Valence States of Copper and Cation Distribution in Submicron Copper Ferrite Spinels CuxFe3-xO4(0≤x≤1)

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Abstract. Valence states studies of copper and iron ions and their cation distribution on both octahedral (B) and tetrahedral (A) sites on the spinel structure of submicron copper-substituted magnetites, $Cu_xFe_{3-x}O_4$ ($0 \leq x \leq 1$) which are oxidized in cation deficient spinels $Cu_xFe_{3-x}O_{4+\delta}$ ($0 \leq \delta \leq 0.5$) have been performed by TG, DTG, FT-IR and XPS when the copper content determine the number of oxidizable cations $1-x = (Fe^{2+} + Cu^+)$ per mole of ferrite. It was demonstrated that Fe^{2+} and Cu^+ ions are oxidized into Fe^{3+} and Cu^{2+} ions below 300°C and that the availability to diffuse could be envisaged as follows : Cu_B^+ (130°C) $< Fe_B^{2+}$ (185°C) $< Cu_A^+$ (240°C). For high copper content ($x \geq 0.4$), the presence of additional interstitial Cu^+ ions in tetrahedral sites has also been found.

1. INTRODUCTION

The cation distribution in submicron $Cu_xFe_{3-x}O_4$ spinels ($0 \leq x \leq 1$) and cation deficient spinels obtained by oxidation at low temperature has been investigated by thermogravimetry (TG and DTG), , FT-IR spectroscopy and XPS. We describe the combined use of these techniques to evaluate the valence and copper ion distribution and its dependence on temperature and oxygen pressure.These spinels were prepared by a "chimie douce" method via decomposition of mixed oxalate precursors as reported in ref. [1], the average cristallite size being close to 35 nm.

2. RESULTS AND DISCUSSION

2.1 Study by thermogravimetry and cation distribution

It has been previously established that the oxidation temperature of B-sites M^{n+} ions is lower than that of A-sites M^{n+} ions because of the weaker ionic bonding of the B-sites as compared with the stronger A-sites covalent bonds [2]. In this context an analysis by thermogravimetry on the basis of a redox-type mechanism of copper has been intented to differentiate the oxidation temperature of each oxidizable cation. Figure 1 (curve a) shows the DTG curve for a sample with x = 0.32. Three oxidations should be implicated with this temperature resolution. The intense peak at 200°C can be attributed to the B-site Fe^{2+} ion oxidation, this oxidation temperature having been largely demonstrated elsewhere [3].The peak at 290°C and the shoulder at 150°C represent the oxidation of copper ions.The comparison with $Cu_xMn_{3-x}O_4$ spinel containing A-site Cu^+ ions [4] permit us to attribute in the copper ferrites the peak appearing at 290°C to the oxidation of A-site Cu^+ ions. The shoulder appearing at about 150°C was as a matter of fact due to the oxidation of B-site Cu^+ ions, a proposition that is supported by one larger cation-oxygen distance [2].
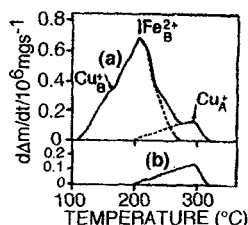

Figure 1: (a) global oxidation curve and desummation peaks, (b) curve showing the disappearance of the first and second peaks

In order to propose a cation distribution, a quantitative analysis of cations from the determination of oxidation peak areas has been carried out. The profile of the peak attributed to the oxidation of Cu^+ ion on A-sites, first determined by desummation (Fig.1, curve a), has been confirmed by DTG after selective oxidation in isothermal conditions at 140°C for 24 h of Cu^+ and Fe^{2+} ions on B-sites. After this procedure, the reoxidation on heating in O_2 corresponding to the curve b represents only the oxidation of Cu^+ ions on A-sites. For differentiate and evaluate quantitatively the oxidation peak areas of these two cations, the Cu^+ ions concentration on B-sites has been determined from oxygen loss due to the unoxidability of copper ions at low oxygen pressure which is the basis of the oxygen analysis. At 27 Pa and above, overall cations $Cu_B^+ Fe_B^{2+}$ and Cu_A^+ are totally oxidized as confirmed by the lattice constant value found to be the lowest. The heating curves for 9 and 6 Pa reveal that the copper ions are oxygen pressure dependent. Thereby, the magnitude of the mass-gain difference between 27 Pa and lower partial pressures of oxygen corresponds to cations which have not been oxidized.The difference in oxygen content reaches a plateau region in the interval $180 < T < 205°C$ which indicates that for an oxygen pressure of 9 Pa, the Fe^{2+} ions have been completely oxidized. We can thus attribute the magnitude of this difference to the amount of $Cu_B^+ + Cu_A^+$ ions initially present in the spinel lattice. With an oxygen pressure of 6 Pa, the plateau region was absent and a significant B site Fe^{2+} ions amount remains after this treatment as supported by the important difference of mass gain above 230°C. The cation distribution obeys the formula :

