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XPS study of $Pr_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.33, 0.4 and 0.84)

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ABSTRACT

We have studied the Mn 2p, Ca 2p, and Pr 4d core levels of $Pr_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.33, 0.4 and 0.84) as a function of x using X-ray photoelectron spectroscopy both at room temperature as well as 77 K. Suppression of chemical potential shifts have been observed at 77 K compared to that of room temperature spectra. We have discussed this result by considering the concept of phase separation.

1. Introduction

Perovskite type manganites having general formula $R_{1-x}A_xMnO_3$ (R is the trivalent rare earth element and A is the divalent alkaline earth element) have become interesting in the field of condensed matter physics due to its so-called colossal magnetoresistance (CMR) behaviour [1–3]. Among these manganites, $Pr_{1-x}Ca_xMnO_3$ is one of the most interesting series due to the varieties of phases [4–6]. At room temperature these are paramagnetic insulators (PMI). At low temperature, the concentrations $x \leq 0.25$ show ferromagnetic insulating (FMI) behaviour. The charge ordered (CO) state has been observed for $0.3 \leq x \leq 0.85$ with antiferromagnetic insulating (AFMI) behaviour. The coexistence of FM clusters in AFM domains have been attracted due to their importance in understanding the role of spin, charge, and orbital ordering in this type of CMR system [7–13]. There are many reports regarding the coexistence of FM and AFM phases in the form of clusters, stripes, etc. in the CO phase of $Pr_{1-x}Ca_xMnO_3$ system [14–19].

X-ray photoelectron spectroscopy (XPS) is one of the powerful tool to study the core levels of the materials. From the core level studies of CMR systems, there are many reports regarding the chemical potential shifts [20–22] as a function of concentraions at room temperature. But a few study has been reported at low temperatures. In this paper we report the comparision of chemical potential shift at room temperature with that of 77 K.

2. Experimental

Single crystals of $Pr_{1-x}Ca_xMnO_3$ with $x = 0.2$, 0.33 and 0.4 were grown by the floating zone method in a mirror furnace and the polycrystalline $Pr_{0.16}Ca_{0.84}MnO_3$ sample was prepared by the standard solid state reaction method. The compositional homogeneity of the crystals had been confirmed using energy dispersive spectroscopic (EDS) analysis. The crystals were characterized by using magnetization, electrical transport and neutron diffraction measurements. Details of the sample preparation and characterization measurements are published elsewhere [16,19,23]. The XPS measurements were performed by using an Omicron μ-metal ultra high vacuum system equipped with a twin anode Mg/Al X-ray source (DAR 400) and a hemispherical electron energy analyzer (EA 125 HR). In our measurements we have used the Mg Kα line with photon energy 1253.6 eV and the resolution was about 1.0 eV. All measurements were performed under a base vacuum of $\sim 1.0 \times 10^{-10}$ mbar. The samples were repeatedly scraped *insitu* by using a diamond file to obtain clean surfaces. For the low temperature measurements, the samples were cooled by pumping liquid nitrogen through the sample manipulator fitted with a cryostat. The sample temperatures were measured by using a silicon diode sensor touching the bottom of the sample holder.

3. Results and discussion

The Mn 2p core level spectra of $Pr_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.33, 0.4, and 0.84) taken at room temperature as well as at 77 K are shown in Fig. 1. All the spectra were normalized and shifted along the Y axis by a constant for clarity. The two prominent peaks at around ~641.5 eV and ~653.5 eV are due to the spin orbit split of $2p_{3/2}$ and $2p_{1/2}$. These spectra look similar to those reported earlier on the similar systems [21,24]. In Fig. 1, the Mn 2p peak positions shift

