Crystallography

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Crystal Structure and Electron Density Distribution of a Pr_2NiO_4-Based Mixed Conductor $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$

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Introduction

Mixed oxide-ionic and electronic conducting ceramics (MIECs) will become increasingly important for future environmentally friendly ("green") societies, because the MIECs are used as materials for oxygen separation membranes and cathodes of solid-oxide fuel cells (SOFCs). For lower temperature devices, novel MIECs with higher oxygen permeation rate are required. A_2BO_4-based oxides with K_2NiF_4-type structure have extensively been studied as new MIECs. Here we report the crystal structure and electron density distribution of a Pr_2NiO_4-Based mixed conductor $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$ [1].

Experiments

Synchrotron x-ray powder diffraction experiments of $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$ were performed at 25 °C using the multiple-detector system installed at the BL-4B$_2$ beam line of the Photon Factory, KEK, Japan. A monochromatized 1.20641 Å x-ray beam was utilized. The crystal structure of the $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$ was refined by the Rietveld method with a computer program RIETAN-FP. Electron-density distribution of $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$ was investigated by a maximum-entropy method (MEM, PRIMA) and Density Functional Theory (DFT) calculations.

Results and discussion

Synchrotron powder diffraction pattern indicated that the $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$ material has a K_2NiF_4-type structure with tetragonal $I4/mmm$ space group. High-angular-resolution synchrotron X-ray diffraction profiles at 25 °C did not exhibit any splitting due to the orthorhombic symmetry, which indicates the tetragonal symmetry. The reliability factors for the analysis of synchrotron data of $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$ at 25 °C were R_{wp} = 13.47% and R_F = 3.72%. The crystal structure of $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$ consists of $(Ni,Cu,Ga)O_6$ octahedron and (Pr,La)-O layers. In the (Pr,La)-O layer, interstitial O3 atoms existed at a 16*n* site. MEM electron and DFT valence electron density maps in Fig. 1 include the information on chemical bonding in $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$. The covalent bonds between the (Ni,Cu,Ga) and O1 atoms are observed on the *ab* planes at z=0 and 1/2 (*B*-O1 in Fig. 1), while the (Pr,La) atoms are more ionic (*A* in Fig. 1). The (Ni,Cu,Ga)-O1 covalent bond is formed by the overlap of Ni 3d, Cu 3d and O1 2p orbitals. The *B*-O1 covalent bonds form a two-dimensional network on the *ab* planes at z=0 and 1/2.

Ref. [1] M. Yashima, N. Sirikanda and T. Ishihara, "Crystal Structure, Diffusion Path and Oxygen Permeability of a Pr_2NiO_4-Based Mixed Conductor $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$", *J. Am. Chem. Soc.*, **132**, [7] 2385-2392 (2010).

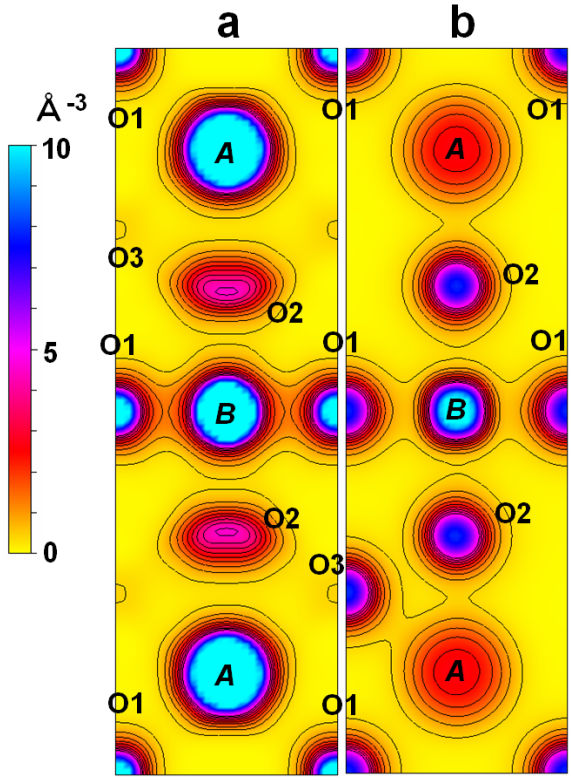

Fig.1. (a) MEM experimental electron density and (b) DFT-based valence electron density distributions of $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$.

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