



# SURFACE STRUCTURAL DISORDER IN MECHANOSYNTHESIZED AND MECHANICALLY ACTIVATED ZINC FERRITE

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## 1. Introduction

Zinc ferrite,  $\text{Zn}^{[4]}\text{Fe}^{[6]}\text{O}_4$ , prepared by a conventional ceramic method forms the structure of a normal spinel with zinc in the tetrahedral <sup>[4]</sup> sites and iron in the octahedral <sup>[6]</sup> sites of a cubic close packing of oxygen atoms. The new mechanochemical method of zinc ferrite synthesis from the mixture of zinc oxide and iron oxide has received increased attention in recent years [1,2]. This new method (mechanosynthesis) offers the possibility of forming zinc ferrite in the inverse spinel structure [3].

The structural disorder in the bulk of mechanosynthesized zinc ferrite (synthesised by the high energy milling of the  $\text{ZnO}/\text{Fe}_2\text{O}_3$  mixture) and of mechanically activated zinc ferrite (synthesised by the conventional thermal method, followed by mechanical treatment) has been studied in previous work [3-9] using a variety of experimental techniques. It has been found that the metastable nanoscale structural states of both mechanically activated and mechanosynthesized zinc ferrites are characterised by the mechanically induced inversion as well as by the deformation of the spinel octahedron geometry.

In the present work the X-ray photoelectron spectroscopy (XPS) study of mechanosynthesized and of mechanically activated spinel has been performed in order to obtain information about the precise sites of atoms in relation to the crystal structure of the mechanically disturbed surface.

## 2. Experimental

Two synthesis routes, a conventional thermal method as well as the mechanochemical route, were used for the preparation of zinc ferrite. Stoichiometric mixtures of powdered reactants containing 66.34%  $\alpha\text{-Fe}_2\text{O}_3$  and 33.76% ZnO by weight (products of Merck) were used as starting materials. The milling process was carried out in a planetary ball mill, AGO 2 (Institute of Solid State Chemistry, Novosibirsk), at room temperature. Ten grams of the starting material were sealed in a stainless steel vial (150 cm<sup>3</sup> in volume) together with stainless steel balls 5 mm in diameter. The ball to powder weight ratio was 20:1. Milling experiments were performed in air at 800 rpm.

The surface analytical studies were performed by an ESCALAB 220iXL spectrometer (Fisons Instruments).

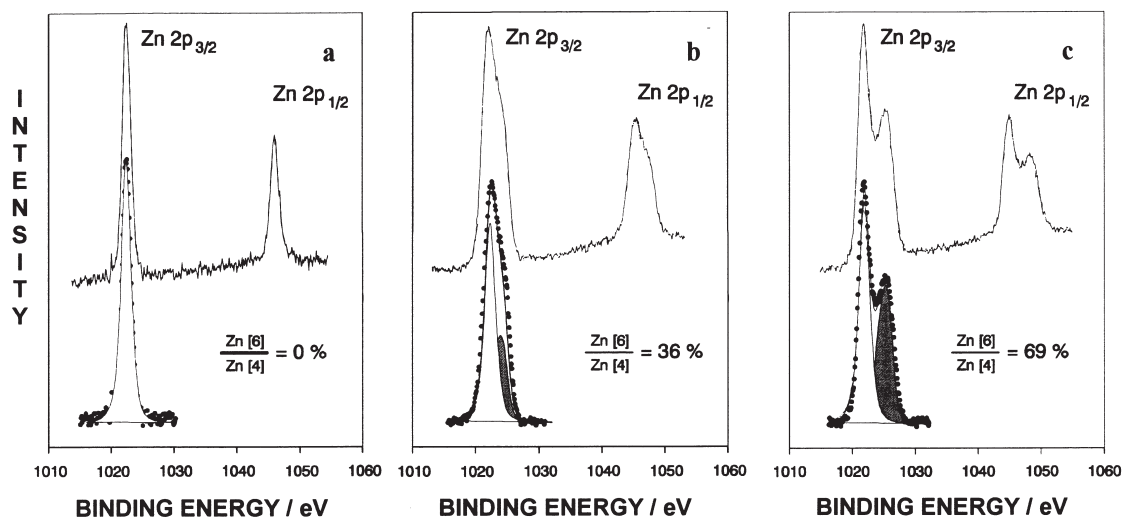
The X-ray source used was monochromatic focused  $\text{AlK}\alpha$  radiation (1486.6 eV) with an input power of 150 W. The XPS spectra of the investigated samples were evaluated on the basis of two well characterised zinc standard compounds, ZnO, the structurally well known tetrahedrally coordinated species and  $\text{Zn}_2\text{TiO}_4$ , the octahedrally coordinated species [10]. Due to the mean free path of the photoelectrons in zinc oxides of 1.961 nm, the information depth of our XPS investigations was  $\sim 6$  nm [10].

