

Mössbauer studies on ferrous-zinc ferrites prepared by a novel technique*

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Abstract. Ferrous-zinc ferrites, $Zn_xFe_{3-x}O_4$ ($0 < x < 1$) have been prepared using a new method involving the stabilization of FeO prior to its reaction with ZnO and Fe_2O_3 . Mössbauer studies on these ferrites have given results regarding the hyperfine fields, quadrupole interactions and isomer shifts in good agreement with those reported earlier on the same ferrites prepared by more elaborate and expensive techniques. This confirms the reliability of the new technique, which being much simpler, is less prone to errors in stoichiometry.

Keywords. Ferrous-zinc ferrites; Fe_3O_4 ; Mössbauer studies.

1. Introduction

Ferrous-zinc ferrites have large values of saturation magnetization and therefore are capable of application in recording heads and transformer-core materials. They have not been industrially exploited however since their preparation is difficult (Stuijts *et al* 1971) because of the need for the existence of large and specific amounts of the highly oxidizable and unstable Fe^{2+} in them. It is obviously not possible to start with the required amount of FeO (along with the other oxides) since FeO not only oxidizes spontaneously in air but even disproportionates in vacuum to Fe_3O_4 and Fe. Elaborate and indirect methods have therefore been used for the preparation of these ferrites. Stuijts *et al* (1971) and Srivastava *et al* (1976 p. 2032) have thermally reduced a mixture of ZnO and Fe_2O_3 to the required extent in a special furnace and in a flowing current of nitrogen. They followed the extent of reduction of Fe^{3+} to Fe^{2+} in the reacting powders by an analysis of the incoming and outgoing gases. Dobson *et al* (1970) have heated Fe_2O_3 and ZnO with the required amount of iron powder in evacuated sealed tubes. The former method is very elaborate, indirect and liable to errors inherent in gas analysis. The latter method involves not only a solid state reaction between oxides but also

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a reduction of Fe^{3+} to Fe^{2+} by metallic iron. It may become difficult in such a method to get the resulting compound with the same homogeneity and stoichiometry as from a simple solid state reaction among metal oxides involving no change of valency in the process.

Two of the present authors (Deshpande and Murthy 1981) have reported earlier a novel and accurate method of preparing ferrous-zinc ferrites without difficulty. Highly active ferric oxide prepared at a low temperature (Murthy *et al* 1979) was heated at 950°C for 8 hr in the presence of (but out of physical contact with) an excess of reduced iron in a gas-tight silica furnace-tube filled with pure nitrogen and provided with a manometer-cum-mercury seal to release any pressure developed during the heating. The iron acted as an oxygen-getter and reduced the Fe_2O_3 to a compound $\text{Fe}_{(1-\delta)}\text{O}$ where δ estimated by chemical analysis was less than 0.1. This material containing mostly FeO and a very small amount of Fe_2O_3 was quite stable in air. Calculated quantities of Fe_2O_3 and ZnO were then mixed with a known weight of the above reduced analysed oxide of iron, and reacted at $1000^\circ\text{C}/12$ hr in a static inert atmosphere under reduced pressure. The initial low pressure of nitrogen in the unit prevented any bubbling out of gases and consequent loss of oxygen on heating, through the mercury cut-off-cum-manometer assembly. The resulting ferrite powder on cooling always analysed to the required composition within the usual limits of accuracy of chemical analysis. The preparation of ferrous-zinc ferrites thus became a straightforward one involving a usual solid state reaction between analysed oxides; and any required composition could be easily reproduced accurately since there was no need to change the valency of iron during the reaction. The resulting powder was pressed with a volatilizable binder such as camphor, polymethyl methacrylate or polyamine sulphones. The binder was then distilled off in a current of oxygen-free nitrogen and the pieces were sintered at $1270^\circ\text{C}/8$ hr in a static nitrogen atmosphere under reduced pressure (so that no gases could bubble out on heating). The sintering unit is given in another earlier paper (Murthy *et al* 1979). The cubic lattice parameters and some magnetic measurements on the sintered ferrous-zinc ferrites $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ with $x = 0.2, 0.3, 0.4, 0.5$ and 0.6 have been reported in the earlier paper (Deshpande and Murthy 1981). We report in this paper some Mössbauer studies on the ferrous-zinc ferrites prepared by this method.

