Preparation and Properties of Fine Particle Nickel–Zinc Ferrites: A Comparative Study of Combustion and Precursor Methods

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Fine particle nickel–zinc ferrites, $Ni_xZn_{1-x}Fe_2O_4$ where $x = 0.2$–0.8 have been prepared, both by the thermal decomposition of the precursor, $(N_2H_5)_3Ni_xZn_{1-x}Fe_2(N_2H_3COO)_9 \cdot 3H_2O$ and combustion of redox mixtures containing nickel nitrate, zinc nitrate, iron(III) nitrate, and oxalic acid dihydrazide (ODH) in the required mole ratio. Both the processes yield submicrometer size (60–90 nm), large surface area (85–108 m^2/g), sinteractive powders which when heated at 1050°C, 3 hr achieve >98% of the theoretical density.   © 1992 Academic Press, Inc.

1. Introduction

Nickel–zinc ferrites, $Ni_xZn_{1-x}Fe_2O_4$ are of interest because of their technological applications (*1–4*) such as high frequency inductors, transformer cores, read/write heads for high speed digital recordings, antenna rods, etc. It is essential that the recording head material should have high density to give a good wear and tear property against the rapidly moving tapes with their abrasive coating of iron oxide (*5*). The magnetic properties of the ferrites are determined by the chemical composition, porosity, grain size, and microstructure. Fine particle, sinteractive Ni–Zn ferrite powders have been obtained by the thermal decomposition/combustion of solid solution precursors of the type $(N_2H_5)_3Ni_xZn_{1-x}Fe_2(N_2H_3COO)_9 \cdot 3H_2O$ (*6–8*). These precursors have low decomposition/ignition tempera-

ture and once ignited burn autocatalytically to yield fine particle ferrites. Although the process is quite attractive, the preparation of the precursors is quite involved and requires a couple of weeks for the crystallization of $(N_2H_5)_3Ni_xZn_{1-x}Fe_2(N_2H_3COO)_9 \cdot 3H_2O$. Moreover, the yield of ferrite is only 15% (weight of the ferrite/precursor). Recently, a novel combustion process has been developed using metal nitrate (oxidizer) and ODH (fuel) mixtures for an instant synthesis of a variety of ferrites (*9*). Presently, we report the preparation of a whole range of Ni–Zn ferrites, $Ni_xZn_{1-x}Fe_2O_4$, by the combustion process and compare the properties with those already reported by the precursor method (*6*).

2.1 Experimental

Ni–Zn ferrites $Ni_xZn_{1-x}Fe_2O_4$ where $x = 0.2$–0.8 were prepared by the combustion of nickel nitrate, zinc nitrate, iron(III) nitrate and oxalic acid dihydrazide (ODH) mixtures

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and also by the decomposition of hydrazine precursor $(N_2H_5)_3Ni_xZn_{1-x}Fe_2(N_2H_3COO)_9 \cdot 3H_2O$. Stoichiometric compositions of metal nitrate (oxidizer) and ODH (fuel) are calculated using the total oxidizing and reducing valencies of the components, which serve as the numerical coefficients for the stoichiometric balance so that the equivalence ratio ϕ_c is unity and the energy released is maximum (10). The mole ratio calculated for the release of maximum energy and for the complete combustion to obtain Ni–Zn ferrite is $x\text{Ni}(NO_3)_2 \cdot 6H_2O : (1 - x)\text{Zn}(NO_3)_2 \cdot 4H_2O : 2\text{Fe}(NO_3)_3 \cdot 9H_2O : 4(CON_2H_3)_2$.

In a typical experiment $\text{Ni}(NO_3)_2 \cdot 6H_2O(1.80$ g), $\text{Zn}(NO_3)_2 \cdot 3H_2O(1.51$ g), $\text{Fe}(NO_3)_3 \cdot 9H_2O(10.0$ g) were taken in a pyrex dish and dissolved in minimum amount of water (15 ml) to which $(CON_2H_3)_2$(ODH) (4.74 g) was added, and the dish containing the solution was introduced in a muffle furnace ($l = 28$ cm, $b = 17$ cm, $h = 9$ cm) maintained at $350 \pm 10°C$. The mixture boils, froths, and ignites to yield voluminous and foamy $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2O_4$ occupying the entire volume of the container in less than 3 min. The formation of Ni–Zn ferrites was confirmed by X-ray powder diffraction, and their fine particle nature was studied using SEM, TEM, particle size analysis, and surface area measurements.

