

# Formation and Surface Structure of Ti-Zn-Double Oxides and of Zn Ferrite\*

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In powder mixtures of ZnO and TiO<sub>2</sub> the compounds Zn<sub>2</sub>TiO<sub>4</sub>, ZnTiO<sub>3</sub>, and Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub> can be formed as a result of solid state reactions. The formation of the double oxides is essentially determined by the microstructure of the powder mixture. Furthermore, the type of the double oxide depends on the TiO<sub>2</sub> modification. There exist structural similarities between Zn<sub>2</sub>TiO<sub>4</sub> (spinel) and TiO<sub>2</sub> (anatase) as well as between ZnTiO<sub>3</sub> and TiO<sub>2</sub> (rutile). Compound Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub> is formed only on the basis of the Zn<sub>2</sub>TiO<sub>4</sub> phase. The Zn<sup>2+</sup> ions on the surface of Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub> occupy only tetrahedral sites and not octahedral ones, like it was derived for the crystal structure of the bulk.

The formation of zinc ferrite, ZnFe<sub>2</sub>O<sub>4</sub> at room temperature is possible by means of mechanical activation in a high-energy ball-milling process of a ZnO—Fe<sub>2</sub>O<sub>3</sub> mixture (mechanosynthesis). The surface structure of mechanosynthesized zinc ferrite corresponds to the inverse spinel structure type. The structure of inverse spinel type is also created by means of mechanical activation of zinc ferrite of the normal spinel type.

The investigation of regenerable sorbents for the desulfurization of hot coal gases is an important task in the field of material science in connection with the development of environmentally friendly techniques of power generation from coal.

Basically, metal oxides as ZnO, Fe<sub>2</sub>O<sub>3</sub>, CuO, SnO<sub>2</sub> are suitable as sorbents for H<sub>2</sub>S forming sulfides. The sorbents can be regenerated with O<sub>2</sub>—N<sub>2</sub> mixtures which may contain also water vapour, at likewise high temperatures. The most frequently investigated sorbent for H<sub>2</sub>S is ZnO. The use of ZnO is limited to gas temperatures lower than 900 K, because the rate of sublimation of ZnO strongly increases at higher temperatures. The undesirable loss of ZnO may be prevented to a larger extent, if mixed oxides are used instead of pure ZnO. Mixed oxides of ZnO and TiO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub> are proved to be universally usable. TiO<sub>2</sub> does not react with the components of the coal gas, but Fe<sub>2</sub>O<sub>3</sub> reacts. Both substances bind ZnO and decrease its sublimation rate.

The system ZnO—TiO<sub>2</sub> is of interest because of the possible formation of three double oxides of different stoichiometries (Zn<sub>2</sub>TiO<sub>4</sub>, ZnTiO<sub>3</sub>, Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub>) and different TiO<sub>2</sub> modifications as well.

Dulin and Rase [1] estimated the phase diagram ZnO—TiO<sub>2</sub>, where above about 870 K the compounds

Zn<sub>2</sub>TiO<sub>4</sub> and ZnTiO<sub>3</sub> are thermodynamically stable. Above 1220 K the authors detected the decomposition of ZnTiO<sub>3</sub> to Zn<sub>2</sub>TiO<sub>4</sub> and TiO<sub>2</sub> rutile.

The existence of the metastable compound Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub> was shown for the first time by Bartram and Slepetyts [2] and they proposed a structure derived from the spinel type. By Wallis [3, 4] a new type of a defect spinel was derived. The crystal structure of Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub> can be described with a cubic close packing of oxygen ions with completely occupied tetrahedral sites (Zn<sup>2+</sup> ions) and not completely occupied octahedral sites. The unoccupied octahedral sites are not arranged statistically, but they are ordered in the structure. This order leads to the decrease of the space group symmetry from Fd-3m to P4<sub>3</sub>32.

The aim of this part of the contribution is to investigate the relation between the microstructure and the kind of the compounds in the system ZnO—TiO<sub>2</sub> and to investigate the surface structure of Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub>.

