



Influence of applied magnetic field and heating on properties of cobalt ferrite films

Kanchan Kumari^{1,*} , Rajesh Kumar¹, and Partha Bir Barman¹

¹Department of Physics and Materials Science, Jaypee University of Information Technology, Solan, Wanknaghat, Himachal Pradesh 173234, India

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ABSTRACT

Cobalt ferrite (CoFe₂O₄) films were grown in the presence of a magnetic field using a solution method. These films were investigated to understand the effect of applied magnetic field and heating on their morphological, structural, and magnetic properties. Investigations showed that the crystallite size in both the unheated and heated films increases with the application of the magnetic field. The crystalline size is observed to increase from 3.57 to 5.65 nm in the case of unheated films and from 21.49 to 23.0 nm in the case of heated films, with the application of a magnetic field. Along with the crystalline size, the applied magnetic field is found to influence the magnetic properties of the films.

1 Introduction

Among a number of ferrite materials, spinel ferrites are of great importance in understanding the fundamentals of nanomagnetism, which makes them an efficient candidate for a wide range of applications, such as spin filters, magneto-electronic devices, permanent magnets, etc. [1–5]. The properties of spinel ferrites depend upon the chemistry of the metal (M) and iron (Fe) cations [6, 7] in the general formula MFe₂O₄. Generally, the spinel ferrites form two types of lattices for cation occupancy; one is in the tetrahedral and the other is in octahedral coordination of the oxygen atom [8]. There are number of spinel ferrites, and among them, the cobalt ferrite (CoFe₂O₄) is an important candidate having an inverse spinel structure, wherein the divalent Co ions occupy

octahedral sites in the lattice [9–13]. The CoFe₂O₄ shows a ferromagnetic ordering with a large magnetic moment that exhibits exclusive properties such as magneto-optic magneto-electric effects, high magnetocrystalline anisotropy, saturation magnetization, magnetostriction, and coercivity at room temperature [14, 15].

For application purpose, the magnetic characteristics of the ferrite materials can be modulated by heat treatment, such as vacuum annealing and temperature variations during the synthesis of material. As the magnetic properties of the ferrites depend upon the distribution of cations among different lattice sites, the cations distribution can itself be manipulated through heat treatment, and thus the magnetic properties of the material can be tuned. With an influenced cations distribution, the heat treatment

Address correspondence to E-mail: thekvs001@gmail.com

can also affect the coordinated oxygen that may influence the exchange interaction among the cations. This occurs because of an indirect coupling of cations through the oxygen anions in the crystal lattice of the ferrites. In addition, a heating process can affect the recombination process of granular nanoparticles and thus the final grain size. The size of the grain greatly influences the magnetic properties of the material as well. Thus, it is quite interesting to study the effect of temperature on the properties of CoFe_2O_4 . Many researchers have made efforts to manipulate the properties during the synthesis of the CoFe_2O_4 , such as in [14, 16–20].

Here in this work, films of CoFe_2O_4 were grown through a solution approach. The films were prepared in the presence of an external magnetic field. Thus formed films were studied to evaluate the influence of the applied magnetic field, as well as the effect of heating on the properties of the films. For comparison, the films were also made in the absence of a magnetic field and without heating. The unheated films were compared with the films which were heated at 300 °C. The effect of heating was studied for both the CoFe_2O_4 films prepared without and with the applied magnetic field. Obtained results demonstrated that the magnetic properties of the CoFe_2O_4 films could be altered by applying a magnetic field during the formation of the film. Our previous study also demonstrated an influence of application of an external magnetic field and heating on the properties of nickel ferrite (NiFe_2O_4) films [21].

2 Experimental procedure

Cobalt chloride (CoCl_2), ferric chloride (FeCl_3), polyvinyl alcohol (PVA), and ammonia gas (NH_3) were used as the materials to form the CoFe_2O_4 films. First, a 0.4 g of PVA was dissolved in distilled water using a hot plate magnetic stirrer at 40 °C for 1 hour. Then 0.02 molar of CoCl_2 and 0.024 molar of FeCl_3 were added to the prepared PVA solution. Thus obtained solution was stirred for 1 hour that resulted in a transparent solution. The obtained precursor solution was then allowed to cool down to room temperature (~ 25 °C), and finally, it was filtered. After filtration, a part of the solution was taken in a petri dish that was placed inside a specially designed reaction chamber. The chamber was designed in such a way that the magnetic field could be applied to the

