Thermal Decomposition of Freeze-dried Complex Acetates of Iron, Nickel and Zinc, and Structural Characterization of Products

H. Langbein,[a] C. Michalk,[b] K. Knese[b] & P. Eichhorn[a]

[a] Dresden University of Technology, Department of Chemistry, O-8027 Dresden, FRG
[b] Leipzig University, Department of Physics, O-7010 Leipzig, FRG

Abstract

Heteronuclear complex acetates with the stoichiometry of metal ions $Ni_{1-x}^{II}Zn_x^{II}Fe_2^{III}$ are prepared by freeze-drying of solutions of metal acetates with appropriate compositions. The amorphous powders are decomposed on heating, releasing H_2O, acetic acid, acetone and CO_2. Depending on the conditions of decomposition, single-phase ferrites with spinel structure or mixtures of ferrites and simple oxides are formed as crystalline products. The phase formation is followed with the help of X-ray powder diffractometry and Mössbauer spectroscopy.

Heteronucleare komplexe Acetate mit der Metallionenstöchiometrie $Ni_{1-x}^{II}Zn_x^{II}Fe_2^{III}$ werden durch Gefriertrocknung entsprechend zusammengesetzter Metallacetatlösungen hergestellt. Die amorphen Pulver zersetzen sich beim Erhitzen unter Abgabe von H_2O, Essigsäure, Aceton und CO_2. In Abhängigkeit von den Zersetzungsbedingungen enstehen als kristalline Produkte Ferrite mit Spinellstruktur oder Ferrite mit einem Anteil an einfachen Oxiden. Die Ausbildung der Phasen wurde mittels Röntgenpulverdiffraktometrie und Mössbauerspektroskopie verfolgt.

On a préparé des acétates complexes hétéronucléaires possédant la stoichiométrie des ions métalliques $Ni_{1-x}^{II}Zn_x^{II}Fe_2^{III}$ par lyophilisation de solutions d'acétates métalliques de compositions appropriées. Les poudres amorphes se décomposent lors du chauffage, libérant H_2O, de l'acide acétique, de l'acétone et du CO_2. Les produits cristallins formés sont, selon les conditions de décomposition, des ferrites de structure spinelle ou des ferrites avec une partie d'oxydes simples. La formation des phases a été suivie à l'aide de la diffractométrie X et de la spectroscopie Mössbauer.

1 Introduction

In connection with the synthesis of ferrites with spinel structure MFe_2O_4 the authors were interested in $(Fe_2MO(CH_3COO)_6(H_2O)_3) \cdot nH_2O$ (I) compounds. The compounds can be precipitated from solutions of Fe(III) salts and salts of bivalent metal ions M(II) with M = Fe, Co, Ni, Mn or Zn by addition of acetate solution.[1,2] In **I** the cation stoichiometry of the spinel is already present; however, to realize a precise 2:1 stoichiometry of metal ions in the complex acetates requires specific precipitation conditions for each M(II).[3] Observing definite conditions, crystalline samples are thermally decomposed, giving off consecutively H_2O, acetic acid, acetone and CO_2, and crystalline ferrite MFe_2O_4 is produced from an amorphous intermediate. The ferrite formation was investigated, taking especially $NiFe_2O_4$ as an example.[4,5] Because the 2:1 stoichiometry of metal ions is only realized with difficulty for crystalline Fe_2M–acetato complexes, this becomes nearly impossible for defined compositions with different M(II) ions, which, when decomposed, should produce technically interesting ferrites, e.g. $Ni_{1-x}Zn_xFe_2O_4$ or $Mn_{1-x-y}Zn_xFe_{2+y}O_4$. With regard to the latter aim, the method of freeze-drying is a possible solution which, in principle, allows the transformation of solutions of metal salts into powders, while maintaining the stoichiometry.

By the investigations described in the following section, the authors intended to prepare complex metal acetate powders by freeze-drying of appropriately composed initial solutions and to characterize the oxides produced by thermal decomposition. To determine structural changes within the decomposition, in addition to X-ray phase analysis, mainly Mössbauer spectroscopic investigations were carried out.

