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Determination of valence state of Mn ions in $Pr_{1-x}A_xMnO_{3-\delta}$ (A = Ca, Sr) by Mn-L_3 X-ray absorption near-edge structure analysis

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ABSTRACT

The valence states of the Mn ions in $Pr_{1-x}A_xMnO_{3-\delta}$ (A = Ca, Sr) are investigated by Mn-L_3 X-ray absorption near-edge structure (XANES) analysis. The spectral fine structures in the Mn-L_3 XANES analysis show a significant difference between $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$ and $Pr_{0.5}Sr_{0.5}MnO_{3-\delta}$, a paramagnetic insulator and a ferromagnetic metal, respectively, at room temperature, whereas the spectral structures of $Pr_{0.7}Ca_{0.3}MnO_{3-\delta}$ and $Pr_{0.7}Sr_{0.3}MnO_{3-\delta}$, paramagnetic insulators, are almost identical. These results indicate that the valence states of the Mn ions in these materials are highly correlated with their magnetic and electrical properties. A significant difference was also found between the Mn-L_3 XANES profiles of $Pr_{1-x}Ca_xMnO_{3-\delta}$ and the profiles formed by the linear combination of the Mn-L_3 XANES spectra of $PrMnO_3$ (Mn^{3+}) and $CaMnO_3$ (Mn^{4+}). This difference indicates that the Mn ions in these materials do not have a mixed-valence state of 3+ and 4+, but have an intermediate valence state o 3+ and 4+.

1. Introduction

Perovskite manganites have attracted both scientific and technological interest since the 1950s because these materials exhibit interesting phenomena such as charge/orbital ordering and metal–insulator transitions through the application of external fields (e.g., magnetic, electric, strain, and photonic fields) [1,2]. Historically, the phase transition in these materials has been explained in terms of the double-exchange effect, wherein the 3d electrons in Mn^{3+} and Mn^{4+} ions interact with each other [3]. However, recently, this ionic charge-ordering model has been disputed [4], and the intermediate valence-state model, or the so-called Zener polaron model, has been proposed as an alternative explanation [5]. It was also reported that the electronic state of these manganites is separated into two dissimilar phases and this separation contributes to the phase transition [6–8]. Jooss et al. proposed a new model of phase transitions. In this model, polaronic ordering and disordering states coexist in $Pr_{0.6}Ca_{0.4}MnO_{3-\delta}$ and phase transition occurs when the ordered phase is subjected to electric or magnetic fields [9]. Although a few theoretical and experimental studies support this result [10,11], the mechanism of the phase transition in these materials is still a controversial topic.

Many crystallographic and theoretical studies on perovskite manganites have been reported. In order to understand the characteristic electrical and magnetic properties of perovskite manganites, it is essential to determine the valence state of Mn ions. For such studies, a spectroscopic technique is one of the most powerful approaches. Several spectroscopic studies on rare-earth manganites by Mn-K X-ray absorption near-edge structure (XANES) have already been reported [12–16]. In these studies, it was reported that the threshold energy of Mn-K XANES shifted toward higher energy sides with an increase in the concentration of doped divalent ions such as Ca^{2+} and Sr^{2+}; that is, so-called chemical shifts were observed in the Mn-K XANES spectra. However, in these Mn-K XANES studies, it could not be clearly determined whether the valence state of Mn ions in these manganites was a mixture of Mn^{3+} and Mn^{4+} or an intermediate state between Mn^{3+} and Mn^{4+}. On the other hand, it is well known that Mn-L_3 XANES profiles are sensitive to changes in the valence states of Mn ions [17], which can be observed through the electronic transition from Mn L_3 ($3p_{3/2}$) to Mn $M_{4,5}$ (3d). Several studies on Mn-L_3 XANES analysis of rare-earth manganites have been reported [18–20]; in one of these studies, a continuous change in the Mn-L_3 XANES of $LaMnO_3$ with an increase in doped Sr^{2+} concentration was demonstrated [18]. However, the valence state of Mn ions was not discussed in detail; in addition, the relationship between Mn valence states, determined by the Mn-L_3 XANES profiles, and their characteristic properties was not discussed. To the best of our knowledge, among these rare-earth manganites, the valence state of Mn ions in $PrMnO_3$ doped

