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The boron speciation quantification in alkali borosilicate glasses by electron energy loss spectroscopy

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Transmission electron microscopy and related analytical techniques have been widely used to study the microstructure of different materials. However, few research works have been performed in the field of glasses, possibly due to the electron-beam irradiation damage(1). In this study, based on our previous research, we have developed a method based on electron energy loss spectroscopy (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 for the fast acquisition of EELS has been designed and a new fitting criterion was developed, from which the fraction of BO_4 tetrahedra can be obtained by fitting the experimental data with linear combinations of reference spectra. Figure 1 illustrates the boron K-edge spectra (strictly speaking energy loss near edge structure, "ELNES") of three glasses (LBS, NBS and KBS are lithium-, sodium- and potassium borosilicate glass) with different fitting methods(2). The peak A was solely from trigonal BO_3 and peak B was mainly attributed by tetrahedral BO_4, while peak C contains signals from both configurations. The measured BO_4 fractions (N_4) obtained by the new fitting method are consistent with those from ^{11}B MAS NMR data, suggesting that EELS be an alternative and convenient way to determine the N_4 fraction in glasses.
In addition, in order to investigate the effect of cerium oxide on the glass microstructure, 5 mol% CeO_2 was added to the KBS glass (Ce-KBS). The BO_4 fraction in the Ce-KBS glass was found to be lower than that in the KBS glass and the Ce oxidation state was quantified to be close to 4^+. The boron time-resolved EELS spectra were recorded to quantify the electron beam irradiation effect to the glass network. The results clearly demonstrate that the transformation from BO_4 to BO_3 units can be efficiently suppressed by adding CeO_2 to the borosilicate glasses. Meanwhile, Ce oxidation state was found to decrease during the electron beam irradiation, which indicates that Ce ions act as a buffer to retard the damage of the glass network during TEM observation. More details about the EELS analysis of the borosilicate glasses will be discussed.

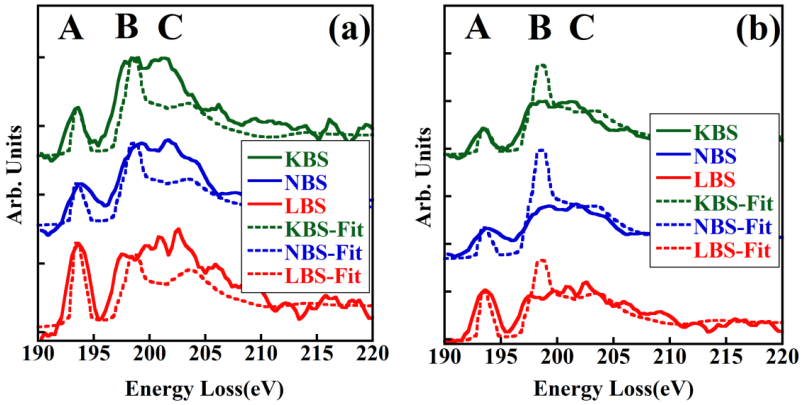

Figure 1: Experimental boron K-edge EELS spectra of the lithium-, sodium- and potassium borosilicate glasses (solid lines) along with the fitted spectra (dashed lines) by (a) the previously reported method and (b) the fitting method developed in this work

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2) S. D. Cheng, G. Yang, Y. Q. Zhao, M. Y. Peng, J. Skibsted and Y. Z. Yue: "Quantification of the boron speciation in alkali borosilicate glasses by electron energy loss spectroscopy", *Scientific Reports* 5 (2015) 17526.