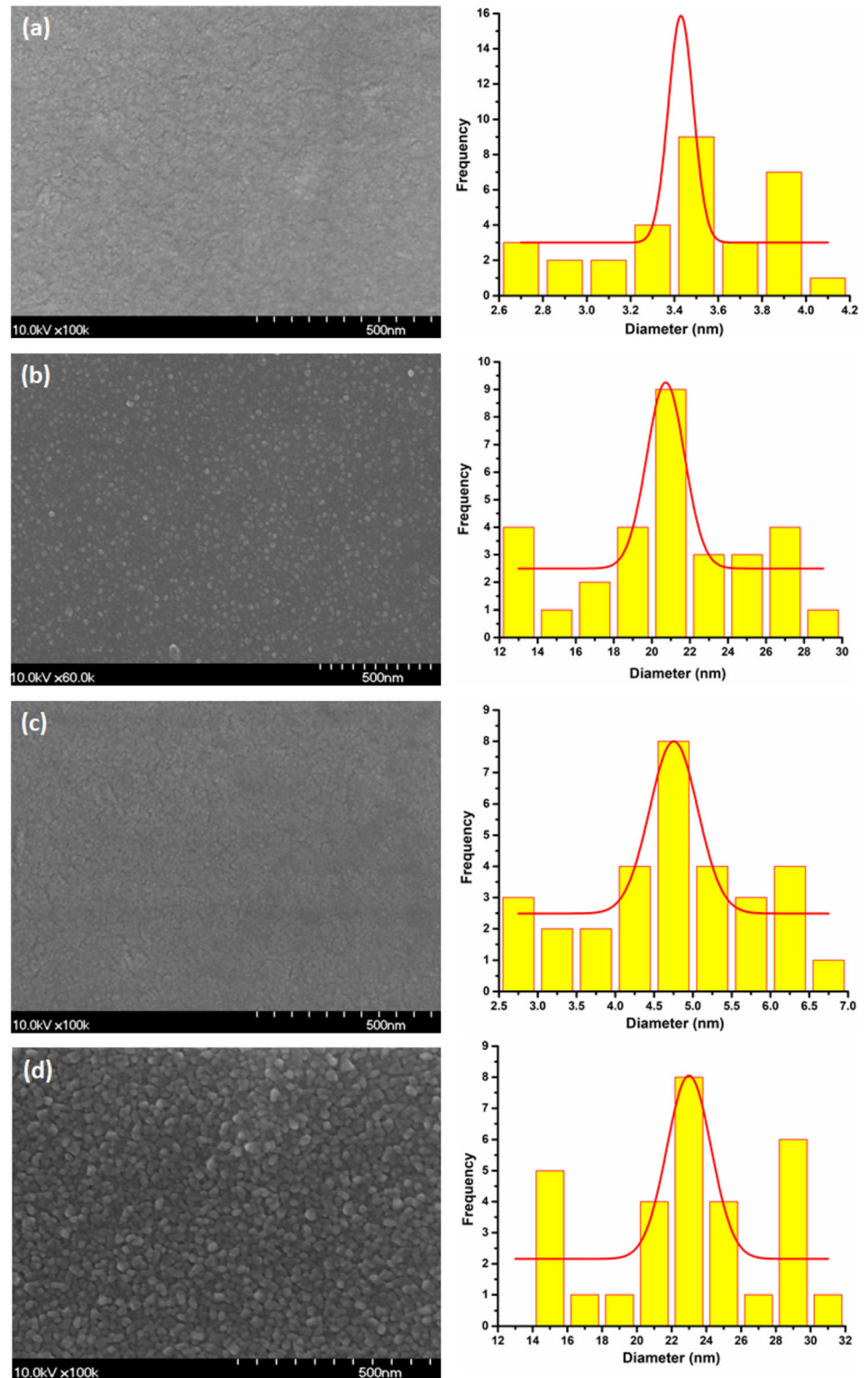
solution placed in the petri dish. To form a film of CoFe_2O_4 , a measured volume (70 ml) of NH_3 vapors/gas was purged inside the reaction chamber, and the chamber was kept closed for about 20 min. Inside the chamber, the NH_3 vapors/gas was allowed to react with the surface of the precursor solution that resulted in a floating film of CoFe_2O_4 . During the reaction of the precursor solution with NH_3 gas, an external magnetic field (1 T) was applied to study the effect of the external magnetic field on the properties of the film. After formation, the film was taken on a glass substrate, and then it was heated at 300 °C for 1 h. To study the effect of both of the formation parameters i.e., the externally applied magnetic field during formation and the heating, one of the samples from both the sets (formed without and with applying magnetic field) was heated at 300 °C, whereas another set of the films was studied without heating. The obtained films were characterized using scanning electron microscopy (SEM), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), and vibrating sample magnetometer (VSM) for their morphological, structural, and magnetic properties, respectively.

