

Keywords: electro-conductivity, thermoelectromotive, impurities

### P11.13.84

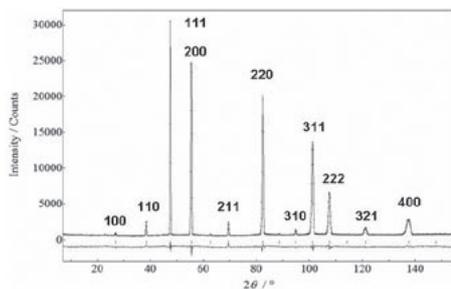
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#### Structural investigation of the cubic perovskite-type doped lanthanum cobaltite $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-x}$

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Lanthanum strontium cobaltites,  $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-x}$ , which have a perovskite-type structure, are promising electrode materials for solid oxide fuel cells (SOFCs). The purpose of the present study is to investigate the crystal structure of the cubic Pm-3m perovskite-type  $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-x}$  at room temperature and at high temperature by neutron diffractometry. Neutron diffraction data were collected in air by a diffractometer HERMES with a 150 multi-detector system. A furnace with  $\text{MoSi}_2$  heaters was placed on the sample table, and used for neutron diffraction measurements at high temperatures (J. Am. Ceram. Soc. 85 (2002) 2925). The experimental data were analyzed assuming the cubic perovskite-type structure by Rietveld method. La and Ba atoms were placed at the special position 1b  $1/2, 1/2, 1/2$  of the Pm-3m symmetry. Co and O atoms were put at the 1a 0, 0, 0 and 3d  $1/2, 0, 0$  sites, respectively. The calculated profile agreed well with the observed one taken at room temperature (Figure). The refined crystal structure of  $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-x}$  is similar with that of cubic  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-x}$  at 1531K reported in our previous work [J. Appl. Crystallogr., 40 (2007) 1166].



Keywords: neutron diffraction, solid oxide fuel cells, perovskite-type structure

### P11.13.85

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#### Synchrotron XRD and EXAFS studies on nanocrystalline $\text{ZrO}_2$ -CaO solid solutions

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The crystal structure and the local atomic order of a series of nanocrystalline  $\text{ZrO}_2$ -CaO solid solutions with varying CaO content were studied by synchrotron radiation X-ray powder diffraction and extended X-ray absorption fine structure (EXAFS) spectroscopy. These samples were synthesized by a pH-controlled nitrate-glycine gel-combustion process. For CaO contents up to 8 mol%, the t<sup>+</sup>-

form of the tetragonal phase ( $c/a > 1$ ) was identified, whereas, for 10 and 12 mol% CaO, the t<sup>-</sup>-form ( $c/a = 1$ ; oxygen anions displaced from their ideal positions in the cubic phase) was detected. Finally, the cubic phase was observed for solid solutions with CaO content of 14 mol% CaO or higher. Thus, the t<sup>+</sup>/t<sup>-</sup> and t<sup>-</sup>/cubic compositional boundaries were determined to be at  $(9 \pm 1)$  and  $(13 \pm 1)$  mol% CaO, respectively. EXAFS study demonstrated that this transition is related to a tetragonal-to-cubic symmetry change of the first oxygen coordination shell around Zr atoms.

Keywords: zirconia, XAFS, synchrotron X-ray diffraction

### P11.13.87

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#### Novel long period structures in hydrogen storage $\text{La}_x\text{Y}_{1-x}\text{Ni}_{3.8}$ compounds

