

XANES AND X-RAY PHOTOEMISSION OF THE $\text{La}_{0.67}(\text{Ca,Pb})_{0.33}(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ COMPOUNDS

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Polycrystalline compounds $\text{La}_{0.67}\text{Ca}_{0.33}(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ ($x = 0, 0.08$) and $\text{La}_{0.67}\text{Pb}_{0.33}(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ ($x = 0, 0.01, 0.03, 0.06, 0.10, 0.15$) were prepared by the sol-gel low-temperature method followed by heat treatment at 1273 K in air [1].

High resolution Mn *K*-edge XANES spectra of the samples and the reference oxides have been acquired in total *K* fluorescence yield using undulator fundamental mono-chromatized by a pair of Si (311) single crystals at the XAS-XES ID26 beamline of the ESRF, Grenoble. The spectra of all the samples reveal similar shape with a small, but significant gradual shift of the edge energy (Fig. 1), which is attributed to Mn charge disproportionation upon Fe substitution. A shift towards higher energy can be interpreted within the model of preferential Fe $3d^5$ configuration and gradual decrease of the average Mn $3d$ occupation upon substitution. **Conclusion:** the shift by $\sim 0.25\text{eV}$ from $x = 0.0$ to $x = 0.15$ agrees well with the expected average valence change from $\text{Mn}^{3.33+}$ to $\text{Mn}^{3.45+}$, assuming linear relationship between edge position and Mn oxidation [2].

Special attention was focused to the analysis of the Mn $2p$ core-level lines and the multiplet splitting (MS) of the lines was taken into account. It arises when, upon

ejection of core electron, the angular momenta of the partially filled core shell can couple with the angular momenta of open atomic valence shell to form several multiplets of different energies [3]. The MS is expected to be observed if the specimen possesses unpaired electrons in its outer valence shells, e.g. for the ground-state configuration $2p^53d^3$ for Mn^{+4} and $2p^53d^4$ for Mn^{+3} ions. To analyse the MS of the Mn $2p$ core-level line we have adopted the results of the MS calculations for Mn^{+3} and Mn^{+4} ions presented in [3,4] in order to fit the Mn $2p_{3/2}$ spectra. The selected spectra and the fittings are shown in Fig. 2.

Photoemission measurements were carried out by use of the angle resolved X-ray and ultraviolet XPS/ARUPS Omicron photoemission spectrometer. The XP spectra were measured for $x = 0, 0.08$ and 0.10 with the Al- K_α X-ray source with energy resolution about 1 eV at 300 K.

As the result of the fit the areas under the Mn^{3+} and Mn^{4+} lines were obtained and the ratio of $\text{Mn}^{3+}/\text{Mn}^{4+} = 1.9 \pm 0.2$ for $\text{La}_{0.67}\text{Ca}_{0.33}(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ ($x = 0.08$) and 1.6 ± 0.2 $\text{La}_{0.67}\text{Pb}_{0.33}(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ ($x = 0.10$) were obtained. **Conclusion:** the ratios are in fairly good agreement with the expected values and with assumption that for $x=0$ the ratio is equal to 2.0.

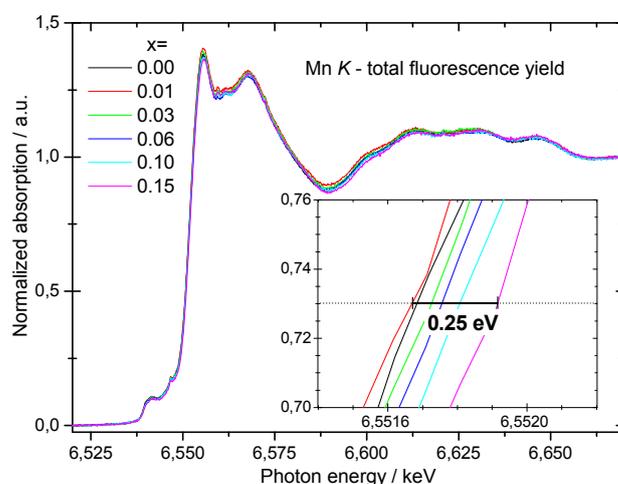


Figure 1. The normalized Mn *K*-edge XANES spectra of $\text{La}_{0.67}\text{Pb}_{0.33}(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$. Insert: magnified part of the spectra at half of maximum to extract the edge shift vs the Fe content.

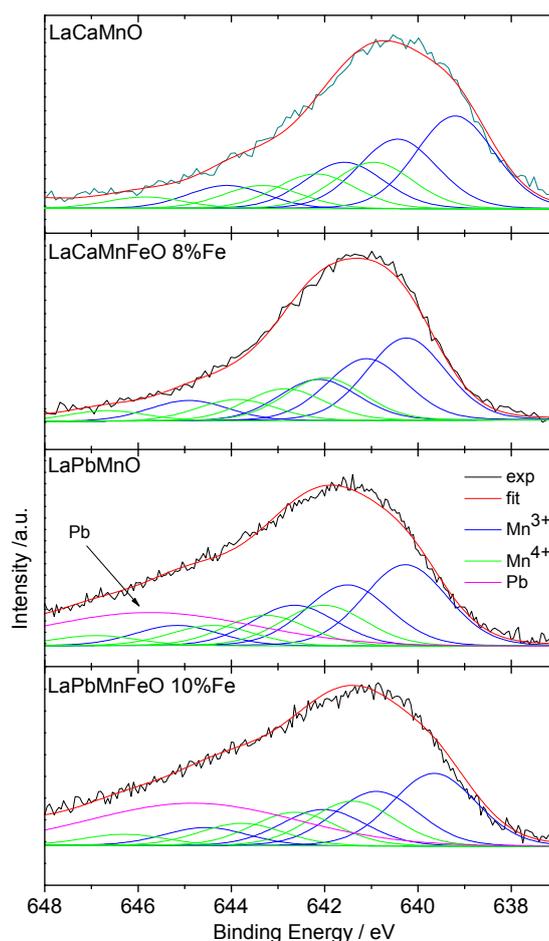


Figure 2. The Mn $2p_{3/2}$ spectra and the fitting of four multiplet for each $Mn^{3+} 2p_{3/2}$ and $Mn^{4+} 2p_{3/2}$ ions according to the analysis in [3,4], as well as with the Pb $4p_{3/2}$ line overlapping the Mn $2p_{3/2}$ lines. The XPS Peak program was used [5].

References

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