



STRUCTURE AND MAGNETIC PROPERTIES OF NANOCRYSTALLINE FERRIMAGNETIC CdFe_2O_4 SPINEL

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Introduction

Fine particles of spinel ferrites exhibit magnetic properties markedly different from their bulk counter parts (1). For example, ZnFe_2O_4 , which is a well known normal spinel and exhibiting antiferromagnetic order below 10 K in the bulk form, has been shown to be ferrimagnetically ordered at much higher temperatures because of the cation inversion when the grain size is reduced to a few nanometers (2). CdFe_2O_4 also has a normal spinel structure in the bulk form similar to that of ZnFe_2O_4 . It is, therefore, our interest to study the magnetic properties of CdFe_2O_4 in the nanocrystalline form for various grain sizes. In this paper we report our results on the effect of grain size on cation distributions, magnetic properties, spin structure and the type of magnetic ordering in nanocrystalline CdFe_2O_4 using various techniques such as XRD, magnetisation studies and in-field Mössbauer spectroscopy.

Experimental

Cadmium ferrite was synthesized in the polycrystalline form by the conventional ceramic technique. Particles of different sizes in the nanometer range were prepared by milling the spinel in a high energy Fritsch Pulverisette (P7) ball mill using tungsten carbide balls and vials. X-ray powder diffraction patterns were obtained by using $\text{Fe-K}\alpha$ ($\lambda = 1.9373 \text{ \AA}$) radiation. The saturation magnetisation, coercivity and thermomagnetic measurements were performed with a Vibrating Sample Magnetometer (VSM) in an applied field of 1 T. The zero-field cooled (ZFC) and field-cooled (FC) magnetisation measurements were carried out from 5 K to 300 K in an applied field of 9 T at Tohoku University, Sendai, Japan by using the VSM of PPMS, (Model 6000), Quantum Design, USA. The low temperature and in-field ^{57}Fe Mössbauer spectra were recorded at Le Mans, France and other spectra were recorded at University of Madras, India with a 25 mCi ^{57}Co source in Rh matrix.

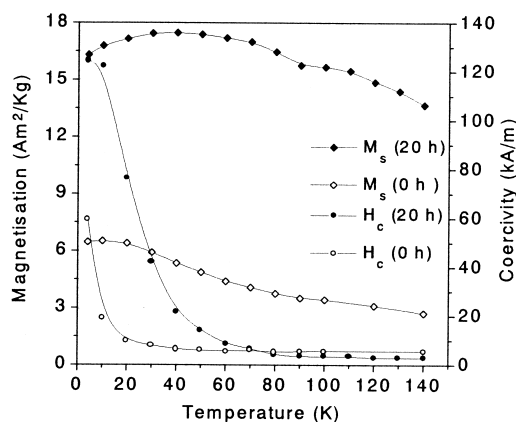


Figure 1. Magnetisation and coercivity as a function of temperature measured in an applied field of 1 T for the 0 h (77 nm) and the 20 h (7 nm) milled CdFe₂O₄.

Results and Discussion

XRD patterns confirmed the formation of the pure spinel phase. The average grain size was determined by using the Scherrer formula for various times of milling and the values ranged from 77 nm for the as-prepared sample to 7 nm for 20 h of milling. The lattice parameter initially increased from 8.701 to 8.715 Å upto 3 h of milling but decreased to 8.692 Å on milling for 20 h. The initial increase may be due to lattice expansion when the larger Cd²⁺ ions replace the Fe³⁺ ions at the octahedral sites as confirmed by our Mössbauer studies and the subsequent decrease can be explained based on the possible lattice contraction because of the deformation of the Fe³⁺ [B]-O²⁻-Fe³⁺ [B] bonds as observed by S epelak et al (3).

