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Mixed-Valence Defect Ferrites: a New Family of Fine Powders and Thin Films of Spinel Ferrites

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Abstract: When highly divided spinel ferrites become reactive enough with oxygen, to allow the oxidation of the Fe^{2+} ions at low temperature and of substitute cations too, when these cations are capable of different valence states. We prepared fine particles of spinel ferrites substituted by Mn, Mo, Cu, by "chimie douce", especially from oxalate precursors and used them to reveal and to study the oxido-reduction phenomena occurring in these finely divided materials. It was shown that the oxidation created a new family of spinel ferrites: the mixed-valence defect ferrites, having specific characteristics and properties. The ferrites of this type can be fine powders prepared at low temperature, or ground ferrites obtained at high temperature, or thin films.

1. INTRODUCTION

Many different spinel ferrites $\text{X}_x\text{Fe}_{3-x}\text{O}_4$ (X=metallic cations) have already been prepared at high temperature ($>1000^\circ\text{C}$) by solid-solid reactions. These methods are very useful, not only in preparing samples for fundamental studies, but also for producing devices for microwave or other applications. Such applications mainly requires "bulk" ferrites (coarse particles, sintered ceramics, single crystals). Oxides prepared at high temperature are generally close to stoichiometry, with a metal/oxygen ratio (M/O) close to 3/4. However, the cation oxidation is difficult in these "bulk" oxides because of their poor reactivity to oxygen while the spinel structure is also generally lost as the M/O ratio decreases. In fact, during the oxidation of coarse grains (>300 nm) of ferrites, the crystallographic transformation of the spinel lattice in corundum structure, has already been demonstrated [1][2]. It has been shown [3], however, that it is possible to oxidize Fe^{2+} cations in fine particle or thin film form, while keeping the spinel structure. Cation deficient spinel ferrites ($\text{M/O} < 3/4$) could then be obtained. These have been the subject of many works too, and they are, currently, widely used for magnetic recording pigments ($\gamma\text{-Fe}_2\text{O}_3$, Co-doped $\gamma\text{-Fe}_2\text{O}_3$). Certain authors have tried to put the ferrite reactivity to use in preparing high performance magnetic materials. Their works mainly focused on the oxidation of the Fe^{2+} ions alone, in either pure [3][4] or substituted magnetite [5-7].

This paper concerns finely divided spinel ferrites substituted by mixed valence transition metals. The main feature of interest of these materials is that Fe^{2+} ions, and their substitution cations can both be oxidized to lead to the formation of defect spinel ferrites with mixed valence. Some of the resulting specific characteristics and properties, that make these phases a new family of ferrites are presented.

2. PREPARATION OF FINE PARTICLES OF SUBSTITUTED SPINEL FERRITES

Many methods have already been proposed for preparing small particles of spinel ferrites. Most are "chimie douce" methods, which can be subdivided into two main classes. In the first, the spinel ferrite particles are prepared directly by precipitating different metallic and iron salts in an alkaline medium. Depending on the pH, concentrations, temperature and other conditions, the required particles are formed after ageing. The second class of methods consists in precipitating a precursor, containing the desired metallic ion/ iron ion ratio, and then heat-treating it at low temperature to obtain a single spinel ferrite. Fine particles can be prepared by either of these methods.

A process of the second class was chosen to prepare our fine particles of substituted ferrites. The basic precursor was the ferrous oxalate $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. In this compound, iron can be totally or partially replaced by any of several metallic elements, especially Mg, Mn, Co, Ni, Zn, Cu... Two types of heat treatment are generally required in succession to transform the precursor into a spinel ferrite. The first, in air, breaks the oxalate particles down into both a spinel oxide and a corundum type-phase. The second is carried out under a reductive $\text{H}_2\text{-N}_2\text{-H}_2\text{O}$ atmosphere, to form a pure spinel phase. If small needle-like particles are wanted (fig. 1), a very slow decomposition of oxalates particles, precipitated in an alcoholic medium, is required [8]. Moreover, all the heat treatments have to be performed at as low as possible temperature.

Figure 1: Acicular particles of Co-Mn spinel ferrites prepared from oxalic precursors.

Most of the spinel powders studied in this paper were elaborated from oxalic precursors. Mixed oxide particles, precipitated in alkaline medium, were used to prepare the $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ samples, because of the difficulties involved in precipitating Fe-Mo mixed oxalates.

