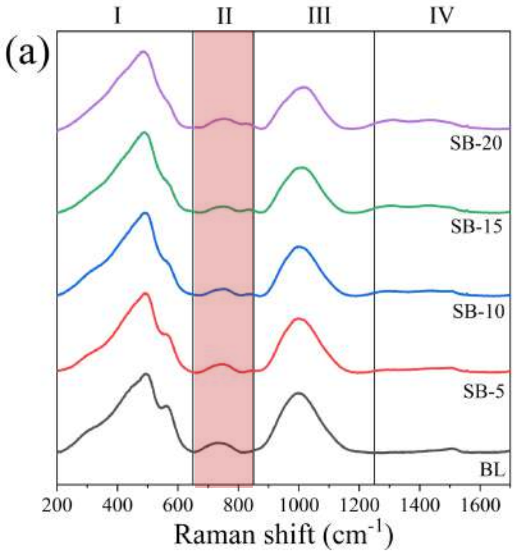
- The broad ^{11}B MAS-NMR spectra of glass-ceramics suggest that all the boron is in the glassy phase.
- ^{27}Al MAS NMR spectroscopy suggests majority of Al^{3+} in glasses is in four-coordination.

MAS NMR spectroscopy could not help us find an answer.

Crystallization in $NaAlSiO_4 – B_2O_3$ glass system

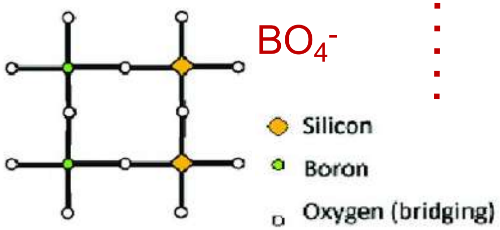
Structural investigation of glasses by Raman spectroscopy

$25Na_2O–25Al_2O_3–xB_2O_3–(50\text{-}x)\ SiO_2$
$x = 0 – 20$ mol.%

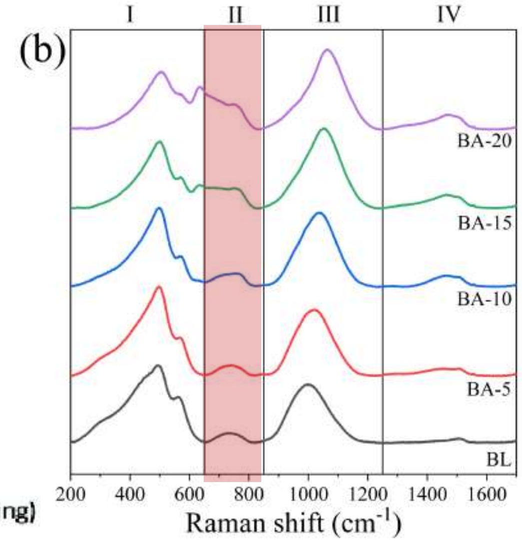


No Raman band at 630 cm^{-1}

Danburite – like borosilicate rings
$Na_2O•B_2O_3•2SiO_2$



$25Na_2O–(25\text{-}x)Al_2O_3–xB_2O_3–50\ SiO_2$
$x = 0 – 20$ mol.%



Raman band at 630 cm^{-1} in glasses with $B_2O_3 \geq 10$ mol.%

Raman spectra of glasses

An increase in B/Al in $25Na_2O–25Al_2O_3–50SiO_2$ leads to an increase in Si–O–B linkages at the expense of Si–O–Al linkages.
Lee and Lee, Geochim. Cosmochim. Acta 268 (2020) 325

- **Hypothesis:** It is the replacement of Si–O–Al linkages by Si–O–B linkages with increasing B/Al ratio that suppresses nepheline crystallization.
- In glasses with varying B/Si ratio, Si–O–Al linkages dominate over Si–O–B linkages, thus leading to the incomplete suppression of nepheline crystallization.

Crystallization in $NaAlSiO_4 – B_2O_3 – P_2O_5$ glass system

Does breaking the Si–O–Al linkages suppress nepheline crystallization?

