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Mixed Metal Oxides of the Type $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ as Photocatalysts for Malachite Green Degradation Under UV Light Irradiation

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Abstract

A combination of thermal and mechanical (high energy ball milling) treatment was applied in an attempt to obtain polycrystalline mixed metal binary and ternary oxides of the type $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0; 0.25; 0.5; 0.75; 1$). The synthetic procedure used successfully produced single-phased, homogeneous ZnFe_2O_4 , CoFe_2O_4 , and $\text{Co}_{0.75}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$, as well as mixed oxides, whose composition depended both on the duration of the high energy ball milling and the ratio Zn(II)/Co(II) . The formation of spinel-like structures was proved by XRD, Mössbauer spectroscopy and Raman spectroscopy. For the characterization of the samples low-temperature N_2 adsorption, UV/Vis spectroscopy and transmission electron microscopy were applied. The energy band gap of the samples was calculated, suggesting they are promising photocatalysts. The decomposition of the Malachite Green in model water solutions under UV-light irradiation was successfully achieved in the presence of the samples as photocatalysts. The highest rate constant was obtained for the sample synthesized at longer milling time in combination with higher Zn(II)/Co(II) ratio. The photocatalytic activity of the ternary mixed oxides was compared with the pure hematite, $\alpha\text{-Fe}_2\text{O}_3$, and the binary ZnFe_2O_4 and CoFe_2O_4 ferrites with spinel structure that were treated in the same way. A synergetic effect of $\alpha\text{-Fe}_2\text{O}_3$ and the spinel-like structure on the photocatalytic properties of ternary mixed metal oxides was detected.

Keywords: ferrites; mechanoactivation, Mossbauer spectroscopy; powder diffraction, photocatalysis, malachite green

1. Introduction

Ferrites with spinel-like structure with the formula MFe_2O_4 , where M represents a divalent metal ion, are technologically important and have been used in many applications including magnetic recording media and magnetic fluids for the storage and/or retrieval of information, magnetic resonance imaging enhancement, catalysis, magnetically guided drug delivery, sensors, pigments, etc.^{1–3}

Among all the properties they possess, ferrites offer the advantage of having a band gap capable of absorbing ultra violet and visible light. Ferrites with spinel-like structure prepared through solid state reaction have been used for photocatalytic hydrogen generation.⁴ The spinel crystal structure enhances the efficiency of light absorption due to the available extra sites in the crystal lattice.⁵ Some organic molecules have been decomposed under UV irradiation in the presence of different spinels as pho-

tocatalysts, such as methyl orange by BaFe_2O_4 ,⁶ phenolphthalein by $\text{CoFe}_2\text{O}_4\text{-ZnO}$,⁷ rhodamine B by $\text{Ag/ZnFe}_2\text{O}_4$ nanocomposites,⁸ and methylene blue by $\text{Zn-Fe}_2\text{O}_4$ nanorods.⁹ There are not many data available for CoFe_2O_4 used as a photocatalyst, but it has been used for decomposition of H_2O_2 .¹⁰ The testing of ferrites as photocatalysts for degradation of inorganics, bacteria as well as organic molecules such as methylene blue, methyl orange and rhodamine B has been summarized,¹¹ but no data are available for malachite green degradation. Malachite Green, MG, is a water-soluble azo dye that is widely used in research laboratories and in the textile, pharmaceutical and food industries. It appears in waste waters, so the water need treatment and purification.

Among the spinel ferrites, ZnFe_2O_4 has significant absorbance in the 450–700 nm wavelength range.¹² It is regarded as a promising photocatalyst with a band gap of 1.92 eV (646 nm), which makes it possible to utilize solar energy.^{11,12} Possessing photochemical stability and low toxicity, ZnFe_2O_4 has been applied to degrade organic pollutants,^{13,14} modified by multiwall carbon nanotubes,¹⁵ by SrTiO_3 ,¹⁶ by TiO_2 ,^{15,17,18} etc. In those cases no energy band gaps have been calculated, but it can be expected that the modification influences the energy band gap of the samples: for example, for bulk CoFe_2O_4 , the band gap was found to be 2.7 eV,^{4,19} while for modified nanostructure $\text{CoFe}_2\text{O}_4/\text{ZnO}$ it was found to be 4.5 eV.⁷ One can therefore expect that polycrystalline mixed metal ternary oxides of the type $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ will have energy band gaps different from that of pure CoFe_2O_4 and ZnFe_2O_4 and therefore can have different photocatalytic activities for malachite green degradation.

Different methods for synthesis of ferrites have been developed, among them co-precipitation and sol-gel techniques. These usually result in large particles and a broad size distribution.^{17,20,21} A combination of mechanical and thermal treatment is often used in a procedure that includes several steps. Mechanical treatment with a ball milling technique has been applied to synthesize Ni-Zn ferrite from initial mixtures of NiO, ZnO and Fe_2O_3 ,^{22,23} while polycrystalline $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ was prepared by mechanical alloying of stoichiometric mixtures of MnO ²⁴ or MnO_2 ²⁵ and ZnO and Fe_2O_3 powders. Variations of the mechanical treatment method include the duration of the pre-heating process as well as the number and the duration of heating steps to anneal after the mechanical treatment. The annealing of a milled powder is usually applied to reduce the lattice defects and strains and to improve the magnetic properties of the ferrites (internal strain has a negative effect on the magnetic properties).^{24,26} The annealing includes heating at a constant rate and isothermal holding, followed by cooling down to room temperature. The milled powders can be annealed at different temperatures to obtain a single-phase powder.¹⁷ During the ball milling, crystal defects can be created so they might have various life times and different natures. The crystal

defects influence the properties of oxides such as electrical,^{27,28,29} magnetic³⁰ and optical,³¹ and may act both as a source and as a trap of electrons. In the synthetic procedure applied in the work presented, we tried to preserve the potential defects formed by first pre-grinding the oxides in order to mix them carefully, then calcining them at high temperature and finally ball milling them in order to stimulate crystal defects in the structure. The later should be preserved if further annealing is not applied.

Shortly, in the work presented, by a two-step procedure combining high temperature treatment and mechanical treatment, polycrystalline binary and ternary mixed metal oxides were synthesized and characterized. The photocatalytic decomposition of Malachite Green under UV irradiation in model water solutions in the presence of the samples obtained was tested. By this an attempt was made to evaluate the application of the synthesized catalysts. Ferrites are seldom used for the decomposition of Malachite Green, so the results obtained increase the range of photocatalysts that can be used for degradation of this dye.

