Fine structure EELS analysis of glasses and glass composites

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Abstract. EELS is a powerful technique for the study of complex oxide ceramics, especially when exploiting the ELNES sensitivity to cation valency and coordination. The same applies for oxide glasses, with the additional benefit of gaining information about glass order parameters and structural units. The major benefit of ELNES in comparison to Raman, NMR and X-ray alternatives is the high resolution of measurement which makes it particularly suitable for nanocomposites. For doped glasses with some of the extra cations exceeding the solubility limit, we have also analysed the systematic change of oxidation state in transit from the glass matrix into precipitates using the example of CeO₂ and the Ce-M-edge pair of spin-orbit split lines.

1. Introduction
The assessment of doping element chemistry, such as rare earth elements, in silicate glasses has multiple industrial and basic science relevance, e.g. for optical properties (laser active materials, photochromic effects, UV-absorption). Another separate motivation is to predict the chemistry of accommodation of radionuclides for long term immobilization (“vitrification”) in a repository [1]. Cerium is a major target of such studies, partially due to its multiple valence flexibility, and also because it is claimed to be the most similar surrogate for Pu [1,2].

The currently preferred methods for glass spectroscopy are optical and magnetic resonance techniques, along with X-ray absorption/ fine structure (XAS/EXAFS). Electron energy loss spectroscopy (EELS) has the potential to extract similar glass structure and chemistry information as XAS/EXAFS due to the complementary processes of inelastic electron scattering and X-ray absorption. The major benefit of EELS in comparison to Raman, NMR and X-ray alternatives is the high resolution of measurement which makes it particularly suitable for nanocomposites. EELS has been used to study the oxidation states of Ce in glass [3], crystals [4] and also to evaluate the electron beam damage on ceria [5]. However, to our knowledge no research on the variation of Ce oxidation states within a glass-precipitate system was done. EELS spectrum imaging (SI) can be employed to acquire a series of spectra dot by dot according to a predefined line, which makes it possible to investigate glass structure parameters or oxidation states of elements down to the nano-scale.

2. Experimental procedure
The glass composition studied here was Na₂O: Li₂O:B₂O₃: SiO₂= 8.6: 4.3: 25.7: 51.4 (mol%), and the metal oxides ZrO₂, CeO₂, Cr₂O₃ were 4, 4, 2 (mol%), respectively. The reagent grade chemicals were batched to an accuracy of ±0.005g, to give a 300g glass melt. They were placed in a Pt crucible and put into a 147cm³ (internal volume) electric furnace with SiC elements. The melting temperature was 1400°C and the total melting time was 5 hours with 1 hour batch free time and 4 hours stirring. After
melting all the glasses were poured into a preheated steel mould to form a rectangular glass block approximately 2x2x10cm in size. This block was then transferred to an annealing furnace where it was held at 570°C for 1 hour and then cooled to room temperature at the rate of 1°C/min to relieve the stresses in the glass. The main specimen (Fig 1a) was prepared by ion milling, while the reference powders were prepared by crushing in agate mortar and pestle with acetone, then mounted on holey-carbon-film-covered copper grids. The sizes of those fragments are in the range of 10 to 500nm.

A JEOL 2010F Field Emission Gun TEM with an accelerating voltage of 200 kV was used for all the analysis. EELS were obtained using a Gatan Image Filter (GIF) using DigitalMicrograph software. Spectrum images (SI) were acquired in STEM mode at a magnification of 100k. Ce reference spectra (CeO₂ and CePO₄) were acquired in TEM mode at a same magnification as SI.

3. Results
Fig. 1 (a) shows the high angle annular dark field (HAADF) STEM image of the observed specimen. The bright regions in the image are Ce-rich crystals, which are 50 to 200 nm in average diameter; the remaining is glass phase. The line shown from 0 to x (~370nm) indicates the direction of the spectra acquisition sequence. The line crosses one crystal and ended in another. Fig. 1 (b) shows the unprocessed surface plot of 50 EELS SI spectra with 3 seconds exposure per point (one spectrum recognize by an outlier peak in the O-K-edge was later discarded). The oxygen peak at 532 eV helps to calibrate the energy scale (x axis), and the two peaks at ~883 eV and ~901 eV indicated the cerium M5/M4 edge (double white line). The nominal molar Ce content in the glass of 4%, likely depleted to <2% after crystal precipitation, renders the Ce peaks in the glass very noisy, hardly seen in Fig 1b. The SNR is high enough, however, to confirm a strong change of the white-line ratio from the glass into the crystals. The 28th spectrum from 0 point (top) was chosen as the representative crystal spectrum (Fig 1c, top). For the glass matrix, the 8th spectrum had to be averaged by +/- 2 neighbour spectra to achieve a similar SNR for Fig 1c (bottom). In order to quantify the valence states of Ce, CeO₂ and CePO₄ powders have been examined, and their spectra were taken as Ce⁴⁺ and Ce⁵⁺ references, respectively (Fig 1d). From the reference spectra it can be seen that M5/M4 peaks of Ce⁴⁺ were in the position of 883 eV and 901 eV, and those of Ce⁵⁺ were at 880 eV and 897 eV, respectively. As outlined in [6], and confirmed in our work, the position of the peaks in the glass matrix and crystals indicates therefore valences of Ce just as well as the white line ratio does. However, the noisy peaks in the glass would not allow to use any one criterion alone.

