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Synthesis and Stability Region of Stoichiometric Nanocrystalline Vanadium−Iron Spinel Powders

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Vanadium−iron spinels with nanometric sizes have been synthesized by a soft chemistry route. This way of elaboration consists of a coprecipitation followed by thermal treatments at low temperatures. The last thermal annealing is performed under a reducing atmosphere in order to obtain the exact oxygen stoichiometry (four oxygen atoms for three metal atoms in AB_2O_4). Because of the low temperatures used, very low oxygen partial pressures (between 10^{-20} and 10^{-30} Pa) have to be applied. For this purpose, a reducing setup has been used. It consists of $H_2/N_2/H_2O$ gas mixtures, creating a reducing atmosphere with low oxygen partial pressure. This atmosphere can be applied to a sample in a thermobalance, so the mass variations are correlated with the oxygen content (or oxygen stoichiometry) in the sample. Thermal annealing under low oxygen partial pressure allows one to obtain stoichiometric spinels of $Fe_{3-x}V_xO_4$ ($0 \leq x \leq 2$).

Introduction

Recent investigations on mixed-valency spinel ferrites reveal that these compounds show interesting properties for magnetic and magnetooptical recording, especially if the spinel grains have nanometric sizes.[1,2] The oxidation of substituted magnetites $Fe_{3-x}M_xO_4$ may lead to the formation of cation-defect phases (γ-Fe_2O_3 type) a phenomenon which is not observed in micrometric-sized particles of spinels, where the precipitation of hematite phase α-Fe_2O_3 occurs. In the case of nanometric-sized spinels, the deficient phases result from the oxidation of the several cations initially present. As the content of vacancies depends on the amount of oxidizable cations, it is interesting to try to introduce, in addition to iron, other oxidizable cations,[3] for example, vanadium. In addition, the coercivity in such spinels is enhanced by the introduction of a small amount of Co^{2+} cations in the spinel lattice. This phenomenon is due to their strong magnetocrystalline anisotropy, and it is increased when the spinel contains vacancies.[4] Up to now, preparation of spinels containing iron and vanadium consisted of a classical ceramic route, which leads to grains with sizes of several micrometers. This large grain size does not allow total oxidation while retaining the spinel structure.

In this paper, a soft chemistry synthesis is developed that requires thermal annealings at moderate temperatures and reducing atmospheres with low oxygen partial pressures.

Experimental

1. Materials. The first stage of the elaboration consist of a precursor precipitation at room temperature. The starting solutions are prepared by dissolving the solid compounds VCl_3, $FeCl_3$, and if necessary $CoCl_2$ into water, and $FeCl_2$ into HCl.

After those solutions are mixed, the precipitation is performed by adding the chloride solution to an aqueous solution of triethylamine. The precipitate, after maturing for 10 min, was then washed with water and acetone and freeze-dried.

A calcination of the sample is then necessary to fix a grain size and to eliminate organic compounds contained in the precipitate. The calcining temperature is determined by thermogravimetry: this temperature agrees with the end of mass loss for the coprecipitate. At the end of the treatment, the powder is quenched in air. The powder mass is about 0.5 g to prevent agglomeration.

After calcination, all of the cations are in an oxidized state, with their highest valencies. A reducing treatment has to be performed to reduce their valency state and to form a stoichiometric spinel phase. This treatment requires low oxygen partial pressures, obtained with a $H_2/N_2/H_2O$ gas mixture. The conditions of temperature and oxygen partial pressure are also determined by thermogravimetric experiments.

2. Procedure. Mass variations were followed by thermogravimetry with a Setaram TAG 24 microbalance (symmetrical setup; resolution and noise level, 0.1 μg).

The elaborated powders are characterized by X-ray diffraction and infrared spectrometry. X-ray diffraction patterns were performed with a Siemens D5000 diffractometer using Cu Kβ radiation. FT-IR spectra were recorded with Perkin-Elmer spectrometers FT-1725X (4000−400 cm^{-1}) and FT-1700X (500−50 cm^{-1}). Transmittance spectra were realized on 1 mg of powdered sample dispersed in 200 mg of CsI pellets pressed under vacuum at 10 Pa.

The sizes of the grains were determined by measurements of specific surface areas (with a Quantachrome Autosorb 1).