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with Ca^{2+} and Sr^{2+} has not been determined yet. In this study, the high-resolution Mn-L_3 XANES measurements are systematically carried out for $Pr_{1-x}A_xMnO_{3-\delta}$ (A = Ca, Sr). We have successfully analyzed the Mn-L_3 XANES of $Pr_{1-x}A_xMnO_{3-\delta}$ in detail; further, we have also found the strong correlation between the valence states of Mn ions and their characteristic electrical property.

2. Experimental procedure

Polycrystalline samples of $Pr_{1-x}A_xMnO_{3-\delta}$ (A = Ca, Sr) were prepared by the conventional solid-state reaction method. Commercially available high-purity powders of $SrCO_3$, $CaCO_3$, Mn_2O_3, and Pr_6O_{11} were used as starting materials. $CaCO_3$ and $SrCO_3$ were preheated at 773 K in air for 30 min to remove hydrated water. All the powders were mixed and ground in an agate mortar for 20 min and then were calcined in air at 1273 K for 10 h. After calcination, the powders were mixed and ground again and then were pressed into pellets (10 mm ϕ). Finally, these pellets were sintered in air at 1473 K for 12 h.

Mn-L_3 XANES spectra were measured at BL-4B in UVSOR (Okazaki, Japan) by the total electron yield method. Synchrotron radiation from a storage ring was monochromatized by a varied-line-spacing plane grating (800 lines/mm). The energy resolution of the incident beams ($E/\Delta E$) was set to 3000 by tuning the slit width at the upper and lower reaches of the grating. The sample powders were mounted on carbon adhesive tape and deposited on the first Cu–Be dynode of an electron multiplier. NaF powders were mixed with the sample powders to calibrate the energy scale of all samples through simultaneous measurement of the F-K XANES spectra of NaF.

3. Results and discussion

Prior to the XANES analysis, the crystal structures of all samples were characterized by powder X-ray diffraction (XRD) with Cu-Kα X-rays. The observed XRD patterns are shown in Fig. 1. The observed XRD patterns of $Pr_{0.7}Ca_{0.3}MnO_{3-\delta}$, $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$, $Pr_{0.7}Sr_{0.3}MnO_{3-\delta}$, and $Pr_{0.7}Sr_{0.5}MnO_{3-\delta}$ agree well with those listed in the Inorganic Crystal Structure Database (ICSD) (Nos. 54902, 85650, 72183, and 72184, respectively), all of which have an orthorhombic perovskite structure with the space group *Pnma*. Hence, it can be concluded that all the samples analyzed in this study were single-phased polycrystalline powders of $PrMnO_3$ in which doped Ca^{2+} and Sr^{2+} ions were substituted at Pr sites.

The electrical properties of the materials synthesized were evaluated by measuring the temperature dependence of electrical resistivity using a standard direct-current (DC) four-probe method; the results are shown in Fig. 2. As shown in this figure, the electrical resistivity of Ca-doped $PrMnO_3$, i.e., $Pr_{0.7}Ca_{0.3}MnO_{3-\delta}$ and $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$, shows a monotonic decrease with an increase in temperature, which is typical behavior of insulating materials. On the other hand, $Pr_{0.5}Sr_{0.5}MnO_{3-\delta}$ shows a gradual monotonic increase in electrical resistivity with an increase in temperature; this behavior is typical one of metallic materials. Further, the electrical resistivity of $Pr_{0.7}Sr_{0.3}MnO_{3-\delta}$ increases up to approximately 275 K and decreases beyond this temperature; this result indicates that the metal-to-insulator transition occurs at approximately 275 K. In summary, the above results confirm that $Pr_{0.7}Ca_{0.3}MnO_{3-\delta}$, $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$, and $Pr_{0.7}Sr_{0.3}MnO_{3-\delta}$ act as insulating materials at around room temperature, whereas $Pr_{0.5}Sr_{0.5}MnO_{3-\delta}$ is metallic. These results are consistent with the results of earlier reports [21].

