IMPROVING THE CHEMICAL DURABILITY OF RADIATION STABLE GLASSES: THE EFFECT OF $\text{Al}_2\text{O}_3$ OR $\text{ZnO}$ INCORPORATION

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Outline of Presentation

- Overview of composition dependence in radiation stability
  - In Pile
  - Radiation Bombardment
  - Important Conclusions
- Chemical Durability Aspects
  - Effect of ZnO incorporation
  - Effect of Al₂O₃ incorporation
  - Conclusions
  - Further Studies Planned
Dose and Atomic Displacement: What does the Damage?

- Cumulative $\alpha$ dose will exceed cumulative $\beta + \gamma$ dose at $10^5$ yr
- $\alpha$ decay events produce 3 – 4 orders of magnitude greater cumulative atomic displacements than $\beta$ decay events
Glass Properties: Effects

**Structural Changes:**
- Atoms displaced
- Thermal energy deposited into network
- Polymerization/De-polymerization (crystallization possible)

**Consequences:**
- Production of occluded gases (He & O₂)
- Changes in waste form properties
  - ✓ Leach resistance
  - ✓ Hardness
  - ✓ Fracture toughness
  - ✓ Stored energy
  - ✓ Glass transition temperature – Tᵥ
  - ✓ Compaction/ Swelling – Density variation
Post Irradiation Characterization

Density Variation

<table>
<thead>
<tr>
<th></th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTRS (Base)</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>LTRS (Waste)</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>R7T7 (Base)</td>
<td>2.4</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Density increases 1 – 3 %

Chemical Durability \( \left( L_{Na}, \text{g/cm}^2/\text{d} \right) \)

<table>
<thead>
<tr>
<th>Code</th>
<th>Before Irradiation</th>
<th>After Irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTRS (base)</td>
<td>( 3.2 \times 10^{-5} )</td>
<td>( 2.7 \times 10^{-5} )</td>
</tr>
<tr>
<td>LTRS (waste)</td>
<td>( 6.0 \times 10^{-6} )</td>
<td>( 4.6 \times 10^{-6} )</td>
</tr>
<tr>
<td>R7T7 (base)</td>
<td>( 2.2 \times 10^{-5} )</td>
<td>( 3.3 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

Chemical Durability Unchanged

Summary of Results of In-Pile Irradiation

- Microhardness: \( \downarrow \sim 20\% \)
- Tg: \( \downarrow \sim 1 – 3\% \) (Thermal relaxation/annealing effect?)
- Stored Energy: LTRS base: 93 J/g; R7T7 base: 44 J/g
Observations and Inferences

• No oxygen release at lower temperature (573K)
• Total He: ~2 \times 10^{19} \text{ atoms} (20\% of expected value)
• Total O_2: ~4 \times 10^{20} \text{ atoms}
• Occluded He and O_2 in irradiated glass indicates breaking of oxide bonds, due to He and recoil damage
Post Irradiation characterization

Raman spectroscopy

AVS glass

Increasing boroxyl rings

Evolution of silicate polymerization

• Hints at phase separation under irradiation
• Tetrahedral $BO_4$ converted into trigonal $BO_3$
• Possible reduction in microhardness by plastic flow