Figure 2: DTG curves of $\text{Mo}_{0.49}\text{Fe}_{2.51}\text{O}_4$ (Oxygen pressure: 40 hPa, heating rate: 2°C/min)

3. FINELY DIVIDED SUBSTITUTED SPINEL FERRITES : CATIONIC DISTRIBUTION AND REACTIVITY

As small $\text{X}_x\text{Fe}_{3-x}\text{O}_4$ particles of spinel ferrites oxidize, the oxygen lattice remains cubic close packed, and the oxygen ions are added to the structure as soon as the cations migrate to the surface and change their valence state. The reaction can be described as: $\text{X}_x\text{Fe}_{3-x}\text{O}_4 + \delta/4 \text{O}_2 \rightarrow \text{X}_x\text{Fe}_{3-x}\text{O}_{4+\delta/2} = \text{X}_{8x/(8+\delta)}\text{Fe}_{(24-8x)/(8+\delta)}\square_{3\delta/(8+\delta)}\text{O}_4$. (δ is the number of exchanged electrons per formula unit, $\square$ represents the cationic vacancies). This equation shows that the resulting ferrite has a defect structure. If we assume that the molar mass of the ferrite is always close to 230 grams, the relative weight gain associated to the reaction is $(\delta \cdot \text{Oxygen atomic mass}) / (\text{molar mass of the ferrite}) = 3.5 \cdot 10^{-2} \cdot \delta$. The symmetric thermobalances, able to measure weight variations less than 0.01%, can thus detect less than 0.003 electrons exchanged per formula unit during the oxidation. This very high sensitivity makes thermogravimetry a very good tool for studying the specific reactivity of the spinel ferrites. Moreover, because the crystallite size distribution is not too large in ferrites prepared by the process previously described, differential thermogravimetry (DTG) reveals one single peak for each type of cation oxidized. Each peak is centered around a temperature depending on the coordination, the chemical nature, and the valence of the cations.

In fact, because the cation-oxygen bondings are more covalent on tetrahedral sites, the cations are more difficult to oxidize in this coordination than on octahedral sites. This is well demonstrated by the oxidation of powders of Fe_3O_4 and Cr_2FeO_4 with crystallite sizes close to 50 nm. Fe^{2+} ions alone can be oxidized in these compounds, but in the first one, Fe^{2+} ions are

Table 1: Structural formulae determined from DTG measurements for the fine particles (crystallite size # 50 nm) of manganese, molybdenum and copper ferrites. $[\text{M}^{n+}]$ and M^{n+} : represents cations on octahedral and tetrahedral sites respectively, $\alpha \neq 0.1$, $\gamma \neq 0.015$, β and a are increasing functions of x , b is a decreasing function of x . Reaction 3 is partial (#50% of Mn^{2+} oxidized).

$\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ ($0 < x \leq 1$)			$\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ ($0 < x \leq 0.6$)			$\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($0 < x \leq 0.6$)		
$\text{Mn}_{0.8x}^{2+} \text{Fe}_1^{3+} - 0.8x$ $[\text{Fe}_{1+0.6x}^{3+} \text{Fe}_{1-0.8x}^{2+} \text{Mn}_{0.2x}^{3+}] \text{O}_4^{2-}$			$\text{Mo}_{\gamma x}^{4+} \text{Fe}_{\beta}^{2+} \text{Fe}_1^{3+} - \beta - \gamma x$ $[\text{Fe}_{1+\beta-(1+\alpha-\gamma)x}^{3+} \text{Fe}_{1-\beta+\alpha x}^{2+} \dots$ $\dots \text{Mo}_{(1-\alpha)x}^{3+} \text{Mo}_{(\alpha-\gamma)x}^{4+}] \text{O}_4^{2-}$			$\text{Cu}_{ax}^{+} \text{Fe}_{1-ax}^{3+}$ $[\text{Fe}_{1+(2a+b)x}^{3+} \text{Fe}_{1-(1+a+b)x}^{2+} \dots$ $\dots \text{Cu}_{bx}^{+} \text{Cu}_{(1-a-b)x}^{2+}] \text{O}_4^{2-}$		
T (°C)	Ox. or red. cations		T (°C)	Oxidized cations		T (°C)	Oxidized cations	
(1)	$\approx 200^\circ\text{C}$	$[\text{Fe}^{2+}] \rightarrow [\text{Fe}^{3+}]$	(6)	$\approx 200^\circ\text{C}$	$[\text{Fe}^{2+}] \rightarrow [\text{Fe}^{3+}]$	(11)	$\approx 180^\circ\text{C}$	$[\text{Cu}^{+}] \rightarrow [\text{Cu}^{2+}]$
(2)	$\approx 300^\circ\text{C}$	$[\text{Mn}^{3+}] \rightarrow [\text{Mn}^{4+}]$	(7)	$\approx 280^\circ\text{C}$	$[\text{Mo}^{3+}] \rightarrow [\text{Mo}^{6+}]$	(12)	$\approx 200^\circ\text{C}$	$[\text{Fe}^{2+}] \rightarrow [\text{Fe}^{3+}]$
(3)	$\approx 350^\circ\text{C}$	$\text{Mn}^{2+} \rightarrow [\text{Mn}^{3+}]$	(8)	$\approx 380^\circ\text{C}$	$[\text{Mo}^{4+}] \rightarrow [\text{Mo}^{6+}]$	(13)	$\approx 250^\circ\text{C}$	$\text{Cu}^{+} \rightarrow [\text{Cu}^{2+}]$
(4)	$\approx 450^\circ\text{C}$	$[\text{Mn}^{4+}] \rightarrow [\text{Mn}^{3+}]$	(9)	$\approx 420^\circ\text{C}$	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$			
(5)	$>500^\circ\text{C}$	$\text{Mn}^{2+} \rightarrow [\text{Mn}^{3+}]$	(10)	$\approx 500^\circ\text{C}$	$\text{Mo}^{4+} \rightarrow \text{Mo}^{6+}$			

