Oxygen stoichiometry control of nanometric oxide compounds: The case of titanium ferrites

N. Millot [a,*], P. Perriat [b]

[a] Laboratoire Interdisciplinaire Carnot de Bourgogne, U.M.R. 5209 C.N.R.S./Université de Bourgogne, BP 47 870, 21078 Dijon Cedex, France
[b] Matériaux, Ingénierie et Sciences, CNRS UMR 5510, INSA de Lyon, 69621 Villeurbanne Cedex, France

A B S T R A C T

Three techniques have been coupled with an original device, based on H_2/H_2O equilibrium, controlling oxygen partial pressure: XRD, TGA and DC conductivity in order to characterize very reactive compounds such as nanometric powders. From XRD, both the structure and the oxygen stoichiometry (thanks to their lattice parameter) were investigated *in situ*. From TGA, it was the oxygen stoichiometry (thanks to mass gain or loss) which was determined. From DC conductivity, it was both the structure and the oxygen stoichiometry (thanks to the activation energy) which were obtained. The advantages were to determine very rapidly and with a small amount of powder the equilibrium conditions (T, pO_2) necessary to obtain the desired phase and stoichiometry. These methods have been evaluated for nanometric titanium ferrites. Two phenomena have been observed during the reducing process: the precipitation of a rhombohedral phase and a significant grain growth linked together.

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1. Introduction

The field of nanoparticles in materials research sparks intense interest due to their drastic size-dependent properties. In particular, these materials are very reactive with their outside environment due to high surface/volume ratio. For example, at the nanometric scale, to avoid the oxidation of metals, it is necessary to study them under reductive atmosphere [1,2]. Such constraints are also required for nanometric metal oxides containing unstable cations under ambient conditions (such as Fe^{2+} [3]; U^{4+} [4,5]; Mn^{2+} [6]; Cu^{2+} [7]). It is then necessary to develop synthesis routes under appropriate atmosphere (low pO_2, without water, etc.) coupled with *in situ* characterization tools.

"*Post mortem*" characterizations are usually used to determine both the structure and the oxygen stoichiometry of inorganic metallic oxides. Nevertheless, this methodology presents two major drawbacks. First, in order to obtain appropriate oxygen stoichiometry and structure, several time taking (usually days) thermal treatments and subsequent characterizations of a compound are necessary. Second, homogeneous samples are difficult to obtain. Indeed, as some cations (for example Fe^{2+}) are not thermodynamically stable in air, a significant amount of them can be oxidized when powders are studied under air atmosphere. This

phenomenon leads to chemical heterogeneities in nanometric particles [8,9]. The purpose of this study was then to develop three *in situ* techniques: XRD, TGA and DC conductivity measurements to solve these problems and to determine precisely and rapidly the (T, pO_2) required for a desired nanomaterial

- From XRD experiments, it was both the structure and the oxygen stoichiometry (thanks to the lattice parameter) which can be investigated.
- From TGA measurements, it was the oxygen stoichiometry (thanks to mass gain or loss) which can be determined.
- From DC conductivity experiments, it was both the structure and the oxygen stoichiometry (thanks to the activation energy which was related to M^{n+}/M^{n+1} cations pairs numbers) which could be investigated.

To valid these methods, ferrites, key materials in several important processes due to their magnetic and catalytic properties [10], in particular for biomedical applications [11], have been chosen, especially titanium ferrites ($Fe_{3-x}Ti_x)_{1-\delta}O_4$, with x the Ti content in the spinel structure (between 0 and 1), and δ the deviation from oxygen stoichiometry. Very recently, titanium ferrites were used as magnetically separable sorbent for elemental mercury capture from the flue gas of coal-fired power plants [12]; it has also been shown that the introduction of Ti into magnetite structures has a remarkable effect on promoting the decolorization of synthetic dyes, proving that titanomagnetite

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could be useful for environmental remediation [13]. Titanomagnetites were also studied due to their paleomagnetic interest, since they were found in the earth crust as nanometer-scaled clusters [14,15]. Apart the evidence of a Verwey transition temperature shift in nanostructured Ti-ferrites [16], the choice of this material was also motivated by the fact that their cationic distribution has been extensively studied using several methods. Among the two types of sites occupied by the cations in the spinel structure [17], tetrahedral (A) or octahedral (B), the Ti^{4+} cations reside only on the octahedral sites whatever the scale, micrometer [18,19] or nanometer-sized [20]. Only when the Fe cations are not completely oxidized, the location of the Fe^{2+} cations is still subjected to controversial discussions [21,22].

2. Experimental procedure

Five compositions of titanium ferrites $(Fe_{3-x}Ti_x)_{1-\delta}O_4$ corresponding to: $x = 0$, 0.25, 0.5, 0.75 and 1 have been synthesized according to a classical soft chemistry procedure. Such synthesis has already been reported elsewhere [23,24]. It is well known that the presence of divalent and trivalent cations is required in the formation of the spinel structure [25]. Briefly, after dissolution of suitable amounts of ferrous, ferric and titanium chloride (cations concentration 0.3 mol L^{-1}, pH < 1, $T = 20\,^\circ C$) this mixture was added to an ammonia solution continuously stirred at 800 rpm at 20 °C, leading to instantaneous precipitation of nanometric particles. The equation of the reaction is the following:

$$(1+x)Fe^{2+} + (2-2x)Fe^{3+} + xTi^{4+} + 8OH^- \rightarrow Fe_{3-x}Ti_xO_4 + 4H_2O \quad (1)$$
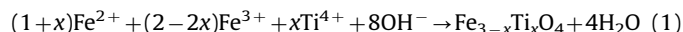
In accordance with the Ti and Fe solubility constants, the precipitate composition was the same as in the liquid phase (proven in Ref. [26] thanks to EDS, EELS, ICP and XPS analyses). The particles were then separated by centrifugation at 3500 rpm for 5 min and washed with deionized water under ultrasonication for 5 min followed by another centrifugation. After four successive washings, a sol was formed without surfactant nor dispersant addition. The sol was freeze-dried leading to a dry spinel precipitate. Calcination under optimized conditions was carried out to eliminate remaining impurities and to oxidize all the Fe^{2+} cations while limiting crystallite growth. It consisted of a thermal treatment for 10 h under air at 380 °C for titanium amount $0.25 \leq x \leq 1$ and 330 °C for $x = 0$ after a temperature ramp of 10 °C/h.

