

Electronic state analysis of oxygen storage perovskite-type oxides

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Most famous oxygen storage material (OSM) is the solid solution material of CeO₂ and ZrO₂ (CZ). CZ stores and releases oxygen by the redox reaction of Ce⁴⁺/Ce³⁺. OSMs are attracting attention in many fields not only as catalysts for automobile exhaust gas purification but also as electrode materials for solid oxide fuel cells and metal-air cells. Researches are actively working toward the further enhancements of OSMs. We are focusing on the perovskite-type oxides as a new material aiming to further improve the performance of OSMs [1]. Perovskite-type oxides are characterized by an extremely large degree of freedom in their compositions. In the perovskite-type oxide, ABO₃, B-site ion and oxygen ion are covalently bonded, and A-site ion forms a structure by ionic bond. The strongly bound B-site ion and O ion determines the electronic structure of ABO₃, and hence determines the basic physical properties of the perovskite oxides. Oishi *et al.* reported that mixing different elements in the B-site of LaCrO_{3-δ} materials increased the amount of oxygen desorption at high temperatures [2]. Unlike the simple SrFeO_{3-δ} and SrMnO_{3-δ} perovskite oxides, the B-site mixed SrFe_{1-x}Mn_xO_{3-δ} (SFM) may exhibit a specific valence changes of Fe and Mn ions in the B-site mixed system, and show desired properties as OSMs.

We synthesized SFM in which the mixing ratio of Fe and Mn was changed, and measured the Mn and Fe *K*-edge X-ray absorption fine structure (XAFS) using the hard X-ray. Regardless of the mixing ratio of Mn and Fe, the change of the Fe *K*-edge XAFS spectrum was not confirmed, but the Mn *K*-edge XAFS spectrum changed depending on the Mn concentrations. Therefore, the symmetry of the Fe-O polyhedron does not change independent of Fe concentrations, but the Mn-O polyhedron symmetry or electronic states of Mn ion varied depending on the Mn ion concentrations. Since the Mn *K*-edge XAFS spectrum is sensitive to the crystal structure changes, it is difficult to evaluate the electronic structure of Mn from the Mn *K*-edge XAFS spectrum. In this study, the Mn *L*-edge of SFM was evaluated in partial electron yield (PEY), total electron yield (TEY), partial fluorescence yield (PFY), and inverse partial fluorescence yield (IPFY) at BL-11 of SR Center, Ritsumeikan University.

Figure 1 shows the Mn *L*-edge XAS spectra in the PEY mode. The Mn *L*-edge spectrum of SrMnO_{3-δ} matched with the peak positions of MnO₂, which implied the Mn⁴⁺ state. The *L*_{III}-edge exhibits a main peak and a sub-peak due to the spin multiplicity and the crystal field effect. In SFM no significant peak shift was observed at both *L*_{III} and *L*_{II}-edge spectra. This indicates that the electronic state does not change independent of Mn ion concentrations in SFM. On the other hand, the valley between the main peak and the sub-peak at the *L*_{III}-edge decreased with the decrease of the Mn concentration. It is due to the variations of the local structure around Mn ions, which depended on the Mn ion concentrations.

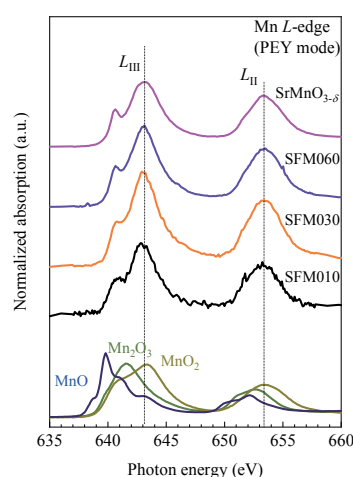


Fig. 1 Mn *L*-edge XAS spectra in PEY mode. SFM010, SFM030, SFM060 are SrFe_{1-x}Mn_xO_{3-δ} (*x*= 0.1, 0.3, 0.6).

References

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