2 Experimental Procedure

X-Ray phase analysis was made using an X-ray powder diffractometer with an equipment HZG1 of Fa. Freiberger Präzisionsmechanik operated by a M62 X-ray generator of Fa. Transformatoren und Röntgenwerk Dresden (iron filtrated Co-K_α radiation, $\lambda = 179 \cdot 02$ pm). For the thermal analysis, a Q1500D derivatograph (system Paulik-Paulik-Erdey) was used. The ^{57}Fe Mössbauer spectra were taken by means of a SM-6T spectrometer (Atomic Physics Institute, Swierk, Poland) at 293 K and were analysed by the computer assuming that the lines were of Lorentz shape. For the measurements in the outer magnetic field, a permanent 1 tesla induction magnet was applied.

3 Preparation and Characterization of Complex Acetates

To make the initial solutions, Fe(II) acetate, produced by dissolving Fe powder in acetic acid in an inert atmosphere, was oxidized in a 10^{-2}M acetic acid solution with double H_2O_2 excess. On heating, a deep red solution was formed containing the complex ion $(Fe_3O(CH_3COO)_6(H_2O)_3)^+$. To this solution, with a concentration of $C_0(Fe^{3+}) = 1$ mol litre^{-1}, the adequate quantity of 0·5M nickel acetate solution and/or zinc acetate solution was added. Poured over with liquid nitrogen, the deeply red-brown coloured solution was quickly frozen and dried in the vacuum chamber of a freeze-drying apparatus. Loose powders, amorphous by X-rays, were formed, the water content of which varied to some extent depending on the intensity of freeze-drying. Following the results of the C–H and metal analyses, the various products contained $5 \pm 0 \cdot 2$ acetate residues/Fe_2M unit. The medium composition of the samples can be described by the formula $(Fe_2Zn_xNi_{1-x}O(CH_3COO)_5(OH)(H_2O)_2)$ **(II)**. Hence the water and acetate content are lower than in the crystalline samples of formula I obtained by precipitation from solutions rich in acetate.
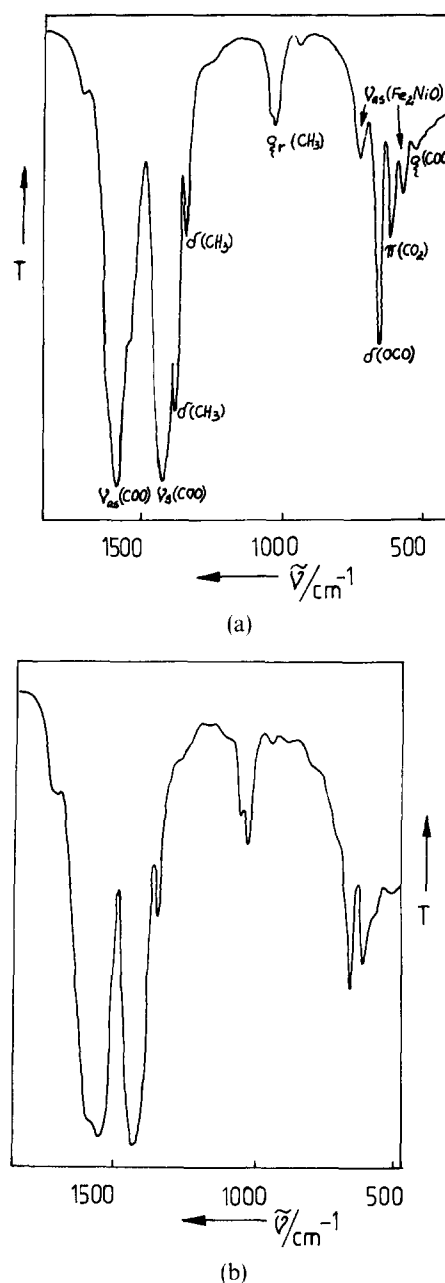

Fig. 1. Parts of IR spectra of (a) $(FeNiO(CH_3COO)_6(H_2O)_3)$. $2H_2O$ and (b) a freeze-dried sample II ($x = 0$).