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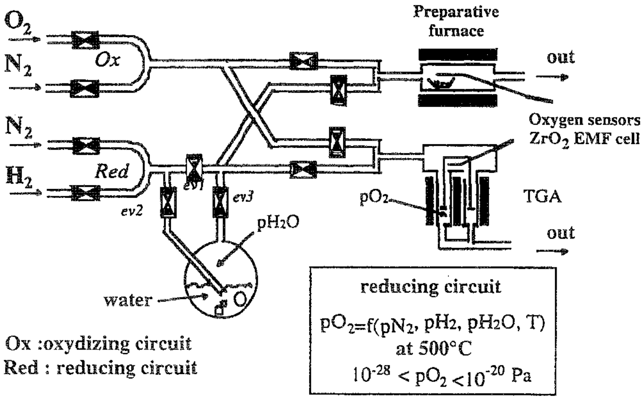

Figure 1. Experimental setup for determining the temperature and oxygen partial pressure conditions in order to obtain stoichiometric spinels.

The experimental apparatus used to reduce the oxides is described as follows: a gas mixture of N_2 and H_2, passing through a water vessel, is sent into either a preparative furnace or a TGA apparatus[5] (Figure 1). In the thermobalance, mass variations are recorded simultaneously under the flow of gas mixture. Previously, annealings under a $N_2/H_2/H_2O$ gas mixture have also been used, but the oxygen content in the spinel phase was checked after quenching, by using X-ray diffraction to determine the cell parameters.[6,7] The correct value of the cell parameter (known from spinels prepared at high temperature) means that the experimental conditions were the appropriate ones. The present system allows one to determine the oxygen stoichiometry at the time when the sample is in contact with the gas mixture, inside the thermobalance. The exact stoichiometry is reached when the mass loss corresponds to the presence of four oxygen atoms for three metal atoms (for a structural formula of AB_2O_4). The apparatus is also designed to perform oxidation reactions, so the several pathways for the gases are called oxidation or reduction pathways (Figure 1).

The low oxygen partial pressure is obtained after achieving the H_2/H_2O equilibrium:

$$H_2 + {}^{1}/_{2}O_2 \Leftrightarrow H_2O \qquad (1)$$

whose equilibrium constant K is given as a function of temperature by the relation:[8]

$$\ln(K) = \frac{30\,272.76}{T} - 7.061\,75 \qquad (2)$$

The oxygen partial pressure associated with this equilibrium is

$$\ln(\mathrm{pO_2}) = 2\ln\left(\frac{\mathrm{pH_2O}}{\mathrm{pH_2}}\right) - 2\ln(\mathrm{K}) \qquad (3)$$

The vessel containing water is maintained at a temperature of 20 °C so that the H_2O water partial pressure (pH_2O) is 0.0227 atm.[8]

The hydrogen partial pressure pH_2 is expressed by the formula

$$\mathrm{pH_2} = \frac{\mathrm{dH_2}}{\mathrm{dtotal}} \qquad (4)$$

where dH_2 is the hydrogen flow and dtotal is the total gas flow (hydrogen and nitrogen).

The oxygen partial pressure, in atmosphere, may be written as

$$\mathrm{pO_2} = \left(\frac{\mathrm{pH_2O}}{K \times \mathrm{pH_2}}\right)^2 \qquad (5)$$

and then

$$\mathrm{pO_2} = \left(\frac{0.0227}{K \times \frac{\mathrm{dH_2}}{\mathrm{dtotal}}}\right)^2 \qquad (6)$$

The oxygen partial pressure is measured near the sample, inside the thermobalance or inside the furnace, with an in situ ZrO_2 sensor (reference Pd/PdO from Setnag). The pressures are measured with an accuracy of 10%, and they agree with the calculated values (Table 1).

