

Magnetic Properties of Mechanochemically Synthesized Mixed Oxides

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The mixed oxides Fe₂O₃-ZnO have been obtained in nanocrystalline state by reactive milling in a high-energy planetary mill, from a stoichiometric mixture of hematite and ZnO. The magnetic properties of samples were evaluated by magnetization measurements and Mössbauer spectrometry. A post milling annealing promotes the solid state reaction and improves the zinc ferrite formation, paramagnetic ZnFe₂O₄ phase is formed. Further mechanical activation leads to structural transformation into Wüstite-type (FeZn)O mixed oxide, with ferromagnetic hysteresis and increased magnetization.

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1. Introduction

Mixed oxides are the oxygen-containing combination of two or more metallic ions. They have many industrial applications in electronics, ceramics and catalysis. Wide-gap diluted magnetic oxide semiconductors, like the Fe₂O₃-ZnO mixed oxide, combine their electric conductivity with ferromagnetism and optical transparency, thereby opening up the possibility of new device concepts. Spinel ferrites have very important technological applications in sensor techniques, medical diagnostics, drug-delivery and information storage. Various synthesis methods, such as a chemical route [1] sol-gel combustion method [2], thermal decomposition of metal-surfactant complexes [3] have been used for preparation, which can lead to magnetic properties on diverse scales. Mechanical activation, especially ball milling is a simple and suitable alternative method for preparation of mixed oxides [4]. The aim of this work is to prepare mechanically synthesized Fe₂O₃-ZnO mixed oxides and characterize their magnetic properties.

2. Experimental

Mechanochemical synthesis of Fe₂O₃-ZnO mixed oxides was performed in a laboratory planetary mill Pulverisette 6 (Fritsch, Germany) by high-energy milling of hematite and ZnO in stoichiometric ratio 1:1. For the mechanochemical synthesis the following experimental conditions were applied: loading of the mill, 50 balls of 10 mm in diameter; material of milling chamber and balls was tungsten carbide; volume of milling chamber, 250 ml; room temperature; rotational speed of the mill planet carrier 400 min⁻¹; milling time, 10 min. dry milling and subsequent wet milling in the presence of ethylcellulose. Sample 1 is as-synthesized, Sample 2 is annealed at 600 °C, Sample 3 is annealed at 700 °C, and additionally mechanically activated for 4 h.

X-ray powder diffraction patterns (XRD) of the samples were taken at room temperature using a D8 Advance

diffractometer (Bruker, Germany), equipped with a Θ/Θ goniometer, Cu-K α radiation, secondary graphite monochromator and scintillation detector in Bragg-Brentano geometry. The diffraction data were collected over an angular range $15^\circ < 2\Theta < 80^\circ$ with steps of 0.03° and a fixed counting time of 25 s/step. For the phase identification and full profile fitting the *Diffra^{plus}Eva* and *Diffra^{plus}Topas* software has been utilized, respectively.

Transmission ⁵⁷Fe Mössbauer spectra were obtained at room temperature with a Wissel electromechanical Mössbauer spectrometer (Wissenschaftliche Elektronik GmbH, Germany) working at a constant acceleration mode. A ⁵⁷Co/Cr source and a α -Fe foil standard were used.

The magnetization curves were investigated using a vibrating sample magnetometer, operating in magnetic fields up to 6 T in temperature range of 4–290 K.

3. Results and discussion

XRD analysis (Fig. 1) reveals the different phase composition of the samples. Mechanical activation at the given conditions does not lead to complete conversion of reagents to mixed oxide. The product consists of un-

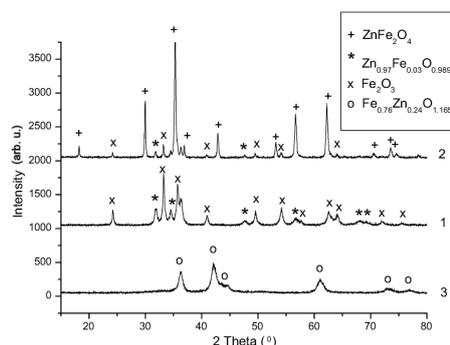


Fig. 1. X-ray diffraction spectra of the samples: (1) as-mechano-synthesized (2) annealed at 600 °C (3) annealed at 700 °C and additionally mechanically activated.