In Fig. 1 parts of the IR spectra of a crystalline sample, $(Fe_2NiO(CH_3COO)_6(H_2O)_3) \cdot 2H_2O$, prepared by precipitation and of a freeze-dried sample of the same metal ions ratio are shown. The IR spectrum of the crystalline sample is identical with literature references.[6] In the figure the assignment of bands made on the basis of additionally plotted spectra of deuterated samples and of samples enriched by ^{18}O following Ref. 6 is also indicated. The high degree of similarity in the spectra of the crystalline and amorphous sample indicates an extensively analogous short-range order. Distinct differences only occur in the $v_{as}(Fe_2NiO)$ range. Whereas the crystalline compound shows two

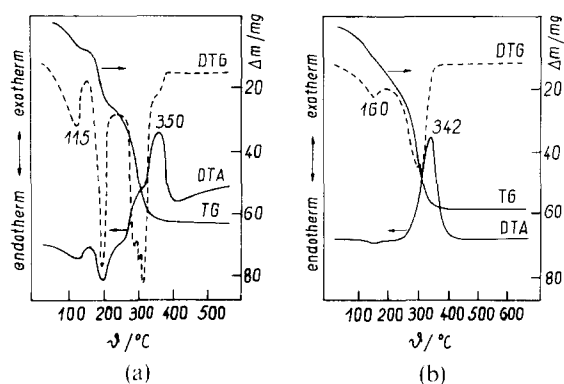**Fig. 2.** Thermal analysis of (a) $(Fe_2NiO(CH_3COO)_6(H_2O)_3)$. $2H_2O$ (crystalline) and (b) freeze-dried sample II $(x = 0)$. Weighed portion: 100 mg; heating rate: $10\,K\,min^{-1}$.

clearly separated absorption bands, these are detectable only as shoulders in the spectrum of the amorphous substance. The IR spectrum of the amorphous substance in the range between 550 and $750\,cm^{-1}$ is interpreted as superimposition of the designated oscillations of the COO group with a wide absorption band caused by asymmetric stretching vibrations of the undoubtedly present M_3O units (M = Fe, Ni), the individual arrangement and composition of which is less definite than in the crystalline compounds. According to Ref. 7 the occurrence of wide absorption bands and the simultaneous reduction of the number of bands is a characteristic of amorphous solids.

Figure 2 illustrates, as well, the result of thermal analysis, taking Fe_2Ni samples as an example. Again, the decomposition behaviour of the crystalline and freeze-dried amorphous samples is very similar. It is remarkable that the effects considerably superimposed for the freeze-dried sample occur clearly separated as two endothermic and at least one exothermic effect for the crystalline sample. Decomposition proceeds up to $200\,°C$, giving off H_2O and CH_3COOH; from $250\,°C$ acetone and CO_2 are formed as decomposition products, where the oxidation of acetone (by oxygen) causes the whole exothermic reaction. When the samples are decomposed in N_2 atmosphere, only endothermic effects are detectable in the total temperature range investigated.

4 Characterization of Solid Decomposition Products

In part (a) of both Figs 3 and 4 parts of the X-ray powder diffractograms are represented for the decomposition products of freeze-dried samples of the metal ions of stoichiometry, $Ni_{0.5}Zn_{0.5}Fe_2$, obtained by various modes. After a short thermal

(a)

(b)

