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Structural, Magnetic, and Magnetostriction Properties of Flexible, Nanocrystalline CoFe$_2$O$_4$ Films Made by Chemical Processing

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ABSTRACT: We report on the simple, single-step, and cost-effective fabrication, characterization, and performance evaluation of cobalt ferrite (CoFe$_2$O$_4$; CFO) nanocrystalline (NC) thin films on a flexible mica substrate. The chemical solution-based drop-casting method employed to fabricate crystalline CFO films and their characterization was performed by studying the phase formation, surface morphology, and magnetic parameters, while sensor applicability was evaluated using combined magnetic and magnetostrictive properties. X-ray diffraction (XRD) indicates the single-phase and nanocrystalline nature of CFO films, where the crystallite size is ∼60 nm. The optimum conditions employed resulted in CFO NC films with surface particles exhibiting a spherical shape morphology with a homogeneous size distribution, as revealed by scanning electron microscopy analyses. Raman spectroscopic characterization of the chemical bonding indicates all of the active bands that are characteristic of the ferrite phase confirm the spinel structure, which is in agreement with XRD studies. The saturation magnetization (M_S) and coercivity (H_C), which are extracted from the field-dependent magnetization data, of CFO NC films were found to be 15.8 emu/g and 1.6 kOe, respectively, while the first-order magnetocrystalline anisotropy constant K_1 was ∼1.07 × 10^6 erg/cm^3. The magnetostriction strain curve indicates that the CFO NC films exhibit a strain value of ∼86 ppm at an applied magnetic field of 8 kOe, indicating their suitability for flexible sensor devices.
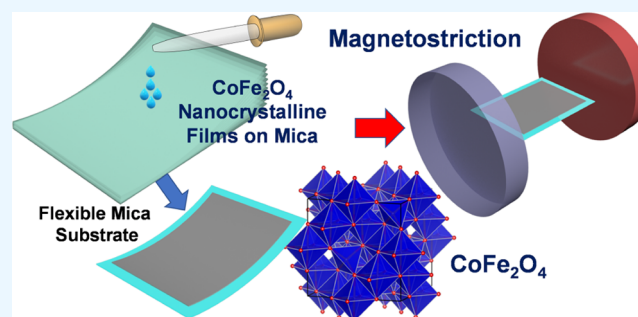
INTRODUCTION

Magnetostriction is a process where the physical dimension of a magnetic material changes under the application of an applied magnetic field, which is of enormous interest to develop advanced sensors for automotive and energy technologies.[1−6] Typically, magnetostriction is a reversible exchange of energy between the mechanical form and the magnetic form. In fact, the ability of magnetostrictive materials to convert a specific amount of energy from one form into another allows their utilization in industrial applications, especially in sensors and actuators.[4] Thus, magnetostrictive smart materials (MSMs), which exhibit magnetostriction, belong to an important class of functional materials. Due to their magneto-elastic features, these materials find widespread usage in numerous technological applications, such as stress sensors, actuators, magnetostrictive filters, controlled fuel injection systems, sonar transducer systems, sensors, micro-actuators, vibration control, and ultrasonic generation.[3,4,6−8] Alloy-based MSMs, such as Terfenol-D and Galfenol, exhibit outstanding magnetostriction strain (λ), along a particular crystallographic direction/s, but only in the single-crystal form.[3,9−11] However, in the polycrystalline or nanocrystalline

form, their magnetostriction parameters (λ and dλ/dH) are significantly low.[12]

In recent years, great attention has been directed toward the design and development of thin-film-based MSMs as these films can be employed to miniaturize devices and enhance their overall performance.[3,5,8] Shirsath et al. developed a single-crystal-like textured cobalt ferrite thin film over an amorphous SiO$_2$/Si substrate and reported giant magnetic parameters (H_C = 14.1 kOe, M_S = 475 emu/cm^3, and remanent ratio of 0.92) at room temperature.[13] In another study, Shirsath et al. demonstrated that high magnetization is achieved for cobalt ferrite thin films decorated on 4 nm-sized gold (Au) quantum dots deposited on an amorphous SiO$_2$/Si substrate.[14] These quantum dots provide a high degree of surface area and minimize the surface area at the interface. At low temperatures,
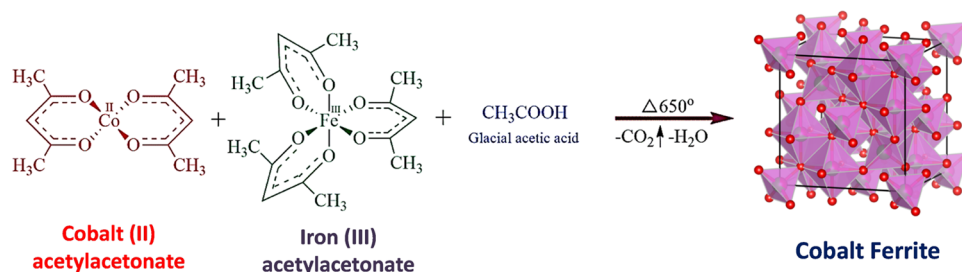
Scheme 1. Chemical Reaction between Co- and Fe-Acetylacetonates Yielding CFO


a strong preferred oriented cobalt ferrite thin film of thickness 40 nm has been grown and reported a very high coercivity of 11.3 kOe.[15] Compared to alloy-based MSMs, metal oxide-based magnetostrictive materials are highly recommended for applications owing to their simple synthesis and processing, cost-effectiveness, high chemical and mechanical stabilities, and suitability for high-frequency devices.[1,5−8] In this context, cubic-structured metal oxide-based cobalt ferrite ($CoFe_2O_4$; CFO) has received significant attention in recent years.[5−7,16−19] CFO is known for its higher magnetostriction parameters at ambient conditions owing to the presence of a higher content of anisotropic Co^{2+} ions in the octahedral sites of the spinel ferrite lattice.[5,7,20] Numerous studies exist in the literature on the magnetostrictive properties of cobalt ferrite and its metal substituted counterparts; however, in the majority of the cases, these are mostly sintered from their bulk or micron-sized powders.[6,7,19,21−23] However, studies on the magnetostrictive properties of cobalt ferrite thin films are limited. On the other hand, there is immense scope for developing thin-film-based cobalt ferrite magnetostrictive materials aiming to design miniaturized and flexible devices such as sensors, actuators, and transducers.[5,23]

