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⁵⁷Fe Mössbauer Spectroscopy of Zinc Ferrite Prepared by a Variety of Synthetic Methods

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Abstract: Confirmation of the suggestion of B site Zn^{2+} in nanocrystalline ZnFe_2O_4 has been sought through X-ray diffraction, ^{57}Fe Mössbauer spectroscopy, magnetic susceptibility and TEM measurements on bulk and nanocrystalline samples prepared by different techniques. Measurements on bulk samples are in agreement with previously reported ones. Samples prepared at low temperature from solutions of salts exhibit broadened XRD patterns, susceptibilities 4-5 times that of bulk samples, broadened Mössbauer spectra and particle sizes between 5-20nm. Low-impact, ball-milled bulk samples exhibited properties similar to the low temperature, nanocrystalline samples. At 298K, the Mössbauer spectra exhibit no magnetic hyperfine splitting and no evidence for a significant proportion of A site Fe^{3+} ions. The unusually high susceptibilities appear to result mainly from the decreased particle size and not from profound changes in the cation distribution of a well-defined, spinel structure.

1. INTRODUCTION

The cation distributions in spinels are the key to their importance as magnetic materials. Some exhibit variable cation distributions, as in CuFe_2O_4 , and others, such as NiFe_2O_4 and ZnFe_2O_4 , have cation distributions that are generally insensitive to temperature and synthesis methods. Zinc ferrite, ZnFe_2O_4 , has a spinel structure and represents a model ferrite compound whose structural property relationships provide clues to the behavior of more complex, mixed ferrites. Recent investigations [1, 2] of nanocrystalline zinc ferrite have suggested that the cation distributions in this material are partially inverted and thus open the possibility of new technical and economically important applications for this inexpensive and easily synthesized spinel ferrite. This result, however, is quite surprising in view of the unusual crystal chemistry of spinels with zinc on the octahedral site. Because of the unusual nature of this claim, we have sought, in this investigation, to explore the systematics of the cation distributions in nanocrystalline ZnFe_2O_4 prepared by a variety of techniques.

2. EXPERIMENTAL

Zinc ferrite was prepared by several different techniques. These included (1) a traditional ceramic synthesis at 1180°C, (2) a low temperature (100°C) hydroxide coprecipitation from a ZnCl_2 , FeCl_3 aqueous solution as described in [1], (3) a low temperature synthesis (100°C) involving the air oxidation of the alkaline precipitation products from an aqueous ZnSO_4 , FeSO_4 solution as described in [3]; and finally (4) the hydrothermal synthesis of zinc ferrite in supercritical methanol as described in [2]. Samples prepared by the above techniques were also comminuted in agate ball and/or agate shaker mills for up to 5 hours.

Phase purity, lattice parameters and particle size (Scherrer method) were determined by X-ray powder diffraction (XRD). Crystallite size was also estimated using transmission electron microscopy (TEM). Magnetic measurements were made between 5 and 150K using a SQUID susceptometer. The ^{57}Fe Mössbauer spectroscopic measurements were made at 298K: measurements and data analysis are similar to those reported in [4].

3. RESULTS

^{57}Fe Mössbauer spectral parameters are given in Table 1, with typical spectra presented in Figure 1. Data obtained for the ceramic zinc ferrite sample(1) are consistent with those previously reported [5], while the spectra of samples which were synthesized by the other techniques (2-4) exhibited line shapes that required at least two quadrupole doublets for an adequate fit. This strategy, while useful for describing the absorption envelope of these spectra, does not imply the presence of two distinct iron sites. On the contrary, the invariance of the isomer shift values for these spectra indicates an absence of crystallographically distinct iron sites. The milling of zinc ferrite synthesized by the ceramic method resulted in samples with spectra not unlike those of the samples synthesized at lower temperatures (cf. Table 1, columns 3, 5 and 6). For example, the spectrum of zinc ferrite prepared by method 1, and then milled for 5 hours, was fitted with two doublets ($\Delta E_Q(1)=0.39 \text{ mms}^{-1}$ and $\Delta E_Q(2)=0.64 \text{ mm s}^{-1}$; $\delta=0.34 \text{ mm s}^{-1}$). One of the most noteworthy features of the Mössbauer spectra is the absence of any asymmetry that would result from the simultaneous occupation of the A and B sites by iron.

Particle sizes, as determined by both TEM and XRD, ranged from 5 to 20 nm for samples prepared by low temperature techniques 2-4. As expected, the particle size is much larger for the zinc ferrite prepared by the ceramic method, although the milling of this sample resulted in a particle size ranging from 15 to 20 nm.

