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PREPARATION OF COBALT DOPED γ-Fe_2O_3 AND Mn–Zn FERRITES BY THE THERMAL DECOMPOSITION OF THE HYDRAZINE PRECURSORS

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Fine particle cobalt doped γ-Fe_2O_3 and Mn–Zn ferrites have been prepared by the thermal decomposition of $N_2H_5Co_xFe_{1-x}(N_2H_3COO)_3 \cdot H_2O$ where $x = 1$–10 atom% and $(N_2H_5)_3Mn_xZn_{1-x}Fe_2(N_2H_3COO)_9 \cdot 3H_2O$ where $x = 0.2$–0.8, respectively. Formation of these oxide materials has been confirmed by thermogravimetry and X-ray powder diffraction patterns. The fine particle nature of these oxide materials is evident from particle size analysis and surface area measurements.

γ-Fe_2O_3 is the most widely used recording material in magnetic tapes and disks. The magnetic requirement for such materials is that it must have high coercive field and saturation magnetisation as well as large remanance ratio. Also for better recording properties the particle size should be small. The limited coercivity range obtained by γ-Fe_2O_3 is overcome by adding 2–10% cobalt ions which increases the coercivity many folds [1].

High density Mn–Zn ferrites are used in readwrite heads, high speed digital tapes, broad band transformer core [2] etc. Important requirements are very high purity, chemical homogeneity, fine grain size and high density.

The preparation of these oxide materials is quite complicated and lengthy. Fine particle oxide materials are usually prepared by spray drying, freeze drying, sol-gel method, co-precipitation of hydroxides [3] and carbonates [4].

In continuation of our studies on the low temperature preparation of γ-Fe_2O_3 [5] and fine particle ferrites [6, 7] using hydrazine precursors, we now report the preparation of cobalt doped γ-Fe_2O_3 and Mn–Zn ferrites.

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Experimental

a) Preparation of. $N_2H_5Co_xFe_{1-x}(N_2H_3COO)_3 \cdot H_2O$ *(A)*

An aqueous solution containing iron(II)sulphate and cobalt(II)sulphate in the required ratio was treated with a solution of N_2H_3COOH in $N_2H_4 \cdot H_2O$ until the precipitate formed just dissolved. On keeping this solution exposed to air rose red crystals separated in about a week. The crystals were washed with alcohol and dried over P_2O_5 in a vacuum desiccator. The composition of the crystals was checked by chemical analysis and found to be $N_2H_5Co_xFe_{1-x}(N_2H_3COO)_3 \cdot H_2O$ (Table 1).

b) Preparation of $(N_2H_5)_3Mn_xZn_{1-x}Fe_2(N_2H_3COO)_9 \cdot 3H_2O$ *(B)*

An aqueous solution containing Mn(II)sulphate, zinc(II)sulphate and iron(II)sulphate in the required ratio was treated with N_2H_3COOH in $N_2H_4 \cdot H_2O$ until the precipitate formed just dissolved. On keeping the solution exposed to air, greenish yellow crystals separated in a couple of weeks. Crystals were washed with alcohol and dried over P_2O_5 in a vacuum desiccator. The composition of the crystals was checked by chemical analysis and found to be $(N_2H_5)_3Mn_xZn_{1-x}Fe_2(N_2H_3COO)_9 \cdot 3H_2O$ (B) (Table 1).

Table 1 Chemical analysis data of A and B

A) $N_2H_5Co_xFe_{1-x}(N_2H_3COO)_3 \cdot H_2O$ [$x = 1$–10 atom%]

x, atom%	% of iron		% of hydrazine	
	found	theoretical	found	theoretical
1	16.41	16.69	38.50	38.57
2	16.38	16.56	38.52	38.57
3	16.31	16.42	38.45	38.56
5	16.01	16.15	38.51	38.56
10	15.28	15.49	38.47	38.54

B) $(N_2H_5)_3Mn_xZn_{1-x}Fe_2(N_2H_3COO)_9 \cdot H_2O$ [$x = 0.2$–0.8]

x	% of Mn		% of Zn		% of Fe		% of hydrazine	
	found	theor.	found	theor.	found	theor.	found	theor.
0.2	1.03	1.09	5.11	5.18	11.02	11.14	38.11	38.30
0.3	1.58	1.65	4.51	4.57	11.10	11.15	38.15	38.33
0.5	2.71	2.75	3.20	3.27	11.12	11.17	38.31	38.41
0.7	3.57	3.85	1.92	1.97	11.10	11.20	38.25	38.49
0.8	4.38	4.41	1.27	1.31	11.09	11.21	38.41	38.53

Instrumental techniques

Simultaneous TG–DTA–DTG experiments were carried out using a ULVAC Sinku–Riko TA–1500, Japan instrument. About 5–8 mg of the samples were used for the experiments. The heating rate employed was 20 deg/min. All experiments were carried out in air.