Recent rapid developments and the continuously increasing need for flexible devices, which are expected to contribute significantly to the emerging electronic, optoelectronic, and magnetic technologies, in turn impose restrictions on the processing and performance of component functional materials. Specifically, functional materials, such as CFO, must be fabricated easily using simple methods without needing expensive equipment and/or elevated processing conditions. Furthermore, specifically in the case of CFO films, rigid substrates, such as Si, Ag, MgO, Al_2O_3, $SrTiO_3$, and $MgAl_2O_2$, are frequently used to realize high-quality epitaxial thin films.[24−26] Moreover, in terms of processing, to fabricate high-quality epitaxial CFO films or multilayered structures, methods employed are typically based on physical vapor deposition methods, such as pulsed laser deposition (PLD), molecular beam epitaxy (MBE), and atomic layer deposition (ALD),[5,23−26] where elevated processing conditions or special processing gases are required to realize such high-quality films. Therefore, based on our previous contributions and understanding developed toward the structural, electrical, and magnetic properties of nanomaterials based on CFO and its derivatives,[6,7,23] we directed our efforts in the present work on the fabrication, characterization, and performance evaluation of CFO films over the surface of single-crystal mica substrates through a simple, single-step, and cost-effective solution drop-casting route. The impetus is to produce high-quality CFO layers with reasonably good magnetic and magnetostriction properties using a simple chemical approach onto flexible mica substrates. The choice of single-crystal mica as a substrate was

primarily due to its flexible nature and other properties, such as thermostability, transparency, being cheaper, nontoxic, and rich in resources.[5,27−29] In fact, in view of the excellent advantages and high-temperature resistance, different electronic oxide films were successfully grown on mica for a wide variety of applications.[28,29] Furthermore, magnetic thin films and devices fabricated on flexible substrates are attractive in emerging applications, where flexibility, biocompatibility, reduced dimensionality, portability, and survivability under harsh conditions are the key requirements. Furthermore, magnetostrictive materials like CFO with magnetostrictive effects are also expected to contribute to the development of biosensors, which can effectively be used in detecting dangerous viruses that have emerged suddenly (COVID-19).[30] Therefore, the simple chemical processing, flexibility, and magnetostriction properties of cobalt ferrite films as presented and discussed in this paper are expected to contribute to the development of flexible sensors for integration into various technologies.