$25Na_2O–25Al_2O_3–\boldsymbol{xP_2O_5–(50\text{-}x)\ SiO_2}$
$x = 0 – 35$ mol.%

$25Na_2O–\boldsymbol{(25\text{-}x)Al_2O_3–xP_2O_5}–10B_2O_3–40\ SiO_2$
$x = 0 – 20$ mol.%

$25Na_2O–25Al_2O_3–\boldsymbol{yP_2O_5}–10\ B_2O_3–\boldsymbol{(40\text{-}y)\ SiO_2}$
$y = 0 – 15$ mol.%

$25Na_2O–25Al_2O_3–\boldsymbol{zP_2O_5–(10\text{-}z)\ B_2O_3}–40\ SiO_2$
$z = 0 – 10$ mol.%

$[25Na_2O–\boldsymbol{(15\text{-}x)Al_2O_3–xFe_2O_3}–15B_2O_3–45\ SiO_2]_{\boldsymbol{(100\text{-}y)}} – \boldsymbol{yP_2O_5}$
$x = 0 – 5$ mol.%; $y = 0 – 7.5$ mol.%

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Structure and crystallization behavior of phosphorus-containing nepheline ($NaAlSiO_4$) based sodium aluminosilicate glasses

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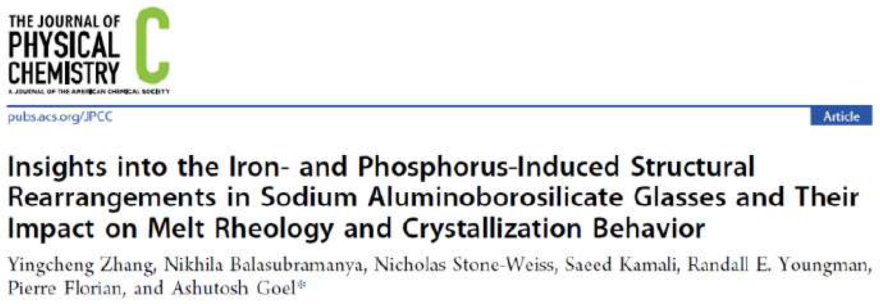
RESEARCH ARTICLE

Journal

Structural dependence of crystallization in phosphorus-containing sodium aluminoborosilicate glasses

Ping Lu[1,2] | Saurabh Kapoor[3] | Libor Kobera[4] | Jiri Brus[4] | Ashutosh Goel[1]



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Article

Insights into the Iron- and Phosphorus-Induced Structural Rearrangements in Sodium Aluminoborosilicate Glasses and Their Impact on Melt Rheology and Crystallization Behavior

