Influence of mechanical milling and thermal annealing on electrical and magnetic properties of nanostructured Ni–Zn and cobalt ferrites

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Abstract. The present article reports some of the interesting and important electrical and magnetic properties of nanostructured spinel ferrites such as $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and CoFe_2O_4 . In the case of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, d.c. electrical conductivity increases upon milling, and it is attributed to oxygen vacancies created by high energy mechanical milling. The real part of dielectric constant (ϵ') for the milled sample is found to be about an order of magnitude smaller than that of the bulk nickel zinc ferrite. The increase in Néel temperature from 538 K in the bulk state to 611 K on the reduction of grain size upon milling has been explained based on the change in the cation distribution. The dielectric constant is smaller by an order of magnitude and the dielectric loss is three orders of magnitude smaller for the milled sample compared to that of the bulk. In the case of cobalt ferrite, the observed decrease in conductivity, when the grain size is increased from 8–92 nm upon thermal annealing is clearly due to the predominant effect of migration of some of the Fe^{3+} ions from octahedral to tetrahedral sites, as is evident from in-field Mössbauer and EXAFS measurements. The dielectric loss ($\tan \delta$) is an order of magnitude smaller for the nano sized particles compared to that of the bulk counterpart.

Keywords. Nanocrystalline cobalt and nickel zinc ferrite; electrical properties; Mössbauer; EXAFS.

1. Introduction

Nanocrystalline spinel ferrite materials are of practical interest in a wide range of applications like high-density information storage, magnetic resonance imaging, targeted drug delivery, etc (Bulte *et al* 1999; Lübke *et al* 1999). Spinel ferrites have high electrical resistivities and low eddy current and dielectric losses and therefore, they are found to be very useful in technological applications (Igarash and Okazaki 1977; Kulikowski 1984). In this article, we report the details of synthesis and electrical and magnetic properties of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and CoFe_2O_4 .

2. Experimental

The $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and CoFe_2O_4 ferrites were synthesized using the ceramic and co-precipitation route, respectively. In the case of Ni–Zn ferrite, the powders of $\alpha\text{-Fe}_2\text{O}_3$, NiO and ZnO in the required stoichiometry were thoroughly mixed in a high energy ball mill using zirconia balls and vials with a speed of 300 rpm. The mixture was presintered at 1173 K for 5 h in air, which was then furnace-cooled to room temperature. The cold ferrite powder was ground in an agate mortar and pelletized. The pellets were then sintered at 1473 K for 5 h in air and furnace-cooled. The pellets were reduced to powders by milling using zirconia

vials and balls at 300 rpm for 30 min and taken to be the as-prepared sample. The as-prepared sample was milled up to 25 h using planetary high-energy ball mill (Fritsch pulverisette 7) with zirconia vials and balls. The milling speed was 600 rpm with a ball to powder weight ratio of 8 : 1. The crystallographic phase analysis for the as-prepared and milled samples was carried out using X-ray diffraction (XRD) with a Rigaku-make high precision Guinier X-ray diffractometer and Cu-K α radiation. The Néel temperature was determined using thermogravimetric analyser (Perkin-Elmer series 7) by applying a small magnetic field of 4 mT using a horse-shoe magnet. Magnetization studies were carried out at 298 K by using a vibrating sample magnetometer (VSM, EG&G, PARC, Model 4500, USA) with a maximum available field of 0.7 T. The extended X-ray absorption fine structure (EXAFS) measurements were done using a laboratory X-ray absorption spectrometer (Rigaku R-XAS Lopper) at Ni K (8332 eV) and Zn K (9663 eV) absorption edges. The CoFe_2O_4 ferrite was prepared using the conventional co-precipitation route. In the conventional co-precipitation technique, 800 ml of mixed 0.11-M Fe and 0.055-FeCo solution was added into the reaction vessel containing 1.5 l of boiling 0.725 M NaOH aqueous solution under mechanical stirring at 500 rpm. The ferrite formation was monitored by sampling the suspension during the contact period. The ^{57}Fe Mössbauer spectra were recorded at 15 K with 8 T magnetic field applied parallel to the direction of gamma rays. For both $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and CoFe_2O_4 ,

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the electrical conductivity and dielectric measurements were carried out as a function of both frequency and temperature in the range 1 Hz–10 MHz and 300–823 K, respectively using an impedance/gain phase analyser (Solartron 1260) with a personal computer and software to acquire the impedance data.

