Understanding the influence of iron on crystallization kinetics of nepheline based glasses

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Introduction

- Hanford site in Washington is home to 55 million US gallons of high level radioactive waste rich in sodium, alumina and iron.
- The strategy is to vitrify this waste in borosilicate glasses.
- Crystallization of nepheline/carnegeite ($NaAlSiO_4$) in glass melts during vitrification and canister cooling is a big challenge as it severely deteriorates the chemical durability of the glass.
- As the HLW borosilicate glasses are similar to basalt glass on a borate-free basis and as no borate phase crystallize on the liquidus, the crystallization chemistry of waste glasses can be described by the known phase relations of the geochemical basalt quaternary Na_2O-Al_2O_3-Fe_2O_3-SiO_2 system.
- The objective of this study is to understand the influence of iron on the thermal stability and crystallization kinetics of model sodium- and alumina- rich simplified silicate glasses in the Na_2O-Al_2O_3-Fe_2O_3-SiO_2 system designed in the primary crystallization field of nepheline.
- The results obtained from this study will form the baseline for understanding the nucleation and crystallization kinetics of multicomponent complex nuclear waste glasses in future.

Experimental

- **Glass synthesis**
  - A series of glasses with compositions $25Na_2O$ – (25-z) Al_2O_3 – zFe_2O_3 – $50SiO_2$ (mol.%) where z varies between 0 – 5% has been prepared by melt-quench technique. Glasses have been labelled in reference to their Fe_2O_3 content, i.e. Fe-z.
  - We could not obtain amorphous glasses with Fe_2O_3 > 5 mol.% .
  - Glass batches comprising oxides and carbonates were melted at 1650 ºC in Pt-Rh crucibles for 2 h. The melts were quenched in cold water to yield ~90 g of glass.
- **Crystallization kinetics during heating of glasses**
  - Thermal stability and crystallization kinetics of glasses was studied using differential thermal analysis (DTA). Thermal scans (30 – 1580 ºC) were collected on glass particles (particle size: 0.5 mm – 1 mm) at four different heating rates: 5, 10, 15 and 20 K min^{-1} in air and inert (N_2) atmosphere.
  - Non-isothermal crystallization kinetics of the glasses was studied using the Augis-Bennett method (Eq. 1) and Ozawa method (Eq. 2):

$$\ln(\beta/T_p) = -E_A/RT_p + \ln k_0 \quad (1)$$

$$\ln[-\ln(1-x)] = -n\ln\beta + \text{constant} \quad (2)$$

E_A is the activation energy of crystallization, T_p is the peak temperature of crystallization (obtained from DTA), β is the heating rate, x is the crystallization fraction and n is the Avrami parameter.

  - In accordance with the crystallization data obtained from DTA, glasses were heated in the crystallization temperature range and air quenched.
  - Glasses were also heated from 30 ºC to 800, 900 and 1000 ºC for 1 h, respectively, in air and inert (N_2) atmospheres, at heating rate of 10 K min^{-1}.
  - Resulting glass-ceramics were characterized for their crystalline phase evolution by X-ray diffraction (XRD) and scanning electron microscopy (SEM).
- **Conversion of melt – to glass-ceramic during cooling**
  - DTA data was also collected for all the glasses during their conversion from melt – to – glass-ceramic during cooling at different cooling rates, in air and inert (N_2) atmosphere.
  - In accordance with the DTA data, conversion of melt to glass-ceramic during cooling was studied by re-melting the glass frit in Pt-Rh crucibles at 1650 ºC.
  - The melt was allowed to cool at 10 K min^{-1} and was air quenched at different temperatures (as per DTA data).
  - The as obtained glass-ceramics were characterized by XRD and SEM