2.2 Physical Methods

The X-ray powder diffraction patterns were recorded using a Phillips model PW 1050/70 X-ray diffractometer using CoK_α radiation with Fe filter. SEM micrographs were taken using a Cambridge Stereoscan Model S-150 scanning electron microscope. TEM observations were made using Phillips EM-301 transmission electron microscope operated at 100 kV. Particle size measurements were carried out using a Micron Photo Sizer Model SKC-2000 employing sedimentation principle. The surface area

of the oxides were measured by nitrogen adsorption employing Micromeritics Accusorb 2100E instrument. A vibration sample magnetometer (VSM) (EG&G Princeton Applied Research Model 155) was used to determine the saturation magnetization of the ferrites at room temperature. The powder and sintered densities of the ferrites were determined by using a pyknometer employing xylene as medium.

3.1 Results and Discussion

The formation of the spinel ferrites was confirmed by their characteristic powder XRD patterns. The X-ray patterns show considerable broadening as in the case of precursors, indicating the fine particle nature of ferrites. The average crystallite sizes calculated from X-ray line broadening using Scherrer's equation (11) are in the range 10–15 nm. Some properties like density, surface area, particle size, etc., of the combustion-synthesized ferrites are given in Table I. Table II gives a comparative account of the properties of Ni–Zn ferrites prepared by both methods. The lattice constant varies linearly with zinc concentration (Table I) as expected, indicating the atomic level substitution of Ni^{+2} by Zn^{+2} in the ferrites. The green densities of the ferrites are in the range of 3.43–3.56 g/cc (65–75% of the theoretical density). The surface area of the ferrites range from 85–95 m^2/g. These values are higher compared to those of precursor-derived ferrites, particularly for the higher values of "x," i.e., $x \geq 0.5$. This behavior can be attributed to the decomposition nature of the precursors, which is accompanied by the shrinking of the product due to the pyrophoric nature of the combustion. This is more evident in NiFe_2O_4 which has the least surface area (42 m^2/g) in the precursor method. The TEM picture (Fig. 1) shows that $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2O_4$ particles are platelets with sizes in the range 60–70 nm. The SEM micrograph of the as-prepared

TABLE I

SOME PROPERTIES OF COMBUSTION SYNTHESIZED Ni–Zn FERRITES

No.	Composition[a]	Product	XRD lattice constant (nm)	Crystallite size (nm)	Surface area (m^2/g)	Particle size from surface area (nm)	Powder density (g/cc)	Average agglomerate size (μm) (sedimentation)	Saturation magnetization (emu/g)
1.	Zn (3.012)	$ZnFe_2O_4$	0.844	11.3	67.5	26.0	3.43	3.6	—
2.	Ni(0.72), Zn(2.41)	$Ni_{0.2}Zn_{0.8}Fe_2O_4$	0.842	12.1	91.2	20.0	3.45	3.6	55.6
3.	Ni(1.44), Zn(1.82)	$Ni_{0.4}Zn_{0.6}Fe_2O_4$	0.840	11.7	85.6	20.0	3.47	3.4	66.0
4.	Ni(1.80), Zn(1.51)	$Ni_{0.5}Zn_{0.5}Fe_2O_4$	0.838	12.7	90.1	20.0	3.47	1.8	73.4
5.	Ni(2.15), Zn(1.21)	$Ni_{0.6}Zn_{0.4}Fe_2O_4$	0.837	12.1	85.2	21.0	3.48	1.8	69.5
6.	Ni(2.88), Zn(0.60)	$Ni_{0.8}Zn_{0.2}Fe_2O_4$	0.835	13.2	91.3	20.0	3.43	1.6	62.1
7.	Ni(2.60)	$NiFe_2O_4$	0.833	10.3	98.1	17.0	3.56	1.6	43.2

[a] = 10.00 g $Fe(NO_3)_3 \cdot 9H_2O$ + 4.74 g ODH + $Ni(NO_3)_2 \cdot 6H_2O$ (x g) + $Zn(NO_3)_2 \cdot 3H_2O$ (1 − x g).

$Ni_{0.5}Zn_{0.5}Fe_2O_4$ foam (Fig. 2) exhibits the inherent nature of a combustion process. Pores and voids are formed by the escaping gases during combustion.

The sintering behavior of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ as a function of temperature is shown in Fig. 3. It can be seen that the ferrites could be sintered to ~98% density at 1050°C, 3 hr, which is low compared to conventional ceramic method (>1200°C).