3. Results and discussion

3.1 $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$

3.1a Phase analysis: Figure 1 shows the XRD patterns of the Ni–Zn ferrite for the as-prepared and 25 h milled sample. The peaks could be indexed to a single phase spinel ferrite. The grain size was calculated from the full-width at half-maximum of the (311) peak using Scherrer's formula. The grain size of the as-prepared and 25 h milled samples were 50 and 14 nm, respectively.

Figure 1. The XRD patterns of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ spinel samples: (a) as-prepared and (b) 25 h milled sample.

Figure 2. The thermogravimetric plots for the $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$: (a) as-prepared (50 nm) and (b) 25 h milled (14 nm) samples.

3.1b Néel temperature measurements: Thermogravimetric plots of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ obtained with a small magnetic applied field of 4 mT are shown in figure 2 for as-prepared and 25 h milled samples. The Néel temperature is found to increase from 573 K for the as-prepared sample to 611 K for the 25 h milled sample. The rise in Néel temperature for the smaller grain size is due to the increase in the strength of A – B superexchange interaction as a result of increase in the population of Fe^{3+} ions in A site upon milling as confirmed by our in-field Mössbauer study (Sivakumar *et al* 2006).

3.1c Magnetization studies: Figure 3 shows the M – H loops obtained using VSM for the as-prepared and 25 h milled sample. The magnetization of the as-prepared sample is 72 emu/g which is almost equal to that of the bulk sample (micron size particle: 73 emu/g) (Smit and Wijn 1959). For the 25 h milled sample, magnetization decreases by about 15% to 61 emu/g due to the migration of some of the Fe^{3+} ions from B to A sites and Zn^{2+} ions from A to B sites upon milling (Sivakumar *et al* 2006). The coercivity increases from 88 Oe for the as-prepared sample to 349 Oe for the 25 h milled sample and it is due to both the surface anisotropy of the small particles and the strain induced in the sample during milling.

3.1d Extended X-ray absorption fine structure analysis (EXAFS): We have carried out EXAFS measurements to study the local atomic environment around the absorption atom and to study the changes in the cation distribution in the nanostructured $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ upon milling. Figures 4(a) and (b) show the Fourier-transformed EXAFS spectra at Zn and Ni–K edge, respectively, for both as-prepared and 25 h milled samples. From figure 4(a), it can easily be understood that the atomic environment

Figure 3. The M – H loops of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ at 300 K for the (a) as-prepared and (b) 25 h milled sample (14 nm).

Figure 4. (a) Fourier transforms of EXAFS spectra at Zn K absorption edge of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite samples and ZnFe_2O_4 reference and (b) at Ni K absorption edge of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite samples and NiFe_2O_4 reference.

Figure 5. Arrhenius plots for electrical conductivity of the as-prepared and 25 h milled $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples. The solid lines are the linear fit to the experimental data.

around Zn^{2+} ion in the as-prepared sample is quite similar to that in the reference sample with a strong r -space peak near $3 \text{ \AA}$, which indicates that all Zn^{2+} ions occupy the tetrahedral site. For the 25 h milled sample, one can eas-

ily observe that the atomic environment around Zn^{2+} ion is quite different from that in the normal structure. The new peak at $2.6 \text{ \AA}$ is due to B - B correlation with a substantial intensity showing that there is a partial transfer of Zn^{2+} ions from A to B sites after milling. From figure 4(b), we find that the EXAFS spectra of the reference, as-prepared and 25 h milled $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ are quite similar to each other. Hence, one can conclude that the Ni^{2+} ions occupy only the octahedral sites and that they do not migrate from the octahedral to the tetrahedral site upon milling.

3.1e D.C. conductivity: Figure 5 shows the Arrhenius plots for the electrical conductivity of both the as-prepared and 25 h milled samples in the temperature range between 400 and 798 K. The grain boundary resistance was obtained by analysing the data using the non-linear least-squares (NLLS) fitting routine. The d.c. conductivity of the grain boundary was calculated from the resistance value and by using the geometrical dimension of the sample. The conductivity increases with temperature as expected from the semiconducting behaviour of spinel ferrites. The activation energy for the thermally activated hopping process was obtained by fitting the d.c. conductivity data with the Arrhenius relation

Table 1. The values of activation energies and the Curie temperatures of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ for the as-prepared and 25 h milled sample. E_{a1} is the activation energy obtained from the conductivity data for the low temperature region and E_{a2} is that for the high-temperature region.