2. Experimental

2. 1. Materials and Synthetic Procedure

The initial materials used were hematite, $\alpha\text{-Fe}_2\text{O}_3$ (>99%, p.a.), ZnO (>99%, p.a.) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (p. a.) (all Alfa Aesar). Cobalt nitrate was used to produce CoO after calcination at 900 °C for 5 hours. The synthetic procedure for the samples used in the work included calcination at 900 °C for 5 h and then milling for two different periods of time (4 or 8 hours). A high energy ball mill (Pulverisette 7, Fritsch) with zirconium oxide vials and balls was used. The milling intensity was 600 rpm and the ball-to-milled powder ratio was 8:1. By treating in the same way the commercial hematite $\alpha\text{-Fe}_2\text{O}_3$, three different samples were obtained, namely Fe-TS, Fe-4MA and Fe-8MA, where TS is the symbol for the calcined sample and it comes from Thermal Synthesis, MA presents the treatment by milling at 4 or 8 hours, respectively and it means MechanoActivated sample. The *binary* mixed metal oxides ZnFe_2O_4 ($\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ where $x = 0$) and CoFe_2O_4 ($\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ where $x = 1$) were synthesized in two steps. In the first step, the stoichiometric mixture of the oxides was hand-grinded for 30 min to ensure complete homogenization, and then compacted to disks 50 mm in diameter and 1–2 mm thick and finally sintered at 900 °C for 5h. In the second step, the as prepared samples were milled for 4h. For the powders obtained, the symbols ZFO-TS, ZFO-4MA, CFO-TS and CFO-4MA, respectively (TS and MA as mentioned above) are used, where ZFO is for Zinc Ferrite Oxide and CFO for Cobalt Ferrite Oxide. The synthetic procedure for *ternary mixed metal oxides* included the same two steps, and the samples produced can be presented by the stoichiometric formula $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ where $x = 0.25; 0.5; 0.75$ and denoted as

ZC31/4, ZC11/4 and ZC13/4 after 4h milling and ZC31/8, ZC11/8 and ZC13/8 after 8h milling where ZC is for Zinc-Cobalt ferrite. The mole ratio of the ions Zn(II)/Co(II) (3:1, 1:1, 1:3) as well as the duration of the milling (4 or 8 hours) are mentioned in the symbols by 31/4, 11/4, 11/4 and 31/8, 11/8, 11/8.

2. 2. Methods for Characterization of the Samples

X-ray powder diffraction (XRD) patterns for phase identification were recorded in the angle interval 10–80° (2 θ), on a Philips PW 1050 diffractometer, equipped with a Cu K α tube and a scintillation detector. Data for cell refinements were collected in θ –2 θ , step-scan mode in the angle interval from 25 to 70° (2 θ), at steps of 0.04° (2 θ) and a counting time of 1 s/step. The cell refinement analysis was carried out in BRASS (Bremen Rietveld Analysis and Structure Suite).³²

Internal strain of the samples was estimated by analysis of XRD peaks using the Williamson-Hall formula³³ $(\beta/2)\cot\theta = 0.45\lambda/(\sin\theta D) + \epsilon$, where β is the peak width at half maximum, θ is the Bragg diffraction angle, λ is the X-ray wavelength, D is the average crystallite size and ϵ is the value of the strain.

Mössbauer spectra were recorded with an electro-mechanical spectrometer (Wissenschaftliche Elektronik GmbH) in constant acceleration mode at room temperature. The source of radiation is ⁵⁷Co/Rh (activity $\approx$ 50 mCi) and standard α -Fe. The recorded spectra were used for calculations using software working with the method of least squares. The following parameters of the hyperfine interactions were calculated: isomer shift (IS), quadrupole splitting (QS), effective inner magnetic field in the site of iron nuclei (H_{eff}), as well as the full width at half maximum (FWHM) and relative weights (G) of the components.

The texture characteristics were determined by low-temperature (77.4 K) nitrogen adsorption using a Quantachrome Instruments NOVA 1200e apparatus. The specific surface area (S_{BET}) was calculated using the Brunauer–Emmett–Teller (BET) surface area method.

Raman spectroscopy – The measurements were carried out in a HORIBA Jobin Yvon Labram HR 800 micro-Raman spectrometer with a He–Ne (633nm) laser, the absolute measurement accuracy being 0.5 cm^{–1} or better.

UV-VIS absorption spectroscopy – an Evolution 300 UV-Vis spectrometer (Thermo Scientific) was used for measuring the absorption of the samples in the range 200–900 nm.

Transmission electron microscopy (HRTEM) was done using a JEM 2100 (JEOL), with an accelerator voltage of 200 kV and up to 1 500 000 times magnification, to follow the morphology of the samples.

Band gap energy calculations. The optical properties (absorption and optical band gap energy) of the sam-

ples were studied using UV-Vis absorption spectra. In all cases broad absorption was registered in the 300–900 nm range of the spectra. The UV-Vis data were analysed for the relation between the optical band gap, absorption coefficient and energy ($h\nu$) of the incident photon for near edge optical absorption in semiconductors. The band gap energy was calculated from the measured curves by fits according to Tauc's equation³⁴ $\alpha h\nu = A(h\nu - E_g)^n$, where A is a constant independent of $h\nu$, E_g is the semiconductor band gap and n depends on the type of transition. In addition, the well-known approach for semiconductor band gap energy determination from the intersection of linear fits of $(\alpha h\nu)^{1/n}$ versus $h\nu$ on the x-axis was used, n being 1/2 and 2 for direct and indirect band gap, respectively.

2. 3. Photocatalytic Activity

The photocatalytic tests were performed in a slurry (1 g catalyst/l), using a 10^{–5} M aqueous solution of Malachite Green oxalate (Chroma GmbH) as a model pollutant. After a 30-min “dark” period (in order to establish the equilibrium of the sorption process), the system was UV-illuminated by a lamp (Sylvania 18 W BLB T8, emission in the 345–400-nm region with a maximum at 365 nm), situated at 9.5 cm distance above the slurry (illumination intensity 0.5 W/m²), under continuous magnetic stirring (400 min^{–1}) and bubbling with air (45 L/h). The initial pH of the solutions were between 5.8 and 5.9. Periodically, a 5-ml aliquot was taken from the solution and filtered through a 0.20- μ Minisart filter. The dye concentration was determined spectrophotometrically using the band at 622 nm. The data obtained were plotted in coordinates $(C/C_0)/t$ and $-\ln(C/C_0)/t$ (where C_0 is the concentration after the “dark” period, and C is the concentration after t min irradiation), and apparent rate constants of the degradation process were determined assuming first-order kinetics. The sorption capacity was calculated as the ratio $(C_{00}-C_0)/C_{00}$, where C_{00} is the starting solution concentration (before the “dark” period). The malachite green degradation at moment t is determined by the formula: degradation, % = $(A_0 - A_t)/A_0 \times 100$, where A_0 is the initial absorption of the malachite green solution at moment $t = 0$ min, and A_t is the absorption at moment t min.

3. Results

3. 1.Characterization of the Samples

3. 1. 1. Phase Composition and Crystal Structure of the Hematite and the Binary Mixed Oxides With Spinel-like Structure (ferrites).

The XRD patterns of the samples Fe-TS, Fe-4MA, Fe-8MA (Figure S1), those of the binary metal oxides ZF-TS, ZF-4MA (Figure S2, *a*), and CF-TS and CF-4MA

(Figure S2, *b*) reveal a single phase without detectable secondary phase (within the limit of X-ray detection, typically 5 %). The calculated unit cell parameters are in good agreement with the data from the crystallographic databases (ZFO 8.4430 Å, ICSD 98-002-8511; CFO 8.3550 Å, ICSD 98-018-4063) (Table 1). The data for the crystallite sizes for ZF-4MA and CF-4MA are close and are similar to those for the ternary oxides milled for 4h (Table 1). For CF-TS and CF-4MA, the unit cell parameters slightly decrease with the milling time, although they are bigger in comparison with the literature data (CFO 8.3550 Å, ICSD 98-018-4063). The intensity of the reflexes is slightly higher for the TS (only calcined) samples compared with those for the MA (calcined and milled) samples (Figure S2). With increasing milling time, the unit cell parameters and the crystallites size decrease for both the zinc and cobalt ferrites, while the lattice distortion increases. An inducing of cation redistribution in spinel ferrites by the high energy ball milling^{35,36} as well as contraction of the lattice caused by lattice defects³⁵ have been pointed out as probable reasons for reduction of lattice parameters.