Results and Discussion

1. Obtaining an Intimate Mixture of Vanadium and Iron Oxides. *1.1. The Precipitation Stage.* X-ray diffraction patterns for freeze-dried coprecipitates show a structural evolution with the atomic ratio V/Fe: the precipitate without vanadium (V/Fe = 0) reveals the crystallization of a spinel phase, with a cell parameter of 0.8386 nm. This value indicates that this phase is constituted of partially oxidized magnetite, since the theoretical cell parameter for Fe_3O_4 is 0.8396 nm. Samples with V/Fe = 0.20 and 0.50 are almost amorphous to X-rays, and for the ratio 2, the powder is completely amorphous.[9]

In the case of the coprecipitation Fe/Mn(II), T. Kodama et al.[10] link the crystallization to the presence of Fe(II) cations. The amorphization is induced by the substitution of Mn(II) for Fe(II), while Fe^{2+} cations facilitate the formation of complex hydroxides containing both Fe^{2+} and Fe^{3+} ions. After dehydration, these complexes lead to the crystallization of Fe_3O_4. The presence of Fe^{3+} cations prevent the crystallization because they rapidly polymerize to form amorphous Fe(III) hydroxides.

If the formula of magnetite is presented by $(Fe^{3+})_A(Fe^{2+}Fe^{3+})_BO_4$, the substitution of vanadium for iron will induce the replacement of Fe^{3+} by V^{3+} cations. So, the formula for Fe_2VO_4 is $(Fe^{2+}Fe^{3+}V^{3+})O_4$ and for FeV_2O_4 it is $(Fe^{2+}V^{3+}V^{3+})O_4$. One can see that the increase of the vanadium content does not change the amount of Fe^{2+} cations for one formula unit. As the amount of Fe^{2+} cations remains the same, the explanation claiming the fact that Fe^{2+} cations disappearance induces the amorphization is not valid. It is probable that, in this case, V^{3+} cations do not replace Fe^{3+} to form the complex hydroxide leading to crystallized magnetite, but they induce the formation of amorphous hydroxides. This is similar to the substitution of Fe^{3+} by Cr^{3+} ions, where it has been reported that incorporation of chromium modifies the microstructure of the precipitates and leads to amorphization, tending to form larger aggregates with a decrease in the size of the primary particles.[11] This last observation concerning the particle size is

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Table 1. Values of PO_2 Obtained by $H_2/N_2/H_2O$ Mixtures at 500°C: Comparison of the Calculated and the Measured Oxygen Partial Pressures

dN_2 (l/min)	0.158	0.155	0.15	0.145	0.14	0.13	0.12	0.11
dH_2 (l/min)	0.002	0.005	0.01	0.015	0.02	0.03	0.04	0.05
dtotal	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
pO_2 (Pa) (measured)	4.80×10^{-23}	7.02×10^{-24}	1.59×10^{-24}	1.03×10^{-24}	4.82×10^{-25}	2.08×10^{-25}	1.14×10^{-25}	6.91×10^{-26}
pO_2 (Pa) (calculated)	4.39×10^{-23}	7.02×10^{-24}	1.75×10^{-24}	7.80×10^{-25}	4.39×10^{-25}	1.95×10^{-25}	1.10×10^{-25}	7.02×10^{-26}

Table 2. Values of Specific Surface Areas for the Several Compounds (expected formula) after the Calcination Stage

expected spinel formula	Fe_3O_4	$Fe_{2.5}V_{0.5}O_4$	Fe_2VO_4	$Fe_{1.5}V_{1.5}O_4$	FeV_2O_4	$Fe_{1.8}V_{0.95}Co_{0.25}O_4$
V/Fe	0	0.2	0.5	1	2	0.5 + Co
S (m^2/g)	23.6	55.6	40.3	23.7	13.38	29.71

verified in the case of the iron–vanadium coprecipitates: specific surface area measurements of the aggregates lead to about 100 m^2/g for a ratio V/Fe = 0 and 20 m^2/g for V/Fe = 2. However, scanning electron microscopy does not allow one to distinguish elementary grains for ratios V/Fe higher than 0.2.

1.2. The Calcination Stage. To remove the impurities adsorbed during the precipitation stage, the powder mass evolution as a function of temperature is followed by thermogravimetry under air flow. The removal of water is observed around 120 °C and that of organic species at up to 350 °C. The selected temperature for the calcination is then 500 °C, and the required time for this treatment is 10 h, so that the grain size distribution is homogeneous. After this calcination stage, values of specific areas depend on the vanadium content (Table 2). The highest specific area, which corresponds to the smallest grains, is measured for the oxide with a V/Fe ratio of 0.2.

