

Synthesis and Magnetic properties of $\text{Mg}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ oxides

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Abstract. We report the magnetic properties of $\text{Mg}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ ($x = 0.3, 0.5, 0.7$ and 0.9) compounds. The oxides were produced by hydrothermal process and sintered at $600\text{ }^\circ\text{C}$ for 12 hours. The X-ray diffraction (XRD) data indicate single phase corundum structure in all the samples. The Mössbauer spectra recorded at about 300 K show transition from paramagnetic to ordered magnetic spin state at $x = 0.5$. The magnetization data reveals superparamagnetic nature of the oxides presented. The shift in hysteresis loops observed along the magnetic field axis is associated with exchange bias effect.

1. Introduction

The design, synthesis, and characterization of nanophase materials of the type $\alpha\text{-Fe}_2\text{O}_3$ have been the subject of intense research in recent years [1-4]. These studies are motivated by the novel properties of these materials at nanoscale as well as by their potential applications in heterogenous catalysts, biomedicine and biotechnology. Various methods have been reported for the synthesis of iron oxide nanoparticles, such as sol-gel reactions and chemical solutions [9-11]. These methods have the advantage that no surfactant need to be removed from the nanoparticles before application into precision industry and biomedical field. In this work we report the exchange bias effect observed in $\text{Mg}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ produced by hydrothermal technique.

2. Experimental details

The compounds $\text{Mg}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ ($x = 0.3, 0.5, 0.7, 0.9$) were produced from a mixture of required stoichiometric proportions of magnesium chloride, chromium (III) chloride and iron (III) chloride hexahydrate solutions. Excess aqueous ammonia was slowly added to the chloride mixture until full precipitation. The precipitate was boiled under reflux for 3 hours. The products were then filtered, washed with deionised water for several times until no chloride ions were detected by addition of silver nitrate standard solution. The clean products were finally washed with ethanol and then dried under an infrared lamp. The resulting homogeneous powders were heated in air at $600\text{ }^\circ\text{C}$ for 12 hours. The XRD patterns of the samples were obtained by using CoK_α radiation ($\lambda = 1.7903\text{ \AA}$) on a Phillips diffractometer (type: PW1710). The Mössbauer spectra were recorded at about 300 K using a conventional constant acceleration spectrometer with a ^{57}Co source sealed in Rh matrix. Magnetization measurements were obtained by using a Quantum Design vibrating sample magnetometer between 10 K and 400 K

3. Results and discussion

In Fig. 1 we show the XRD spectra of $\text{Mg}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ ($x = 0.3, 0.5, 0.7, 0.9$) oxides. The patterns confirm the formation of the basic corundum structure in all samples. The XRD spectra are similar to that of Sn doped $\alpha\text{-Fe}_2\text{O}_3$ [3]. No other impurity phases were observed. The refinement of XRD spectra was performed by a Rietveld analysis (FullProf Suite for Windows) using a model involving a combination of both interstitial and substitutional Mg^{2+} ions in octahedral coordination. The lattice parameters deduced from XRD data are shown in Table 1. There was no significant change in lattice constants with increasing Fe concentration. The average particle sizes calculated by using the Debye Scherrer formula [6] are also shown in Table 1. The particle sizes appear to be sensitive to Cr concentration. The smallest grains (about 33 nm) were formed in a sample with the smallest Cr concentration ($x = 0.9$).