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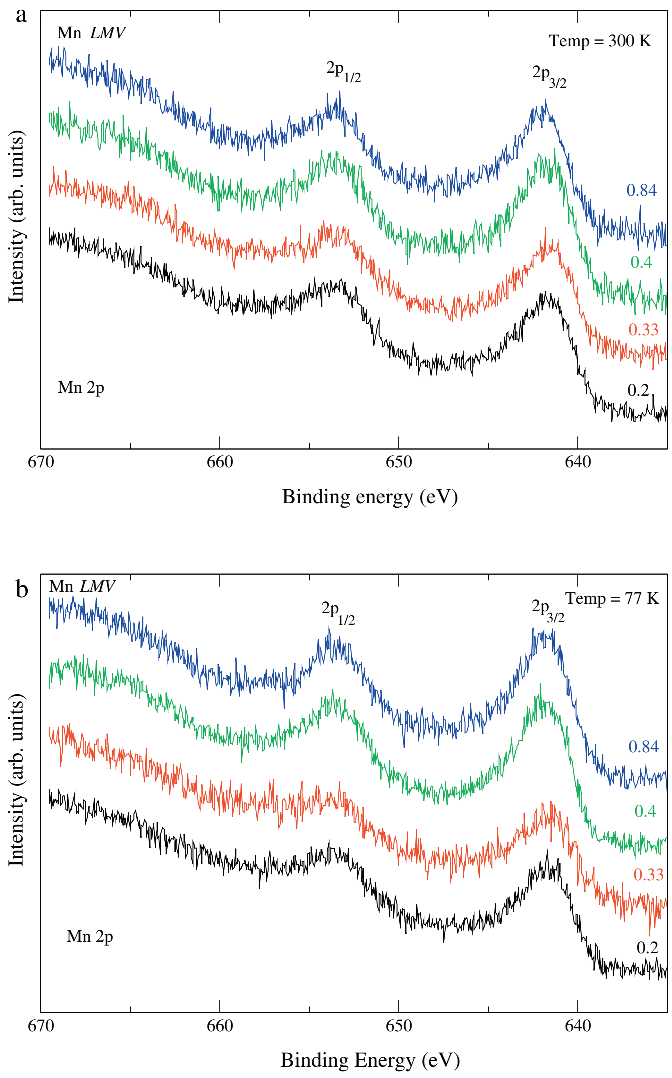

Fig. 1. The Mn 2p core-level XPS (Mg Kα) spectra of $Pr_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.33, 0.4 and 0.84) taken at room temperature (a) and 77 K (b).

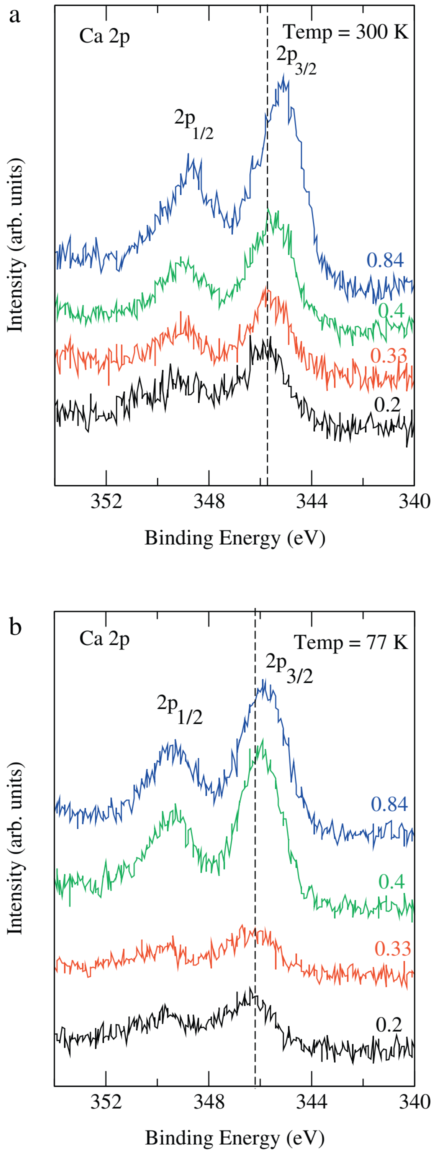

Fig. 2. The Ca 2p core-level XPS (Mg Kα) spectra of $Pr_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.33, 0.4 and 0.84) taken at room temperature (a) and 77 K (b).

towards the higher binding energy for $x = 0.4$ and 0.84 at room temperature (Fig. 1(a)) as well as at 77 K (Fig. 1(b)). But the binding energy shift is higher incase of room temperature spectra as compared to that of 77 K. The Mn *LMV* Auger peaks are observed on the higher binding energy side of $2p_{1/2}$ peak for all four concentrations at room temperature, whereas at 77 K these Auger peaks are absent for $x = 0.2$, and 0.33. Such Mn *LMV* Auger peaks were earlier observed in other hole doped manganites [24].

