Characterization of Oxide Phases Generated during the Synthesis of NiFe$_2$O$_4$

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Oxide phases generated during the synthesis of NiFe$_2$O$_4$ from aqueous Ni(NO$_3$)$_2$/Fe(NO$_3$)$_3$ solution were characterized by X-ray diffraction, Fourier transform IR spectroscopy and ^{57}Fe Mössbauer spectroscopy. Nitrate salts and α-Fe$_2$O$_3$ were observed in the samples prepared at temperatures up to 300 °C. The formation of nickel ferrite was observed at temperatures of 500 °C and higher. Stoichiometric NiFe$_2$O$_4$ was obtained at 1350 °C. NiO and α-Fe$_2$O$_3$ were intermediate phases in the process of nickel ferrite formation. A decreased hyperfine magnetic field was observed for α-Fe$_2$O$_3$ prepared at lower temperatures. Decomposition of nitrate groups was followed by Fourier transform IR spectroscopy.

INTRODUCTION

The influence of the preparative procedure on the physical, chemical and structural properties of different ferrites has been extensively investigated. Particular attention has been paid to the properties of ferrites suitable for technical and commercial use. Nickel ferrite and substituted nickel ferrites were the subject od these investigations because of their specific magnetic and microwave energy absorption properties.

Regazzoni and Matijević[1] investigated the formation of nickel ferrite particles in the system Ni(OH)$_2$/Fe(OH)$_3$-KNO$_3$ in aqueous medium at 90 °C. Spherical particles of a relatively narrow size distribution were obtained at given experimental conditions. Formation of nickel ferrite by incorporation of Ni^{2+} ions into Fe$_3$O$_4$ (magnetite) during its crystallization was suggested. Tamura *et al.*[2] investigated the formation

of magnetite and nickel ferrite films. They found that the content of Ni^{2+} in nickel ferrite films increased with increasing the Ni^{2+} concentration and temperature.

Mixed hydroxides, $Ni(OH)_2/Fe(OH)_3$, containing up to 10 mol% NiO, were treated at elevated temperatures.[3] The solubility of NiO into Fe_2O_3 was 2 mol% for samples prepared at 550 °C. The formation of α-FeOOH (goethite) was suppressed when Ni^{2+} ions were added to Fe^{3+} ions in aqueous solution.[4] After heating at $\simeq$ 185 °C the co-precipitate $Ni(OH)_2/Fe(OH)_3$, with the ratio Ni : Fe = 1 : 2, indicated the presence of precursor $NiFe_2O_4 \cdot H_2O$, which converted to »amorphous« NiF_2O_4 at $\simeq$ 275 °C and, finally, to crystalline $NiFe_2O_4$ at 400 °C.

Aerosol droplets, prepared from a dilute aqueous solution of $Ni(NO_3)_2 + Fe(NO_3)_3$, underwent pyrolysis[5] between 450 and 810 °C. Spherical and hollow particles of nanocrystalline structure were obtained at 480 °C. Above 660 °C, tiny, magnetically active crystallites of NiF_2O_4 were produced.

Morrish and Haneda[6,7] investigated the magnetic structure of fine $NiFe_2O_4$ particles. When they applied longitudinal magnetic field, the Mössbauer spectra indicated a non-collinear magnetic structure of these particles. The authors suggested that the fine $NiFe_2O_4$ particles consisted of a core with the usual spin arrangement and of a surface layer with atomic moment inclinded in the direction of net magnetization.

Nickel ferrite[8] was also prepared by thermal decomposition of the double salt $Ni_{0.33}Fe_{0.67}(NH_4)_2(SO_4)_2 \cdot 6H_2O$. The optimum temperature for the preparation of $NiFe_2O_4$ was found to be 900 °C.

MacKenzie and Cardile[9] investigated the formation of $NiFe_2O_4$ from a mixture of α-Fe_2O_3 (hematite), Fe_3O_4 or spinel ironsand with NiO. The origin of the magnetite-like spinel ironsand was the west coast of the North Island of New Zealand. Nickel ferrites formed under inert conditions had an increased lattice constant due to the presence of Fe^{2+}. Mössbauer spectroscopy suggested that the Fe^{2+} ions in this spinel were located preferentially at the octahedral sites. Calculation of the lattice constant indicated that $NiFe_2O_4$ formed in air was not fully inverse, as usually assumed, and also that it contained a varying fraction of tetrahedral Ni^{2+} ions.

