MS25. Magnetic structures

Chairs: Oksana Zaharko, Wieslawa Sikora

MS25-P1 Tuning a cation distribution and microstructure of $CoMn_2O_4$ nanoparticles: structural and magnetic studies

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Complex metal oxides, especially one crystallizing in the spinel-type family AB_2O_4, represent an important class of functional materials. Their unique chemical, electric, magnetic and mechanical properties have found versatile applications ranging from energy storage and conversion to magnetism, electronics and catalysis.[1–3] Majority of recent work on spinels appears to be strongly focused on electrochemical properties, while the structural and magnetic studies have been scarce in spite of few papers reporting on very intriguing and complex but still poorly understood magnetic behaviour.[4,5]

In this study we have exploited the possibility of novel synthetic route to tune the structural and microstructural properties by simple alternations in preparation conditions,[6,7] and to, furthermore, correlate these effects to magnetic behaviour. The samples were prepared by thermal decomposition of a heterometallic single-molecular precursor $\{[Co(bpy)_3][Mn_2(C_2O_4)_3]\cdot H_2O\}_n$ (**1**) (bpy = 2,2'-bipyridine) at T = 500, 700, 800 and 1000 °C. The X-ray powder diffraction revealed increase in the unit-cell parameters of $CoMn_2O_4$ with the increase of formation temperature. This indicated on thermally induced increase of the inversion parameter within spinel lattice. Pronounced changes in the cation distribution, i.e. substitution of Co^{2+} by Mn^{3+} on the tetrahedral A site, and vice versa on the octahedral B site, were confirmed by the increase of octahedral ^{oct}M–O and decrease of tetrahedral ^{tet}M–O bond distances. Crystal structure and graphical result of the final Rietveld refinement for the $CoMn_2O_4$ phase, heat treated at 800 °C, is shown in Fig. 1. Increase of the applied decomposition temperature was reflected greatly on the magnetic behavior of $CoMn_2O_4$, including the increase of hysteresis width, increase of blocking temperature and raised expression of the low temperature antiferromagnetic-like transition. Those effects could originate from the nano-particle growth and increased anisotropy due to change of the inversion, as well as from the rearrangement of interactions between the spins.

References: 1. Hemberger, J. et al., *Nature*, 2005, *434*, 364. **2.** Fan, H. J. et al., *Nature Mater.*, 2006, *5*, 627. **3.** Matsuda, M. et al., *Nature Phys.*, 2008, *3*, 397. **4.** Bordeneuve H. et al., *Solid State Sci.*, 2010, *12*, 379. **5.** Zhang, H. T., Chen, X. H., *Nanotechnology,* 2006, *17*, 1384. **6.** Habjanič, J. et al., *Inorg. Chem.*, 2014, *53*, 9633. **7.** Popović, J. et al., *Cryst. Growth Des.*, 2013, *3*, 2161.

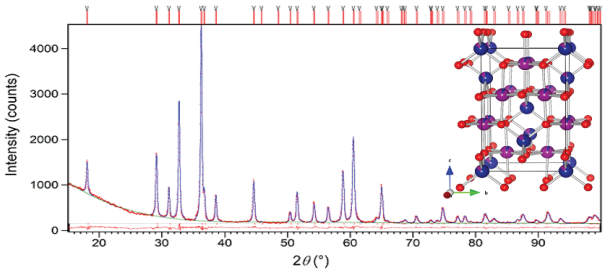

Figure 1. Graphical result of the final Rietveld refinement for the $CoMn_2O_4$ phase, obtained by heating compound 1 at 800 °C. Inset: Crystal structure of $CoMn_2O_4$.

Keywords: spinel structure, inversion parameter, magnetic properties