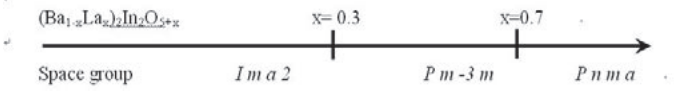
electron microscopy. Synchrotron powder diffraction data of the sample were obtained using high resolution powder diffraction beam line (8C1) at Pohang Acceleration Laboratory. In a system of $(Ba_{1-x}La_x)_2In_2O_{5+x}$, two phase boundaries was existed in accordance with x, as shown in below diagram. Rietveld method was used for refining the structure parameter of the $(Ba_{1-x}La_x)_2In_2O_{5+x}$. The cell parameters of each phase was refined as a=5.94239(2)Å, b= 8.21858(3)Å, c=5.72480(2)Å for $LaInO_3$, a=16.73045(31)Å, b= 6.09718(11)Å, c=5.96295(15)Å for $BaIn_2O_5$, and a=4.15398(2)Å for $(BaLa)In_2O_5$ 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 $(Ba_{1-x}La_x)_2In_2O_{5+x}$ (0<= x<= 1) will be discussed.



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

P11.13.89

Acta Cryst. (2008). A**64**, C534

High temperature crystallographic study of perovskite-type mixed conductor, $(La_{0.5}Sr_{0.5})CoO_{3-\delta}$

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In this study, we aimed at elucidating the crystal structure of perovskite-type mixed conductor, $(La_{0.5}Sr_{0.5})CoO_{3-\delta}$ (LSC) at high temperatures under controlled oxygen partial pressures, $P(O_2)$. 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-Kα radiation, a parallel-beam optics, 298 $\leq T \leq$ 1173K, $2\times10^{-3} \leq P(O_2) \leq$ 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-3c) from 298 to 373K under $P(O_2)$ = 0.21atm, and as a cubic one (Pm-3m) from 473 to 1173K under $P(O_2)$ range from 2×10^{-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%O_2-N_2, and 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%O_2-N_2, and 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 $P(O_2)$, 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 $P(O_2)$, suggesting that Co-O interactions (i.e. chemical bonds) decreases under these conditions.

Keywords: perovskite oxides, high-temperature diffractometry, XAFS

P11.13.90

Acta Cryst. (2008). A**64**, C534

Synthesis and crystal structure of novel proton-conductor, $RbMg(PO_3)_3\cdot3(H_2O)$

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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, CsH_2PO_4 and $CsHSO_4$, 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, $RbMg(PO_3)_3\cdot3(H_2O)$, was synthesized by co-precipitation method. The conductivity at intermediate temperatures was found to exceed 10^{-3} Scm^{-1}. Their structures were determined by the combined neutron and x-ray Rietveld analysis from room temperature to 300°C. The 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 PO_4 chains, these is one dimensional tunnel where water molecules situate and form a spiral chain. The deference 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

Acta Cryst. (2008). A**64**, C534–535

Structural studies on lithiation process of nano-size γ-Fe_2O_3 using neutron scattering technique

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Iron oxides are one of the most ideal cathodes for lithium secondly 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 γ-Fe_2O_3 as a lithium battery cathode materials. Lithiation mechanism of nano-size material for lithium battery electrode was studied by neutron scattering technique.

The nano-size iron oxide, γ-Fe_2O_3, lithiated chemically was subjected to neutron scattering studies for crystal structure analysis by Rietveld method and for local structure analysis by total diffraction technique. The lithium intercalation of the nano-size γ-Fe_2O_3 proceeded by a biphasic reaction through the defect spinel and the disordered rock-salt phases. Pair distribution functions calculated from the total scattering data indicated a correlation of Li-O with a distance of 2.36 Å, which is much longer than the bond distance in ionic crystals. Lithiation mechanism of the nano-size materials will be discussed based on the bulk and local structure changes clarified by these neutron scattering techniques.

[1] M. M. Thackeray, *et. al.*, Mater. Res. Bull., 17, 785 (1982).
[2] B. Bonnet, *et. al.*, Mater. Sci. Forum, 91-93, 345 (1992).
[3] M. Pernet, *et. al.*, Solid State Ionics, 66, 259 (1993).