located on octahedral sites, while they are in a tetrahedral surrounding in the second. The DTG analyses reveal that octahedral and tetrahedral Fe^{2+} ions are oxidized around 200°C and 400°C respectively [9][10]. Moreover, the oxidation temperature depends on the chemical nature and the valence state of the ions [10]. For this reason, besides the peaks ascribed to the Fe^{2+} ion oxidation, other DTG peaks may appear for ferrites substituted by those ions capable of adopt several valence states (fig. 2). By combining several techniques we were able to identify each peak in the oxido-reduction process of manganese [11][12], molybdenum [13][14] and copper [15] substituted ferrites elaborated by a "chimie douce" process. Because the surface area of a given DTG peak is proportional to the quantity of the oxidized ions, by measuring the surface area of each peak after desummation of the DTG curves, we can calculate the quantity of each oxidizable cation in the stoichiometric ferrite. This makes thermogravimetry a quantitative method for determining the structural formula of the spinel ferrites. The structural formulae of $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ ($0 < x \leq 1$) [16], $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ ($0 < x \leq 0.5$) [13] or $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($0 < x \leq 0.6$) [15] fine particles of spinel ferrites were refined by this method (tab. 1).

Ferrites obtained at high temperature can also be ground to sufficiently small grain sizes to make the above oxido-reduction phenomena possible. Therefore, the reactivity of ground $\text{Mo}_x\text{Fe}_{3-x}\text{O}_4$ ($0 < x \leq 1$) [17], $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($0 < x \leq 1$) [15] and $\text{V}_x\text{Fe}_{3-x}\text{O}_4$ ($0 < x \leq 1$) [18] was studied and it was found, in spite of certain slight differences, these have cationic distributions similar to what is obtained by "chimie douce". Moreover, the heat treatments in air also lead to the formation of the high valence state of manganese (Mn^{4+}) and molybdenum (Mo^{6+}). V^{5+} ions were found in spinel ferrites for ground samples [18].

More complicated fine powders of Co-Mn, Co-Mo and Co-Cu spinel ferrites were also prepared by "chimie douce". In these oxides the cobalt ions are Co^{2+} . They are mainly located on octahedral sites when the cobalt content is low, and they are distributed on both sites when the cobalt content per formula unit, is relatively high (0.8-1) [19][8]. Therefore, cobalt ions replace the bivalent cations of the lattice (Fe^{2+} , Mn^{2+} , Cu^{2+}) [8][19-21]. Most of the oxido-reduction reactions, given in table 1, remain the same in spite of the cobalt substitution. As soon as the bivalent cations are replaced by stable Co^{2+} ions, the reactions involving these cations are obviously removed [8].

4. A NEW FAMILY OF SPINEL FERRITES

The oxidations previously described generate unusual high valence states for Mn, Mo and V cation in spinel ferrites. This is one of the specific characteristics of the phases studied. For instance, Mn^{4+} ions are not encountered in bulk ferrites, whose poor reactivity makes oxidation possible only in a range of temperatures where Mn^{4+} ions are not stable. Another consequence is the creation of spinel phases having a great number of vacancies. This can be shown by the oxidation of molybdenum ferrites (reactions (6) to (10) in table 1). In fact, the complete oxidation is described by:

When x is close to 0.6, for the richest molybdenum ferrite prepared now by "chimie douce", the oxidation can generate a defect spinel phase containing around 0.78 vacancy per formula unit. The M/O ratio (0.56) is then very much less than 3/4 and even less than 2/3, which are the M/O ratios for the non-oxidized ferrites and the well-known $\gamma\text{-Fe}_2\text{O}_3$ defect spinel phase, respectively.