The structure and properties of zinc ferrite, ZnFe<sub>2</sub>O<sub>4</sub>, as a result of mechanical activation in ball mills and of the thermal relaxation have been studied in previous works [5, 6]. The mechanically induced reactivity of zinc ferrite was clarified in [7, 8]. The novel synthesis pathway (mechanosynthesis) to zinc ferrite of ZnO—Fe<sub>2</sub>O<sub>3</sub> mixtures is described in [9].

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The part devoted to zinc ferrite in this paper focuses on the surface structure of mechanically activated as well as mechanosynthesized zinc ferrite.

## EXPERIMENTAL

For the preparation of zinc ferrite two synthetic routes were used, a conventional thermal method as well as a high-energy ball milling. Stoichiometric mixtures of powdered reactants (products of Merck) were used as starting materials.

The experiments were carried out with powdered oxides of different particle sizes and specific surface areas  $s(\text{TiO}_2)/(\text{m}^2 \text{ g}^{-1})$ : 9, 30, and 50;  $s(\text{ZnO})/(\text{m}^2 \text{ g}^{-1})$ : 3 and 70. The  $\text{TiO}_2$  powders consisted of rutile or anatase or mixtures of both phases. The powdered oxides were mixed in ball mills with mole ratios  $n(\text{ZnO})/n(\text{TiO}_2) = x_n = 2/1, 1/1, \text{ and } 2/3$ .

The milling process for the mechanical activation of crystalline zinc ferrite as well as the mechanosynthesis to zinc ferrite of  $\text{ZnO}-\text{Fe}_2\text{O}_3$  powder mixtures was carried out in a planetary ball mill AGO 2 (Institute of Solid State Chemistry, Novosibirsk). A stainless steel vial ( $150 \text{ cm}^3$  in volume) and balls of 5 mm in diameter were used. The ball-to-powder mass ratio was 20:1. The milling was done in air.

The courses of the phase formations were investigated by temperature-dependent X-ray diffraction (XRD) methods. The initial stage of the solid state reactions was detected by *in situ* XRD measurements.

X-Ray diffraction patterns were collected using a URD 6 diffractometer (Seifert-FPM, Germany), a STADI P (Stoe, Germany), and a Guinier-Lenné camera (Nonius, The Netherlands). The radiations were  $\text{CuK}\alpha$  and  $\text{CoK}\alpha$ . Data interpretation was carried out using the database of the JCPDS with software by Stoe.

The surface analytical studies were performed by an ESCALAB 220iXL spectrometer (Fisons Instruments, Great Britain) consisting of two vacuum chambers: the analyzer and the fast entry air lock/preparation chamber. The powdered samples were fixed on a carbon tape (carbon conductive tape, Pelco International) at the top of the sample holder and transferred into the UHV. The X-ray source was monochromatic  $\text{AlK}\alpha$  radiation (1486.6 eV) with an input power of 300 W. The emerging charge of the sample was equalized with the installed charge compensation. The final peak position was determined using the C1s peak (shifted to 285.0 eV) corresponding to absorbed carbon species. The XPS measurements were performed at a constant pass energy of 25 eV. The ESCALAB was calibrated routinely with the appropriate XPS lines of Au, Ag, and Cu as given in Ref. [10].

After background correction according to [11] the XPS spectra were described and the correct peak positions were determined by Gaussian—Lorentzian peaks

if necessary with a tail function to take care of the asymmetry of the XPS signal of transition elements [12]. The information depth of these surface studies was estimated by the mean free path of electrons in solid state with approximately 7.5 nm.

## RESULTS AND DISCUSSION

### Formation of Zn-Ti-Double Oxides and Surface Structure of $\text{Zn}_2\text{Ti}_3\text{O}_8$

At temperatures below 1220 K mixtures of  $\text{Zn}_2\text{TiO}_4$ ,  $\text{ZnTiO}_3$  or  $\text{Zn}_2\text{Ti}_3\text{O}_8$  are formed from  $\text{ZnO}$

