EELS studies of nano-precipitates in borosilicate glasses

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Abstract. The sequence of precipitation in five different alkali-borosilicate glasses is studied by HREM, HAADF-STEM and EELS. The glasses are doped or supersaturated with 4 mol% of CeO₂, and have varying concentrations of other dopant oxides, such as Fe₂O₃, Nd₂O₃, Cr₂O₃, and Ag₂O. The shape and distribution of precipitates range from amorphous droplet shape to dendritic crystals. Oxidation states of Ce and other cations in glass and precipitates are measured by ELNES. It is found that Ce in glass preferentially adopts +IV valence in Ce-crystal-free glasses while it adopts +III valence in glass nanocomposites that contain Ce(+IV)O₂ nanocrystals.

1. Introduction

For several decades alkali-borosilicate glasses have been the preferred option for the industrial scale vitrification of radioactive wastes containing a wide distribution of radionuclides from the periodic table [1]. While elements are dissolved at the atomic level in the glass matrix, immobilization into glass-nanocomposites, where part of the elements are stored in particles surrounded by glass, is another promising option. A systematic study of the precipitation of cerium in such glasses has therefore two functions: on the one hand it helps identify mechanisms by which precipitation can be avoided in waste forms where this is unwanted; on the other hand, it can serve as model system for the deliberate generation of finely dispersed nanocrystals with the potential of significantly increasing the maximum waste loading ratio. Ce is chosen as a widely accepted actinide surrogate with multiple valence (+III/+IV) in this study, while at the same time interest exists within the wider glass and ceramic research community with respect to optical properties of Ce in glasses, whether for UV absorption, opacifying, or photochromic applications. The accommodation of Ce will be influenced by other bi-valent redox partners, especially Fe and Cr. Conversely, Ce will influence other glass components, e.g. the precipitation of Ag₂O into metallic Ag nanoparticles.

 Most often spectroscopies, such as NMR, ESR, Raman or XAS/EXAFS are used to assess accommodation of dopant atoms in glasses. Here we have employed EELS/ELNES for this purpose, as it allows simultaneous study of the nanoscale microstructure, such as formation of sub-100 nm sized precipitates, within the same electron microscope using HREM or HAADF-STEM imaging techniques. Solubility limits for lanthanides and other actinide surrogates, such as Hf, Zr have been established by many authors [1], in the particular case of Ce, Hf, and Nd results indicate limits below 4 mol% depending on melting temperature [2].
2. Materials and Microscopy.

Five compositions of borosilicate glasses have been produced for this study using a standard melting and annealing route. The glasses are designed around a common glass matrix with constant Si/B and alkali/boron oxide ratio (except (v)), with different alkalis, and also a constant dopant loading of 10% in total. All percentages given are molar data for the respective oxides.

| Glass-Acronym | Network formers & modifier elements | Dopant elements |
|---------------|--------------------------------------|-----------------|
| (i) KBS-CFC:  | K$_2$O: B$_2$O$_3$: SiO$_2$          = 12.9: 25.7: 51.4 | CeO$_2$: Fe$_2$O$_3$: Cr$_2$O$_3$ = 4:4:2 |
| (ii) NLBS-CZC: | Li$_2$O: Na$_2$O: B$_2$O$_3$: SiO$_2$ = 4.3: 8.6: 25.7: 51.4 | CeO$_2$: ZrO$_2$: Cr$_2$O$_3$ = 4:4:2 |
| (iii) KBS-CZC: | K$_2$O: B$_2$O$_3$: SiO$_2$          = 12.9: 25.7: 51.4 | CeO$_2$: ZrO$_2$: Cr$_2$O$_3$ = 4:4:2 |
| (iv) KBS-CH:   | K$_2$O: B$_2$O$_3$: SiO$_2$          = 12.9: 25.7: 51.4 | CeO$_2$: HfO$_2$ = 4:6 |
| (v) KBS-ACFN:  | K$_2$O: B$_2$O$_3$: SiO$_2$          = 15: 15: 60 | CeO$_2$:Ag$_2$O:Fe$_2$O$_3$:Nd$_2$O$_3$= 4:1:3:2 |

Glasses were melted at 1400 °C followed by annealing at 570 °C. The TEM specimens were prepared by crushing the bulk sample in an agate mortar and pestle with acetone, some suspended particles are mounted on copper grids with carbon film. The advantage of this method is that there is less damage as compared with the ion milling process.

A JEOL 2010F Field Emission Gun TEM with STEM controller and with an accelerating voltage of 200 kV was used for all the analysis. EELS was obtained using a Gatan Image Filter (GIF) in combination with Gatan Digiscan and Spectrum Imaging software. The methods for measuring oxidation states for transition elements and rare earth elements using EELS have been well described elsewhere [3-6]. EELS of the borosilicate glass matrix is detailed in [7].

