PA06

XAS STUDY OF BROWNMILLERITES AND RUDDLESDEN-POPPER MANGANITES

W. Szczerba[1], C.J. Oates[1], M. Sikora[1], M. Borowiec[1*], Cz. Kapusta[1], L. Spałek[2], M. Allix[3], M.R. Rosseinsky[3], R. Ruiz-Bustos[4], and P.D. Battle[4]

[1]*Department of Solid State Physics, Faculty of Physics & Applied Computer Science, AGH University of Science and Technology, Cracow, Poland*

[2]*Institute of Nuclear Physics, Polish Academy of Science, Cracow, Poland*

[3]*Department* of *Chemistry, The University of Liverpool, Crown Street, Liverpool L69 7ZD, United Kingdom*

[4]*Inorganic Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QR, United Kingdom*

Keywords: XANES, EXAFS, Ruddlesden-Popper manganite, brownmillerite, XAS, $Sr_2Mn_{0.5}Ru_{0.5}O_4$, Sr_3MnRuO_7

**) e-mail:yass@agh.edu.pl*

X-Ray Absorption Spectroscopy study of selected compounds of the Ruddlesden-Popper and the browmillerite families is presented. Experiments were carried out at the beamline A1 in HASYLAB/DESY, Hamburg. The n = 1 and n = 2 compounds of the Ruddlesden Popper series, $Sr_2Mn_{0.5}Ru_{0.5}O_4$ and Sr_3MnRuO_7 as well as oxygen nonstoichiometric and gallium doped brownmillerite compounds, $Ca_{2.5}Sr_{0.5}Ga_{1+x}Mn_{2-x}O_{8-\delta}$ have been studied. Polycrystalline powder samples were measured at room temperature in transmission mode.

From the analysis of XANES results, the Mn and Ru valences different from that of +4 expected for Ru only and Mn only compounds were obtained. For manganese the average valence of +3.5, equal in both Ruddlesden Popper compounds was derived. Ruthenium shows a valence of +4.9 in $Sr_2Mn_{0.5}Ru_{0.5}O_4$ and +4.7 in Sr_3MnRuO_7, which indicates a possible nonstoichiometry of the compounds. The EXAFS analysis showed that the distances between Mn and O in the manganese octahedra are almost equal in both compounds, whereas the average distances between Ru and O in the ruthenium octahedra are different and Sr_3MnRuO_7 shows a slightly larger distance than $Sr_2Mn_{0.5}Ru_{0.5}O_4$. These results indicate the same average valence of Mn and different average valences of Ru in the compounds, which is consistent with the results obtained from the XANES measurements.

An analysis of the EXAFS spectra using the FEFF software has been carried out for the Ruddlesden-Popper compounds. The fits of the simulated spectra to the experimental data have shown that the distribution of the Ru and Mn ions on their site is of random type.

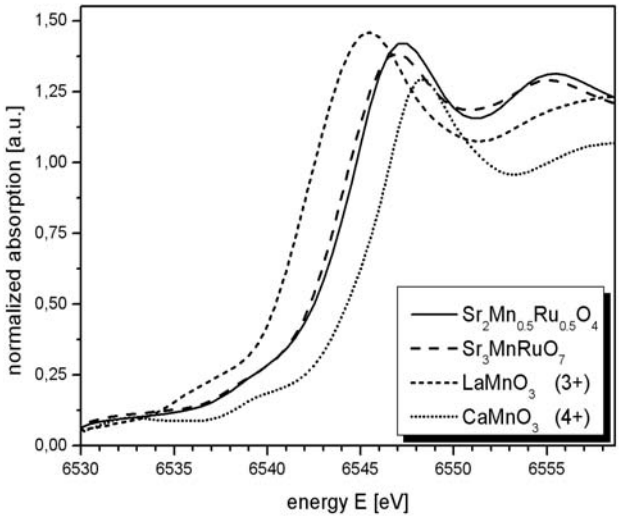

Figure 1. Mn:K edge XANES spectra of $Sr_2Mn_{0.5}Ru_{0.5}O_4$and Sr_3MnRuO_7 together with references samples: $LaMnO_3$ (Mn^{3+}) and $CaMnO_3$ (Mn^{4+}).