Figure 1 shows the variation of magnetisation and coercivity as a function of temperature measured in an applied field of 1 T. The 20 h (7 nm) milled sample has a higher magnetic moment and coercivity compared to that of the 0 h (77 nm) milled sample. The Neel temperature of the 20 h milled sample is found to be very large as seen from the slow decrease in its magnetisation with temperature. The higher coercivity of the 20 h milled sample is because of the smaller grain size and the structural disorder introduced when milled for a longer time. The grain boundary volume increases with decrease in grain size and the structural defects increase with milling time. The grain boundaries and the structural defects act as pinning centres for domain walls which are partly responsible for the increase in coercivity. The increase in surface anisotropy of small particles also contributes to the increase in coercivity. CdFe₂O₄, in the bulk form, is known to be a normal spinel exhibiting antiferromagnetic ordering below 10 K. The observed large magnetic moment for the nanocrystalline CdFe₂O₄, therefore, indicates that the sample is not an antiferromagnet. It should be either a ferromagnet or a ferrimagnet. Our M ossbauer results presented in a later section confirm that nanocrystalline CdFe₂O₄ exhibits ferrimagnetic ordering. The ferrimagnetic ordering is possible only if the cation distribution in cadmium ferrite changes from the normal to the mixed type when the grain size is reduced to a few nanometers. In the mixed spinel some Fe³⁺ ions will occupy the tetrahedral sites and an equal amount of Cd²⁺ ions will be pushed to the octahedral sites. The A-B superexchange interaction between Fe³⁺ ions in A and B sites gives rise to ferrimagnetic ordering. The increase in magnetisation at about 90 K for the 20 h milled sample in 1 T field may be due to the Hopkinson's effect as has been observed in the case of nickel ferrite (4).

Yokoyama et al. (5) have observed a large value of about 80 Am²/kg for the saturation magnetisation at 6 K in an applied field of 1T. Their CdFe₂O₄ particles, prepared by the coprecipitation method with

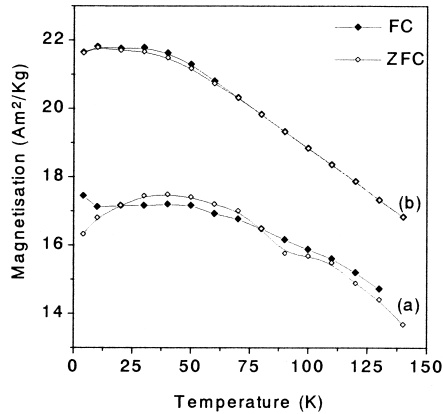


Figure 2. FC and ZFC curves for the 20 h milled (7 nm) CdFe₂O₄ (a) in 1 T applied field and (b) in 9 T applied field.

a grain size of 8 nm, were shown to exhibit ferromagnetic behaviour. The present spinel with 7 nm grain size, however, has a smaller saturation magnetisation of 21.7 Am²/kg at 5 K even in an applied field of 9 T. This indicates the presence of a larger anisotropy in our sample prepared by the mechanical milling method. Figure 2 shows the zero-field cooled (ZFC) and field-cooled (FC) magnetisation curves for the 20 h milled sample measured in two different fields of (a) 1 T and (b) 9 T respectively. These curves suggest that the sample exhibits spin-glass like surface structure as has been observed by Zins et al. (6) in the case of Mn_{1-x}Zn_xFe₂O₄ spinel.

The room temperature Mössbauer spectrum was satisfactorily fitted with a paramagnetic doublet due to quadrupole interaction for all grain sizes except for the sample with the grain size of 7 nm in which case the fitting was improved with two quadrupole doublets. The additional doublet may be assigned to Fe³⁺ ions from the A site.

The Mössbauer spectra of the 7 h and 20 h milled samples at 77 K are presented in Figure 3(a). Both