In a previous work,[10] we investigated the oxide phases in the system NiO-Fe_2O_3 formed after thermal treatment of the $Ni(OH)_2/Fe(OH)_3$ coprecipitates up to 1100 °C. X-ray diffraction indicated the presence of α-Fe_2O_3, NiO and $NiFe_2O_4$ in the samples prepared at 800 °C, while a phase with a structure closely related to $NiFe_2O_4$ was additionally detected in the samples prepared at 1100 °C.

The aim of the present work was to obtain further information about the chemical and structural changes in the solid phase during the formation of $NiFe_2O_4$. X-ray diffraction, Fourier transform IR spectroscopy and ^{57}Fe Mössbauer spectroscopy were used as experimental techniques.

EXPERIMENTAL

Chemicals of *p.a.* purity and doubly distilled water were used. An aqueous solution of $Ni(NO_3)_2/Fe(NO_3)_3$ of the molar ratio NiO : Fe_2O_3 = 1 : 1 was prepared. The excess of water was evaporated using an infrared lamp. The solid residue (samples S_1) was heated in a laboratory furnace at different temperatures in air. An LKO II furnace with Kanthal heaters was

used for heating above 1000 °C. Experimental conditions for the preparation of the samples are given in Table I.

X-ray powder diffraction measurements were performed at room temperature using a Philips counter diffractometer with monochromatized Cu $K\alpha$ radiation (graphite monochromator).

FT-IR spectra were recorded at room temperature using a Perkin-Elmer (model 1720-x) spectrometer. The FT-IR spectrometer was coupled with a personal computer loaded with the IR Data Manager (IRDM) program. The samples were pressed into discs using spectroscopically pure KBr.

^{57}Fe Mössbauer spectra were recorded with a spectrometer produced by WISSEL. Mathematical deconvolution of the Mössbauer spectra was performed using the SIRIUS program.

TABLE I

Experimental conditions for the preparation of samples S_2 to S_9
(hours of heating at given temperatures)

Sample	Temperature / °C							
	200	300	400	500	700	900	1100	1350
S_2	1							
S_3	1	1						
S_4	1	1	1					
S_5	1	1	1	1				
S_6	1	1	1	1	1			
S_7	1	1	1	1	1	1		
S_8	1	1	1	1	1	1	1	
S_9	1	1	1	1	1	1	1	1

RESULTS AND DISCUSSION

The results of X-ray diffraction phase analysis of the prepared samples are given in Table II. The observed phases, α–Fe_2O_3, NiO, NiFe₂O₄ and $Ni(NO_3)_2 \cdot 6H_2O$ were identified according to the JCPDS-PDF card numbers 13–534, 4–835, 10–325 and

TABLE II

The results of X-ray diffraction phase analysis of samples S_1 to S_9

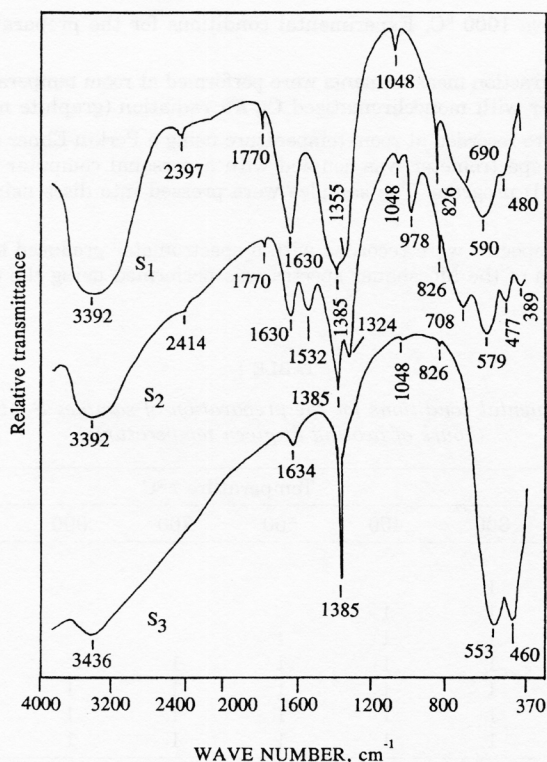| Sample	Phase composition	Remarks
S_1	$Ni(NO_3)_2 \cdot 6H_2O + Fe(NO_3)_3 \cdot nH_2O(?)$	increased broadening of diffraction lines of α-Fe_2O_3 and NiO
S_2	α-Fe_2O_3 + $Ni(NO_3)_2 \cdot 6H_2O$ + ...	
S_3	NiO + α-Fe_2O_3	
S_4	NiO + α-Fe_2O_3	
S_5	NiO + α-Fe_2O_3 + NiFe₂O₄	
S_6	NiFe₂O₄ +NiO	sharpening of NiFe₂O₄ diffraction lines and no shifts of diffraction lines
S_7	NiFe₂O₄	
S_8	NiFe₂O₄	
S_9	NiFe₂O₄	