The experimental Mössbauer spectra of the samples ZF-TS and ZF-MA analysed contain a typical doublet spectrum for the spinel ferrite paramagnetic phase (Figure S3 *a, b*). The experimental Mössbauer spectra of CF-TS and CF-MA include only components expressing super-fine magnetic structure i.e. sextets (Figure S3 *c, d*) that correspond to tetrahedral and octahedral sites of Fe³⁺, indicating the inverse spinel structure of CoFe₂O₄ at ambient temperature (the inverse spinel structure of CoFe₂O₄ has oxygen atoms which make up an fcc lattice, with half of the Fe³⁺ ions occupying the tetrahedral A sites and the other half, together with the Co²⁺ ions located at the octahedral B sites³⁷). The third component (Sextet-3) is likely

due to the presence of ferrite spinel particles having a smaller size. So far the analysis confirms that the synthetic procedure used resulted in CoFe₂O₄ and ZnFe₂O₄ binary mixed metal oxides with spinel structure both after calcination only and after a combination of calcination and milling for 4 hours.

3. 1. 2. Phase Composition and Crystal Structure of Ternary Mixed Metal Oxides

The XRD patterns of the mixed oxides show single phases of well crystallized Co_xZn_{1-x}Fe₂O₄ (*x* = 0.25; 0.5; 0.75) (Figure 1). The longer milling time is the reason for the weak amorphous halo in the XRD of the samples ZC11/8 and ZC13/8. The calculated unit cell parameters are smaller than those for pure ZnFe₂O₄ and bigger than those for pure CoFe₂O₄, compared both with the literature data and with the samples synthesized by us. The uncertainty of the calculations for 8h-milled samples is high due to the smaller size of the crystallites, which leads to higher full width at half maximum (FWHM) values.

The results of the Rietveld analysis are summarized in Table 1. The shape factor used for determination of the crystallite size with the Scherrer formula is 1. The samples milled for 4h have bigger crystallite sizes (almost double the size of 8h-milled samples). The tendency in the decrease of the cell parameters with decrease of the ratio Zn(II)/Co(II) is analogous to reported data (8.4210 Å for Zn/Co = 0.6/0.4: (ICSD 98-016-6203); 8.4120 Å for Zn/Co = 0.4/0.6: (ICSD 98-016-6202)).

The Mössbauer spectra of the powdered samples are a result of a superposition of lines of components without resolved hyperfine magnetic structure i.e. *quadruple doublets* and components with expressed superfine magnetic structure, i.e. *sextets* (Figure 2). The models for

Figure 1. XRD patterns of the samples, from bottom to top (a) ZC31/4, ZC11/4, ZC13/4 and (b) ZC31/8, ZC11/8, ZC13/8, respectively.

Table 1. Unit cell parameter (a_0), average crystallite size (D) and lattice strain (ϵ).

Sample	a_0 (Å)	D , nm	ϵ , $\times 10^{-3}$, a.u.
Fe-TS	$a = 5.0352 \pm 0.0001$ $c = 13.7440 \pm 0.0001$	76.3 ± 2.7	0.006
Fe-4MA	$a = 5.0334 \pm 0.0002$ $c = 13.6846 \pm 0.0030$	21.5 ± 0.5	1.20
Fe-8MA	$a = 5.0342 \pm 0.0001$ $c = 13.6940 \pm 0.0025$	19.8 ± 1.9	1.23
ZF-TS	8.4428 ± 0.0005	77.3 ± 0.9	1.70
ZF-4MA	8.4418 ± 0.0013	53.2 ± 0.5	1.90
CF-TS	8.3840 ± 0.0022	73.5 ± 0.2	2.05
CF-4MA	8.3827 ± 0.0031	57.9 ± 0.3	2.31
ZC31/4	8.4230 ± 0.0012	56.1 ± 0.2	1.95
ZC11/4	8.4160 ± 0.0013	57.4 ± 0.4	1.86
ZC13/4	8.4090 ± 0.0023	56.5 ± 0.3	1.96
ZC31/8	8.4260 ± 0.0025	26.3 ± 0.5	0.91
ZC11/8	8.4173 ± 0.0031	28.0 ± 0.6	1.37
ZC13/8	8.4101 ± 0.0401	24.1 ± 0.5	1.00

Mössbauer spectra processing include these two types of components i.e. two sextets and one doublet for samples ZC31/4 to ZC11/8 and two sextets for the sample ZC13/8. In the calculations, both components are included. The results are summarized in Table S1.

The five ternary mixed metal oxides ZC31/4, ZC11/4, ZC13/4, ZC31/8 and ZC11/8 have a similar composition of the three components i.e. Sx1-hematite

(17–20% of the sample), Sx2-spinel (50–55%) and a superparamagnetic component (26–33%). A possible explanation of the presence of hematite is either because of some incompletely reacted initial hematite material or because some partial destruction of the spinel phase during the milling process. The absence of reflections of hematite in the XRD patterns (Figure 1) suggests that the hematite is present as very small crystals. Taking into account

Figure 2. Mössbauer spectra of ZC31/4, ZC11/4, ZC13/4 (a) and ZC31/8, ZC11/8, ZC13/8 (b), from top to bottom.

that the oxides in the initial source system were present in stoichiometric ratios for the formation of ferrite, the presence of hematite suggests that unreacted free ZnO and CoO should also be present in the samples. The latter are not registered by XRD either because of their very small crystals (just like the hematite) or because of their low concentration.

The hyperfine parameters of the other two components in the Mossbauer spectra of samples ZC31/4, ZC11/4, ZC13/4, ZC31/8 and ZC11/8 can be attributed to the presence of a spinel phase. Its relatively small particle size gives rise to an incompletely resolved magnetic structure. A bidisperse particle size distribution is evidenced by both sextet and doublet components of bigger particles with collective magnetic excitations behaviour and smaller spinel particles with completely collapsed magnetic structures due to thermally activated reversals of particle magnetisation moments³⁸. The lower than typical values of H_{eff} of the crystalline spinel phases may also be a result of the mixed nature of the spinel component. The described composition of the samples from ZC31/4 to ZC11/8 can be explained with their heterogeneity. Sample ZC13/8 has a different spectrum, consisting of two sextets of a spinel phase i.e. Sx1 that includes Fe^{3+} ions in tetrahedral coordination and Sx2 with Fe^{3+} ions in octahedral coordination.

The spinel-like structure of the sample ZC13/8 shown to be homogeneous by Mössbauer spectrum is confirmed by its Raman spectrum (150–1200 cm^{-1}) (Figure 3), which shows clear bands at 468, 612 and 682 cm^{-1} . According to the literature, both Raman modes at 612 and 682 cm^{-1} are reflecting the local lattice effect in the tetrahedral sublattice, while the peak at 468 cm^{-1} is probing the local lattice effect in the octahedral sublattice.^{39,40} The

same Raman bands mentioned above as well as additional bands at 222 cm^{-1} and 286 cm^{-1} can be seen in samples ZC31/4 to ZC11/8; these additional bands can be assigned to $\alpha\text{-Fe}_2\text{O}_3$, which has very intense bands at these positions, shown in the Figure 3 for convenience. The Raman data thus confirm the observed significant difference between sample ZC13/8 and samples ZC31/4 to ZC11/8 by Mossbauer spectroscopy, i.e. the presence of $\alpha\text{-Fe}_2\text{O}_3$. The broadening and the asymmetry of the Raman peaks may be related to a high degree of cation disorder induced by the milling.⁴¹ No ZnO and CoO are detected as separate phases in the Raman spectra of the samples (no distortion of the lattice cell was observed by XRD either). No peaks induced by CoO could be detected according to literature.⁴²

3. 1. 3. The Lattice Strain

The influence of the milling on the samples can be evaluated by the lattice strain data. From the data of Table 1, it appears that for the *individual oxide Fe-TS* the annealing at 900 °C causes the biggest relaxation, as the lattice strain observed is insignificant. The milling for 4h leads to a distortion and introduces point defects, but the further milling for 8h does not change crystallites size and the lattice strain. For the *binary oxides* the decrease of the crystallites size leads to higher values of the lattice strain. Between pure CF and ZF, CF shows the higher lattice strain. A possible reason could be the inverse spinel structure of CoFe_2O_4 at ambient temperature, as proved by Mossbauer spectroscopy (Table S1). For the *ternary oxides* the shorter milling time (4 h) causes bigger lattice strain than the longer 8 h. The fact that the samples contain three metal cations, with different ratio Zn(II)/Co(II) and a more complicated heterogeneous phase composition makes the interpretation of the values for these samples complicated. In conclusion, the milling introduces energy in the system, which partially dissipates but partially causes point defects i.e. lattice strain.