X-ray diffraction patterns for the calcinated coprecipitates reveal some differences depending on their composition. For ratios V/Fe lower than 0.5, the only crystallized phase is a rhombohedral α-Fe_2O_3 type. Beyond this ratio, some phases containing vanadium with valencies higher than three appear, whose nature depends on the amount of vanadium: V_3O_7, V_2O_5, and $Fe_2V_4O_{13}$. The substitution of vanadium for iron also leads to an amorphization of the oxidized phases, which can be deduced easily from the decreasing intensities of the diffraction peaks while the substitution rate increases.[9]

The cations in the products obtained after the previous procedure are in their highest valencies (3+ for Fe, 5+ for V, and 2+ for Co), and therefore they have to be reduced to obtain the spinel phase.

2. Obtaining Stoichiometric Spinel Phases and Determining Reduction Conditions (*T*, pO_2). To maintain the nanometric grain sizes, the reducing treatments have to be performed at temperatures around 500 °C. By referring to the Ellingham diagram of an iron and vanadium system,[6] one can note that for such thermal conditions, the values of oxygen partial pressures which have to be applied are very low (between 10^{-15} and 10^{-25} Pa), inside the existence domain of Fe_3O_4. For these moderate temperatures, the values of oxygen partial pressure (pO_2) may only be reached with gas mixtures of $N_2/H_2/H_2O$.

The experiments are performed using the following procedure: (i) The sample is heated to the selected synthesis temperature (usually 500 °C) with a heating rate of 2 °C/min, under nitrogen flow. (ii) During this heating, the $N_2/H_2/H_2O$ mixture is sent outside the thermobalance in order to establish the equilibrium, for the pressure to be reached before the reduction starts. (iii) When the reduction temperature is reached, the $N_2/H_2/H_2O$ mixture is sent to the sample, replacing the nitrogen atmosphere. The expected oxygen partial pressure is attained almost instantaneously, and the reduction starts as soon as the gases arrive in the thermobalance. Indeed, even if the gas mixture is diluted in nitrogen at the beginning, the ratio pH_2/pH_2O remains constant, and as seen in eq 3, this ratio determines the oxygen partial pressure. This partial pressure varies from 10^{-1} Pa under nitrogen to 10^{-15} Pa under a reducing atmosphere within a few seconds, and the expected pressure is reached within 1 min.

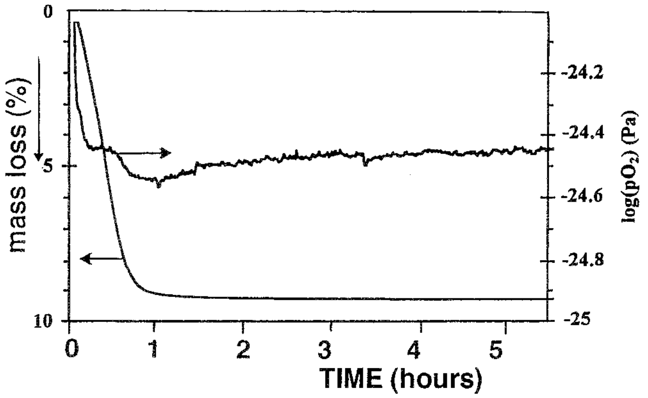

Figure 2. Simultaneous loss of mass and oxygen partial pressure at 500 °C for a calcined coprecipitate (V/Fe = 0.5): dN_2 = 0.14 L/min and dH_2 = 0.02 L/min.

The contact between the sample and the gas mixture is maintained for a few hours for the reduction to be complete. An example of reduction followed by thermogravimetry is given in Figure 2.At this level of the synthesis, two types of experiments have been performed: (i) A quenching of the sample at room temperature, while replacing the reducing atmosphere by nitrogen to prevent any oxidation or water adsorption. This experiment is used to measure the cell parameters as a function of the applied pO_2. (ii) A changing of the composition of the reducing atmosphere, to vary the oxygen partial pressure. The new mixture is then applied for a few hours. These experiments are used to measure the mass variations as a function of pO_2.