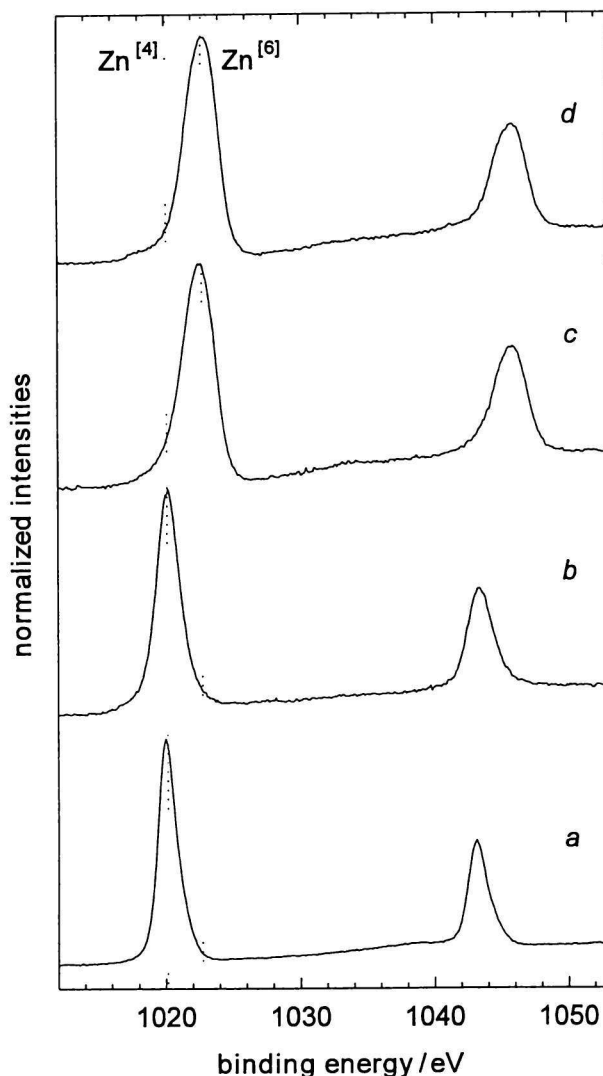
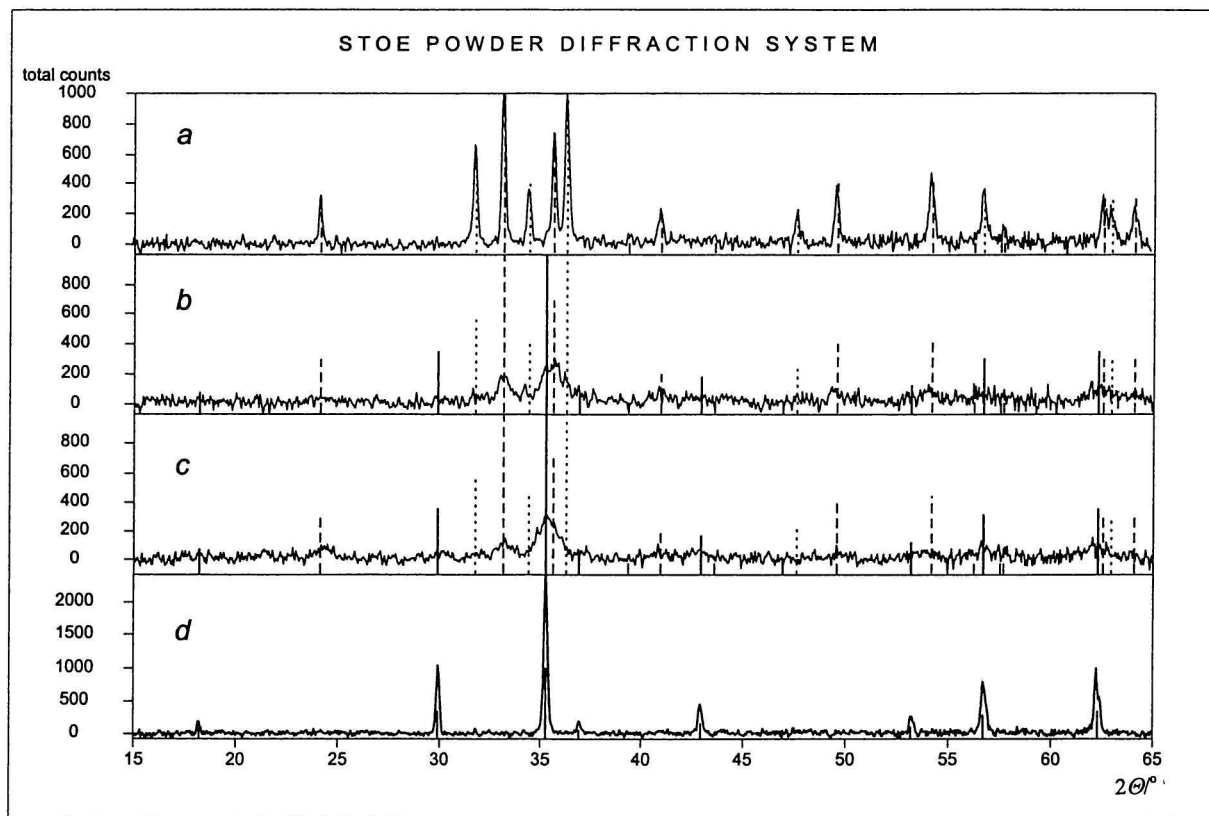