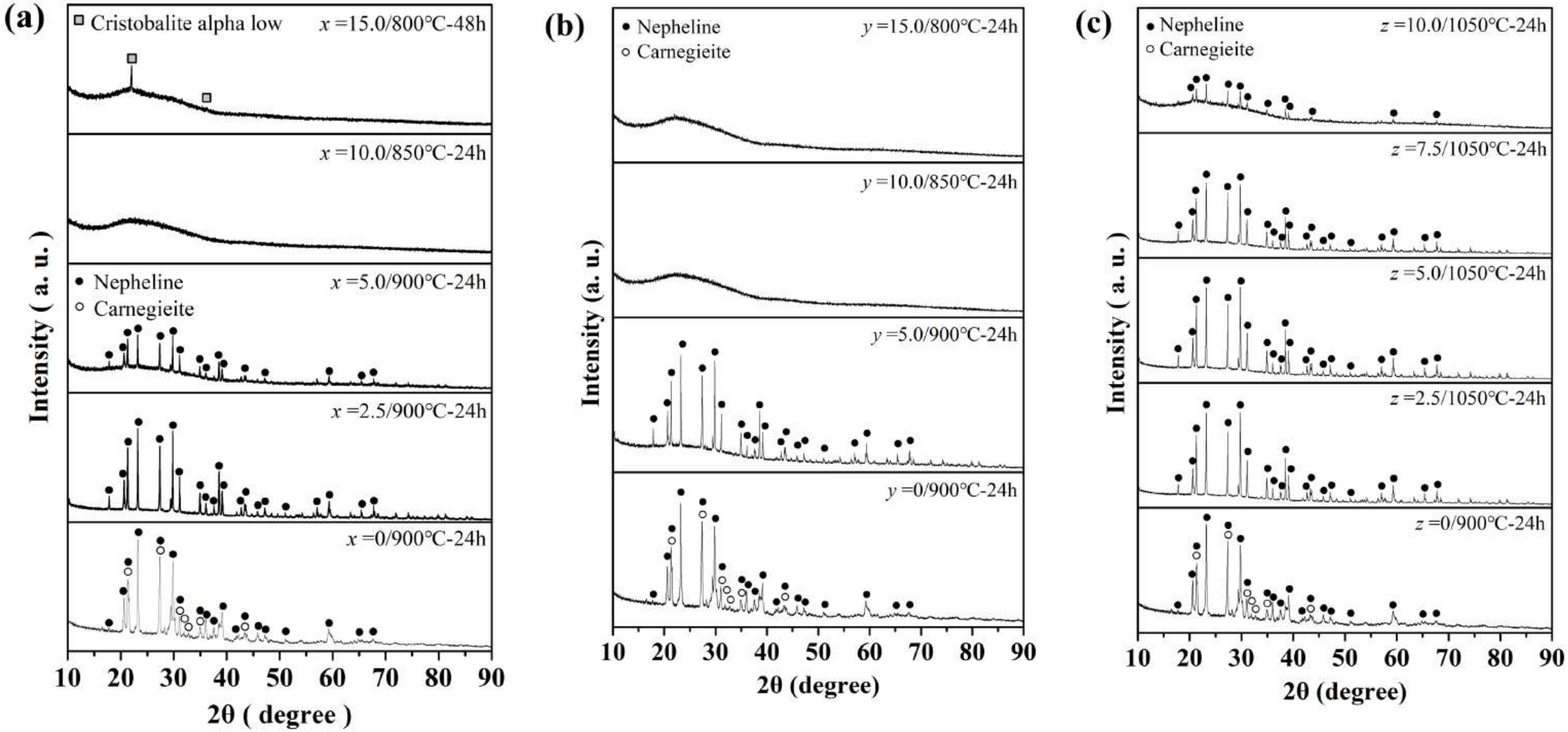
Yingcheng Zhang, Nikhila Balasubramanya, Nicholas Stone-Weiss, Saeed Kamali, Randall E. Youngman, Pierre Florian, and Ashutosh Goel*

Crystallization in $NaAlSiO_4 - B_2O_3 - P_2O_5$ glass system

$25Na_2O–\mathbf{(25\text{-}x)Al_2O_3}–10B_2O_3–\mathbf{xP_2O_5}–40\ SiO_2$
$x = 0 – 15$ mol.%

$25Na_2O–25Al_2O_3–10B_2O_3–\mathbf{yP_2O_5}–\mathbf{(40\text{-}x)\ SiO_2}$
$x = 0 – 15$ mol.%

$25Na_2O–25Al_2O_3–\mathbf{(10\text{-}z)B_2O_3}–\mathbf{zP_2O_5}–40\ SiO_2$
$x = 0 – 10$ mol.%



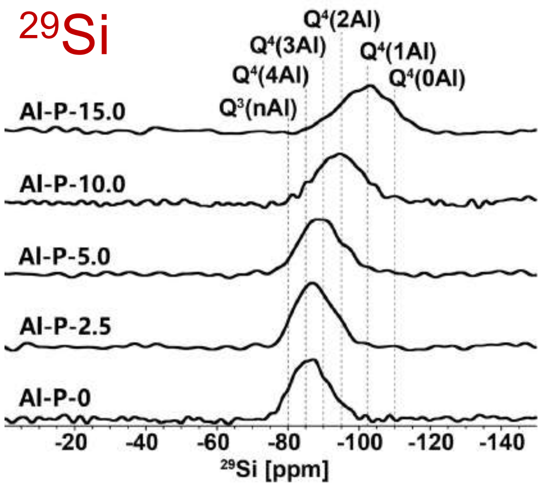
Al/P: $P_2O_5 \geq 10$ mol.% suppresses nepheline crystallization