Table 1. ⁵⁷Fe Mössbauer parameters for ZnFe₂O₄ prepared by methods noted in text.

⁵⁷ Fe Mössbauer Parameters	Method 1	Method 1- milled	Method 2	Method 3	Method 4
ΔE _Q (1)	0.32	0.39	0.45-0.54	0.38	0.36-0.41
ΔE _Q (2)	---	0.64	0.64-0.92	0.61	0.66-0.67
δ [†]	0.34	0.34	0.34	0.35	0.34
Line width	0.28	0.27-0.63	0.32-0.43	0.28-0.50	0.32-0.46

All values in table are in units of mm s⁻¹. Relative errors ~0.01 mm s⁻¹.

[†]Isomer shift, w.r.t. iron metal. For two doublet fits, isomer shifts were approximately equal.

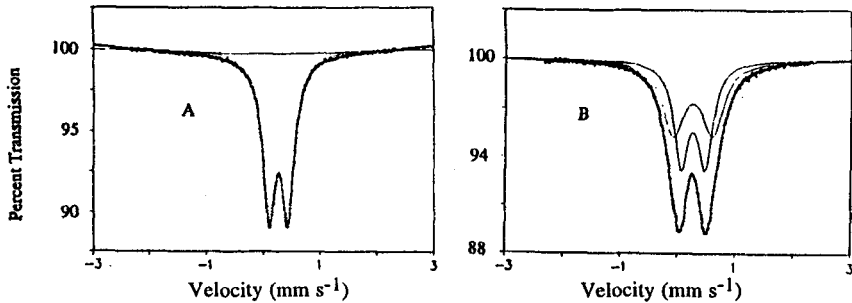


Figure 1. ⁵⁷Fe Mössbauer spectra for ZnFe₂O₄ prepared by (A) method 1 and (B) method 4

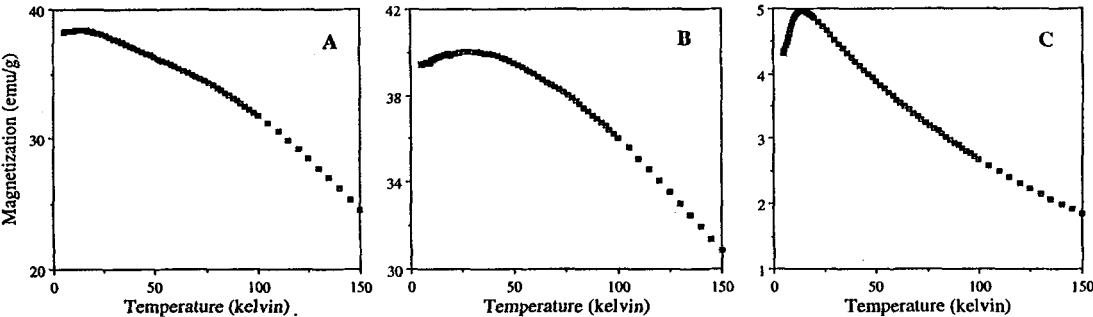


Figure 2. Magnetization vs. temperature for (A) ZnFe₂O₄ prepared by method 4, (B) by method 1 and milled, and (C) method 1.

Magnetic measurements indicate that all of these zinc ferrite samples are paramagnetic above approximately 125K and exhibit a Curie law temperature dependence. A μ_{eff} of 5.7 μ_B per iron atom for the ceramic sample is in agreement with previously published values. The samples prepared by techniques 2-4 typically have significantly larger μ_{eff} values, ranging from approximately 19 to 27 μ_B / Fe atom. It is noteworthy that the sample prepared at high temperature and then milled also displays an enhanced magnetic moment of 19 μ_B per iron atom. The ferromagnetic phase transition reported for zinc ferrite near 9K is clearly present for the ceramic sample. This transition is present for samples prepared by techniques 3 and 4, although it is of a relatively smaller magnitude and occurs at lower temperatures.

4. CONCLUSIONS

The synthesis of ZnFe₂O₄ by a variety of different techniques has allowed a qualitative description of its properties in relation to particle size. The magnetic moment of zinc ferrite nanoparticles, for example, are clearly increased relative to the bulk material. This increase, however, appears to be mainly a function of particle size which is independent of the synthesis method, and is also observed to occur when the particle size of bulk samples is decreased through ball milling.

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