$$\left(Cu_{\alpha x}^+ \ Fe_{1-\alpha x}^{3+}\right)_A \quad \left(Cu_{(1-\alpha-\beta)x}^{2+} \ Cu_{\beta x}^+ \ Fe_{1+(2\alpha+\beta)x}^{3+} \ Fe_{1-(1+\alpha+\beta)x}^{2+}\right)_B \ O_4^{2-} \quad \text{with } \alpha = 0.50 \text{ and } \beta = 0.20 \text{ for } x = 0.32.$$

However, this distribution cannot be generalized, the α and β coefficients being dependent on the copper content and thermal treatment which leads, for samples quenched from temperatures higher that 600°C, to deficient oxygen spinels $Cu_xFe_{3-x}O_{4-\delta}$. For these non-stoichiometric phases, the oxidation reveals a larger mass gain than that calculated with 1-x per mole of ferrite. This is ascribed to the presence, of both additional interstitial Cu^+ ions and octahedral Fe^{2+} ions at sites normally occupied in the original deficient spinel. For deficient oxygen spinel, $CuFe_2O_{4-\delta}$ (x=1), the observed mass gain is due to the oxidation of Cu^+ ions interstitial. In all cases, the oxidation temperature for Cu^+ ions interstitial associated with the spinel structure is higher than that for Cu^+ ions in A site implying that intercalated copper ions are also located in A sites.

2.2 Distribution in cation deficient spinels

When the copper is substituted for iron in Fe_3O_4, the FT-IR spectrum exibits two broad absorption bands near 353 and 562 cm^{-1}, typical of a "chemical" disorder resulting from Fe^{2+} and Fe^{3+} ions on equivalent sites. The Cu 2p3/2 spectrum shows an intense peak at 932 eV. It has a large value of the full width at half maximum (FWHM=3.7 eV) compared with those of oxidized samples, that seems to be a strong evidence for the presence of Cu in different binding states. As a matter of fact, Cu 2p3/2 peak contains several signals whose the binding energies have the following values : 930.7 eV , 932 eV and 934 eV. In comparison with other results [5], the peak at 934 eV in the spectrum can be interpreted as belonging to Cu^{2+} on B-sites, the peak at 932 eV to Cu^+ on A-sites and at 930.7 eV to Cu^+ on B-sites.

The FTIR spectra of oxidized samples under non-isothermal conditions ($PO_2 = 4x10^3$ Pa, 2°C min^{-1}) and quenched from various temperatures exhibit, in the temperature range 150-450°C when cation deficient spinels are formed, a large number of absorption bands, those being well-resolved for samples oxidized at 250, 300 and 340°C . For these three temperatures, the similarity with the FTIR spectrum of ordered γ-Fe_2O_3 [6], both in the position and number (at least 20) of absorption bands permits us to postulate the same type of order between vacancies and cations on B-sites, i.e. a □/cation ratio of 1/5. Indeed, the complete oxidation of Cu_B^+, Fe_B^{2+}, and Cu_A^+ leads to a maximum of vacancies. For the same composition, the spinel oxidized at 180 and 450°C shows the disappearance of some absorption bands, especially in the region 500-150 cm^{-1}. The observed difference may be reasonably explained by a lower number of vacancies resulting from a partial oxidation of cations. At 180°C, only Cu_B^+ and a part of Fe_B^{2+} ions are oxidized, that strongly reduces the number of vacancies and thereby only a partial ordering occurs [6]. On the other hand, at 450°C the decrease of vacancy content is related to reduction process occurring at this temperature.

The spectrum of Cu 2p3/2 of a sample oxidized at 180°C shows a Cu 2p3/2 signal with a small value of the FWHM (3.1 eV) consequently to the absence of Cu_B^+ in the structure. Curve fitting yields only two signals caused by Cu^+ on A-sites (932.3 eV) and Cu^{2+} on B-sites (934.3 eV). With increasing temperature more and more Cu ions are placed as Cu^{2+} on B-sites and at 300°C, where the mass gain is maximum, the signal is solely caused by Cu^{2+} ions on these sites .The existence of an intense satellite peak at 944 eV in the spectrum clearly proves the presence of Cu^{2+} ions. For the reduction temperature domain (350-480°C) where the spinel structure was maintained, Cu^{2+} is partly reduced and the signal of Cu^+ on A -site again appears.

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