The XANES analysis of the Mn:*K* an Ga:*K* edges spectra of the brownmillerite series, $Ca_{2.5}Sr_{0.5}Ga_{1+x}Mn_{2-x}O_{8-\delta}$, has shown that the valences of Mn are very close to those expected from the proposed stoichiometry. Gallium, which is expected to retain its +3 valence, shows no change of it with doping. The differences in the amplitude of the first peak of the EXAFS spectra of the manganese edge suggests, that the structural modification caused by the change of number of oxygen layers in the structure concerns mainly the manganese double layers. The EXAFS spectra of gallium reveal that its next environment does not show any noticeable changes.

The Ga-doping for manganese shows no influence on the oxygen nearest neighbour shell of manganese, whereas a change in the first neighbour shell of gallium is observed.

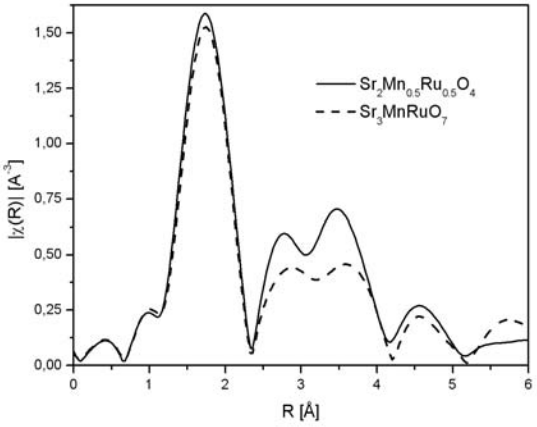

Figure 2. Fourier transform of EXAFS spectra of $Sr_2Mn_{0.5}Ru_{0.5}O_4$ and Sr_3MnRuO_7 at the Mn:K edge.

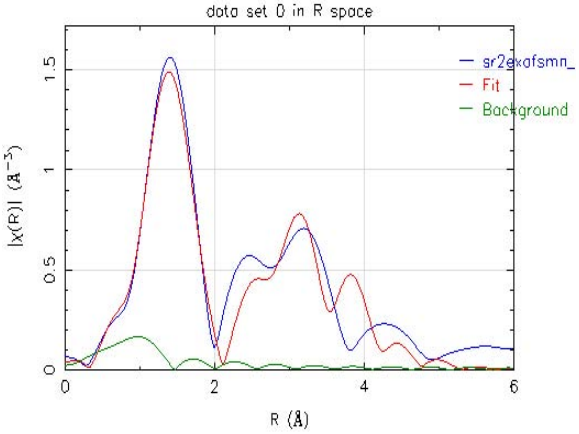

Figure 3. Fourier transform of the EXAFS spectrum of $Sr_2Mn_{0.5}Ru_{0.5}O_4$ at the Mn:K edge. with a fit assuming an ordered Mn/Ru distribution

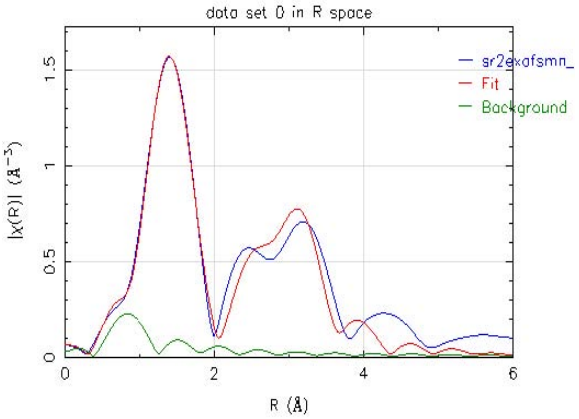

Figure 4. Fourier transform of the EXAFS spectrum of $Sr_2Mn_{0.5}Ru_{0.5}O_4$ at the Mn:K edge with a fit assuming a disordered Mn/Ru distribution.