Fig. 3. (a) Parts of X-ray powder diffractograms of decomposition products of the sample II $(x = 0.5)$ and (b) Mössbauer spectra of the appropriate samples. Decomposition conditions: sample b-1, 1 h, $300\,°C$; sample b-2, 1 h, $300\,°C$ then 3 h, $800\,°C$; sample b-1', measurement in the external magnetic field (1 T).
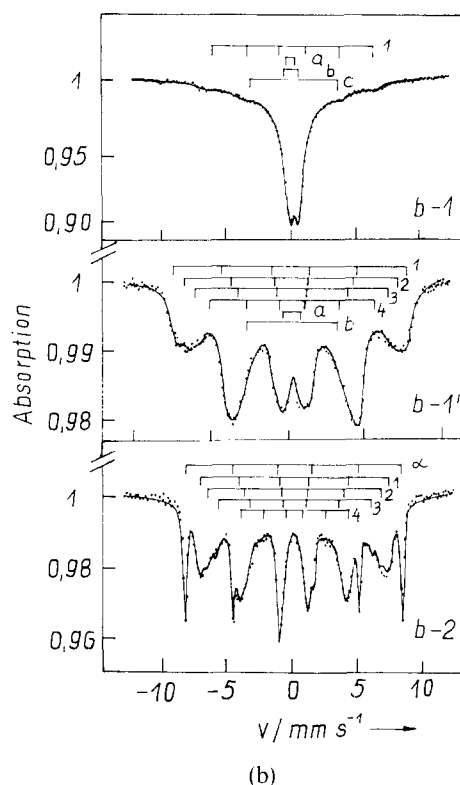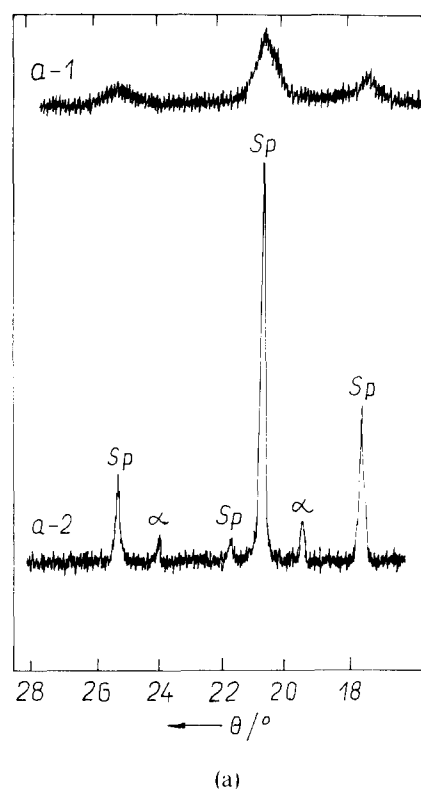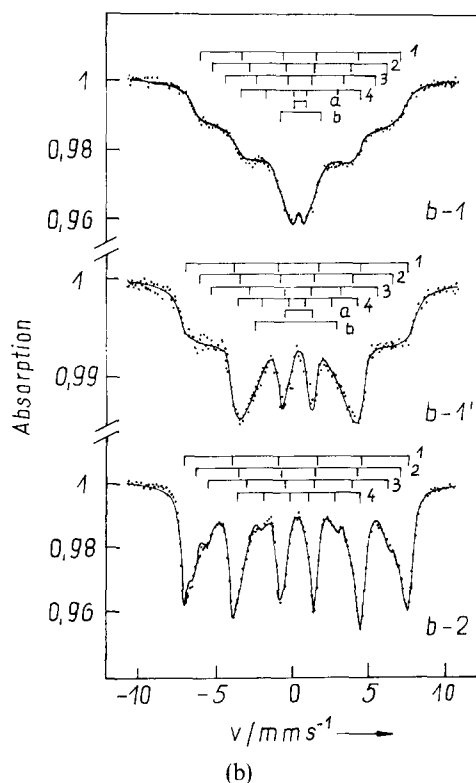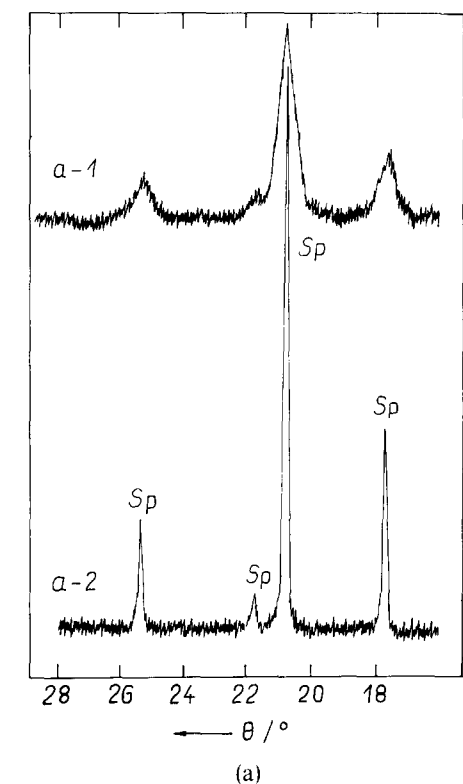
(a)

