

Analytical STEM of Borosilicate Glasses Containing Molybdates.

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ABSTRACT

Borosilicate nuclear waste glasses with various amounts of simulated waste elements have been examined by analytical TEM. This preliminary Scanning Transmission Electron Microscopy (STEM) study evaluates the capability of EELS for mapping coordination parameters of the base glass structure, to apply EDX-mapping and HAADF Z-contrast mapping for the characterisation and shape-mapping of common precipitates in nuclear glasses, such as molybdates, and to study irradiation effects.

INTRODUCTION

Borate, borosilicate, and alkali-borosilicate glasses have been the subject of a large number of studies applying a multitude of characterisation techniques [1-5], such as NMR, X-ray absorption spectroscopy, Raman spectroscopy, XPS, ESR, TEM, and others. The aims of these spectroscopies are to determine the glass structure (radial distribution function), short and medium range order, and local coordination, e.g. of boron as a function of alkali content. Solute elements or precipitates have been analysed for valence and/or coordination [6-7]. However, it is still not clear to what extent the basic glass structure examinations on binary / ternary systems can be extrapolated to complex compositions of nuclear waste glasses with more than 20 elements present. Borosilicates as the basis for nuclear waste glasses and current research needs are e.g. summarised in [8-9].

A promising technique which can be used simultaneously for the nanoscale imaging of inhomogeneous or phase separated glasses and for local structural analysis of glass coordination is scanning transmission electron microscopy (STEM), using three signals on three detectors: (i) EDX-spectroscopy in STEM leading to 2D chemical maps of glass/precipitate systems, (ii) High-angle annular dark field (HAADF)-STEM leading to Z-contrast images with intensity roughly proportional to $t \cdot Z^2$, where t is thickness and Z atomic number, and (iii) EELS (electron energy loss spectroscopy) with a focused beam, especially near-edge-fine-structure (ELNES), aiming at chemical and coordination information with resolution down to nm-sized volumes.

The glass precipitation studies in this work are aimed at establishing the dependency of crystal formation in nuclear borosilicate waste glasses on the conditions of glass melting (oxidising vs reducing) and on post-melt heat treatments. Molybdates are an important model system of both practical and scientific relevance due to the varying Mo valence leading to different solubility limits and different overall glass durability values [10].

EELS ANALYSIS OF GLASS STRUCTURE

Of the six borosilicate glasses A-F (table 1), three TEM samples I-III have been analysed by EELS to test the sensitivity and reliability of coordination measurements (see also [11-13]) against established techniques, such as NMR. The studies have to consider every preparation step which may influence glass structure, ranging from the glass making details, annealing sequence, thin foil preparation to exposure to a strong electron beam.

- Sample I is a ground plus ion-milled thin foil of glass **A**, carbon coated against specimen charging/drift.
- Sample II is a milled fine powder of glass **A**, suspended on carbon support film,
- Sample III is the ternary sodium-borosilicate (NBS) model glass **C** with composition in the high-tetrahedral range, ion milled to very thin thickness (<10nm), and uncoated.

Table 1: Glass compositions used in wt% of oxides as batched (unless otherwise stated):

| Glass | Si | B | Na | Li | comments and waste simulants |
|----------|-----------|----|----|-----|---|
| A | 49 | 18 | 13 | 4.2 | +20% waste, incl.: Mo:2.4; Nd:3; Gd:2.8; Zr:2.2 + 15 others; air melted and 48h-heated at 600 ^o C (A1) or 650 ^o C (A2), |
| B | same as A | | | | reducing atmosphere (N ₂ /5% H ₂) and heated at 600 ^o C. |
| C | 62 | 22 | 17 | | ternary glass; mol%: 63.4; 20; 16.6 : K=3.17; R=0.83 *) |
| D | 40 | 14 | 11 | 5.2 | +35% waste as A ; air-melted (D1) or reduced (D2), 600 ^o C. |
| E | 62 | 22 | 11 | 5.3 | +1% Mo-oxide as only waste, reducing atmosphere |
| F | 46 | 16 | 16 | - | +4.8% Mo; 3.1% Cs; 13.6% Nd; reducing atmosphere. |

*The definitions are $K = [\text{SiO}_2/\text{B}_2\text{O}_3]$ and $R = [\text{Na}_2\text{O}/\text{B}_2\text{O}_3]$ expressed in molar %.

Borates and borosilicates were amongst the first glasses to be studied by NMR, and extensive data are available on the coordination data of boron, especially the relationship $N_4 = N_4(K, R)$, where $N_4 = \text{BO}_4 / [\text{BO}_4 + \text{BO}_3]$.

