Local structural changes in amorphous $NaAlGe_3O_8$ upon compression to 50 GPa

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Silicate melts are key agents for heat and matter transport within the Earth. However, to understand their physico-chemical properties, precise structural data at relevant conditions of the deep Earth are needed. In particular, significant densifications accompanied by coordination number changes of the network forming cation (here Ge, in nature Si) are expected upon compression. Despite paramount influence of these changes on transport properties and their underlying mechanism on the atomic scale [1], the progress of densification remains not fully understood.

Here, we report on the pressure induced structural changes in a synthetic $NaAlGe_3O_8$ glass, that presents an analogue system to sodium rich polymerized silicate melts. The local structural changes of Ge were studied using extended x-ray absorption fine structure spectroscopy (EXAFS) coupled to the diamond anvil cell (DAC) up to 50 GPa. In the probed glass, Si is fully substituted by Ge in order to circumvent experimental restrictions caused by combination of EXAFS with the DAC. We acquired high-quality EXAFS data up to 16 $Å^{-1}$ thanks to the use of nano-polycrystalline diamonds. Data were analysed up to the third coordination shell, using both single and multiple scattering paths.

We found that under compression the bond distances for the first Ge-O shell increase from ca. 1.72 to 1.79 Å. This result is invariant to the fit model (path numbers). The Ge-O bond length reaches a maximum between 25 and 32 GPa. In this pressure range also the fitted coordination number of Ge reaches about 6. Dominant tetrahedral coordination is observed up to 8 GPa. At higher pressure fitted parameters imply a gradual change of the coordination from tetrahedral to octahedral coordination up to pressures of 25-32 GPa. From EXAFS we cannot conclude whether, during the transition, the system is governed by a mixture of tetrahedral and octahedral symmetry or if five-fold symmetry is also present as suggested for Si in amorphous SiO_2 [2]. In contrast to the fit results of the first shell, the fits for the second shell do not provide clear distinction for Ge-Ge correlations only, or significant presence of Ge-Na correlations. Presence of Ge-Al correlations seems unlikely, though.

Previous EXAFS results on amorphous GeO_2 [3, 4] show the change in Ge coordination at much lower pressure. The structure of both compounds at ambient conditions is dominated by the fully polymerized network of Ge tetrahedra. Thus, this comparison may imply that replacement of Ge by Al and Na considerably influences the compression behaviour. The results of this study provide valuable reference data for further investigation of the structural changes of Ge as a monitoring element for Si under compression in complex glassy materials relevant for geological systems.

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