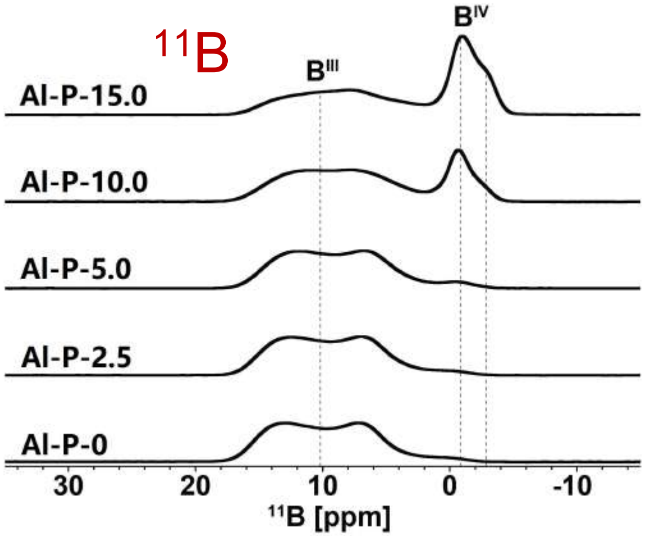
Si/P: $P_2O_5 \geq 10$ mol.% suppresses nepheline crystallization

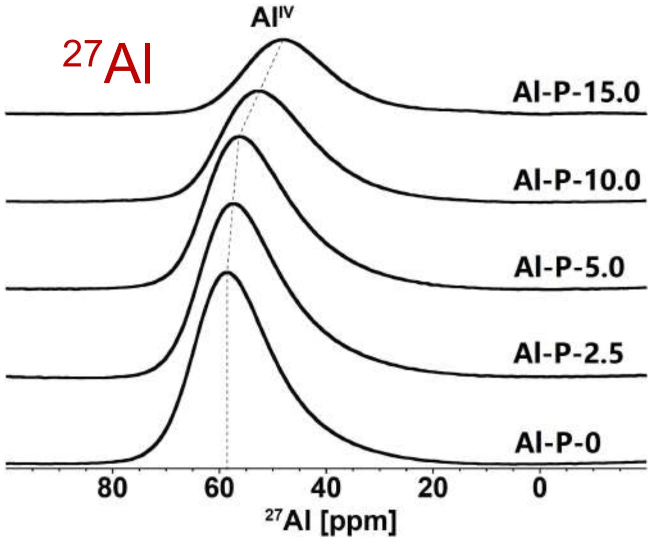
B/P: Does not completely suppress nepheline crystallization

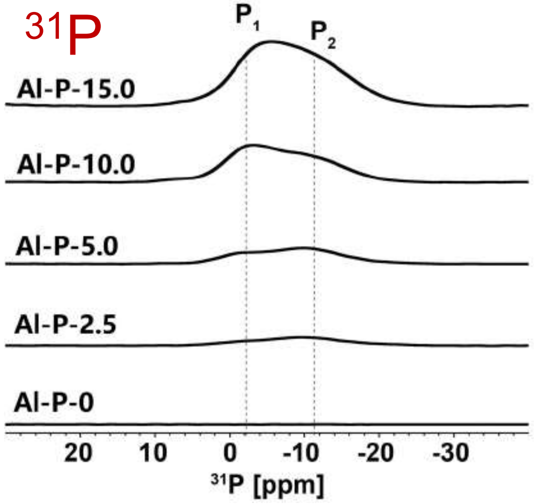
Crystallization in $NaAlSiO_4$ – B_2O_3-P_2O_5 glass system

Structural investigation of glasses by MAS NMR spectroscopy









MAS NMR spectroscopy suggests the formation of Al–O–P linkages over Si–O–Al linkages in the glass structure, thus, suppressing the crystallization in the investigated glasses.