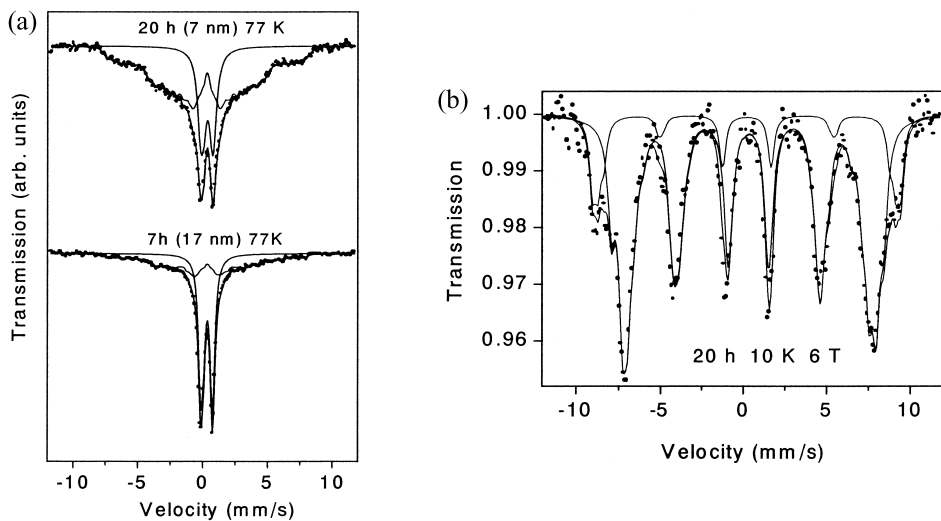


Figure 3. Mössbauer spectra recorded (a) at 77 K for the 7 h (17 nm), 20 h (7 nm) and (b) at 10 K for the 6 T in-field spectrum for the 20 h (7 nm) milled CdFe₂O₄

TABLE 1

Mössbauer Parameters of Nanocrystalline CdFe₂O₄ for 17 nm and 7 nm Grain Sizes at 77 K in Zero Magnetic Field and That for 7 nm (20 h) Grain Size at 10 K in an External Magnetic Field of 6 T Applied Parallel to the Direction and Gamma Rays

Sample	Site	δ (mm s ⁻¹) ±0.02	$\langle 2\epsilon \rangle$ (mm s ⁻¹) ±0.02	$\langle B \rangle$ (T) ±0.1	$\langle B_{\text{eff}} \rangle$ (T) ±0.1	$\langle \beta \rangle$ (°) ±5	I_{rel} (%) ±2
17 nm	—	0.46	0.80	—	—	—	55
77 K	—	0.46	0.04	24	—	—	45
7 nm	—	0.47	0.81	—	—	—	26
77 K	—	0.44	0.01	26	—	—	74
7 nm	A-site	0.40	0.00	50.2*	55.4	20	18
10 K	B-site	0.50	-0.01	50.1*	46.0	50	82
6 T							

Isomer shift values δ relative to that of α -Fe at 300K, quadrupole splitting 2ϵ , hyperfine field B , effective field B_{eff} , average canting angle β and relative proportions L_{rel} .

* Hyperfine field estimated from B_{eff} and β .

the spectra have a magnetically ordered component and a quadrupole doublet with the relative intensity of the sextet increasing with milling time. The Mössbauer parameters resulting from the least-squares fitting are given in Table 1. Figure 3(b) shows the Mössbauer spectrum of the 20 h (7 nm) milled sample at 10 K in an external magnetic field of 6 T applied parallel to the direction of gamma rays. The in-field Mössbauer spectrum, which could be satisfactorily fitted with three sextets for the A-site and with six sextets for the B-site, may be arising from the various local environments of Fe³⁺ sites in a highly disordered spinel. In Table 1 the average values of the parameters alone are presented for each site. It requires to record the Mössbauer spectrum in a larger field with a better statistics to have a correct estimate of the Fe³⁺ ions in the tetrahedral and octahedral sites. A comparison between the spectrum brings out two interesting results. The first one is that the spectra of the tetrahedral and octahedral sites are getting separated when the external magnetic field is applied which is a clear evidence for the presence of Fe³⁺ ions on the A-site. Hence, it can be said without any ambiguity that CdFe₂O₄ with nanometer grain size is a mixed spinel ferrite exhibiting ferrimagnetic ordering as a result of the Fe³⁺(A)-O²⁻-Fe³⁺(B) superexchange interaction. This is contradictory to the findings of Yokoyama et al. (5) from their magnetic measurements that ultrafine particles of CdFe₂O₄ exhibit ferromagnetic behaviour. The second observation is that the second and fifth lines of the Mössbauer spectra have appreciable intensity even under a field of 6 T applied parallel to the direction of gamma rays. The particles, therefore, have a large anisotropy and the Fe³⁺ spins in both the sites are canted. The canting angles were calculated from the ratios of the line intensities of A_{2,5} to A_{1,6} and the values are given in Table 1.

Conclusions

The nanocrystalline CdFe₂O₄ with various grain sizes were synthesized by ball milling the bulk material. The magnetisation measurements reveal a spin-glass like surface structure and the material is found to have a large anisotropy. Mössbauer effect experiment at 10 K in an external magnetic field of 6 T applied parallel to the direction of gamma rays could clearly show that CdFe₂O₄ behaves like a mixed spinel on reducing the grain size to a few nanometers and that it exhibits ferrimagnetic ordering. Fe³⁺ spins at both the sites exhibit spin canting. The cation inversion is found to increase with decrease in grain size.

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