A Structural Study of Alkali-Germano-Phosphate Glasses by Ge K-edge EXAFS: Is 5-fold Ge Present?

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Introduction

Germanate (Ge) glasses undergo very pronounced physical changes with the addition of alkalis. The densities and refractive indices of these glasses exhibit a maximum called the "germanate anomaly". This behavior makes these glasses useful as self-focusing optical fibers. The proposed mechanism for the anomaly is a coordination change of $^{[4]}$Ge to $^{[6]}$Ge. This mechanism is based on an observed lengthening of the Ge-O bond length with added alkali. However, on close examination, the bond lengthening does not correlate with the anomaly maximum.[1,2] The anomaly must be due to some other mechanism. More recently it has been suggested that $^{[5]}$Ge, indicated by neutron scattering,[3] may be responsible.

In this study we examine the coordination environment of Ge in a series of germano-phosphate glasses using Ge *K*-edge EXAFS. The presence of P in silicate glasses induces a coordination change of Si from 4- to 6-fold coordination. We had anticipated that a similar effect might occur in Ge glasses with added phosphorous.

Methods and Materials

Alkali-germano-phosphate glasses were prepared with compositions of R_2O-GeO_2-P_2O_5 (R = Na, K, and Rb) and with varying GeO_2:P_2O_5 mole ratios (8:1, 6:1, 4:1 and 2:1 with R_2O varying from 5 to 30 mol% in 5 mol% increments for each GeO_2:P_2O_5 ratio). Data were obtained at the bending magnet beamline, ID-20, PNC-CAT. Powdered glass samples were mounted on Kapton tape, and Ge *K*-edge EXAFS were collected in both transmission and fluorescence mode.

Results

Density measurements (Fig. 1) for a series of Na_2O-GeO_2-P_2O_5 glasses with varying GeO_2:P_2O_5 ratios (8:1, 6:1, 4:1, and 2:1) indicate that for the low P_2O_5 (8:1, 6:1, 4:1) glasses a density maximum is observed, similar to that observed in pure alkali-germanate glasses. The Ge *K*-edge data obtained for the Na_2O glasses (8:1, 6:1, and 4:1) have been modeled using FEFF74 with input from rutile GeO_2 ($^{[6]}$Ge), trigonal GeO_2 ($^{[4]}$Ge), and $K_2Ge_8O_{17}$ ($^{[5]}$Ge,$^{[4]}$Ge). Preliminary analysis of the data suggests that no higher coordinated species are present (i.e., $^{[6]}$Ge or $^{[5]}$Ge) and that the Ge-O bond distances are relatively unchanged (~1.74 Å) until compositions >25-30 mol% Na_2O, where a slight increase in the Ge-O bond length is observed (~1.75 Å).

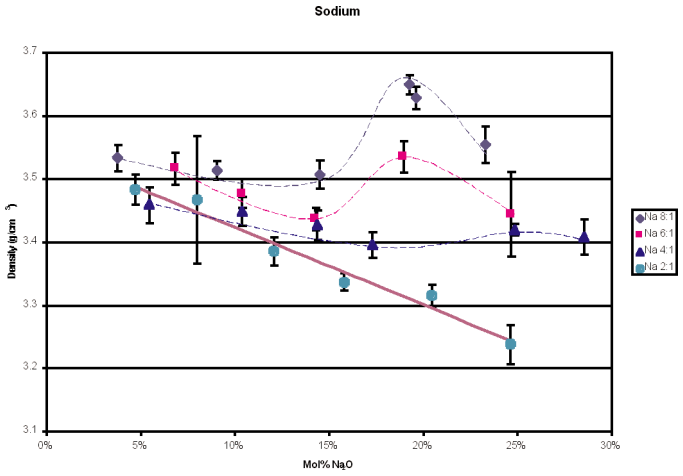

FIG. 1. Density measurements for a series of alkali-germanate glasses.

Discussion

The lack of significant bond lengthening for compositions, that exhibit a density maximum lends support for the existence of a structural mechanism responsible for the anomaly that does not involve higher coordinated germanium species. Furthermore, it also suggests that the germanium part of the network, when P is present, is relatively unaffected by the addition of alkalis.

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