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LABORATOIRE

DE PHYSIQUE DE L'ETAT CONDENSE

U.M.R. C.N.R.S. 6087

Report on the PhD thesis manuscript of Mr **Petr Brázda**
to be presented at the University of Strasbourg
Title: **Preparation of Fe_2O_3/SiO_2 Nanocomposites from Molecular Precursor by Sol-Gel Method and Doping of Iron(III) by Trivalent Metal Cations**

The manuscript of the thesis presented by Mr Petr Brázda reports on experimental studies devoted to the preparation of Fe_2O_3/SiO_2 nanocomposites, Ga and Al substituted ones using sol-gel route and the characterization of their structural and magnetic properties by means of different techniques. It is important to emphasize that this work has been realized in two Institutes, Inorganic Chemistry and Physique et Chimie des Matériaux from Praha (Czech Republic) and Strasbourg (France), respectively.

The manuscript consists of 6 chapters: after the general introduction, reviewing aspects of sol-gel method, general features of magnetism, nanoparticles and local probe techniques, i.e. ^{57}Fe NMR and Mössbauer spectrometry, are reported in the first chapter with the structural and magnetic characteristics of ferric crystalline oxide forms. The second one is rather concerned by instrumental conditions while the elaboration of the different samples and their further high temperature annealing treatment protocols are described in the following section. The structural and magnetic characterizations of Fe_2O_3/SiO_2, $Al_xFe_{2-x}O_3/SiO_2$, and $Ga_xFe_{2-x}O_3/SiO_2$ nanocomposites are described in the next three chapters, respectively, before concluding remarks.

The manuscript of Mr Petr Brázda is rather well written, well illustrated and rather well documented but the presentation with a systematic and repetitive description could be improved with a section focused on the synthesis of the results to better compare the different samples and their respective interests. I want to mention that the good labelling procedure is helpful for the reader to rapidly identify the sample.

The main objective of the present thesis was the synthesis of nanoparticles of ferric oxides, Al- and Ga-substituted ferric oxides, embedded in a silica matrix by means of the sol-gel method and to apply then subsequent annealing to favour the transformation of the ferric oxide into the ε-Fe_2O_3 phase, the hard magnetic characteristics of which are known to be of great interest for applications. The results presented by Mr Petr Brázda clearly demonstrate that the main goals were achieved.

The first point is concerned by the search of optimal sol-gel chemical conditions and heat treatments to prepare the nanocomposites. Mr Petr Brázda has used many instrumental techniques to check first the macroscopic homogeneity, then to identify the present phases, to follow the evolution of lattice parameters, grain size, hyperfine parameters and magnetic characteristics as a function of annealing temperature and annealing regimes. This part is quite important and required expertise in the different experimental techniques. In addition, the atomic substitution mechanism has been investigated by means of local Fe probe techniques. It is concluded that the optimal annealing temperature to get pure ε-Fe_2O_3 phase inside silica matrix is 1100°C while the mean grain size of oxide particle is close to 30 nm. The higher stability of the ε-Fe_2O_3 phase is explained by the lower tendency of cationic migration from tetrahedral into octahedral coordination. Such a mechanism is consistent with the evolution of magnetic properties (coercive field, magnetic ordering temperature) suggesting their lowering when the diamagnetic substituting ion content increases. So the contribution of Mr Petr Brázda based on large experimental studies gives rise to a better understanding of the elaboration of the present nanocomposites with non substituted and substituted ferric oxides and their structural and magnetic properties.

Nevertheless, some points remain unclear, at least after reading the manuscript: the Mössbauer spectra are recorded either at 300K or 4.2K and the hyperfine structure may result from both static and dynamic effects at elevated temperature since low temperature does favour the observation of blocked magnetic structure. Consequently, the description of hyperfine structure has to be done at low temperature because room temperature hyperfine structure prevents from a clear modelling in terms of atomic environments. In addition, from effective field values estimated from in-field Mössbauer spectra, one does calculate the corresponding hyperfine field in order to compare with that directly obtained from zero-field Mössbauer spectra. Finally, NMR data have to be compared to those of Mössbauer spectrometry providing the registration be the same! Tables of experimental data do contain error bars.

In conclusion, Mr Petr Brázda has reported many interesting experimental results obtained by means of a large variety of instrumental techniques: I feel that he acquired a good standard of attainment in materials science. Consequently, I recommend Mr Petr Brázda to defend his thesis at the University of Strasbourg (France).

Le Mans, November 2009 the 5th

Jean-Marc Greneche
CNRS Research Director