

XAFS study of local structure and oxygen stoichiometry in $(\text{La}_{0.25}\text{Ca}_{0.75})\text{MnO}_3$ nanoparticles

Manganites are natural or self-assembled nanophase materials whose bulk properties have been largely studied during the last 15 years by several techniques, including the synchrotron radiation ones.

This class of compounds of chemical formula $(\text{Ln}_{1-x}\text{Ca}_x)\text{MnO}_3$ (with $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \dots$) presents huge magneto-conductive and structural properties clearly tuned by the coexistence of nanometric metallic and insulating domains percolating as a function of temperature and external magnetic field.

Therefore manganites can be ascribed not only in the context of strongly correlated electron systems but also in that of nanostructured materials, due to the possibility to modulate their physical and chemical properties on a nanoscopic scale. This result may be of great interest both from the fundamental and applicative point of view since the nanoscopic phase texture of manganites could allow to continue to miniaturize transistors and electronic components useful for technological applications. Recently their study has received a new impulse due to the possibility to synthesize such compounds with reduced dimensionality thus determining a magneto-conductive behaviour different from that observed in the same bulk materials. In this framework we have investigated the effects of nanometric grain size on magnetic and electronic properties of different single-phase $(\text{La}_{1-x}\text{Ca}_x)\text{MnO}_3$ nanocrystalline samples obtained by sol-gel route.

In particular manganites with $x > 0.50$, presenting bulk charge ordering of Mn^{3+} and Mn^{4+} ions in different sublattices and antiferromagnetism at lower T , have never been studied previously on nanoscale. We have synthesized $(\text{La}_{0.25}\text{Ca}_{0.75})\text{MnO}_3$ compounds obtaining powder grain size of 60 nm up to 300 nm, as calculated by the Scherrer formula on the diffraction peaks broadening of X-ray powder diffraction patterns. Their magnetic characterization indicates that powders reduced dimensionality enhances the ferromagnetic component (FM), weakening the charge ordered and antiferromagnetic one. The samples are anyway phase-separated materials: the magnetization versus temperature behaviour and the magnetization decays with aging phenomena indicate that the ferromagnetic component manifests as a spin-cluster glass.

This kind of nanostructured materials can be accurately studied by XAFS techniques able to investigate the local structure and disorder around the absorbing Mn atom on the scale of the first neighbouring shells.

Moreover carrying out a study on the effects of grain size on the material structural and magnetoconductive properties, the problem to correctly define the oxygen stoichiometry is basic due to the critical dependence of these properties also on the oxygen content and on the related hole concentration.

We need to minimize changes in this parameter in order to uncouple the oxygen non-stoichiometry effects from those determined by the grain size variation. Since the manganite nanometric grains are characterized by a central magnetic core and by a non-magnetic outer grain shell containing all the crystallographic and oxygen defects and whose thickness increases decreasing the grain nanosize, we also have to quantify possible oxygen vacancies varying the nanometric grain size. Such a careful determination of the oxygen content can be successfully addressed performing high resolution EXAFS and mainly XANES measurements at the Mn K-edge in order to determine the local bonds geometry, the local symmetry and stereochemistry of the nanoscopic system besides the manganese electronic configuration.

Comparing the XANES spectra with those of model compounds having different O stoichiometry and also performing a quantitative fitting analysis we could determine the oxygen content of the sample with an error much lower than traditional analytical measurements like thermogravimetric or titration methods. In fact, in these last cases the measurement statistical error can also be of the same magnitude of the estimated off-stoichiometry.

EXAFS and XANES measurements have been performed at the Mn K-edge and further XANES spectra have been acquired at the La L-III edge, all in transmission geometry. Since high resolution XRD analysis evidenced a peculiar behaviour of lattice parameters as a function of grain nanosize we were interested to investigate what happens in local structure at various temperatures, selected for each sample on the bases of magnetization and resistivity data, in a range between 10 and 300 K. In particular we measured a total of 5 powder pellets of nanometric $(\text{La}_{0.25}\text{Ca}_{0.75})\text{MnO}_3$ compounds having 5 different average grain sizes of 60 nm up to 300 nm. Each compound was previously characterized by different and complementary techniques like X-ray powder diffraction (XRD) and High Resolution Transmission Electron Microscopy (HRTEM). Magnetic properties were previously explored by means of dc and ac magnetic measurements in the temperature range 5-350 K in order to organize in the right way the XAS measurements.

Moreover in our previous studies performed by EXAFS, neutron diffraction and anelastic spectroscopy on bulk polycrystalline samples we have reached an advanced knowledge of the structural and dynamical phenomena associated with the various phase transitions (PM-FM, spin glass or charge ordering). We also measured at room temperature an iso-structural reference $(\text{La}_{0.25}\text{Ca}_{0.75})\text{MnO}_3$ bulk sample in order to better analyse the XANES spectral features.

Therefore we determined the oxygen stoichiometry with a confidence level largely higher than that obtained by the traditional thermogravimetric or analytical techniques like titration and locally characterizing with a good resolution what structurally happens when the grain dimension is varied on a nanometric scale by different thermal treatments and conditions.