Study of modulated structure and ionic conduction in misfit-layered cobalt oxides applicable to IT-SOFC cahode

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A good suite of materials are currently available for SOFC operation above 800 ℃; however, possible issues with long-term stability and availability of suitable, low cost seals and interconnects have focused considerable attention for intermediate-temperature (IT) SOFCs ', working below 800 ℃. The main requirements for SOFCs ' cathodes are (i) high electronic conductivity with a possible anionic contribution, (ii) a good stability under oxidative conditions, (iii) a significant catalytic activity towards oxygen dissociation, and (iv) long-term chemical/thermal/mechanical stabilities in the concerned thermal range with the electrolyte and other contact components. The misfit-layered Co oxides Ca3Co4O9 ([Ca2CoO3+δ]0.62 CoO2) has been investigated for its relatively high thermoelectric performances. Its crystal structure consists of an alternate stack of a distorted three-layered rock salt ?type [Ca2CoO3] layer and a CdI2 ?type [CoO2] conducting sheet parallel to the c-axes. Therefore, this material could be also considered as a regular intergrowth between electronic and oxygen ion conducting units, which inspired the possibility of mixed ionic-electronic conductivity (MIEC) properties as SOFC mixed conducting cathode. Polycrystalline [Ca1.8Y0.2CoO3+δ] 0.62 CoO2 were prepared by a conventional solid-state reaction method. Appropriate amount of starting from a mixture of CaCO3 (99.9%) , Y2O3 (99.9%) and Co3O4 (99.9%) powders were mixed with an agate mortar and pressed into pellets. Neutron powder diffraction (ND) data were collected at room temperature using a Kinken powder diffractometer for the high-ef.ciency and high-resolution measurements (HERMES) of Institute for Materials Research (IMR), Tohoku University, installed at a JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI). The ND data were collected on thoroughly ground powders in a multiscanning mode in the 2 θ range from 5.0 to 153.9 °with a step width of 0.1 °.The incident neutron beam was monochromatized to a wavelength of 1.8478 .The XRD and ND data were simultaneously analyzed using a Rietveld re.nement program PREMOS 91designed for modulated structure analyses. We adopt a superspace group of C2/m (1p0)s0 because the CdI2-type [CoO2] subsystem has a C2/m symmetry, whereas the RS-type BL subsystem has a C21/m symmetry. The crystal structures and interatomic distance plots were obtained using the PRJMS and MODPLT routines, respectively; both are included in the PREMOS 91 package. Figure 1 shows the observed, calculated and difference intensities of the HERMES data for the sample. Short vertical lines below the patterns indicate the peak positions of the main (upper) and satellite (lower) reflections of the two subsystems. The final Rwp factor is 5.98 %.
Fig. 1. Observed, calculated and difference intensities of powder ND data for the. The inset is the final crystal structure.