3 Results and discussion

Figure 1a–d shows the SEM images of the CoFe_2O_4 ferrite films along with their particle size distribution. The surface morphology of the unheated films is shown in Fig. 1a and c, and that of the heated films is shown in Fig. 1b and d. These images show that all the films possess almost a uniform surface morphology. Looking at the morphological images of the unheated films, which were formed without and with applying magnetic field, show no variation in the particle size. The particle size calculated from the distribution of particles for unheated film prepared without and with applying the magnetic field is obtained as 3.42 nm and 4.75 nm, respectively. For heated films, from both of the sets of films, the particle size is 20.5 nm and 21.0 nm, respectively. These results show that the particle size inside the films increases with the heating of films and also with the magnetic field applied during the formation of the films.

The XRD patterns of the as-grown films and those of the heated at temperature 300 °C are shown in Fig. 2. Both of the heated and unheated films formed

Fig. 1 SEM images and particle size distribution of the CoFe_2O_4 films. **a** and **b** corresponds to the films formed without a magnetic field, **c** and **d** corresponds to the films formed with a magnetic field for unheated and heated samples, respectively



without applying magnetic field show two diffraction peaks at diffraction angles (2θ), 15.94° and 31.68° that corresponds to lattice planes (111) and (220). Similarly, the films, heated and unheated, formed with

applying a magnetic field, show diffraction peak at an angle 2θ equal to 31.66° that corresponds to the lattice plane (220). These peaks, in all the diffraction patterns, are matched–well with the JCPDS cards No.

22-1086, but at the same time, some of the peaks are missing from the spectra. It is well known that the appearance of a number of diffraction peaks in XRD spectra depends on the direction of crystal growth, which is generally dependent on the preparation method [17, 22]. As in the present case, a magnetic field was applied during the formation of the films; it may have resulted in an orientation of the magnetic moments of the atoms/crystallites inside the film and thus a directional growth of the film. However, the films were heated at a comparatively lower temperature (300 °C), which may have resulted in a poor crystallinity inside the films. In addition, as it is well known that the scattering of X-rays from atoms produces a diffraction pattern in XRD, and thus the

obtained diffraction pattern contains information about the atomic arrangement in crystal. The film formed in the presence of a magnetic field shows only one diffraction peak at (220) that indicates the atoms inside the crystal are highly oriented in a direction which results in a single diffraction peak in the XRD pattern. This suggests that the applied magnetic field appears to produce an oriented growth in the films [23].

From the XRD pattern, it is also observed that with the magnetic field applied during the film formation, and the heating, the intensity of all the peaks increases, whereas the full-width at half maxima (FWHM) decreases. These two synthesis parameters have influenced the average size of crystallites, as

