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Charge ordering transition of $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$ studied by Mn 3s photoemission spectroscopy

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Introduction

$Pr_{0.5}Ca_{0.5}MnO_3$ shows a charge-ordering transition around 230 K [1, 2]. The transition results from the modification of the electronic state owing to the correlation among the charge carriers, that is, Mn 3d electrons. It is considered that the valence of Mn in $Pr_{0.5}Ca_{0.5}MnO_3$ changes through the transition from an averaged value of +3.5 in the high-temperature paramagnetic insulating phase to 1:1-ordered trivalent and tetravalent states in the low-temperature charge-ordered insulating phase. Very recently Galakhov *et al.* have shown that the exchange splitting of the Mn 3s x-ray photoemission (XP) spectra of manganese oxides reflects Mn valency [3].

In this work we have measured the Mn 3s XP spectra of $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$ at 300 and 100 K in order to investigate the change in the valence of Mn through the charge-ordering transition. We have found that the Mn 3s XP spectra of $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$ changes through the charge-ordering transition and the Mn valency changes as expected.

Results and Discussion

The sample used was $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$ multigrain crystal. The oxygen deficiency was estimated to be about 0.05 by magnetic susceptibility measurements. The sample surface was cleaned in situ by scraping. The excitation energy was 850 eV and was calibrated by measuring the Au 4f XP spectrum.

The Mn 3s XP spectrum of $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$ at 300 K is shown by dots in Fig. 1. Thick and thin lines represent the Mn 3s XP spectra of $La_{1.2}Sr_{1.8}Mn_2O_7$ and $Pr_{0.5}Ca_{0.5}MnO_3$, respectively, at room temperature [3]. The spectrum of $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$ is almost identical to that of $La_{1.2}Sr_{1.8}Mn_2O_7$ not to $Pr_{0.5}Ca_{0.5}MnO_3$. This is consistent with the fact that the formal Mn valency of the present sample is +3.4 by taking account of $\delta \approx 0.05$.

The Mn 3s XP spectrum of $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$ at 100 K is shown by open circles in Fig. 2. The spectrum is well reproduced by the superposition of that for the trivalent manganese oxide, $LiMnO_3$, reduced to 60% and that for tetravalent $SrMnO_3$ reduced to 40%. Thus the Mn 3s XP spectrum of $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$ at 100 K reflects the charge-ordered state of Mn. This illustrates that Mn 3s XP spectroscopy is useful tool to detect the charge-ordering transition of the manganese oxides. Usually Mn 3s XP spectra are measured with low signal to noise ratio, but they carry rich information as is the present case.

The population of Mn^{3+} and Mn^{4+} estimated in this work is somewhat different from the previous results [1]. The reason is now under investigation.

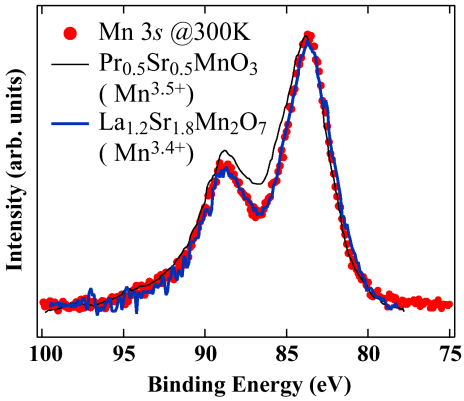

Fig. 1. Mn 3s photoemission spectrum of $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$ measured at 300 K (dots).

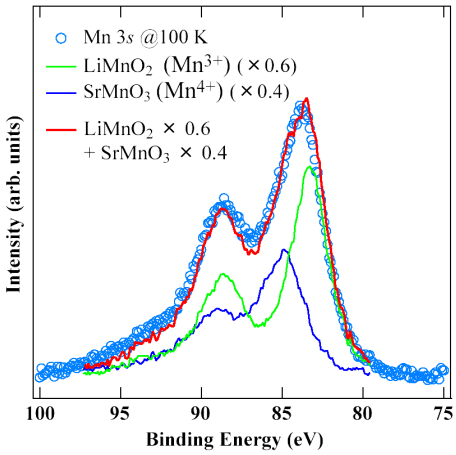

Fig. 2. Mn 3s photoemission spectrum of $Pr_{0.5}Ca_{0.5}MnO_{3-\delta}$ measured at 100 K (open circles).

References

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