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$CoFe_2O_4$ NANOSTRUCTURED MAGNETIC MATERIALS: INFLUENCE OF NOT-CONVENTIONAL METHODS OF COMPACTION (SPS, HIP) ON THE MICROSTRUCTURE AND PHYSICAL CHARACTERISTICS

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1. OBJECTIVE

This work presents a Bottom-Up strategy implementing methods of soft chemistry followed by processes of not-conventional compaction for making of $CoFe_2O_4$ spinel nanostructured materials. The optimization of the process routes to obtain bulk and dense materials will be described in details along with the material nanostructures and magnetic properties.

Initially, the nanopowders (10 nm) are obtained in solution by hydrolysis forced in polyol medium. $CoFe_2O_4$ nanoparticles have been obtained starting from ionic salts (cobalt acetate and iron chlorate) dissolved in a polyol and heated at a boiling point. The chemical reactions are made possible by several properties of polyols, including high boiling point, dissolving, complexing, hydrolysing and protective properties. This route enables to synthesize particles of size and morphology controlled. These powders prove to have interesting magnetic properties in comparison with those worked out by other ways of soft chemistry [1] : high saturation magnetization near to the bulk materials and temperature of blocking higher than the ambient one.

2. SYNTHESIS METHOD

Then, the massive parts are obtained using two non conventional methods of compaction: Hot Isostatic Pression (HIP) and Spar Plasma Sintering (SPS). The aim is to obtain nanostructured materials preserving or improving the magnetic characteristics of the objects (increase in the temperature of blocking for example). SPS sintering was carried out under a force of 5 kN and at a temperature going from 500 to 700°C. HIP sintering was obtained under temperatures going from 500 to 700°C and a pressure varying in the field 1500 to 2000 bars. For comparison, the powders have been sintered in air at atmospheric pressure at several temperatures up to 800°C.

All the obtained materials have been subject to several analyses mainly MET, DRX and magnetic measurements (Hysterisis loops, ZFC/FC susceptibility).

3. RESULTS

3.1. Obtention of a pure $CoFe_2O_4$: Influence of the compaction method

X-Ray diffraction analysis shows that a secondary phase (the hematite Fe_2O_3) is observed aside CoFe2O4 when the SPS experiments are conducted under air (Figure 1). Whereas a pure CoFe2O4 is recovered when argon is used instead of air (Figure 1). It is interesting to note that despite a higher pressure employed in HIP compaction, a pure $CoFe_2O_4$ phase is also obtained (Figure 1). In all cases, the cell parameter inferred from the patterns is very close to that of bulk $CoFe_2O_4$ (a = 8,395 Å).

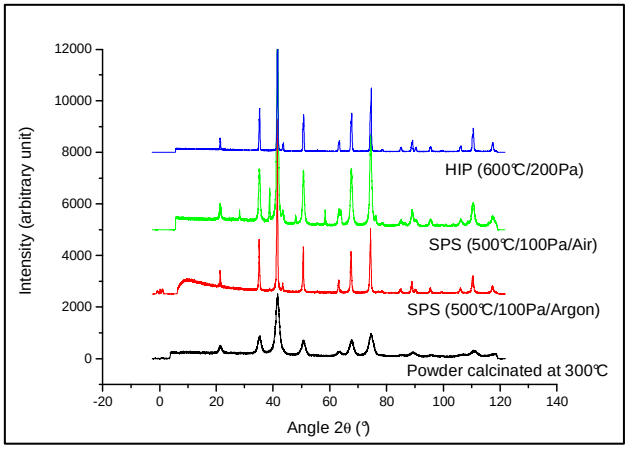

Figure 1 : X-Ray diffractograms of $CoFe_2O_4$ powders

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3.2. Influence of the compaction method on the texture

The texture has been studied by both of X-ray diffraction and microscopy techniques. The X-ray diffraction allowed obtaining the crystallite size using the Debye Scherer relation. The crystallite size increases with increasing the temperature with the highest size obtained for the HIP conditions (Table 1). The microscopy observations show that the particles are indeed formed by aggreation of crystallites. It is interesting to note that in the nanostructured material obtained by SPS the particles remain in the nano-size range indeed each particle appears to be formed of few crystallites (Figure 2c). Whereas the particles obtained by HIP are micrometric (Figure 2d).