■ EXPERIMENTAL DETAILS

Crystalline Cobalt Ferrite Thin-Film Synthesis. In this work, a simple, economically viable, and eco-friendly wet-chemical method (solution drop-casting) involving acetonates of the respective cations, i.e., Co and Fe, was used to prepare CFO NC thin films. Our choice of the simple solution drop-casting method is due to the fact that, over other chemical methods, it is a relatively easy and inexpensive method to prepare films. Furthermore, unlike other conventional methods based on either physical or chemical vapor deposition methods, sophisticated instrumentation is not required to fabricate the films, and moreover, a high degree of particle homogeneity can be achieved after calcination at a suitable temperature. Also, multilayering becomes much easier; it is possible to coat multiple layers of ferrite particles over the substrate to have better contact between the ferrite particles, which is an essential requirement for magnetostriction strain. The chemical reaction yielding CFO NC films is presented in Scheme 1. In this chemical processing, initially, 0.01 M cobalt acetyl acetonate ($Co(acac)_2$) and 0.02 M iron acetyl acetonate ($Fe(acac)_3$) solutions were transferred into a beaker containing 5 mL of glacial acetic acid. The reaction mixture was subjected to magnetic stirring for about 30 min to obtain homogeneity of the solution. Later, a single layer of mica substrate having the dimension 1 cm^2 was taken, washed with acetone, and then placed on a hot plate under a temperature of ∼180 °C. In the subsequent step, the precursor solution was drop-cast on the mica substrate followed by calcination at 620 °C (lower than the melting point of mica) for 2 h at the heating rate of 5 °/min. The same procedure was replicated 10 times to have multiple layers of coating. Using SEM cross-section imaging,
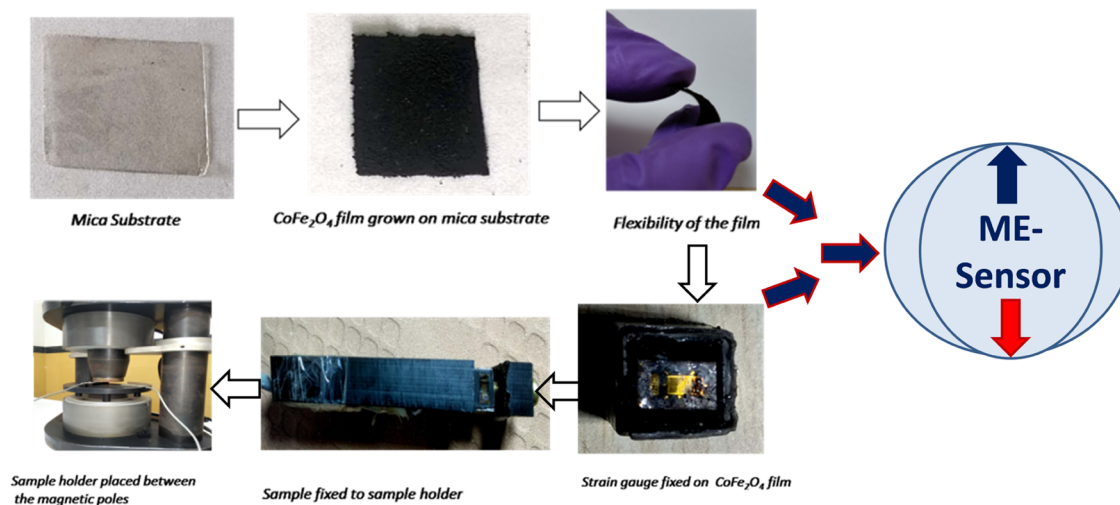
Figure 1. Schematic illustration of $CoFe_2O_4$ thin-film fabrication on a mica substrate and magnetostriction measurement leading to sensor development.
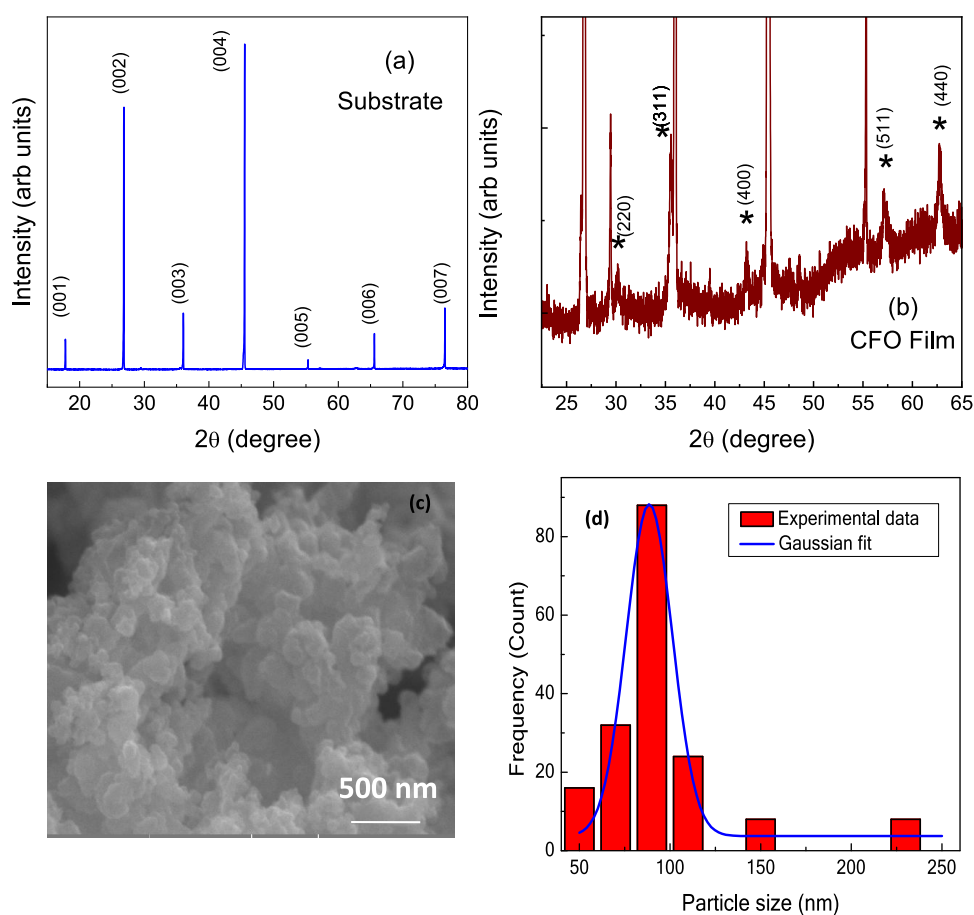
Figure 2. XRD patterns of (a) mica muscovite single-crystal substrate and (b) $CoFe_2O_4$; the peaks labeled with * symbols are attributed to the $CoFe_2O_4$ phase. (c) SEM image and (d) the corresponding particle size distribution histogram of cobalt ferrite thin films grown on the mica substrate.

the estimated CFO film thickness was ∼500 nm. We performed several studies with sample growth to optimize conditions to realize the crystalline CFO films. Specifically, CFO films obtained at room temperature and at intermediate temperatures were all amorphous and/or showed problems of adhesion to the substrate in order to result in the formation of well-adhered and mechanically robust crystalline CFO films.

This study is thus focused on evaluating the structure, properties, and performance of crystalline CFO films to demonstrate that simple chemical processing can result in the formation of near-epiquality CFO layers for sensor applications.

Cobalt Ferrite Thin-Film Characterization. The X-ray diffraction (XRD) patterns of the mica substrate and $CoFe_2O_4$-

coated mica substrate samples were recorded at room temperature by means of a "PANalytical X'pert pro" diffractometer using an X-ray source of Cu Kα radiation. Morphological features of the $CoFe_2O_4$ thin-film sample were investigated by SEM (Quanta 200, FEI). Using a Renishaw Raman spectrophotometer (U.K., Model inVia), the Raman spectrum of the fabricated cobalt ferrite film was recorded using an excitation source of 532 nm.