Recorded under Indo-French CEA Project
Composition Range of Boro-Silicate Glass

<table>
<thead>
<tr>
<th>Composition and structural parameters of NBS glasses</th>
<th>NBS-1 (Mole %)</th>
<th>NBS-2 (Mole %)</th>
<th>NBS-3 (Mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Component</strong></td>
<td><strong>SiO₂</strong></td>
<td><strong>B₂O₃</strong></td>
<td><strong>Na₂O</strong></td>
</tr>
<tr>
<td></td>
<td><strong>55.00</strong></td>
<td><strong>20.00</strong></td>
<td><strong>25.00</strong></td>
</tr>
<tr>
<td></td>
<td><strong>60.00</strong></td>
<td><strong>20.00</strong></td>
<td><strong>20.00</strong></td>
</tr>
<tr>
<td></td>
<td><strong>53.40</strong></td>
<td><strong>26.66</strong></td>
<td><strong>20.00</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Na₂O/B₂O₃</strong></td>
<td><strong>1.25</strong></td>
<td><strong>1.00</strong></td>
</tr>
<tr>
<td></td>
<td><strong>(R) 2.75</strong></td>
<td><strong>3.00</strong></td>
<td><strong>2.00</strong></td>
</tr>
<tr>
<td><strong>SiO₂/B₂O₃</strong></td>
<td><strong>2.75</strong></td>
<td><strong>3.00</strong></td>
<td><strong>2.00</strong></td>
</tr>
</tbody>
</table>

Calculations using Dell, Yuan and Bray model of Borosilicate glass:

- \( R_{\text{max}} = 0.5 + \frac{K}{16} \)
- \( R_{d1} = 0.5 + \frac{K}{4} \)
- \( R_{d2} = 1.5 + \frac{3K}{4} \)

- Three types of networks probed
- Characterized by different R and K values

- Planar BO₃ converted into BO₄
- No NBO on Si tetrahedra
- Additional Na forms NBO on silicate reedmergnerite groups
- Conversion of planar diborate into pyroborate by formation of NBO on BO₃ planar rings
- Further formation of Si NBOs and breakup of reedmergnerite units
- High depolymerization of all structural units
- Glass stability low
Comparing NBS-1, 2 and 3

NBS-1

No Crystallization post irradiation

NBS-2

- Crystallization covers full surface
- Caused by spherical cascade region localized just below the surface
- Gas bubbling also evident

NBS-3

- He ions penetrate ~10μm into the sample
- Most of the crystallization too far into the sample to observe near the end of the ion track
- Small amount of crystallization at ion impact site, causing raster like feature
Variable Dose Experiments

• Change in network polymerization evident at $10^{13}$ and $10^{14}$ ion/cm²
• Possible network re-amorphization in $10^{15}$ ions/cm² sample
• High doses can lead to reamorphization (but higher fictive temperature structure: still looking into this)
Important Conclusions

• Glasses with high Na$_2$O content but low B$_2$O$_3$ and high $T_g$ are resistant to radiation damage
• **BUT:** These glasses are vulnerable to leaching!
• Chemical durability concerns addressed by Al$_2$O$_3$/ZnO addition in NBS-1?
• How will this affect phase separation?
• Melting behaviour?
Compositions Chosen

<table>
<thead>
<tr>
<th>Oxide</th>
<th>NBS-1 (mol%)</th>
<th>NBS-Al-2 (mol%)</th>
<th>NBS-Al-6 (mol%)</th>
<th>NBS-Al-10 (mol%)</th>
<th>NBS-Zn-2 (mol%)</th>
<th>NBS-Zn-6 (mol%)</th>
<th>NBS-Zn-10 (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>55.00</td>
<td>53.9</td>
<td>51.7</td>
<td>49.5</td>
<td>53.9</td>
<td>51.7</td>
<td>49.5</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>20.00</td>
<td>19.6</td>
<td>18.8</td>
<td>18</td>
<td>19.6</td>
<td>18.8</td>
<td>18</td>
</tr>
<tr>
<td>Na₂O</td>
<td>25.00</td>
<td>24.5</td>
<td>23.51</td>
<td>22.5</td>
<td>24.5</td>
<td>23.5</td>
<td>22</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>2</td>
<td>6</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>Na₂O/B₂O₃ (R)</td>
<td>1.25</td>
<td>1.14</td>
<td>0.93</td>
<td>0.69</td>
<td>1.14</td>
<td>0.93</td>
<td>0.69</td>
</tr>
<tr>
<td>SiO₂/B₂O₃ (K)</td>
<td>2.75</td>
<td>2.75</td>
<td>2.75</td>
<td>2.75</td>
<td>2.75</td>
<td>2.75</td>
<td>2.75</td>
</tr>
</tbody>
</table>

