A Study of the Reduction and Reoxidation of Substoichiometric Magnetite

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Magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) are ferrimagnetic compounds with unique electric and magnetic properties. They are widely used as material in catalysis, magnetic separation, ceramics processing, energy and magnetic data storage, and as protection from microwave radiation. Moreover, both magnetite and maghemite have been extensively investigated for application in biomedicine. For example, they have been recognised as suitable magnetic materials for MR imaging, drug delivery, drug targeting, cell labelling and magnetic separation, as well as a hyperthermia agent. Magnetite has better magnetic properties than maghemite, however, magnetite tends to oxidise easily due to the presence of Fe^{2+}, whereas maghemite is chemically and physically very stable. The oxidation of magnetite deteriorates its magnetic properties.

In the present work, the substoichiometric magnetite particles ($Fe_{2.90}O_4$) of micrometer dimensions were subjected to reduction and reoxidation at a temperature of up to 600 ºC. The reduction of substoichiometric magnetite by hydrogen was performed under static conditions, whereas the reoxidation experiments were performed in a stream of oxygen. Samples were characterized by field emission scanning electron microscopy (FE-SEM), XRD, FT-IR and Mössbauer spectroscopy. The experimental condition for stoichiometric magnetite (Fe_3O_4) was obtained. It was found that Mössbauer spectroscopy is a powerful technique for monitoring the stoichiometry of magnetite, but limiting in terms of distinguishing a magnetite-maghemite mixture. FT-IR spectroscopy showed that samples, which by means of Mössbauer spectroscopy were characterised as nonstoichiometric magnetite, contained bands characteristic of magnetite and maghemite. After investigating the micrometer sized particles, all the three peaks present in the XRD patterns of maghemite, but not in the XRD patterns of magnetite, at $2\theta(\mathrm{Cu}K\alpha) = 15$, 24 and 26 degrees turned out clearly visible. The magnetite-to-maghemite transition mechanism will be discussed.

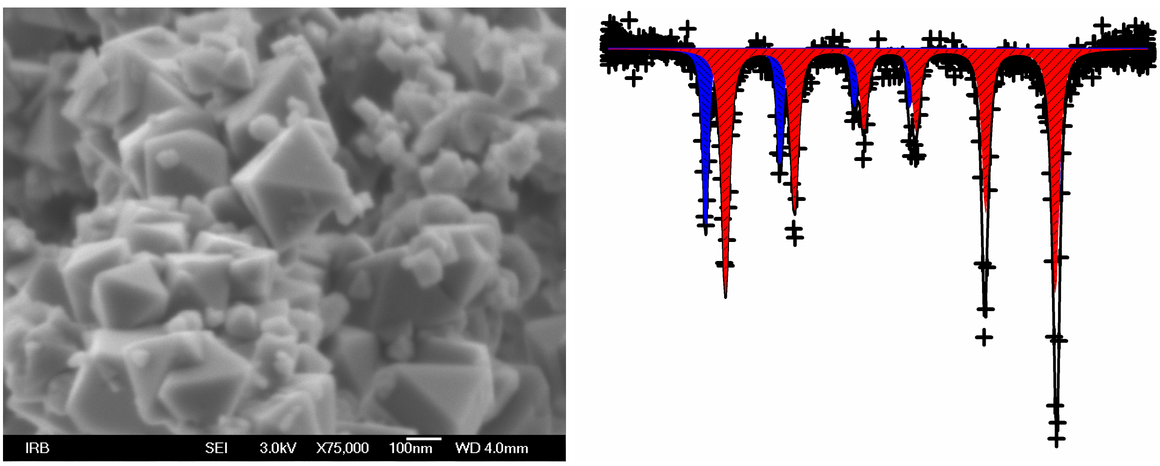

Fig. 1: FE-SEM image (left) and Mössbauer spectrum (right) of stoichiometric magnetite (Fe_3O_4).