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XAS and XMCD studies of spinel-type HEOs

V. Bilovol[1]*, M. Sikora[2], M. Szymczak[3], K. Berent[1] and J. Cieślak[3]

[1]*Academic Centre for Materials and Nanotechnology, AGH University of Krakow, 30-059, Krakow, Poland*
[2]*National Synchrotron Radiation Centre SOLARIS, Jagiellonian University, 30-392 Krakow, Poland*
[3]*AGH University of Krakow, Faculty of Physics and Applied Computer Science, 30-059 Krakow, Poland*

*e-mail: vbilovol@agh.edu.pl

A new class of oxide systems known as High Entropy Oxides (HEOs) was for the first time formulated and reported only ten years ago [1]. The fundamental concept behind high-entropy materials is to employ a variety of principal elements (usually 5 or more in nearly equal molar ratios) to achieve a high configurational entropy of the system, thereby enhancing the formation of a simple, one-phase solid solution. The study of their structural and functional properties is of great interest [2], as these properties cannot be simply deduced from the crystal structure and the nature of the individual elements. Therefore, the band structure is highly likely not that of a statistical average of the five binary oxides, and it is not clear if structural and magnetic correlations can be preserved despite the chemical disorder.

The magnetic properties of HEOs are strongly dependent on the elemental composition and distribution between octahedral and tetrahedral sites of the spinel structure. We were able to collect at the PIRX beamline of SOLARIS synchrotron a comprehensive set of XAS and XMCD spectra from five HEO samples, namely $Co_x(Cr,Fe,Mn,M)_{3-x}O_4$, where x = 0.33, 0.50, 0.60, 0.82, 1.00 at% in TEY mode at L edge of Co, Cr, Mn, Fe and Ni.

The L_3 XMCD spectra showed the evolution of signs that clearly demonstrate ferromagnetic (negative sign) and anti-ferromagnetic (positive sign) alignment of spin moments of the given element sublattice with respect to the external magnetic field. Upon comparison of the XAS and XMCD spectra of all the metals distributed in the spinel lattice, it was qualitatively confirmed that Cr and Fe ions are trivalent, Mn shows a mixed valence (2+/3+/4+), and Ni ions are divalent, while Co is predominantly 2+ with admixture of 3+ in the high entropy magnetic spinel oxides. Based on the XMCD shape and amplitude, the occupancy tendency is unambiguous for Cr and Ni (both octahedral) and Co (tetrahedral), while for Mn and Fe it varied as follows: for $x <= 0.6$, Fe ions were situated exclusively on tetrahedral positions, while Mn ions for $x > 0.6$ on octahedral ones. Based on the above information, the profile of cation distribution in spinel HEOs, where Co content is a variable, is derived experimentally and compared to theoretical predictions provided by DFT.

References

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2. J. Cieślak, M. Reissner, K. Berent, et al., Acta Materialia 206 (2021) 116600.