2. Experimental

2.1. Preparation of the compounds

The compounds $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ with $x = 0.2, 0.4, 0.6$ and 0.8 were prepared by the method outlined in the introduction and reported earlier (Deshpande and Murthy 1981). The compound with $x = 0$ *i.e.* Fe_3O_4 was prepared by a solid state reaction between calculated quantities of Fe_2O_3 and the analysed compound $\text{Fe}_{(1-\delta)}\text{O}$ ($\delta < 0.1$) referred to earlier in the introduction. This reaction was carried out under the same conditions as those used for the other compounds $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ with $0 < x < 1$. The compound with $x = 1$, *i.e.* ZnFe_2O_4 was prepared as usual by a straightforward reaction between ZnO and Fe_2O_3 . The ZnO required in making these ferrites was prepared in an active form by the decom-

position of precipitated zinc oxalate at 600° C. All the above compounds were sintered at 1270° C/8 hr in a static inert atmosphere and under conditions in which no gases bubbled out of the closed reaction tube-furnace (as mentioned earlier in the introduction). Chemical analysis of all the compounds showed agreement between the expected and analysed compositions of $Zn_xFe_{3-x}O_4$ within the usual limits of accuracy of volumetric analysis. X-ray diffraction studies with Philips PW 1730 x-ray generator using Fe K_α radiation indicated a single phase in each case with cubic lattice parameters varying linearly with x . The initial permeability (μ_i) and the quality factor (Q) at 800 kHz were measured on sintered toroids (2 cm O.D., 1 cm I.D. and 0.5 cm thickness) with Hewlett Packard 4342 A Q-meter. All these data are given in table 1.

2.2. Mössbauer experiments

Mössbauer spectra were recorded with a conventional constant acceleration electromechanical drive coupled to ND 100 multichannel analyser operating in time mode. A 5 mCi⁵⁷Co : Rh source was used to record the spectra at room temperature. A metallic iron foil (25 μ) was used to calibrate the spectrometer and all isomer shifts were measured with respect to that of metallic iron. All the hyperfine (hf) interaction parameters were computed using an iterative least squares MOSFIT program on ICL 1409 computer.

3. Results and discussion

Figure 1 shows the typical Mössbauer spectra recorded at room temperature for various compositions of $Zn_xFe_{3-x}O_4$ where $x = 0$ (*i.e.* Fe_3O_4), 0.2, 0.4, 0.6, 0.8 and 1.0 (*i.e.* $ZnFe_2O_4$). Figure 1a clearly shows the hyperfine (hf) split spectrum with characteristic parameters attributable to Fe_3O_4 . These parameters are $H_n(A) = 485 \pm 5$ kOe, $H_n(B) = 453 \pm 5$ kOe, $\Delta E_q(A) = 0.10 \pm 0.04$ mm/sec, $\Delta E_q(B) = -0.08 \pm 0.04$ mm/sec., $IS(A) = 0.36 \pm 0.02$ mm/sec, $IS(B) = 0.75 \pm 0.02$ mm/sec. These values are in excellent agreement with those reported earlier in the literature (MEDI 1974); and are particularly significant since the Fe_3O_4 was prepared by a new method which was exactly similar to the one used for preparing ferrous-zinc ferrites also.