Sample	Activation energy from conductivity data		T_c from		
	E_{a1} (eV)	E_{a2} (eV)	Arrhenius plot (K)	TGA (K)	Thermomagnetic measurements (K)
As-prepared (50 nm)	0.57 (± 0.01)	0.93 (± 0.01)	569 (± 2)	573 (± 1)	569 (± 1)
25 h milled (14 nm)	0.66 (± 0.02)	0.93 (± 0.01)	607 (± 3)	611 (± 1)	607 (± 1)

Figure 6. (a) Real part of the dielectric constant (ϵ') at 373 K as a function of frequency for the as-prepared and 25 h milled $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples and (b) dielectric loss factor ($\tan \delta$) at 373 K as a function of frequency for as-prepared and 25 h milled $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples.

$$\sigma T = \sigma_0 \exp \left[\frac{E_a}{kT} \right], \quad (1)$$

where σ_0 is the pre-exponential factor with dimensions of $(\Omega \text{ cm})^{-1} \text{ K}$, E_a the activation energy for d.c. conductivity and k the Boltzmann constant. The values of activation

energies for the as-prepared and 25 h milled samples are given in table 1. The change of slopes in Arrhenius plot for both as-prepared and 25 h milled samples corresponds to the ferromagnetic to paramagnetic transition temperatures as confirmed by the thermogravimetric measurements as shown in table 1. The conductivity is expected to decrease upon milling because of the grain size reduction and also because of the decrease in the number of $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ pairs in the octahedral site arising from the partial displacement of Fe^{3+} ions from octahedral site to tetrahedral site due to milling as evident by the in-field Mössbauer studies reported earlier (Sivakumar *et al* 2006). On the contrary, we have observed an increase in conductivity with the reduction of grain size upon milling. Earlier, it (Goya and Rechenberg 1999) has been observed that oxygen ions escape from the spinel structure, thereby creating anion vacancies during milling. In the present study, therefore, the increase in conductivity with the reduction of grain size can be attributed to oxygen vacancies created during high energy ball milling. In general, the activation energy for conductivity due to electron hopping in bulk $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrites is of the order of 0.4 eV (Abdeen 1999). In the present work, the high values (0.57 and 0.66 eV) of activation energies for the as-prepared and 25 h milled samples, respectively obtained in the low temperature region may be due to hole hopping in addition to electron hopping contributing to conduction. The anion vacancies are activated at higher activation energy (≈ 0.93 eV), which is characteristic of diffusion of oxygen vacancies (Waster 1991).

3.1f Dielectric behaviour: (i) *Frequency dependence of dielectric constant and dielectric loss:* Figure 6(a) shows the frequency dependence of dielectric constant (ϵ') for the as-prepared and 25 h milled samples. The dielectric constant decreases with grain size reduction upon milling. In general, the electron exchange between Fe^{2+} and Fe^{3+} ions which results in local displacement of electrons in the direction of electric field determines electric polarization in spinel ferrites. The dielectric constant of ferrites varies mainly due to the fluctuations in the concentration of Fe^{2+} ions (Koops 1951; Rezlescu and Rezlescu 1974; Waster 1991). The polarization and dielectric constant are expected to increase with the concentration of

Fe^{2+} . In the present work, for the 25 h milled sample, there is a migration of some of the Fe^{3+} ions from octahedral (B) to tetrahedral (A) sites, which is clearly evident from the in-field Mössbauer studies (Sivakumar *et al* 2006). Therefore, the dielectric constant (ϵ') is lower for the 25 h milled (14 nm) sample compared to that of the as-prepared sample (50 nm). Verma *et al* (1999) obtained a value of about 100 for ϵ' at room temperature and at 100 kHz for the bulk (8 μm grain size) $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite. In our measurements, ϵ' is found to be an order of magnitude smaller for the 25 h milled $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ sample at the same temperature and frequency.

In general, the dielectric constant should decrease monotonically with frequency in ferrites, because the electron exchange between $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ ions cannot follow the alternating electric field beyond a certain critical frequency. However, in the present sample, ϵ' shows anomalous behaviour with frequency for both as-prepared

and 25 h milled samples. Initially it increases with the frequency, reaches a maximum and then decreases with further increase in the frequency. The presence of Ni^{3+} and Ni^{2+} ions in B sites gives rise to p -type carriers which also contribute to the net polarization in addition to the n -type carriers. However, the contribution of the p -type carriers should be smaller than that from the n -type carriers with an opposite sign. Since the p -type carriers have a lower mobility than the n -type carriers, the contribution to polarization from the former will decrease more rapidly even at low frequencies than the latter. Therefore, the net contribution will increase initially and then decrease with frequency as observed in the present samples and shown in figure 6(a). Rezlescu and Rezlescu (1974) also reported a similar behaviour in the case of Cu–Ni ferrites.