3. 2. Optical Properties and Band Gap Energy Calculation

The absorbance in the UV/Vis range (450–700 nm, spectra not shown here) showed a clear maximum at around 400 nm and a weaker band at around 750 nm. Based on these data, the band gap energy, E_g , was determined after plotting α/E , where α is the absorption coefficient. Examples for ZC31/4 are shown in the range of direct and indirect transitions (Figure 4 a, b).

The crossing point with the x-axis was found after applying different analyses.³⁴ For the direct transition, α^2/E was plotted against energy and the linear part of the graph was extrapolated to zero where a value of 1.83 eV was obtained; for the indirect transition, $\alpha^{1/2}/E$ was plotted against energy and in a similar way, a value of 1.3 eV was

Figure 3. Raman spectra of the samples ZC31/4, ZC11/4, ZC13/4, ZC31/8, ZC11/8, ZC13/8 compared with the spectra of pure hematite and ZnO.

Figure 3. Raman spectra of the samples ZC31/4, ZC11/4, ZC13/4, ZC31/8, ZC11/8, ZC13/8 compared with the spectra of pure hematite and ZnO.

found. Similar graphs were obtained for ZC11/4, ZC13/4, ZC31/8, and ZC11/8. However, the data for ZC13/8 are different from the other samples and a linear fit is obtained if the expression accounting for Urbach tails for amorphous material is used, $\alpha(h\nu) \sim \exp(h\nu/E_u)$.⁴³ The fit gives one linear part of the graph and a value of 1.3 eV was obtained by extrapolation of the straight section to the x-axis (Figure 4, c). This model accounts for static disorder in amorphous solids. The fact that sample ZC13/8 has the smallest particle size of all samples (24 nm, Table 1) could be the reason for the similarity of sample ZC13/8 with an amorphous sample. The band gap in the range 1.1–1.3 eV for the samples ZC31/4, ZC11/4, ZC13/4, ZC31/8, ZC11/8 (Table 2) confirms the presence of spinel phase as detected by IR (not included here), Raman and Mössbauer spectroscopy and XRD, along with mono metal oxides like hematite.

Table 2. Calculated data for E_g1 and E_g2 .

Sample	E_g1 (direct), eV	E_g2 (indirect), eV
ZC31/4	1.83	1.3
ZC11/4	1.79	1.3
ZC13/4	1.69	1.21
ZC31/8	1.68	1.22
ZC11/8	1.72	1.11
ZC13/8	–	1.3

It can be speculated that the values found for E_g1 are due to the presence of hematite, ZnO and CoO. The band gap data E_g1 (direct) for ZC31/4, ZC11/4, ZC13/4 show a clear tendency of a decrease upon substitution (according the experimental stoichiometry) by a lighter cation, i.e. Co(II). A similar observation was made for Co(II) doped ZnO,^{44,45} an increase is observed for cations such as Al(III) and Ga(III), with a larger mass difference than Zn(II) and Co(II).⁴⁶ Considering the literature data for the values of the band gap i.e. $\alpha\text{-Fe}_2\text{O}_3$ with 2.2 eV⁴⁷, ZnO with 3.77 eV¹² or

3.3 eV, according⁴⁵ ZnFe_2O_4 with 1.92 eV,^{11,12} and CoFe_2O_4 with 2.7 eV^{4,19} it is obvious that the resulting ternary oxides have lower values of the band gap than the individual components. It is an indication that the composite oxides can absorb more photons and generate more e[−]/h⁺ pairs so the photocatalytic activity can be enhanced. Similar behaviours for composite systems has been reported.⁴⁸

3. 3. Specific Surface Area (SSA), Pore Volume and Average Pore Diameter

The BET specific surface areas (Table 3) were found to be low, which is probably caused by the high temperature for calcination during the first step of the synthetic procedure. The value for $\alpha\text{-Fe}_2\text{O}_3$ calcined, Fe-TS, is the lowest among all the samples and increased with the milling time for Fe-4MA and Fe-8MA, which is to be expected. The highest observed values are those for ZF-4MA, 30 m²/g, and for CF-4MA, 21 m²/g, in agreement with expectations for higher SSA after the milling

Table 3. Specific surface area (SSA), pore volume and average pore diameter of the samples

Sample	S_{BET} , m ² /g	Pore volume, cm ³ /g	Average pore size, nm
Fe-TS	2		
Fe-4MA	8		
Fe-8MA	12		
ZF-TS	7		
ZF-4MA	30		
CF-TS	9		
CF-4MA	21		
ZC31/4	14	0.02	5.4
ZC11/4	14	0.03	8.1
ZC13/4	14	0.03	9.4
ZC31/8	12	0.02	7.4
ZC11/8	14	0.03	8.0
ZC13/8	22	0.20	32.8

Figure 5. TEM-micrographs of ZC31/4 (a), ZC31/8 (b) x100k and ZC13/8 (c) and (d), respectively at x100k and x 40k.

procedure. Among the ternary oxides the sample ZC13/8 shows a substantially higher S_{BET} than the other ternary oxides, $22 \text{ m}^2/\text{g}$.

The values for pore volume were determined only for the ternary oxide systems. It was determined from the amount of nitrogen adsorbed at the end of the isotherm at $p/p_0 = 0.98$ according to the Gurvitch rule. Nitrogen adsorption – desorption isotherms conducted at -196°C over powdered samples (Figure S4, a, b) show different shapes. The samples ZC31/4, ZC11/4, ZC13/4, ZC31/8, and ZC11/8, showed II type isotherms according to the IUPAC classification⁴⁹ (non-porous or macroporous forms which allow monolayer-multilayer adsorption to occur at high p/p_0); the H3 loop is usually assigned to aggregates of plate-like particles which possess non-rigid slit-shaped pores. The isotherm of ZC13/8 is of the II type with H1 loop, which shows well-defined cylindrical pores or agglomerates of approximately uniform spheres appearing probably as secondary intra-particle porosity (Figure S4, b). The hysteresis loops are characteristic of mesoporous solids and their shape reveals a change in the pore structure.

The average pore size is rather close for ZC31/4, ZC11/4, ZC13/4, ZC31/8 and ZC11/8 (Table 3) and different from that of the sample ZC13/8. The S_{BET} , pore volume and average pore diameter are changing in the order ZC31/4, ZC11/4, ZC13/4, ZC31/8, ZC11/8, ZC13/8 in the same way. The change of the porous structure is clearly shown (Figure S5) for the pore size distribution of the samples, where ZC13/8 shows a large amount of mesopores in the range 15–100 nm.