Magnetic and Magnetostrictive Property Evaluation. Magnetic field-dependent magnetization measurements were carried out using a Lakeshore vibrating sample magnetometer (VSM), with a step size of 150 Oe. For magnetostriction measurements, a strain gauge of resistance 350 Ω was cemented on a fabricated film using M-bond resin followed by curing at 80 °C for 10 h. Later, the sample was attached to the sample holder and placed between the poles of an electromagnet, as illustrated in Figure 1. The magnetostriction strain of the fabricated film was measured along the direction parallel to the applied magnetic field.

■ RESULTS AND DISCUSSION

Crystal Structure, Phase, and Surface Morphology. The XRD patterns of the mica muscovite single-crystal substrate and CFO NC thin films are shown in Figure 2b. The substrate exhibits a layer structure with weak van der Waals interactions between the layers, and it also belongs to a monoclinic crystal system with unit cell parameters of $a = 5.19$, $b = 9.01$, $c = 19.96$ Å, $\alpha = \gamma = 90°$, and $\beta = 95.89°$. The XRD (Figure 2b) of CFO NC films indicates the phase purity. As is evident in XRD (Figure 2b), the reflections marked with * correspond to a spinel-structured cobalt ferrite film. The XRD data indicate the formation of a single-phase cobalt ferrite film on the surface of the mica substrate. However, the CFO film XRD peaks are considerably broader due to their nanocrystalline nature. The average crystallite size, estimated from the Scherrer formula, is found to be around ~60 nm. Estimated from XRD, the unit cell parameter of the CFO films is 8.38 Å, which is comparable to those reported in the literature.[7,31] However, while the CFO films deposited in this work are crystalline, chemically processed films are not epitaxial compared to PLD CFO films deposited onto mica substrates.[5,24] On the other hand, as discussed later under chemical bonding and magnetic/magnetostriction properties, the CFO films are comparable to those deposited using PLD.[5,24] The SEM image of the CFO films is shown in Figure 2c. The corresponding histogram of particle size distribution is presented in Figure 2d. It is clear from the SEM image that the ferrite particles are in the nanometer size with an average grain size of 80 nm. Also, the ferrite particles are nearly spherical shaped and agglomerated into the form of clusters, which is due to the magnetic nature of the particles.

Chemical Bonding. To further assess the chemical bonding and structural quality of CFO films, we relied on spectroscopic characterization, particularly Raman scattering, which provides direct information on chemical bonding.[32−34] Cation distribution, which is one of the primary factors, strongly affects the magnetic properties of spinel ferrites.[16,19,23,35] As the spinel ferrite exhibits two crystallographically distinguishable sites (tetrahedral and octahedral), the magnetic cations' distribution among these sites dictates the magnetization of the spinel ferrite samples.[35] Raman spectroscopy can be employed as an effective tool to identify the cation distribution and also the phase formation of the

nano and bulk ferrite samples.[32] Therefore, Raman scattering measurements on CFO films on mica substrates are expected to provide information on their structural quality and chemical bonding. The Raman spectrum of CFO NC films is shown in Figure 3. All of the observed Raman scattering bands
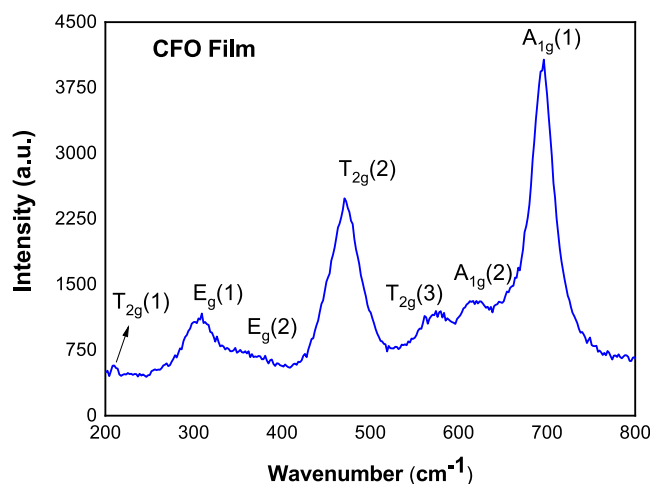
Figure 3. Raman spectrum of CFO NC films. The observed Raman bands are as indicated.

correspond to the spinel ferrite ($CoFe_2O_4$) phase. As seen in the spectrum (Figure 3), seven active bands, more than the number of bands predicted by factor group analysis, are present, signifying that the ferrite particles are crystallized in a mixed spinel structure. The presence of seven active bands has been reported for single-phase cobalt ferrite systems.[6,31,32] The present Raman spectrum of CFO NC films is consistent with those reports. The observed Raman bands situated at wavenumbers of 696.5, 616.5, 570, 470.7, 365, 309.3, and 210 cm^{-1} are assigned to $A_{1g}(1)$, $A_{1g}(2)$, $T_{2g}(3)$, $T_{2g}(2)$, $E_g(2)$, $E_g(1)$, and $T_{2g}(1)$, respectively. $A_{1g}(1)$ and $A_{1g}(2)$ bands correspond to symmetric stretching vibrations of Fe−O and Co−O bonds in FeO_4 and CoO_4 tetrahedral units, respectively. The $T_{2g}(2)$ is due to the stretching vibration of the Fe−O bond in the FeO_6 octahedral unit, whereas the $T_{2g}(3)$ band is due to the asymmetric bending vibration of the oxygens coordinated to the cobaltous ion (Co^{2+}) in the tetrahedral sites. E_g bands correspond to the symmetric bending motion of the oxygen atom within the AO_4 units (CoO_4 and FeO_4). The weak signal at 210 cm^{-1}, due to $T_{2g}(1)$, pertains to the translational motion of the BO_6 units against the A-site cations.[32]