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A series of  $(\text{La},\text{Y})\text{Ni}_z$  ( $3 < z < 4$ ) alloy compounds show polymorphic block-stacking superstructures. These structures can be interpreted as rhombohedral stacking sequence of ABC (3R-type) and hexagonal stacking sequence of AB (2H-type), where the structural unit is composed of  $\text{LaNi}_5$  (Haücke phase) and  $\text{YNi}_2$  (Laves phase, C15) type structures at unit-cell scale. In this presentation, we describe the differences of local chemistry between non-reacted and after gaseous- $\text{H}_2$  reacted  $(\text{La},\text{Y})\text{Ni}_z$  ( $3 < z < 4$ ) compounds through the direct observation by Z-contrast scanning transmission electron microscopy (STEM). All of  $(\text{La}_x\text{Y}_{1-x})\text{Ni}_{3.8}$  ( $x=0.4, 0.5, 0.6$ ) superstructures annealed at 1023K for 14 days are identified as 5:19R-type (3R) [1] based on electron diffraction analysis. Interestingly, for all the images there appear Z-contrast modulations at nanometer scales, which become significant for the  $\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{3.8}$ . These directly represent local chemical fluctuations, namely the occurrence of La-rich/Y-rich chemical domains in these alloys: that is to say, 'chemical mosaicism'. STEM image of  $\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{3.8}$  reacted with 2MPa hydrogen shows disappearance of 'chemical mosaicism', and to transform a novel long period Y-ordered 9R superstructure with c-length approximately 167Å. On the basis of Z-contrast analysis, we find that the novel structure contains Y-hydride layers, whose structure is well interpreted by referring structure local atomic configurations within  $\text{YH}_3$  compound.

References

[1] T. Ozaki, et al., J. Alloys Compd., 446-447, (2007) 620-624.

Keywords: hydride compounds, STEM, chemical domain structure

### P11.13.88

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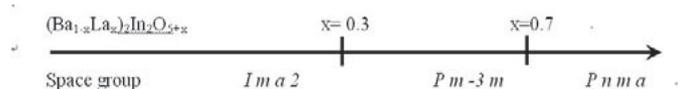
#### Structural investigation of the Ba doped $\text{LaInO}_3$

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A high ionic conductor Ba doped lanthanum indium oxide was investigated by synchrotron powder diffraction and transmission

electron microscopy. Synchrotron powder diffraction data of the sample were obtained using high resolution powder diffraction beam line (8C1) at Pohang Acceleration Laboratory. In a system of  $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ , two phase boundaries was existed in accordance with  $x$ , as shown in below diagram. Rietveld method was used for refining the structure parameter of the  $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ . The cell parameters of each phase was refined as  $a=5.94239(2)\text{\AA}$ ,  $b=8.21858(3)\text{\AA}$ ,  $c=5.72480(2)\text{\AA}$  for  $\text{LaInO}_3$ ,  $a=16.73045(31)\text{\AA}$ ,  $b=6.09718(11)\text{\AA}$ ,  $c=5.96295(15)\text{\AA}$  for  $\text{BaIn}_2\text{O}_5$ , and  $a=4.15398(2)\text{\AA}$  for  $(\text{BaLa})\text{In}_2\text{O}_5$  respectively. The electrical conductivity of the sintered samples was measured by DC four-probe method. The relationship between the oxide-ion conductivity and crystal structure of  $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$  ( $0 \leq x \leq 1$ ) will be discussed.



Keywords: synchrotron X-ray diffraction, Rietveld refinement, phase transitions and structure

### P11.13.89

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#### High temperature crystallographic study of perovskite-type mixed conductor, $(\text{La}_{0.5}\text{Sr}_{0.5})\text{CoO}_{3-\delta}$

