Microsc. Microanal. 8 (Suppl. 2), 2002
10.1017.S143192760210585X

ANALYSIS OF 4 d TRANSITION METAL OXIDES BY EELS

Y. Ito[*,**], R.E. Cook[**], P.W. Klamut[*], B. Dabrowski[*,**], and M. Maxwell[*]

[*]Department of Physics, Northern Illinois University, DeKalb, IL 60115-2872
[**]Materials Science Division, Argonne National Laboratory, 9700 S. Cass Ave. Argonne, IL 60439-4838

The $SrRuO_3$ is a poor metallic itinerant ferromagnet with the transition temperature T_C = 165 K. Recently, we found that T_C for this system could be substantially lowered (to about 90K) by high-pressure oxygen annealing. This may be explained by imposed changes to the electronic state of Ru octahedrally coordinated by oxygens in this compound. The similar coordination exists in the $RuSr_2(RE_{2-x}Ce_x)Cu_2O_{10-y}$ (Ru-1222) (RE = Gd, Eu)[1] and $RuSr_2RECu_2O_8$ (Ru-1212)[2,3], which exhibit the apparent coexistence of superconductivity and ferromagnetism possibly influenced by the electronic state of Ru. This has triggered a tremendous interest in 4d transition metal complex oxides containing ruthenium ions in octahedral coordination.

Here, we investigate the microscopic origins of differences in T_C due to the high pressure oxygen annealing of $SrRuO_3$ and the relationship between microstructure, composition, and electronic structure by electron energy-loss spectroscopy (EELS) and (S)TEM imaging techniques. The Ru L_{23}-edges are sensitive to the 4d- occupancy, i.e. the valence state[4,5]. However, these edges are located at considerably high energy-losses (2967 eV and 2838 eV), hence higher beam current and longer acquisition time are required with a sacrifice of the spatial resolution. On the other hand, the M-edges (Fig. 2) are more easily accessible but complex to analyze. In this respect, the correlation between L- and M- (particularly M_{23}-) edges is also investigated. The 200kV Schottky field emission TEM/STEMs (Philips FEI Tecnai F20 and JEOL 2010F) and the Philips 300 kV CM 30 TEM with a LaB_6 gun have been used. The CM 30 was used for the acquisition of the Ru L_{23}-edges.

Two polycrystalline $SrRuO_3$ samples were prepared (1) in the conventional manner (T_C = 165K) and (2) by the high pressure oxygen annealing resulting in substantially lower T_C (= 90K) (Fig.1). The Mössbauer Ru^{99} analysis of the sample (1) showed a unique hyperfine magnetic field and, corresponding to one Ru site (+4) and a broad single line above the T_C (96K), indicating the presence of multiple sites and/or electric quadrupole interaction for the sample (2)[6].

A close examination revealed the changes in the L_3/L_2 and M_3/M_2 ratios (the derivative method[7]) and 1.5 eV higher energy shift of M_{23}-edges (see Fig. 3). This is consistent with the behavior of the Ru M- and L-edges of RuO_2 (Ru 4+) and Sr_2YRuO_6 (Ru 5+), suggesting the increase of the valence state after annealing. It is also apparent that the intensity of the pre-peak of O K-edge is increased after the annealing, i.e. increase of the hybridization of the O 2p orbital with the Ru 4d states. Furthermore, decrease of the Ru/O intensity ratio is also observed after the annealing (sample (2)). If this is due to the depletion of some Ru atoms, it may segregate at the interface. Detailed investigation at the grain interface will be conducted. Furthermore, other 4d electron systems containing Mo ions will also be investigated.

References

[1] Felner et al., *Phys.Rev.* B **55**, (1997) R3374.
[2] C. Bernhard et al., *Phys.Rev.* B **59** (1999) 14099.
[3] L. Bauernfeind et al., *Physica* C **254**, (1995) 151
[4] J.K. Okamoto, et al, *Transmission Electron Energy Loss Spectrometry in Materials Science* (The Minerals, Metals, Materials Society, 1992), 183.
[5] R.S. Liu et al., *Phys. Rev.* B **63** (2001) 212507.
[6] M. DeMarco, et al. Private communication (2002)
[7] G. A. Botton et al., *J. Microscopy* **180** (1995) 211.