In a spinel $AB_2O_{4+\delta}$, mass variations are linked to the deviation from stoichiometry δ. Evolutions of δ as a function of oxygen partial pressure and at a given temperature is represented by a curve schematized in Figure 3 for $Fe_2VO_{4+\delta}$. This curve is centered on the value of pO_2 leading to the exact stoichiometry, showing a plateau (δ = 0). It exhibits negative or positive deviation from stoichiometry, depending on values of

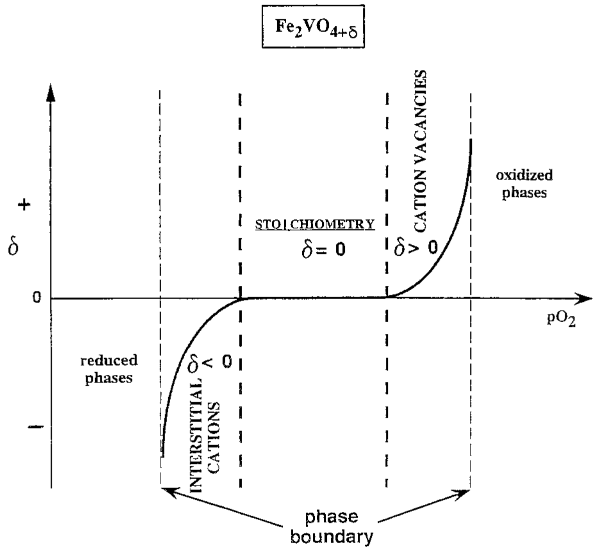

Figure 3. Schematic representation of the deviation from stoichiometry δ as a function of the oxygen partial pressure in $Fe_2VO_{4+\delta}$.

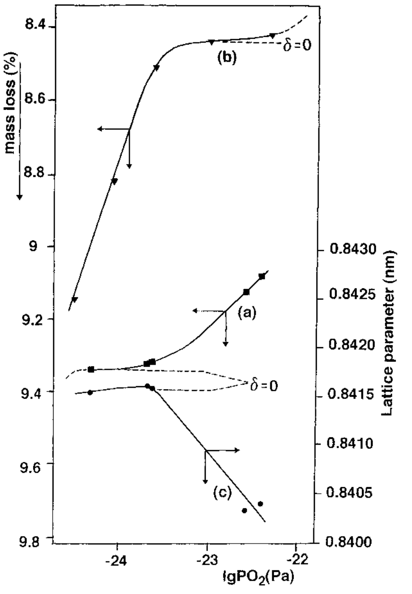

Figure 4. Mass losses after reduction at 500 °C obtained in TG as a function of the oxygen partial pressure in the case of $Fe_{2.05}V_{0.95}O_4$ (a) and $Fe_{1.88}V_{0.89}Co_{0.23}O_4$ (b) and lattice parameter evolution after quenching as a function of pO_2 at 500 °C in the case of $Fe_{2.05}V_{0.95}O_{4+\delta}$ (c). The stoichiometry $\delta = 0$ is reached when the mass loss or the cell parameter shows a plateau (around 10^{-24} Pa).

pO_2. For positive values of δ, the spinel phase contains cation vacancies, whereas for negative values of δ, interstitial cations may be present. For δ values higher or lower than the previous ones, a demixation occurs, leading to oxidized phases for $\delta > 0$ (Fe_2O_3, V_2O_3, ...) or reduced phases for $\delta < 0$ (FeO, Fe, ...).

Experimental mass losses may be measured by thermogravimetry in a reducing atmosphere, for several oxygen partial pressures at 500 °C. In the case of calcined coprecipitates containing Fe + V and Fe + V + Co (synthesized to obtain $Fe_{2.05}V_{0.95}O_4$ and $Fe_{1.88}V_{0.89}Co_{0.23}O_4$, respectively), the curves are represented in Figure 4 (curves a and b). For both curves, the exact stoichiometry $\delta = 0$ is reached in the range of oxygen partial pressure where the mass does not vary with pO_2.