The oxidations proceed from the surface to the core of the grains. When the particles are partially oxidized, the outer part (highly oxidized) and the inner part (weakly or not oxidized) have small and large unit cells respectively. In fact, the more the ferrite is oxidized, the lower its lattice constant. To simplify, it may be assumed that the accommodation of the two spinel lattices thus tends to develop a tension near the surface and a compression in the core. The resulting stress, which reaches a maximum at around half oxidation, may cause an enhancement of the coercive force due to induced magneto-elastic effects, and also probably creates a directional order (DO) [22]. In fact, the DO, which reveals the minimization of the lattice free energy, appears under the effect of the magnetization and not only heat treatments or irradiation, but also mechanical stress. The establishment of the DO has a very low kinetic. Generally, special heat treatments are required to complete the DO creation.

Experimentally, enhancements in coercivity (H_c) due to partial oxidations are mainly revealed in cobalt-substituted ferrites because of the strong magneto-elastic effects of octahedral Co^{2+} ions. For the same reasons, major variations in the remanent Faraday rotation are also observed in these oxides ($\theta_{F,R}$) [23]. The curves of room temperature H_c (or $\theta_{F,R}$) versus oxidation temperature for these materials show different peaks centered in the regions where approximately half of each type of oxidizable cation have changed valence. The more important oxidations are then revealed by the coercive force measurements (fig. 3-4), not only for fine powders but also for thin films made of fine crystallites. However, in spite of the small crystallite sizes (about 20 nm) in the films, the oxidations occur at higher temperatures than for powders. In fact, the films surface in contact with air during oxidation is very small, because of the close packing crystallites and the protection of one side of the film by a substrate. This slows down the oxidation kinetics and shifts the reactions to high temperatures.

In spite of the enhancements in H_c due to the partial oxidation, it is possible to improve H_c further by a more complete DO. This can be done by cooling the samples very slowly at about 10°C/h from their oxidation temperature to room temperature. Extraordinary/coercivities (of about 4000 Oe for $\text{Mo}_{0.1}\text{Co}_{0.92}\text{Fe}_{1.98}\text{O}_4$ [21]) can be achieved this way for fine powders of spinel ferrites.

For pure manganese ferrites, oxido-reduction phenomena around 450°C create many Mn^{3+} ions. When the total manganese content is high ($x \geq 1$), the Mn^{3+} content is above the critical concentration for which the spinel lattice becomes tetragonally distorted, because of the cooperative Jahn-Teller effect. Besides creating the mixed valence defect structure, the reactivity in this case causes the loss of the lattice cubic symmetry. The unit cell distortion generates an anisotropy

Figure 3: Coercivity versus oxidation temperature for $\text{Mn}_{0.4}\text{Co}_{0.18}\text{Fe}_{2.42}\text{O}_4$, $\text{Cu}_{0.18}\text{Co}_{0.18}\text{Fe}_{2.64}\text{O}_4$, $\text{Mo}_{0.1}\text{Co}_{0.92}\text{Fe}_{1.98}\text{O}_4$ quenched after oxidation at different temperatures. $[\text{M}^{n+}]$ and M^{n+} are octahedral and tetrahedral cations oxidized or reduced.

Figure 4: Coercivity and remanent Faraday rotation for $\text{Mn}_{0.13}\text{Co}_{0.73}\text{Fe}_{2.14}\text{O}_4$ thin film and $\text{Mn}_{0.12}\text{Co}_{0.08}\text{Fe}_{2.08}\text{O}_4$ fine powder oxidized at different temperatures.

which has an effect on the coercivity. Fine acicular particles of MnFe_2O_4 and $\text{Mn}_{1.8}\text{Fe}_{1.2}\text{O}_4$ have coercivities close to 175 and 90 Oe respectively, before oxidation, but these last reach 325 and 860 Oe after an oxidation at 425°C for 2 hours.

From the above examples, it is clear that the formation of mixed valence cations and vacancies endows ferrites with specific characteristics and properties. This makes the mixed-valence defect ferrites a truly new family of spinel ferrites.

5. CONCLUSION

Finely divided ferrites have enough reactivity with oxygen that it becomes possible not only to oxidize the ferrous ion in the spinel lattice, but also the substitute cations, when these cations are capable of different valence states. Mixed-valence defect ferrites can then be created. Their properties are sufficiently different from those of the stoichiometric ferrites from which they derive, that they can be considered to constitute a new family. These new materials may be fine particles, prepared by a "chimie douce" or by grinding ferrites obtained at high temperature; or they may be thin films. Some of the mixed valence defect ferrites properties (H_c , θ_F , R) are already of interest for information storage purpose, and careful study of their electric, electromagnetic, and optical properties should reveal other potential applications of this new family of spinel ferrites.

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