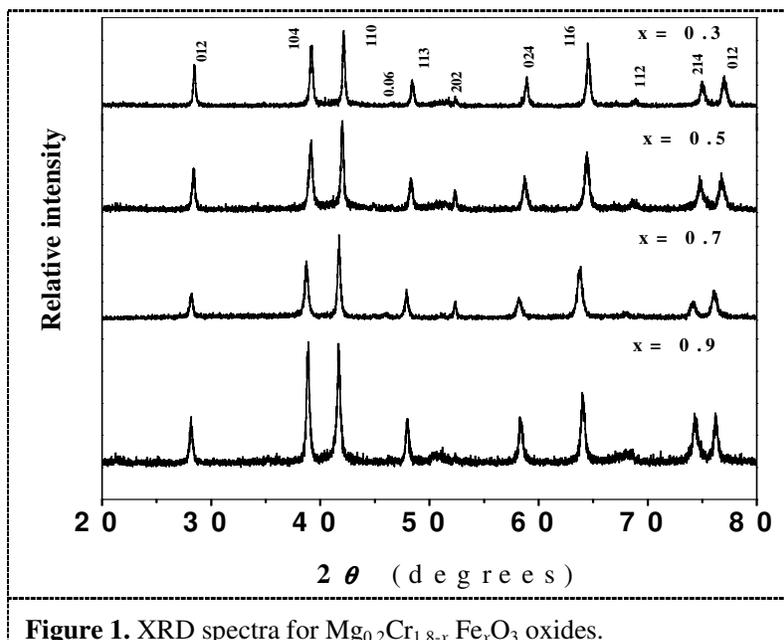
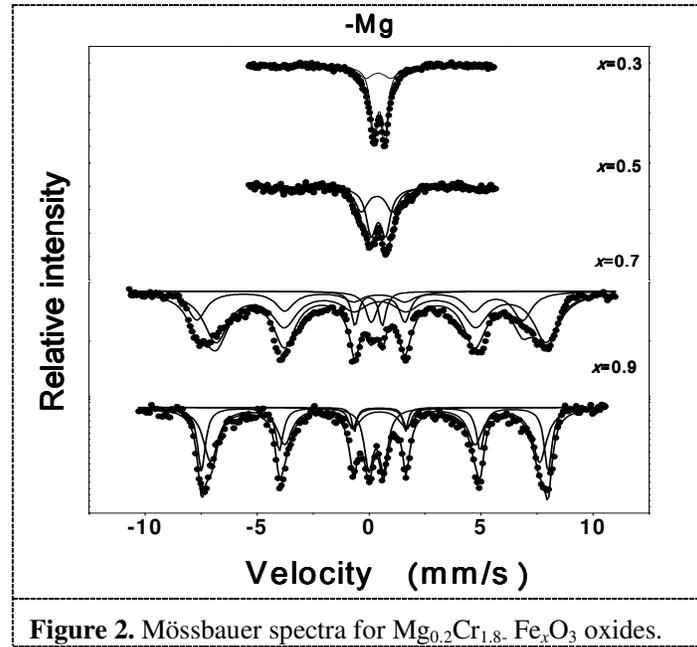


Figure 1. XRD spectra for $\text{Mg}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ oxides.

The variation of Mössbauer spectra as a function of x is shown in Fig. 2. The spectra for compounds with low Fe concentration ($x \leq 0.5$) were best fitted to two doublets. Doublets are associated with Fe ions in paramagnetic spin state. For $x = 0.7$ and 0.9 magnetic splitting is observed. The spectra could be fitted with two sextets and one doublet. There was no significant change in isomer shifts and quadrupole splitting with increasing x . A slight increase in hyperfine fields from 433 kOe to 455 kOe and 439 kOe to 480 kOe with increasing x has been observed for the two fitting sextets. This can be explained by an increasing Fe concentration in the structure.

The zero field (ZFC) and FC (50 Oe) magnetization curves are shown in Fig. 3. During field cooling (FC), the oxides were cooled from 400 K to 10 K in the presence of an external magnetic field of 50 Oe. For ZFC measurements, the applied field of 50 Oe was kept constant during cooling to 10 K and the magnetization was recorded during warming up to 400 K in the presence of the same external field. The magnetization in the FC curve decreases continuously with increasing temperature. In ZFC the state of magnetization increases with increasing temperature. This behaviour is characteristic of spin glass like behaviour [7]. The width of the peak in ZFC curve is associated with particle size distribution. Each particle with a particular size has a certain blocking temperature [11]. A narrower peak observed in ZFC curve for $x = 0.9$ indicates narrow distribution of particle sizes. The

linear fits for the temperature dependence of the inverse magnetization shows that the samples exhibit Curie-Weiss type behaviour above about 286 K and 290 K for $x = 0.7$ and $x = 0.9$ respectively. The corresponding extrapolated paramagnetic Curie temperatures θ_p are -354 K and -722 K. In Fig. 4 we show typical results for $x = 0.9$. The large negative values of θ_p indicate that the antiferromagnetic (AFM) interactions in $\text{Mg}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ are strong.