[8] Supported by NSF-DMR-0105398 and HECA. The JEOL 2010F microscope, operated by the RRC at the University of Illinois at Chicago, is supported by NSF (NSF-DMR-9601792).

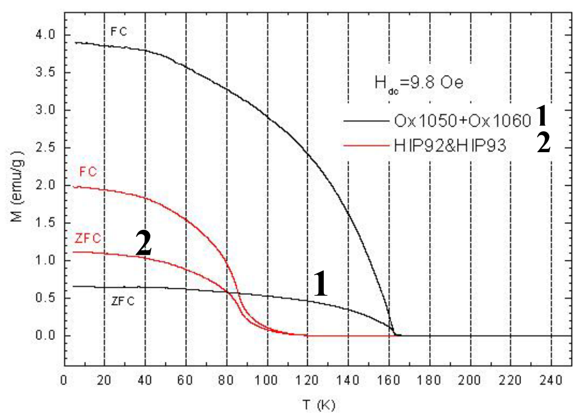

Figure 1. Magnetization measurement as a function of temperature. (1) Before annealing, $T_C = 165K$. (2) After high pressure oxygen annealing, $T_C = 90K$.

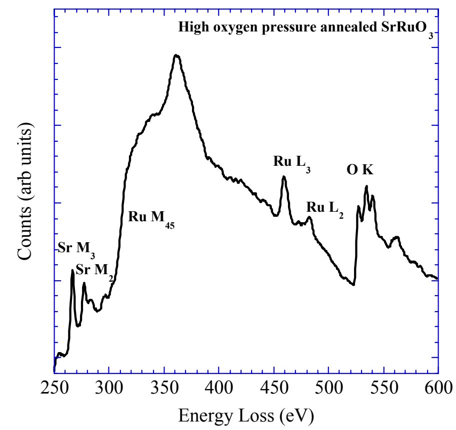

Figure 2. O K-, Ru M_{45}-, M_{23}- and Sr M_{23}-edges from the high oxygen pressure annealed $SrRuO_3$.

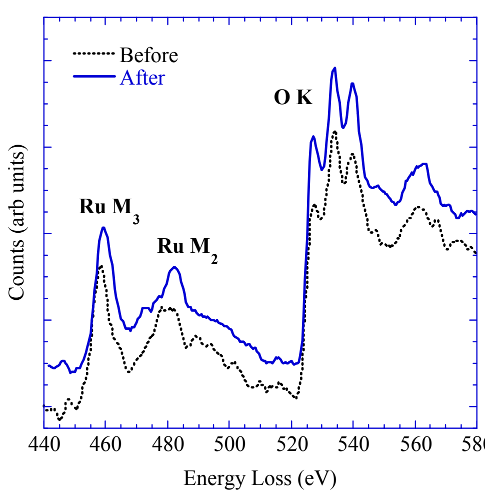

Figure 3. O K- and M_{23}-edges before and after the high oxygen pressure annealing.

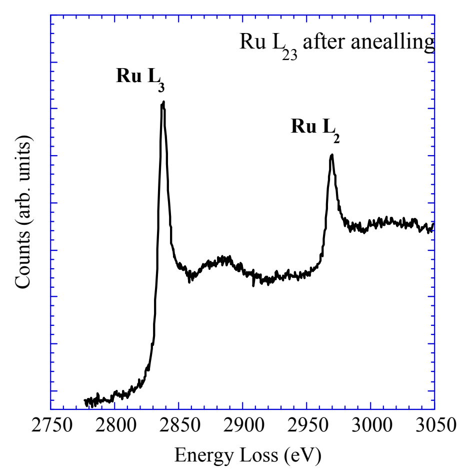

Figure 4. Ru L_{23}-edge after annealing.

https://doi.org/10.1017/S143192760210585X Published online by Cambridge University Press