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Spark plasma sintering of cobalt ferrite nanopowders prepared by coprecipitation and hydrothermal synthesis

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Abstract

Cobalt ferrite exhibits a high coercivity at room temperature and a strong magnetic anisotropy compared to the other spinel ferrites and, consequently appears as an interesting material for permanent magnets and high-density recording. The magnetic properties depend also on the crystallite size. In order to keep the powder properties in a bulk material, dense nanostructured cobalt ferrite has to be sintered. A field activated sintering process like spark plasma sintering (SPS) may be promising for such challenge. The present paper deals with: (i) the preparation of cobalt ferrite by two methods: coprecipitation and hydrothermal synthesis in supercritical water; (ii) the SPS sintering of the cobalt ferrite nanopowder prepared by coprecipitation. The sintering of the as-processed powder and that obtained after a thermal treatment resulting in the spinel phase has been investigated. The influence of the starting powder and the sintering parameters such as the temperature, the duration of the SPS stage on the grain growth and the densification degree of bulk materials will be presented.

Keywords: Sintering; Powders-chemical preparation; Grain size; Magnetic properties; Ferrites

1. Introduction

Cobalt ferrites are hard ferrites with a positive crystalline anisotropy due to the cobalt, which confers on them better magnetic properties than on γ-Fe_2O_3. Besides the composition, the magnetic properties, particularly the coercive field, are strongly dependent on the oxidation degree, cation distribution and crystallite size. For instance, coercivity is known to be maximal for a cobalt ferrite crystallite size between 30 and 40 nm.[1–7] More generally, nanostructured ceramic materials for both electronic and biomedical applications draw industry and scientist attention because of their physical properties depending on grain size.[8] Consequently, synthesis methods of nanometric powders are very attractive.

In preliminary works about ferrites obtained by soft chemistry and mechanosynthesis, our research group has presented a complete comparison.[9] Nevertheless, these two technologies do not allow to have a huge production and cannot be developed at industrial level. Continuous synthesis technologies, allowing a several tens grams/hour production, are then very interesting. In this perspective, a continuous production prototype of hydrothermal synthesis in subcritical and supercritical water has been developed.[10–12] Oxide powders synthesized in supercritical water have revealed several interesting qualities. Indeed, the grains are nanometric with controlled particle morphology and very well crystallized. The first aim of this paper is to compare two synthesis methods: coprecipitation (soft chemistry) and hydrothermal synthesis, in a continuous way and in supercritical water. The second aim is to study a quite new sintering process: spark plasma sintering (SPS). This process has been seldom used in the case of ferrites.[13–15] The consolidation of nanopowders to produce dense bodies while maintaining their fine crystallite size is usually difficult by conventional methods such as hot pressing, etc. Recently, spark plasma sintering (SPS)[16,17] appears as a new sintering method to avoid or minimize the grain growth because of short processing times. While the synthesis of cobalt ferrite powders has been the subject of many papers, whose aim was to obtain fine particles with controlled shapes, sizes and oxygen stoichiometries, and high coercivity,[18–20] almost no studies have been devoted to their sintering. The present paper focuses on the sintering by SPS of cobalt ferrite powders processed by the coprecipitation route.

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2. Experimental procedure

2.1. Synthesis

The synthesis conditions are described in Table 1 and the experimental apparatus used for hydrothermal synthesis in supercritical conditions is described in other publications.[10,12] A stream of distilled water is pressurized and then heated to a temperature that is above the desired temperature in the reactor. The basic solution and the metal salt aqueous solution are also pressurized in separate lines. Then the three reactants are combined at a mixing point, located just before the reactor. The rapid heating leads to a subsequent reaction in the reactor. The residence time of the solution in the reactor is about 10 s. The reactor is an Inconel serpentine with a 2 m length and a 2.3 mm inner diameter. After the reactor, the solution is rapidly quenched and filters remove agglomerated particles. Then, the suspension obtained is centrifuged and washed with deionized water under ultrasonification during 5 min. After about 10 washings, the centrifugation is not more possible because a sol is formed. This suspension is freeze-dried and leads to a powder hereafter called SC-Fe_2CoO_4. This powder has been thermally treated during 4 h at 600 °C (2 °C/min) in order to control the oxygen stoichiometry and to remove the remaining impurities (the thermal treatment conditions have been deduced from TGA experiments).

