

Valence-to-core X-ray emission spectroscopy of complex amorphous germanium oxides: Sensitivity with respect to network polymerization and coordination

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The structure of germanate glasses in systems like $\text{GeO}_2\text{-Na}_2\text{O}$ and $\text{GeO}_2\text{-SiO}_2$ is of fundamental and practical importance in glass research and related fields since germanates are considered structural analogs to silicates. Two important parameters are 1) the degree of tetrahedral polymerization at pressures below about 10 GPa, and 2) the germanium coordination at higher pressures, where the network character is gradually replaced by a close-packing of oxygen atoms.

Today, there is a need for analytical techniques capable of detecting the degree of polymerization of chemically complex glasses in confined environments like diamond anvil cells. While X-ray absorption techniques can retrieve from glasses bond distances and – with larger uncertainty – coordination, they are generally not sensitive to second-coordination-shell effects like the degree of tetrahedral polymerization. Diffraction techniques are capable to detect both first and second coordination shell effects usually only in those chemically simple cases, where the partial radial distribution functions do not strongly overlap. With this work, we aim at exploring the extent to which valence-to-core X-ray emission spectroscopy (vtc-XES) can provide first- and second-coordination-shell information on amorphous and chemically complex compounds.

We measured the vtc-XES spectra of germanium oxides at ambient and high pressure with von-Hamos spectrometers and we compared inferred structural information to XRD measurements. The interpretation of our results is corroborated by Bethe-Salpeter calculations with the OCEAN code.

The results show that the $\text{K}\beta''$ emission line is sensitive to coordination and oxygen-germanium bond distance as first coordination shell effects. Furthermore, it reflects the different binding energies of bridging and non-bridging oxygen atoms. The $\text{K}\beta''$ emission line may thus allow for tracking the state of polymerization of a germanium oxide glass under pressure in diamond anvil cells or in other confining environments.