

Structural and Magnetic Properties study of CoFe₂O₄ Nanopowder prepared by Mechanical Milling using metallic Cobalt and Hematite powder Blend

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ABSTRACT

In this work we report the phase formation and magnetic properties of CoFe₂O₄ nanopowder prepared by mechanical alloying technique using metallic cobalt and hematite powder (1:1 molar ratio) as the initial raw material in ambient air atmosphere. The formation of single phase cobalt ferrite of (Co²⁺_{0.18}Fe³⁺_{0.82})[Co²⁺_{0.82}Fe³⁺_{1.18}]O₄ stoichiometry was confirmed for the samples milled above 15 hours without any heat-treatment by XRD and Mössbauer techniques. The average crystallite size of the sample milled for 30 h was ~ 13 nm. The highest room temperature value of the saturation magnetization (51 e.m.u./g) was obtained for the sample milled for 25h which was much lower than the corresponding value of the bulk cobalt ferrite due to the size effect.

KeyWords: CoFe₂O₄, Nanopowder, Mechanical Alloying, Magnetic Properties

1 INTRODUCTION

Nano-sized spinel ferrite particles has been investigated widely in recent years because of their potential applications in microwave devices, magnetic recording and magnetic fluids[1,2]. Cobalt ferrite (CoFe₂O₄) amongst various spinel type ferrites is an interesting magnetic material because of its very high magnetocrystalline anisotropy as well as a reasonable saturation magnetization. Various preparation techniques such as: co-precipitation[3], sol-gel[4], hydrothermal[5] and mechanical alloying[6] have been utilized to prepared nanosized cobalt ferrite particles. Amongst these methods mechanical alloying/activation(MA) technique lend itself as a simple rout for the synthesis various metallic and oxide compounds[7] . Synthesis of CoFe₂O₄ nanoparticles using a combination, chemical precipitation, mechanical alloying and subsequent heat treatment is already reported[8] . However we report here the successful synthesis, phase formation and magnetic properties of this compound prepared by MA technique using metallic cobalt and hematite powders as the starting row materials in ambient atmosphere.

2 EXPERIMENTALS

The starting raw materials were α -Fe₂O₃ (>99% purity, Merck, Germany) and Co (>99% purity, Merck, Germany) powders. Mixture of Co and α -Fe₂O₃ powders with a molar ratio of Co to α -Fe₂O₃ 1:1 were loaded together. The ball to powder weight ratio (BPR) was 10:1. The mechanical alloying was performed in a Spex 8000 high energy vibratory mill for a maximum of 30 hours. The activated powders were collected after 1, 5, 15, 25 and 30 hours of milling. Phase development in the samples was monitored using a Philips X-ray diffractometer (XRD) with Cu-K α radiation. The average crystallite sizes of the milled samples were also determined from the full-width at half maximum (FWHM) of the strongest reflection, the (311) peak using the Williamson-Hall method[9] after applying the standard correction for instrumental broadening. Room temperature Mössbauer spectra were recorded on a conventional gamma-resonance spectrometer operating in constant-acceleration mode with ⁵⁷Co(Cr) as source. Isomer shifts (IS) are reported relative to α -Fe at room temperature. The spectra were computer-analyzed using the standard program. Room temperature magnetic measurements were carried out using a vibrating sample magnetometer at a maximum field of 1.5 T.

3 RESULTS AND DISCUSSION

3.1 XRD Data

Fig. 1 shows XRD multiplet pattern of Co/Fe₂O₃ powder blend mechanically activated for 0.0, 1, 5, 15, 25 and 30 hours. As expected prior to mechanical activation, the powder mixture exhibited sharp crystalline peaks related to metallic Co and hematite (α -Fe₂O₃) phases. For the samples milled above 1 h, almost all of previously observed sharp diffraction peaks vanished. The pronounced broadening observed for various diffraction peaks (Fig.1) could be related to the significant refinement in crystallite and particle sizes of the constituting powders, increase of defect concentration, as well as the formation of some solid solution compounds. For the sample milled for 1 h, although XRD pattern could not clearly detect the formation of trace amounts of CoFe₂O₄ phase formed but the Mössbauer spectra obtained confirmed the existence of this phase in this sample (Fig.2 and Table 1).