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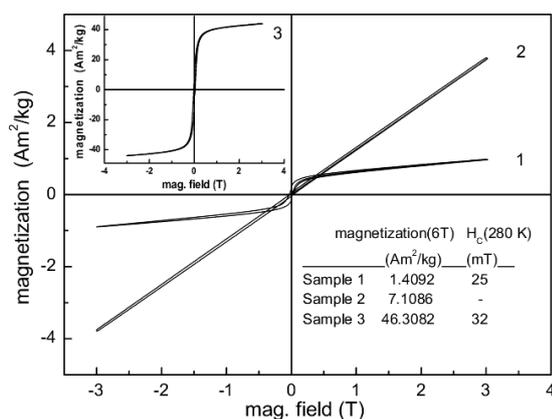


Fig. 2. Room temperature magnetization curves of the samples.

reacted hematite and ZnO, with a small degree of Fe incorporation. The average crystallite size is between 10–20 nm. Annealing of the product at 600 °C leads to the formation of ferrite type mixed oxide ZnFe₂O₄ with crystallite size of about 60 nm, but considerable amount of reagents remains unreacted. Annealing at 700 °C promotes the formation of zinc ferrite, which is the major phase (not shown). Further mechanical activation re-

sulted in Wüstite-type tetragonally distorted mixed oxide, with prevalence of Fe, and fine crystalline structure in the range below 10 nm.

Mössbauer technique was used to study the magnetic properties and ionic state of the iron in Fe₂O₃-ZnO mixed oxides (Table). The measured spectra represent doublets or combination of a doublet (Db) and sextet (Sx). The hyperfine parameters for the sextets are in correspondence with those for Fe³⁺ ions, octahedrally coordinated in hematite (α -Fe₂O₃-substance with antiferromagnetic or weakly ferromagnetic properties). The parameters of the doublet components are those of the Fe³⁺ ions of octahedral coordination in the paramagnetic ZnFe₂O₄ phase. One can estimate the approximate ratio between the iron-containing phases in the samples based on the ratio between the relative weights of the components G (Table).

The results of magnetization measurements at room temperature are summarized in Fig. 2. Sample 1 shows hysteresis (coercivity $H_C \sim 25$ mT) and its magnetization does not saturate in magnetic field of 6 T. Sample 2 is paramagnetic at room temperature, however, at 4 K, hysteresis loops with $H_C \sim 80$ mT have been observed (not shown) and the magnetization does not saturate as well. Sample 3 has the largest magnetization and shows ferromagnetic-like hysteresis with $H_C \sim 32$ mT.

TABLE

Parameters of the Mössbauer spectra of the investigated samples. IS—isomer shift, QS—quadrupole splitting, H_{eff} —hyperfine field, FWHM—full width at half maximum, G —relative weights.

Sample code	Components	IS (mm/s)	QS (mm/s)	H_{eff} (T)	FWHM (mm/s)	G (%)
Sample 1	Sx- α -Fe ₂ O ₃ -Fe ³⁺	0.37	-0.17	51.5	0.37	98
	Db-ZnFe ₂ O ₄ -Fe ³⁺	0.35	0.40	-	0.46	2
Sample 2	Sx- α -Fe ₂ O ₃ -Fe ³⁺	0.38	-0.19	51.6	0.28	22
	Db-ZnFe ₂ O ₄ -Fe ³⁺	0.35	0.39	-	0.36	78
Sample 3 before second milling	Db-ZnFe ₂ O ₄ -Fe ³⁺	0.35	0.40	-	0.41	100

4. Conclusions

Mechanochemical reaction between hematite and ZnO in planetary mill formed a precursor, which was subsequently heated to successfully produce ZnFe₂O₄. The reaction begins after the amorphization of ZnO, whereas α -Fe₂O₃ is still crystalline. It has been found that the obtained milled powder after annealing is a spinel-type structure with paramagnetic behaviour. Additional mechanical activation leads to the formation of Wüstite-type (FeZn)O mixed oxide showing ferromagnetic hysteresis and increased magnetization.

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