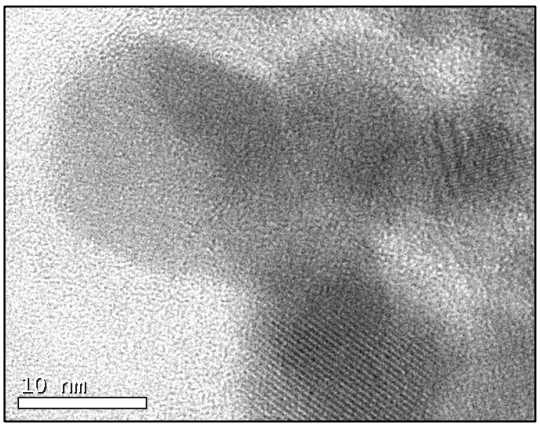

Figure 2a : Powder calcinated at 300°C

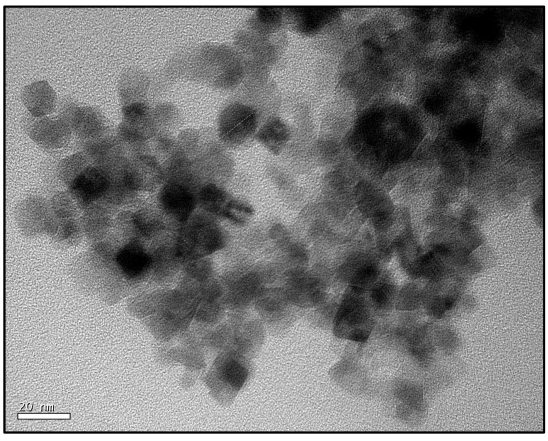

Figure 2b : Powder calcinated at 500°C

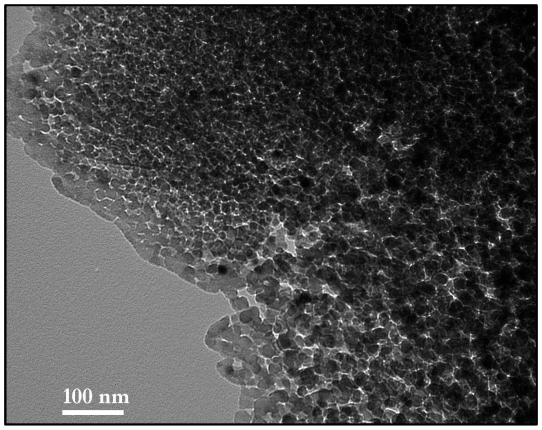

Figure 2c : SPS (500°C/100Pa/Argon)

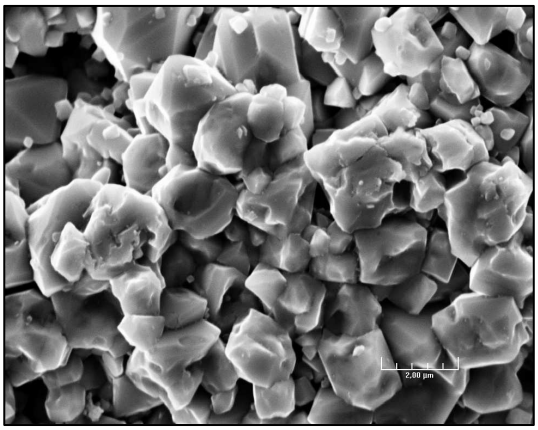

Figure 2d : HIP (600°C/200Pa)

Sample	Powder after synthesis	Powder calcinated at 300°C/6h	Powder calcinated at 400°C/6h	Powder calcinated at 500°C/6h	Powder calcinated at 800°C/6h	SPS (500°C / 100Pa /Argon)	SPS (600°C / 100Pa /Argon)	SPS (700°C / 100Pa /Argon)	HIP (600°C /200Pa)
Cristallite size (nm)	4,49	6,07	8,81	10,48	61,19	10,5	12,76	31,13	55,62
Particle size (nm)	5	10/12	12/15	15/20	Between 100 and 150	10	12/15	40/50	Between 500 nm and 2µm

Table 1: Crystallite size of the sintered powders

3.3. Magnetic behavior of the nanostructured materials.

Magnetic measurements show that all studied materials exhibit a superparamagnetic behaviour. The main magnetic characteristics are indicated in the table 2. The saturation magnetization (Ms) has been calculated thanks to the relation M_{mes}= Ms(1 – a/H) (figure 3).