Increasing the milling time to 5 hours gave rise to the appreciable increase of the level of formation of cobalt ferrite phase and the disappearance of the main diffraction peak of metallic cobalt powder (Fig.1c). However, the XRD pattern obtained for this sample confirmed the existence of some non reacted hematite phase of appreciably smaller average crystallite size (17 nm) compared to that of the initial iron oxide (average particle size 0.5 μm) used as the starting raw material. Furthermore, increasing the milling time to above 5 hours, i.e., 15, 25 and 30 hours, caused a noticeable increase of the intensities of the diffraction peaks related to cobalt ferrite phase at the expense of the reduction of those of $\alpha\text{-Fe}_2\text{O}_3$ phase and the only major phase observed was CoFe_2O_4 for these samples, within the detection accuracy limit of XRD technique.

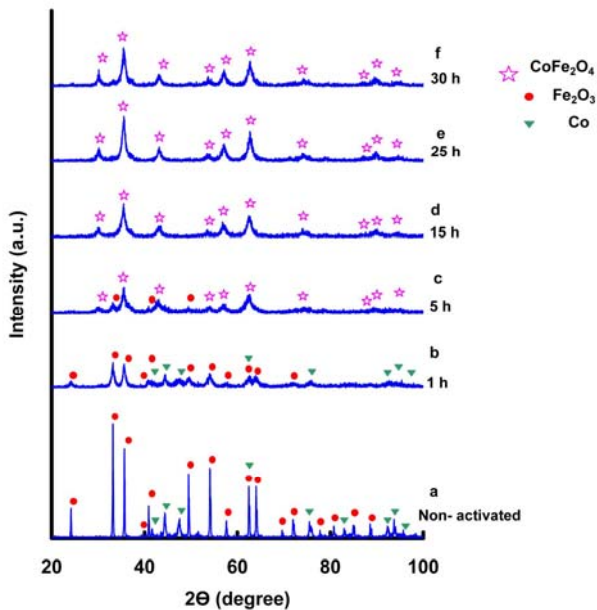


Fig 1: XRD multiplet patterns of $\text{Co}/\text{Fe}_2\text{O}_3$ powder blend mechanically activated for 0 h (a), 1h (b), 5h (c), 15h (d), 25h (e) and 30h (f).

Fig. 3 displays the variations of the average crystallite sizes of the cobalt ferrite phase formed versus the milling time. As can be realized from this figure, increasing the milling time from 5h to 30h gave rise to a rather linear increase of the average crystallite sizes of this compound. A similar crystallite size rise due to the increase of milling time is also previously reported for magnetite samples prepared by mechanical alloying technique[10]. The observed increase of the average crystallite sizes of the formed cobalt ferrite is possibly related to the increased injection of energy and diffusion rate of previously formed nuclei[11]. The formation of structural defects and disorder induced by mechanical activation will favor diffusion and atomic rearrangements at considerably low temperatures.

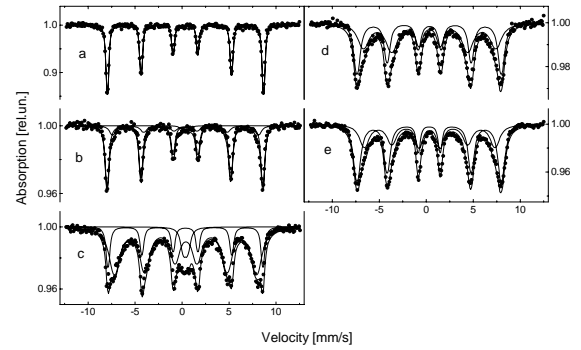


Fig 2: Room temperature Mössbauer spectra of various samples milled for 0 h (a), 1 h (b), 5 h (c), 25 h (d) and 30 h (e) in ambient atmosphere.

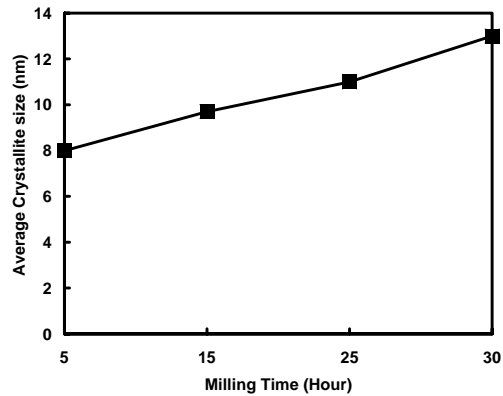


Fig 3: Average crystallite size variation of CoFe_2O_4 phase versus the milling time.

