

Valence states analysis of Pr ions and Co ions in $\text{Pr}_{1-x}\text{A}_x\text{CoO}_{3-\delta}$ (A = Ca and Sr)

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Perovskite type cobalt oxides doped with alkaline-earth ions, $\text{R}_{1-x}\text{A}_x\text{CoO}_{3-\delta}$ (R = rare-earth, A = alkaline-earth), have been of much interest for last fifty years, because they have unique electronic and magnetic properties such as colossal magnetoresistance and metal-insulator transition [1-3]. In order to understand such characteristic properties, it is essential to know the electronic structures of these materials. When the alkaline-earth ions are substituted at rare-earth site in RCoO_3 , one or both of the followings should occur to keep the system electrically neutral, i) Co and/or R ions change their valences, i.e., $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$ or $\text{R}^{3+} \rightarrow \text{R}^{4+}$, or ii) oxygen vacancy is created. However, these mechanisms of charge compensation have not yet been thoroughly investigated for these materials.

In the present study, the electronic structure analysis have been systematically carried out by the X-ray absorption near-edge structure (XANES) measurements with the aid of the first-principles calculations to investigate the valence states of Pr ions and Co ions in $\text{Pr}_{1-x}\text{A}_x\text{CoO}_{3-\delta}$ (A = Ca, Sr). All the sample specimens were fabricated by the conventional solid-state reaction method. Pr-L₃ and Co-K XANES spectra were collected at BL01B1 in SPring-8 with a transmission mode. Prior to the XANES analysis, all the samples were examined by the powder X-ray diffraction method, which show all the samples were crystallized in a single phased orthorhombic perovskite structure.

Observed Pr-L₃ XANES spectra of $\text{Pr}_{1-x}\text{A}_x\text{CoO}_{3-\delta}$ are shown in FIG. 1. XANES profiles of $\text{Pr}_{1-x}\text{A}_x\text{CoO}_{3-\delta}$ are almost identical and show only one intense peak originating from the Pr^{3+} , which indicate that the valence states of Pr ions are trivalent in $\text{Pr}_{1-x}\text{A}_x\text{CoO}_{3-\delta}$. Observed Co-K XANES spectra of $\text{Pr}_{1-x}\text{A}_x\text{CoO}_{3-\delta}$ are shown in FIG. 2. Although all samples of $\text{Pr}_{1-x}\text{A}_x\text{CoO}_{3-\delta}$ show similar profiles, the peak energies of the first intense peaks changes slightly and continuously from lower to higher energy sides, i.e, chemical shift, depending upon the concentration of doped Ca^{2+} and Sr^{2+} ions was confirmed at the Co-K XANES spectra in $\text{Pr}_{1-x}\text{A}_x\text{CoO}_{3-\delta}$. These peak energies of the first intense peaks in Co-K XANES spectra are plotted in FIG. 3. These results indicate that valence state of Co ions in $\text{Pr}_{1-x}\text{A}_x\text{CoO}_{3-\delta}$ increases as increment of doped Ca^{2+} and Sr^{2+} concentration. Details of the chemical shift were also investigated by the theoretical XANES calculations with the first-principles method within the density functional theory, which could explain the change in the charge state of Co ions in these materials.

References

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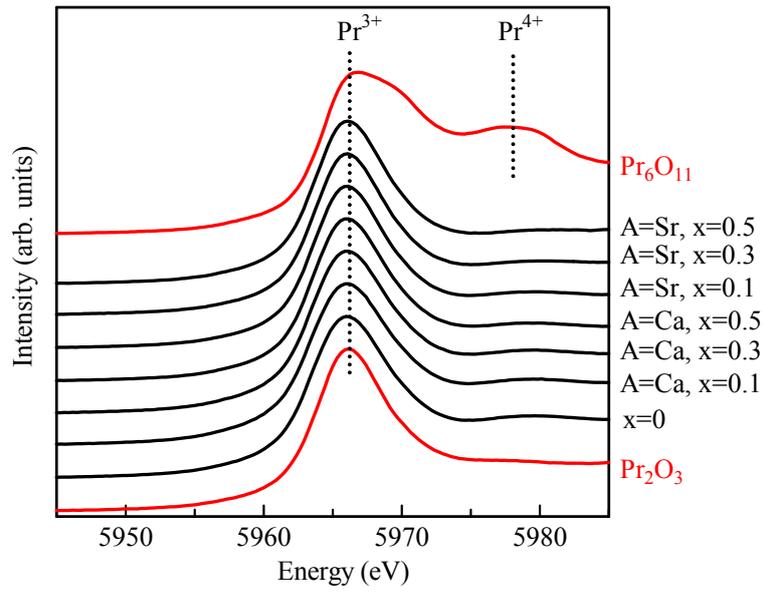