3. 4. Transmission Electron Microscopy

TEM micrographs show agglomerates for ZC31/4, ZC31/8 (Figure 5, a, b) and crystallites for ZC13/8 (Figure 5 c, d). Agglomeration was present even after sonification, and can be attributed to the mechanotreatment of the

samples without the addition of surfactants. This can lead to partial melting of the edges of the smaller particles during the milling and can play the role of glue between the bigger particles. Because of the agglomeration in the ZC31/4, ZC11/4, ZC13/4, ZC31/8, ZC11/8 samples, evaluation of the particles size distribution on the base of TEM micrograph was attempted only for the ZC13/8 sample (Figure 6). Nanosized particles in the broad range between 5–45 nm can be observed, while sizes between 15–25 nm are the most typical (more than 60% of all particles) (Figure 6).

Figure 6. Particles size distribution for ZC13/8 (based on the TEM micrograph, Figure 5, c).

3. 5. Photocatalytic Properties of the Samples

$\alpha\text{-Fe}_2\text{O}_3$: hematite is an n-type semiconductor with a band gap in the region 2.0–2.2 eV.⁴⁷ The rate constants

for $\alpha\text{-Fe}_2\text{O}_3$ shown in Table 4 are decreasing with increasing milling time, so Fe-TS is showing the highest value of $(6.6 \pm 0.4) \times 10^{-3} \text{ min}^{-1}$; the values for the rate constants for Fe-4MA and Fe-8MA are only half of that. The rate constant per unit surface area shows the same tendency i.e. high for Fe-TS, lower for Fe-4MA and Fe-8MA; the difference is bigger here because of the high SSA of Fe-TS. The lattice strain (Table 1) is higher for the less photocatalytically active samples.

Binary mixed metal oxides ZnFe_2O_4 and CoFe_2O_4 : Among the binary mixed oxides, the highest rate constant is observed for ZF-TS, $(12.7 \pm 0.73) \times 10^{-3} \text{ min}^{-1}$. The values for ZF-4MA, CF-TS and CF-4MA are smaller and similar. The lattice strain increases with the milling for CF-4MA, but there is no difference in the rate constants for CF-TS and CF-4MA. The very big difference in the rate constants for ZF-TS and ZF-4MA can hardly be explained with the insignificant difference in the lattice strain. The activity per unit surface for ZF-4MA and CF-4MA are the same; apparently the milling is causing the same effect on the surface and on the photocatalytic activity.

Ternary oxides: The data in Table 4 show the rate constants and sorption, and those in Table 5 show the degradation of Malachite Green with the time. It is obvious that the samples are active as photocatalysts. They suc-

cessfully degrade more than 50% of the Malachite Green present in the suspension within 90 min. The highest conversion of 68% (Table 5) was obtained by sample ZC31/8 with the highest rate constant observed, $12.3 \times 10^{-3} \text{ min}^{-1}$ (Figure 7, Table 4).

Figure 7. Photocatalytic degradation of Malachite Green by the samples ZC31/4, ZC11/4, ZC13/4, ZC31/8, ZC11/8, ZC13/8 under UV-irradiation

The photocatalytic rate constants (Table 4) increase both with increasing Zn(II)/Co(II) ratio in the samples and with increasing milling time. The values for the rate constants for the ternary oxides ZC31/4, 10.6×10^{-3} , ZC11/4, 8.4×10^{-3} , and ZC13/4, $8.1 \times 10^{-3} \text{ min}^{-1}$ are higher than those for $\alpha\text{-Fe}_2\text{O}_3$, $6.6 \times 10^{-3} \text{ min}^{-1}$ (the highest value among Fe-TS, Fe-4MA, Fe-8MA) as well as higher than those for the binary mixed metal oxides made at the same milling time, ZF-4MA, 6.53×10^{-3} , and CF-4MA, $5.33 \times 10^{-3} \text{ min}^{-1}$. This may be explained by $\alpha\text{-Fe}_2\text{O}_3$ and the spinels in the ternary mixed metal oxides having a synergetic effect on the photocatalytic activity.

4. Discussion

The aim of the work was to obtain polycrystalline ternary spinel ferrites with different Zn/Co ratios and to test their photocatalytic activity. In order to reveal the inf-

Table 4. Photocatalytic activity: rate constants and sorption

Sample	Rate constant, $\times 10^{-3}, \text{ min}^{-1}$	Rate constant to $S_{\text{BET}}, \times 10^{-4}, \text{ min}^{-1} \cdot \text{g} \cdot \text{m}^{-2}$	Sorption, %
Fe-TS	6.6 ± 0.41	3.30	53.03
Fe-4MA	2.9 ± 0.35	0.37	37.32
Fe-8MA	3.3 ± 0.35	0.28	43.46
ZF-TS	12.70 ± 0.73	1.81	78.13
ZF-4MA	6.53 ± 0.40	0.22	70.82
CF-TS	5.73 ± 0.38	0.64	77.80
CF-4MA	5.33 ± 0.31	0.25	68.34
ZC31/4	10.6 ± 0.45	7.57	78.32
ZC11/4	8.4 ± 0.25	6.00	75.89
ZC13/4	8.1 ± 0.25	5.78	78.18
ZC31/8	12.3 ± 0.71	10.25	82.46
ZC11/8	9.0 ± 0.3	6.43	78.28
ZC13/8	8.3 ± 0.25	3.77	79.35

Table 5. Degradation of Malachite Green with the time, %

Time, min	Samples					
	ZC31/4	ZC11/4	ZC13/4	ZC31/8	ZC11/8	ZC13/8
15	17.76	8.69	12.26	9.16	13.85	12.98
30	29.61	22.46	19.24	23.89	20.72	22.25
45	34.69	33.92	28.71	36.53	34.16	27.41
60	56.31	43.94	36.93	56.56	44.00	38.76
90	56.55	50.35	53.29	68.13	54.26	53.95

fluence of the synthetic procedure on the photocatalytic properties of the samples, a combination of solid state reaction with high-energy ball-milling was applied both to treat a commercial ferric oxide (hematite) and to synthesize oxides with spinel structure of the type $M'_xM''_{1-x}Fe_2O_4$ ($M' = Zn$, $M'' = Co$; $x = 0, 0.25, 0.5, 0.75, 1$). Homogeneous $ZnFe_2O_4$ and $CoFe_2O_4$ ferrites with spinel structure were obtained both by solid state reaction and by a combination of solid state reaction with high-energy ball-milling. The ternary mixed metal oxide $Co_{0.75}Zn_{0.25}Fe_2O_4$ was obtained as a well-crystallized homogeneous spinel structure after 8 hours of milling. In spite of the XRD data showing single phases of well crystallized oxides $Co_xZn_{1-x}Fe_2O_4$ ($x = 0.25; 0.5$), the Mössbauer and Raman spectroscopy measurements revealed the presence of both a spinel-like structure and hematite. This illustrates the importance of combining different methods for analysis of the structure in ferrite multicomponent systems, and gives a chance to test a potential synergism in the photocatalytic activity of the spinel structure and hematite, when they are treated at the same experimental conditions. Some considerations on the photocatalytic activity are worth mentioning:

(i) *The composition and the photocatalytic properties of ternary mixed metal oxides:* Considering the composition of the ternary mixed metal oxides presented, they can be divided in two groups, namely ZC31/4, ZC11/4, ZC13/4, ZC31/8, and ZC11/8 in first group and ZC13/8 the other one. The five samples ZC31/4, ZC11/4, ZC13/4, ZC31/8 and ZC11/8 are phases, containing spinel-like ferrite (50–55%) and hematite, $\alpha-Fe_2O_3$ (17–20%). The hematite, with an energy band gap of 2.2 eV, absorbs light up to 550 nm and (as other iron oxides) possesses photocatalytic activity.⁴⁷ Any of the components can be active during the photocatalytic decomposition of Malachite Green; their activity is difficult to be separated, especially because of the fact that they have close energy band gap values. The sample ZC13/8 is the only one with a homogeneous spinel structure, $Co_{0.75}Zn_{0.25}Fe_2O_4$, but its photocatalytic behaviour does not differ from the samples ZC31/4, ZC11/4, ZC13/4 and ZC11/8 (containing both hematite and spinel-like ferrite). Taking into account the data from Table 4, an increasing of the rate constant with the increasing of Zn(II) content in the samples is observed for both milling periods applied. The samples ZC31/4 and ZC31/8 show the best activity among the others, with rate constants of 10.6×10^{-3} and $12.3 \times 10^{-3} \text{ min}^{-1}$, respectively.