What if we do not change any network former ratios. Instead, what if we substitute non-framework cations, for example, Na^+/Ca^{2+}?

Impact of CaO on nepheline crystallization

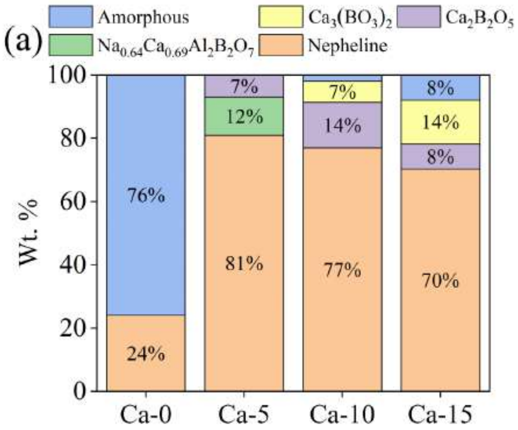
$Na_2O – CaO – Al_2O_3 – B_2O_3 – SiO_2$

$[25Na_2O–25Al_2O_3–10B_2O_3–50SiO_2]_{100-x} – x\text{CaO}$
$x = 0 – 15$ mol.%

OB > 0.57

$(25-y)Na_2O–y\text{CaO}–17.5Al_2O_3–12.5\ B_2O_3–50\ SiO_2$
$x = 0 – 15$ mol.%

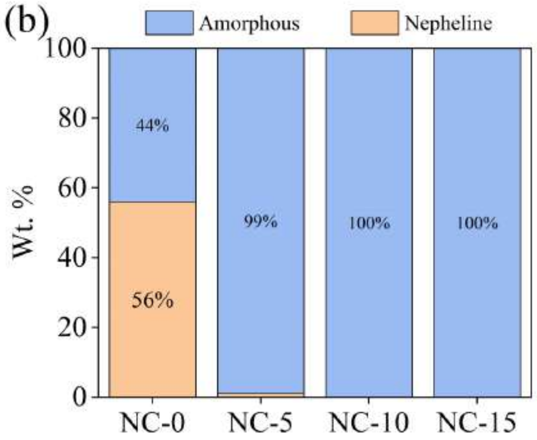
OB ≤ 0.57



CaO addition increased propensity toward nepheline crystallization

Rationale for glass composition design

1. Since the ratio of network formers is not being changed, there should be minimal impact on Si–O–Al linkages in the glass structure.
2. According to optical basicity model, if the optical basicity of a glass composition is <0.57, it will not crystallize nepheline.



5 mol.% CaO substitution for Na_2O suppressed nepheline crystallization

Why do glasses with optical basicity lower than 0.57 show minimal tendency towards devitrification, while the glasses with OB > 0.57 crystallize rapidly?

Is our hypothesis still valid?

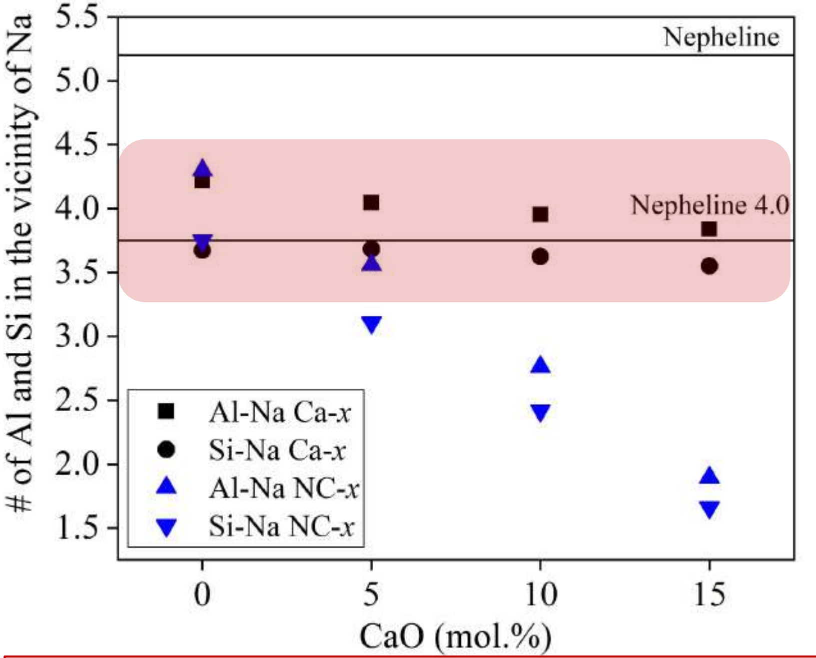
Impact of CaO on nepheline crystallization