A Fe_2CoO_4 powder has been also synthesized by soft chemistry. It results from the coprecipitation of iron chloride ($FeCl_2{\cdot}4H_2O$) and cobalt chloride ($CoCl_2{\cdot}6H_2O$) in the presence of boiling potassium hydroxide. The precipitate has been separated from the medium by centrifugation, washed (in the same way than the supercritical powder) and freeze-dried. This powder (hereafter called P-Fe_2CoO_4) has been calcinated during 2 h at 650 °C (2 °C/min), under air. This treatment has been optimized in order to remove the remaining impurities (such as chlorides), to obtain the spinel structure while limiting grain growth.

2.2. Sintering

The two soft-chemistry powders (freeze-dried and calcinated) have been sintered in a SPS apparatus (Model 515S, Sumitomo Coal Mining Co.) under primary vacuum. In such apparatus, the heating is performed by the passing of a pulsed dc current through the graphite die containing the powder (10 mm in diameter). Simultaneously, an uniaxial pressure is applied. The powders were heated at a rate of about 100 °C/min under a pressure of 40 MPa. All samples were held 5 min at the sintering temperature. The sintering conditions are summarized in Table 3.

Table 1

Synthesis conditions of Fe_2CoO_4 powders obtained by coprecipitation (P-Fe_2CoO_4) and thermohydrolysis in a continuous way and in supercritical water (SC-Fe_2CoO_4)

	Precursors	P (bar)	T (°C)
P-Fe_2CoO_4	$CoCl_2{\cdot}6H_2O$ 1.07 mol/L $FeCl_2{\cdot}4H_2O$ 2.14 mol/L KOH 7 mol/L	P_{atm}	90
SC-Fe_2CoO_4	$Co(NO_3)_2$ 0.025 mol/L $Fe(NO_3)_3$ 0.05 mol/L NaOH 0.25 mol/L	300	440

2.3. Characterizations

Surface area measurements are performed using an AUTOSORB apparatus with N_2 adsorbing gas. Samples (150–200 mg of powder) are outgassed at 220 °C. The B.E.T. method is used to determine the surface area values from the isotherm of nitrogen adsorption.

All samples are characterized by X-ray diffraction (XRD) using a Siemens D5000 automatic powder diffractometer, operating at 35 mA and 50 kV with the $\lambda_{Cu\,K\beta} = 1.39222$ Å radiation. The instrumental broadening correction is determined from a standard reference material, annealed BaF_2. Pseudo-Voigt peak profile analysis, using the Langford method,[21] is performed to determine both the average crystallite size (size of a region over which the diffraction is coherent) and crystallographic imperfections (microdistorsions, stacking faults, etc.). The lattice parameters of the powders are deduced from XRD line positions using Topas software, taking into account the effect of sample gap.

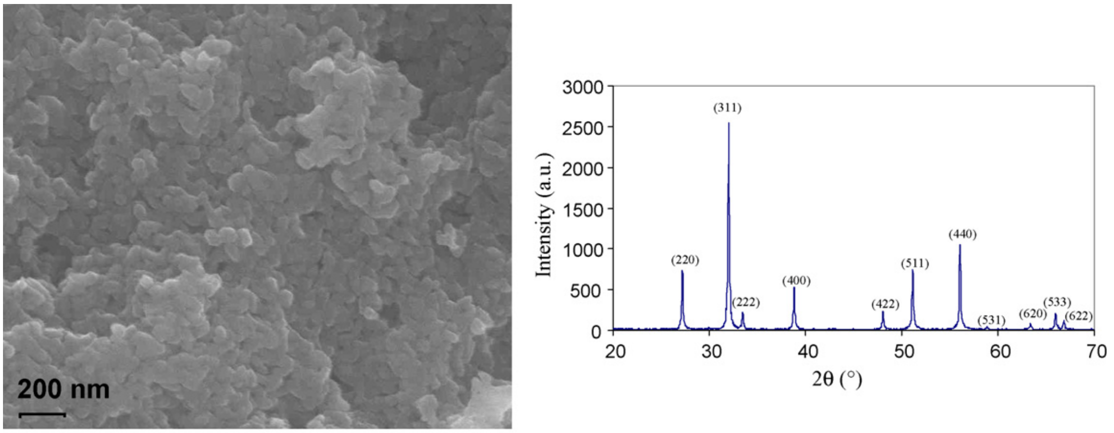
Samples are all characterized by scanning electron micrographs (SEM) (JEOL JSM-6400F) coupled with a LINK OXFORD energy dispersive X-ray analyzer which allows the determination of the chemical composition of the samples.

