

XAFS Measurement of Germanate Melts under High-temperature and High-Pressure

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Structural and physical properties of liquid under pressures are a very interesting issue for earth and material science. Like crystalline phases, it has been proposed that structures of liquid phase change with pressure. However, the number of experimental study on this phenomenon is still very limited. Using a high-pressure XAFS technique, we have investigated the local structure of $\text{Li}_2\text{O}-4\text{GeO}_2$ melts and demonstrated that a dense liquid phase with GeO_6 octahedron appears under pressure⁽¹⁾. Germanates are structural analogs of silicates. Because they show phase transitions at lower pressure than silicates, they can be used as model compounds that are more accessible to high pressure experiments. In this study, we have investigated the local structure of SrGeO_3 melts by using a high-pressure and high-temperature XAFS technique.

High-pressure and high-temperature XAFS experiments were performed at BL14B1 using SMAP 180 system. We used WC anvils of 6 mm edge square faces. SrGeO_3 powder was synthesized by mixing SrCO_3 and GeO_2 and firing 1000 °C for 24 hours. SrGeO_3 was mixed with B_2O_3 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 LaCrO_3 disk was used for a heater. Temperature was monitored by a W-Re thermocouple. Generated pressure was estimated using the calibration curve based on NaCl pressure scale. XAFS experiments were performed using a Si(111) double-crystal

monochromator. The beam was focused vertically by two mirrors. The incident X-ray intensity and the transmitted X-ray intensity were detected by using two ionization chambers filled with pure N_2 and pure Ar gases, respectively. X-ray absorption spectra near Ge *K*-edge were measured.

The XANES spectra of the present germanate recorded at various conditions are shown in Fig. 1. The results show slightly difference in spectra forms and peak positions, which correspond to the coordination environments of Ge atoms. Further quantitative analysis is being undertaken.

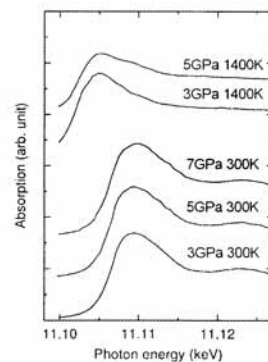


Figure 1 Experimental Ge *K*-edge XANES spectra of the present germanate.

(1) Ohtaka et al., Phys. Rev. Lett. (2004), in press.

Surface-structure study on lithium battery materials using surface x-ray diffraction

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Lithium batteries have attracted much attention in recent years because of their high specific energy and longcycle-life. For the battery performances, interfacial reactions at the electrode/electrolyte interface play important role. Previously, the interfacial phenomena were studied on thin film cathode made by various thin film formation technique. These cathodes have usually been constructed by poly-crystalline state; the effect of grain boundary and the anisotropy on crystal plane are difficult to estimate. Electrodes with epitaxial film are a novel approach for clarifying and controlling interfacial electrode reaction of lithium battery by making ideal interface between the electrode and electrolyte. In the present study, we could successfully grow single-crystal thin-films of LiCoO_2 and LiMn_2O_4 on single crystal substrates by pulsed laser deposition (PLD) method. We

examined surface structure changes at the electrode/electrolyte by in-situ surface X-ray reflectivity using SPring-8(BL14B1) with keeping different constant potentials. This measurement clarified thickness and roughness of the electrode surface. For the thin-film of LiCoO_2 deposited on the (1 1 0) plane of SrTiO_3 substrate, no change at the interface was observed. For LiMn_2O_4 deposited on the (1 1 0) and the (1 1 1) plane of SrTiO_3 , the surface structure changed with the potential applied. Furthermore, the surface structure change depends on the orientation of the LiMn_2O_4 plane. Based on our experimental results, interfacial reactions at the electrode/electrolyte interface will be clarified.