Table 3. Comparison of Theoretical and Experimental Mass Loss During Reduction of Fe_2VO_4 and $Fe_{1.8}V_{0.95}Co_{0.25}O_4$

	theoretical mass loss (%)	experimental mass loss (%)
Fe_2VO_4	9.57	9.31
$Fe_{1.8}V_{0.95}Co_{0.25}O_4$	8.33	8.43

Table 4. Characteristics of the Stoichiometric Spinels $Fe_{3-x}V_xO_4$[a]

x	V mass %[b]	Fe mass %[b]	pO_2 values (Pa)	av. particle size (nm)[f]	lattice param. (nm)
0			4.6×10^{-23} [c]	143	0.8396
0.49	9.85	55.03	1.6×10^{-23} [c]	43	0.8403
0.95	18.85	44.75	4.4×10^{-25} [c]	65	0.8416
1.46	28.35	32.90	6.8×10^{-21} [d]	101	0.8430
2	39.35	21.10	6.2×10^{-20} [e]	120	0.8450

[a] Here, x is the number of vanadium atoms in one formula unit. [b] V and Fe mass % are obtained from chemical analysis. [c] At 500 °C. [d] At 600 °C. [e] At 700 °C. [f] The average particle size is calculated from the values of specific surface areas.

For $Fe_{2.05}V_{0.95}O_4$, pO_2 is around 10^{-24} Pa (curve a), and for $Fe_{1.88}V_{0.89}Co_{0.23}O_4$, it is around 10^{-23} Pa. (curve b). This value of pO_2 depends on the elements (and their content) present in the spinel phase. For the spinel containing cobalt, the cobalt cations have their highest valency after the calcination stage, and they stay in the 2^+ valency state in the spinel. Concerning the vanadium and iron cations, they have to be reduced to form the spinel phase. Globally, the amount of cations that has to be reduced is more important for the spinel without cobalt, and the pO_2 has to be smaller, as verified experimentally.

The values of mass losses to reach the exact stoichiometry may be predicted, by considering that, after the calcination, the phases contain the oxidized states of each element: α-Fe_2O_3, V_2O_5 and CoO. The difference in atomic weights between this oxidized state and the spinel phase gives the theoretical mass loss (Table 3). Values of mass loss are very sensitive to the vanadium content; for example, if the composition of the spinel phase is $Fe_{2.05}V_{0.95}O_4$ in place of Fe_2VO_4, the mass loss becomes 9.27% instead of 9.57%. So, the slight difference between the calculated values and the experimental ones (Table 3) may be explained by the variation of the real composition compared with the expected one.

To compare this new method for determining the stoichiometry in spinels with the previous one,[6,7] some samples have been quenched after the reducing treatment is achieved, and X-ray patterns were recorded. The only spinel phase is detected after all of the reducing treatments, and its cell parameters are represented in Figure 4 (curve c) as a function of the oxygen partial pressure. The variations of mass loss detected by thermogravimetry are correlated with the values of cell parameters: for the smallest mass losses, the spinel phase is oxidized, with a lower cell parameter.

With the temperature and oxygen partial pressure conditions determined by thermogravimetry, the reduction can be performed in the furnace on a larger amount of powder to study the reactivity by other techniques.[9]

Pure spinel phases are obtained for vanadium contents smaller than 1, by reducing treatments. The reducing conditions are summarized in Table 4. The attempts of synthesis at 500 °C of $Fe_{3-x}V_xO_4$ where $x >$

1, show that, in addition to the spinel phase, other phases appear such as an Fe and a rhombohedral $Fe_2O_3-V_2O_3$ phase. For example in $Fe_{1.5}V_{1.5}O_4$, the simultaneous presence of a reduced and an oxidized phase led us to think that a variation of the oxygen partial pressure cannot lead to a single spinel phase. Indeed, higher pO_2 values may increase the amount of oxidized phase, and lower pO_2 values may increase the amount of reduced phase. The solution is to perform the synthesis at a higher temperature to prevent the precipitation of vanadium in a rhombohedral phase. While increasing the synthesis temperature, it is necessary to decrease the hydrogen proportion in the gas mixture because it is not a strong reducer. Several attempts at 550 and 600 °C lead to a spinel phase, almost stoichiometric, in which the iron phase previously detected at 500 °C has disappeared.

The selected temperature condition is 600 °C, even if a weak peak of a rhombohedral phase is detected, because a higher temperature synthesis would increase the grain size to micrometric sizes, which is not the aim of this study. The conditions used to synthesize $Fe_{1.5}V_{1.5}O_4$ and FeV_2O_4 are reported in Table 4.