(b)

Fig. 4. (a) Parts of X-ray powder diffractograms of decomposition products of the sample II ($x = 0.5$) and (b) Mössbauer spectra of the appropriate samples. Decomposition conditions: sample b-1, 6 h, 400°C; sample b-2, 6 h, 400°C then 3 h, 800°C; sample b-1', measurement in the external magnetic field (1 T).

treatment at 300°C, the diagram shows reflections of relatively great half-intensity width which, according to the position and intensity ratio, can be assigned to the spinel structure of a Ni–Zn ferrite (sample 3a-1). By a subsequent treatment of the sample for 3 h at 800°C the reflection intensity is increased, with a simultaneous decrease in the half-intensity width (sample 3a-2). Besides the spinel reflections, other reflections also occur which are characteristic of α-Fe_2O_3. ZnO and NiO reflections are not apparent; the NiO reflections coincide with spinel reflections at $\vartheta = 21.8°$ and $\vartheta = 25.6°$ in the represented angular range. Hence, under the decomposition conditions selected, predominantly, but not exclusively, ferrite with spinel structure is produced. Only by re-treating the sample obtained at 800°C for several hours at 1150°C is single-phase ferrite obtained. These facts are substantiated by Mössbauer spectroscopic investigations. The Mössbauer spectra belonging to the samples 3a-1 and 3a-2 are represented in Fig. 3(b). After the 300°C treatment, the Mössbauer spectrum shows a wide doublet which is typical of relaxation effects. The sextet structure to be expected for Ni–Zn ferrite due to magnetic hyperfine interaction is only slightly indicated (sample 3b-1). When measuring in a 1-tesla outer magnetic field perpendicular to the γ-ray direction (sample 3b-1'), the relaxation portion of 34.5% is considerably lower than in the measurement without outer field (91%), whereas the sextet spectrum characteristic of Ni–Zn ferrite more distinctly occurs than in the zero-field measurement. Such a change of the Mössbauer spectrum influenced by an outer magnetic field is typical of the so-called superparamagnetic behaviour of small particles of diameters <15 nm.

It is known that, depending on the thermal energy kT, such small particles quickly change their direction of magnetization.[8] With an outer magnetic field fluctuation of magnetization is suppressed. Because the medium particle diameter of the ferrite powder is much greater than 15 nm, these superparamagnetic particles are magnetic clusters within the ferrite particles which are separated by still amorphous areas. The small crystallinity of the sample 3a-1 confirms that fact. After heating to 800°C, a spectrum is obtained which is typical of Ni–Zn ferrite, and this spectrum is superimposed by the Mössbauer spectrum of α-Fe_2O_3 (18%). The spectrum's portion to be explained by relaxation effects is only small. The ferrite spectrum's adjustment as superimposition of several sextets is understandable when taking into account that the Fe ions on A places form a sextet with another magnetic splitting

than that of the sextet of Fe ions on B places of the spinel lattice. Because of different metal ions in the vicinity, and thus different effective magnetic fields in the Mössbauer spectra, lines are widened, which corresponds to a distribution of hyperfine interactions and can be adjusted by computers when superimposing more than two sextets (see Table 1). Figure 4(a) shows a detail from the X-ray powder diffractogram of a sample tempered for 6 h at 400°C. Only spinel reflections occur, and the sample's crystallinity is higher compared with that of the sample 3a-1. Accordingly more striking, the sextet structure which occurs is characteristic of the ordered ferrite phase (sample 4b-1). Its portion is about 50% in the zero-field spectrum. By measuring in the outer magnetic field (sample 4b-1') a ferrite phase percentage exceeding 94% was identified.

By using a 3-h tempering phase at 800°C following the 400°C treatment, according to the X-ray diffractogram (sample 4a-2) and the Mössbauer spectrum (sample 4b-2), a single-phase Ni–Zn ferrite of high crystallinity is obtained. Completely analogous results were achieved when the decomposition products of freeze-dried samples of metal ions stoichiometry of Fe:Ni = 2:1 were investigated.