Fig. 1. Photoelectron spectra of model substances with zinc in tetrahedral and octahedral coordination. a)  $\text{ZnO}$  (Zn tetrahedrally coordinated), b)  $\text{Zn}_2\text{Ti}_3\text{O}_8$  (Zn tetrahedrally coordinated), c)  $\text{ZnTiO}_3$  (Zn octahedrally coordinated), d)  $\text{Zn}_2\text{TiO}_4$  (Zn octahedrally coordinated).  $\text{Zn}^{[4]}$  = Zn tetrahedrally coordinated,  $\text{Zn}^{[6]}$  = Zn octahedrally coordinated.



**Fig. 2.** XRD patterns of the ZnO—Fe<sub>2</sub>O<sub>3</sub> mixtures. The intensity in total counts in dependence on  $2\theta/^\circ$ . XRD patterns generated by URD 6 diffractometer with CuK $\alpha$  radiation, XRD diagram created by Stoe software. *a*) Unmilled, *b*) ball-milled for 8 min, *c*) ball-milled for 18 min, *d*) ball-milled for 18 min followed by the thermal treatment (400 min at 1100 K). Fe<sub>2</sub>O<sub>3</sub>, ZnO, — ZnFe<sub>2</sub>O<sub>4</sub>.

and TiO<sub>2</sub> as a result of solid state reactions. The formation of double oxides takes place in the temperature range between 870—1220 K. That temperature at which the solid state reaction starts decreases with an enlargement of the specific surface areas and a decrease of the particle sizes. The lowest temperatures are obtained with nanocrystalline powders and very homogeneous mixtures.

Compound Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub> originates only from the Zn<sub>2</sub>TiO<sub>4</sub> phase. The double oxide formation with ZnO is overlapped by the transformation of the modification anatase → rutile taking place in the temperature range between 800—1100 K. The speed of transformation depends on the temperature and the particle size of the anatase powder.