FIG. 1. Observed Pr-L₃ XANES spectra of Pr₂O₃, Pr₆O₁₁ and Pr_{1-x}A_xCoO_{3-δ} (A = Ca, Sr).

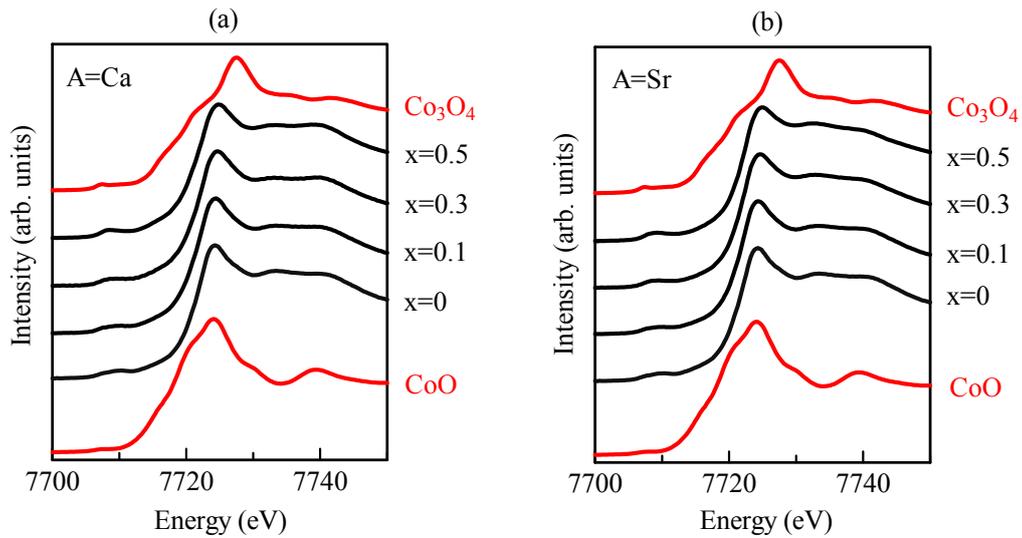


FIG. 2. Observed Co-K XANES spectra of (a) Pr_{1-x}Ca_xCoO_{3-δ} and (b) Pr_{1-x}Sr_xCoO_{3-δ}. Those of CoO and Co₃O₄ are also plotted as references.

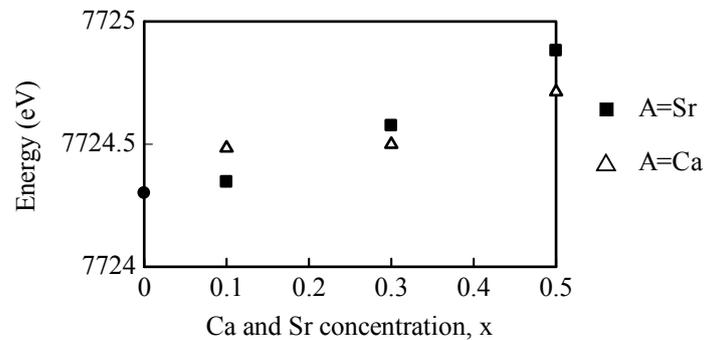


FIG. 3. Energies of the first intense peaks in Co-K XANES spectra of Pr_{1-x}A_xCoO_{3-δ} (A=Ca, Sr).