The hysteresis loops of powders are measured with a M2100 50 Hz magnetometer, those of densified materials are measured with a VSM apparatus.

3. Results and discussion

3.1. Synthesis

The Fe_2CoO_4 powder obtained by thermohydrolysis is very well dispersed and homogeneous with a grain size of about 3 nm deduced from XRD results. This value matches quite well the average particle diameter deduced from specific area measurements ($S_{BET} = 236\ m^2/g$ which corresponds to a diameter of 4.8 nm). The grain size distribution is quite narrow, even after a thermal annealing of 4 h at 600 °C (Fig. 1). This treatment leads to a grain size increase: $\Phi_{XRD} = 34$ nm. The lattice parameter of the Fe_2CoO_4 spinel phase treated during 4 h at 600 °C is $a_{exp} = 8.3839 \pm 0.0001$ Å (Table 2) whereas the value reported in literature is $a_{lit} = 8.35 \pm 0.01$ Å for a powder obtained by soft chemistry and heated at 500 °C.[18] The calculated value $a_{cal} = 8.3878$ Å by the Poix method is in relatively good agreement with the experimental one (the cation–oxygen distances used for the calculation of the lattice parameter are given in reference 22). The difference could be explained by a possible oxidation of the cobalt cation in Co^{3+} (2.4% in order to obtain the experimental value). It cannot be explained by a redistribution of the cobalt cation in tetrahedral sites, phenomenon which increases the lattice parameter (8.4099 Å if all the Co^{2+} cations



(a) (b)

Fig. 1. (a) SEM micrograph of the Fe_2CoO_4 powder obtained by thermohydrolysis in supercritical conditions and treated during 4 h at 600 °C and (b) XRD pattern of the same powder. The ICDD card used to label the XRD patterns is 22-1086.

Table 2
Specific area measurements and X-ray diffraction analysis of Fe_2CoO_4 powders

	S_{BET} (m^2/g)	Phase	EDXS Fe/Co	a (Å)	Φ_{XRD} (nm)	Hc (Oe) at −204 °C	σ_m (uem/g)
SC-Fe_2CoO_4	236 ± 2	Spinel	2.04	–	3 ± 1	3730	9.5
SC-Fe_2CoO_4 treated (4 h at 600 °C)	15.4 ± 1	Spinel	2.03	8.3839 ± 0.0001	34 ± 1	7350	51.8
P-Fe_2CoO_4	25 ± 1	Oxides + hydroxides		–	–	–	–
P-Fe_2CoO_4 treated (2 h at 650 °C)	20 ± 1	Spinel		8.3813 ± 0.0004	27 ± 1	6330	12.4

The XRD profile analysis is performed according to Halder and Wagner method. Due to very large diffraction peaks, the lattice parameter cannot be determined for the powder obtained just after the thermohydrolysis. The EDXS ratios are determined by doing the average of about 10 measurements.

are in tetrahedral sites). As we can see in Table 2, the coercive field of the freeze-dried powder is about 3730 Oe at −204 °C (the powder has a superparamagnetic behavior at room temperature). The coercive field of the powder obtained after the thermal annealing is higher: 7350 Oe at −204 °C (1180 Oe at room temperature). This higher value is due to the bigger particle size of the annealed powder. This powder could be a good candidate for magnetic recording.

Now concerning powders obtained by coprecipitation: the as-processed powder does not present only the Fe_2CoO_4 spinel phase but a mixture of oxide and hydroxide phases. This powder is more agglomerated than the supercritical powder, since its surface area is 25 m^2/g (see Table 2). After the calcination, the desired cobalt ferrite has been obtained. Its surface area is quite the same (20 m^2/g) and the crystallite size determined by XRD equal to 27 nm (Table 2). The coercivity of the calcinated powder is approximately the same as that of the treated supercritical powder (6330 Oe instead of 7350 Oe at −204 °C); this difference may be attributed to the crystallite size difference (27 nm instead of 34 nm). Another explanation could come from the lattice parameter values. Indeed, if we compare the lattice parameter of the coprecipitated powder treated at 650 °C under air with that of the supercritical powder, we can see that it is smaller (8.3813 Å instead of 8.3839 Å). The content of Co^{3+} cations in the soft-chemistry powder may be higher than in the supercritical powder (4.2% instead of 2.4%). This cationic difference can also explain the saturation magnetization difference between the two powders, which can also be linked to density differences between the two samples.

