Changes in the electronic state of SrCeO₃ thin films by PVDF-mediated fluorination

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1 Introduction

Topotactic fluorination of metal oxides with polyvinylidene fluoride (PVDF) is an effective way to synthesize metal oxyfluorides without forming undesired impurity phases [1]. Our previous research revealed that topotactic fluorination of the single crystalline thin films of SrCoO_{2.5} and BaBiO₃ using PVDF can reduce Co and Bi in the films together with fluorine substitution [2,3]. In this study, we performed topotactic fluorination of single crystalline thin films of perovskite SrCeO₃ with Ce⁴⁺. In general, Ce ions favor Ce³⁺ and Ce⁴⁺ states and thus the fluorinate of SrCeO₃ with PVDF might accompany the reduction of Ce oxidation state.

2 Experiment

Perovskite SrCeO₃ precursor thin films were deposited on SrTiO₃ (001) substrates using pulsed laser deposition. The obtained films were subjected to the subsequent reaction with PVDF pellets at 430°C for 1 h in a tubular furnace under Ar gas flow. Crystal structures were characterized by X-ray diffraction (XRD), and chemical compositions were analyzed by energy dispersive X-ray spectrometry (EDS). The oxidation states of Ce were evaluated by X-ray absorption spectroscopy (XAS) measurements, which were performed at the BL-2A beamline of the Photon Factory, KEK. The XAS spectra were measured by the total electron-yield method at 300 K.

3 <u>Results and Discussion</u>

From the EDS measurements of the SrCeO₃ precursor and fluorinated films, we confirmed that the cation ratio of Sr and Ce was unchanged before and after the fluorination. Meanwhile, fluorine was doped and oxygen was completely removed from the film after the reaction.

Figure 1 shows the XRD patterns of the SrCeO₃ precursor and fluorinated films. The precursor film had perovskite structure with the *c*-axis length of 0.429 nm. After the fluorination, each XRD peak of the film moved to higher 2θ , indicating that the crystal structure of the film transformed into fluorite structure with the *c*-axis length of 0.588 nm.

Figure 2 shows the Ce *M*-edge XAS spectra of the SrCeO₃ precursor and fluorinated films. The Ce M_4 and M_5 peaks were clearly observed in all spectra. The spectra of the precursor and fluorinated films are similar to those of the Ce⁴⁺Cl₆²⁻ and Ce³⁺Cl₆³⁻ references [4], respectively, in both peak shapes and positions. This indicates that the

oxidation states of Ce in the film changed from 4+ to 3+ through the fluorination. From these results, the chemical composition of the fluorinated film can be inferred as SrCeF₅.



Fig. 1: X-ray diffraction patterns of the SrCeO₃ precursor and fluorinated films.



Fig. 2: Ce *M*-edge XAS spectra of the SrCeO₃ precursor and fluorinated films.

References

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