It should be mentioned that diffusion process during mechanical activation is a dynamic process and hence it can be assumed that the inter diffusion layer is broken by the activation process, thus enabling new surfaces with very different compositions to contact each other. Furthermore, the diffusivity rises with the decrease of the grain size and the formation of more free surfaces.

3.3 Magnetic Data

Fig. 4 display the variations of saturation magnetization (M_S) and intrinsic coercive field (iH_C) versus the milling time respectively. For the non activated sample (0 h milled) the magnitudes of the measured iH_C and M_S parameters were 100 Oe and 27 e.m.u/g which are related to the presence of metallic cobalt powder used. As can be seen in Fig. 4 increasing the milling time gave rise to the increase of both M_S as well as iH_C of the samples.

The magnitude of the latter showed a sharp rise for the samples mechanically milled up to 25 hours. Further, the observed rising trend for M_S with increasing milling

Hours	Fe sites	IS	QS	ϵ_Q	Γ	H_{in} , $\pm 0.5T$	Rel. cont., ± 0.05	s_A/s_B
		$\pm 0.03 \text{ MM/C}$						
0	$\alpha\text{-Fe}_2\text{O}_3$	0.38	-	0.20	0.28	51.6	1.00	-
1	$\alpha\text{-Fe}_2\text{O}_3$	0.35	-	0.18	0.40	51.3	0.78	-
	Fe^{3+} : CoFe_2O_4	0.36	-	0.04	~ 0.70	47.8	0.20	-
	Fe^{3+} (paramag.) ¹⁾	0.34	0.88	-	0.60	-	0.02	-
5	$\alpha\text{-Fe}_2\text{O}_3$	0.38	-	0.21	0.40	51.2	0.19	-
	Fe^{3+} : CoFe_2O_4	0.39	-	0.04	~ 1.20	47.0	0.74	-
	Fe^{3+} (paramag.) ¹⁾	0.38	0.45	-	0.60	-	0.07	-
25	Fe^{3+} (B): CoFe_2O_4	0.32	-	0.02	0.66	47.8	0.59	0.69
	Fe^{3+} (A): CoFe_2O_4	0.34	-	0.02	1.20	43.5	0.41	
30	Fe^{3+} (B): CoFe_2O_4	0.31	-	0.01	0.65	47.8	0.59	0.69
	Fe^{3+} (A): CoFe_2O_4	0.34	-	0.02	1.00	43.0	0.41	

Table 1: Mössbauer parameters of the Fe sites for the samples milled for 0, 1, 5, 25 and 30 hours (IS – isomer shift, relative to $\alpha\text{-Fe}$; QS- quadruple splitting; ϵ_Q -quadruple shift; Γ - line width, H_{in} - internal magnetic field, s_A/s_B is the area ratio of the tetrahedral and octahedral lines).

time is due to the increased rate of formation of cobalt ferrite as confirmed with XRD (Fig.1) and Mössbauer results (Fig.2 and Table 1). However, it should be mentioned that the rate of increase of M_S is influenced by the volume fraction of CoFe_2O_4 phase formed. The highest value of saturation magnetization obtained in this work was 51 e.m.u /g for the sample milled for 25h. This value is much lower than that of the bulk cobalt ferrite. The lower M_S values associated with nanocrystalline CoFe_2O_4 powder could be attributed to the structural distortions in the surface compared to the bulk [12].

The net magnetic moment is reduced in ultrafine particles as the surface has significantly large surface to volume ratio. Thus a large proportion of metal ions are in structurally distorted particle surface, where in, the bond lengths, and bond angles would be different compared to the bulk to give reduced magnetic moment. It is also likely that the cation site occupancy in nanosized CoFe_2O_4 could be different from the bulk to give reduced magnetic moment [13].

3.3 Mössbauer Data

Fig.2 shows room temperature Mössbauer spectra of the samples obtained at various milling periods. The results of computer fittings of the spectra are summarized in Table 1. The spectrum in fig.1a was found to be similar to the typical spectra normally seen for polycrystalline hematite ($\alpha\text{-Fe}_2\text{O}_3$) coarse grain particles. Mössbauer spectra of the sample milled for 1 hour revealed the coexistence of hyperfine structure (HFS) lines arising from $\alpha\text{-Fe}_2\text{O}_3$ as well as two new subspectra; HFS lines with relative content 0.2 that may belong to octahedral B-sites of CoFe_2O_4 [14] and weak “paramagnetic” doublet. The presence of the latter suggests

