

XANES analysis of the valence states of Mn ions in $\text{Pr}_{1-x}\text{A}_x\text{MnO}_{3-\delta}$ (A=Ca, Sr)

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Praseodymium manganite doped with alkali-earth elements, $\text{Pr}_{1-x}\text{A}_x\text{MnO}_{3-\delta}$ (A=Ca, Sr), have been attracted great interest since 1950s, because of their unique electric and magnetic properties such as colossal magnetoresistance and metal-insulator transition [1]. The theoretical model for these properties was proposed by Zener [2] and others [3], in which mixed-valence Mn ion interacts each other over O ion. In order to understand the unique properties of perovskite manganite, it is very important to know the valence states of Mn ions in those materials. Although few suggestions were reported for those states by XPS, it has still been unclear whether the valences of Mn are different (mixed state) or equal (intermediate state).

In this study, X-ray Absorption Near Edge Structure (XANES) and X-ray Photoemission Spectroscopy (XPS) analysis of $\text{Pr}_{1-x}\text{A}_x\text{MnO}_{3-\delta}$ (A=Ca, Sr) were carried out to investigate the valence states of Mn ions. The first principles calculations were also performed to investigate the defect formation mechanism in $\text{Pr}_{1-x}\text{A}_x\text{MnO}_{3-\delta}$ (A=Ca, Sr) and the electronic structure of the materials.

Mn $L_{2,3}$ -edge XANES spectra of $\text{Pr}_{1-x}\text{A}_x\text{MnO}_{3-\delta}$ (A=Ca, Sr) were recorded by total electron yield method at BL 4B at UVSOR in Okazaki, Japan. Observed XANES spectra of PrMnO_3 and CaMnO_3 show similar profiles to those of Mn_2O_3 and MnO_2 , respectively, which suggests the valence states of Mn ions in PrMnO_3 and CaMnO_3 are 3+ and 4+, respectively. As x increases in $\text{Pr}_{1-x}\text{A}_x\text{MnO}_{3-\delta}$ (A=Ca, Sr), the structure of the spectrum of $\text{Pr}_{1-x}\text{A}_x\text{MnO}_{3-\delta}$ (A=Ca, Sr) gradually changes from the spectral profile of Mn^{3+} to that of Mn^{4+} , which indicate the valence states change with increase of x.

Although the gradual valence change was indicated from Mn $L_{2,3}$ -edge XANES spectra of $\text{Pr}_{1-x}\text{A}_x\text{MnO}_{3-\delta}$ (A=Ca, Sr), whether the valences of Mn ions in this materials are mixed (both 3+ and 4+ exist) or intermediate (only +3.x exist) is not clear yet. The ground state of Mn ions is very hard to observe by spectroscopic methods using X-rays or other beam. Then the charge distributions of Mn ions were investigated by the first-principles calculations. Total electronic energies were compared for the different four types of magnetic structures, which were reported by Goodenough [4].

References

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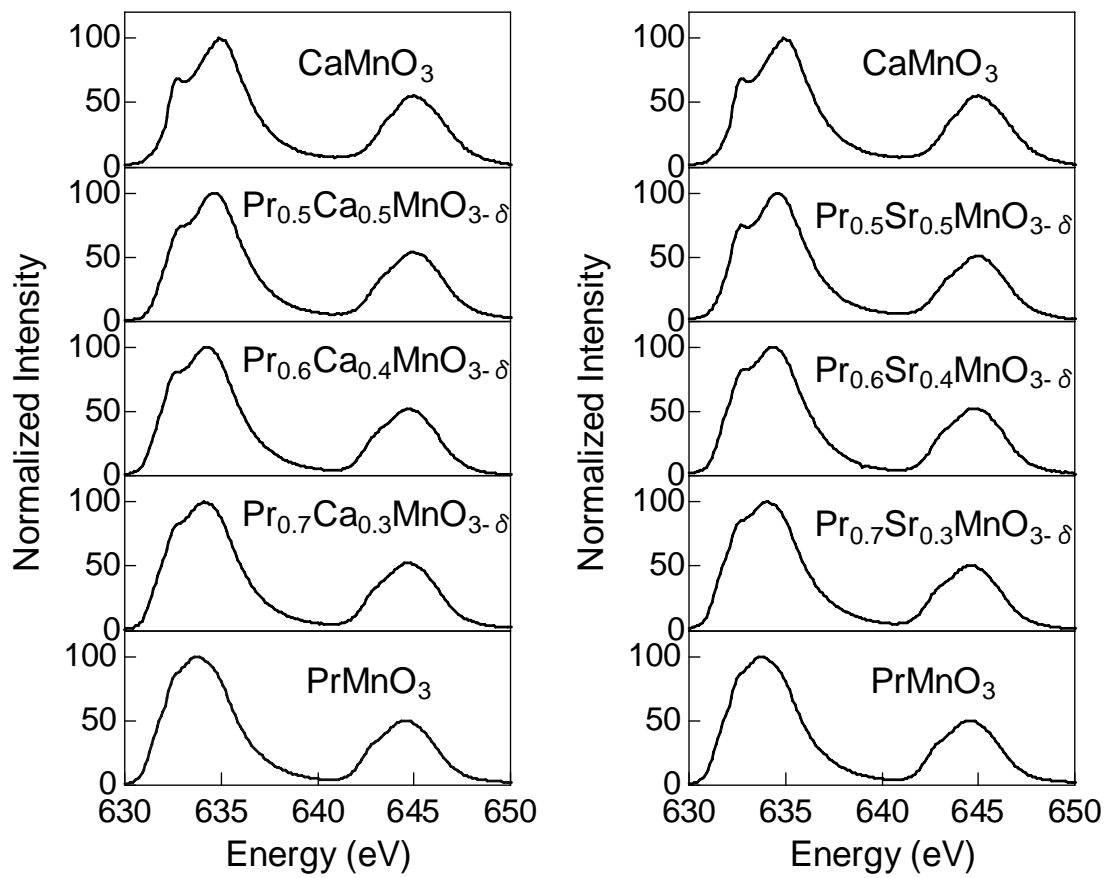


Fig. 1. The XANES spectra of Mn L_{2,3}-edge in Pr_{1-x}A_xMnO_{3-δ} (A=Ca, Sr)