Mössbauer spectra figures 1(b) to 1(f)—for the various compositions of $Zn_xFe_{3-x}O_4$ show the effect of dilution with zinc on the hyperfine field experienced by the iron ions at the tetrahedral and the octahedral sites. It is well-known that the Zn^{2+} ions occupy the tetrahedral sites in spinel ferrites and are therefore expected to decrease the hf field at these sites. However the decrease in hf field is also observed for the iron ions at the octahedral sites. Due to the zinc substitution it seems that the cation distribution (Fe^{2+}/Fe^{3+}) has effectively altered, reflecting the decrease in the hf field. For all the compositions except $x = 0.8$, hf parameters have been computed and given in table 2. For $x = 0.6$, strong broad absorption wings extending over to ~ 4 mm/sec in the centre of the spectrum are observed. These results agree qualitatively with those reported earlier by Dobson *et al* (1970) and Srivastava *et al* (1976, p. 2041) although the method of

Table 1. xrd, chemical analysis and magnetic measurements on $Zn_xFe_{3-x}O_4$.

Sl. No.	X	Cubic lattice parameter 'a', $\pm 0.005 \text{ \AA}$	Fe ²⁺ /g		Total Fe/g		μ_t at 800 kHz	Q at 800 kHz	μQ
			Anal.	Cal.	Anal.	Cal.			
1.	0.0	8.393	0.2380	0.2412	0.7240	0.7236
2.	0.2	8.405	0.1938	0.1913	0.6752	0.6698	75.96	30.5	2316.78
3.	0.4	8.416	0.1448	0.1447	0.6201	0.6169	165.00	17.5	2887.50
4.	0.6	8.430	0.0946	0.0941	0.5679	0.5649	298.00	5.75	1713.50
5.	0.8	8.439	0.0470	0.0467	0.5141	0.5137
6.	1.0	8.450	0.0000	0.0000	0.4653	0.4633

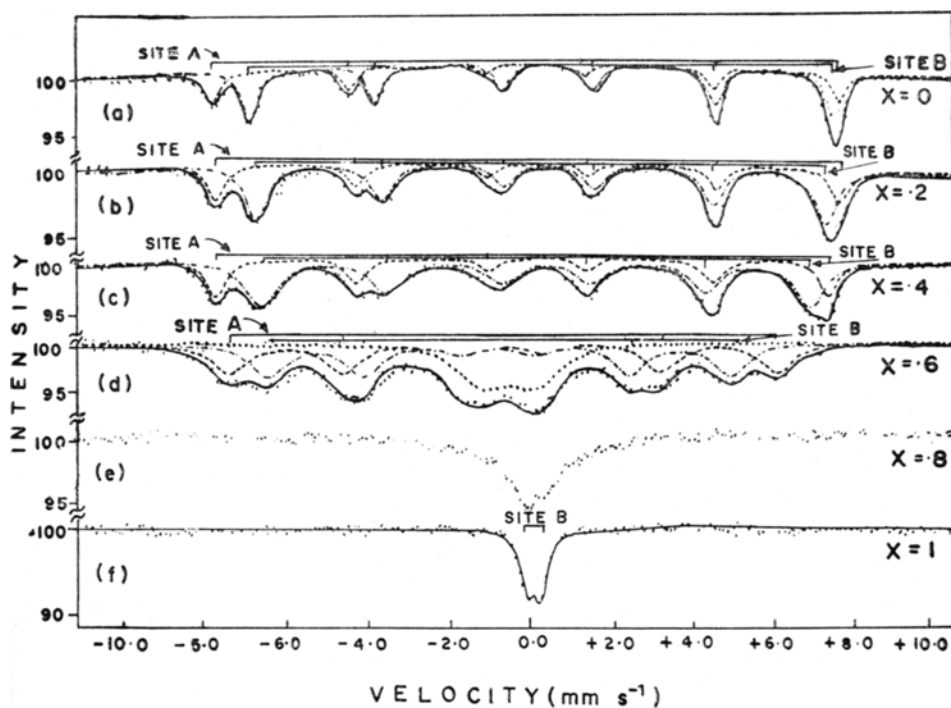


Figure 1. Mössbauer spectra of $Zn_xFe_{3-x}O_4$ at room temperature ;
 (a) $x = 0.0$ (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$, (f) $x = 1.0$.