Magnetic and Magnetostrictive Properties and Performance. The magnetization dependence of the DC magnetic field (M × H) hysteresis loop of the cobalt ferrite film, measured at room temperature in the magnetic field ranging from −20 kOe to +20 kOe, is presented in Figure 4a. The presence of a well-defined magnetic hysteresis loop in the M−H curve indicates the long-range ferromagnetic behavior of the $CoFe_2O_4$ NC film sample with a saturation magnetization (M_S) of 15.8 emu/g. The saturation magnetization of cobalt ferrite depends strongly on the particle/grain size. If the grain size of cobalt ferrite is more than 2 μm, the magnetization will be closer to bulk magnetization (~80 emu/g).[36] However, in the present study, the cobalt ferrite particles are nanocrystalline in nature with an average size of ~60 nm and, therefore, have less magnetization in comparison with bulk magnetization of
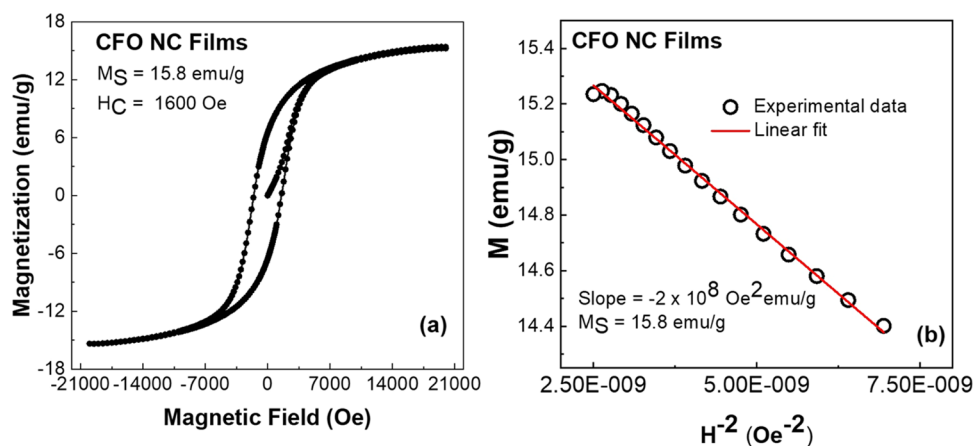
Figure 4. (a) M × H hysteresis loop of the $CoFe_2O_4$ NC film at 300 K; (b) fitting of M−H data in the high-field region for the $CoFe_2O_4$ thin film.
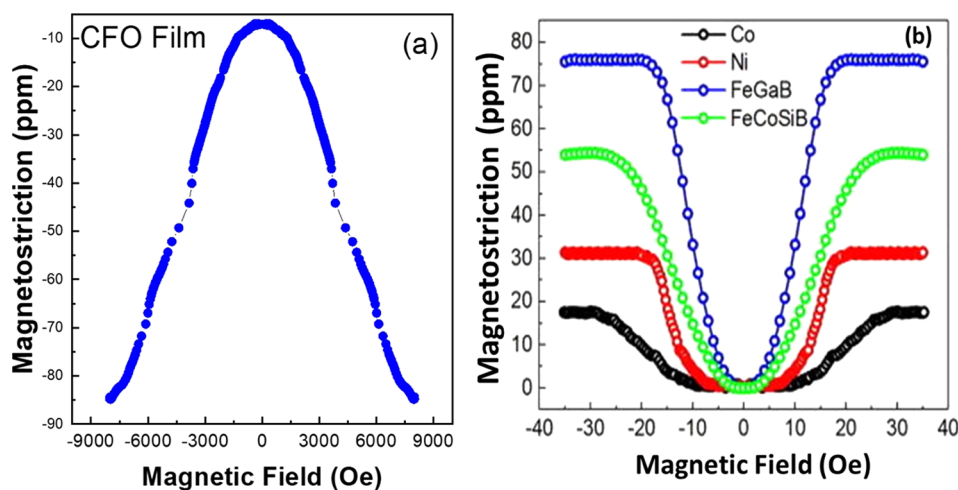
Figure 5. (a) Magnetostriction strain curve of the $CoFe_2O_4$ thin film recorded at room temperature using the strain gauge technique. (b) Measurement results of the magnetostriction constant in the absolute value of different magnetic thin films. Reprinted from ref 3 with the permission of AIP Publishing.

the material. The coercivity (H_C) of the CFO NC film amounts to 1.6 kOe, which is larger than that reported for sintered polycrystalline cobalt ferrites.[31] The higher coercivity associated with the sample is primarily attributed to the smaller crystallite size of the CFO NC films, as the coercivity of the spinel ferrites is inversely proportional to crystallite size through the Brown equation (except in single-domain particles).[37] The other magnetic parameters, namely, saturation magnetization (M_S) and magnetocrystalline anisotropy constant (K_1), of the CFO NC films extracted using the law of approach to saturation (LAS),[38] is described by

$$M = M_S\left[1 - \frac{a}{H} - \frac{b}{H^2}\right] \quad (1)$$

The term with a/H is related to the inhomogeneity parameter, while the other term b/H^2 corresponds to the magnetocrystalline anisotropy of the sample. For cubic ferrite systems, b can be expressed by

$$b = \frac{8K_1^2}{105M_S^2} \quad (2)$$

At a sufficiently high magnetic field, eq 1 can be rewritten as

$$M = M_S\left[1 - \frac{8K_1^2}{105H^2M_S^2}\right] \quad (3)$$

Herein, the initial magnetization data of the CFO films obtained at a higher magnetic field has been plotted as M vs $1/H^2$. The resultant data was fitted with a linear equation (see, Figure 4b). The intercept on the magnetization axis gives the M_S, while K_1 of the sample can be estimated from the slope. The obtained M_S and K_1 values of the CFO NC films are 15.8 emu/g and 1.07×10^6 erg/cm^3, respectively. The anisotropy constant obtained in the present study is comparable to the reported value.[31]