Structural investigation of glasses by MAS NMR spectroscopy and MD simulations

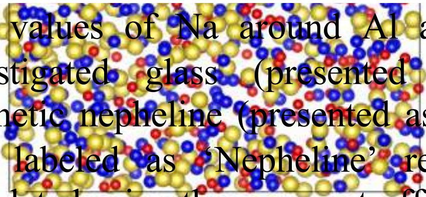
Structure of glasses with OB > 0.57

- The addition of CaO pushes Na^+ closer to AlO_4 units in the glass structure, while Ca^{2+} prefers to associate with borate phase (from MAS NMR and MD simulations).
- The addition of CaO promotes de-mixing between borate and silicate units in glasses with OB > 0.57, while the mixing between aluminate and silicate units (Si–O–Al) increases or remains identical (from ^{29}Si-^{11}B and ^{29}Si-^{27}Al D-HMQC NMR spectroscopy).
- The environment of aluminosilicate network in these glasses is similar to that observed in nepheline crystal (as per MD simulations).

Nepheline crystallization is favored!



The values of Na around Al and Si units in the investigated glass (presented as symbols) and synthetic nepheline (presented as a solid lines). The line labeled as 'Nepheline' represents the value calculated using the same cut-off radius as those used in glass and the line labeled as 'Nepheline 4.0' represents the value calculated using a fixed cut-off radius of 4.0 Å. (Note: Al-Na and Si-Na numbers are identical in crystalline nepheline, thus represented as one single line)



Snapshot of the MD structure of Ca-15 glass showing the aggregation of Ca and B atoms (upper panel), and Na, Al and Si atoms (lower panel).

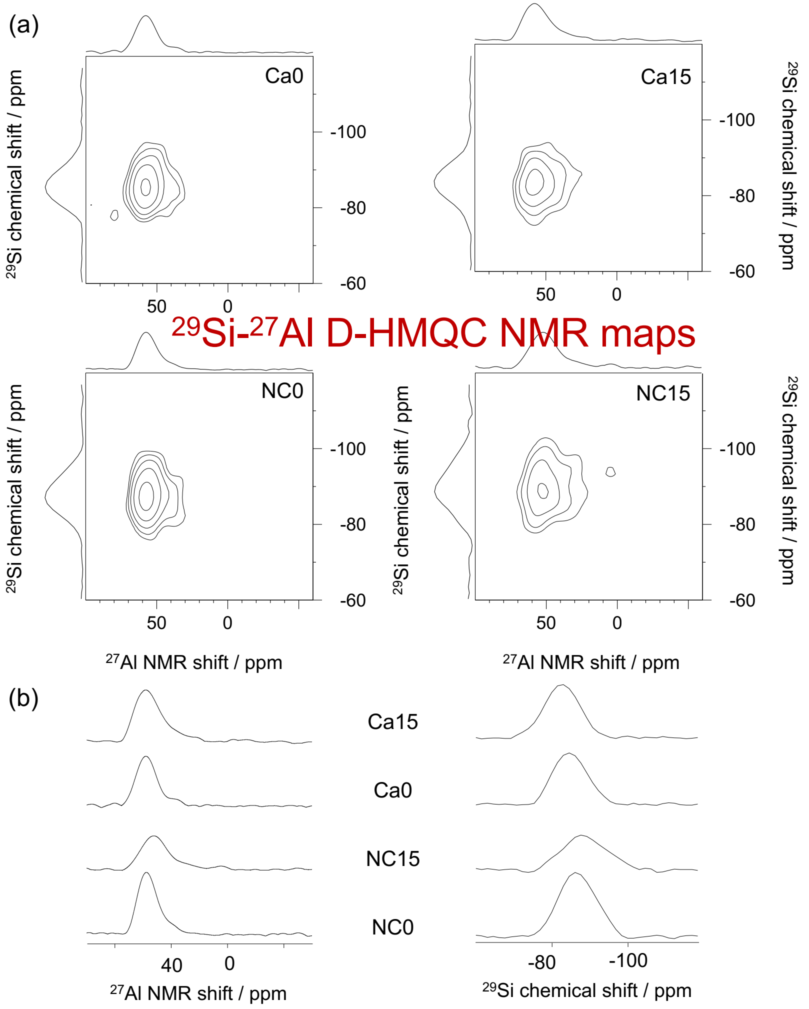
Impact of CaO on nepheline crystallization