Figure 1. Fourier transform IR spectra of samples S_1, S_2 and S_3, recorded at room temperature.

25–577, respectively. Since the lattice constant of $NiFe_2O_4$ is almost twice as large as that of NiO, there are no diffraction lines of NiO independent of the ones of $NiFe_2O_4$. The presence of NiO was proved[10] by comparison of the intensities of the overlapped diffraction lines belonging to both NiO and $NiFe_2O_4$. Besides $Ni(NO_3)_2$ · $6H_2O$, sample S_1 contained an additional phase, which might be considered as an iron nitrate hydrate; however, its positive identification by the JCPDS-PDF data was not possible with certainty.

The results, obtained by FT-IR spectoscopy, are summarized in Figures 1, 2 and 3. The FT-IR spectrum of sample S_1 showed a very intensive band at 3392 cm^{-1} which can be ascribed to the stretching modes of surface water molecules or to the envelope of the H-bonded surface OH groups,[11] while the characteristic band at 1630 cm^{-1} is due to the H_2O bending mode. The bands at 1770, 1385 and 826 cm^{-1} in the same spectrum are well visible and correspond to the nitrate groups.[12]

The presence of α–Fe_2O_3 in sample S_1 cannot be recognized with certainty on the basis of the FT-IR spectrum because a very strong band at 590 cm^{-1}, with shoulders at 690 and 480 cm^{-1}, is the superposition of several IR bands of different origin. The nature of IR bands corresponding to α–Fe_2O_3 was discussed in previous papers.[10,13,14]
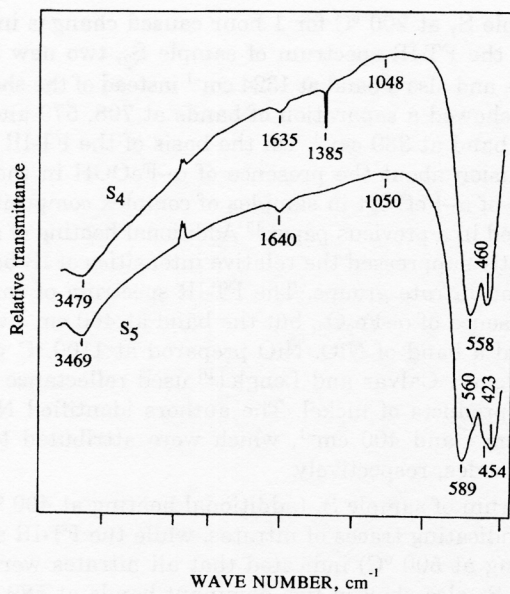
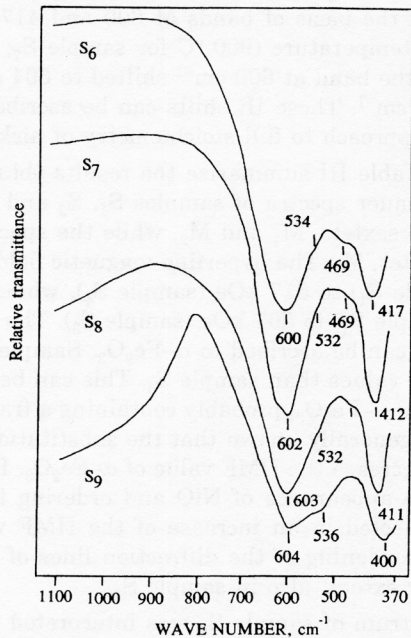Figure 2. Fourier transofrm IR spectra of samples S$_4$ and S$_5$, recorded at room temperature.