The magnetostriction strain curve of the cobalt ferrite film grown on the mica substrate was measured using the standard strain gauge method. The magnetostriction strain curves of the CFO NC films were recorded at room temperature along the direction parallel to the applied magnetic field. The measured magnetostriction strain curve of the cobalt ferrite film is presented in Figure 5a. It is evident (Figure 5a) that there is no appreciable magnetostriction strain up to a magnetic field of 1 kOe. After 1 kOe, the magnetostriction strain increases almost linearly with an increase in the applied magnetic field. For instance, the magnetostriction values are found to be 0, −3, −16, −45, −67, and −86 ppm at magnetic fields of 0 kOe, 1

kOe, 2 kOe, 4 kOe, 6 kOe, and 8 kOe, respectively. The magnetostriction constant and the behavior seen for flexible CFO films are comparable to the magnetic alloy films reported in the literature.[3] For comparison, the magnetostriction constant of different magnetic thin films is shown in Figure 5b.

The magnetostriction strain of −86 ppm is obtained at a maximum magnetic field of 8000 Oe (8 kOe). This value is comparable to the best-quality single-crystal or polycrystalline cobalt ferrite thin films made by PLD.[5,30,39] In fact, in a recent contribution, Liu et al. already demonstrated the superior performance of CFO films made by PLD onto mica.[5] They attributed the superior performance of the CFO−mica bimorph to the nature of weak interaction between the film and the substrate. Liu et al. convincingly presented that such a flexible CFO/muscovite bimorph provides a new platform to develop next-generation flexible magnetic devices.[5] Furthermore, as seen in Figure 5a, for chemically processed CFO films on mica, even at a maximum measuring field, magnetostriction does not attain saturation, indicating that there is a possibility of achieving an even higher magnetostriction strain at higher magnetic fields. Note that the magnitude of magnetostriction of cobalt ferrite depends on various factors such as grain size, porosity, density, grain connectivity, cation distribution, and grain orientation.[5,7,30,39] Additionally, the robust magnetic behavior against mechanical bending for the CFO/mica film−substrate pair has been already demonstrated by Liu et al.[5] and Oh et al.[24] Therefore, taking those results into consideration, the present work and the results of the CFO NC films made by the simple, eco-friendly chemical processing are outstanding (better H_C, M_S, and K) compared to all trials of Co-ferrite thin films, making them applicable in many technological areas, such as sensors, and in data storage.[39]

CONCLUSIONS

Summarizing the results, we have demonstrated the fabrication of high-quality magnetic cobalt ferrite thin films onto a flexible mica substrate. The present simple, eco-friendly, and economically viable approach results in CFO/mica flexible films with a quality and magnetostrictive performance comparable to those of PLD CFO/mica films reported in the literature. The average crystallite size of cobalt ferrite nanocrystalline films made by the present approach involving chemical processing is 60 nm, and the morphology is characterized by uniform distribution of ferrite particles that are spherical in shape. The magnetic parameters, namely, M_S, H_C, and K_1, of the cobalt ferrite nanocrystalline films are 15.8 emu/g, 16 kOe, and 2.03×10^5 J/m^3, respectively. These films exhibit a linear increase in the magnetostriction strain with an applied magnetic field. The highest value of magnetostriction was obtained as −86 ppm at an applied magnetic field of 8 kOe. The CFO NC films, which are flexible in nature, with relatively high-quality structural, magnetic, and magnetostriction parameters, are suitable for the development of flexible sensor devices.

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) G Saiz, P.; de Luis, R. F.; Lasheras, A.; Arriortua, M. I.; Lopes, A. C. Magnetoelastic Resonance Sensors: Principles, Applications, and Perspectives. *ACS Sens.* **2022**, *7*, 1248−1268.

(2) Gibbs, M.R.J.*Modern Trends in Magnetostriction Study and Application*; Kluwer Academic: Dordrecht, 2001; pp 283−305.

(3) Dong, C.; Li, M.; Liang, X.; Chen, H.; Zhou, H.; Wang, X.; Gao, Y.; McConney, M. E.; Jones, J. G.; Brown, G. J.; et al. Characterization of Magnetomechanical Properties in FeGaB Thin Films. *Appl. Phys. Lett.* **2018**, *113*, No. 262401.

(4) Olabi, A. G.; Grunwald, A. Design and Application of Magnetostrictive Materials. *Mater. Des.* **2008**, *29*, 469−483.

(5) Liu, H. J.; Wang, C. K.; Su, D.; Amrillah, T.; Hsieh, Y. H.; Wu, K. H.; Chen, Y. C.; Juang, J. H.; Eng, L. M.; Jen, S.-U.; Chu, Y. H. Flexible Heteroepitaxy of CoFe$_2$O$_4$/Muscovite Bimorph with Large Magnetostriction. *ACS Appl. Mater. Interfaces* **2017**, *9*, 7297−7304.