X-ray powder diffraction patterns of the oxide samples were recorded using a Philips X-ray diffractometer model PW 1050/70. Cobalt source was used with nickel/iron filter.

Particle size analysis of the oxides was carried out using a Seishin Micron Photo sizer model SKC 2000, Japan, employing sedimentation and light scattering principle.

BET surface areas of the oxides were determined using a Micromeritics Accusorb 2100E instrument by nitrogen adsorption.

The IR spectra of the precursors were recorded as Nujol mull using a Perkin–Elmer 781 spectrophotometer.

The densities of the oxides were measured employing a pyknometer using xylene medium.

Results and discussion

The results of chemical analysis of A and B (Table 1) show that the precursors are solid-solutions of the corresponding metal salts. Formation of solid solution is expected due to the comparable ionic sizes of Co^{2+}, Mn^{2+}, Zn^{2+} with Fe^{2+} [8]. Typical infrared spectra of $N_2H_5Co_xFe_{1-x}(N_2H_3COO)_3 \cdot H_2O$ ($x=2$ atom%) and $(N_2H_5)_3Mn_{0.8}Zn_{0.2}Fe_2(N_2H_3COO)_9 \cdot 3H_2O$ are shown in Fig. 1. Both precursors show characteristic absorption frequencies of $N_2H_3COO^-$ at 3200, 3260, 3300 (ν_{n-H}), 1590 (NH_2 band) 1650 (ν_{COO-}), 1100 (ν_{N-C}), 900 ($\nu_{N-N}N_2H_3^+$) and 960 ($\nu_{N-N}N_2H_5^+$) cm^{-1}. Formation of solid solution is evident by the similarity of IR spectra of A ($x=2$ atom%) and B ($x=0.8$) (Fig. 1) with that of Fe complex [8].

The TG–DTA–DTG curves of A ($x=1$ atom%) and B ($x=0.5$) are shown in Fig. 2. Both precursors decompose in single step at ~170° to give corresponding oxides i.e., γ-Fe_2O_3 (1 atom% cobalt) $Mn_xZn_{1-x}Fe_2O_4$ ($x=0.5$), respectively. The DTA of precursor A shows a doublet corresponding to the single TG step. On the other hand the precursor B showed a single exotherm. The doublet observed in the case of A has been attributed to the decomposition of metathetically formed iron oxalate hydrazine intermediate [8]. The results of TG–DTA of the complexes are summarised in Table 2. The mass loss observed in TG is in good agreement with that calculated for the formation of these oxides.

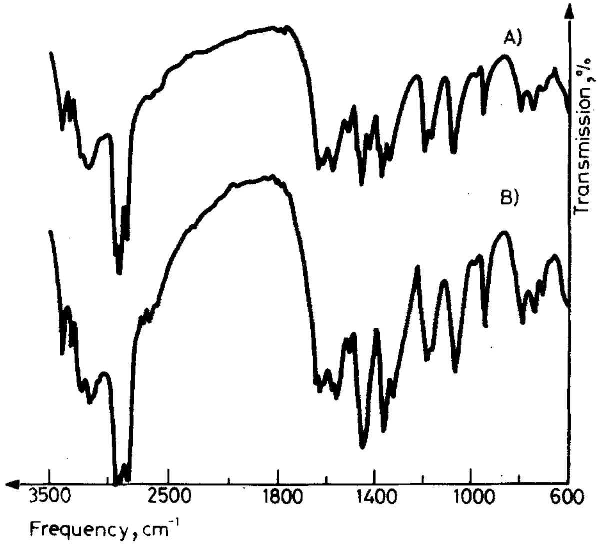

Fig. 1 Infrared absorption spectra of (A) $N_2H_5Co_xFe_{1-x}(N_2H_3COO)_3 \cdot H_2O$ ($x=2$ atom%); (B) $(N_2H_5)_3Mn_xZn_{1-x}Fe_2(N_2H_3COO)_9 \cdot 3H_2O$ ($x=0.8$)