## 3 Results and Discussion

The XPS study of the  $\text{ZnFe}_2\text{O}_4$  and of the  $\text{Fe}_2\text{O}_3/\text{ZnO}$  mixture submitted to the high energy milling process revealed that the Zn  $2p_{3/2}$  signal of the non-activated zinc ferrite and of the starting  $\text{ZnO}/\text{Fe}_2\text{O}_3$  mixture consists of a single sharp peak corresponding to tetrahedrally coordinated zinc (Fig. 1a). With increasing milling time, the Zn  $2p_{3/2}$  signal in the spectra of both zinc ferrite and the oxide mixture became broader, and a second new component gradually appeared on the right side of the signal. We notice that the new component of the signal was clearly visible in the XPS spectra of mechanically treated samples after 2 min of milling (Fig. 1b). Further milling of the  $\text{ZnFe}_2\text{O}_4$  and of the  $\text{ZnO}/\text{Fe}_2\text{O}_3$  mixture led to an increase of the structural disorder of the spinel structure and to a progressive mechanochemical synthesis of zinc ferrite, respectively [3, 5, 8]. This process is accompanied by the gradual increase of the relative weight of the new signal component in the XPS spectra of the investigated systems in both the mechanically activated as well as the mechanochemical zinc ferrite samples (Fig. 1).

An interesting observation is that in the spectra of both mechanochemical and mechanically activated zinc ferrites, the newly created component of the Zn  $2p_{3/2}$  signal has the same peak position as the signal assigned to octahedrally coordinated zinc in the  $\text{Zn}_2\text{TiO}_4$  10, i.e. in mechanically treated samples, the Zn  $2p_{3/2}$  signal corresponds not only to tetrahedrally but also to octahedrally coordinated zinc. Taking into account that zinc ferrite prepared by the conventional ceramic method adopts the normal spinel structure, in which the  $\text{Zn}^{2+}$  cations occupy only sites tetrahedrally coordinated by oxygen while the octahedrally co-

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**Fig. 1.** The X-ray photoelectron spectra of zinc ferrite: (a) non-activated  $\text{ZnFe}_2\text{O}_4$ ; (b)  $\text{ZnFe}_2\text{O}_4$  mechanically activated for 2 min; (c)  $\text{ZnFe}_2\text{O}_4$  mechanically activated for 18 min.

ordinated sites are occupied by the  $\text{Fe}^{3+}$  cations, an appearance of zinc in octahedral sites is evidence that, in addition to the bulk structure [3-9], also the surface structure ( $< 6$  nm) of both mechanothesized and mechanically activated zinc ferrites corresponds to the structure of the inverse spinel. In both cases, the content of  $\text{Zn}^{2+}$  ions in octahedral positions increases with increasing milling time (Fig. 1).

The XPS study of mechanically treated zinc ferrites after the thermal treatment at various temperatures revealed that the relaxation of the surface structure starts at  $T > 800$  K and finishes at a temperature above 1000 K within a period of 4 hours. Thus, a metastability of the surface structure of both mechanically activated and mechanothesized zinc ferrites upon heating is manifested by a gradual disappearance of the mechanically induced inversion. The re-equilibration of the surface structure terminates by a complete relaxation, i.e. during heating the surface structure of mechanically activated and of mechanothesized spinel is transformed into a normal spinel structure (typical of the crystalline zinc ferrite prepared by the conventional thermal method).

#### 4. Conclusions

The results obtained in this work indicate that, from the qualitative point of view, the surface structure of the nano-scale mechanothesized zinc ferrite is similar to that of the mechanically activated zinc ferrite. The main feature of the surface structural disorder of both mechanically activated and mechanothesized zinc ferrites is the mechanically induced inversion. In both cases, the inversion degree increases with increasing milling time. At temperatures above 800 K the mechanically induced inversion disappears and the re-equilibration terminates by a complete relaxation of the disordered surface structure.

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