Figure 6(b) shows the plot between dielectric loss ($\tan \delta$) and frequency for the as-prepared and 25 h milled

Figure 7. (a) Temperature dependence of dielectric constant (ϵ') for the as-prepared and 25 h milled $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples at 100 kHz and (b) temperature dependence of dielectric loss factor ($\tan \delta$) for the as-prepared and 25 h milled $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples at 100 kHz. (The line joining the data points is a guide to the eye).

Figure 8. XRD patterns of CoFe_2O_4 spinel samples.

Figure 9. 8 T in-field Mössbauer spectra of the CoFe_2O_4 spinel ferrite for (a) as-prepared (8 nm) and (b) annealed at 1473 K for 2 h (92 nm).

Table 2. Mössbauer parameters: Isomer shift $\langle IS \rangle$, quadrupole shift $\langle 2\epsilon \rangle$, effective hyperfine field $\langle B_{\text{eff}} \rangle$, hyperfine field $\langle B_{\text{hyp}} \rangle$, canting angle $\langle \beta \rangle$ and relative intensity of the sextets $\langle I_{\text{rel}} \rangle$ for the CoFe_2O_4 samples at 12 K in an external magnetic field of 8 T applied parallel to the direction of γ -rays.

Sample (grain size in nm)	Fe site	$\langle IS \rangle^*$ (mm/s) ± 0.01	$\langle 2\epsilon \rangle$ (mm/s) ± 0.02	$\langle B_{\text{eff}} \rangle$ (T) ± 0.5	$\langle B_{\text{hyp}} \rangle$ (T) ± 0.5	$\langle \beta \rangle$ (degrees) ± 5	I_{rel} (%) ± 1
As-prepared (8 nm)	A	0.34	-0.00	59.8	52.3	20	36
	B	0.49	-0.02	46.7	53.9	29	64
Annealed at 1473/2 h (92 nm)	A	0.34	0.01	60.3	52.7	17	42
	B	0.50	-0.03	49.0	56.5	22	58

*with respect to α -Fe at 300 K.

Figure 10. Arrhenius plots for the electrical conductivity of nanocrystalline CoFe_2O_4 spinel ferrite for (a) as-prepared (8 nm) and (b) annealed at 1473 K for 2 h (92 nm) samples. The solid lines are the least-squares fit to (1) (g, grain and gb, grain boundary).

samples. We attribute the increase in $\tan \delta$ from the as-prepared to 25 h milled sample due to oxygen vacancy upon milling. The Zn^{2+} ions, because of the volatile nature of zinc, are known to escape from the spinel structure on thermal treatment at high temperature or upon mechanical milling in a high energy ball mill (Goya and Rechenberg 1999). Therefore, in the present study, it is possible that the number of Zn^{2+} ions that escape from the spinel structure increases with milling, which results in oxygen vacancies and hence higher dielectric losses as observed for the 25 h milled sample.

(ii) *Temperature dependence of ϵ' and $\tan \delta$* : Figures 7(a) and (b) show the temperature dependence of ϵ' and $\tan \delta$ for the as-prepared and 25 h milled sample, respectively. The dielectric constant and dielectric loss increase with temperature for both the samples, which is normally an expected behaviour and observed in most of the ferrites (Hiti 1968; Ponpandian and Narayanasamy 2002;

Ponpandian *et al* 2002). The hopping of charge carriers is thermally activated with the temperature rise and hence the dielectric polarization increases causing an increase in ϵ' and $\tan \delta$ with temperature.

3.2 CoFe_2O_4

3.2a Phase analysis: Figure 8 shows the XRD patterns of the as-prepared sample (A) and the sample annealed at 1473 K/2h (B). The two patterns in figure 8 could be indexed to single spinel phase. The average grain sizes were calculated using Scherrer's formula taking into account the instrumental line broadening. The average grain sizes of samples A and B were 8 and 92 nm, respectively.