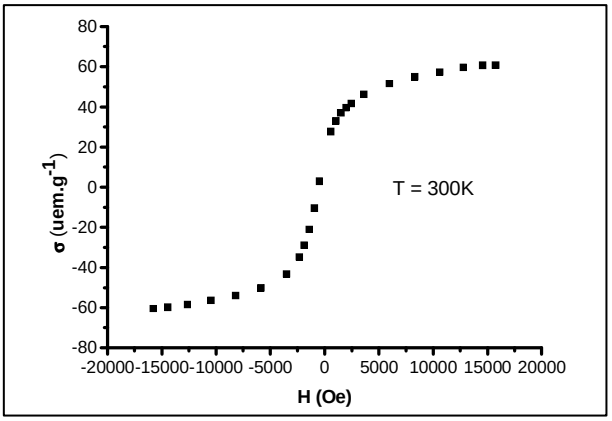

Figure 3a : Hysteresis loop of the $CoFe_2O_4$ SPS sample obtained at 500 °C

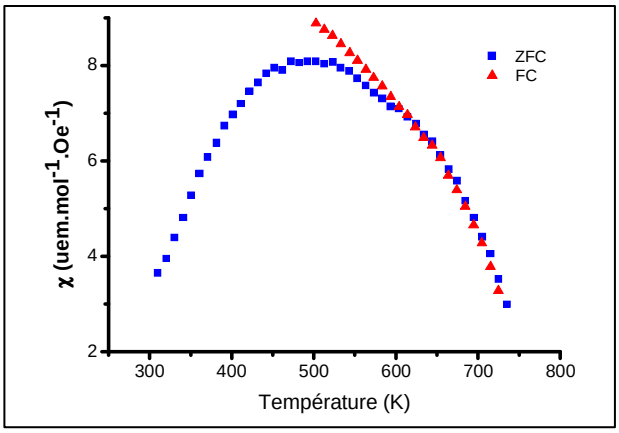

Figure 3b : Susceptibility χ(T) measured in ZFC and FC modes for $CoFe_2O_4$ SPS sample obtained at 500 °C

Two main important results have to be underlined. First the blocking temperature appears to depend mainly on the crystallite size and none on the particle size. Indeed it increases when the crystallite size increases (Figure 4). It

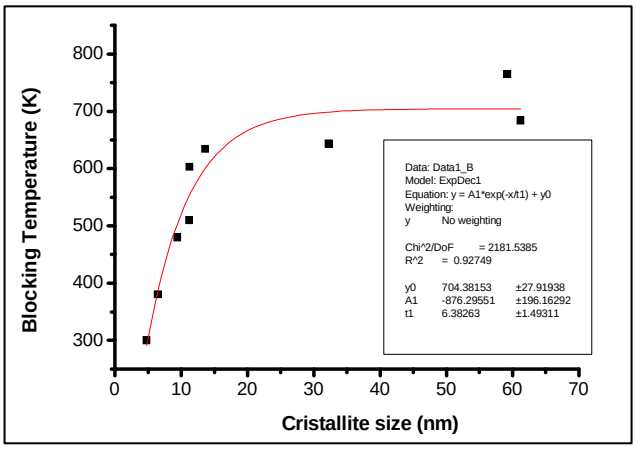

Figure 4 : Variation of the blocking temperature in function of crystallite size.

is interesting to note that the blocking temperature approaches the critical temperature (Tc = 810K) for the HIP nanostructured materials for which the crystallite size has the highest value from over all studied materials. The second result concerns the saturation magnetization. The as-prepared powder has a high saturation magntezation near to that of the bulk $CoFe_2O_4$ (80 emu/g). When the powder is calcinated at 300°C, its saturation magnetization decreases slightly. For the nanostructured materials, the saturation magnetization increases with the crystallite size to reach that of the bulk material.

It should be noted that the saturation magnetization obtained here are higher than that observed recently on nanostrutured $CoFe_2O_4$ obtained by SPS compaction of powder prepared by coprecipitation or thermolysis (51 emu/g) [2].

Sample	Powder after synthesis	Powder calcinated at 300°C/6h	Powder calcinated at 400°C/6h	Powder calcinated at 500°C/6h	Powder calcinated at 800°C/6h	SPS (500°C / 100Pa /Argon)	SPS (600°C / 100Pa /Argon)	SPS (700°C / 100Pa /Argon)	HIP (600°C /200Pa)
Blocking temperature (K)	300	380	480	510	684	603	634	644	765
σ (uem/g)	69	57	61	64	85	67	69	70	90

Table 2 : Magnetic properties of cristallites

3. CONCLUSION

In conclusion, this work shows that consolidation of nanopowder to obtain dense CoFe2O4 can be achieved via a Bottom-up strategy combining chimie douce and non-conventionnal compaction methods. The as-obtained material is nanostructured: the crystallite size is maintained in the nanometer range. Thus the dense nanostructured material exhibits a superpramagnetic behaviour with high blocking temperature and saturation magnetization.

4. REFERENCES

[1] S. Ammar, A Helfen, N. Jouini, F Fiévet, I. Rosenman, F Villain, P. Molinié and M. Danot, "Magnetic properties of ultrafine cobalt ferrite particles synthesized by hydrolysis in a polyol medium" *J. Mater. Chem.*, Royal Society of Chemistry, **11**, pp 186-192 (2001).

[2] N. Millot, S. Le Gallet, D. Aymes, F. Bernard and Y. Grin, "Spark Plasma Sintering of cobalt ferrite nanopowders prepared by coprecipitation and hydrothermal synthesis", *J. Eur. Ceram. Soc.*, Elsevier, **27**, pp 921 – 926 (2007).