

Syncrystallization of CoFe_2O_4 from Ferric and Cobaltous Chlorides: Physical Properties of the Precipitate

A. MALATS I RIERA, G. POURROY,* AND P. POIX

Groupe des Matériaux Inorganiques, IPCMS, EHICS, 1 rue Blaise Pascal, BP296, 67008 Starsbourg Cedex, France

Received June 19, 1991; in revised form April 10, 1992; accepted April 20, 1992

The precipitate CoFe_2O_4 obtained from cobaltous and ferric chlorides and potassium hydroxide is a well-crystallized spinel phase, indicating that the term "coprecipitation" is not suitable for describing this synthesis. The term "syncrystallization," which means crystallization of a definite compound directly during the precipitation, is preferred. The fine powder of CoFe_2O_4 is very reactive toward oxygen. CoFe_2O_4 contains mixed valences Co^{2+} and Co(III) between 100 and 600°C, which has a great influence on the crystallographic parameter and the saturation magnetization. © 1992 Academic Press, Inc.

Introduction

Cobalt-substituted magnetites of spinel structure (space group $Fd\bar{3}m$) have been known for several decades (1). Interest in these compounds increased when progress in recording required higher coercivities to prevent demagnetization. Indeed, coercivity higher than 300 Oe could not be obtained with $\gamma\text{-Fe}_2\text{O}_3$. Furthermore, the magneto-crystalline anisotropy of iron oxide could be greatly increased by substituting a small amount of cobalt for the iron atoms. Several synthesis methods have been developed in order to obtain fine particles with controlled shapes and sizes and high coercivity, such as substitution of iron in $\gamma\text{-Fe}_2\text{O}_3$ (1–4) or impregnation of $\gamma\text{-Fe}_2\text{O}_3$ by cobalt (5). Despite the importance of ferrites in general

and of Co ferrite in particular, very few published reports deal with the preparation of these materials by precipitation from aqueous solution. The simplest method consists of precipitating cobaltous and ferric chlorides with NaOH (6–8). Other methods have been developed in which ferrous and cobaltous chlorides, nitrates, or sulfates are precipitated by oxalic acid, KOH, or NaOH in order to obtain powders of controlled granulometry and particular magnetic properties (9–12). Nevertheless, no studies have been devoted to the chemical characteristics and the evolution of the precipitate. We focus here on the physical properties of the powder precipitated from cobaltous and ferric chlorides.

Experimental

Iron chloride, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and cobalt chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, are dissolved in wa-

* To whom correspondence should be addressed.

ter and then heated at 80–100°C. This solution is poured into boiling potassium hydroxide, which is vigorously stirred. The precipitate is then boiled for 30 min to increase the grain sizes and facilitate the filtration. Boiling water is used for washing. This last operation is finished when no chloride ions are detected in the filtrate. The powder is then heated under air at different temperatures, 100, 200, 300, 500, and 800°C, for 1 hr.

The crystallographic parameters are determined by means of X-ray diffraction measurements at room temperature by using a Kristalloflex Siemens diffractometer and monochromatic cobalt radiation ($\lambda = 1.78897 \text{ \AA}$). Thermal gravimetric and thermal differential analyses (TG and DTA) are performed in platinum crucibles under air using a Setaram 92 apparatus. The loss or gain of weight is calculated after removing the signal of the empty crucible. Magnetization measurements are performed at room temperature using a Foner-type magnetometer.

Results and Discussion

All the phases are well crystallized and present the pure spinel structure without impurities such as iron or cobalt hydroxide or oxide. X-ray diffraction lines, those of the precipitate after filtration as well as those of the precipitate annealed under air up to 800°C, are fine. The presence of an appreciable amount of an amorphous phase is ruled out because of the weak background intensity. That means that the precipitate is not a mixture of crystallized or amorphous phases whose heating leads to definite compounds such as those encountered in the low-temperature synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ or NbFeO_4 and TaFeO_4 (14, 15). Accordingly, the term "coprecipitation" is not suitable in this case. The term "syncrystallization," which means crystallization of a compound as soon as the precipitate is formed, describes this synthesis more precisely.

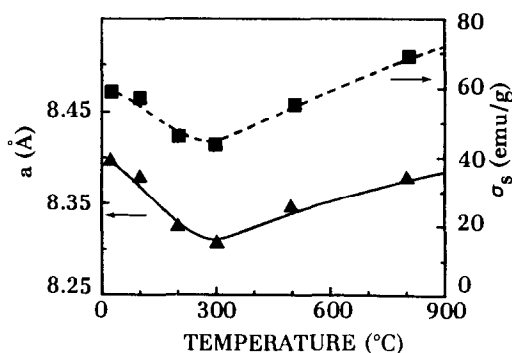


FIG. 1. Variation of the crystallographic parameter and the magnetization saturation of the CoFe_2O_4 precipitate versus annealing temperature.

However, when the precipitate is heated under air up to 800°C, the crystallographic parameter varies substantially, from 8.39 Å (± 0.01) at room temperature to 8.29 Å (± 0.01) at 300°C. It increases again above 400°C and reaches 8.38 Å (± 0.01) at 800°C (Fig. 1). The minimum value of the crystallographic parameter at about 250–350°C must be related to the anomaly of the TG curve and to the strong exothermic peak of the DTA curve, occurring at about 200–250°C (Fig. 2). Let us note the temperature differ-