It can be assumed that peculiarities of the synthetic procedure namely a heat treatment, followed by mechanotreatment without annealing in combination with the Zn(II)/Co(II) ratio, favoured the photocatalytic activity. That the highest rate constant was observed for the sample with the longest mechanotreatment and highest Zn(II)/Co(II) ratio, ZC31/8, is an illustration for this. Additional reason for the highest rate constant value for ZC31/8 is the synergetic effect of the spinel-like structure and $\alpha-Fe_2O_3$. Considering the data from Mossbauer (Tab-

le S1), the amount of hematite in all five samples ZC31/4, ZC11/4, ZC13/4, ZC31/8, ZC11/8 is very close, so the difference in their activity could be a result of the different Zn/Co ratios and different milling times.

(ii) *The specific surface area, S_{BET} , and the photocatalytic activity:* The specific surface area is rather low, which is to be expected taking into account the high temperature for heat treatment of the samples, 900 °C. The samples ZC31/4, ZC11/4, ZC13/4, ZC31/8, ZC11/8 have similar values of S_{BET} , but have different photocatalytic behaviour. The sample ZC13/8 is very different from the others, with a specific surface area twice as high, but it does not show the highest rate constant obtained. It looks like S_{BET} is not decisive for the photocatalytic activity in our case because no correlation between specific surface area and photocatalytic activity is observed. If the degradation rate constant is divided by the specific surface area (the same approach as applied in⁵⁰) the “normalized” values ($\text{min}^{-1} \text{ g. m}^{-2}$, Table 4) show the weakest catalytic activity for ZC13/8 while the best sample is still ZC31/8. According to Bubacz et al.⁵¹ the process of photodegradation is not determined only by the specific surface area, S_{BET} . The peculiarities of the surface structure are responsible for differences in the catalytic activity. The size of the particles and crystallites is influencing the activity of the catalyst by influencing the processes of recombination of the electron-hole couples.^{52,53} The best catalyst among the synthesized, ZC31/8, has the smallest crystallite size. That the crystallite size for ZC31/4 (56 nm) is twice as large as that for ZC31/8 (26 nm) does not reflect in their catalytic activity, which are similar ($10.3 \times 10^{-3} \text{ min}^{-1}$ for ZC31/4 and $12.3 \times 10^{-3} \text{ min}^{-1}$ for ZC31/8).

The rate constants for some of the samples (ZC31/4, ZC31/8) are close to those obtained by us for TiO_2 (Degussa P-25) when decomposing Malachite Green with UV light irradiation, namely $11.6 \times 10^{-3} \text{ min}^{-1}$, but at higher specific surface area ($52 \text{ m}^2/\text{g}$).⁵⁰ The “normalized” value for Degussa P25 (rate constant/ S_{BET}) is $2.2 \times 10^{-4} \text{ min}^{-1} \text{ g. m}^{-2}$, which is rather low compared with the values for our samples (Table 4), even including our weakest result, the one for the sample ZC13/8. This is in accordance with the values for the energy band gap (Results, 3.2), obtained for our samples that are considerably smaller than the one for Degussa-P25.

(iii) *Comparison of the homogeneous ZC13/8 and the other five inhomogeneous samples ZC31/4, ZC11/4, ZC13/4, ZC31/8, ZC11/8* shows that ZC13/8 has the same UV/Vis and IR spectra as the other samples although it is the only one with a clearly crystallised spinel structure. ZC13/8 differs in some physicochemical parameters such as S_{BET} , pore volume, average pore size and composition, but its photocatalytic activity is similar to ZC13/4 (and ZC11/4), synthesised at shorter milling time (Table 4). Probably the activity of ZC13/4 (and ZC11/4) is similar to ZC13/8 because of the synergetic effect observed. The photocatalytic activity of sample ZC13/8 is the only one repor-

ted in the literature for a pure spinel-like structure for degradation of Malachite Green under UV light irradiation.

If the reason for inhomogeneity of the five ternary oxides ZC31/4, ZC11/4, ZC13/4, ZC31/8, ZC11/8 is the milling procedure, which could cause some decomposition, the reason to obtain ZC13/8 could be a combination of successful synthesis by the longer mechanotreatment assisted by the stabilizing role of the smaller Co^{2+} ions.

(iv) *The relation between the defects in the structure of the samples and their photocatalytic activity:* Apparently the milling increases the defects and the lattice strain for $\alpha\text{-Fe}_2\text{O}_3$, but the photocatalytic activity of $\alpha\text{-Fe}_2\text{O}_3$ decreases, so it looks like for $\alpha\text{-Fe}_2\text{O}_3$ the defects do not have a positive effect on its activity as a photocatalyst. For the binary mixed metal oxides the one with the lowest strain has the highest activity, i.e. the pure $\text{Zn-Fe}_2\text{O}_4$. No positive effect of the lattice strain is observed for the ternary oxides: the sample with the lowest strain possesses the best activity. It is known that cationic vacancies (and/or interstitial atoms) can be observed in the structure of spinels.⁵⁴ The possible defects in the powdered samples are evaluated on the base of the calculated lattice strain. In spite of the expectations that the lattice strain induces structural distortion and by that transforms the properties,⁵⁵ we did not observe a correlation between the lattice strain and the photocatalytic activity. The sample with the best activity among the ternary oxides, ZC31/8, has the lowest value of lattice strain. We can suggest there are factors which are compensating the lattice strain caused by the defects.

5. Conclusions

Polycrystalline spinel-like ferrites were synthesized and tested for degradation of Malachite Green in model solutions under UV light irradiation. The values for the rate constant and the degree of degradation obtained show that these samples have potential to be used as photocatalysts to purify contaminated waters. The rate constants observed are similar to that obtained for TiO_2 Degussa P25, but at lower specific surface area. Considering all the factors influencing the photocatalytic activity, differences in photocatalytic behavior are observed depending on the duration of high energy ball-milling and Zn(II)/Co(II) ratio. A synergetic effect of the $\alpha\text{-Fe}_2\text{O}_3$ and spinel-like structure on the photocatalytic properties was detected.