(6) Anantharamaiah, P. N.; Joy, P.A. Magnetic and Magnetostrictive Properties of Aluminium Substituted Cobalt Ferrite Synthesized by Citrate-Gel Method. *J. Mater. Sci.* **2015**, *50*, 6510−6517.

(7) Keswani, B. C.; Patil, S. I.; Kolekar, Y. D.; Ramana, C. V. Improved Magnetostrictive Properties of Cobalt Ferrite (CoFe$_2$O$_4$) by Mn and Dy Co-substitution for Magneto-Mechanical Sensors. *J. Appl. Phys.* **2019**, *126*, No. 174503.

(8) Liang, X.; Dong, C.; Chen, H.; Wang, J.; Wei, Y.; Zaeimbashi, M.; He, Y.; Matyushov, A.; Sun, C.; Sun, N. A Review of Thin-Film Magnetoelastic Materials for Magnetoelectric Applications. *Sensors* **2020**, *20*, No. 1532.

(9) Wang, N.-j.; Liu, Y.; Zhang, H.; Chen, X.; Li, Y. Fabrication, Magnetostriction Properties and Applications of Tb-Dy-Fe Alloys: A Review. *China Foundry* **2016**, *13*, 75−84.

(10) Clark, A. E.; Hathaway, K. B.; Wun-Fogle, W.; Restorff, J. B.; Lograsso, T. A.; Keppens, V. M.; Petculescu, G.; Taylor, R. A. Extraordinary Magnetoelasticity and Lattice Softening in bcc Fe-Ga Alloys. *J. Appl. Phys.* **2003**, *93*, No. 8621.

(11) Bergstrom, R.; Wuttig, M.; Cullen, J.; Zavalij, P.; Briber, R.; Dennis, C.; Garlea, V. O.; Laver, M. Morphotropic Phase Boundaries in Ferromagnets: Tb$_{1-x}$Dy$_x$Fe$_2$ Alloys. *Phys. Rev. Lett.* **2013**, *111*, No. 017203.

(12) Gou, J.; Ma, T.; Liu, X.; Zhang, C.; Sun, L.; Sun, G.; Xia, W.; Ren, X. Large and Sensitive Magnetostriction in Ferromagnetic Composites with Nanodispersive Precipitates. *NPG Asia Mater.* **2021**, *13*, No. 6.

(13) Shirsath, S. E.; Wang, D.; Zhang, J.; Morisako, A.; Li, S.; Liu, X. Single-Crystal-like Textured Growth of CoFe$_2$O$_4$ Thin Film on an Amorphous Substrate: A Self-Bilayer Approach. *ACS Appl. Electron. Mater.* **2020**, *2*, 3650−3657.

(14) Shirsath, S. E.; Liu, X.; Assadi, M.H.N.; Younis, A.; Yasukawa, Y.; Karan, S. K.; Zhang, J.; Kim, J.; Wang, D.; Morisako, A.; Yamauchi, Y.; Li, S. Au quantum dots engineered room temperature crystallization and magnetic anisotropy in CoFe$_2$O$_4$ thin films. *Nanoscale Horiz.* **2019**, *4*, 434−444.

(15) Shirsath, S. E.; Liu, X.; Yasukawa, Y.; Li, S.; Morisako, A. Switching of magnetic easy-axis using crystal orientation for large perpendicular coercivity in CoFe$_2$O$_4$ thin film. *Sci. Rep.* **2016**, *6*, No. 30074.

(16) Amrillah, T.; Hermawan, A.; Bitla, Y.; Baqiya, M. A.; Quynh, L. T.; Taufik, A.; Yin, S.; Juang, J.-Y. Preferentially Oriented Nanometer-Sized CoFe$_2$O$_4$ Mesocrystals Embedded in the BiFeO$_3$ Matrix for Opto-Magnetic Device Applications. *ACS Appl. Nano Mater.* **2021**, *4*, 11249−11259.

(17) Moriya, M.; Ito, M.; Sakamoto, W.; Yogo, T. One-Pot Synthesis and Morphology Control of Spinel Ferrite (MFe$_2$O$_4$, M=Mn, Fe, and Co) Nanocrystals from Homo- and Heterotrimetallic Clusters. *Cryst. Growth Des.* **2009**, *9*, 1889−1893.

(18) Raveendran, S.; Kannan, S. Polymorphism and Phase Transitions in t-ZrO$_2$/CoFe$_2$O$_4$ Composite Structures: Impact of Composition and Heat Treatments. *Cryst. Growth Des.* **2019**, *19*, 4710−4720.

(19) Kakade, S. G.; Kambale, R. C.; Kolekar, Y. D.; Ramana, C. V. Dielectric, Electrical Transport and Magnetic Properties of Er^{3+} Substituted Nanocrystalline Cobalt Ferrite. *J. Phys. Chem. Solids* **2016**, *98*, 20−27.

(20) Slonczewski, J. C. Anisotropy and Magnetostriction in Magnetic Oxides. *J. Appl. Phys.* **1961**, *32*, 253S−263S.

(21) Bhame, S. D.; Joy, P. A. Enhanced Magnetostrictive Properties of CoFe$_2$O$_4$ Synthesized by an Autocombustion Method. *Sens. Actuators, A* **2007**, *137*, 256−261.

(22) Mohaideen, K. K.; Joy, P. A. Enhancement in the Magneto-striction of Sintered Cobalt Ferrite by Making Self-composites from Nanocrystalline and Bulk Powders. *ACS Appl. Mater. Interfaces* **2012**, *4*, 6421−6425.