3.2b In-field Mössbauer studies: To find the changes in the cation distribution of CoFe_2O_4 with heat treatment, we have recorded the in-field ^{57}Fe Mössbauer spectra for both A and B samples which are shown in figure 9. The Mössbauer spectra were fitted with two magnetic components arising from the tetrahedral (A) and octahedral (B) sites of Fe^{3+} ions. The experimental data have been fitted by using the least-squares MOSFIT program (Teillet and Varret). The refined values of hyperfine parameters are listed in table 2. The sextet with the smaller value of isomer shift of 0.34 mm/s is unambiguously assigned to the tetrahedral Fe^{3+} ions, and the other one to the octahedral Fe^{3+} ions. The relative intensities of the A-site and B-site sextets obtained from the fitting of the in-field Mössbauer spectra are reliable as the spectra of the two sites are now well resolved. The ratio of intensity of the A-site sextet to that of the B-site sextet is expected to be 1, which is the ratio of the population of the Fe^{3+} ions in A sites to that in B sites, provided Co^{2+} ions are only in the B sites as observed in bulk sized particles. But the experimental values obtained from the intensities of the A- and B-site sextets are 0.56 and 0.72 for samples with 8 and 92 nm grain sizes, respectively. It is possible only if some of the Fe^{3+} ions from the octahedral sites migrate to the tetrahedral sites on thermal annealing at 1473 K for 2 h.

3.2c D.C. conductivity: Figure 10 shows the Arrhenius plots for the electrical conductivity of the as-prepared and

heat treated samples, plotted in the temperature range from 475–625 K. For the two samples there is a change in the slope of the straight lines at about a temperature of 540 ± 3 K, which is much below their Néel temperatures. Figure 10 shows that the conductivity decreases when the grain size increases from 8–92 nm whereas it is expected to increase with the grain size. The possible change in cation distribution on annealing at 1473 K for 2 h might have contributed to the observed decrease in the conductivity. The in-field Mössbauer gave a clear evidence for the migration of some of the Fe^{3+} ions from the octahedral to tetrahedral sites as discussed in detail in §3.2b. In cobalt ferrites, the hopping of both electrons and holes contributes to the electrical conductivity. The decrease in the number

of iron ions in octahedral site will result in the decrease of $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ pairs contributing to the decrease in conductivity.

3.2d Variation of ϵ' and $\tan \delta$ with frequency: Figure 11(a) shows the effect of frequency on the real part of the dielectric constant ϵ' at 473 K for both A and B samples. Mahajan *et al* (2002) observed that the real part, ϵ' , of the dielectric constant is of the order of 10^2 at 473 K at a frequency of 1 kHz for the bulk cobalt ferrite. In the present work, the real part of the dielectric constant for sample A is of the order of 10^3 at 473 K at a frequency of 1 kHz. The dielectric constant is found to be an order of magnitude higher for the 8 nm particles compared to that of the bulk cobalt ferrite (Mahajan *et al* 2002). The high dielectric constant for 8 nm CoFe_2O_4 particles, therefore, makes them suitable for microwave applications. Moreover, the dielectric constant decreases by more than an order of magnitude when the grain size increases from 8–92 nm. This is due to the reduction of $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ pairs in B sites as a consequence of the decrease in the number of iron ions in B-sites, as revealed by the in-field Mössbauer studies as discussed in detail in §3.2b.

The plots between dielectric loss ($\tan \delta$) and frequency for samples A and B are shown in figure 11(b). Shitre *et al* (2002) observed that $\tan \delta$ is around 0.4 at 300 K in the frequency range of 1 kHz for the bulk cobalt ferrite prepared by ceramic method. In the present study, $\tan \delta$ for sample A (8 nm) is about 0.0325 at 300 K in the same frequency range. The dielectric loss is thus found to be an order of magnitude lower for the 8 nm particles compared to that of the bulk cobalt ferrite (Shitre *et al* 2002). The sample A (8 nm) can, therefore, be used for high frequency communication because of the low value of dielectric loss.

4. Conclusions

In the case of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, the Néel temperature is found to be enhanced to 611 K for the 25 h milled sample which is attributed to the increase in the superexchange interaction strength resulting from the migration of Fe^{3+} ions from the octahedral to tetrahedral sites upon milling. The oxygen vacancies created upon milling increase the conductivity. The dielectric constant for the 25 h milled sample is smaller by an order of magnitude and the dielectric loss is three orders of magnitude smaller compared to that of the bulk. The anomalous frequency dependence of the dielectric constant arises from the two types of charge carriers present in this ferrite. In CoFe_2O_4 , we conclude that the electrical conductivity and the dielectric properties could be tailor made by controlling cation distribution through thermal annealing. The dielectric loss is found to be smaller for the nanometer sized particles.

Figure 11. (a) Real part of the dielectric constant (ϵ') at 473 K as a function of frequency for as-prepared (8 nm) CoFe_2O_4 sample and sample annealed at 1473 K for 2 h (92 nm) and (b) dielectric loss factor ($\tan \delta$) at 473 K as a function of frequency for as-prepared (8 nm) CoFe_2O_4 sample and sample annealed at 1473 K for 2 h (92 nm).

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