Results

Crystallization kinetics of glasses during heating

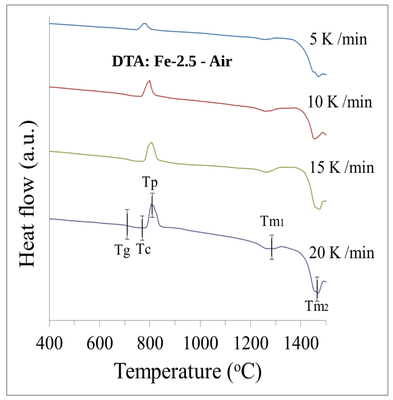


Figure 1: DTA scans of glasses containing 2.5 mol.% Fe_2O_3, in air atmosphere

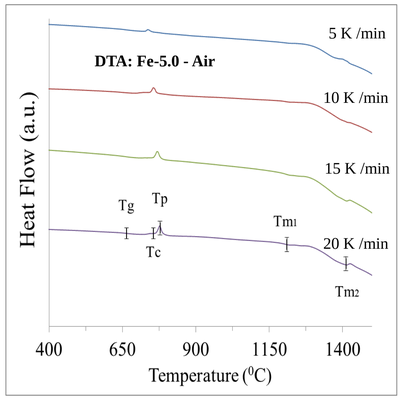


Figure 2: DTA scans of glasses containing 5 mol.% Fe_2O_3, in air atmosphere

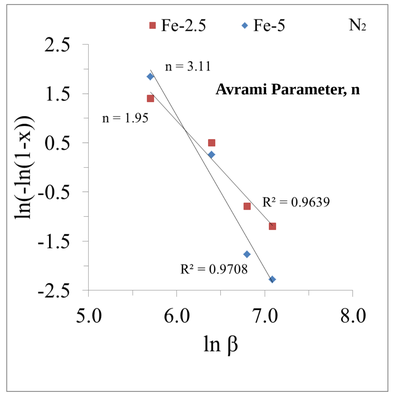


Figure 3: Avrami Parameter, n, indicates the type of crystallization mechanism. **Fe-2.5**: n = 1.95 indicates simultaneous surface and volume (mixed) nucleation. **Fe-5**: n = 3.11 indicates volume nucleation.

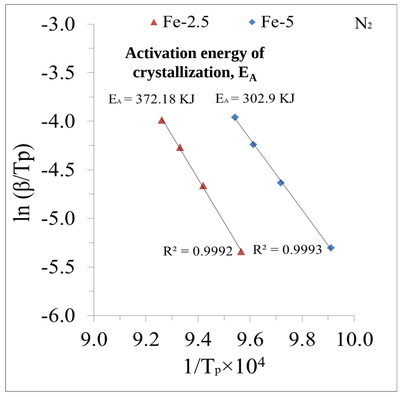


Figure 4: Activation energy of crystallization, E_A, indicates the crystallization tendency. Glass Fe-5 has a lower E_A than Fe-2.5, so it is has a higher crystallization tendency.

- Incorporation of Fe_2O_3 in glasses decreases their crystallization temperature and increases their crystallization tendency.
- Parent glass (stoichiometric nepheline composition) is prone to surface crystallization. Incorporating 5 mol.% Fe_2O_3 in these glasses transforms the crystallization kinetics from surface to volume nucleation.
- Crystallization kinetics of glass Fe-2.5 is affected by the environment (N_2 vs. Air) while no significant impact of environment could be seen for glass Fe-5.

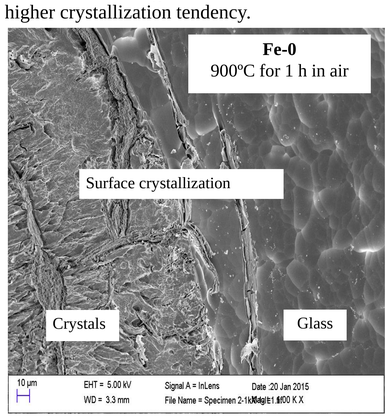
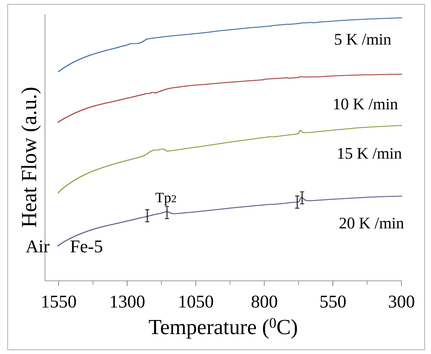