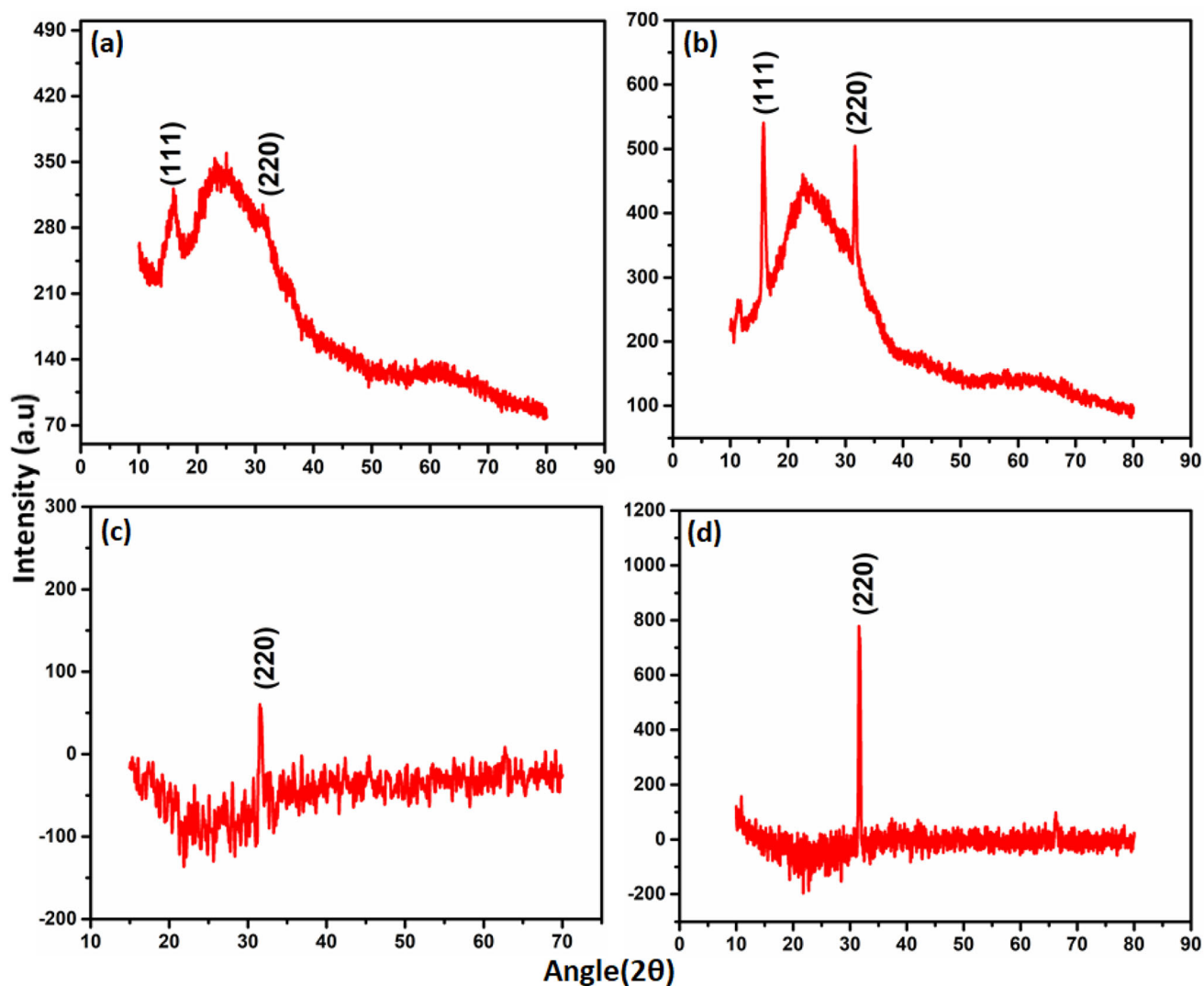


Fig. 2 XRD pattern of the CoFe_2O_4 films. **a** and **b** XRD pattern of unheated and heated films formed without a magnetic field, **c** and **d** XRD pattern of unheated and heated films formed with the magnetic

determined by Scherrer's formula. The crystallite size was studied for the typical peak (220) in all the samples. The average crystallite size increases from 3.57 to 5.65 nm for the unheated films and from 21.49 to 23.0 nm for the heated films, which were formed without and with applying the magnetic field, respectively. From the XRD data, the lattice spacing was also calculated, which is found to be 2.83 and 2.82 Å, respectively in the case of unheated and heated films prepared without applying a magnetic field. On the other hand, in the case of the films which were formed with the magnetic field, the lattice spacing of 2.81 and 2.80 Å is obtained for unheated and heated films, respectively.

Further, the lattice constant is also calculated, which in the case of the films formed without applying the magnetic field is 8.2 Å and 7.8 Å for unheated and heated films, respectively. Similarly, the lattice constant in the films formed with the magnetic field is obtained as 8.4 Å and 8.0 Å, respectively, for the unheated and heated films. The decrease in the lattice constant with the heating can be correlated with a decrease in the oxygen ions in the lattice [24]. Nonetheless, the thermal vibrations due to the heating of the sample may result in a decrease of the point defects inside the crystal lattice, exhibiting a reduction in the lattice parameters [21, 25].