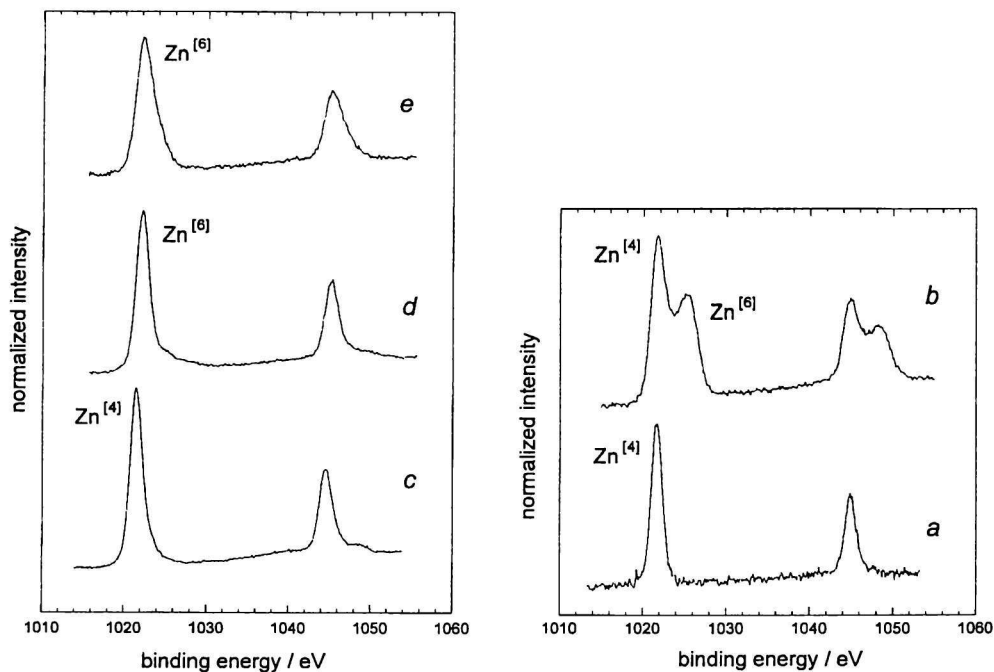
There are correlations between the TiO<sub>2</sub> modification and the formation of certain titanium-zinc-double oxides. The formation of Zn<sub>2</sub>TiO<sub>4</sub> and Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub> is confined only in the presence of anatase, while ZnTiO<sub>3</sub> is only formed in the presence of rutile. Between TiO<sub>2</sub> anatase and Zn<sub>2</sub>TiO<sub>4</sub>, or Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub> on the one hand and TiO<sub>2</sub> rutile and ZnTiO<sub>3</sub> on the other, structural similarities could be demonstrated. The symmetries of packing of the oxygen ions (cubic close packing and hexagonal close packing) show already fundamental

relationships between the structures of anatase and Zn<sub>2</sub>TiO<sub>4</sub>, or Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub> as well as rutile and ZnTiO<sub>3</sub> (ilmenite). The structures of TiO<sub>2</sub>, Zn<sub>2</sub>TiO<sub>4</sub>, and ZnTiO<sub>3</sub> consist of TiO<sub>6</sub> octahedra which are connected over common edges. In rutile and in ZnTiO<sub>3</sub> the connection of the TiO<sub>6</sub> octahedra leads to chains and/or layers, but in anatase and in spinel (Zn<sub>2</sub>TiO<sub>4</sub> and Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub>) to three-dimensional frameworks.

Fig. 1*b* shows the photoelectron spectroscopic surface studies of Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub> in comparison to ZnO, Fig. 1*a*, ZnTiO<sub>3</sub>, Fig. 1*c*, and Zn<sub>2</sub>TiO<sub>4</sub>, Fig. 1*d*. It is known that the Zn<sup>2+</sup> ions occupy in ZnO only tetrahedral sites and in ZnTiO<sub>3</sub> and Zn<sub>2</sub>TiO<sub>4</sub> octahedral sites. The Zn<sup>2+</sup> ions in Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub> have the same peak position and structure of the Zn 2p<sub>3/2</sub> signal like the well known ZnO with zinc only in tetrahedral positions. This is another indication of the tetrahedral coordination of zinc in the defect spinel structure of Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub> [3, 4].

#### Formation and Surface Structure of Zn Ferrite

ZnFe<sub>2</sub>O<sub>4</sub> is formed in ZnO—Fe<sub>2</sub>O<sub>3</sub> mixtures at temperatures above 1100 K. Results of the investigation of the influence of mechanical activation of ZnO—



**Fig. 3.** Photoelectron spectra of ZnO—Fe<sub>2</sub>O<sub>3</sub> mixtures and of zinc ferrite. *a*) ZnFe<sub>2</sub>O<sub>4</sub>, normal spinel structure, *b*) ZnFe<sub>2</sub>O<sub>4</sub>, inverse spinel structure, created by mechanical activation (18 min) of ZnFe<sub>2</sub>O<sub>4</sub> with normal spinel structure [5, 6], *c*) ZnO—Fe<sub>2</sub>O<sub>3</sub>,  $x_n = 1:1$ , nonmechanically activated, *d*) ZnO—Fe<sub>2</sub>O<sub>3</sub>,  $x_n = 1:1$ , 8 min activated, *e*) ZnO—Fe<sub>2</sub>O<sub>3</sub>,  $x_n = 1:1$ , 18 min activated. Zn<sup>[4]</sup> = Zn tetrahedrally coordinated, Zn<sup>[6]</sup> = Zn octahedrally coordinated.