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6. References

1. P. Laokul, V. Amornkitbamrung, S. Seraphin, S. Maensiri, *Curr. Appl. Phys.* **2011**, *11*, 101–108.
2. V. B.-Gutierrez, M. J. T. - Fernandez, R. Saez-Puche, *J. Phys. Chem. C* **2010**, *114*, 1789–1795.
3. Y. B. Li, R. Yi, A. G. Yan, L. W. Deng, K. C. Zhou, X. H. Liu, *Solid State Sci.* **2009**, *11*, 1319–1324.
<https://doi.org/10.1016/j.solidstatesciences.2009.04.014>
4. S. Saadi, A. Bouguelia, M. Trari, *Renew. Energy* **2006**, *31*, 2245–2256. <https://doi.org/10.1016/j.renene.2005.10.014>
5. A. V. Ravindra, P. Padhan, W. Prellier, *Appl. Phys. Lett.* **2012**, *101*, 161902.
<https://doi.org/10.1063/1.4759001>
6. Y. Yang, Y. Jiang, Y. Wang, Y. Sun, L. Liu, J. Zhang, *Mat. Chem. Phys.* **2007**, *105*, 154–156.
<https://doi.org/10.1016/j.matchemphys.2007.04.050>
7. C. Borgohain, K. K. Senapati, K. C. Sarma, P. Phukan, *J. Mol. Catal. A: Chem.* **2012**, *363–364*, 495–500.
<https://doi.org/10.1016/j.molcata.2012.07.032>
8. X. Cao, Li Gu, X. Lan, C. Zhao, D. Yao, W. Sheng, *Mat. Chem. Phys.* **2007**, *106*, 175–180.
<https://doi.org/10.1016/j.matchemphys.2007.05.033>
9. Z. Jia, D. Ren, Y. Liang, R. Zhu, *Mat. Lett.* **2011**, *65*, 3116–3119. <https://doi.org/10.1016/j.matlet.2011.06.101>
10. G. A. El-Shobaky, A. M. Turky, N. Y. Mostafa, S. K. Mohamed, *J. Alloys Compd.* **2010**, *493*, 415–422.
<https://doi.org/10.1016/j.jallcom.2009.12.115>
11. E. Casbeer, V. K. Sharma, X. - Zh. Li, *Sep. Purif. Techn.* **2012**, *87*, 1–14.
<https://doi.org/10.1016/j.seppur.2011.11.034>
12. M. Su, Ch. He, V. K. Sharma, M. A. Asi, D. Xia, X. - Li, H. Deng, Y. Xiong, *J. Hazard. Mater.* **2012**, *211–212*, 95–103.
13. S. H. Xu, D. L. Feng, W. F. Shangguan, *J. Phys. Chem. C* **2009**, *113*, 2463–2467. <https://doi.org/10.1021/jp806704y>
14. S. D. Jadhav, P. P. Hankare, R. P. Patil, R. Sasikala, *Mater. Lett.* **2011**, *65*, 371–373.
<https://doi.org/10.1016/j.matlet.2010.10.004>
15. C.-H. Chen, Y.-H. Liang, W. - D. Zhang, *J. Alloys Compd.* **2010**, *501*, 168–172.
<https://doi.org/10.1016/j.jallcom.2010.04.072>
16. S. Boumazza, A. Boudjemaa, A. Bouguelia, R. Bouarab, M. Trari, *Appl. Energy* **2010**, *87*, 2230–2236.
<https://doi.org/10.1016/j.apenergy.2009.12.016>
17. B. P. Zhang, J. L. Zhang, F. Chen, *Res. Chem. Intermed.* **2008**, *34*, 375–380.
<https://doi.org/10.1163/156856708784040669>
18. G. Y. Zhang, Y. Q. Sun, D. Z. Gao, Y. Y. Xu, *Mater. Res. Bull.* **2010**, *45*, 755–760.
<https://doi.org/10.1016/j.materresbull.2010.03.025>
19. R. S. Gaikwad, S. - Y. Chae, R. S. Mane, S. - H. Han, O. - S. Joo, *Int. J. Electrochem.* **2011**, *ID 729141*, 6 pages,
<https://doi.org/10.4061/2011/729141>
20. M. Yokoyama, T. Oku, T. Taniyama, T. Sato, E. Ohta, T. Sato, K. Haneda, S. Itoh, K. Kurahashi, M. Takeda, *Phys. B* **1995**, *213–214*, 251–253.
[https://doi.org/10.1016/0921-4526\(95\)00121-O](https://doi.org/10.1016/0921-4526(95)00121-O)
21. P. P. Hankare, R. P. Patil, R. Sasikala, *Mater. Lett.* **2011**, *65*, 371–373. <https://doi.org/10.1016/j.matlet.2010.10.004>

