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Reversible phase transition of metal-organic framework by de/rehydration

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The phase transition of a new coordination polymer, [Zn(HBTC)(BPE)_{0.5}(H₂O)]_n·nH₂O, HBTC²⁻=dianion of trimesic acid, DPE = 1,2-bis-(4-pyridyl)ethane, during dehydration and rehydration processes has been monitored by in-situ synchrotron powder X-ray diffractometry. The complex with an extended 1D ladderlike metal-organic framework (MOF) has been synthesized and structural characterized by single-crystal X-ray diffraction method. Structural determination reveals that the Zn(II) ion is four-coordinated in a distorted tetrahedral geometry, bonded to one nitrogen atom from one BPE ligand, and three oxygen atoms from two monodentate carboxylate groups of two HBTC²⁻ ligands and one coordinated water molecule. The 1D ladderlike MOF **1** dehydrates up heating of the solid to 180°C to form a new 2D MOF, [Zn(HBTC)(DPE)0.5]n (**2**). The reversible solid-state structural transformation between crystalline **1** with 1D ladderlike framework and its dehydrated powder **2** with 2D framework via the displacement of coordinated water molecule to HBTC²⁻ ligand, by thermal de/rehydrated processes has been monitoring by in situ PXRD measurements. In the crystal lattice, during heating process, one oxygen atom of the uncoordinated carboxylate group of HBTC²⁻ ligand moves toward the neighboring Zn(II) ion, with concomitant removal of the water molecule, and form a new Zn-O bond without expanding the coordination geometry of metal center. The dehydrated structure for **2** at 180°C was determined from the powder diffraction data with program DASH. Powder pattern was indexed with Dcivol and Treor programs. The structure factors of the powder patterns were extracted with Pawley's method, and simulated annealing method was employed to determine the crystal structure. The final refinement with the Rietveld method was performed using GSAS-EXPGUI program.

Keywords: powder crystallography, metal-organic framework, dehydration

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Origin of giant tetragonal lattice strain in (1-x)BiFeO₃-xPbTiO₃ System

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Electron charge density studies are carried out to reveal the origin of the large tetragonal lattice distortion in multiferroic perovskites (1-x)BiFeO₃-xPbTiO₃ (BF-xPT) by analyzing synchrotron radiation powder diffraction data measured at SPring-8 BL02B2 using the MEM/Rietveld method. The characteristic chemical bondings that are Fe/Ti in 5-fold O coordination and covalent Bi/Pb-O bonding are clearly visualized in the MEM charge density maps in the entire tetragonal composition range $x > 0.31$, which implies BF-xPT is a layered material in the tetragonal phase. The largest tetragonal lattice strain of $c/a = 1.187$ is observed at $x = 0.31$ in the vicinity of the morphotropic phase boundary (MPB) to the rhombohedral structure [1]. Note that all perovskite-type solid solutions with tetragonal structures never show the largest tetragonal distortion near the MPB, for example the smallest tetragonal distortion in PZT near the MPB [2, 3]. The crystal structure of BF-0.31PT, together with PT, is shown in Fig. 1. With decreasing x from 1 (PT) to 0.31, the lattice parameter a decreases, while c increases. Significant changes in the lattice parameters a and c are attributed to changes in the Bi/Pb-O (covalent) and Fe/Ti-O (ionic) bond lengths, respectively. The extrapolated lattice parameters and bond lengths at $x = 0$ (BF) on the basis of the experimentally observed ones well coincide with those optimized by *ab initio* calculations assuming the tetragonal structure with $P4mm$ symmetry. We consider that the tetragonal structure of BF-0.31PT with large tetragonal distortion is originated from the hidden tetragonal structure of BF. By substituting BF for PT in the BF-xPT system, the rotational mode of the Fe/Ti-O₆ octahedron is suppressed, and the tetragonal structure is established by the dominated soft phonon at the Γ point in the Brillouin zone. The Bi/Pb-O covalent bonding plays an important role for the large tetragonal distortion. It is quite natural to consider that the layered structure involving the Fe/Ti-O₅ pyramids are materialized by the contraction on the Bi/Pb-O bonding.

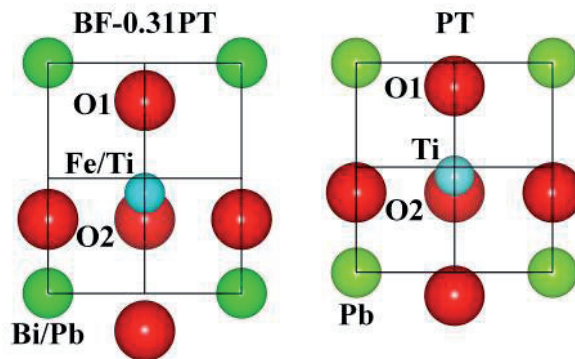


Fig. 1 Crystal structure of BF-0.31PT and PT.

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Crystal structure of BaTiO₃-based ceramics in MLCCs under applied high voltage

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