The variation of hysteresis curves of $\text{Mg}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ as a function of x recorded at 400 K and 10 K is shown in Fig. 5. The amplified view of hysteresis loops at low fields is also shown in the insets. An anomalous variation of magnetization with low magnetic field is observed. This behavior might have application in magnetic switching devices. The small values of coercive fields observed in hysteresis curves measured at room temperature indicate superparamagnetic nature of the compounds. An increase in coercivity was observed from 400 K to 10 K. The measurements of hysteresis loops at 10 K were performed after FC and ZFC measurements. The loops are not symmetrical about the origin but are slightly shifted to the left side. The shift of the hysteresis curves along the field axis is associated with exchange bias effects [8]. The direct exchange interaction between ferromagnetic and anti-ferromagnetic spins in a common interface results in an unidirectional magnetic anisotropy seen as exchange bias. The theory on exchange bias effect is discussed in reference [2]. In the present case for $\text{Mg}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ compounds we suspect the exchange bias to be due to exchange interaction between antiferromagnetic and ferromagnetic spins in Cr and Fe, respectively. The exchange bias phenomenon has applications in magneto-electronic switching devices, random access magnetic storage units, magnetic sensors and spintronics devices [1]. The exchange bias field is defined as $H_{EB} = (H_{C1} - H_{C2})/2$, where H_{C1} and H_{C2} are coercive fields at the left and right side of the shifted magnetization curve [1]. The values of exchange bias deduced from hysteresis loops measured at 10 K are shown in Table 2.

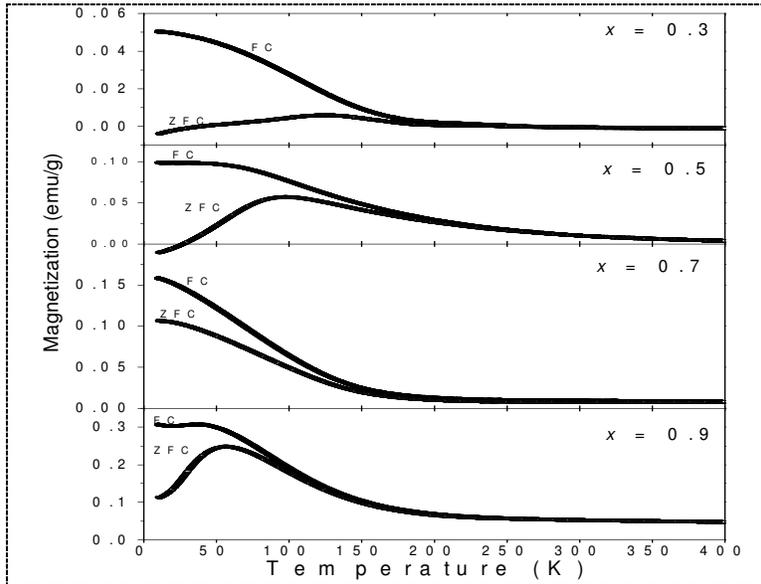


Figure 3. ZFC and FC (50 Oe) curves for $\text{Mg}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ oxides

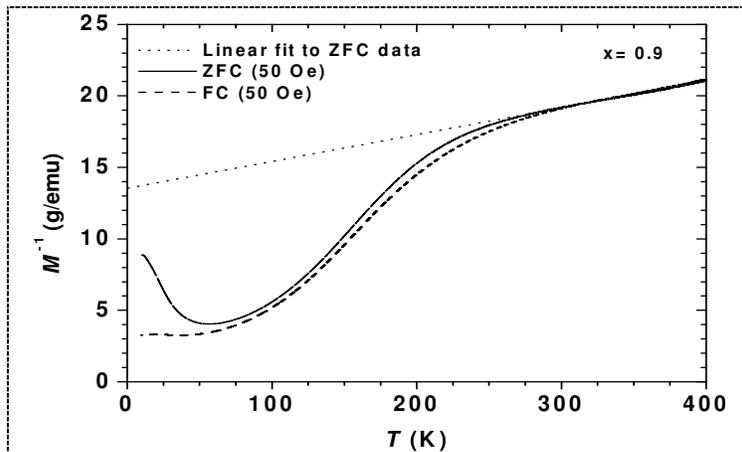


Figure 4. Linear fit for the temperature dependence of the inverse magnetization.

