

Structural changes in complex silicate glasses at high pressure and temperature conditions probed by X-ray absorption spectroscopy

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Silicate melts play an important role in the dynamics of the Earth's interior. They represent a multicomponent system and consist of a polymerized network built by network forming cations, such as Si, and network modifying cations, such as Na, Ca or Mg. The competing behaviour of both cation types shapes the macroscopic physical properties of magmas as a function of their composition (rheology, density, trace element transport capacity).

X-ray absorption fine structure spectroscopy (XAFS) is one of the most suitable techniques to probe the local structural environment of elements. XAFS has often been combined with high-pressure and temperature instrumentation, such as the resistively heated diamond anvil cell (RH-DAC) to monitor local structural changes. However, because diamond exhibits a very high absorbance for energies below 10 keV most geologically relevant elements, such as Si and Na that are low Z elements cannot be investigated using this approach.

In order to overcome the experimental restrictions we substituted the elements of interest by their chemical and structural analogues that are high Z elements (i.e., Ge monitors the behavior of the network formers Si or Al, whereas Sr the network modifiers such as Na or Ca).

As a first step we investigated the compression of amorphous NaAlGe₃O₈ up to 144 GPa, which represents the simplified Ge-analogue of natural Na and Al-bearing silicate melts. We observed a coordination change for Ge from [4] to [6]-fold in the P range between ~3 and 34 GPa, revealed by the increase of the Ge-O bond length (Figure 1). Compared to pure GeO₂ glass the observed structural change appears at slightly lower P and extend over larger pressure interval [1, 2, 3]. We related these differences in the compaction behavior to the presence of the network modifying cation (Na) in this study. Compared to pure SiO₂ glass [4], the structural changes in Ge-bearing glasses start at significantly lower pressures and the octahedral coordination is reached at lower pressure (Figure 1).

Beyond 34 GPa the Ge-O bond length decreases up to 144 GPa, which can be related to compaction of the Ge-oxide octahedron without increase of the coordination number. Distortion of the octahedra as found by [6] cannot be ruled out and could explain the slight deviation from a continuous bond-length reduction as observed around 90 GPa and 120 GPa (Figure 1).

In a second step we studied the compression behaviour of a more complex multi-component glass composition (Na_{0.45}Ca_{0.1}Mg_{0.05}Sr_{0.5}Al_{1.35}Si_{1.95}Ge_{0.5}O_{7.8}) up to 140 GPa, resembling closely natural melts. In addition we monitored the effect of temperature on the 4-6-fold coordination transition and performed heating runs in the P/T domain of 3-23 GPa and 520°C. Preliminary results reveal a slight shift of the [4]-[6]-fold transition to lower P with increasing T.

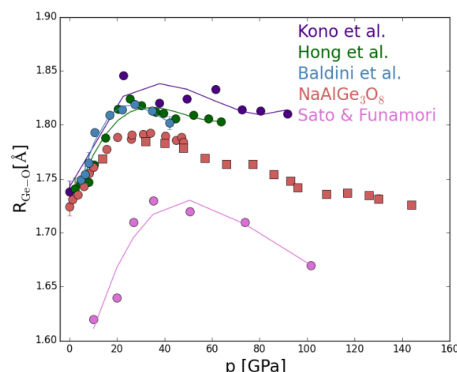


Figure 1. Evolution of the Ge – O distance as a function of pressure for NaAlGe₃O₈ compared to the literature data for GeO₂ [1], [2], [3] and SiO₂ [4]

The results give important insight into the role of network modifiers on the compaction behaviour of silicate and germanate glass structures, which in turn governs chemical distribution processes in the deep Earth. This is the first attempt to constrain the temperature effect on the compaction of complex alumina-silicate-germanate glasses which is of great importance for understanding the relation between thermodynamic behaviour and the atomic-scale properties of matter in the deep planetary interior.

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