Barium titanate $BaTiO_3$ is the inorganic compound with a cubic perovskite structure as a prototype structure. Successive phase transitions take place with decreasing temperature, and $BaTiO_3$ with a tetragonal structure shows prominent ferroelectric properties at room temperature. Thus far, $BaTiO_3$ 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 $BaTiO_3$ 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 $BaTiO_3$ 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 $BaTiO_3$ [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 $BaTiO_3$-based MLCCs. In this paper, we report *in situ* crystal structure analysis of $(Ba_{0.94}Gd_{0.06})(Ti_{0.97}Mg_{0.03})O_3$ (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 ($\lambda = 0.35$ Å), 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 $T_C = 293$ 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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MS81.P48

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

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Layered double hydroxide (LDH), of which general formula is $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n} \cdot mH_2O$ 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 $[Mg_{2/3}Al_{1/3}(OH)_2](A^{n-})_{1/3n} \cdot mH_2O$ (MgAl-LDH) with $A^{n-} = CO_3^{2-}$, Cl⁻, and NO_3^- are investigated by synchrotron radiation powder diffraction measurements at SPring-8 BL02B2.

MgAl-LDH($A^{n-} = CO_3^{2-}$) was synthesized by hydrothermally treating a mixed aqueous solution of $Mg(CO_3)_2$, $Al(CO_3)_3$, and hexamethylenetetramine at 140°C for 48 hours. The obtained MgAl-LDH($A^{n-} = CO_3^{2-}$) were converted to MgAl-LDH($A^{n-} = $ Cl⁻) by acetate buffer method [1]. MgAl-LDHs with other anions were synthesized by immersing MgAl-LDH($A^{n-} = $ Cl⁻) into aqueous solution with appropriate anions.

Crystal structures of MgAl-LDHs($A^{n-} = $ Cl⁻ and NO_3^-), which had been unknown, were refined by assuming the structure parameters of MgAl-LDH($A^{n-} = CO_3^{2-}$) [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($A^{n-} = NO_3^-$). The site of water molecules is located on the almost same *z*-coordinate in MgAl-LDH($A^{n-} = CO_3^{2-}$, Cl⁻). In MgAl-LDH($A^{n-} = NO_3^-$), 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.
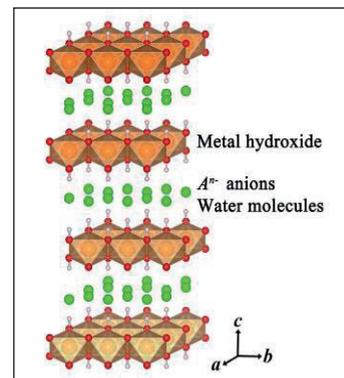

Fig. 1 Crystal structure of LDH (hexagonal crystal system). Metal hydroxide nanosheet and interlayer region, which contains A^{n-} anions and water molecules respectively, stack alternatively along the *c* axis.

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MS81.P49

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

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There is a great interest in the multiferroic compounds and in mechanisms of the magnetic-ferroelectric coupling in view of promising wide technological applications of such materials. Recently, a cascade of the magnetic and structural phase transitions were discovered in the new multiferroic $GdFe_3(BO_3)_4$ [1], [2], [3]. A single-crystal X-ray structural study [2] showed the presence of two different iron helicoidal chains at 90 K, which becomes identical at room temperature. However, the relationship between magnetism and structure of $GdFe_3(BO_3)_4$ is still unclear.

In this work, the single-crystal of gadolinium iron borate $GdFe_3(BO_3)_4$ was investigated by the ^{57}Fe Mössbauer spectroscopy and X-ray diffraction in the temperature range between 5 and 295 K. Computer analysis of the Mössbauer data shows the presence of two close but nonequivalent sites for the Fe ions in the whole temperature range 5 - 295 K. Temperature dependences of the hyperfine parameters of the Mössbauer spectra indicate some structural and magnetic anomalies at $T < T_N$ and near the structural phase transition points, that are well correlated with our single-crystal X-Ray data.

The unit cell parameters of $GdFe_3(BO_3)_4$ single crystal were determined in a temperature range from room temperature to 30 K on a HUBER-5042 four-circle X-ray diffractometer equipped with a DISPLEX DE-202 two-stage closed-cycle cryostat (ADP Cryogenics Inc.), which affords the temperature stabilization within ± 0.05 K. The accuracy of setting the angular positions of the goniometer is $0.001°$. The unit cell parameters were measured at $T = 295$ K and in the 220 - 30 K range with the 5 - 10 K intervals. The measurements were based on 32 diffraction reflections at $19° < \theta < 22°$. It was found that the a and b init cell parameters do not change until the phase transition at 155 K, and then they decrease dramatically with lowering temperature. After that they reduce as $a \sim T^2$-law. Yet, the c parameter decreases uniformly from the room temperature down to 155 K, and then some anomalies appear near 80 K when it starts to increase. The unit cell volume shows properly the phase transition at 155 K and has some anomalies in the 80 - 60 K interval.

