

P-48

Structural transformations in Mn₃O₄ at high pressure and high temperature

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Structural transformations are a very fertile research area where physicochemical ceramics and earth sciences overlap to investigate basic aspects of the materials and possible applications. At high pressures, spinel compounds can transform to CaMn₂O₄, CaFe₂O₄, or CaTi₂O₄-type structures, often regarded as post-spinel phases [1]. In this work the results of *in-situ* synchrotron X-ray diffraction studies of hausmannite up to 7.2 GPa and 1273 K are reported. The Mn₃O₄ tetragonal spinel is found to transform to a 9.6 % denser polymorph of the CaMn₂O₄-type structure at 7.2 GPa and 673 K, under milder conditions than those of any transformations to postspinel phase described so far. Upon heating at high pressure, the Mn₃O₄ phase undergoes decomposition and finally disappears in favor of MnO at temperatures above 1073 K [2]. Finally, a reconstructive hausmannite-to-postspinel transformation is connected with a full octahedral movement. Manganese cations go from one octahedral site to the next by edge-crossing, which requires energy input. This is the likely reason why together with high pressure the high temperature is also needed to facilitate a transformation of the highly stable hausmannite to marokite-like structure. One interesting property of the post spinel compounds is the potentially high mobility of cations through the lattice, what makes post spinel phases promising candidates for cathode research.

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- [1] A. Yamanaka, A. Uchida, Y. Nakamoto, *Am. Mineral.* **93** (2008) 1874.
 [2] J. Darul, C. Lathe, P. Piszora, *J. Phys. Chem. C* **117** (2013) 23487.

P-49

Spin-crossover transition in iron(II) coordination polymers induced by high pressure

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Spin-crossover (SCO) transition can occur in some metal complexes wherein the spin state of the complex changes due to external stimuli like temperature, pressure or light irradiation.[1]

Till now, a vast amount of iron(II) complexes showing temperature- and light-induced spin-crossover transition have been reported, but only several systems have been investigated under high pressure.[2]

We have focused our attention on low-temperature light-induced excited spin-state trapping (LIESST) and high-pressure X-ray diffraction studies of the SCO transitions of one-dimensional iron(II) coordination polymers. For these purposes we have chosen two isostructural complexes [Fe(3L)₃]X₂ (where L=1,3-di(tetrazol-1-yl)propane, X = BF₄⁻ or ClO₄⁻). Both complexes form hexagonal crystals of space group $P\bar{3}c1$.

A series of high-pressure single-crystal diffraction experiments on [Fe(3L)₃](BF₄)₂, [Fe(3L)₃](ClO₄)₂ and [Zn(3L)₃](ClO₄)₂ (reference sample) have been performed at High Pressure ID09A Beamline at ESRF using parallel monochromatic X-ray beam (E = 30 keV, λ = 0.413 Å) focused to 30 × 30 μm² on the sample loaded into membrane Diamond Anvil Cell and topped by silicon oil. A significant transformation of Fe-N bonds compressed up to 1.4 GPa have been observed, which allow us to postulate an occurrence of spin-crossover transition.

- [1] P. Gutlich, Y. Garcia, H. A. Goodwin, *Top. Curr.Chem.* **233** (2004) 1;
 M. A. Halcrow, *Spin-crossover materials: properties and applications*, John Wiley & Sons, Ltd., 2013.
 [2] P. Gutlich, V. Ksenofontov, A. B. Gaspar, *Coord. Chem. Rev.* **249** (2005) 1811;
 D. Pinkowicz, M. Rams, M. Misek, K. V. Kamenev, H. Tomkowiak, A. Katrusiak, B. Sieklucka *J. Am. Chem. Soc.* **137** (2015) 8795.