

In-situ high-pressure x-ray diffraction study of unquenchable ZnGeO₃ perovskite

Hitoshi Yusa[1]; Masaki Akaogi[2]; Nagayoshi SATA[3]; Hiroshi Kojitani[4]; Ryo Yamamoto[5]

[1] NIMS; [2] Dept. of Chem., Gakushuin Univ.; [3] IFREE, JAMSTEC; [4] Dept. of Chemistry, Gakushuin Univ.; [5] Dept. Chem., Gakushuin Univ.

Several high-pressure perovskite phases of germanate and titanate [e.g. MgGeO₃; Leinenweber et al. (1994), MnTiO₃; Ross et al. (1989)] exhibit a transformation to lithium niobate phase during decompression to ambient condition. In ZnGeO₃ compound, it is reported that the lithium niobate phase are recovered as a quench products of high P, T experiments. Until now, however, the direct confirmation of the ZnGeO₃ perovskite phase has not been observed yet. We have tried to make in-situ x-ray diffraction experiments to identify the perovskite phase under high pressure.

The high P, T experiments have been done at BL-10XU (SPring8) using a symmetrical diamond anvil cell (DAC) combined with Nd:YLF laser. The angle dispersed x-ray diffraction (30 keV) was detected by an imaging plate and x-ray CCD camera. The starting ZnGeO₃ ilmenite phase, which was synthesized at 10 GPa and 1200 degC by a multi-anvil apparatus (Kawai-type), was compressed in the DAC without any pressure medium. After compression to 34 GPa, the sample was heated at 1300 - 1400 K. Any absorber, such as platinum, is not necessary to add to enhance laser heating, because the gray brownish sample has absorption band in the near-infrared laser wavelength. The pressure decreased to 31 GPa after 30 minutes heating. The color of heated area changed to transparent. Then, the diffraction profile exhibits drastic change from broad peaks of ilmenite to sharp peaks. Peaks more than the number of 20 appear in the range of $2\theta=18\text{deg}$. All new peaks can be assigned to the indices by Pbnm orthorhombic perovskite. The refinement calculation give the lattice parameters of $a=4.817(2)$, $b=4.943(1)$ and $c=7.019(2)$ at 31 GPa. This shows the orthorhombic perovskite close to tetragonal form as compared to MgGeO₃ and MnTiO₃. The structure of the recovered sample was confirmed to be the lithium niobate type.

Recompression experiment on the recovered lithium niobate phase was successively carried out using a quasi hydrostatic pressure medium to investigate the transformation to perovskite phase at room temperature. High-resolution x-ray diffraction experiments were performed at BL-04B2 with the long film distance (600 mm) and high energy x-ray of 38 keV. As a result, the transition pressure was determined to the range between 10.5 to 13.3 GPa. Whereas, the back transition to the lithium niobate phase exhibits a hysteresis. The perovskite phase reverted to the lithium niobate phase around the pressure from 10.7 to 6.8 GPa. It is interesting that these results give the similar transition pressure to the perovskite - lithium niobate transition in MgGeO₃ [Leinenweber et al. (1994)].