Fe<sub>2</sub>O<sub>3</sub> mixtures on the formation of zinc ferrite have shown that it is possible to achieve the mechano-synthesis of zinc ferrite (from zinc oxide and iron oxide powders) at room temperature in a planetary mill [9].

Before milling the size of the powder particles of the Fe<sub>2</sub>O<sub>3</sub>—ZnO mixture varies from 10 μm to 50 μm. After a relative short time of milling (8 min) the material consists of agglomerates of many small particles (1—3 μm) with a rounded shape. With further milling the powders become much finer and uniform in shape with an average particle size of about 1 μm.

XRD pattern (Fig. 2*a*) of the starting powder is characterized by the sharp crystalline peaks corresponding to ZnO (JCPDS 36-1451) and α-Fe<sub>2</sub>O<sub>3</sub> (JCPDS 33-664). During the early stages of milling XRD reveals only a decrease of the intensity and an associated broadening of the Bragg peaks of the individual oxides.

With increasing milling time, the weak diffraction lines of both phases completely disappear and the strongest diffraction lines gradually merge together producing two broad peaks and new peaks of ZnFe<sub>2</sub>O<sub>4</sub> (JCPDS 22-1012) are formed (Fig. 2*b, c*). The results of Mössbauer spectroscopy give an additional confirmation on the formation of ZnFe<sub>2</sub>O<sub>4</sub> during the mechanical activation of the oxides at room temperature [9]. Fig. 2*d* shows for comparison the XRD diagram of crystalline zinc ferrite.

Under standard conditions zinc ferrite forms the

structure of a normal spinel with zinc in the tetrahedral sites and iron in the octahedral sites of a cubic close packing of oxygen atoms Zn<sup>[4]</sup>Fe<sup>[6]</sup><sub>2</sub>O<sub>4</sub>, shown in Fig. 3*a*. It is the same peak position like the tetrahedrally coordinated zinc in ZnO (Fig. 1*a*). The mechanical activation leads to a change of the normal spinel structure to the inverse spinel structure [5] with zinc in octahedral sites and iron in tetrahedral and octahedral sites of the cubic close packing oxygen matrix Zn<sup>[6]</sup>Fe<sup>[4,6]</sup><sub>2</sub>O<sub>4</sub>.

The mechanoactivated zinc ferrite has a disordered structural state. The ESCA investigation of mechanoactivated zinc ferrite (Fig. 3*b*) indicates that there are two signals. One is the signal with the same peak position like the tetrahedrally coordinated zinc in ZnO (Fig. 1*a*) or in normal zinc ferrite (Fig. 3*a*) and an additional peak is that with the same position like the octahedrally coordinated zinc in ZnTiO<sub>3</sub> or in Zn<sub>2</sub>TiO<sub>4</sub> (Fig. 1*c, d*). Zn<sup>2+</sup> ions in mechanically activated zinc ferrite are tetrahedrally and octahedrally coordinated. This means that a part of the surface structure (< 7.5 nm) of the mechanically activated zinc ferrite corresponds already to the structure of the inverse spinel.

The mechanical activation of a mixture of zinc oxide and iron(III) oxide shown in Fig. 3*c—e* leads to the same result of the surface analytical studies like the mechanical activation of the normal spinel of ZnFe<sub>2</sub>O<sub>4</sub> and of the coordination sphere of zinc. In the oxide

mixture (Fig. 3c) zinc is tetrahedrally coordinated, but in the mechanically activated mixture the  $Zn^{2+}$  ions occupy octahedral positions (Fig. 3d, e). Zinc is octahedrally coordinated in mechanosynthesized zinc ferrite. This means that also the surface structure of mechanosynthesized zinc ferrite corresponds to the inverse spinel type.

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