22. M. Jalaly, M. H. Enayati, F. Karimzadeh, P. Kameli, *Powder Techn.* **2009**, *193*, 150–153.
<https://doi.org/10.1016/j.powtec.2009.03.008>
23. N. H. Vasoya, L. H. Vanpariya, P. N. Sakariya, M. D. Timbadiya, T. K. Pathak, V. K. Lakhani, K. B. Modi, *Ceram. Int.* **2010**, *36*, 947–954.
<https://doi.org/10.1016/j.ceramint.2009.10.024>
24. S. Dasgupta, K. B. Kim, J. Ellrich, J. Eckert, I. Manna, *J. Alloys Compd.* **2006**, *424*, 13–20.
<https://doi.org/10.1016/j.jallcom.2005.12.078>
25. M. Mozaffari, F. Ebrahimi, S. Daneshfouzan, J. Amighian, *J. Alloys Compd.* **2008**, *449*, 65–67.
<https://doi.org/10.1016/j.jallcom.2006.03.107>
26. K. Maaz, A. Mumtaz, S. K. Hasanain, A. Ceylan, *J. Magn. Magn. Mater.* **2007**, *308*, 289–295.
<https://doi.org/10.1016/j.jmmm.2006.06.003>
27. Z. Q. Liu, C. J. Li, W. M. Lü, X. H. Huang, Z. Huang, S. W. Zeng, X. P. Qiu, L. S. Huang, A. Annadi, J. S. Chen, J. M. D. Coey, T. Venkatesan, Ariando, *Phys. Rev. X* **2013**, *3*, 021010.
<https://doi.org/10.1103/PhysRevX.3.021010>
28. Z. Q. Liu, D. P. Leusink, X. Wang, W. M. Lü, K. Gopinadhan, A. Annadi, Y. L. Zhao, X. H. Huang, S. W. Zeng, Z. Huang, A. Srivastava, S. Dhar, T. Venkatesan, Ariando, *Phys. Rev. Lett.* **2011**, *107*, 146802.
<https://doi.org/10.1103/PhysRevLett.107.146802>
29. Z. Q. Liu, D. P. Leusink, W. M. Lü, X. Wang, X. P. Yang, K. Gopinadhan, Y. T. Lin, A. Annadi, Y. L. Zhao, A. Roy Barman, S. Dhar, Y. P. Feng, H. B. Su, G. Xiong, T. Venkatesan, Ariando, *Phys. Rev. B* **2011**, *84*, 165106.
<https://doi.org/10.1103/PhysRevB.84.165106>
30. Z. Q. Liu, W. M. Lü, S. L. Lim, X. P. Qiu, N. N. Bao, M. Motapothula, J. B. Yi, M. Yang, S. Dhar, T. Venkatesan, Ariando, *Phys. Rev. B* **2013**, *87*, 220405(R).
<https://doi.org/10.1103/PhysRevB.87.220405>
31. Z. Q. Liu, W. Lu, S. W. Zeng, J. W. Deng, Z. Huang, C. J. Li, M. Motapothula, W. M. Lü, L. Sun, K. Han, J. Q. Zhong, P. Yang, N. N. Bao, W. Chen, J. S. Chen, Y. P. Feng, J. M. D. Coey, T. Venkatesan, Ariando, *Adv. Mater. Interfaces* **2014**, *1*, 1400155. <https://doi.org/10.1002/admi.201400155>
32. J. Birkenstock, R. X. Fisher, T. Messner, BRASS, Ber. DMG, Beih, *Eur. J. Mineral.* **2003**, *15*, 21–28.
33. K. Williamson, W. H. Hall, *Acta Metall.* **1953**, *1*, 22–31.
[https://doi.org/10.1016/0001-6160\(53\)90006-6](https://doi.org/10.1016/0001-6160(53)90006-6)
34. J. Tauc, R. Grigorovici, A. Vancu, *Phys. Status Solidi* **1966**, *15*, 627–637. <https://doi.org/10.1002/pssb.19660150224>
35. S. D. Shenoy, P. A. Joy, M. R. Anantharaman, *J. Magn. Magn. Mater.* **2004**, *269*, 217.
[https://doi.org/10.1016/S0304-8853\(03\)00596-1](https://doi.org/10.1016/S0304-8853(03)00596-1)
36. K. B. Modi, S. N. Dolia, P. U. Sharma, *Indian J. Phys.* **2015**, *89*, 425–436.
<https://doi.org/10.1007/s12648-014-0604-5>
37. P. D. Thang, G. Rijnders, D. H. A. Blanket, *J. Magn. Magn. Mat.* **2005**, *295*, 251–256.
<https://doi.org/10.1016/j.jmmm.2005.01.011>
38. F. Bodker, S. Morup, C. A. Oxborrow, S. Linderroth, M. B. Madsen, J. W. Niemantsverdriet, *J. Phys. Condens. Mat.* **1992**, *4*, 6555–6568.
<https://doi.org/10.1088/0953-8984/4/31/008>
39. J. Kreisel, G. Lucazeau, J. Vincent, *J. Solid State Chem.* **1999**, *137*, 127–137.
<https://doi.org/10.1006/jssc.1997.7737>
40. F. Nakagomi, S. W. da Silva, V. K. Garg, A. C. Oliveira, P. C. Morais, A. F. Junior, E. C. D. Lima, *J. Appl. Phys.* **2007**, *101*, 09M514.
41. L. Ben Tahar, L. S. Smiri, M. Artus, A. - L. Joudrier, F. Herbst, M. J. Vaulay, S. Ammar, F. Feivet, *Mater. Res. Bull.* **2007**, *42*, 1888.
<https://doi.org/10.1016/j.materresbull.2006.12.014>
42. C. - W. Tang, C. - B. Wang, S. - H. Chien, *Thermochim. Acta* **2008**, *473*, 68–73.
<https://doi.org/10.1016/j.tca.2008.04.015>
43. D. L. Wood, J. S. Tauc, *Phys Rev B* **1972**, *5*, 3144.
<https://doi.org/10.1103/PhysRevB.5.3144>
44. M. Boulouddeine, N. Viart, S. Colis, A. Dinia, *Chem. Phys. Lett.* **2004**, *397*, 73.
<https://doi.org/10.1016/j.cplett.2004.08.064>
45. S. V. Bhat, F. L. Deepak, *Solid State Commun.* **2005**, *135*, 345–347. <https://doi.org/10.1016/j.ssc.2005.05.051>
46. H. Dixit, N. Tandon, S. Cottenier, R. Saniz, D. Lamoén, B. Partoens, V. Van Speybroeck, M. Waroquier, *New J. Phys.* **2011**, *13*, 063002.
<https://doi.org/10.1088/1367-2630/13/6/063002>
47. J. Bandara, J. A. Mielczarski, A. Lopez, J. Kiwi, *Appl. Catal. B: Environ.* **2001**, *34*, 321–333.
[https://doi.org/10.1016/S0926-3373\(01\)00225-9](https://doi.org/10.1016/S0926-3373(01)00225-9)
48. L. Zhang, Y. He, P. Ye, Y. Wu, T. Wu, *Catal. Commun.* **2013**, *30*, 14–18. <https://doi.org/10.1016/j.catcom.2012.10.013>
49. F. Rouquerol, J. Rouquerol, K. Sing, Adsorption by powders and porous solids: Principles, methodology and applications, Acad. Press, San Diego, **1999**.
50. R. Kralchevska, M. Milanova, D. Hristov, A. Pintar, D. Todorovsky, *Mater. Res. Bull.* **2012**, *47*, 2165–2177.
<https://doi.org/10.1016/j.materresbull.2012.06.009>
51. K. Bubacz, J. Choina, D. Dolat, E. Borowiak-Paleń, D. Moszyński, A. W. Morawski, *Mater. Res. Bull.* **2010**, *45*, 1085–1091.
<https://doi.org/10.1016/j.materresbull.2010.06.024>
52. R. Scotti, M. D'Arienzo, F. Morazzoni, I. R. Bellobono, *Appl. Catal. B* **2009**, *88*, 323–330.
<https://doi.org/10.1016/j.apcatb.2008.11.012>
53. A. Testino, I. R. Bellobono, V. Buscaglia, C. Canevali, M. D'Arienzo, S. Polizzi, R. Scotti, F. Morazzoni, *J. Am. Chem. Soc.* **2007**, *129*, 3564–3575.
<https://doi.org/10.1021/ja067050+>
54. M. Gaudon, N. Pailhe, A. Wattiaux, A. Demourgues, *Mat. Res. Bull.* **2009**, *44*, 479–484.
<https://doi.org/10.1016/j.materresbull.2008.12.005>
55. L. Zhao, H. Yang, X. Zhao, L. Yu, Y. Cui, S. Feng, *Mat. Lett.* **2006**, *60*, 1–6.
<https://doi.org/10.1016/j.matlet.2005.07.017>

Povzetek

Kombinacijo toplotne in mehanske (krogelni mlini) obdelave smo uporabili pri pripravi polikristalničnih mešanih binarnih in ternarnih kovinskih oksidov tipa $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.25, 0.5, 0.75, 1$). S takšnim sinteznim pristopom smo uspešno pripravili homogene ZnFe_2O_4 , CoFe_2O_4 , in $\text{Co}_{0.75}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$ ter tudi mešane okside, katerih sestava je odvisna tako od trajanja mletja s kroglicami in razmerja Zn(II)/Co(II) . Tvorbo spinelu podobnih struktur smo dokazali z rentgensko praškovo difrakcijo (XRD), Mössbauerjevo spektroskopijo in Ramansko spektroskopijo. Za nadaljnjo karakterizacijo vzorcev smo uporabili nizko-temperaturno adsorpcijo N_2 , UV/VIS spektroskopijo in transmisijsko elektronsko mikroskopijo (TEM). Izračunana energija prepovedanega pasu (band gap) vzorcev kaže, da so materiali potencialni fotokatalizatorji. V prisotnosti vzorcev, ki smo jih uporabili kot fotokatalizatorje, je barvilo malahitno zeleno v modelnih vodnih raztopinah pri obsevanju z UV svetlobo razpadlo. Najboljšo fotokatalitsko učinkovitost smo opazili pri vzorcu za katerega smo pri sintezi uporabili daljši čas mletja in višje razmerje Zn (II)/Co (II) . Primerjali smo tudi fotokatalitsko aktivnost ternarnih mešanih oksidov s čistim hematitom $\alpha\text{-Fe}_2\text{O}_3$ in binarnima ZnFe_2O_4 in CoFe_2O_4 feritoma s spinelno strukturo, ki smo jih pripravili na enak način. Zaznali smo sinergijski učinek $\alpha\text{-Fe}_2\text{O}_3$ in strukture podobne spinelu na fotokatalitske lastnosti ternarnih mešanih kovinskih oksidov.