

# Local Electronic and Atomic Structure of $\text{SrFe}_{1-x}\text{Mn}_x\text{O}_{3-\delta}$ Studied with Surface Sensitive X-ray Absorption Spectroscopy in the Partial Electron Yield Mode

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Perovskite-type oxides are characterized by a large degree of freedom in their composition and can be composed by combining various elements.<sup>1</sup> In the perovskite-type oxide,  $\text{ABO}_3$ , the electronic structure is established by the state of strongly bound B-site ions and oxide ions, which determines the fundamental physical properties of the material.<sup>2</sup> To unambiguously evaluate the valence state of Fe and Mn ions in the perovskite-type materials, we used Mn and Fe *L*-edge XAS. In addition, O *K*-edge XAS was also evaluated to discuss the coordinated oxide ions around Mn and Fe ions.

The  $\text{SrFe}_{1-x}\text{Mn}_x\text{O}_{3-\delta}$  ( $x=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, \text{ and } 1.0$ ) were prepared using a chemical solution method.<sup>3</sup> From the X-ray diffraction analysis, we confirmed a structure of orthorhombic  $\text{Sr}_4\text{Fe}_4\text{O}_{11}$  (*Cmmm*, no.65) at  $x=0$ , a cubic perovskite-type structure (*Pm $\bar{3}m$* , no.221) for  $x=0.1-0.6$ , and a hexagonal  $\text{SrMnO}_{3-\delta}$  (*P6 $_3$ /mmc*, no.194) at  $x=1.0$ . The Mn, Fe *L*-edge, and O *K*-edge spectra were collected at the soft X-ray beamline, BL-11, SR Center, Ritsumeikan University (Shiga, Japan). The XAS spectra were obtained in the partial electron yield (PEY) mode.

The Mn *L*-edge spectra of  $\text{SrFe}_{1-x}\text{Mn}_x\text{O}_{3-\delta}$  are consistent with the peak position of  $\text{MnO}_2$  [Fig. 1(a)], suggesting the tetravalent state. No significant peak shift was observed indicating that the electronic state of Mn ion does not change for the different Mn content samples.

However, the main peak at the  $L_{\text{III}}$ -edge of the samples with  $x=0.1$  and  $0.2$  slightly shifts toward the lower photon energy. Similarly, the Fe *L*-edge spectra are mostly unchanged [Fig. 1(b)], but the main peak at the  $L_{\text{III}}$  and  $L_{\text{II}}$ -edges slightly shifts toward the higher photon energy, i.e. the peak energy of  $\text{Sr}_4\text{Fe}_4\text{O}_{11}$  phase ( $x=0$ ), with the decrease in Mn contents. Although the samples with low Mn contents ( $x=0.1, 0.2$ ) have the cubic perovskite that is the same crystal structure of Mn-rich samples, the changes in the peaks observed in the Mn and Fe *L*-edge spectra suggest that the atomic structure at the sample surface is different, which is partially similar to that of the oxide ion vacancy-ordered  $\text{Sr}_4\text{Fe}_4\text{O}_{11}$  phase.

Figure 1(c) shows the O *K*-edge spectra. The peak observed at 531.5 eV for all the samples is ascribed to a carbon tape. The pre-edge peak observed below 533 eV shifts to the lower photon energy as the Mn contents decreases, the energy of the pre-edge peak is the lowest for the  $\text{SrFeO}_3$  sample. Hence, the shift of the pre-edge peak suggests the change in bonding state between oxygen and B-site ions, which is responsible for the slight change in the Mn and Fe *L*-edge spectra as observed.

## References

- [1] M. Oishi, T. Sakuragi, N. Oshima, F. Fujishiro, J. Solid State Chem. **2021**, 294, 121893.
- [2] J. Mizusaki, Solid State Ionics **1992**, 52, 79.
- [3] F. Fujishiro, N. Oshima, N. Kamioka, T. Sakuragi, M. Oishi, J. Solid State Chem. **2020**, 283, 121152.

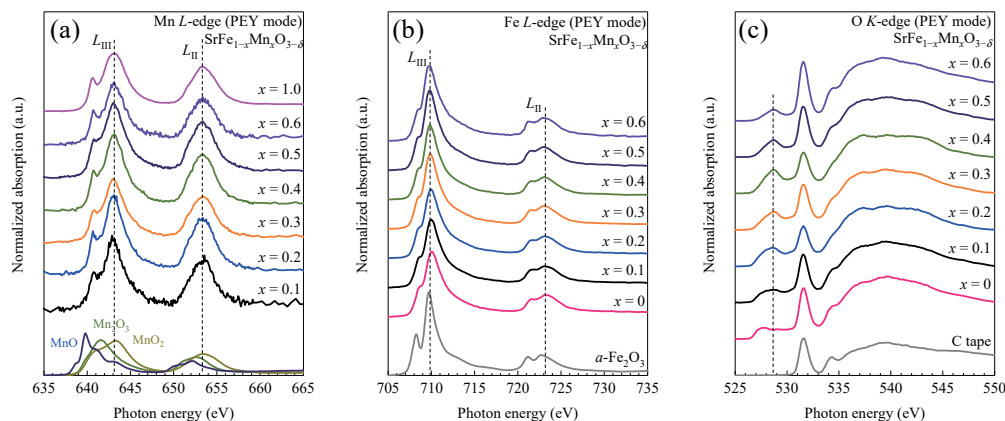


Fig. 1 (a) Mn-edge, (b) Fe *L*-edge, and (c) O *K*-edge XAS spectra of  $\text{SrFe}_{1-x}\text{Mn}_x\text{O}_{3-\delta}$ .