3. Microstructures

Apart from large-scale (tens-of-microns in size) platelet shaped precipitates of Cr$_2$O$_3$ in all our Cr-containing glasses, the glasses were homogeneous. Glass (iv) was fully amorphous, while glass (v) contained metallic Ag nanoparticles as the only precipitate (Fig 1). All Fe, Zr, Nd and Hf fully dissolved in the respective glasses. Ce precipitated in all but the last two glasses (iv) and (v). The Ce-nanostructure is however complex, as highlighted in Fig 2 using glass (i) as example. We discriminate three hierarchies of particle phases:

- **Level A**: 200-500 nm precipitates of pronounced dendritic structures (Fig 2a,c,d). They are expectedly confirmed as single crystalline and have a cubic (fluorite) crystal structure. Similarly the were found in the other glasses, however their average diameter with glass type being 70-120 nm in glass (ii) and 200-600 nm in glass (iii). Minor differences in the cooling scheme could likewise influence the size. The branching statistics are quite diverse, however, with there is a consistent perpendicularity of the central branches.

- **Level B**: 100-150 nm roundish particles/phases, which appear amorphous in HREM. They are Ce-rich and exclusive to glass (i) and not found in any of our other compositions (Fig 2b, large particles).

- **Level C**: 10nm-50 nm roundish particles/phases, which are again amorphous. They are found in glasses (i), (ii) and (iii) and are also Ce-rich (Fig 2b, small particles).

All of the aforementioned particles are distributed randomly and are found homogeneously throughout the glass blocks, with the exception of some CeO$_2$ dendrites growing on the Cr$_2$O$_3$-plates, where present, surrounded by a Ce depletion zone.

4. Spectroscopy

The Ce-M-edge fine structure was selected from the EELS spectrum and recorded for all glasses and for selected particles within the glasses with high dispersion (Figs 3+4). To evaluate the oxidation state (valence) of Ce, the ratio of the integral areas under the peaks for the M5 and M4 white line needs to be quantified. For this study we select the 2nd derivative method [4], Fig 4. A fractional formal valence is interpreted as meaning there is a distribution of both Ce(+III) and Ce(+IV) in the material, which could happen at certain temperatures and redox-partner environments. However, for
particles clearly smaller than the specimen thickness, fractional data probably indicate overlap of particle and glass matrix and require correction. The quantification of Ce-edges is fairly robust and suffers less from energy-calibration problems than L-edges of transition elements.

Fig 1: ADF-STEM images of 4 glasses with acronyms and numbers as detailed in section 2.

Fig 2: ADF-STEM images of 4 groups of precipitates from glass (i)

Fig 3: Example of a raw EELS signal from glass (v) including Fe, Ce, and Nd double white lines

Fig 4: 2nd derivative EELS spectra of Ce-M5,4 white lines for 3 glasses (a,d,e) and two particles (b,c) from the glass (i) as detailed in the inset text. Axes: X: energy loss ~ 870-930 eV, Y: a.u.
A collection of all Ce-valence quantification results reveals details of the complex redox-chemistry of
these glasses:

| Glass or Particle | Integrals: M5/M4 | Formal valence | Rounded**/* corrected** |
|-------------------|-----------------|----------------|-------------------------|
| (i) Glass matrix  | 1.31            | 3.01           | 3.0*                    |
| (i) Dendrites     | 0.91            | 3.99           | 4.0*                    |
| (i) Large drops   | 1.29            | 3.04           | 3.0*                    |
| (i) Small drops   | 1.16            | 3.37           | ~4**                    |
| (iv) Glass matrix | 0.93            | 3.9            | ~4*                     |
| (v) Glass matrix  | 0.93            | 3.9            | ~4*                     |

Further measurements on the glasses (ii) and (iii), not included here, confirmed identical chemistry to
glass (i). However an evaluation of various statistical methods of M5/M4 quantification, conducted on
glass (ii), lead to spread of results from 3.0 to 3.3 for the glass matrix depending on the data
processing method used [6]. Apart from such systematic errors we estimate the statistical error on the
formal valences to be ± 0.1. By adopting one quantification procedure for all of the glasses, we
consider the relative comparisons to be safe. For spectra of crystalline reference materials [6] and
minerals used for immobilization in ceramics, see [8].

5. Discussion and Conclusions
It is found that Ce is accommodated as Ce(+IV) in all glasses where no CeO₂ crystals were formed
(iv,v). Once dendritic precipitates form, in which Ce is present in the (+IV) state in a fluorite structure,
the residual Ce left in the glass matrix switches to (+III). The nature of the two sorts of Ce-rich drop-
shaped particles, and their differing Ce-valences has not been resolved. Their amorphous nature in
HREM points to phase separation effects, albeit not of the traditional borate-vs-silicate type of phase
separation. The particles have a bimodal size distribution and probably originate at different time
during cooling/annealing. The smaller droplets seem to increase in number, although not in size,
during intense electron irradiation. An initial population is, however, already present at the start of any
TEM imaging. The morphology of all the glasses appeared to be stable under moderate beam
intensities. Only under high-intensity illumination has phase separation been demonstrated for glass
(ii). The Ce-signal is also unaltered after extensive irradiation, unlike the EELS edges for alkalis and
boron [7].

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