

Oxygen Nonstoichiometry, Crystal structure, and Mechanical Properties of $\text{La}_2\text{NiO}_{4+\delta}$

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Introduction

K_2NiF_4 type oxides show high oxygen diffusivity and catalytic activity which is caused by interstitial oxygen in the rock salt layer. Diffusion coefficient and surface exchange coefficient of K_2NiF_4 type oxides is larger than those of conventional perovskite type oxides [1]. Because of these excellent electrochemical properties, K_2NiF_4 type oxides are expected as a promising cathode material for solid oxide fuel cells (SOFCs) [2, 3]. Rice et al. reported that the interstitial oxygen formation induces the change of the crystal structure [4]. While oxygen nonstoichiometry provides functional properties, it may depress the mechanical strength because of the structural variation. The effect of oxygen nonstoichiometry on the mechanical properties is essential knowledge to construct reliable SOFC generation systems.

In order to observe the crystal structure and to evaluate the mechanical properties at given oxygen content and temperature, we carry out in-situ X-ray diffraction measurement and in-situ small punching test on $\text{La}_2\text{NiO}_{4+\delta}$. These results are compared with our previous study on the oxygen nonstoichiometry of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ [5]. The relationship among oxygen nonstoichiometry, crystal structure, and the mechanical properties is elucidated in the present work.

Experimental

$\text{La}_2\text{NiO}_{4+\delta}$ was synthesized by a citric acid method. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved into deionized water. The concentration of each solution was determined by a chelate titration. The metal nitrate solutions were mixed in a proper ratio. Excess amount of citric acid was added to the mixed solution. They were heated at 573 K to obtain precursors. The precursors were fired at 1273 K for 10 hours. They were grinded with ethanol, and fired again at 1473 K for 10 hours.

In-situ XRD measurement was carried out with D8 Advance X-ray diffractometer (Bruker AXS). $\text{N}_2\text{-O}_2$ gas mixture was introduced to control the $P(\text{O}_2)$ in the sample chamber. Temperature around the sample was controlled by a Pt heater. Lattice parameter was obtained from the diffraction pattern by Whole Powder Pattern Decomposition with TOPAS software [6].

Dense specimen for the small punching test was obtained as follows. Powder samples were pressed by 180 MPa by CIP. They were sintered at 1773 K for 10 hours. The dense specimen with relative density of more than 95% was obtained. Electric furnace and gas-tight sample chamber were equipped in the apparatus for small punching test. $P(\text{O}_2)$ in the chamber was controlled by the introduction of $\text{O}_2\text{-Ar}$ gas mixture.

Results and Discussion

The crystal structure of $\text{La}_2\text{NiO}_{4+\delta}$ is a tetragonal symmetry (space group $I4/mmm$). Figure 1 shows the

$P(\text{O}_2)$ dependence of lattice parameters of $\text{La}_2\text{NiO}_{4+\delta}$ at 873-1173 K. In the present study, a is the lattice parameter parallel to the perovskite and rock salt layers and c is that perpendicular to the layers. The structural change due to the nonstoichiometry is clearly observed from Fig. 1. As $P(\text{O}_2)$ increases, c increases linearly while a slightly decreases. Since the amount of interstitial oxygen increases with increasing $P(\text{O}_2)$, these structural changes are caused by the incorporation of the interstitial oxygen. It is easy to assume that the structural change due to the oxygen nonstoichiometry affects mechanical properties. Now, mechanical properties at given T and $P(\text{O}_2)$ are evaluating by in-situ small punching measurement.

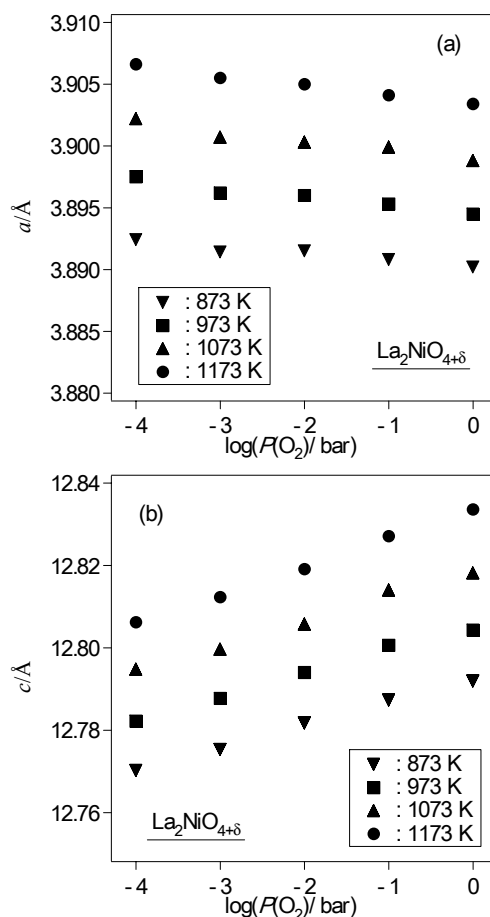


Figure 1. Lattice parameters of $\text{La}_2\text{NiO}_{4+\delta}$.

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