

論文の内容の要旨

論文題目

Control of Structures and Properties of Transition Metal Oxide Thin Films by Soft Chemical Processes

(ソフト化学的手法による遷移金属酸化物薄膜の構造・特性制御)

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1. Introduction

Transition-metal oxides are rich sources of interesting phenomena such as superconductivity, multiferroicity, and metal–insulator transition. Traditionally, they have been synthesized using a sintering process, where a mixture of starting metal oxides is heated up to high (> 1000 °C) temperature. On the other hand much attention has been paid to soft chemical, or low-temperature processes for the synthesis of metal oxide samples in the past several decades. Among them, topotactic reactions, during which a large part of the crystal structure of the starting material is maintained, are rather kinetic process because they exploit higher mobility of particular elements over others in a single material, and thus they are powerful methods to prepare thermodynamically metastable materials.

Although soft chemical synthesis using topotactic reactions has been developed on powder samples, thin films possess potential advantages over bulk studies, such as enhanced reactivity and high crystallinity. For example, it was reported that the topotactic reaction between SrFeO_{2.5} thin films and polyvinylidene fluoride proceeds at much lower temperature than bulk powder. However, most of the topotactic studies on thin films focused on preparation of already reported materials rather than exploration of novel materials. Thus, in this thesis, I explored topotactic reactions on transition-metal oxide thin films to prepare novel oxide-based materials. In particular, I used anion exchange and insertion reactions to control the structures and properties of perovskite nickel oxides and copper oxides.

2. Synthesis of defect-fluorite NdNiO_xH_y from NdNiO₃ precursors

First, I chose perovskite NdNiO₃, which shows temperature-dependent metal–insulator transition, as a precursor material. Observation by scanning transmission electron microscopy revealed that by hydride (H⁻) exchange reaction using CaH₂, a defect fluorite structured phase was obtained as thin films on SrTiO₃ substrate, as shown in Figure 1. This phase was identified as new oxyhydride NdNiO_xH_y. This is in contrast to previous literature on the reaction using powder samples of NdNiO₃, where only oxygen deintercalation and not hydride incorporation took place. Furthermore, the epitaxial relation of the fluorite phase to the substrate could be changed by reaction conditions. When the reaction was performed at 240 °C, I obtained [001] oriented growth with a thin layer of oxygen-deficient phase NdNiO₂ at the interface between the film and the substrate. On the other hand, at higher temperature of 400 °C, [110]-oriented NdNiO_xH_y film was obtained without NdNiO₂.

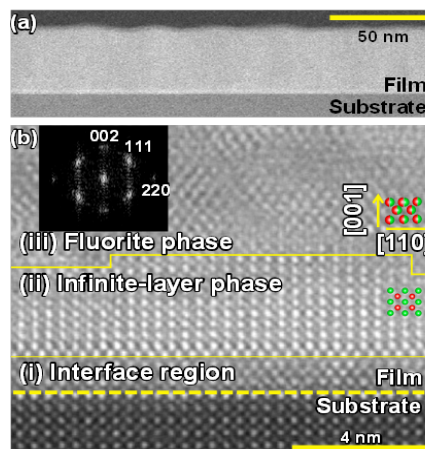


Figure 1. (a) Wide and (b) magnified views of HAADF-STEM images after reacting NdNiO₃ and CaH₂ at 240 °C for 12 h. Inset shows Fourier transform of the region (iii). Reprinted from *Dalton Transactions*, **30**, 12114 (2016), licensed under CC BY 3.0, Copyright 2016 the Royal Society of Chemistry.

3. Reversible changes in resistance of perovskite nickelate NdNiO₃ by fluorine substitution

Next, with the same starting material of NdNiO₃, I performed topotactic fluorination using polyvinylidene fluoride (PVDF). Though H⁻ and F⁻ possess the same formal valence and similar ionic radius, the reactions of NdNiO₃ with CaH₂ and PVDF proceeded very differently. That is, the perovskite framework was completely maintained throughout the reaction, and perovskite oxyfluoride NdNiO_{3-x}F_x was formed. As shown in Figure 2, the fluorine content *x* inside the film was systematically controlled by the reaction time with PVDF. The fluorinated films were highly insulating in contrast to NdNiO₃ with metallic conduction, and showed a bandgap of up to 2.1 eV. Hard X-ray photoelectron and soft X-ray absorption spectroscopies were performed to investigate the electronic states of the obtained films. They revealed the suppression of the density of states at the Fermi level as well as electron doping into nickel ions. The changes in the spectra indicated that the insulating characteristics of the NdNiO_{3-x}F_x thin films were induced by Mott transition as a result of change in

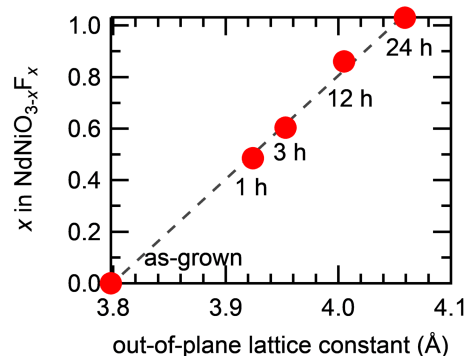


Figure 2. Relationship between fluorine contents *x* and out-of-plane lattice constants of NdNiO_{3-x}F_x thin films prepared by PVDF fluorination. Reprinted with permission from *ACS Applied Materials & Interfaces*, **9**, 10882 (2017), Copyright 2017 American Chemical Society.

nickel valence states. Furthermore, I also found that the fluorine ions incorporated into the films could be removed by annealing under oxygen atmosphere, yielding the original NdNiO_3 with metallic conduction.

4. Fluorination of perovskite cuprate LaCuO_x

Like $\text{NdNiO}_{3-x}\text{F}_x$, most of the transition-metal oxyfluorides with perovskite (ABX_3) structure are insulating because of the strong ionicity of metal-fluorine bonds. To obtain conducting oxyfluorides with perovskite structure, I chose another starting material, LaCuO_x . Since some copper oxyfluorides with $2 \pm \delta$ valence states, such as $\text{Sr}_2\text{CuO}_2\text{F}_{2+x}$ show high-temperature superconductivity, I supposed that conducting materials could be obtained by synthesizing oxyfluoride LaCuO_xF_y . By using CuF_2 as a fluorine source,

fluoride ions were successfully introduced into the LaCuO_x films. Figure 3 shows temperature dependence of resistivity of the films before and after fluorination. Although the sample contained spatial inhomogeneity in chemical composition, the fluorinated LaCuO_xF_y film showed metallic conduction with resistivity of the order of $\text{m}\Omega \text{ cm}$ at 300 K.

5. Conclusion

In conclusion, I performed different soft chemical processes on two different transition-metal oxide thin films, NdNiO_3 and LaCuO_x . The results revealed that introduction of F and H into thin-film samples could drastically alter their crystal structures and/or electrical transport properties. These methods are a promising way to synthesize new materials containing multiple anions and to modify the physical properties of oxide materials.

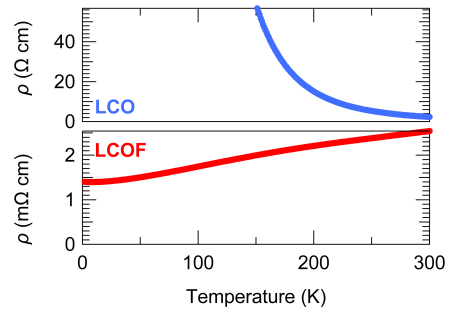


Figure 3. Temperature dependence of resistivity of LaCuO_x and LaCuO_xF_y thin films.