Table 2. Mössbauer data on $Zn_xFe_{3-x}O_4$

Sl. No.	x	Pattern	$iS \pm 0.02$ mm/sec w.r.t. iron metal	$E_Q \pm 0.04$ mm/sec.	$H_n \pm 5$ kOe
1.	0	A	0.36	0.1	485
		B	0.75	-0.08	453
2.	0.2	A	0.40	0.14	480
		B	0.75	0.08	440
3.	0.4	A	0.40	0.21	464
		B	0.71	0.15	414
4.	0.6	A	0.49	0.08	420
		B	0.62	0.09	350
		C	Central doublet contribution present.		
5.	0.8	Complex non-Lorentzian spectrum.			
6.	1.0		0.49 ± 0.04	0.34	

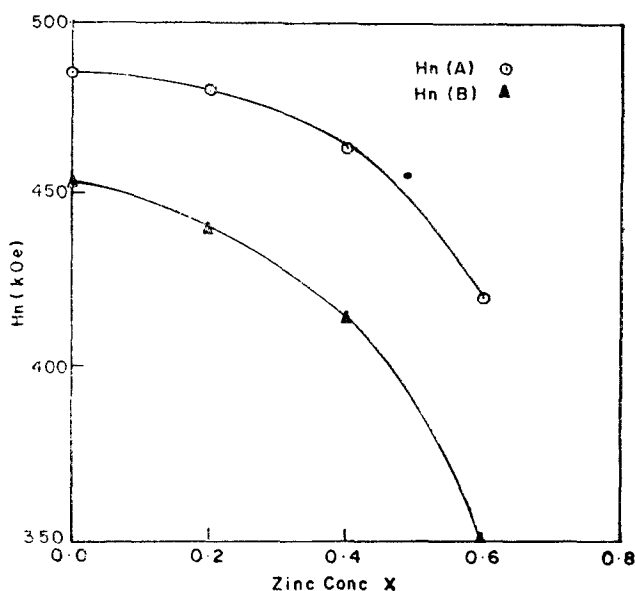


Figure 2. Hyperfine fields, H_n (kOe) corresponding to (A) and (B) sites vs x in $Zn_xFe_{3-x}O_4$.

preparation of ferrite samples is totally different. For the zinc concentration of $x = 0.8$ [figure 1 (e)] the Mössbauer spectrum is a broad non-Lorentzian, showing either the hf field distribution effects and/or electron spin relaxation effects. It is difficult to differentiate the contributions from these two effects and therefore no attempt is made to compute hf interaction parameters.

In figure 2 we have plotted $H_n(A)$ and $H_n(B)$ vs the amount of zinc substituted in ferrite samples. It is seen clearly that the fields at (A) and (B) sites decrease regularly with increase in zinc concentration. At $x = 0.6$ the hyperfine fields at both the sites, (A) and (B), have decreased appreciably. We have not computed any hf interaction parameters in the concentration range $0.6 < x < 0.8$ due to the unresolved broad hyperfine structure. For the zinc concentration of $x = 1.0$ the Mössbauer spectrum as expected is very simple showing only the quadrupole split partners. The hf parameters are $\Delta E_Q = 0.34 \pm 0.04$ mm/sec. and $IS = 0.49 \pm 0.04$ mm/sec. exhibiting the unique octahedral site of Fe^{3+} in zinc ferrite. All our results agree very well with those of Dobson *et al* (1970) and Srivastava *et al* (1976, p. 2041) except for the compound $Zn_{0.4}Fe_{2.6}O_4$ (corresponding to $x = 0.4$) in the latter paper.

4. Conclusion

Mössbauer spectra of $Zn_xFe_{3-x}O_4$ with $0 < x < 1$ prepared by a new and simple technique using a stabilized oxide of iron very rich in FeO, indicate that hyperfine interactions at the (A) and (B) sites in the spinel ferrite agree very well with those reported earlier on the same compounds synthesized by much more

elaborate indirect methods. The straightforward preparative technique employing a stabilized FeO is very convenient, reliable and reproducible.

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