In order to reach the desired cation/oxygen ratio leading to $\delta = 0$, powders were then annealed under $N_2/H_2/H_2O$ gas mixture [27]. Indeed, these gases were more appropriate than CO/CO_2 gas mixtures classically used at higher temperature (1000 °C). H_2/H_2O mixtures ensured reducing atmosphere ($10^{-15} < pO_2 < 10^{-25}$ Pa) at the low temperatures required to limit grain growth (400–700 °C).

Each powder was studied by thermogravimetry using a symmetric thermobalance SETARAM TAG 24 capable of measuring weight variations of about 0.001%. The deviation from oxygen stoichiometry, δ, was deduced from the mass changes observed during the oxidation and reduction treatments.

For infra-red spectroscopy (IR), nanoparticles (2 mg) were supported on 100 mg potassium bromide (KBr). Samples were mixed and ground using an agate morter and pestel. After grinding, samples were pressed into a disk of 13 mm diameter, using a pressure of 150 kg/cm^3. All spectra were recorded on a Perkin-Elmer 1725X FTIR spectrophotometer.

In situ X-ray diffraction (XRD) experiments were carried out using an INEL diffractometer equipped with a curved position-sensitive detector (CPS 120 INEL). Monochromatic Co-$K\alpha_1$ X-rays ($\lambda = 0.17889$ nm) were obtained with a primary focusing Ge
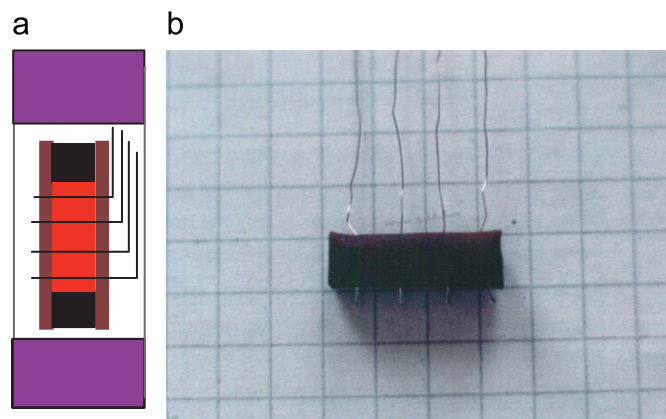
Fig. 1. (a) Scheme of the double encapsulation system developed in order to obtain cylindrical samples of nanopowders, with four platinum electrodes, by isostatic pressing. (b) Micrograph of such a cylindrical sample with four platinum electrodes used for DC conductivity measurements (scale: 5 mm × 5 mm).

monochromator. The diffraction pattern was scanned over the 2θ range 20–130° in steps of 0.03° and a counting time of 3600 s/step. *In situ* XRD experiments, using the XRK900 reaction chamber from Anton Parr, were carried out in the same oxido-reduction scheme as that performed in the thermobalance. *Ex situ* XRD patterns at room temperature were collected on a Siemens D5000 automatic powder diffractometer, operating at 35 mA and 50 kV. Fluorescence effects were minimized by using Cu $K\beta$ radiation and correction for instrumental broadening was determined from a standard reference material, annealed BaF_2. The lattice parameters of the powders were deduced from XRD line positions using a least-squares refinement method.[1] XRD line profile analysis[2] was performed in order to determine the average crystallite size (size of a region over which the diffraction is coherent) and the degree of crystallographic imperfections (microdistorsions, stacking faults, planar defects, etc.) [28,29].

The DC conductivity measurements were carried out under controlled atmosphere (air or reducing $N_2/H_2/H_2O$ mixtures) on compressed cylindrical samples using four-probe technique. The compact must satisfy the following compromises: to be sufficiently dense to have a good mechanical behavior but to be sufficiently porous to facilitate oxygen transport in its bulk. Also, by isostatic compaction under 250 MPa and thanks to a system of double encapsulation, cylindrical samples with four platinum electrodes were obtained (Fig. 1). Measurements were carried out with a Keitley 236 using the conventional four-probe technique. A current was applied through the outer probes inducing a voltage in the inner probes. Thus, the conductivity of the material was given by the formula $\sigma_{ferrite} = 1/R_{ferrite} = I/U_{int}$.

Preparative furnace, in which DC conductivity measurements were realized, and TGA apparatus both contain an *in situ* ZrO_2 emf cell to measure pO_2.

Particle sizes were determined thanks to scanning electron microscopy (SEM) using a JEOL 6400F microscope.

Surface area measurements have been performed using an AUTOSORB apparatus and 150–200 mg of powder. Samples were outgassed *in situ* at 200 °C and the measurements were performed at liquid N_2 temperature with N_2 adsorbing gas. The generalized equation of BET has been used in calculation of surface area values from the isotherm of nitrogen adsorption. The mean

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[1] In-house software taking into account the effect of sample gap.
[2] Available in the PC software package DIFFRACT AT supplied by SIEMENS.