(23) Ansari, S. M.; Sinha, B. B.; Phase, D.; Sen, D.; Sastry, P. U.; Kolekar, Y. D.; Ramana, C. V. Particle Size, Morphology, and Chemical Composition Controlled CoFe$_2$O$_4$ Nanoparticles with Tunable Magnetic Properties via Oleic Acid Based Solvothermal Synthesis for Application in Electronic Devices. *ACS Appl. Nano Mater.* **2019**, *2*, 1828−1843.

(24) Oh, K. L.; Kwak, Y. M.; Kong, D. S.; Ryu, S.; Kim, H.; Jeen, H.; Choi, S.; Jung, J. H. Mechanical Stability of Ferrimagnetic CoFe$_2$O$_4$ Flexible Thin Films. *Curr. Appl. Phys.* **2021**, *31*, 87−92.

(25) Ramos, A. V.; Santos, T. S.; Guittet, M.-J.; Miao, G.-X.; Moussy, J.-B.; Moodera, J. S. Influence of Oxidation on the Spin-filtering Properties of CoFe$_2$O$_4$ and the Resultant Spin Polarization. *Phys. Rev. B* **2008**, *78*, No. 180402.

(26) Pham, C. D.; Chang, J.; Zurbuchen, M. A.; Chang, J. P. Magnetic Properties of CoFe$_2$O$_4$ Thin Films Synthesized by

Radical-Enhanced Atomic Layer Deposition. *ACS Appl. Mater. Interfaces* **2017**, *9*, 36980−36988.

(27) He, Y.; Dong, H.; Meng, Q.; Jiang, L.; Shao, S.; He, L.; Hu, W. Mica, a Potential Two-Dimensional-Crystal Gate Insulator for Organic Field-Effect Transistors. *Adv. Mater.* **2011**, *23*, 5502−5507.

(28) Liu, Y. X.; Cai, Y.; Zhang, Y. S.; Deng, X.; Zhong, N.; Xiang, P. H.; Duan, C. G. Van der Waals Epitaxy for High-quality Flexible VO$_2$ Film on Mica Substrate. *J. Appl. Phys.* **2021**, *130*, No. 025301.

(29) Zhang, Y.; Cao, Y.; Hu, H.; Wang, X.; Li, P.; Yang, Y.; Zheng, J.; Zhang, C.; Song, Z.; Li.; et al. Flexible Metal−Insulator Transitions Based on van der Waals Oxide Heterostructures. *ACS Appl. Mater. Interfaces* **2019**, *11*, 8284−8290.

(30) Narita, F.; Wang, Z.; Kurita, H.; Li, Z.; Shi, Y.; Jia, Y.; Soutis, C. A Review of Piezoelectric and Magnetostrictive Biosensor Materials for Detection of COVID-19 and Other Viruses. *Adv. Mater.* **2021**, *33*, No. 2005448.

(31) Anantharamaiah, P. N.; Shashanka, H. M.; Kumar, R.; Chelvane, J. A.; Sahoo, B. Chemically Enabling CoFe$_2$O$_4$ for Magnetostrictive Strain Sensing Applications at Lower Magnetic Fields: Effect of Zn Substitution. *Mater. Sci. Eng. B* **2021**, *266*, No. 115080.

(32) Puli, V. S.; Adireddy, S.; Ramana, C. V. Chemical bonding and magnetic properties of gadolinium (Gd) substituted cobalt ferrite. *J. Alloys Compd.* **2015**, *644*, 470−475.

(33) Kalidindi, N. R.; Manciu, F. S.; Ramana, C. V. Crystal Structure, Phase, and Electrical Conductivity of Nanocrystalline W$_{0.95}$Ti$_{0.05}$O$_3$ Thin Films. *ACS Appl. Mater. Interfaces* **2011**, *3*, 863−868.

(34) Hussain, O. M.; Rao, K. S.; Madhuri, K. V.; Ramana, C. V.; Naidu, B. S.; Pai, S.; John, J.; Pinto, R.; Julien, C. M. Growth and characteristics of reactive pulsed laser deposited molybdenum trioxide thin films. *Appl. Phys. A: Mater. Sci. Process.* **2002**, *75*, 417−422.

(35) Anantharamaiah, P. N.; Rao, P.; Shashanka, H. M.; Khopkar, V.; Chelvane, J. A.; Sahoo, B.; Ramana, C. V. Tunable Dielectric Properties of Nickel Ferrite Derived via Crystallographic Site Preferential Cation Substitution. *J. Phys. Chem. C* **2022**, *126*, 9123−9134.

(36) Anantharamaiah, P. N.; Joy, P. A. Effect of co-substitution of Co^{2+} and V^{5+} for Fe^{3+} on the magnetic properties of CoFe$_2$O$_4$. *Phys. B* **2019**, *554*, 107−113.

(37) Maria, K. H.; Choudhury, S.; Hakim, M. A. Structural Phase Transformation and Hysteresis Behavior of Cu-Zn Ferrites. *Int. Nano Lett.* **2013**, *3*, No. 42.

(38) Tanwar, K.; Gyan, D. S.; Gupta, P.; Pandey, S.; Prakash, O.; Kumar, D. Investigation of Crystal Structure, Microstructure and Low Temperature Magnetic Behavior of Ce^{4+} and Zn^{2+} Co-doped Barium Hexaferrites (BaFe$_{12}$O$_{19}$). *RSC Adv.* **2018**, *8*, 19600−19609.

(39) Eskandari, F.; Porter, S. B.; Venkatesan, M.; Kameli, P.; Rode, K.; Coey, J.M.D. Magnetization and Anisotropy of Cobalt Ferrite Thin Films. *Phys. Rev. Mater.* **2017**, *1*, No. 074413.