The Mn-L_3 XANES spectra of $Pr_{1-x}A_xMnO_{3-\delta}$ (A = Ca, Sr) are shown in Fig. 3. All the spectra are composed mainly of two peaks labeled peaks A and B, as shown in Fig. 3. As x increases

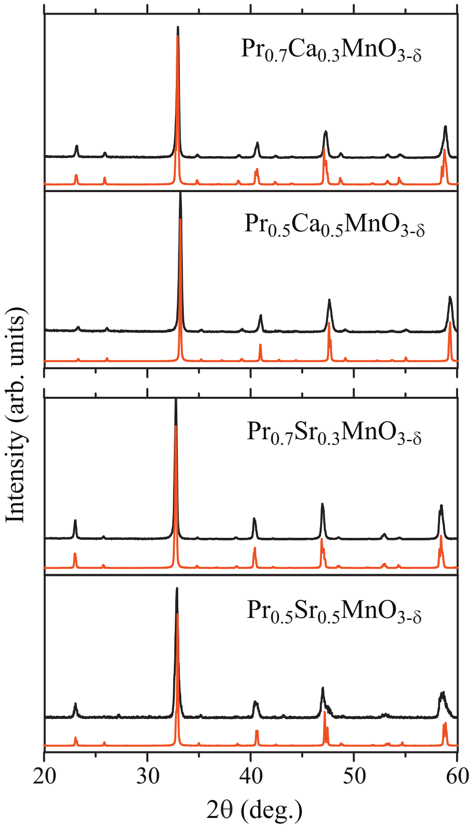

Fig. 1. Observed (upper; black) and referenced (lower; red) XRD patterns of $Pr_{1-x}A_xMnO_{3-\delta}$ (A = Ca, Sr). From top to bottom, ICSD numbers of the referenced XRD patterns are 54902, 85650, 72183, and 72184. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

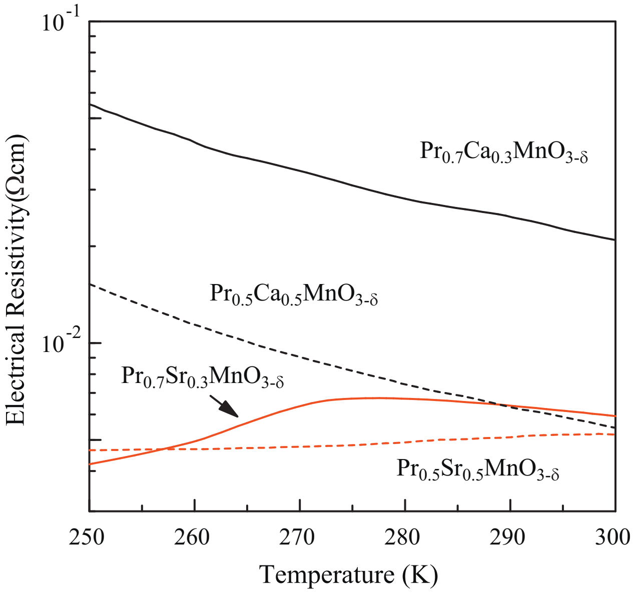

Fig. 2. Temperature dependence of electrical resistivity of $Pr_{1-x}A_xMnO_{3-\delta}$ (A = Ca, Sr). The black solid and dashed lines are $Pr_{0.7}Ca_{0.3}MnO_{3-\delta}$ and $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$, respectively, and the red solid and dashed lines are $Pr_{0.7}Sr_{0.3}MnO_{3-\delta}$ and $Pr_{0.5}Sr_{0.5}MnO_{3-\delta}$, respectively.