3.2. Sintering

Results concerning the different SPS experiments are summarized in Table 3.

An example of shrinkage curve recorded during the SPS experiment is reported in Fig. 2. The shrinkage observed for the FeCoT-001 sample may be attributed to both impurities volatilisation (between 150 and 700 °C) and sample densification. The shrinkage due to densification starts really after 700 °C for this sample. For the as-processed powder, the shrinkage (between 150 and 700 °C) is more important.

In all cases, the desired cobalt ferrite with a spinel structure has been obtained (Fig. 3 and Table 2). However, all samples sintered from the as-processed powder and those sintered at 1000 °C from the heat-treated powder are also composed of a

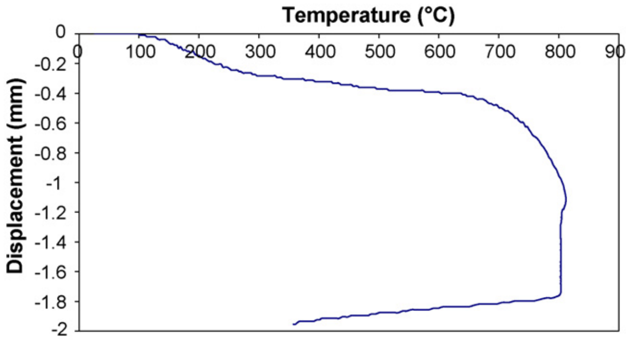


Fig. 2. Shrinkage of the FeCoT-001 sample (sintered at 800 °C during 5 min).

Table 3
Sintering conditions and results of the SPS experiments

Sample		Phases	Sintering temperature (°C)	Apparent density	Relative density (%)	Grain size Φ_{XRD} (nm)
As-processed powder	FeCo-001	Fe_2CoO_4 (+CoO)	700	4.06	77	–
	FeCo-002	Fe_2CoO_4 (+CoO)	700	5.20	99	67
	FeCo-003	Fe_2CoO_4 (+CoO)	800	5.15	98	133
	FeCo-004	Fe_2CoO_4 (+CoO)	800	4.64	88	–
Heat-treated powder	FeCoT-001	Fe_2CoO_4	800	3.19	60	31
	FeCoT-002	Fe_2CoO_4	900	4.81	91	28
	FeCoT-003	Fe_2CoO_4 (+CoO)	1000	5.17	98	–
	FeCoT-004	Fe_2CoO_4 (+CoO)	1000	5.15	98	–
	FeCoT-005	Fe_2CoO_4 (+CoO)	1000	5.16	98	–

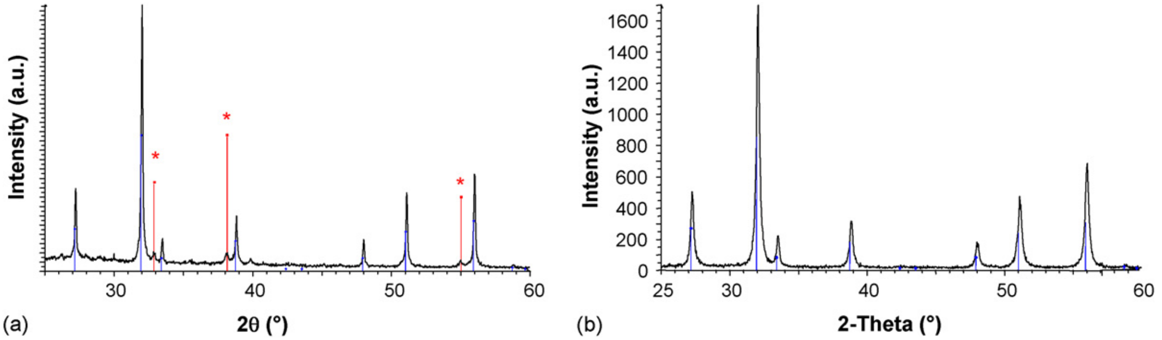


Fig. 3. X-ray diffractograms of Fe_2CoO_4 pellets (a) as-processed powder sintered at 800 °C (*CoO phase) and (b) heat-treated powder sintered at 900 °C.