The relative magnetization (M/M_s) of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ as a function of field/tem- perature quotient (H/T) is shown in Fig. 4. The magnetization curves of the as-pre- pared ferrites by both methods at room tem- perature are characterized by lower satura- tion value and a single-line M–H curve, indicating superparamagnetic nature of the ferrites. As-formed ferrites did not attain saturation even at 18 KOe. However, on sintering the ferrites at 1050°C, 3 hr, satura- tion was attained. This effect is obviously due to the particle size dependence of M_s. The magnetic saturation moment reaches

TABLE II

COMPARISON OF PROPERTIES OF Ni–Zn FERRITES PREPARED BY BOTH PRECURSOR AND COMBUSTION METHODS

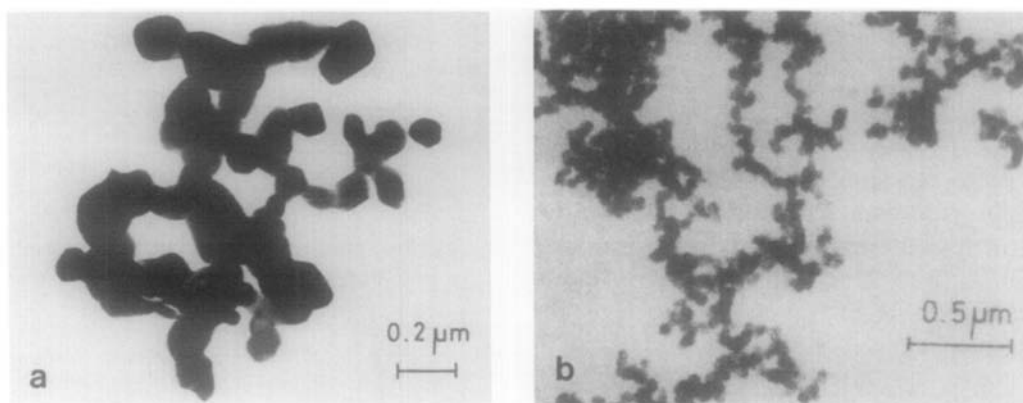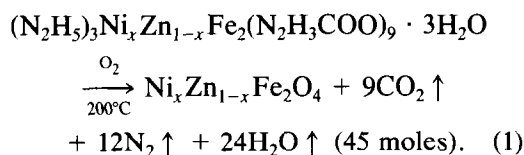| No.	Property	Precursor method	Combustion method
1.	Crystallite size from X-ray line broadening	10–15 nm	10–15 nm
2.	BET Surface area	42–108 m^2/g	85–95 m^2/g
3.	Powder density (% theoretical density)	65–75%	65–75%
4.	TEM (particle size)	60–90 nm	60–90 nm
5.	Sinterability (>98% density)	1000°C, 24 hr	1050°C, 3 hr
6.	Average grain size (SEM)	1–2 μm	3–5 μm
7.	Initiation temperature	250 ± 40°C	350 ± 10°C
8.	Homogeneity	100%	100%
9.	No. of moles gas evolved	45 moles	32 moles
10.	Average agglomerate size	1–5 μm	1–5 μm
11.	Time taken to prepare Ni–Zn ferrite	1–2 weeks to prepare the precursor, decomposition of the precursor in <5 min	Instantaneous (3 min)

FIG. 1. Transmission electron micrograph of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ prepared by (a) combustion method and (b) precursor method.

a maximum value of 73.6 emu/g for $Ni_{0.5}Zn_{0.5}Fe_2O_4$. This can be explained on the basis of Yafet–Kittel type of spin arrangement (12). With increase in "Zn" concentration the Fe^{+3} ions will have no magnetic neighbor and spins become uncoupled (13).

