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Correlation Between the Reactivity Towards Oxygen and the Coercitivity in Submicron Vanadium Ferrite Spinels

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Abstract. Nanometric powders of Fe_2VO_4 and $Fe_{1.84}V_{0.92}Co_{0.23}O_4$ have been synthetised by "chimie douce" process. The cations in the spinel structure can oxidize at low temperatures without any phase transformation leading to cation-deficient spinel with formula $Fe_2VO_{4+\delta}$ and $Fe_{1.84}V_{0.92}Co_{0.23}O_{4+\delta}$, where δ is the deviation from stoichiometry, due to a change of the anion-cation ratio, consecutive to formation of vacancies. The oxidation, investigated by thermogravimetry, involves several stages, each stage corresponding to the oxidation of one oxidizable cation, Fe^{2+}, V^{2+}, V^{3+} on B (octahedral) or A (tetrahedral) sites. Coercivity has also been studied, revealing that the coercive field increases with the rate of oxidation.

1. ELABORATION OF VANADIUM FERRITES

The nanocrystalline particles were prepared by coprecipitation by adding an aqueous solution containing suitable amounts of Co^{2+}, Fe^{2+}, Fe^{3+}, V^{3+} to triethylamine. It is followed by a heat treatment which includes calcination at 500°C for 10 hours under O_2, and reduction at 500°C for 5 hours under $H_2/N_2/H_2O$ mixtures. The relative contents of the different gases to obtain stoichiometry were obtained by studying the deviation from stoichiometry, δ, as a function of the oxygen partial pressure, pO_2, given by the gas mixture and measured by an EMF cell : the stoichiometry (δ=0) is obtained, at a given temperature, in the range of oxygen partial pressure where δ does not vary with pO_2 [1]. For the two investigated ferrites, the atmospheric conditions for obtaining the stoichiometry depends on the composition of the spinel: $pO_2=10^{-28}$ atm at 500°C (N_2=98.4%, H_2=1.6%) for $Fe_{1.84}V_{0.92}Co_{0.23}O_4$, $pO_2=10^{-29}$ atm at 500°C (N_2=87.5%, H_2=12.5%) for Fe_2VO_4. The particles have a size of 40 nm, and are identified to be a pure spinel structure. The lattice constant is equal to 8.382 Å for $Fe_{1.84}V_{0.92}Co_{0.23}O_4$ and to 8.411 Å for Fe_2VO_4.

2. REACTIVITY TOWARDS OXYGEN: COMPARISON BETWEEN NANOMETRIC AND COARSE GRAINS

The oxidation of Fe_2VO_4 is followed by thermogravimetry for linear heating rate experiments. Figure 1 compares the rate of oxidation in Fe_2VO_4 for coarse (300 nm) and nanometric powders (40 nm) and the rate of oxidation in nanometric vanadium ferrites containing or not Co cations. For coarse grains, the DTG curve has been carefully studied by additional experiments : X-ray diffraction, XPS and FT-IR spectroscopy. Three peaks (Figure 1a) have been evidenced, corresponding successively to the oxidation of the Fe^{2+} cations on B sites, the V^{2+} cations on B sites and finally the V^{3+} cations on B sites [2]. The oxidation temperature of a cation is strongly correlated to the cation-oxygen distance, which depends both on the valence state and the location on A or B sites [3]. Compared with coarse grain, the DTG curve relative to the nanometric powder is quite different. First, there is a strong difference in the shape of the DTG curves, which indicates that the cation distribution is not the same in coarse and fine particles. This can be explained by the fact that the two types of powders are prepared at different temperatures (500°C for nanometric powders, 850°C for coarse powders). Second, the oxidation begins sooner in fine powders, which is consistent with the fact that oxidation involves some diffusion mechanisms [3]: for instance, whereas the temperature of oxidation of the Fe^{2+} cations on B sites, (which is the oxidation more precisely studied in this paper) is around 250°C in coarse powders, it is below 200°C concerning the nanometric one. Concerning the comparison between the DTG curves of nanometric powders containing or not Co ions, it can be emphasized that, when all the oxidizable cations in the spinel

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structure are oxidized, the deviation from stoichiometry is lower in the samples which contain Co (δ=1.17 in $Fe_{1.84}V_{0.92}Co_{0.23}O_4$, δ=1.34 in Fe_2VO_4). This is consistent with the fact that in $Fe_{1.84}V_{0.92}Co_{0.23}O_4$, some Fe^{2+} and/or V^{2+} cations are replaced by some Co^{2+} cations which can not oxidize. This point can be also justified by noticing that the rate of oxidation decreases mainly at low temperatures [100-300°C], which is the range in temperature where there are the bivalent cations which are oxidizing.

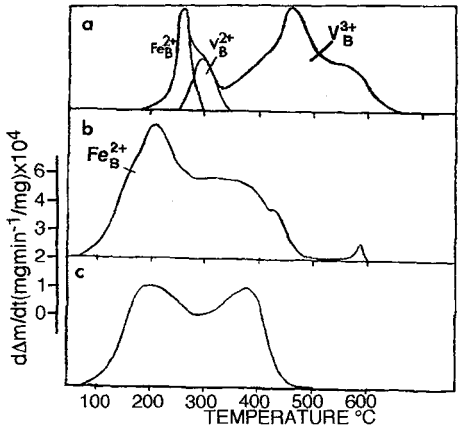

Figure 1: DTG curves of (a) coarse powder of Fe_2VO_4, (b) nanometric powder of Fe_2VO_4, (c) nanometric powder of $Fe_{1.84}V_{0.92}Co_{0.23}O_4$

3. EVOLUTION OF THE COERCIVITY WITH THE Fe^{2+} CATIONS OXIDATION

When the vanadium ferrites contain some Co cations, there is a strong correlation between the oxidation of the Fe^{2+} on the B sites and the coercivity, as one can see by comparing Figure 1 and Figure 2. In Figure 2, the coercivity is measured at room temperature after the same linear heating experiments and quenching at different temperatures. This increase in coercivity is attributed to the creation of a directional order [4] linked to the reorganization of Co cations enhanced by the high content of vacancies created during the Fe^{2+} oxidation.

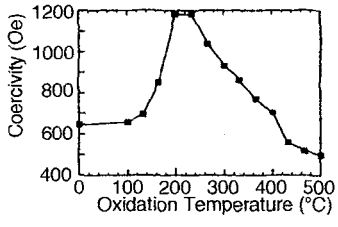

Figure 2: Evolution of the coercive field versus the oxidation temperature in $Fe_{1.84}V_{0.92}Co_{0.23}O_4$

4. CONCLUSION

The reactivity towards oxygen has been investigated in submicron vanadium ferrite spinels using thermogravimetry analysis, FT-IR spectroscopy and XPS. These spinels were prepared by "chimie douce", and the conditions to elaborate the spinel phase were obtained by using $N_2/H_2/H_2O$ mixtures at 500°C. When the vanadium ferrites contain some Co cations, correlations have been revealed between the oxidation of the Fe^{2+} cations on B sites and the coercivity.

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