5 Conclusions

By the findings of the investigations described many analogies in the decomposition behaviour of crystalline complex acetates and freeze-dried samples of the respective composition are substantiated. The advantage of freeze-drying is the possibility of preparation of submicroscopically homogeneous samples, the stoichiometry of metal ions of which is practically open as to the selection. With regard to the preparation of single-phase ferrites by thermal decomposition at low temperature, the decomposition conditions are of high significance. A longer tempering time between 300 and 400°C is important. However, the interpretation of ferrite formation given in Ref. 4 by means of the intermediate formation of NiO and Fe_3O_4 seems to be improbable. So the Mössbauer identification of Fe_3O_4 is not beyond doubt, as in Ref. 4 the phase in question occurred only in a single sample with a small percentage and, in addition, the Mössbauer parameters were indicated inaccurately. By the Mössbauer investigations of the samples 3b-1 to 4b-2 the Fe_3O_4 occurrence in these samples is excluded.

The product present after the decomposition at about 300°C is of a low crystallinity. Within the tempering process, between 300 and 400°C, obviously ordering processes take place in the considerably disturbed lattice with greater amorphous portions and structure elements of the Ni–Zn (or Ni alone) ferrite are formed. This assumption is substantiated by a comparison of Mössbauer spectra for samples 3b-1 and 4b-1. The more incompletely these ordering processes proceed before the temperature is increased to values of the faster crystallization of the amorphous powders, the higher is the probability for a partial crystallization of the single oxides. It is remarkable that the upper temperature limit for the necessary ordering processes is in a range where γ-Fe_2O_3 is transformed into α-Fe_2O_3 as well.

Table 1. Mössbauer parameters of the samples 2b-1–4b-2 (designation according to Figs 3(b) and 4(b))

Sample	Partial spectrum	Intensity (%)	IS (mm/s)	QS (mm/s)	B (T)	Γ (mm/s)
3b-1	1	8·94	0·39	0·0	38·73	1·64
	a	34·44	0·33	0·66	0·0	0·75
	b	44·23	0·36	1·05	0·0	2·70
	c	12·39	0·41	6·84	0·0	2·93
3b-1'	1	15·21	0·32	0·0	47·33	0·64
	2	17·70	0·40	0·0	43·32	0·76
	3	18·64	0·43	0·0	38·98	0·97
	4	13·91	0·38	0·0	33·29	1·66
	a	18·87	0·37	1·22	0·0	1·17
	b	15·66	0·35	6·01	0·0	2·25
3b-2	x	18·25	0·40	−0·162	52·01	0·29
	1	26·57	0·30	0·0	45·26	0·77
	2	17·61	0·32	0·0	41·56	0·75
	3	18·46	0·33	0·0	36·82	0·94
	4	19·11	0·29	0·0	25·89	1·13
4b-1	1	11·32	0·28	0·0	40·81	0·93
	2	10·80	0·30	0·0	35·72	0·86
	3	8·79	0·29	0·0	30·62	0·88
	4	19·16	0·36	0·0	24·41	1·86
	a	10·32	0·32	0·74	0·0	0·83
	b	39·60	0·33	2·74	0·0	3·41
4b-1'	1	19·02	0·27	0·0	44·85	0·94
	2	29·02	0·31	0·0	39·44	1·27
	3	16·29	0·28	0·0	33·65	1·01
	4	22·03	0·31	0·0	23·95	1·32
	a	11·71	0·32	1·78	0·0	1·04
	b	1·92	0·27	5·31	0·0	0·54
4b-2	1	29·51	0·27	0·0	45·38	0·57
	2	29·12	0·31	0·0	42·39	0·80
	3	24·15	0·35	0·0	36·87	0·97
	4	17·22	0·34	0·0	25·46	0·91

IS = Isomeric shift (relative to α-iron); QS = quadrupole splitting; B = hyperfine splitting; Γ = half-intensity width; 1,2,3,4 = ferrite phases; a,b,c = relaxation parts; x = α-Fe_2O_3.

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