EELS spectra have been recorded with exposure times of several seconds, with Na-concentrations being unavoidably readjusted by beam induced Na migration and therefore subject to deviations from the nominal compositions. Spectra have been background-subtracted and the K-edge fine structure of boron spread to match available literature data for the purely coordinated minerals vonsenite-BO₃ (Fig 1a) and rhodizite-BO₄ (Fig 1b), following the work of Sauer et al. [14]. Superimposing the two fingerprints is iterated until match to the experiment is achieved with a variable factor N_4 .

For sample I, a boron coordination ratio of 2 BO₄ units to 5 BO₃ units (or $N_4 = 0.3$) is found as best match (Fig 2a), while no superposition could exactly reproduce the shape of the second peak, which might indicate a problem with the principle of fingerprinting using crystal minerals. The result is a substantial deviation from the expected NMR-values of $N_4 > 0.5$, which is either due to electron beam damage (see below) or due to the neglect of the 20% waste loading and mixed alkali (Li+Na) composition, while the NMR reference is for pure NBS glasses only (for a recent study on Li-Na mixed alkali borosilicate glasses, see [4]).

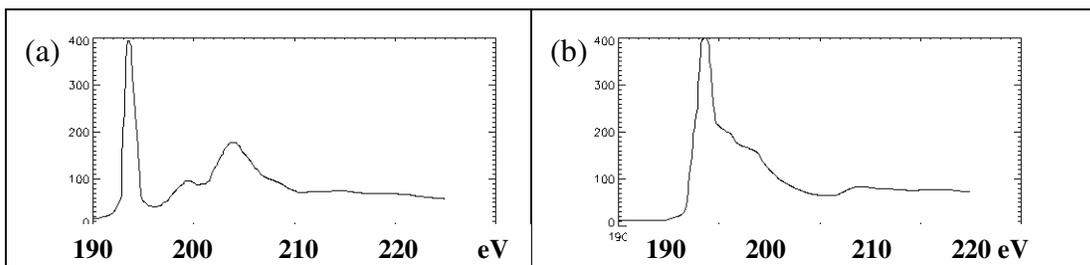


Figure 1: Reference-spectra (after Sauer et al.[14]) as coordination fingerprints: BO_3 (a) with peaks at 193.6 and 204eV and BO_4 (b) with peak at 198.6eV.