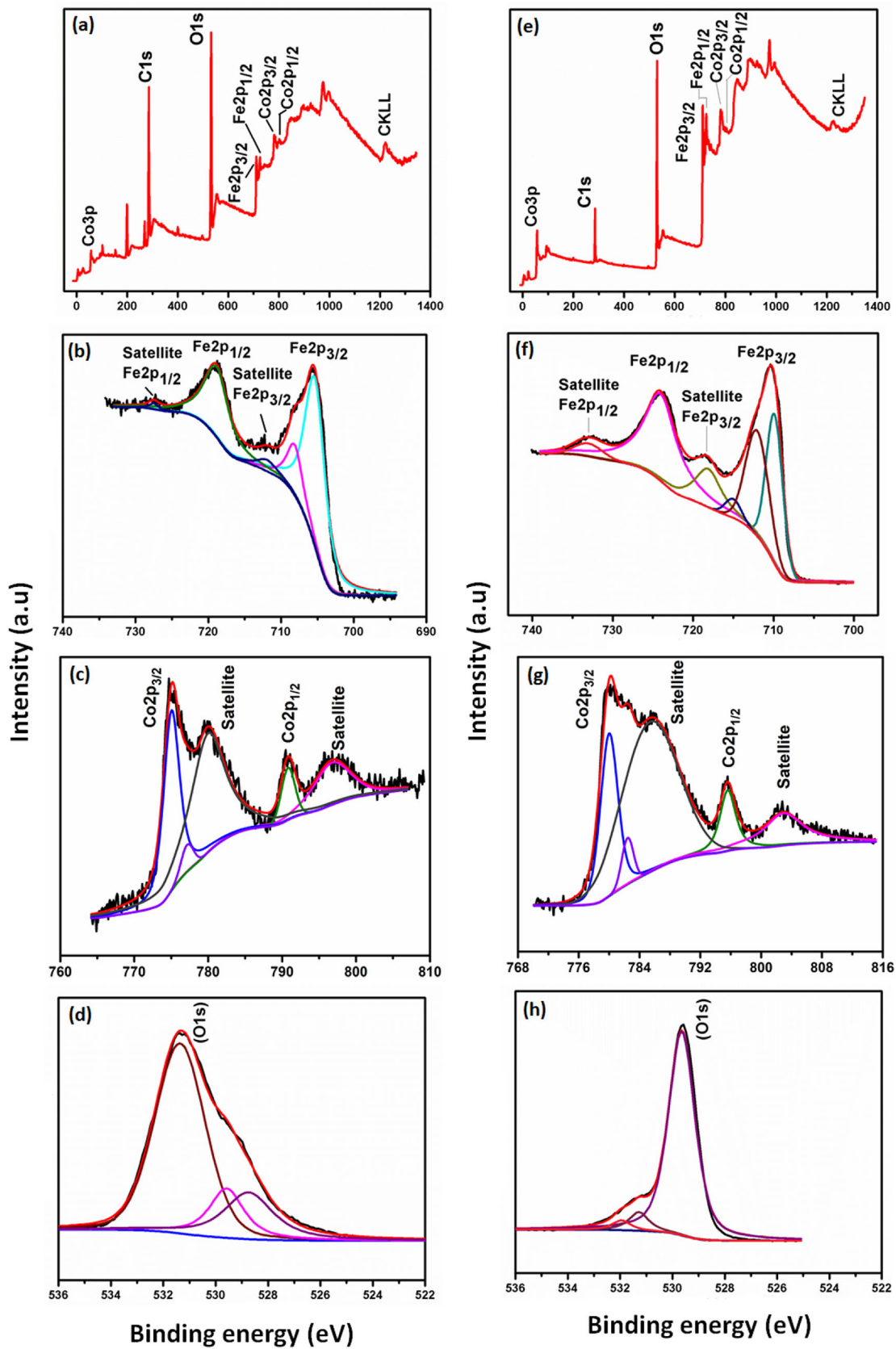
XPS survey spectra of CoFe_2O_4 films are shown in Fig. 3. Figure 3a and e corresponds to unheated and heated films, respectively, which were formed without applying a magnetic field. Both of these survey spectra possess distinct peaks of oxygen, Fe2p and Co2p, along with a carbon peak that may have appeared due to an impurity from the instrument. The high-resolution spectra, corresponding to the peaks Fe2p, Co2p, and O1s in the unheated films, are shown in Fig. 3b–d, and that of the heated films are shown in Fig. 3f–h. Here, the Fe2p_{1/2} peak (Fig. 3b) corresponds to the binding energy of 718.9 eV, and the peak Fe2p_{3/2} corresponds to the binding energy of 705.5 eV. The deconvoluted Fe2p_{3/2} peak has further two components with the binding energies 705.6 eV and 708.2 eV that correspond to the Fe cations at octahedral and tetrahedral sites, respectively. In the XPS spectrum, the existing satellite features of Fe2p spectra reveal the presence of Fe³⁺ cations only. While heating the film at 300 °C, it shows a shift in the spectrum by ~ 6 eV (Fig. 3f). In this case, the

