Observation of structural phase transition in Co$_3$Sb$_4$O$_6$F$_6$ by multi-quantum beam


Department of Materials Science and Engineering, National Defense Academy, Yokosuka, Kanagawa 239-8686, Japan, Department of Physics, Graduate School of Science, Osaka Metropolitan University, Sakai, Osaka 599-8531, Japan, Department of Materials Science, Graduate School of Engineering, Osaka Metropolitan University, Sakai, Osaka 599-8570, Japan, Japan Synchrotron Radiation Research Institute, SPring-8, 1-1 Kouto, Sayo-gun, Hyogo 679-5198, Japan, Neutron Materials Research Division, Materials Sciences Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tokai, Ibaraki 319-1106, Japan, Department of Chemistry, Graduate School of Advanced Science and Engineering, Hiroshima University, 1-3-1, Kagamiyama, Higashi-Hiroshima 739-8530, Japan

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Mixed-anion compounds form unique crystal structures owing to the coordination of the different types of anions with cations such as those of transition metal elements because of the differences in the ionic radii, electronegativities, and polarizabilities of the anions. Moreover, these compounds exhibit attractive physical properties owing to the local symmetry degradation of the coordination polyhedron and changes in the energy level of the crystal field [1]. Recently, the oxyfluorides A$_3$Sb$_4$O$_6$F$_6$ (A = Co, Ni), which contain two types of anions, namely O and F, were synthesized by the hydrothermal method [2]. Hu et al. investigated the crystal structure and magnetic properties of Co$_3$Sb$_4$O$_6$F$_6$. However, the physical properties such as the heat capacity, dielectric property, and details of the low-temperature crystal structure have not been investigated yet. This study aimed to clarify the low-temperature crystal and magnetic structures of Co$_3$Sb$_4$O$_6$F$_6$ by synchrotron radiation and neutron diffraction and investigate its specific heat and dielectric and magnetic properties. In addition, Co$_3$Sb$_4$O$_6$F$_6$ is one of oxyfluorides, and the coordination of oxygen and fluorine is closely related to physical properties, so its information is very important. Therefore, the coordination of oxygen and fluorine was determined by high-resolution synchrotron diffraction and first-principles calculations. Synchrotron powder diffraction (SPD) experiment was conducted at beamline BL02B2 of SPring-8, Japan [3]. Neutron powder diffraction (NPD) experiment was conducted by multi-quantum beam flight (TOF) diffractometer beamline BL08 SuperHRPD of MLF J-PARC, Japan [4]. A structural phase transition was observed at $T_S \sim 180$ K from a cubic phase to a $c > a$ tetragonal phase. Moreover, a magnetic structure analysis using NPD data showed a magnetic transition from a paramagnetic to a G-type antiferromagnetic phase at $T_S \sim 67$ K, at which a cusp was also observed in the temperature dependence of magnetic susceptibility. Rietveld refinements using SPD and NPD data revealed the rotation and deformation of the Co$_3$F$_6$ octahedron due to the large displacement of the F atoms play an important role in the structural phase transition at $T_S$ [5].