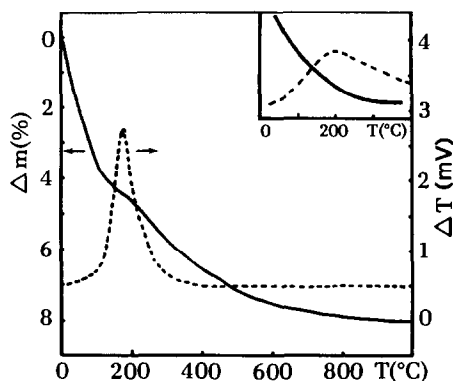
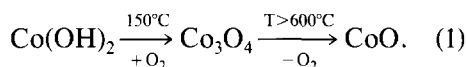
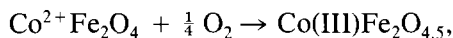


FIG. 2. TG (solid line) and DTA (broken line) curves of CoFe_2O_4 under air. The decomposition of TG variation into a dehydration curve (solid line), and the oxidation and reduction of cobalt (broken line) are displayed in the inset.

ence due to the different ways of measurement, static in the former case and dynamic in the latter. Nevertheless, the three phenomena have the same origin, the oxidation of cobalt. Indeed, the strong exothermic peak of the DTA curve can be associated only with oxidation since it does not appear under vacuum. The unique cation, which can be oxidized, is Co^{2+} . Indeed, it is well known that



The oxidation of Co^{2+} to Co(III), smaller than Co^{2+} , following the reaction



gives rise to the decrease in the crystallographic parameter. By using the method of characteristic distances (invariants) developed by Poix, we can calculate that the variation of parameters arising from the total oxidation of cobalt is $\Delta a = 0.211 \text{ \AA}$ and corresponds to a weight increase of 3.4% (16–20). The observed variation, 0.090 \AA between 350 and 800°C , corresponds to a calculated weight decrease of 1.45%. Let us observe the TG curve: above 300°C , the weight loss (of $\approx 1.5\%$) cannot be assigned to a decomposition of hydroxide (all the cobalt and iron hydroxides decompose below 300°C) and can originate only from cobalt reduction. Therefore, the TG curve is the result of two phenomena: the dehydration of the precipitate which corresponds to a weight loss, and the oxidation and a reduction as shown in the inset to Fig. 2.

The saturation magnetization presents a variation similar to that of crystallographic parameters (Fig. 1). Under air, it decreases until the temperature reaches 250°C and then increases at higher temperatures. Similar considerations can be used to explain the variation of the saturation magnetization. At 0 K, the calculated magnetic moment varies from $3\mu_B/\text{mole}$ for CoFe_2O_4 ($y = 0$) to 1.1

μ_B/mole for the fully oxidized compound ($y = 0.5$), Co(III) being diamagnetic. As for the coercive field, it always increases, from 10 Oe at room temperature up to 620 Oe at 800°C . Very little can be said about that, since it depends both on shapes and sizes of particles and on anisotropy. When heated, the particle sizes probably increase. However, the increasing concentration of Co^{2+} improves the anisotropy, which may have an effect on the coercive field.

Conclusions

Pure and well-crystallized CoFe_2O_4 has been synthesized at ambient temperature. The powder, made up of fine particles, is very reactive toward oxygen. CoFe_2O_4 with cobalt under two oxidation states, Co^{2+} and Co(III), can be obtained by annealing the precipitate under air between 100 and 600°C without crystallization modifications. Applications in catalysis are under consideration.

Acknowledgments

We thank La Caixa de Barcelona for the grant awarded to A. Malats i Riera.

References

1. E. P. WOHLFARTH (Ed.), "Ferromagnetic Materials," North-Holland, Amsterdam (1980).
2. J. C. JESCHKE, U.S. Patent No. 3243375 (1966).
3. F. KRONES, "Technik des Masnetspeicher," p. 479, Springer-Verlag, Berlin (1960).
4. P. MOLLARD, A. COLLOMB, J. DEVENYL, A. ROUSSET, AND J. PARIS IEEE, *Trans. Mag.* **11**, 894 (1975).
5. W. D. HALLER AND R. M. COLLINE, U.S. Patent No. 3573980 (1971).
6. W. J. SCHUELE AND V. D. DEETSCREEK, *J. Appl. Phys.* **32**, 235S (1961).
7. M. KIMAYA, *Bull. Chem. Soc. Jpn.* **51**, 134 (1978).
8. K. MATSUDA AND I. KAYAMA, *Proc. Mac. Sci. Tokai Univ.* **17**, 101 (1982).
9. T. SATO, T. IJIMA, M. SEKI, AND N. INAGAKI, *J. Magn. Mater.* **65**, 252 (1987).
10. H. TAMURA AND E. MATIJEVIC *J. Colloid Interface Sci.* **90**, 100 (1982).
11. R. E. VANDENBERGHE, R. VALEERBERGHE,

- E. DEGRAVE, AND G. ROBBRECHT, *J. Magn. Mater.* **15-18**, 1117 (1980).
12. Y. MAKINO, I. KAMIYA, AND G. SUGUIRA, Japan Patent No. 7415757 (1974).
13. E. PRINCE, *Phys. Rev.* **102**, 674 (1956).
14. S. SILMINOT, S. EL HADIGUI, J. P. KAPPLER, AND J. C. BERNIER, *Superconducting Ceram. Br. Ceram. Proc.* **40**, 15 (1988).
15. G. POURROY, A. MALATS I RIERA, AND P. POIX, *J. Solid State Chem.* **88**, 476 (1990).
16. P. POIX, *Sem. Etat Solide* **1**, 82 (1966-1967).
17. P. POIX, *C.R. Acad. Sci. Paris C* **268**, 1139 (1969).
18. P. POIX, F. BASILE, AND C. DJEGA-MARIADASSOU, *Ann. Chim.* **10**, 159 (1975).
19. P. POIX, *C.R. Acad. Sci. Paris C* **270**, 1852 (1970).
20. P. POIX, *J. Solid State Chem.* **31**, 95 (1980).