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Quantification of the Boron Speciation and Cu Oxidation States in Alkali Borosilicate Glasses by Electron Energy Loss Spectroscopy

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Alkali borosilicate glasses have been widely used for a long time due to their good chemical/physical properties. In borosilicate glasses, boron has two structural configurations: trigonal BO_3 and tetrahedral BO_4 units[1]. The BO_4 tetrahedra participate in the three-dimensional network structures of borosilicate glasses, therefore they are preferred for some special applications, such as nuclear waste immobilization. Several techniques have been developed to quantify the fraction of BO_4 in borosilicate glasses, including X-ray absorption near edge structure (XANES), Raman spectroscopy and nuclear magnetic resonance (NMR)[2]. Among these tools, 11B magic-angle spinning (MAS) NMR is one of the most reliable methods to quantify the BO_4 fraction, N_4= $[BO_4]/([BO_4] + [BO_3])$, in boron glasses. However, solid-state NMR instrumentation is not commonly found in all research laboratories. Electron energy loss spectroscopy (EELS) can also be applied to quantify N_4 since the BO_3 and BO_4 units exhibit characteristic features in the corresponding spectra (Fig. 1a). The quantification of N_4 by EELS has been tried but the obtained N_4 data was lower than the actual N_4 values measured by NMR, due to the electron beam irradiation damage which causes the transformation of BO_4 into BO_3 units during the signal acquisition[3].

In this work, we have developed a method based on EELS data acquisition and analysis, which enables determination of the boron speciation in a series of ternary alkali borosilicate glasses with constant molar ratios. A script in DigitalMicrograph for fast acquisition (~0.05s) of EELS has been designed, from which the boron K-edge spectra can be obtained with minimum electron irradiation damage (Fig. 1b). The fraction of BO_4 tetrahedra can be obtained by fitting the experimental data with linear combinations of reference spectra with special criteria. The measured BO_4 fractions (N_4) obtained by EELS are consistent with those from 11B MAS NMR data, suggesting that EELS be an alternative and convenient way to determine the N_4 fraction in glasses.

Three optically transparent colorful (red, green and blue) glasses were synthesized by sol-gel method. All glasses have the same composition but the annealing atmosphere is different. The exhibiting color is believed to be due to the different oxidation states of Cu in these glasses. XRD and XPS have been applied to these glasses but no crystalline phase or Cu signal was detected. SEM and TEM analysis shows that nano-sized precipitates are homogeneously distributed in the glass matrix. The precipitates were analyzed by STEM-EELS. From the STEM images it is observed that the nano-precipitates are brighter than the glass matrix, with the combination of EELS spectra imaging analysis they are found to be Cu rich precipitates. The oxidation states of Cu are quantified by fitting the Cu $L_{2,3}$ edge spectra from the precipitates with the reference spectra from single valenced Cu reference compounds (Fig. 2). The oxidation states of Cu in the precipitates are found to be 0, +0.7 and +1.94 for the red, green and blue glass, respectively. Density functional theory (DFT) was used to find the qualitative correlation between the oxidation states of Cu and the apparent color of the glass. The calculated optical absorption and reflection spectra could verify the Cu oxidation states obtained by EELS.

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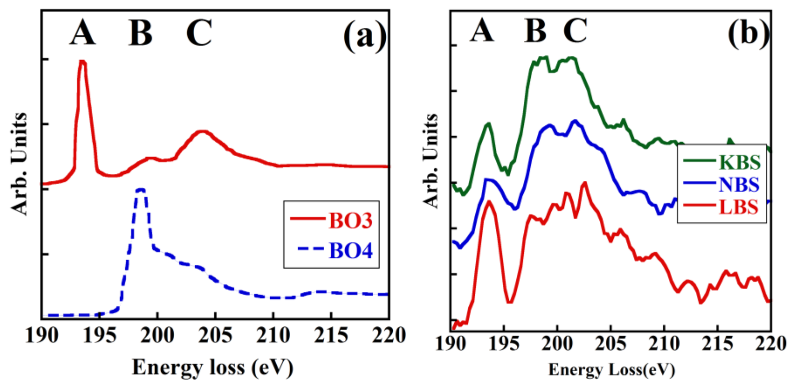

Figure 1. (a) Plots of boron K-edge reference fingerprint spectra of the BO_3 and BO_4 units found in the minerals vonsenite and rhodizite[1], respectively. (b) Experimental boron K-edge spectra of the LBS (red), NBS (blue) and KBS (green) glasses.

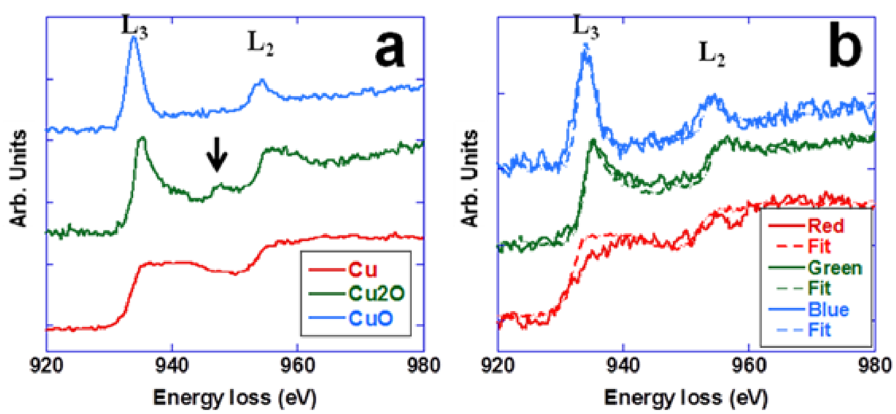

Figure 2. Cu K-edge EELS spectra of (a) Cu reference materials and (b) NPs in different glasses and the corresponding curve fitting. The solid lines are the summed spectra, and the dotted lines are fitted curves

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