small quantity of CoO phase. The CoO phase amount is larger in the samples sintered at 1000 °C. This CoO phase formation may have two different origins according to the nature of the starting powder. Indeed, the cobalt migration may occur from the spinel phase to the CoO phase in samples sintered at 1000 °C from the heat-treated powders whereas in samples sintered from the as-processed powders, the cobalt may have not been completely dissolved in the spinel phase yet because of the short time of the experiments (Fig. 3a).

The densities of the bulk materials are summarized in Table 3. The relative densities have been calculated, assuming that the solid is composed of the Fe_2CoO_4 spinel phase ($d = 5.274$). Table 3 shows that for same sintering conditions, bulk materials are obtained with higher densities from the as-processed powder than from the heat-treated powder. However, for all samples sintered from the as-processed powder, the result is strongly dependent on the sample. It may be correlated to the powder amount poured into the graphite die. Indeed, a smaller powder amount (0.52 g (FeCo-003 sample) instead of 0.82 g (FeCo-004 sample)) may lead to a better control of the densification with a relative density of 98% instead of 88%. In such short processing conditions, the gaseous species amount, which volatilises during the sintering may have to be as small as possible in order not to prevent the porosity elimination. In order to explain such differences between densities in the case of the as-processed powders, another hypothesis may be put forward. Indeed, no attention has been paid to the powder agglomeration, which may have led to non-reproducible filling of the graphite mold. Granulometry analyses were carried out on both powders and showed that the average size of the agglomerates is 26 and 15 μm for the as-processed and heat-treated powders, respectively. The granulometry analyses have also exhibited a narrower agglomerate size distribution for the heat-treated powder. Consequently, the initial characteristics (agglomerate size and distribution) of the powders may have also contributed to lead to a different behavior during the sintering.

SEM observations show that the samples sintered from the as-processed powder exhibit large grains of several microns whereas the grains have never exceeded a few hundreds of nanometers in the samples sintered from the heat-treated powder. The grain size distribution is also very large in the samples sintered from the as-processed powder that reminds the large agglomerate size distribution observed in the starting powder.

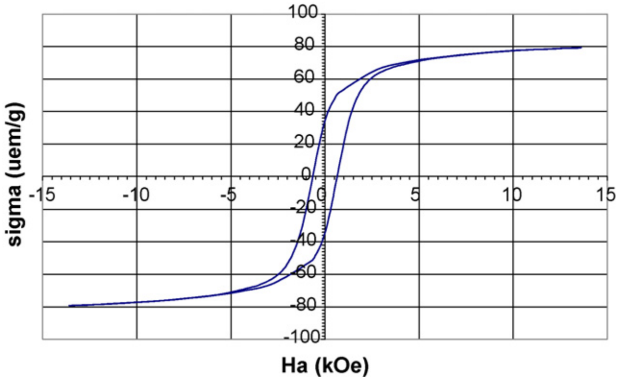


Fig. 4. Hysteresis loop of the FeCoT-002 sample obtained at room temperature.

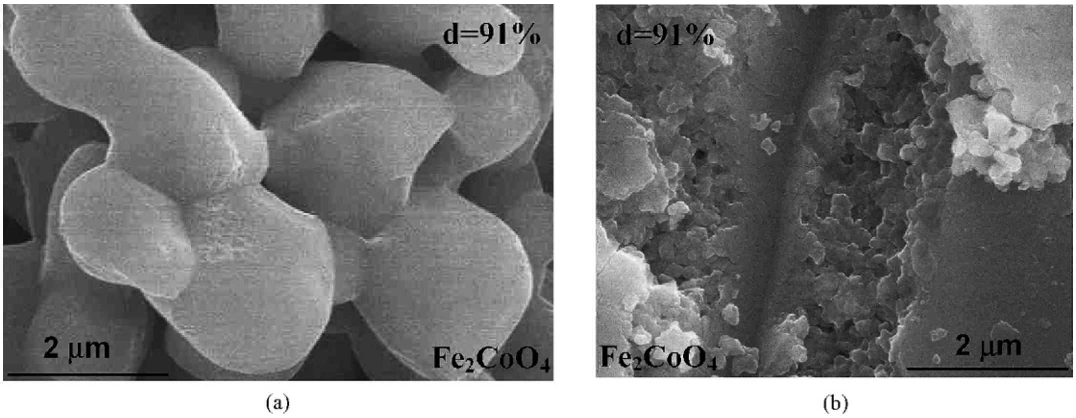


Fig. 5. Comparison of (a) a conventional sintering and (b) a SPS experiment (FeCoT-002) of the same powder.