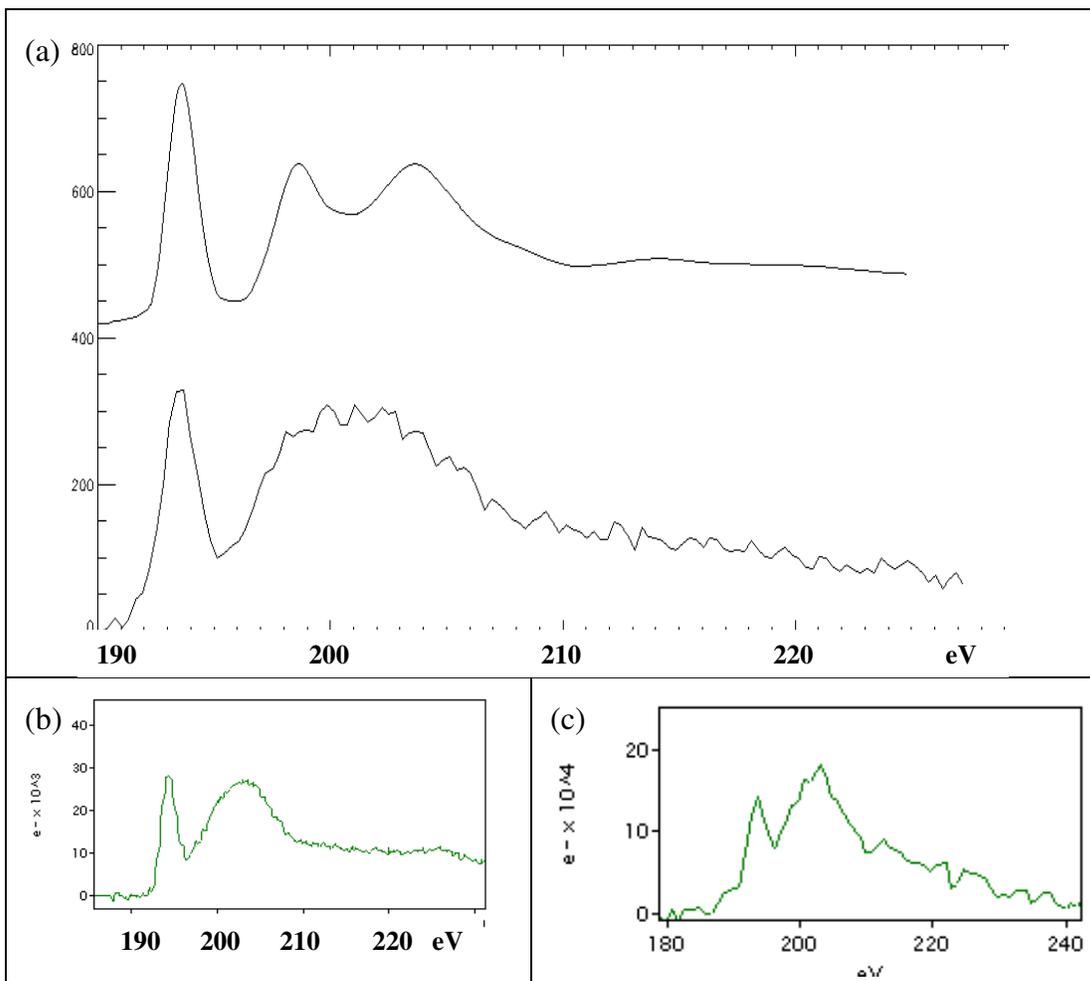


Figure 2: (a) Matched reference-superposition (top) and experimental glass EELS spectrum, sample I (bottom). (b) and (c) are for samples II and III

For sample II, the result is mostly unchanged as expected for the equivalent Si:B:Na ratios, but not obvious due to the largely different preparation route.

For sample III, which is a pure NBS glass, the best match is shifted towards higher N_4 in the region of $N_4=0.4$. However, the lower energy resolution and signal noise ratio of this spectrum could well have reduced the BO_3 peak height. Furthermore the exact maximum and shape of the second peak does not fully match the BO_4 peak. Further studies are in progress to include EELS signals as a function of time and specimen thickness and to minimise beam-sensitivity.

EDX CHEMICAL MAPPING AND HAADF Z-CONTRAST MAPPING

Waste loading and precipitation experiments: The glasses studied here were described in detail in [1], and are summarized in table 1 above. The solubility of high molybdenum content waste in borosilicate glass can be influenced by the redox environment during melting. Mo can be incorporated in various oxidation states into a large number of mixed oxides [1] (e.g. $SrMoO_4$, $AB(MoO_4)_2$ or $AB_2C(MoO_4)_4$), which will determine the overall durability, which is the prime quality criterion for wasteforms.