peaks Fe2p_{1/2} and Fe2p_{3/2} are observed at 724 eV and 710.3 eV, respectively. Here, the deconvoluted spectrum possesses components of the peak Fe2p_{3/2} at 709.8 eV and 712.0 eV, which corresponds to the Fe³⁺ cations located at octahedral and tetrahedral sites, respectively. Again, the satellite positions and separation between the Fe2p_{1/2} and Fe2p_{3/2} peaks show that the Fe cations are in Fe³⁺ oxidation state.

Now, in the case of unheated films formed without applying a magnetic field (Fig. 3c), the Co has a Co2p_{1/2} peak at 790.89 eV and Co2p_{3/2} at 774.90 eV. The deconvoluted components of Co2p_{3/2} peak at 774.99 eV and 775.9 eV corresponds to Co cations at octahedral and tetrahedral sites, respectively [6, 26]. The observed satellite features towards the higher binding energy side of Co2p_{3/2} and Co2p_{1/2} is a direct consequence of the band structure associated with the Co²⁺ cations in the oxide lattice [26, 27].

For the CoFe_2O_4 film heated at 300 °C, a shift of ~ 6 eV is observed throughout the spectrum, which is similar to the change in the case of the Fe2p spectrum. After heating the film, the peaks corresponding to Co2p_{1/2} and Co2p_{3/2} are shifted to the binding energy positions 795.57 eV and 780.15 eV, respectively (Fig. 3g). The Co remains in 2 + oxidation state as revealed from the satellite features of the spectrum. In this case, the components of the deconvoluted Co2p_{3/2} peak are found at 780.3 eV and 781.5 eV, which corresponds to Co²⁺ cations at octahedral and tetrahedral sites, respectively. Ideally, in the inverse structure, the Co²⁺ cations occupy only the octahedral site; however, it depends upon the synthesis method. In the present case, the Co²⁺ cations occupy both the octahedral and tetrahedral sites, which is probably due to the adopted synthesis technique alike to [28, 29].

Figure 3d and h corresponds to unheated and heated CoFe_2O_4 ferrite films formed without applying a magnetic fields, respectively. The deconvoluted O1s spectra have peaks at 531.6, 529.6, and 528.7 eV. Here, the peak at the binding energy 531.6 eV corresponds to structural defects, such as under-coordinated lattice oxygen, chemisorbed oxygen, etc. The peak at the position 529.6 eV represents lattice oxygen (O²⁻) content in the sample [30]. In the unheated film, the intensity of the peak at the binding energy 531.6 eV is higher than that of the other peaks, whereas, in the heated film, the higher intensity peak is observed at 529.6 eV. The obtained higher



◀ **Fig. 3** XPS spectra of CoFe_2O_4 films formed without applying a magnetic field. **a** and **e** the survey spectrum, **b** and **f** are high-resolution Fe2p spectrum, **c** and **g** are high-resolution Co2p spectrum, and **d** and **h** are high-resolution O1s spectrum for unheated and heated samples, respectively

intensities corresponding to 531.6 eV indicate the presence $(\text{OH})^-$ ions in the unheated film, and upon heating the film, it reduces as shown in Fig. 3h.

The in-plane room temperature hysteresis measured for all the films are shown in Fig. 4. The magnetic parameters (saturation magnetization, coercivity, and retentivity) of the films along with their variation with the applied magnetic field and the heating, were calculated from the study of the hysteresis loop. The hysteresis measurements of the heated and unheated films prepared without and with the magnetic field are shown in Fig. 4a and b, respectively.