The crystallite size deduced by XRD profile analysis of the spinel phase is 31 nm for the FeCoT-001 sample and 29 nm for the FeCoT-002 sample. According to these values, no growth of the crystallites has occurred during both sintering, whatever temperature (800 or 900 °C). Although the as-processed powders have been sintered at lower temperatures (700 and 800 °C), the crystallite size of the spinel phase obtained after sintering is larger than that obtained for the heat-treated powder with 67 and 133 nm for the FeCo-001 and FeCo-004 samples, respectively.

The lattice parameter of the FeCoT-002 sample, presenting only the spinel phase, is 8.3883 ± 0.0003Å. The lattice parameter, calculated by using the method of characteristic distances (invariants) developed by Poix, assuming that all the Co^{2+} cations occupy the octahedral sites of the structure, is 8.3878 Å. The FeCoT-002 sample presents consequently the inverse spinel structure as the theory of the crystalline field foresees it.

The FeCoT-002 sample appeared as the best one, since it is the best compromise between structure, density and grain size. Its magnetic parameters have been compared with those of the starting powder (Fig. 4). The higher saturation magnetization observed (79.3 uem/g instead of 12.4 uem/g) is obvious since it suggests fewer pores as well as higher density in the bulk. The evolution of the coercivity (640 Oe instead of 1315 Oe at room temperature) is more complicated to explain since it could not be attributed to a grain size evolution. The only explanation that we can give is that it is known that coercivity depends on the compaction of a powder, linked both to the magnetic interactions between grains and to grain mobility.

In order to compare SPS and conventional sintering, a green compact, prepared from the heat-treated powder, has been conventionally sintered at 1350 °C, with a heating rate of 5 °C/min. This sintered pellet has been compared with the FeCoT-002 sample obtained by SPS. Thanks to Fig. 5, we can notice that the same density has been achieved (about 91%) by both sintering. However, because of a smaller process time (14 min instead of more than 4 h) and a limited grain growth, SPS is more interesting. We should also notice that in all cases, starting from as-processed powder or treated powder, the conventional sintering leads always to the desired cobalt ferrite, without cobalt oxide demixion.

4. Conclusion

Nanocrystalline Fe_2CoO_4 has been synthesized in the spinel structure by two different routes: hydrothermal synthesis in supercritical water and coprecipitation. For the first time, the desired cobalt ferrite has been directly obtained by thermohydrolysis, in a continuous way, and with a very small grain size (about 3 nm). A thermal treatment is necessary in the case of the coprecipitation route. After an annealing of this powder at 650 °C, the spinel structure has been obtained with a grain size always in a nanometric range (27 nm). The coercive field of this latest powder is very high (6330 Oe at −204 °C) and has been compared with those of the supercritical powder treated at 650 °C (the as-processed supercritical powder is superparamagnetic at room temperature). Differences can be attributed both to grain size discrepancy and to various cobalt cations oxidation in the spinel structure.

The spark plasma sintering of the soft-chemistry powders may not allow to get systematically the desired spinel cobalt ferrite from whatever starting powders compared to conventional sintering. It would not be attributed to the nature of the starting powder or to the sintering temperature but to the rapid processing times, which would not allow to reach equilibrium. That is why with SPS, the cobalt may be not completely dissolved in the spinel structure or may have segregated as cobalt oxide. Nevertheless, a pure spinel phase with the theoretical cationic distribution has been obtained with no grain growth observed and with a significant densification of 91%. SPS method seems to be a promising process to produce dense nanostructured ferrites. This study is in progress in order both to compare these sinterings with those of the supercritical powder (3 nm), and to optimize the sintering parameters to obtain higher densities.

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