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In this study, we aimed at elucidating the crystal structure of perovskite-type mixed conductor,  $(\text{La}_{0.5}\text{Sr}_{0.5})\text{CoO}_{3-\delta}$  (LSC) at high temperatures under controlled oxygen partial pressures,  $P(\text{O}_2)$ . The LSC sample was synthesized by a coprecipitation method. High temperature X-ray diffraction (HT-XRD) measurements were carried out under the following experimental conditions: Cu-K $\alpha$  radiation, a parallel-beam optics,  $298 \leq T \leq 1173\text{K}$ ,  $2 \times 10^{-3} \leq P(\text{O}_2) \leq 0.21$  atm). The XRD data were refined by the Rietveld method using the computer program RIETAN-2000. The XRD patterns could be indexed as a trigonal perovskite unit cell ( $R\bar{3}c$ ) from 298 to 373K under  $P(\text{O}_2) = 0.21\text{atm}$ , and as a cubic one ( $Pm\bar{3}m$ ) from 473 to 1173K under  $P(\text{O}_2)$  range from  $2 \times 10^{-3}$  to 0.21atm. Electron density distribution analysis of the XRD data of LSC was carried out by a combination of Rietveld analysis, the maximum-entropy method (MEM), and MEM-based pattern fitting (MPF) using the computer program PRIMA. Electronic states and local structures of metal ions in LSC were analyzed by X-ray absorption fine structure (XAFS). The La K- and Sr K-XAFS of the LSC were measured at 295K-in air, 996K-in air, 1vol% $\text{O}_2\text{-N}_2$ , and  $\text{N}_2$  using the beam line BL01B1 of SPring-8. The Co K-XAFS of the LSC was measured at 295K-in air, 923K-in air, 1vol% $\text{O}_2\text{-N}_2$ , and  $\text{N}_2$  using laboratory equipment EXAC-820 (Technos Co., Ltd.). The peak intensity at around 16.11keV of the Sr K-edge decreased with increasing temperature and decreasing  $P(\text{O}_2)$ , suggesting that Sr-O interactions (i.e. chemical bonds) decreases under these conditions. While the Co K-edge shifted to lower energy with increasing temperature and decreasing  $P(\text{O}_2)$ , suggesting that Co-O interactions (i.e. chemical bonds) decreases under these conditions.

Keywords: perovskite oxides, high-temperature diffractometry, XAFS

### P11.13.90

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#### Synthesis and crystal structure of novel proton-conductor, $\text{RbMg}(\text{PO}_3)_3 \cdot 3(\text{H}_2\text{O})$

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Proton-conductors have been devoted for applications in electrochemical devices such as fuel cells. Among these materials, proton-conductive solid acid salts,  $\text{CsH}_2\text{PO}_4$  and  $\text{CsHSO}_4$ , are well known as high proton conductors at medium temperature range. However, their operating temperature is narrow and the search for new proton conductors are still necessary. In the present study, a novel material with high proton conductivity was synthesized in the solid acid salt systems, and its structure was examined by X-ray and neutron diffraction measurements. New proton conductor,  $\text{RbMg}(\text{PO}_3)_3 \cdot 3(\text{H}_2\text{O})$ , was synthesized by co-precipitation method. The conductivity at intermediate temperatures was found to exceed  $10^{-3} \text{Scm}^{-1}$ . Their structures were determined by the combined neutron and x-ray Rietveld analysis from room temperature to 300°C. The  $\text{PO}_4$  tetrahedra are connected with each other by corner-sharing oxygen atoms and form the spiral-shaped chains along  $c$ -direction. Protons are found to locate at the sites around the chains, and these protons participate in the high proton conductivity. Between one-dimensional  $\text{PO}_4$  chains, these is one dimensional tunnel where water molecules situate and form a spiral chain. The difference in conduction mechanisms was observed between room temperature and high temperatures. The relationship between the structure and the proton conduction mechanism will be discussed.

Keywords: proton conductor, neutron powder diffraction, conduction mechanism

### P11.13.91

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#### Structural studies on lithiation process of nano-size $\gamma\text{-Fe}_2\text{O}_3$ using neutron scattering technique

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Iron oxides are one of the most ideal cathodes for lithium secondary batteries because of its low cost and low environmental impact, in comparison with cobalt or nickel based cathode materials. The binary iron oxide is the simplest system and was previously proposed for positive electrode materials[1]. However, an irreversible phase transformation from the corundum/spinel to the disordered rock-salt type appeared at the first lithiation process prevents reversible reactions and an application for lithium secondary batteries[1-3]. We also proposed the nano-sized crystalline  $\gamma\text{-Fe}_2\text{O}_3$  as a lithium battery cathode materials. Lithiation mechanism of nano-size material for lithium battery electrode was studied by neutron scattering technique.