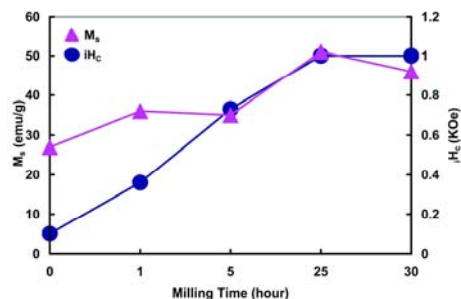


Fig 4: The variations of saturation magnetization (M_S) and intrinsic coercive field (iH_c) of the activated powders at various milling time .

the presence of superparamagnetic particles in the powder mixture. Increasing the milling time for 5 hours (Fig.2c), led to the progressive diminishing of signals from hematite phase with an accompanied increase of the relative content of nanosized CoFe_2O_4 phase in agreement with XRD results.

The presence of a complex hyperfine structure in which a quadrupole doublet is superimposed on a magnetically split sextet suggest that these samples (milled for 1 and 5 hours) can be possibly divided in to two components of superparamagnetic and ferrimagnetic due to size distribution. For the samples milled above 5h i.e. 25 and 30h the contribution of superparamagnetic component were found to be negligible. This was also in agreement with the obtained calculated crystallite sizes for these samples. The average crystallite sizes of the samples milled for 15, 25 and 30 hours were above the critical superparamagnetic size reported earlier for CoFe_2O_4 nanopowder [15]. It is also interesting to note that the magnitude of the relative content (Table 1) of the hematite phase for the sample milled for 5 hours was about 4 times less than that of the sample milled for 1 hour

which was also in agreement with XRD results. Similar spectra (Figs. 2d and 2e) were obtained for the samples milled for 25 and 30 hours where only two superimposed six line hyperfine spectra belonging to tetrahedral (A) and octahedral (B) sites of CoFe_2O_4 were seen. It is noteworthy that the values of internal hyperfine fields $H_{\text{in}}(\text{A}) \sim 43.2$ T and $H_{\text{in}}(\text{B}) \sim 47.8$ T (Table 1) are less than the corresponding values reported for quenched bulk CoFe_2O_4 ; $H_{\text{in}}(\text{A}) = 47.2$ T and $H_{\text{in}}(\text{B}) = 49.4$ T [14]. The observed differences could be related to the particle size effect. The calculated $s_{\text{A}}/s_{\text{B}}$ ratio which is the area ratio of the tetrahedral to octahedral lines was found similar (0.69) for the samples milled for 25 and 30 hours. These ratios are proportional to the ratio of the number of A- and B-site iron ions assuming the recoilless fraction f is the same for the two sites. It should be noted that the value $s_{\text{A}}/s_{\text{B}} = 0.69$ is close to the previously reported value for the quenched sample of CoFe_2O_4 ($s_{\text{A}}/s_{\text{B}} = 0.65$) [14]. The cation distribution in case of the samples milled for 25 and 30 hours using the mixture of metallic cobalt and polycrystalline hematite prepared in this work is therefore suggested to be considered as: $(\text{Co}^{2+}_{0.18}\text{Fe}^{3+}_{0.82})[\text{Co}^{2+}_{0.82}\text{Fe}^{3+}_{1.18}]\text{O}_4$, where $s_{\text{A}}/s_{\text{B}} = 0.69$.

4 CONCLUSION

The below mentioned conclusions were withdrawn based on the work presented here:

1. Single phase CoFe_2O_4 ferrite nanopowder was formed by mechanical milling of a powder blend mixture of metallic cobalt and hematite (Co/ α - Fe_2O_3 molar ratio :1:1) above 15 hour using a high energy vibratory mill.
2. Mössbauer spectroscopy analysis confirmed the coexistence of superparamagnetic and ferrimagnetic particles for the samples milled for 1 and 5 hours.
3. The highest value of saturation magnetization obtained in this work was 51 e.m.u /g for the sample milled for 25h which is much lower than that of the bulk cobalt ferrite. This is believed to be related to the structural distortions on the surface of cobalt ferrite nanopowder.
4. The stoichiometry of the cobalt phase formed was estimated to be $(\text{Co}^{2+}_{0.18}\text{Fe}^{3+}_{0.82})[\text{Co}^{2+}_{0.82}\text{Fe}^{3+}_{1.18}]\text{O}_4$, based on our Mössbauer analysis.

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