Figure 3. Fourier transform IR spectra of samples S$_6$, S$_7$, S$_7$ and S$_9$, recorded at room temperature.

Heating of sample S_1 at 200 °C for 1 hour caused changes in the corresponding FT-IR spectrum. In the FT-IR spectrum of sample S_2, two new bands at 1532 and 978 cm^{-1} were visible, and also a band at 1324 cm^{-1} instead of the shoulder at 1355 cm^{-1}. This spectrum also showed a separation of bands at 708, 579 and 477 cm^{-1} and appearance of a weak band at 389 cm^{-1}. On the basis of the FT-IR spectra of samples S_1 and S_2, no conclusion about the presence of α–FeOOH in these samples can be made. Identification of α–FeOOH in samples of complex composition by FT-IR spectroscopy was discussed in a previous paper.[15] Additional heating of sample S_2 at 300 °C for 1 hour significantly suppressed the relative intensities of IR bands corresponding to H_2O molecules and nitrate groups. The FT-IR spectrum of sample S_3 gave more evidence for the presence of α–Fe_2O_3, but the band at 460 cm^{-1} was an overlap of a band of α–Fe_2O_3 and a band of NiO. NiO prepared at 1100 °C was characterized[10] by the band at 466 cm^{-1}. Calvar and Lenglet[16] used reflectance IR spectra in analyzing the oxidized products of nickel. The authors identified NiO on the basis of bands at 580–615 cm^{-1} and 400 cm^{-1}, which were attributed to longitudinal and transversal optical modes, respectively.

The FT-IR spectrum of sample S_4 (additional heating at 400 °C) showed a sharp peak at 1385 cm^{-1} indicating traces of nitrates, while the FT-IR spectrum of sample S_5 (additional heating at 500 °C) indicated that all nitrates were decomposed. The spectrum of sample S_5 also showed two dominant bands at 589 and 423 cm^{-1} with shoulders at 560 and 454 cm^{-1}. The bands at 584 and 423 cm^{-1} indicated ferritization in sample S_5.

The FT-IR spectrum of sample S_6 (additional heating at 700 °C) showed the presence of nickel ferrite on the basis of bands at 600 and 417 cm^{-1}. With further increasing of the heating temperature (900 °C for sample S_7; 1100 °C for sample S_8; 1350 °C for sample S_9), the band at 600 cm^{-1} shifted to 604 cm^{-1}, while the band at 417 cm^{-1} shifted to 400 cm^{-1}. These IR shifts can be ascribed to the crystal lattice ordering and/or to the approach to full stoichiometry of nickel ferrite.

Figures 4 to 7 and Table III summarize the results obtained by the Mössbauer spectroscopy. The Mössbauer spectra of samples S_1, S_2 and S_3 were interpreted as the superposition of two sextets, M_1 and M_2, while the spectrum of sample S_4 was characterized by one sextet, M_1. The hyperfine magnetic field, HMF, of sextet M_1 increased from 471 (sample S_1) to 517 kOe (sample S_4), while the HMF of sextet M_2 increased from 439 (sample S_1) to 501 kOe (sample S_3). The HMF value of 517 kOe measured for sample S_4 can be ascribed to α–Fe_2O_3. Samples S_1, S_2 and S_3 showed significantly lower HMF values than sample S_4. This can be explained by the presence of poorly crystallized α–Fe_2O_3, probably containing a fraction of Ni^{2+} ions in the α–Fe_2O_3 structure. It is generally known that the substitution of Fe^{3+} ions with certain metal cations can decrease the HMF value of α–Fe_2O_3. Increase in temperature up to 400 °C caused the appearance of NiO and ordering in the crystal lattice of α–Fe_2O_3, which was reflected in an increase of the HMF value. X-ray diffraction showed a pronounced broadening of the diffraction lines of α–Fe_2O_3 in samples S_2 and S_3, and to a smaller extent, also in sample S_4.