Structural investigation of glasses by MAS NMR spectroscopy and MD simulations

Structure of glasses with OB ≤ 0.57

- We studied mixing between network forming moieties using ^{11}B-^{29}Si and ^{27}Al-^{29}Si Dipolar heteronuclear multiple quantum coherence (D-HMQC) NMR spectroscopy.
- An increase in CaO/Na_2O in the glasses results in a decreased Al/Si mixing, i.e., lower Si–O–Al connectivity (from D-HMQC spectroscopy).

Our hypothesis is still valid!



^{29}Si-^{27}Al D-HMQC NMR maps

^{29}Si-^{27}Al D-HMQC NMR projections

Quantitative Structure – Property Relationships (QSPR) based Predictive Models

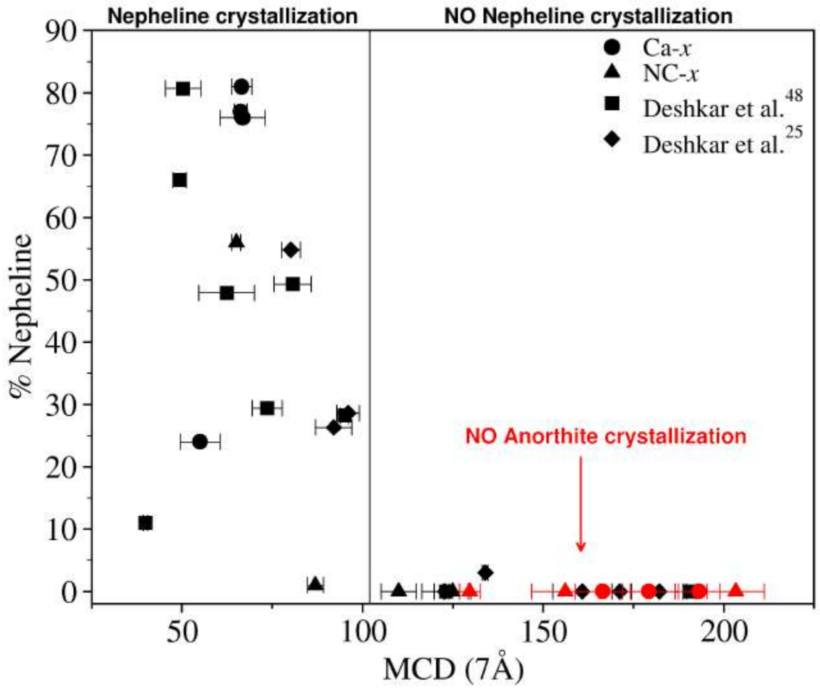
Goal 1: Elucidate the chemo-structural descriptors controlling the crystallization of nepheline in multicomponent glasses.

Goal 2: Development of a QSPR-based predictive model to predict nepheline crystallization in functional glasses

Challenge: Functional glasses, for example, nuclear waste glasses, are compositionally complex – 20-30 oxides.