- Varying concentrations of Al₂O₃ and ZnO substituted into NBS-1
- Sufficient Na⁺ for compensation
- R reducing with substitution, K unchanged: Na⁺ used for charge compensation
Effect of Composition Changes on the Network

MAS-NMR spectra of NBS-1 glasses with Al$_2$O$_3$ and ZnO incorporation.
(a) $^{11}$B, (b) $^{23}$Na, (c) $^{27}$Al and (d) $^{29}$Si MAS-NMR spectra

- Modifier environment not perturbed by incorporation of ZnO or Al$_2$O$_3$
- 2Al glasses show a shift in $^{29}$Si resonance: Under investigation
- All Al present in [4] coordination: Adequate charge compensation
- BO$_3$ fraction increases for high ZnO
Chemical Durability

Degradation performance of NBS-1 glasses with various concentration of Al₂O₃ and ZnO

<table>
<thead>
<tr>
<th>Glass</th>
<th>Density (gm/cc)</th>
<th>Normalized leach rate for Na (gm/cm²/day)</th>
<th>Normalized leach rate for B (gm/cm²/day)</th>
<th>Normalized leach rate for Si (gm/cm²/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBS-I</td>
<td>2.53</td>
<td>2.48 x 10⁻⁴</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NBS-Al-2</td>
<td>2.50</td>
<td>1.33 x 10⁻⁴</td>
<td>6.19 x 10⁻⁶</td>
<td>9.67 x 10⁻⁷</td>
</tr>
<tr>
<td>NBS-Al-6</td>
<td>2.48</td>
<td>1.09 x 10⁻⁴</td>
<td>5.78 x 10⁻⁶</td>
<td>4.02 x 10⁻⁶</td>
</tr>
<tr>
<td>NBS-Al-10</td>
<td>2.50</td>
<td>5.72 x 10⁻⁵</td>
<td>2.59 x 10⁻⁶</td>
<td>6.5 x 10⁻⁸</td>
</tr>
<tr>
<td>NBS-Zn-2</td>
<td>2.56</td>
<td>2.09 x 10⁻⁴</td>
<td>9.04 x 10⁻⁶</td>
<td>1.83 x 10⁻⁶</td>
</tr>
<tr>
<td>NBS-Zn-6</td>
<td>2.58</td>
<td>1.05 x 10⁻⁴</td>
<td>4.40 x 10⁻⁶</td>
<td>7.58 x 10⁻⁷</td>
</tr>
<tr>
<td>NBS-Zn-10</td>
<td>2.43</td>
<td>8.92 x 10⁻⁶</td>
<td>4.34 x 10⁻⁷</td>
<td>8.71 x 10⁻⁸</td>
</tr>
</tbody>
</table>

How is Radiation Stability Affected?

- No significant changes in radiation stability under 2MeV Au ion bombardment
- Radiation stability of the original NBS-1 composition retained
Effect of ZnO/Al$_2$O$_3$ on Glass Formation

• Glass formation observed for all compositions studied: No crystallization tendencies
• Pouring temperature $\sim$1150$^\circ$C for ZnO samples
• Pouring temperature increases to $\sim$1300$^\circ$C for Al$_2$O$_3$ containing samples: Volatility concerns
• Prefer ZnO to Al$_2$O$_3$
Conclusions

• ZnO incorporation seems beneficial to augment chemical durability of radiation stable compositions
• High Na$_2$O content: Cold Crucible melting?
• ZnO induced crystallization not a significant limitation
Further Studies

• Coordination environment of Zn in these glasses
• Electrical conductivity measurements
• Incorporate RO and effect of same on chemical/radiation stability
• Effect of electronic and ballistic damage on the revised compositions
Acknowledgements

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