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Keywords: X-ray_diffraction, EXAFS, miscibility

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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 Dicvol 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.

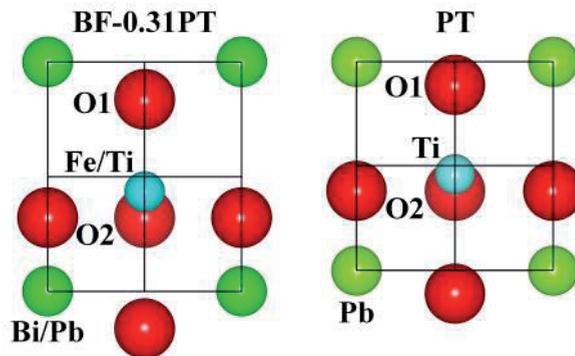


Fig. 1 Crystal structure of BF-0.31PT and PT.

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

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Barium titanate BaTiO₃ is the inorganic compound with a cubic perovskite structure as a prototype structure. Successive phase transitions take place with decreasing temperature, and BaTiO₃ with a tetragonal structure shows prominent ferroelectric properties at room temperature. Thus far, BaTiO₃ has generally been used as a dielectric for multilayer ceramic capacitors (MLCCs) owing to its low dielectric loss and high permittivity. In particular, to satisfy the low dielectric loss and low microphonics requirements, Gd- and Mg-doped BaTiO₃ are proposed as candidates for the dielectric materials [1-3], which enable us to suppress various problems involved in applying the ferroelectric properties of pure BaTiO₃ to MLCCs. The temperature dependence of permittivity can be improved by increasing the Gd and Mg contents, although the Curie temperature (T_C) is significantly decreased. Our electron charge density study reveals that the lowering of T_C is due to the decrease in covalency on the Ti-O bond in BaTiO₃ [4]. We have recently revealed that Gd is the most effective rare-earth element for suppressing insulation degradation for applied high voltage and temperature stress among BaTiO₃-based MLCCs. In this paper, we report *in situ* crystal structure analysis of (Ba_{0.94}Gd_{0.06})(Ti_{0.97}Mg_{0.03})O₃ (BGTM) under variations in applied high electric field and temperature using a sample fabricated based on a MLCC. The electric-field-induced lattice strain and atomic displacement in BGTM are demonstrated in the environments which simulate the electric device operating.

Powder diffraction experiment was carried out using the large Debye-Scherrer camera installed at BL02B2 in Spring-8. The energy of X-rays was 35 keV ($\lambda = 0.35 \text{ \AA}$), which enabled us to investigate the inside of MLCC in transmission geometry. A clear one-to-one correspondence between the crystal structure and the dielectric properties of BGTM in the MLCC, *e. g.*, the phase transition temperature $T_C = 293 \text{ K}$, was confirmed on the diffractometer using the simultaneous measuring system. The tetragonal distortions in the variation of the lattice constants and the atomic displacement of the B-site atoms were investigated as functions of temperature (200 – 400 K) and applied electric field up to 300 kV/cm. The tetragonal distortion observed for the ceramic grains arranged in the electric field was significant in the vicinity of T_C . The lattice strain was increased with increasing the electric field, and saturated above 100 kV/cm at 300 K. The displacements of the B-site ions showed a similar variation as the lattice strain. The fluctuation of the dipole moment at the phase transition can be demonstrated by adopting a Langevin function for the electric-field-induced polarization calculated based on the point charge model. These results give clear evidence that the induced lattice strains are attributed to the displacements of the constituent ions in the electric field.

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Crystal structure of anion exchangeable Mg²⁺-Al³⁺ layered double hydroxides

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C720

Layered double hydroxide (LDH), of which general formula is $[M^{2+}_{1-x}M^{3+}_x(\text{OH})_2](A^{n-})_{x/n} \cdot m\text{H}_2\text{O}$ where M^{2+} and M^{3+} are divalent and trivalent metal ions and A^{n-} is anion, is one of the promising anion exchangeable inorganic materials for cleaning environmental water polluted by toxic anions. Figure 1 shows a typical crystal structure of LDH, which is composed of positively charged metal hydroxide nanosheets and interlayer anions with water molecules [1], [2]. A key to develop LDHs with higher anion selectivity is to understand the interaction between the hydroxide nanosheet and the incorporated anions with water molecules from viewpoint of crystal structure. So far, however, only a few structures of LDHs have been reported. In this study, structural features of $[\text{Mg}_{2/3}\text{Al}_{1/3}(\text{OH})_2](A^{n-})_{1/3n} \cdot m\text{H}_2\text{O}$ (MgAl-LDH) with $A^{n-} = \text{CO}_3^{2-}$, Cl^- , and NO_3^- are investigated by synchrotron radiation powder diffraction measurements at Spring-8 BL02B2.

MgAl-LDH($A^{n-} = \text{CO}_3^{2-}$) was synthesized by hydrothermally treating a mixed aqueous solution of $\text{Mg}(\text{CO}_3)_2$, $\text{Al}(\text{CO}_3)_3$, and hexamethylenetetramine at 140°C for 48 hours. The obtained MgAl-LDH($A^{n-} = \text{CO}_3^{2-}$) were converted to MgAl-LDH($A^{n-} = \text{Cl}^-$) by acetate buffer method [1]. MgAl-LDHs with other anions were synthesized by immersing MgAl-LDH($A^{n-} = \text{Cl}^-$) into aqueous solution with appropriate anions.

Crystal structures of MgAl-LDHs($A^{n-} = \text{Cl}^-$ and NO_3^-), which had been unknown, were refined by assuming the structure parameters of MgAl-LDH($A^{n-} = \text{CO}_3^{2-}$) [3] as initial parameters. The Rietveld analyses revealed that the arrangement of water molecules in the interlayer depends on A^{n-} . The thickness of the metal hydroxide sheet is almost independent of A^{n-} , whereas that of the interlayer is large in MgAl-LDH($A^{n-} = \text{NO}_3^-$). The site of water molecules is located on the almost same z-coordinate in MgAl-LDH($A^{n-} = \text{CO}_3^{2-}$, Cl^-). In MgAl-LDH($A^{n-} = \text{NO}_3^-$), on the other hand, z of water molecules is different from z of NO_3^- . There are two water molecule sheets in the interlayer between NO_3^- layer and hydroxide sheet. There is a possibility that the difference in the site of water molecule controls the anion selectivity of LDH.

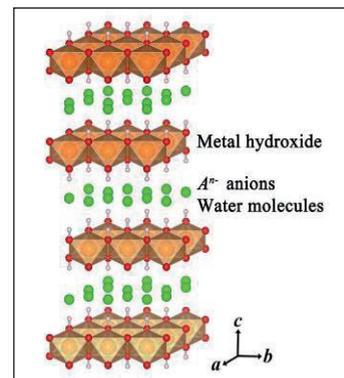


Fig. 1 Crystal structure of LDH (hexagonal crystal system). Metal hydroxide nanosheet and interlayer region, which contains A^{n-} anions and water molecules respectively, stack alternatively along the c axis.

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The low-temperature magnetic and structural properties of a new multiferroic GdFe₃(BO₃)₄

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