Neutron powder diffraction study on quantum paraelectric state of water confined in beryl

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In confined spaces, water molecules exhibit different physical properties from those in a bulk state mainly due to the structural difference of hydrogen bond networks. Beryl, which is a silicate mineral (chemical formula: $Be_3Al_2Si_6O_{18}$, space group: *P6/mcc*), is composed of siloxane nanocages, which can store a single water molecule around the center of the cages. A recent inelastic neutron scattering (INS) study clarified that the dynamical disorder falls into a quantum tunneling state with decreasing temperature; several INS peaks due to tunneling splitting were observed below 25 K [1]. A dielectric study on beryl revealed quantum paraelectric behavior down to 0.3 K, supporting the tunneling state mentioned above [2]. Beryl exhibits anomalous low-temperature behavior of H_2O molecules compared with other usual water systems such as ices, and hydrates. This is because the water molecules in the cages are isolated from the neighboring water molecules [1]. In this study, we have performed the neutron powder diffraction (NPD) experiments of H_2O- and D_2O-enriched beryls to search a possible ordering transition of water molecules and investigate the localization of hydrogen and deuterium atoms in the quantum paraelectric state in beryl. Thus far, neutron diffraction study of hydrous beryl was reported down to 30 K using single crystal of natural samples with low cage occupancy (~30%) [3]. This is the first NPD measurement of both H_2O- and D_2O-molecules enriched samples (cage occupancy: 60%) in a much lower temperature region. The NPD measurements were conducted using the high-efficiency and high-resolution measurements, HERMES, installed at the JRR-3 reactor, with 1K Cryostat which can be cooled down to 0.7 K. The incident neutron wavelength was 1.34 Å. The samples were synthesized under high-pressure (2.5 GPa) and high-temperature (600 °C) conditions using powdered natural beryl and H_2O/ D_2O water as starting materials.

Figure 1 shows the NPD patterns of H_2O- and D_2O-enriched beryls obtained at 0.7 K, the lowest measurement temperature. The red bars represent the peak positions calculated for each of the structures. No significant signs of superlattice reflections accompanied with the expected ordering transition in both the samples. The NPD patterns can be explained based on the crystal structure of beryl determined at room temperature. Further structural analysis of the difference Fourier is on-going to elucidate the localization of hydrogen and deuterium atoms in the quantum paraelectric state.

[1] A. I. Kolesnikov *et al*., Phys. Rev. Lett. **116**, 167802 (2016). [2] B. P. Gorshunov *et al*., Nat. Commun. **7**, 12842 (2016). [3] G. Artioli *et al*., Am. Mineral. **78**, 762 (1993).

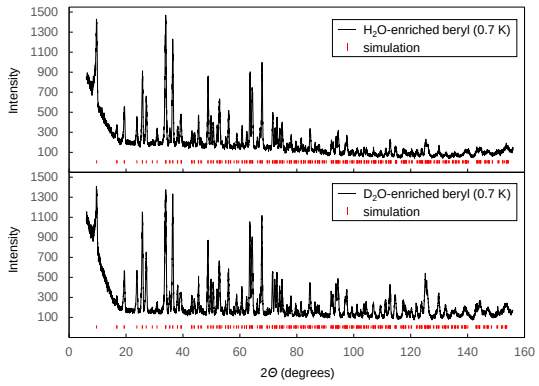

Fig. 1. Neutron diffraction patterns of H_2O- and D_2O-enriched beryls obtained at 0.7 K. The red bars represent the peak positions calculated for each of the structures.