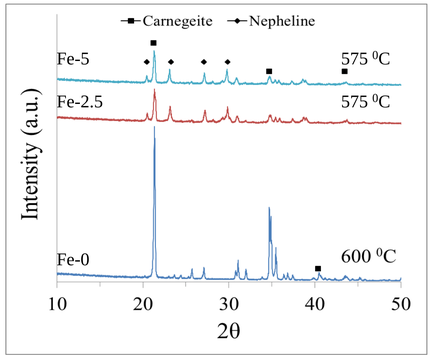
Table 1: Activation energies and Avrami parameters of glass samples in both air and N_2 atmospheres.

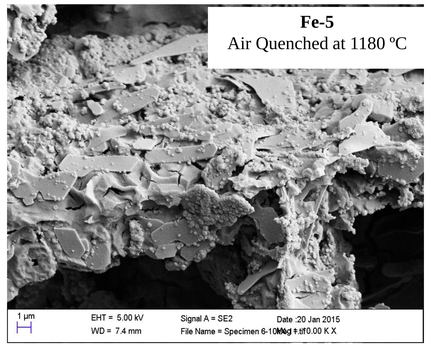
Sample	Environment	Activation Energy (KJ)	Avrami
Fe-2.5	Air	410.89	1.81
Fe-5	Air	295.47	3.06
Fe-2.5	N_2	372.18	1.95
Fe-5	N_2	302.88	3.11

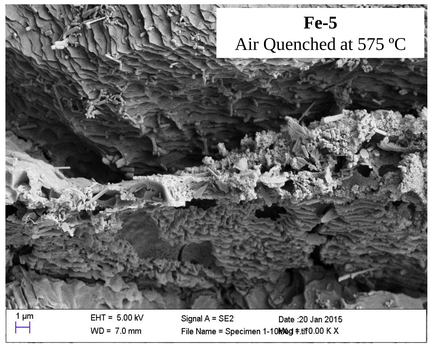
Results (cont'd.)

Conversion of melt to glass-ceramic during cooling









- Devitrification in all the glasses begins with the crystallization of carnegeite ($NaAlSiO_4$, orthorhombic) (~1200 ºC).
- Prolonged heat treatments leads to the crystallization of nepheline ($NaAlSiO_4$, hexagonal) (~1200 ºC) as a secondary phase.
- Fe_2O_3 promotes the crystallization of nepheline over carnegeite *via* formation of magnetite as nucleation site.

Discussion

- Iron incorporation prenucleates the glasses which upon heat treatment result in the formation of magnetite phase as nucleation sites, thus, shifting the mechanism of crystallization from surface to volume.
- Unlike carnegeite, the crystal structure of nepheline allows partial substitution of Fe^{3+}/Al^{3+}. This promotes the crystallization of nepheline over carnegeite in iron-containing glasses.

Conclusions

- Iron incorporation in nepheline-based sodium aluminosilicate glasses shifts crystallization mechanism from surface to bulk
- Our results indicate that atmosphere does affect the crystallization kinetics of iron-containing aluminosilicate glasses but only when Fe_2O_3 concentration is low.
- Since nepheline crystal structure can easily accommodate iron in comparison to carnegeite, iron seems to promote nepheline formation in these glasses at the expense of carnegeite through formation of Fe_3O_4 phase as nucleation site.
- Future work will be focused on adding compositional complexity to these glasses and studying them further for their nucleation and crystallization behavior.

References

- McCloy et al., *J. Non-Cryst. Solids* 409 (2015) 145; Goel et al., *J. Non-Cryst. Solids* 358 (2012) 674
- Jantzen and Brown, *J. Am. Ceram. Soc.* 90 (2007) 1880

Acknowledgments

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