Pressure induced coordination number change in germanate melt

Osamu Ohtaka[1], Hiroshi Arima[2], Hiroshi Fukui[1], yoshinori katayama[3], Wataru Utsumi[3], Akira Yoshiasa[4]

[1] Earth and Space Science, Osaka Univ, [2] Earth and Space Sci., Osaka Univ, [3] JAERI, [4] Earth and Space Sci., Osaka Univ.

http://www.ess.sci.osaka-u.ac.jp/~ohtaka/index.html

Like crystalline phases, it is most likely that structures of liquid phases change with pressure. The number of high-pressure study on this phenomenon is, however, still very limited because of experimental difficulties. Structural and physical properties of silicate melts are very important for geophysics. At high pressure and temperature, coordination number (CN) change of Si in silicate melts will occur and probably result in the change of the physical properties such as viscosity. Germanates are structural analogs of silicates. Since they show phase transitions at lower pressure than silicates, they can be used as model compounds which are more accessible to high pressure experiments. Ge can be conveniently studied with an x-ray-absorption method, while the Si K-edge occurs in the soft X-ray region which makes it impossible to perform the XAFS observation in high pressure apparatus. In this study, we have investigated the local structure of alkali-GeO2 melts by using a high-pressure XAFS technique.

High-pressure and high-temperature XAFS experiments were performed at BL14B1 in the SPring-8 using a cubic type apparatus, SMAP 180 system. We used sintered diamond anvils with 3 mm truncation for single stage compression. Li2O-4GeO2 glass was mixed with B2O3 and BN (1:1:20 wt. ratio), and put in a BN sample chamber. Pressure transmitting medium was boron and epoxy resin. A pair of LaCrO3 or MoSi2 disk was used for the furnace, and temperature was monitored by a W-Re thermocouple. X-ray beam was monochromatized using Si(111) reflection and focused vertically by two mirrors. X-ray absorption spectra near Ge K-edge were measured up to 9 GPa at 1273 K.

EXAFS interference functions were extracted from the measured X-ray absorption spectra and peaks which correspond to the Ge-O distance were observed. The Ge-O distances obtained with the EXAFS and the modification in the XANES indicate that present liquid germanate consists of a mixture of fourfold and sixfold Ge around 3 GPa and of the complete sixfold Ge above 4 GPa. The transition pressure is much lower than that observed in the germanate glass with room temperature compression. This is the first result that the structural data of germanate melts under pressure have been obtained.