The Mössbauer spectrum of sample S_5 was interpreted as the superposition of three sextets, due to the presence of nickel ferrite and α–Fe_2O_3. The spectra recorded for samples S_6 to S_9 were fitted with two sextets corresponding to nickel ferrite. The relative intensities of the spectral lines of the inner sextet, M_2, increased from sam-
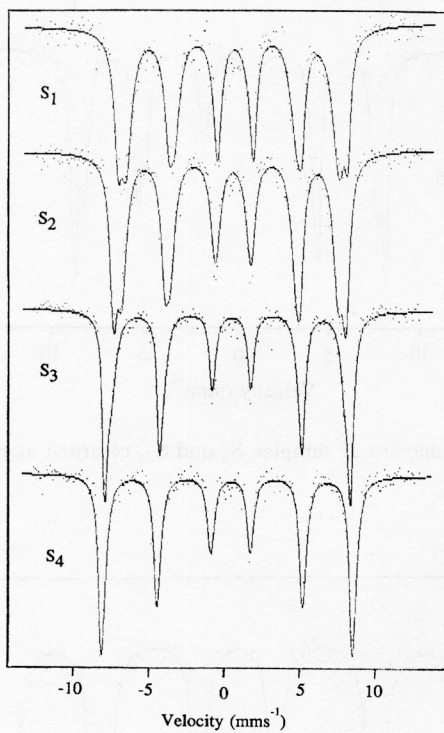
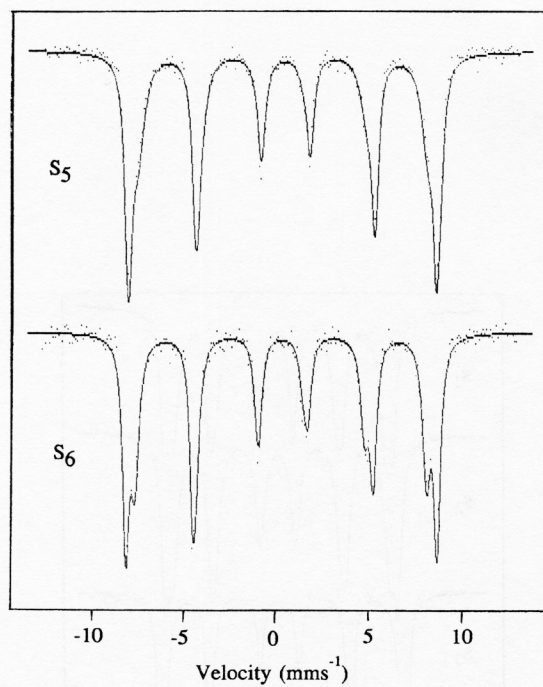Figure 4. ^{57}Fe Mössbauer spectra of samples S$_1$, S$_2$, S$_3$ and S$_4$, recorded at room temperature.

Figure 5. ^{57}Fe Mössbauer spectra of samples S_5 and S_6, recorded at room temperature.
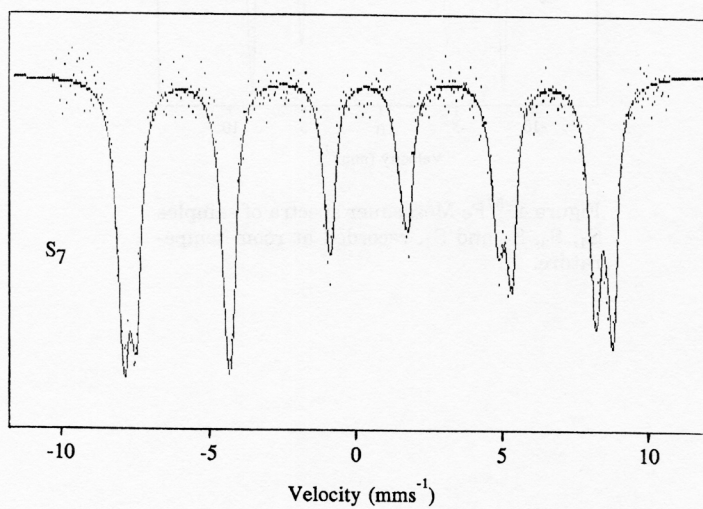

