

Notes

Effect of processing parameters on the magnetic properties of $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$

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Polycrystalline nickel-zinc ferrite powder has been obtained by chemical co-precipitation, involving the corresponding metal nitrates and sodium hydroxide under the different processing parameters for precipitation from those reported in our earlier paper [1, Anilkumar *et al.*, *Mater Lett*, 27(1996) 293]. The precipitate, when dried at 80°C in air shows cubic ferrite with lower values for $M_s \approx 17.7 \text{ emu/g}$ ($M_s \approx 44 \text{ emu/g}$ as reported in the earlier paper cited above). Different modes of drying such as IR drying, microwave drying do not improve M_s values. On the other hand, M_s value improves substantially when the precipitate is further processed hydrothermally. When calcined at 1200°C/4h in air, all the samples reach 96-100% of the saturation value ($M_s \approx 77 \text{ emu/g}$). All these experimental results (XRD, VSM) are analyzed in terms of the microscopic inhomogeneity (structural and chemical) of the precipitated and calcined samples.

There is worldwide interest in improving the performance parameters of nickel-zinc ferrite used in high frequency applications, especially in view of the miniaturization of electronic devices². The desired magnetic properties are achieved by judicious choice of the processing parameters. In general, these ferrites are produced by conventional ceramic routes³ which are known to have some inbuilt drawbacks resulting in non-reproducibility and deterioration of magnetic properties. Wet chemical or solution methods⁴⁻⁷ have overcome some of these problems and improved the performance of Ni-Zn ferrites synthesized at relatively low temperatures. In our laboratory, we have succeeded in preparing sinteractive powders of Ni-Zn ferrite at 80°C with a high saturation magnetization of $\approx 44 \text{ emu/g}$, following a co-precipitation route under optimized processing conditions¹. We also reported the use of these powders in the synthesis of low power-loss ferrites⁸ (in the form of dense compacts) operating in several tens of MHz regions. An excellent performance is achieved by adding selective dopants to enhance the grain-boundary resistivities.⁹⁻¹¹

In order to understand the effects of three important processing parameters on the quality of resulting ferrite powders/compacts (more than 10 parameters were optimized in Ref. 1), we synthesized Ni-Zn ferrite powder using the identical grades of chemicals with suitable changes in three processing parameters: (i) solution concentration, (ii) mode of washing and (iii) drying of the resulting precipitate. Due to these changes, the magnetic properties were found to be relatively poor (i.e. lower M_s value at the low applied magnetic fields). The resulting precipitate was further hydrothermally processed which substantially improved the saturation magnetization value, $M_s \approx 50.7 \text{ emu/g}$. The experimental procedures, data acquisition and its analysis are presented in the paper.

Experimental

Chemical synthesis

The optimum concentrated solutions of nickel nitrate (3.95 M), zinc nitrate (4.2 M), ferric nitrate (2.87 M) and sodium hydroxide (5.3 M) were prepared using Loba and Merck LR grade chemicals. The solutions were filtered through sintered glass funnel (G4) to remove the insoluble impurities. The metal ion solutions were then premixed in a stoichiometric ratio to make 20 g of a typical $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ composition. The premixed nitrate solutions of Ni, Zn and Fe were added rapidly to the sodium hydroxide solution. The precipitation was carried out at room temperature with continuous stirring. Due to exothermic nature of reaction, the temperature of the slurry was found to rise around $\approx 50^\circ\text{C}$, forming the mixed hydrated oxides of iron, nickel and zinc. The precipitate was washed five times with distilled water using the centrifuge machine. The precipitate was further divided into four parts to give different thermal treatments: (i) the sample dried in an electrical oven at $80 \pm 5^\circ\text{C}$ in air (Sample A), (ii) the sample dried under the IR lamp for 20 minutes (Sample B), (iii) the sample dried in microwave oven for 40 minutes (Sample C) and (iv) the sample treated hydrothermally (Sample D). For hydrothermal treatment, the ferrite slurry was added in a Parr bomb and it was sealed with Teflon. The contents were heated hydrothermally in a furnace at 100°C for 48 hr under saturated steam pressure. After

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the hydrothermal treatment, the Parr bomb was allowed to cool down naturally. The contents were taken out and dried at 80°C in oven. Then these as dried samples A, B, C, D were calcined at 1200°C for 4 hr in a furnace.

Characterization

All as-dried samples (A, B, C and D) and those further calcined at 1200°C were characterized using following physico-chemical techniques.

Powder X-ray diffractograms (XRD) were obtained using a Philips PW1730 diffractometer with $\text{CuK}\alpha$ radiation.

Saturation magnetization measurements were carried out at room temperature and at liquid nitrogen temperature by using a vibrating sample magnetometer EG&G PAR model 4500.