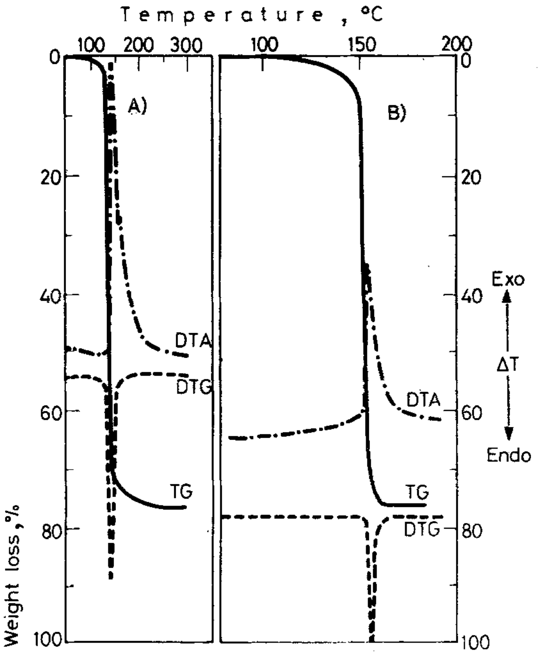

Fig. 2 Simultaneous TG–DTA–DTG of (A) $N_2H_5Co_xFe_{1-x}(N_2H_3COO)_3 \cdot H_2O$ ($x=1$ atom%); (B) $(N_2H_5)_3Mn_xZn_{1-x}Fe_2(N_2H_3COO)_9 \cdot 3H_2O$ ($x=0.5$)

Table 2 Thermal analysis data of A and B

A) $N_2H_5Co_xFe_{1-x}(N_2H_3COO)_3 \cdot H_2O$ ($x=1$–10 atom%)

x, atom%	DTA peak temp., °C	Temperature range, °C	Mass loss, %	
			found	theoretical
1	165(exo) 180(exo)	145–220	74.00	73.52
2	165(exo) 180(exo)	150–220	73.50	73.52
3	160(exo) 180(exo)	145–230	74.00	73.51
5	160(exo) 180(exo)	150–230	74.00	73.50
10	160(exo) 180(exo)	145–220	73.50	73.46

B) $(N_2H_5)_3Mn_xZn_{1-x}Fe_2(N_2H_3COO)_9 \cdot 3H_2O$ ($x=0.2$–0.8)

x, atom%	DTA peak temp., °C	Temperature range, °C	Mass loss, %	
			found	theoretical
0.2	150(exo)	115–210	76.50	76.18
0.2	150(exo)	115–210	76.50	76.25
0.5	155(exo)	120–220	76.50	76.41
0.7	165(exo)	130–230	77.00	76.57
0.8	155(exo)	120–210	77.00	76.65

Formation of γ-Fe_2O_3 ($a=0.837$ nm) and Mn–Zn ferrites ($a=0.8512$ nm) is confirmed by their characteristic XRD patterns (Fig. 3) and their corresponding lattice constants "a" value which correspond to those in the literature [9–11].

Both precursors decompose at fairly low temperatures (~170°) with the evolution of large amounts of gases like CO_2, NH_3, H_2O, N_2 etc. (nearly 75% weight loss) to yield fine, porous and voluminous oxide products. The powder density of cobalt doped γ-Fe_2O_3 was in the range 4.20–4.50 g/cm^3 (~76% of theoretical density) and that of $Mn_xZn_{1-x}Fe_2O_4$ was in the range 3.45–3.75 g/cm^3 (~70% of theoretical density).

The BET surface area of cobalt doped γ-Fe_2O_3 is in the range of 70–75 m^2/g and that of Mn–Zn ferrites varies from 110–130 m^2/g. Typical particle size analysis of 2 atom% cobalt doped γ-Fe_2O_3 is shown in Fig. 4 and it can be seen that the average particle size is 0.83 μm. Similarly, the average particle size of Mn–Zn ferrites was in the range 3–6 μm.

