

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.

[1] T. Nakamura, H. Sano, T. Konoike, K. Tomono, *Key Eng. Mater.* **1999**, 169-170, 19. [2] T. Nakamura, H. Sano, T. Konoike, K. Tomono, *Jpn. J. Appl. Phys.* **1999**, 38, 5457. [3] N. Inoue, K. Kawasaki, H. Sano, T. Morimoto, *Jpn. J. Appl. Phys.* **2006**, 45, 7365. [4] N. Inoue, T. Okamoto, A. Ando, H. Takagi, T. Hashimoto, C. Moriyoshi, Y. Kuroiwa, *Jpn. J. Appl. Phys.* **2009**, 48, 09KF03.

Keywords: X-ray_diffraction, electronic_device, barium_titanate

MS81.P48

Acta Cryst. (2011) A67, C720

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

Chikako Moriyoshi,^a Yoshiki Matsuoka,^a Hiroaki Sato,^b Ryo Sasai,^b and Yoshihiro Kuroiwa,^a ^aDepartment of Physical Science, Graduate School of Science, Hiroshima University, Higashi-Hiroshima (Japan). ^bDepartment of Material Science, Interdisciplinary Faculty of Science and Engineering, Shimane University, Matsue (Japan). E-mail: moriyosi@sci.hiroshima-u.ac.jp

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.

[1] K. Okamoto, N. Iyi, T. Sasaki, *Applied Clay Science* **2007**, 37, 23-31. [2] K.-H. Goh, T.-T. Lim, Z. Dong, *Water Reserch* **2008**, 42, 1343-1368. [3] M. Bellotto, B. Rebours, O. Clause, J. Lynch, D. Bazin, E. Elkaim, *Journal of Physical Chemistry* **1996**, 100, 8527-8534.

Keywords: X-ray_diffraction, anion_exchange, layered_structure

MS81.P49

Acta Cryst. (2011) A67, C720-C721

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

Kirill Frolov, Igor Lyubutin, Olga Alekseeva, Igor Verin, Shubnikov Institute of Crystallography, Russian Academy of Science, Moscow (Russia). E-mail: green@ns.crys.ras.ru