Cluster analysis model (powered by MD simulations)

- **Assumption:** Nucleation and growth of crystalline phases in a multicomponent oxide glass is facilitated by clusters of atoms (known as 'embryos') in the glass structure, with their stoichiometry and structure similar to that of the crystal phase.
- The cluster analysis explores simulated structures quantifying the similarity between the atomic environments in glass and the reference crystal.
- Atomic aggregates (clusters) within a pre-defined cutoff from the central atom in the glass model are compared with the ones of a reference crystalline structure, providing a cumulative displacement between the radial distribution function up to the pre-defined cutoff.

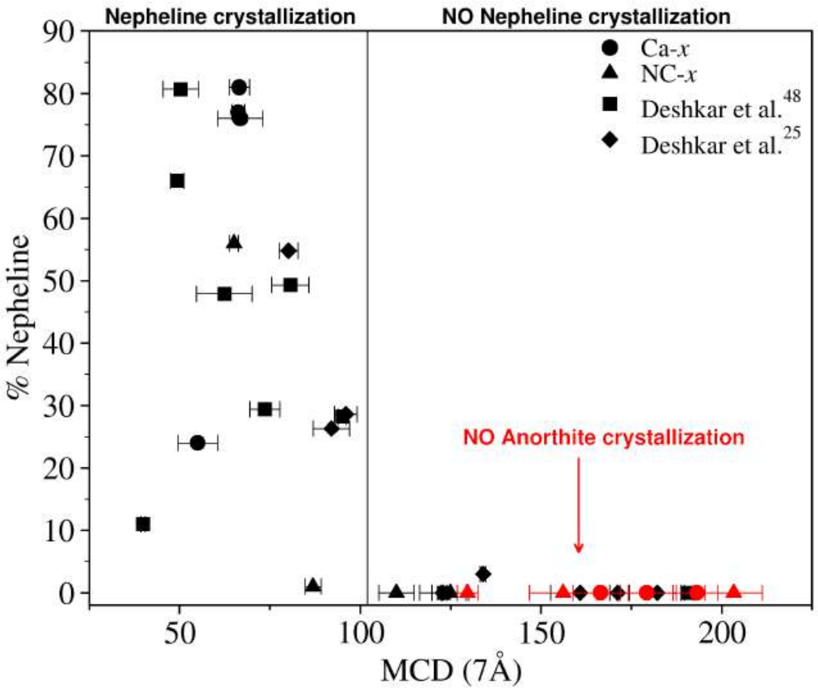


Minimum Cumulative Displacement (MCD) as a function of % nepheline crystallization in the glasses

Quantitative Structure – Property Relationships (QSPR) based Predictive Models

Cluster analysis model (powered by MD simulations)

- We focused on the local environment of oxygen atoms within a cut-off of 7 Å, which can be compared with six different oxygens in synthetic nepheline.
- The minimum cumulative displacement (MCD) averaged among the six oxygen sites in nepheline crystal has been computed and used as a guideline to estimate the possible crystallization of nepheline in glass.
- All the glasses with high propensity of nepheline crystallization exhibit an MCD < 102.



Minimum Cumulative Displacement (MCD) as a function of % nepheline crystallization in the glasses

The cluster analysis model correctly predicted the tendency towards nepheline crystallization in glasses where other empirical models failed.

Conclusions and Future Outlook

- An attempt has been made to elucidate the chemo-structural drivers controlling the sulfur loading and crystallization problem in nuclear waste glasses.

- A similar approach can also be used to understand the drivers controlling molybdenum solubility in borosilicate glasses.

- The knowledge and information derived from these investigations can be used to develop physics-based QSPR models to design glasses with enhanced waste loadings.

- Our future studies will focus on **(1)** developing non-empirical models to predict sulfur solubility in borosilicate glasses; **(2)** testing and improving the predicting ability of the cluster analysis model with glasses exhibiting more compositional complexity; **(3)** Expanding the models over a broad compositional space and phase assemblages.


Graduate
Studies