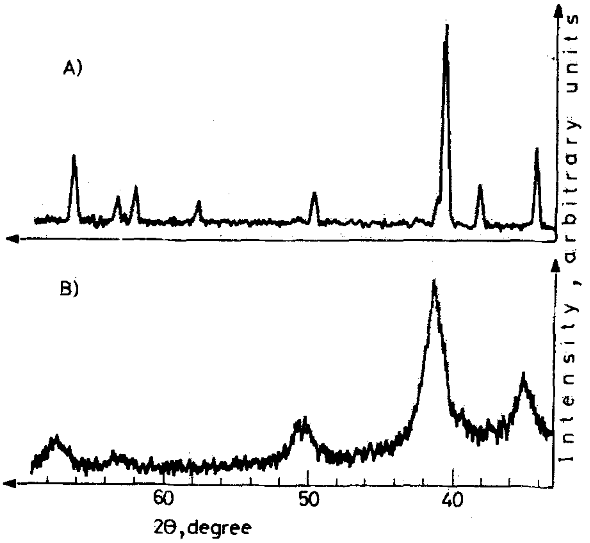

Fig. 3 X-ray powder diffraction patterns of (A) $Mn_{0.5}Zn_{0.5}Fe_2O_4$; (B) γ-Fe_2O_3 (1 atom% cobalt)

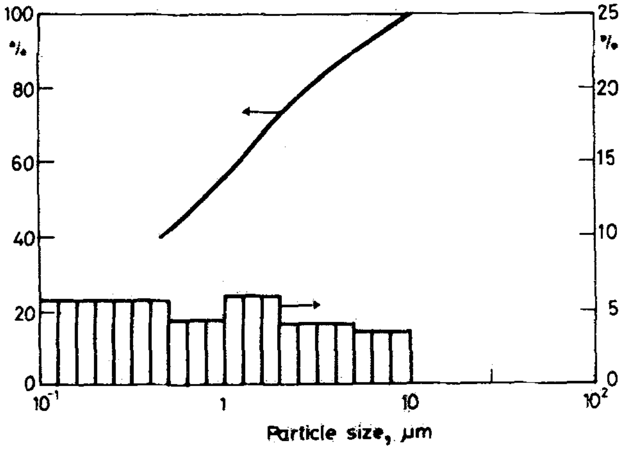

Fig. 4 Accumulated weight percentage curve for γ-Fe_2O_3 (2 atom% cobalt)

Conclusions

Technologically important cobalt doped γ-Fe_2O_3 and Mn–Zn ferrites have been obtained in a single step by thermal decomposition of novel hydrazine precursors at very low temperatures. These fine particle oxides could be sintered below 1000° to achieve almost 99% of theoretical density.

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Zusammenfassung — Mit fein verteiltem Kobalt versetztes γ-Fe_2O_3 sowie Mn–Zn Ferrite wurden durch thermische Zersetzung von $N_2H_5Co_xFe_{1-x}(N_2H_3COO)_3 \cdot H_2O$ mit $x = 1$–10 Atomprozent bzw. $(N_2H_5)_3Mn_xZn_{1-x}Fe_2(N_2H_3COO)_9 \cdot 3H_2O$ mit $x = 0{,}2$–$0{,}8$ hergestellt. Die Bildung dieser Oxidstoffe wurde durch Thermogravimetrie und Pulverdiffraktionsmethoden bekräftigt. Die Feinkornstruktur dieser Oxidstoffe wird durch Korngrößenverteilungs- und Oberflächenmessungen augenscheinlich.

Резюме — Термическим разложением соединений $N_2H_5Co_xFe_{1-x}(N_2H_3COO)_3 \cdot H_2O$, где $x = 1$–10 атомных%, и $(N_2H_5)_3Mn_xZn_{1-x}Fe_2(N_2H_3COO)_9 \cdot 3H_2O$, где $x = 0{,}2$–$0{,}8$, были получены, соответственно, легированный кобальтом порошкообразный γ-Fe_2O_3 и Mn–Zn ферриты. Образование таких оксидных материалов было подтверждено термогравиметрией и порошковым рентгеноструктурным анализом. Тонкопорошковая природа этих оксидных материалов доказана ситовым анализом и измерением площади поверхности.