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**Keywords: multiferroics, phase transitions, low temperature**

MS81.P50

Structural properties of Gd(III) and Y(III) complexes with diimines and crotonate as bridging ligands.

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As a part of our researche of lanthanide complexes we have prepared and determined the crystal and molecular structure of five crotonate Gadolinium and Ytrium complexes displaying crotonates bridges. The diimines are 2,2-bipyridine (bpy), 1,2-bis(4-pyridyl)ethane (bpy-etha), and 1,2-bis(4-pyridyl)ethene (bpy-ethy)

The first one $\{[Gd(crot)_3(H_2O)(bpy)_{1/2}]_2\}$**(1)** is a dimer, built up around a symmetry center, and each cation is coordinated to three crotonato groups binding in dissimilar coordination modes (purely chelanting, tridentate, and purely bridging). There is in addition a bpy unit, also chelating the cation through both nitrogens and protuding outwards at both sides of the dimer [1].

The complexes $\{[Gd(crot)_3(H_2O)(bpy\text{-}etha)_{1/2}]_2\}_n$ **(2)**, $\{[Gd(crot)_3(H_2O)(bpy\text{-}ethy)_{1/2}]_2\}_n$ **(3)**, $\{[Y(crot)_3(H_2O)(bpy\text{-}etha)_{1/2}]_2\}_n$ **(4)**, and $\{[Y(crot)_3(H_2O)(bpy\text{-}ethy)_{1/2}]_2\}_n$ **(5)** are polymers.They crystallize in the triclinic space group P-1, and the asymmetric units are composed of a nine coordinated Ln cation , three crotonato ligands , one aqua and half of a whole diimine unit bisected by a symmetry centre.$[Ln(crot)_3(H_2O)]$ groups are linked by a double O_{crot} bridge into centrosymmetric dimeric units, in turn connected by the corresponding pyridine groups into chains running along [-201] (Figure)
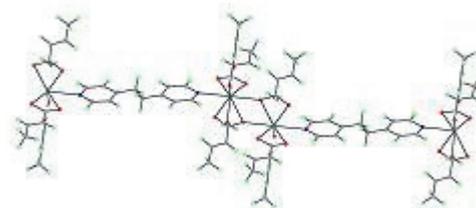
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Keywords : complexes, lanthanides, structures .

MS81.P51

Sillenites: composition, structure, morphology, crystal growth.

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The phases $Bi(1)_{24}M_2O_{40}$ or $Bi(1)_{24}(M,M')_2O_{40}$ with sillenite structure (γ-Bi_2O_3, sp.gr. $I23$, $z=13$ or $Bi(1)_{24}Bi(2)_2O_{40-\delta}$, $z=1$; coordination polyhedron of $Bi(1)$ is distorted semi-octahedron $Bi(1)O_5$ –$Bi(1)O(1)_3O(2)O(3))$ and of $Bi(2)$ or M – tetrahedron $Bi(2)O(3)_4$ or $MO(3)_4)$ have physical properties (photoconductivity, piezo-and electrooptical effects and so on) depending on the crystallochemical properties (ionic radius – r (M_{IV}), and formal charge - FC) of M and M' atoms. *The aim* of this paper is structural characterization of the compounds in the sillenite family.

Basic methods for structural characterization of sillenites with nominal composition $Bi_{24}M_2O_{40}$ (M=Al^{3+}, Fe^{3+}, Ga^{3+}, Si^{4+}, Ge^{4+}, Ti^{4+}, Mn^{4+}, Cr^{4+}, V^{5+}) and $Bi_{24}(M,M')_2O_{40}$ (M=Al^{3+}, Fe^{3+}, Si^{4+}, Ge^{4+}, Ti^{4+}, Cr^{4+}, V^{5+}, M'=Mn^{4+}, V^{5+}) were:

Diffraction study.

– X-ray structure analysis – single crystals: CAD-4 and Xcalibur; ground into fine powder samples: HZG-4A;

– neutron study – single crystal: 5C2, Orphee reactor;

– synchrotron radiation – the 'Belok' station on the synchrotron radiation source from the bending magnet in the Sibir-2 storage ring;

Spectroscopy study.

– Raman-spectroscopy – single crystals: Horiba Jobin Yvon LABRAM HR800, ν=100-1000 см$^{-1}$;

– IR-spectroscopy – ground into fine powder samples: Equinox 55,