The Ca 2p spectra of $Pr_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.33, 0.4 and 0.84) both at room temperature as well as 77 K are shown in Fig. 2. The Ca $2p_{3/2}$ and Ca $2p_{1/2}$, due to spin orbit splitting, are clearly distinguishable at around ∼345.5 and ∼349 eV, respectively. It is clear from Fig. 2(a) that, at room temperature the peak positions shift towards the lower binding energy when we move from $x = 0.2$ to $x = 0.84$. Also the same kind of shift is observed for 77 K spectra (Fig. 2(b)) with a lesser magnitude.

The Pr 4d spectra of $Pr_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.33 and 0.4) taken at room temperature as well as 77 K are shown in Fig. 3. The Pr 4d peaks come around 116 eV binding energy. The peak positions shift towards the lower binding energy at room temperature (Fig. 3(a)) when we move from $x = 0.2$ to 0.4. Here also the similar kind of shift is observed for 77 K spectra (Fig. 3(b)) with a lesser magnitude.

As mentioned above the binding energy shifts with respect to the value of x have been observed at the Ca 2p, Pr 4d and Mn 2p core levels. Incase of Mn 2p core levels, the binding energy shift is towards the higher energy side while the other two levels shift to the lower energy side. The magnitude of the binding energy shifts are found to be higher at room temperature compared to 77 K. The shift to higher binding energy observed in Mn 2p could be due to the increase in the effective Mn valence state from Mn^{3+} towards Mn^{4+} [20,21]. The binding energy shift incase of Ca 2p and Pr 4d core levels could possibly due to the shift in the chemical potential [20,21]. The low temperature data shows a smaller value for this chemical potential shift. Such a suppression of the chemical potential shift have been observed earlier in other transition metal oxides [25,26] is mostly due to the formation of stripes. According to the phase separation model, a pinning of the chemical potential is consequence of the mixed phase nature of these materials. The numerical studies [27,28] have indeed shown the pinning of chemical potential in the composition range, where the phase sep-

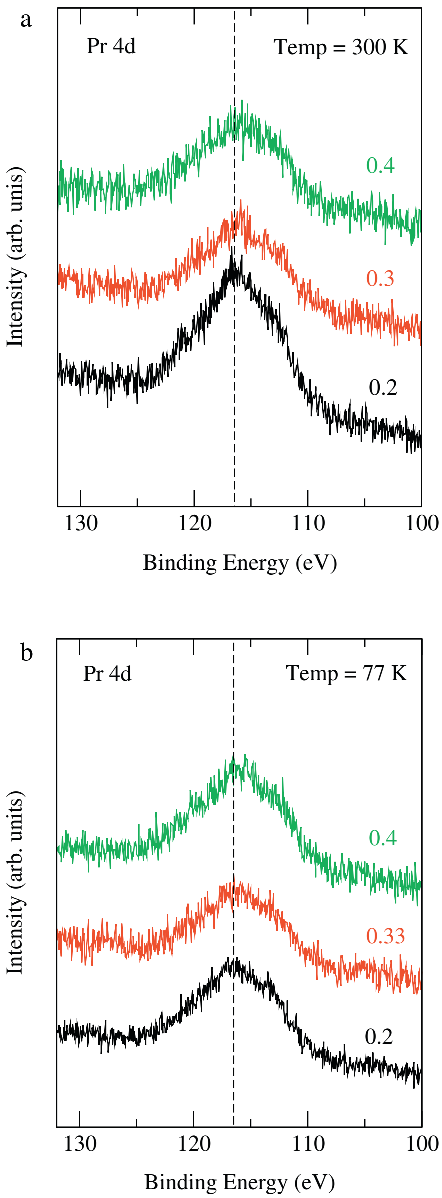

Fig. 3. The Pr 4d core-level XPS (Mg Kα) spectra of $Pr_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.33 and 0.4) taken at room temperature (a) and 77 K (b).

aration is realized. These results also support the model of phase separation in the $Pr_{1-x}Ca_xMnO_3$ system [15,19].

4. Conclusions

Using X-ray photoelectron spectroscopy we have studied the Mn 2p, Ca 2p and Pr 4d core levels of $Pr_{1-x}Ca_xMnO_3$ with $x = 0.2$, 0.33, 0.4 and 0.84 at room temperature as well as at 77 K. From these studies we observed the shift of chemical potential as a function of x and there is a suppression of chemical potential shift at 77 K compared to that of room temeperature spectra. These results support the model of phase separation in $Pr_{1-x}Ca_xMnO_3$ system.

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