

X-ray absorption fine structure study of K edges of Mn and Co in $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.3}\text{Co}_{0.7}\text{O}_{3\pm\delta}$

Umesh A. Palikundwar, Akash A. Deshmukh and Rajashri R. Urkude,
X-ray Research Laboratory, Department of Physics, Rashtrasant Tukadoji Maharaj Nagpur
University, Nagpur 440033, India,
uapali@nagpuruniversity.nic.in

Strontium doped LaMnO_3 and LaCoO_3 have been widely studied for their electrical and magnetic properties. It is found that compounds become ferromagnetic and metallic as an effect of replacement of La^{3+} ions by Sr^{2+} ions. Ferromagnetism and reduction in the resistivity in the LaMnO_3 can be well understood in terms of double exchange (DE) mechanism between Mn^{3+} and Mn^{4+} ions. This mixed state of Mn ions is formed as a result of the Sr doping. In addition to DE mechanism Jahn-Teller (JT) effect also plays an important role through a strong electron lattice coupling. Whereas, in LaCoO_3 , the Co^{3+} ions are found to be in low spin state at low temperature and show progressive conversion from low spin to high spin state with the increase in temperature. On Sr doping, Co^{4+} ions are expected to be created. Similar to the Co^{3+} ions, Co^{4+} ions can be in low spin or in high spin or in the mixed state with both spins. The ferromagnetism exhibited by the compounds is a result of the mixed interactions between Co^{3+} and Co^{4+} ions. The super exchange interaction $\text{Co}^{3+}\text{-O-}\text{Co}^{4+}$ is found to be ferromagnetic while the exchange interactions between similar ions are antiferromagnetic.

In this work we report the effect of Sr doping at A site on the mixed B site ABO_3 type perovskite $\text{LaMn}_{1-x}\text{Co}_x\text{O}_{3\pm\delta}$. Compounds $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.3}\text{Co}_{0.7}\text{O}_{3\pm\delta}$ ($x=0, 0.2, 0.4, 0.5$) have been prepared by an aqueous solution method. Prepared compounds have been then characterized using powder x-ray diffraction (XRD) method. Oxygen stoichiometry in the compounds has been determined by iodometric titrations.

La ions are in trivalent state and their replacement by divalent Sr ions would increase the valence state of the ions of transition metals (Mn and Co) in order to maintain the charge balance in the compounds. Also there is a large difference in the ionic sizes of La^{3+} and Sr^{2+} ions. This leads towards the change in crystal symmetry on an average as well as at local level. Thus it is imperative to carry out X-ray absorption spectroscopic study of these compounds to get information about the ionic states and the local structures of transition metal ions. This information is useful in understanding the electrical and magnetic properties of these compounds.

X-ray absorption fine structure (XANES and EXAFS) spectra associated with Mn and Co K-edges were recorded in transmission mode at EXAFS-1 beamline at ELETTRA synchrotron source using Si(111) double crystal monochromator.

The evolution of pre-edge peaks of Co indicates a change in the hybridization of Co-3d and O-2p states whereas Mn-3d and O-2p hybridization has been observed to remain the same in the compounds. Mn-O bond length is nearly constant in all the compounds whereas Co-O bond length has been found to decrease. Increase in the distortion has been observed in both the MnO_6 and CoO_6 octahedra. A large distortion in CoO_6 octahedra, than that in MnO_6 octahedra, has been observed.

The analyses of XANES and EXAFS have shown that the doping of Sr has more effect on the oxidation state and local environment of Co than that of Mn.

Keywords: XANES, EXAFS, CMR, Jahn-Teller (JT) effect

One of the authors Umesh A. Palikundwar acknowledges Department of Science and Technology (DST) India and Italian Government for the financial support.