The dependency of the ratio of white line intensity R_w on the oxidation state of Ce is described in [3,5,6]. For lanthanides the ratio has a linear relationship with the oxidation state. Amongst the various methods proposed to quantify the R_w evaluation (most elaborate are peak-modelling and fitting procedures), we compare two of the most popular procedures:

(i) 2nd derivative conversion with subsequent peak-area evaluation between zero-crossings.
(ii) Peak-area evaluation after exponential pre-peak background subtraction and post-peak continuum subtraction.

Fig. 2 shows the second derivative spectra taken from Fig. 1 (c). The integral ratio of M5/M4 peaks in glass matrix and crystals are 1.286 and 0.903, respectively. They are very close to those of Ce⁴⁺ and Ce⁵⁺ references, which were calculated to be 0.901 and 1.308. Using a linear relationship, in the glass matrix there are 94.6% Ce⁴⁺ and 5.4% Ce⁵⁺, thus the “formal” oxidation state (representing a mixture of atoms) of Ce in the glass matrix would be +3.05. Similarly in the crystals there are almost 99.5% Ce⁴⁺ and only 0.5% Ce⁵⁺, the formal oxidation state of Ce is 3.995. The peak position difference between crystals and glass and the extra shoulder in Ce⁴⁺ are consistent with findings of Garvie [6].
Fig. 1 (a) HAADF image of specimen (b) surface plot of 50 spectra, x axis shows the length of the line (x< 370 nm), eV-axis shows the energy loss and z axis shows the intensity. (c) ELNES of 16\(^{th}\) (bottom) and 28\(^{th}\) (top) spectra from 0 point. (d) ELNES of CePO\(_4\) (bottom) and CeO\(_2\) (top)

For the continuum subtraction method, a simplified continuum model has been fitted (using IDL software) to all SI-spectra in crystalline regions using rectangular functions the height of which was given by two energy windows at the minima between the peaks and after the M4 peak. For the selected 4 spectra of Fig 1 the continuum has been improved to a smoothed rectangle using two arctan-functions [7]. M5/M4 values from spectra of Fig 1 are: 0.796 for +IV, and 1.107 for +III reference powders. In the glass-composite the ratio amounts to 0.780 in the crystals and ranges from 0.906 to 1.02 in the glass matrix depending on line selection. This corresponds to formal valences of slightly “above” 4.0 for the crystals and between 3.35…3.71 for the glass matrix. Large ratio variations in the glass (0.9 – 1.1) can also be revealed on the line scan evaluation in Fig 4. This is assumed to be a pure SNR effect, not a spatially resolved real valence fluctuation in the glass.
4. Discussion
Importantly, all three criteria, which are (i) peak-position, (ii) peak-shoulders, and (iii) peak-area white line ratio, lead to the same qualitative result of close to pure Ce(+IV)O₂ for the precipitates, while the glass is of mixed, Ce(+III)-rich valence. Crystallisation of CeO₂ is the expected phase from a chemical point of view. Problems are as follows: In the crystals, we have to be aware that the STEM line-scan could have mixed some glass matrix with the crystals due to projection effects, although the specimen thickness (ion-milled) is likely smaller than the particle diameter. Partial reduction of Ce⁴⁺ due to electron beams has also been reported, all of which easily explain the deviation of crystal data from 100% Ce⁴⁺. Also intensity transfer from M5 to M4 due to plasmon multiple-scattering in thicker areas would be a possibility. This effect opposes the others by overestimating formal valence, and might explain artefact results of >4.00 valence. Proper deconvolution would need to acquire a low-loss SI series sequentially at the same positions, which is non-trivial and also needs modified software for bulk-processing of spectra.

In the glass the quantification of the mixed valence of Ce is more difficult, and was found to depend on the method of peak-evaluation. Chemically, mixed Ce-valence in glasses is wide-spread, and would depend on the amount and strength of the redox partner elements in the glass and on the oxidising/reducing environment during glass melting. The 2ⁿᵈ derivative procedure for very noisy data and for pairs of peaks of non-standard line shapes or mutually different shapes might be unreliable.

5. Summary
EELS spectrum imaging (SI) was explored to study the Ce oxidation state variation in glasses and precipitates at high spatial resolution. In spite of problems arising from incompatible peak-area quantification procedures, the results are encouraging, and the beam sensitivity of ELNES measurements particularly on rare-earth element glasses is found relatively small. Further work [8] addresses boron coordination fingerprinting in the same glasses; [9].

References
[1] C. Lopez, X. Deschanels, J.M. Bart, J.M. Boubals, C. Den Auwer, E. Simoni, J. Nucl. Mater., 312 (2003) 76-80.
[2] P.B. Rose, M.I. Ojovan, N.C. Hyatt, W.E. Lee, Mat. Res. Soc. Symp. Proc., 824 (2004) CC5.6.
[3] J. A. Fortner, E.C. Buck, A. J. G. Ellison, J. K. Bates, Ultramicroscopy, 67 (1997) 77-81
[4] H. Xu, Y. Wang, J. Nuclear Materials, 265 (1999)117-123
[5] L. A. J. Garvie, P. R. Buseck, J. Phys. Chem. Solids, 60 (1999) 1943-1947
[6] L. A. J. Garvie, H. Xu, Y. Wang, R.L. Putnam, J. Phys Chem Sol, 66 (2005), 902-905.
[7] R. Egerton, Electron Energy-Loss Spectroscopy, Plenum Press, New York, 1996
[8] G. Yang, G. Möbus, R. Hand, Phys. Chem. Glasses (submitted).
[9] The authors would like to thank ISL for the sponsorship of this project.