Structure Analysis of Oxide Ions in a Doped Pr2NiO4-based Mixed Conductor

Hiroki Yamada †, Masatomo Yashima †, Tomoya Takizawa †, Shinji Yamamoto †, Tatsumi Ishihara ‡

† *Department of Materials Science and Engineering, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta-cho 4259, Midori-ku, Yokohama, Kanagawa 226-8502, Japan and* ‡ *Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan*

Mixed oxide-ionic and electronic conducting ceramics (MIECs) are attracting much interest as materials for oxygen separation membranes. Oxygen can permeate through MIECs membranes when a gradient of oxygen chemical potential exists. A2BO4-based oxides with K2NiF4-type structure have extensively been studied as a new mixed ionic-electronic conductor, where A and B are cations. The development of improved MIECs requires a better understanding of the mechanism of ionic conduction, and crucial to this is a comprehensive knowledge of the oxide ion conduction in the A2BO4-based oxides occurs by diffusion of excess oxide ions along the rock-salt-type AO layers. However, the diffusion of excess oxide ion has not been determined yet. Pr2NiO4-based oxides have high oxygen permeability and high diffusivity of oxide ions. Here, we report the structure analysis of a K2NiF4-type mixed conductor Pr2(Ni0.75Cu0.25)0.95Ga0.05O4+ δ (PNCG), through a high-temperature neutron powder diffraction study. We chose this chemical composition, because it exhibits high oxygen permeability. The present result would give hints for the design of K2NiF4-type conductors.

A PNCG sample was prepared by a solid-state reaction at 1350 oC for 6 h in air. Neutron powder diffraction data of PNCG were in situ measured at 20.4-1011.2 oC using a furnace and 150 detector system HERMES at a neutron wavelength of 1.8204(5) angstrom. Neutron diffraction data were analyzed by Rietveld analysis. A computer program RIETAN-FP was utilized for the Rietveld analysis.

Rietveld refinements of the neutron diffraction data of PNCG at 20.4 oC and 1011.2 oC were performed on the basis of the K2NiF4-type structure with I4/mmm space-group symmetry. Reliability factors and goodness of fit at 20.4 oC were Rwp = 6.66%, RI = 3.06%, RF = 1.78% and GOF = 3.17. Lattice parameters were a = b = 3.8364(2) angstrom, c= 12.5374(7) angstrom. Reliability factors and goodness of fit at 1011.2 oC were Rwp = 6.33%, RI = 2.06%, RF = 0.98% and GOF = 4.93 (Fig.1). Lattice parameters were a = b = 3.8793(4) angstrom, c= 12.7326(13) angstrom.

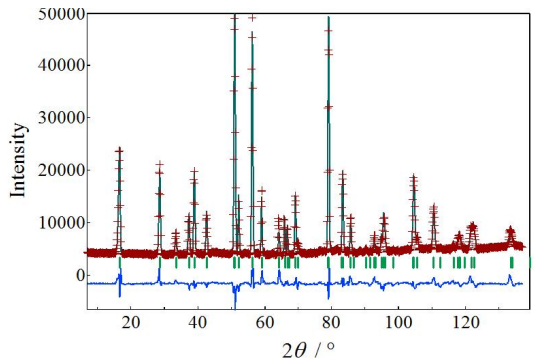

Fig. 1. Neutron diffraction profiles at 1011.2 oC for Pr2(Cu0.75Ni0.25)0.95Ga0.05O4+ δ using a single phase I4/mmm model.