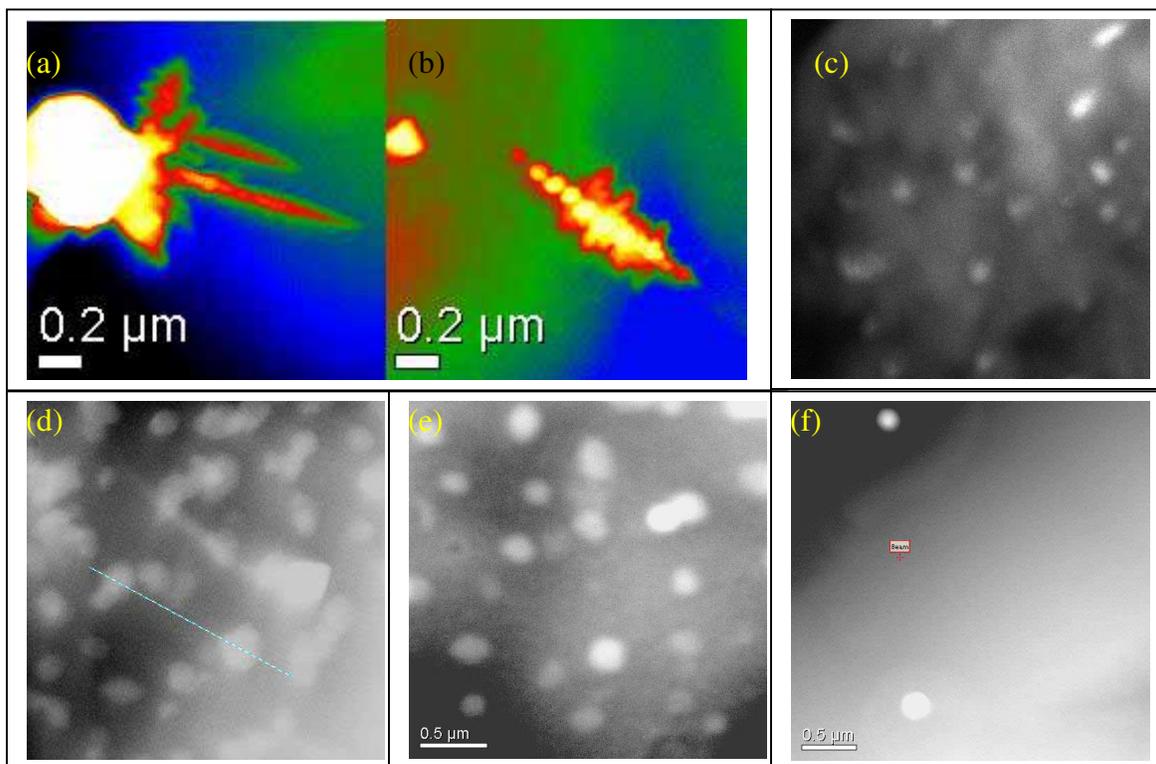


Figure 3: HAADF-STEM on JEM-2010F FEGTEM:

(a+b): Dendritic molybdates (in print: gray; digital proceedings: red/yellow) and round metal Ag-particles (white) of glass **B**

(c+d): Molybdates in glass **A2** (heat treated at $650^{\circ}C$) and **D1** ($600^{\circ}C$), both air melted.

(e+f): Molybdates in glass **D2** and **E**, reducing atmosphere, both heat treated at $600^{\circ}C$.

FEGSTEM mapping: samples of the glasses were ground and ion milled, carbon coated and observed in a JEOL JEM2010F FEGTEM using an Oxford Instruments EDX system and a JEOL scanning unit with high-angle annular dark field (HAADF) detector. EDX-maps have been acquired at 20k magnification over 1h, while HAADF maps are acquired using Gatan Digiscan in ~10sec exposure. Fig 4 shows clearly the enhanced visibility of heavy-atom precipitates by HAADF due to Z-contrast (intensity $\sim Z^2 \cdot \text{thickness}$), such as neodymium oxide (Nd: $Z^2 = 3600$), while molybdates appear light gray (Mo: $Z^2 = 1764$) and borosilicate (Si: $Z^2 = 196$) appears dark. EDX maps assist basic chemical identification, although at slightly lower resolution than the HAADF maps.