The unheated film prepared without magnetic field (Fig. 4a) shows saturation magnetization, coercivity, and retentivity values as 15.74 emu/cm^3 , 96.09693 Oe , and 3.37 emu/cm^3 , respectively. On the other

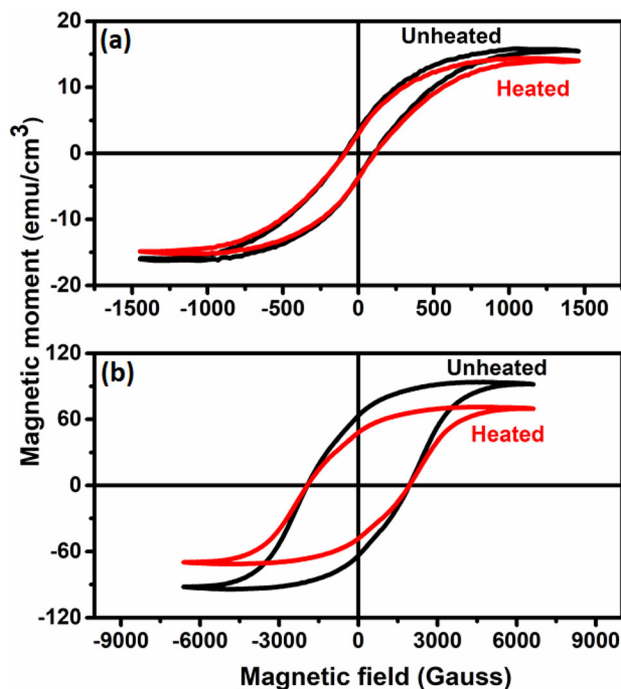


Fig. 4 Hysteresis loops for CoFe_2O_4 films. **a** hysteresis of the heated and unheated films formed without a magnetic field, **b** hysteresis of the heated and unheated films formed with the magnetic field

hand, upon heating, these films showed no variations in the coercivity, retentivity, whereas the saturation magnetization decreases to 14.26 emu/cm^3 . Similarly, the hysteresis loops of the films (unheated and heated) prepared with the magnetic field is shown in Fig. 4b. In the case of unheated films, the values of saturation magnetization, coercivity, and retentivity is 92.37 emu/cm^3 , 1918.531 Oe , and 63.96 emu/cm^3 , respectively. In this case, after heating, the values of saturation magnetization and retentivity decrease to 69.49 emu/cm^3 and 47.72 emu/cm^3 , whereas the coercivity remains the same (1918.531 Oe).

In the magnetic study of the films from the hysteresis loop, the magnetic parameters of the films prepared in the presence of a magnetic field are found to increase as compared to that of the films prepared without a magnetic field. Further, in the films formed without applying a magnetic field, the saturation magnetization decreases with heating, while the coercivity and retentivity remain the same. On the other hand, in the films formed with a magnetic field, saturation magnetization, coercivity, and retentivity decrease upon heating. The increase in the temperature is expected to cause a thermal fluctuation that would have made a change in the occupancy of the cations and the orientation of magnetic moments. These factors lead to influence the magnetic parameters of CoFe_2O_4 as being directly dependent on the occupancy of Co^{2+} in the lattice sites (mainly the octahedral ' O_h ' sites) [31–33].

4 Conclusion

CoFe_2O_4 films were formed with and without applying a magnetic field. The films were transferred successfully on the surface of a glass substrates. The films have been investigated for heating effect on their structural and magnetic properties. The employed studies show that the size of the particles increases with the heating and magnetic field applied during formation. The XPS results show that Co and Fe hydroxide is formed in unheated films, which get transformed into their binary oxides after heating. All the magnetic parameters are found to be increased in the films formed in the presence of a magnetic field irrespective of their heating conditions. Further, upon heating the films, the retentivity and saturation are found to decrease, whereas the coercivity does not change. The adopted method may be applied in the

tuning of magnetic properties of a number of materials possessing a resultant magnetic moment. As a conclusion of this study, it can be said that the presence of a magnetic field during the formation of the film is capable of tuning the magnetic properties of CoFe_2O_4 film. Similar studies can be done for other magnetic materials to tune their magnetic parameters.

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