Results and discussion

XRD patterns of the samples A, B, C, D are shown

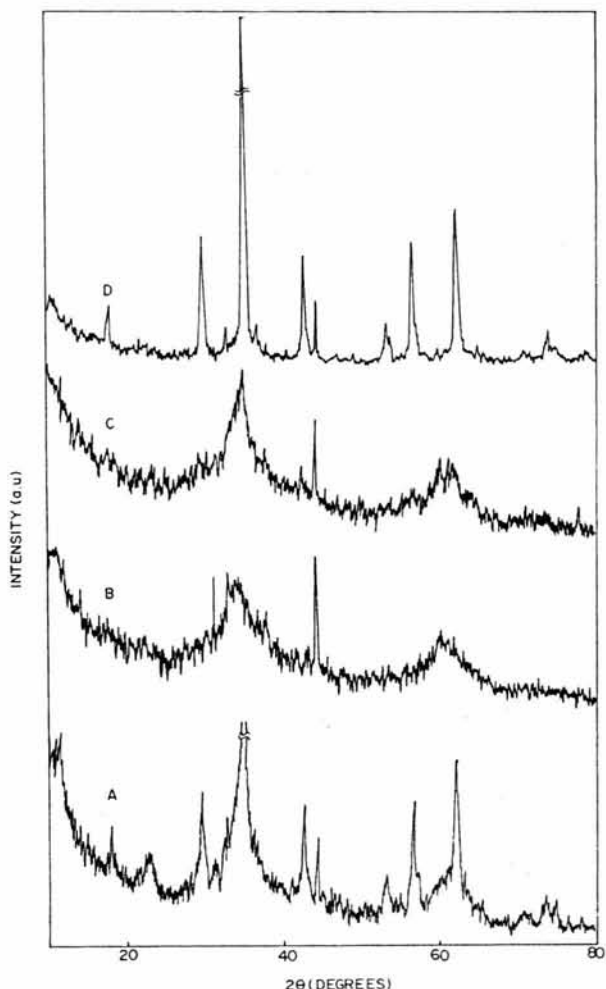


Fig. 1—X-ray diffraction patterns for the as-dried samples A, B, C, D

in Fig.1. Powder pattern for sample A shows all peaks matching with the characteristic reflection of Ni-Zn ferrite as reported in Ref.1 indicating the formation of single phase spinel. Sample B and C do not show the characteristic spinel pattern, as the ferritization is incomplete. The XRD pattern for sample D shows well-defined spinel structure of single-phase compound with better crystallinity. On calcination to 1200°C all these samples show a well-defined and almost identical XRD pattern confirming the complete phase formation of $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$.

The saturation magnetization values of samples A, B, C, D obtained are presented in Table 1. Fig. 2 indicates the nature of hysteresis loop for as-dried samples A, B, C, D. The sample A shows M_s value of $\approx 17.7 \text{ emu/g}$. This value is lower than the M_s value $\approx 44 \text{ emu/g}$ reported earlier¹ for $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$. This decrease is observed because the amount of phase formation in sample A is less (as confirmed from XRD) as compared to that for the sample reported in Ref.1, which differs qualitatively. For sample B and sample C, the M_s value still further decreases to 1.6

Table 1 — Saturation magnetization values of $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ samples at different processing conditions. ($H = 15 \text{ KOe}$)

Sample	Saturation magnetization (emu/g)		
	As-dried sample	After calcination at 1200°C/4h	At liquid nitrogen temp. (83K)
A	17.7	67.0	74.0
B	1.6	63.0	73.5
C	4.0	62.3	73.0
D	50.7	63.2	77.0

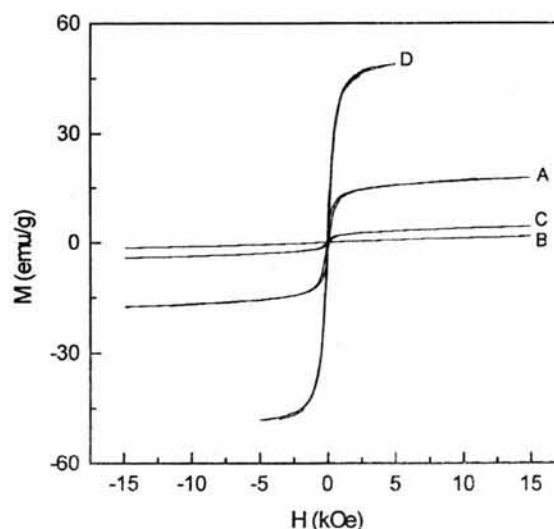


Fig. 2—Variation of magnetization with the applied magnetic field for as-dried samples A, B, C, D.

and 4 emu/g because of the change in the drying condition. These drying conditions do not favour the crystallization/ferritization reaction and, therefore, it does not result in any phase formation of ferrite as seen from XRD plots (Fig. 1B / 1C).

The hydrothermal treatment improves the M_s value to ≈ 50.7 emu/g (sample D). The improvement in the sample D as compared to the M_s value (≈ 44 emu/g) of sample reported in Ref.1 is because of the hydrothermal treatment given to sample D followed by drying at 80°C . Drying the sample at $80\pm 5^\circ\text{C}$ in oven alone does not increase the M_s value. But the pressure and temperature acting together in hydrothermal synthesis enhance the rate of chemical reaction, which facilitates the crystallization/ferritization leading to well defined spinel formation as confirmed by XRD.

However, on calcination to 1200°C for 4hr of all these samples, the saturation magnetization value at room temperature is observed to be >60 emu/g confirming the evolution of well-defined Ni-Zn ferrite. M_s value when measured at liquid nitrogen temperature increases to >73 emu/g for all the samples, approaching the saturation value. This behaviour is also supported by observation of the identical XRD patterns. The calcination at sufficiently high temperature helped (in all cases) in enhancing the rate of solid state diffusion reaction leading to (structurally and chemically on a microscopic scale) formation of well-defined spinel ferrite.

This study shows that any change in the processing changes the completion of ferritization. The hydrothermal method enhances the magnetization value substantially, avoiding further high temperature

calcination step. This major achievement seems to be very promising for synthesis of active powders even when there are forced changes in processing parameters.

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