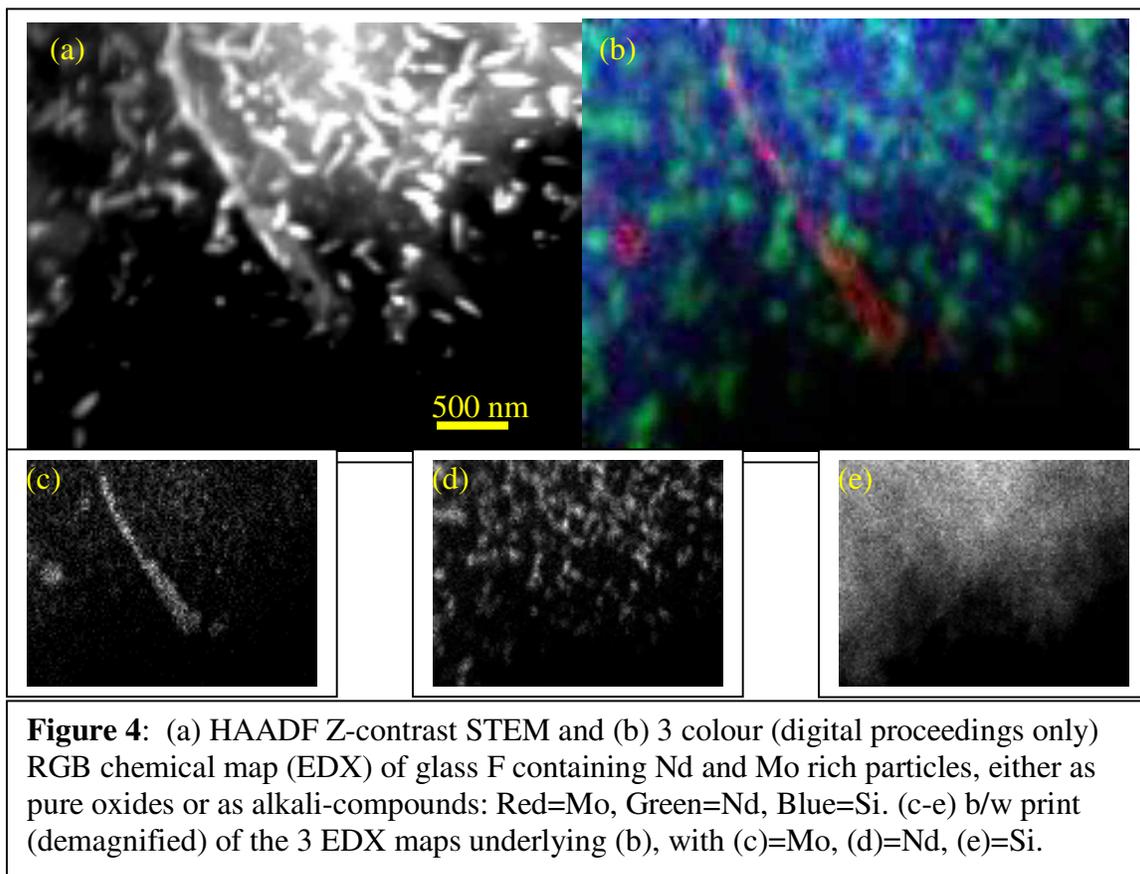


Figure 4: (a) HAADF Z-contrast STEM and (b) 3 colour (digital proceedings only) RGB chemical map (EDX) of glass F containing Nd and Mo rich particles, either as pure oxides or as alkali-compounds: Red=Mo, Green=Nd, Blue=Si. (c-e) b/w print (demagnified) of the 3 EDX maps underlying (b), with (c)=Mo, (d)=Nd, (e)=Si.

Results: All waste loaded glasses showed precipitates with sizes to <100nm, except for glass **A1** (low waste load), while glass **E** had very low density of particles. The molybdate morphology varied from needles to spheroidal. Figs 3a-b suggest that Ag-particles promote molybdate growth, however, isolated dendritic Mo-particles were also found. The exact phase identification, apart from some pure Ag and Mo particles, is mostly difficult due to the multiple choice of molybdates [1] with scheelite structure, and also due to the absence of Li-peaks in EDX.

IRRADIATION DAMAGE

While oxygen bubble formation [15] could not be observed on any of the NBS glasses studied here [however, we found strong oxygen-K-edge pre-peaks in a KMgAl-fluoro-silicate under same conditions], the main damage mechanism in FEGTEM electron irradiation [16] was sodium-loss, dependent on illumination and exposure time. EDX sequences showed the Na/Si peak height ratio dropping by a factor of 2-5 (depending on beam intensity) from the spectrum observed with a fully-spread beam. The Na concentration was observed by EDX to reach a new stable level asymptotically, although EELS confirmation of this fact was not possible. An interesting question is whether the depletion of Na is followed instantly by a regrouping of boron oxide units from BO_4 to BO_3 following the NMR-measured N_4 (K, R) curves [2], or whether the originally higher BO_4 level from the higher Na concentration partially survives during this kinetic (non-thermal) damage mechanism. The change of the K-value upon irradiation is also unclear.

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REFERENCES

1. R.J. Short et al., MRS symp. proceed., vol. 757, II5.4., Boston Fall Meeting, 2002; and Proc. XXVIIth Symp. Scient.Bas. Nucl. Waste Man., Kalmar, Sweden, 2003, in press.
2. P. Stallworth and P.J. Bray, in Glass Science and Technology, D.R. Uhlmann, N.J. Kreidl, eds., vol. 4A, p. 123-130 (1990).
3. R.N. Sinclair et al., Phys. Chem. Glasses 41, 286-289 (2000).
4. J.M. Roderick et al., J. Non-cryst. Solids, 293, 746-751 (2001).
5. K. Sun, L.M. Wang and R.C. Ewing, MRS symp. proceed., vol. 757, 135-140, (2002)
6. G. Calas et al., J. Nuclear materials, 322, 15-20 (2003).
7. C. Lopez et al., J. Nuclear materials, 312, 76-80 (2003).
8. M.J. Plodinec, Glass Technology, 41, 186-192 (2000).
9. W. Lutze, R.C. Ewing, eds., Radioactive Waste Forms for the Future, North Holland, Amsterdam, (1988).
10. W. Lutze, in [9], p 31.
11. L.A.J. Garvie, A.J. Craven, R. Brydson, Am. Mineralogist 85, 732-738 (1995).
12. N. Jiang, J.R. Qiu, J.C.H. Spence, Phys. Rev. B, 66, 054203 (2002).
13. R. Schneider, et al., J. Phys. D, Appl. Phys., **29**, 1709 (1996).
14. H. Sauer et al., Ultramicroscopy 49, 198-209 (1993).
15. R. Egerton, Electron Energy Loss Spectroscopy, Plenum, New York, 2nd ed. (1996).
16. K. Sun, L.M. Wang and R.C. Ewing, Microsc. Microanal. 9 (Sup. 2), 128-129 (2003).