3. Characterization of Stoichiometric Spinel Phases. The composition of the samples (Table 4) is analyzed by atomic absorption spectroscopy after dissolving the sample powder in a concentrated HCl solution. The analysis gives the composition of only Fe and V, and the stoichiometry is assumed to be achieved so the number of oxygen atoms is four.

For the compounds $Fe_{3-x}V_xO_4$ where $x = 0$, 0.49, and 0.95 and for the spinel containing cobalt $Fe_{1.88}V_{0.89}Co_{0.23}O_4$, X-ray diffraction patterns show the presence of the only spinel phase (Figure 5, curves a−d), whereas for $Fe_{1.54}V_{1.46}O_4$ and FeV_2O_4, the spinel phase and two other phases are detected (Figure 5, curves e and f). Those phases are Fe and a solid solution $Fe_2O_3-V_2O_3$. This rhombohedral phase content is about 10 wt % in FeV_2O_4 and less than 4 wt % in $Fe_{1.54}V_{1.46}O_4$.

The values of cell parameters increase with an increase of vanadium content (Table 4). Those values are compared with powders[12−14] synthesized at high temperatures (>1000 °C) by the ceramic method. Our values are smaller than others in the range $x > 1$; this is probably due to the small amount of rhomboedral phase detected in these powders. The difference may also come from, especially in the range $x < 1$, a partial oxidation of the grain surface after quenching, because of the nanometric grain size.

The crystallite sizes are reported in Table 4. Concerning their morphology, the grains have nanometric sizes, with a homogeneous size distribution.[9] The smallest grain sizes are attributed to the spinels $Fe_{2.51}V_{0.49}O_4$ and $Fe_{1.88}V_{0.89}Co_{0.23}O_4$ (whose average particle size is around 50 nm). Thus, replacing iron by other elements seems to favor the synthesis of nanometric grains, but there is an optimal substitution rate ($x = 0.5$ in the case of vanadium) above which the grain size increases.

If the structural formula $(Fe_{\alpha}^{2+}Fe_{1-\alpha}^{3+})_A(Fe_{1-\alpha}^{2+}Fe_{1-x+\alpha}^{3+}V_x^{3+})_BO_4^{2-}$ is assumed,[9] the total amount of vanadium is located at octahedral B sites, whereas the tetrahedral A sites are occupied by ferrous and ferric cations. Infrared spectra of stoichiometric spinels (Figure 6) show a gradual sharpening of both absorption bands around 370 and 579 cm^{-1}. These bands are assigned to the ν_1 (T_{1u}) mode, which is the Fe−O stretching mode of the octahedral and tetrahedral sites (near 570 cm^{-1}), and to the ν_2 (T_{1u}) mode, which is an Fe−O stretching mode of the octahedral sites (near 370 cm^{-1}).[15] The spectrum of magnetite ($x = 0$) show a weak and broad band at 579 cm^{-1}, which is consistent with a random distribution of Fe^{2+} and Fe^{3+} ions on equivalent B sites.