Table 1. Grain size (D), lattice parameters for $\text{Mg}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ oxides

x	$a = b$ (Å)	c (Å)	D (nm)
0.3	4.986	13.621	55.6
0.5	4.986	13.643	42.5
0.7	5.001	13.622	65.9
0.9	4.962	13.586	32.8

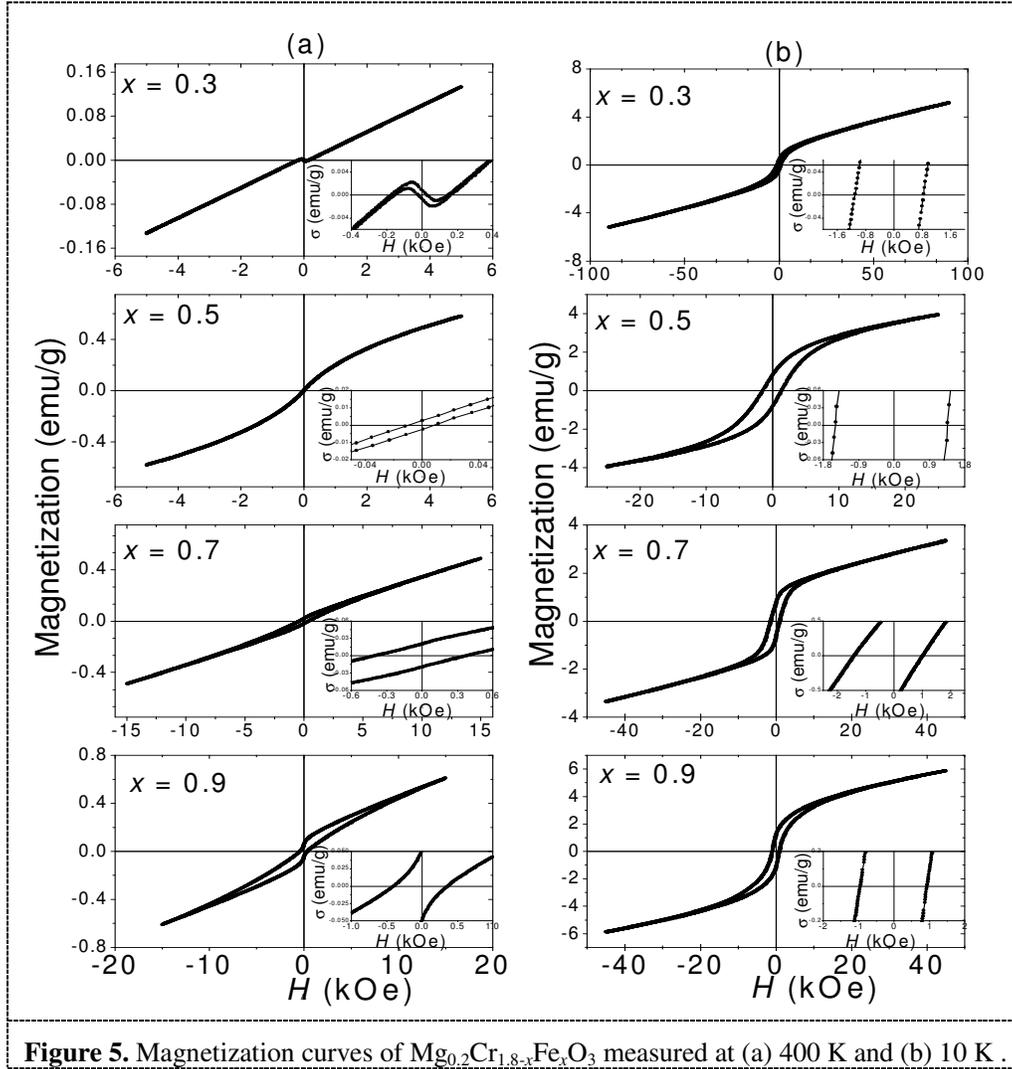


Figure 5. Magnetization curves of $\text{Mg}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ measured at (a) 400 K and (b) 10 K .

Table 2. Values of exchange bias fields for $\text{Mg}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ oxides.

x	0.3	0.5	0.7	0.9
H_{EB} (Oe)	135	64	192	10
± 1				

4. Conclusion

We have successfully made $\text{Mg}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ compounds by hydrothermal process. An anomalous variation of magnetization in low fields has been observed. The oxides exhibit exchange bias effects which appear to be sensitive to grain sizes. Samples with larger grains show more enhanced exchange bias effect. Our results from 400 K to 10 K also show evidence of strong antiferromagnetic interactions in the compounds.

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