The local environment and valency of chromium and copper ions in manganese doping $CuCr_2Se_4$ spinel

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$CuCr_2Se_4$ compound is intensively study because its specific combinations of magnetic and electric properties and its potential applications in magneto-optical and spin-based electronic properties. The investigated material crystallize in a spinel structure $Fd\bar{3}m$ and exhibit ferromagnetic state at room temperature with Curie temperature 430 K. In our studies we analysed impact of manganese doping on sublattice and charges of Cu and Cr atoms.

Polycrystalline samples with a general formula of $CuCr_{2-x}Mn_xSe_4$ (x = 0.1, 0.2) were synthesized using the standard solid-state reaction method. Stoichiometric amounts of high purity Cu, Mn, Cr and Se (Sigma Aldrich, 5N purity) were weighted and mixed using a mortar and pestle. The mixtures were sintered two times in evacuated quartz ampoules at 850°C for 240 hours. Grinding of the materials was repeated after each sintering. The obtained samples were tested to be a single phase by XRD method.

The occupied and un-occupied electronic states were investigated by x-ray absorption (XAS) and x-ray photoelectron (XPS) methods. XANES and EXAFS spectra of the K-edge of Cu, Cr and Se were obtained at the A1 beamline at Hasylab/DESY synchrotron in Hamburg, Germany. Photoemission measurements of Cr2p, Cu2p and Se3d lines were collected using Alk_α-monochromatized X-ray source in a PHI5700/660 Physical Electronics spectrometer.

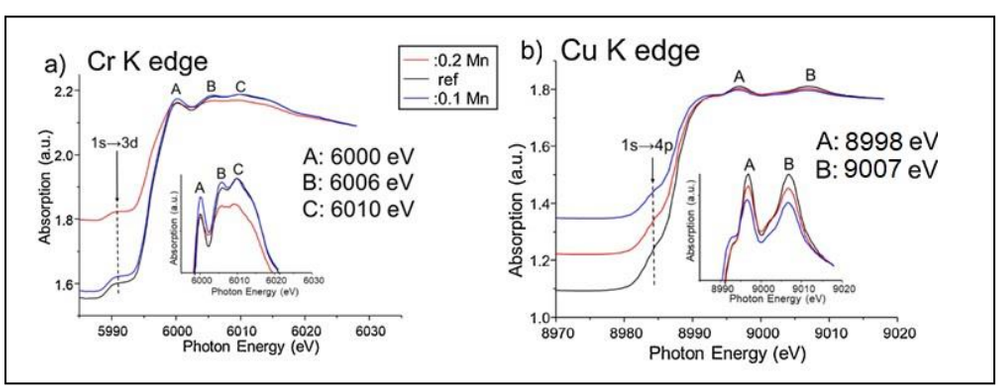

Figure 1. XAS spectra for Cr (a) and Cu (b) of K edges recorded for $CuCr_2Se_4$ reference sample and for sample with 0.10 and 0.20 Mn substitution. Inserts present enlarged energy area around the main absorption peak.

XAS and XPS studied shows that copper exists mainly on 2+ oxidation state while and chromium exists on 3+ oxidation state. The mixed valency of manganese ions (Mn^{3+} and Mn^{4+}) were concluded can suggesting a change in copper ions valency from divalency to monovalency.

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References

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