Iron(III) oxide nanoparticles: formation, structure and magnetic properties

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One of the fundamental questions of nanoscience is how the atomic structure and properties of a material change with the increasing aggregation state, starting from individual atoms, small clusters through nanoparticles (NP) to bulk materials. This knowledge is essential for fabrication of highly functional nanostructured materials with tailored properties. In this work the answer to this question is given for one of the technologically very important materials – iron(III) oxide. This is achieved by combining global structure optimizations at the density functional theory (DFT) level, molecular dynamics simulations by employing accurate, DFT parameterized interatomic potential functions and laser vaporization (LAVA)[1] experiments. With the exception of a nearly tetrahedral, adamantane-like Fe_2O_3 dimer $(Fe_2O_3)_n$ nanoclusters assume compact, virtually amorphous structures with little or no symmetry.[2] Starting from $n = 5$ they increasingly assume tetrahedral shape with an adamantane-like $(Fe_2O_3)_2$ unit as the main building block. The tetrahedral morphology persists for Fe_2O_3 NP with diameters up to 3 nm. Simulated crystallization of larger NP with diameters of about 5 nm demonstrates pronounced melting point depression of 800 K and leads to the formation of ε-Fe_2O_3 single crystals with hexagonal morphology.[3] This is in very good agreement with the results of structure analysis of LAVA generated Fe_2O_3 nanopowders (Fig. 1) providing the first direct indication that ε-Fe_2O_3 may be thermodynamically the most stable phase in this size range. The observed significant melting point depression provides an explanation for the thermal instability of small ε-Fe_2O_3 NP due to sintering and formation of larger agglomerates facilitating conversion to α-Fe_2O_3.

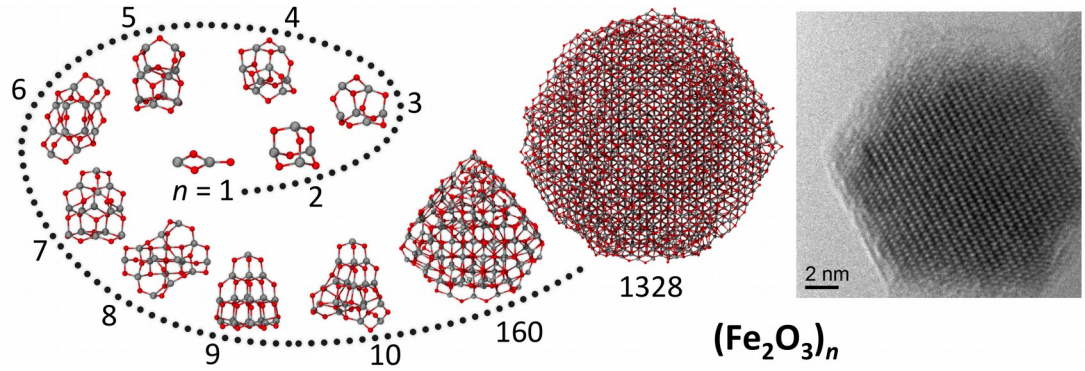

Figure 1. Most stable structures of $(Fe_2O_3)_n$ clusters and nanoparticles (left) and high-resolution TEM micrograph of a LAVA generated Fe_2O_3 nanoparticle (right).

Bibliography

[1] C. Stötzel, H. D. Kurland, J. Grabow, S. Dutz, E. Müller, M. Sierka and F. A. Müller, *Cryst. Growth Des.*, **13**, 4868-4876 **(2013)**.
[2] A. Erlebach, C. Hühn, R. Jana and M. Sierka, *Phys. Chem. Chem. Phys.*, **16**, 26421-26426 **(2014)**.
[3] A. Erlebach, H. D. Kurland, J. Grabow, F. A. Müller and M. Sierka, *Nanoscale*, **7**, 2960-2969 **(2015)**.