Keywords: nanocrystals, iron oxides, neutron scattering

P11.13.92

Acta Cryst. (2008). A**64**, C535

Free oxygen ions in nanoporous material $12CaO{\cdot}7Al_2O_3$ and cage deformation at high temperature

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There has been great interest for a decade in the nanoporous material $12CaO{\cdot}7Al_2O_3$ (C12A7) because of variety of fascinating characteristics the material exhibits, including high ionic conductivity of oxygen ions at high temperature. The characteristics are mostly due to its unique structure. The frame work structure of C12A7 in a unit cell can be represented as $[Ca_{24}Al_{28}O_{64}]^{4+}$ which consists of twelve cages with inner free space of ~ 4 Å in diameter. Two remaining oxygen ions, so called free oxygen ions, are believed to be captured in the inner space of two cages out of the twelve cages. The free oxygen ions are considered to play a important role in the oxide ion conduction. In order to obtain precise structural information, including the position of the free oxygen ions, neutron powder diffraction studies were carried out over a wide temperature range, 50 K - 700 K. The structure analyses clearly indicated that the free oxygen ion is located inside the cage and the position is displaced from the S_4 axis running through the center of the cage. It was also confirmed that the presence of the free oxygen ion in the cage induces a deformation of the cage. Calcium ions at the top and the bottom of the cage are shifted toward the center of the cage when the free oxygen ion is present in the cage. The framework structure was found to be further deformed as the temperature is elevated. The deformation involves; lengthening of aluminum-oxygen bond lengths; shortening of a distance between an oxygen ion in the cage wall and the free oxygen ion. These variations may enhance the oxygen ion migration at high temperature. A complete description of the deformation at high temperature and a possible mechanism of the oxygen ion migration will be presented.

Keywords: crystal structure-physical property relationships, ionic conductors, neutron diffraction

P11.14.93

Acta Cryst. (2008). A**64**, C535

Residual stress investigation of dissimilar overlap-friction stir welds made from Al and steel

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One of the main research topics at the GKSS Research Centre is the investigation and further development of friction stir welding techniques. In this context dissimilar overlap joints of sheets made from aluminum and steel were produced by friction stir welding at GKSS. A set of four different specimens was produced with different welding and tool speeds. Aluminum alloy AA5754-H22 and dual phase steel alloy DP600 were used. The aluminum and steel sheets were 1.5 mm thick and the stirring zone was 12 mm wide. The residual stress distribution in these specimens was investigated at the high energy materials science synchrotron beamline HARWI II operated by GKSS at the HASYLAB / DESY, Germany. A beam with a photon energy of 100 keV and a size of 2 x 0.2 mm^2, with the larger beam dimension being parallel to the weld, was used in transmission geometry. A Mar345 detector system was employed to monitor complete Debye-Scherrer rings. The diffraction peak shifts of the Al {311} and Fe {211} lattice planes were used to determine the residual stress in the respective material. Peak positions were determined relatively to the Cu {220} peak of a Cu-powder directly attached to each specimen. This allowed the correction for peak shifts induced by the distortion of the specimens and the resulting change of the sample-to-detector distance. The results for the weld zone show that the stresses in weld direction are close to the yield strength for the steel and about 70% of the yield strength for Al. Furthermore, high welding and tool rotation speeds result in steeper stress gradients in steel and almost symmetric stress profiles in both materials, whereas low welding and tool rotation speeds result in a broader stress profile in steel and asymmetry of the profiles in both materials.

Keywords: friction stir welding, residual stress, high energy synchrotron radiation

P11.14.94

Acta Cryst. (2008). A**64**, C535-536

Residual stresses associated with laser bending of mild steel plates

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Bending of metal plates with high-energy laser beams presents a flexible materials forming technique where bending results from the establishment of a steep temperature gradient through the material thickness. This inevitably leads to non-uniform thermal expansion/ contraction and subsequently residual stresses. Non destructive residual strain mapping with diffraction techniques through the 8mm thickness of a series WA 300 grade structural steel plate samples, focused on the region straddling the centerline of the heating bead location, shows the presence of large residual stress fields. Directly below the laser track the longitudinal strains are tensile and dominant, normal strains compressive and transverse strains slightly tensile.