3.2 Mechanism

Formation of fine particle Ni–Zn ferrites by the precursor method can be attributed

to their low temperature initiation and exothermic decomposition producing a lot of gases. The combustion reaction can be written as follows:
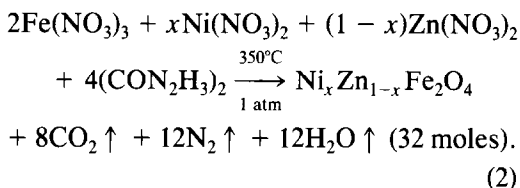
$$(N_2H_5)_3Ni_xZn_{1-x}Fe_2(N_2H_3COO)_9 \cdot 3H_2O$$
$$\xrightarrow[200°C]{O_2} Ni_xZn_{1-x}Fe_2O_4 + 9CO_2\uparrow$$
$$+ 12N_2\uparrow + 24H_2O\uparrow \quad (45 \text{ moles}). \quad (1)$$

Thus, the precursor method (solid-state decomposition) can be considered as a com-

FIG. 2. SEM micrograph of as prepared $Ni_{0.5}Zn_{0.5}Fe_2O_4$ foam prepared by combustion method.

bustion process which uses atmospheric ox-
ygen as oxidizer for combustion of the
precursor which is fuel rich. The decompo-
sition is autocatalytic; once initiated it is
accompanied by the evolution of 45 moles of
gases like N_2, H_2O, and CO_2. This facilitates
the formation fine particle Ni–Zn ferrite by
dissipating the heat and reducing the sin-
tering of the product. On the other hand, the
combustion method involves solution pyrol-
ysis and carries its own oxygen from metal
nitrates. The reaction can be written as
follows:

$$2Fe(NO_3)_3 + xNi(NO_3)_2 + (1 - x)Zn(NO_3)_2$$
$$+ 4(CON_2H_3)_2 \xrightarrow[\text{1 atm}]{350°C} Ni_xZn_{1-x}Fe_2O_4$$
$$+ 8CO_2\uparrow + 12N_2\uparrow + 12H_2O\uparrow \quad (32 \text{ moles}).$$
$$(2)$$

The exothermicity of the redox reaction

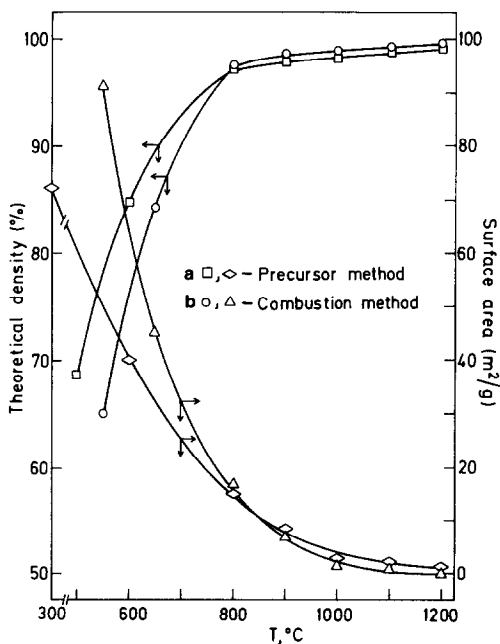FIG. 4. M/M_s vs H/T plot for combustion synthesized
$Ni_{0.5}Zn_{0.5}Fe_2O_4$.

FIG. 3. Sintering behavior of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ pre-
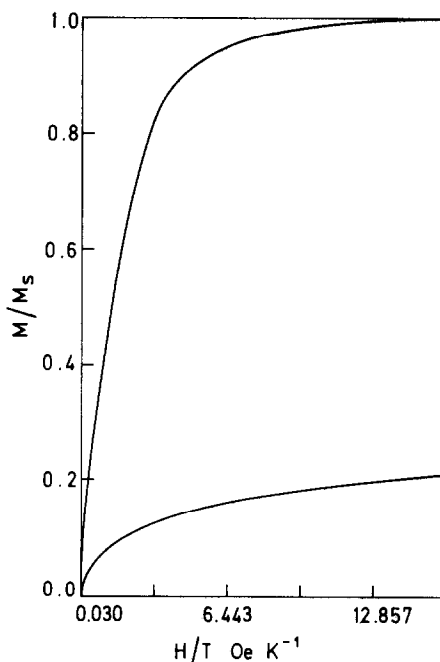pared by (a) combustion method and (b) precursor
method.

provides the energy required to form the
ferrite. The reaction is autocatalytic and
once initiated the Ni–Zn ferrite formed ap-
pears to catalyze oxidation of ODH (fuel).

4. Conclusion

Ni–Zn ferrites obtained by the combus-
tion process have large surface area, narrow
particle size distribution, and are sinterac-
tive similar to those by the hydrazine car-
boxylate precursor method. The combus-
tion process of preparing Ni–Zn ferrites is
simple, rapid, safe, and yields sinteractive
powders which attain >98% (theoretical
density) at 1050°C, 3 hr, holds much promise
over other methods.

Acknowledgment

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