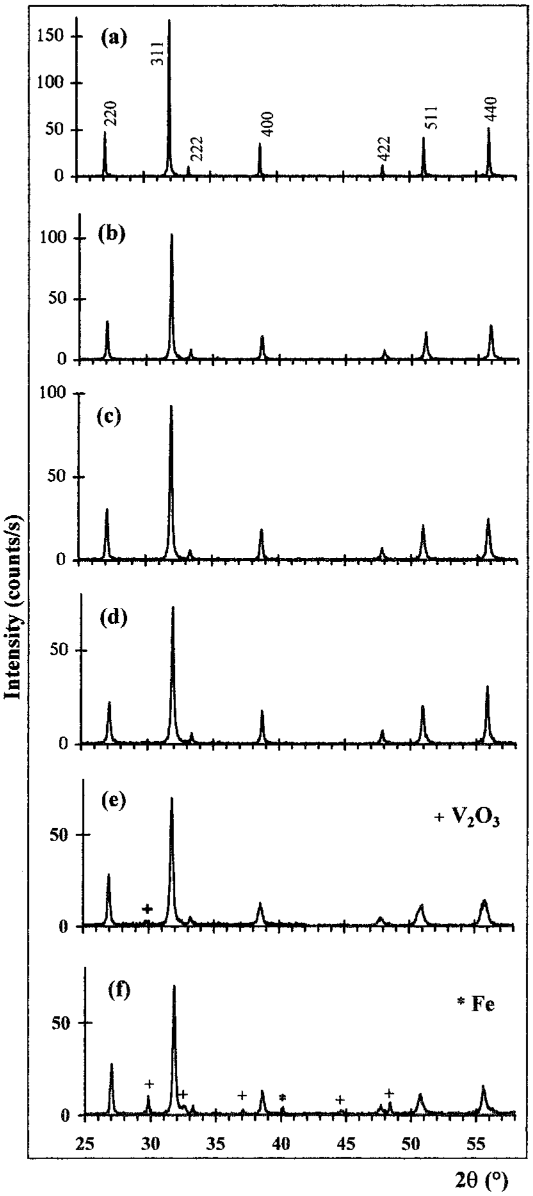

Figure 5. XRD patterns for the stoichiometric spinels: (a) Fe_3O_4, (b) $Fe_{2.51}V_{0.49}O_4$, (c) $Fe_{2.05}V_{0.95}O_4$, (d) $Fe_{1.88}V_{0.89}Co_{0.23}O_4$, (e) $Fe_{1.54}V_{1.46}O_4$, and (f) FeV_2O_4.

The ν_1 and ν_2 bands shift toward higher frequencies with increasing vanadium content, in particular the ν_2 band, which depends only on the nature of octahedral cations. This may be due to a change in the bonding force between the trivalent cation (Fe^{3+} which is gradu-

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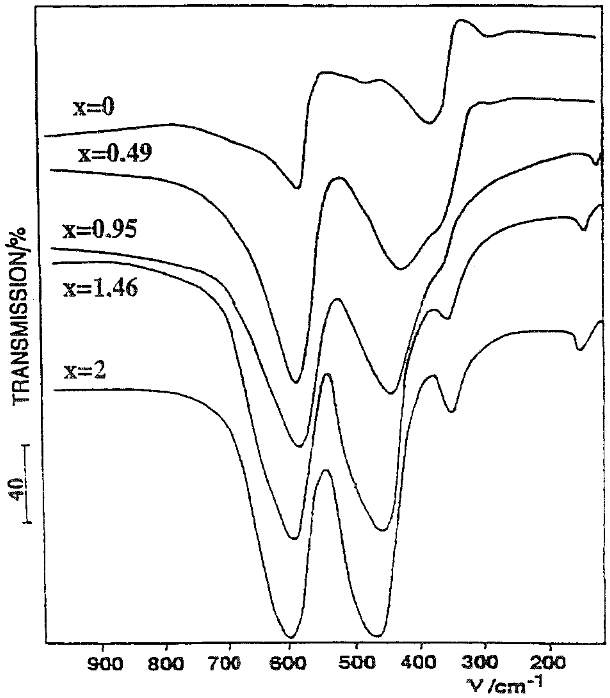

Figure 6. FT-IR spectra for $Fe_{3-x}V_xO_4$ spinels.

ally replaced by V^{3+}) and oxygen anion. The ν_3 and ν_4 bands, which are clearly observed for V contents higher than 1, are assigned to the motion of Fe^{2+} cations on A sites against those of B sites and to a O−Fe−O bending mode of the A and B sites, respectively.[15] The ν_4 band is predominantly related to a tetrahedral site cation,[16] and it does not show shifts with vanadium substitution. This is consistent with the fact that the A sites of end-member spinels (for example, FeV_2O_4) are believed to be occupied largely by Fe^{2+} cations.

Conclusion

Nanometric spinels containing iron and vanadium have been synthesized, using a soft chemistry method followed by a reducing treatment under $H_2/N_2/H_2O$ gas mixtures. After an identification of the species obtained by precipitation, the oxygen stoichiometry has been determined using thermogravimetry, by recording the mass variations as a function of the applied oxygen partial pressure. This method has allowed us to obtain spinels of $Fe_{3-x}V_xO_4$, where x is in the range 0−2, as well as a spinel containing iron, vanadium and cobalt. This last compound reveals that, by oxidation, a directional order is established between the vacancies and the cobalt cations which induces an increase of the coercive field.[17]

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