Figure 6. ^{57}Fe Mössbauer spectrum of sample S_7, recorded at room temperature.
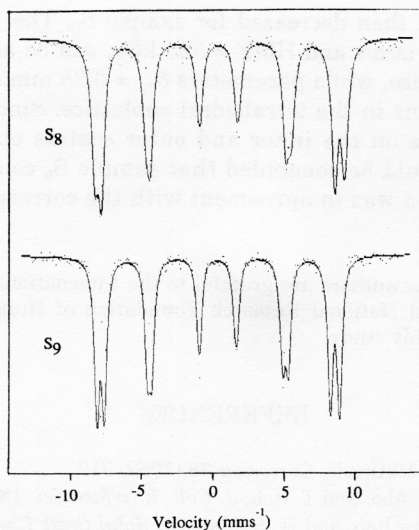
Figure 7. ^{57}Fe Mössbauer spectrum of samples S_8 and S_9, recorded at room temperature.

TABLE III

^{57}Fe Mössbauer parameters calculated on the basis of the
spectra recorded at room temperature

Sample	Lines	δ^*/mm s^{-1}	ΔE_q/mm s^{-1}	HMF/kOe	Γ/mm s^{-1}
S_1	M_1	0.38	−0.21	471	0.45
	M_2	0.37	−0.16	439	0.99
S_2	M_1	0.36	−0.22	478	0.57
	M_2	0.39	−0.16	446	0.75
S_3	M_1	0.38	−0.20	506	0.41
	M_2	0.37	−0.18	501	0.71
S_4	M_1	0.39	−0.14	517	0.54
S_5	M_1	0.37	−0.12	524	0.41
	M_2	0.36	−0.16	513	0.39
	M_3	0.29	−0.01	484	0.83
S_6	M_1	0.36	−0.08	522	0.41
	M_2	0.26	0.01	490	0.55
S_7	M_1	0.36	−0.06	519	0.44
	M_2	0.24	0.01	487	0.50
S_8	M_1	0.35	0.08	535	0.49
	M_2	0.27	0.01	500	0.57
S_9	M_1	0.36	0.04	528	0.42
	M_2	0.28	0.01	494	0.47

*Isomer shift is given relative to α–Fe
Errors: ± 0.01 mm/s and ± 1kOe

ple S_6 to sample S_8, and then decreased for sample S_9. The parameters calculated for sample S_9, $\delta_{Fe} = 0.36$ mm/s and HMF = 528 kOe, can be ascribed to Fe^{3+} cations in the octahedral sublattice, while parameters $\delta_{Fe} = 0.28$ mm/s and HMF = 494 kOe can be asscribed to cations in the tetrahedral sublattice. Since the relative intensities of the spectral lines on the inner and outer sextets observed for sample S_9 were almost equal, it could be concluded that sample S_9 contained stoichiometric $NiFe_2O_4$. This comclusion was in agreement with the corresponding X-ray diffraction measurements.

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SAŽETAK

Karakterizacija oksidnih faza stvorenih tijekom sinteze $NiFe_2O_4$

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Oksidne faze stvorene tijekom sinteze $NiFe_2O_4$ iz vodene otopine $Ni(NO_3)_2/Fe(NO_{23})_3$ karakterizirane su difrakcijom X-zraka, FT-IR spektroskopijom i ^{57}Fe Mössbauerovom spektroskopijom. U uzorcima pripravljenima do 300 °C detektirane su nitratne soli i α–Fe_2O_3. Stvaranje ferita opaženo je pri 500 °C. Stehiometrijski $NiFe_2O_4$ pripravljen je pri 1350 °C. Pokazano je da su NiO i α–Fe_2O_3 međufaze u procesu stvaranja $NiFe_2O_4$. Smanjena vrijednost hiperfinog magnetskog polja izmjerena je za uzorke α–Fe_2O_3 pripravljene pri nižim temperaturama. FT-IR spektroskopijom praćena je razgradnja nitratnih grupa.