Research Article

www.bombaytechnologist.in

BOMBAY TECHNOLOGIST

ISSN: 0067-9925

$Co_{13}Cu_{87}$ and Fe_3O_4 Nanoalloys for Ultrahigh Density Magnetic Storage

Samiksha Uttam Sawant[a] and Prof. Bheemalingam Chittari[b]

[a]*Second year Master of Physics, Department of Physics, Institute of of Chemical Technology, Mumbai, India*
[b]*Assistant Professor, Department of Physical Sciences, Indian Institute of Science Education and Research, Kolkata, India*

Abstract:

Being a part of a globalized society, we are using data at a truly unprecedented rate. Given the daily rise in the need for data and space consumption, it is clear that technology must be developed that will not only conserve space but also expand memory.

Storage capacity is a key factor in the development of portable devices such as mobile, MP3 players, digital cameras, etc. In today's technology data storage capacity is crossing over its limit due to the superparamagnetic effect. This technology with longitudinal recording has an estimated limit of 100-200 gigabytes/sq.inch whereas, by perpendicular recording, it increases almost 100 times.

This study involves analyzing magnetic single domain nanoparticles suitable for the purpose of high density magnetic data storage. In this work, $Co_{13}Cu_{87}$ and Fe_3O_4 have been studied and are speculated to perform satisfying performances. It has been shown that the magnetic characteristics of these nanoalloys can be easily tailored, making it versatile and scalable for storing data.

Keywords: magnetization, nanoparticle, coercivity, hysteresis, density, magnetism, anisotropy.

1. Introduction

At present, because of the unparalleled use of data, the data storage industry is considered to be one among the largest and fastest growing industry ever. This benefit goes not just to the service sector but to the industry sector as well. According to the Indian Brand Equity Foundation, in 2020, the IT industry accounted for 9.3% of India's GDP.[1] The fact is not worth deniable that today, everyone needs efficient and long-term data storage solutions to provide a stable foundation. Hence, the introduction of some technology in this field is the need of the hour.

Various devices were tried and tested as a tool for data storage. Usually, the maximum data that can be stored with CDs go up to 700 megabytes, DVDs can hold up to 7

gigabytes, whereas pendrives can store up to 128 gigabytes. And today, we have hard disks developed that can store as high as 20 terabytes of data. Hard disk drives (HDD) being considered legacy technology, provide the basis for data storage. Currently, researchers have made a breakthrough in developing hard disk drives with materials that will lead to ultrahigh density magnetic storage. With the advent of the field of nanotechnology, it has been observed that nanoparticles have superior magnetic properties (saturation magnetization, coercivity, and others) than bulk materials. This leads to the conclusion that nanoparticle-containing devices have a lot of potential for storing data.[2] On inspecting the properties of Fe, Pt, Co, Cu, etc, it can be understood that the magnetic properties of FeO and CuCo nanoalloys suit the best for this purpose.

The curve of Magnetization versus coercivity (M vs. Hc) is called the hysteresis loop, which can help reveal a wealth of information about the material's magnetic properties. The intrinsic mechanism of the hysteresis loop can play a very important role in determining the type of magnetism that materials possess. On the basis of coercivity, materials can be classified into two basic sections- soft magnets and hard magnets. Lesser coercivity (Hc) implies a soft magnet, whereas larger coercivity implies a hard magnet. Similarly, higher magnetization and lower magnetization imply soft and hard magnets, respectively.

Fig.1 shows typical curves of a strong and weak magnetic material. The electric and magnetic properties of the nanostructured systems depend not only on the intrinsic properties of the nanostructures but also on their interactions with the matrix. Thus, the magnetic behavior of the system can be controlled by the particle size, shape, chemical composition, and structure of the nanoparticles and/or by the nature of the matrix in which they are embedded.

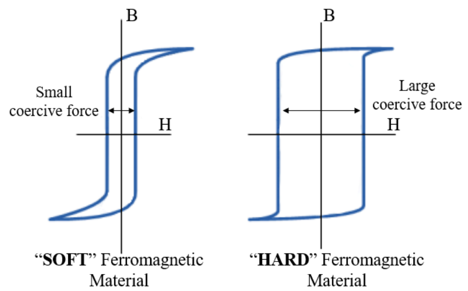

Fig. 1. Hysteresis curve for soft and hard magnets[3]

Apart from the material chosen, the way in which the arrangement is done also plays an important role. To avoid wastage of space, a perpendicular recording process is more convenient since a huge amount of data is restored within a minimum space. Perpendicular magnetic recording can provide a 100 times higher recording density than traditional longitudinal magnetic recording.[4]

2. Aim and objective

The problem of data storage can be handled with the help of nanotechnology. Few nanoparticles are found to be promising in this regard. The areal data density on magnetic media, especially hard disk memory, has increased at an astonishing rate. A combination of superparamagnetic nanoalloys is observed to be more effective.

The main aim of this work is to study the properties of FeCo and CuCo nanoalloys containing magnetic single domain nanoparticles with the promising behaviour of high density magnetic data storage.

3. Discussion

In the traditional method, to store a bit, a lot of space was required. This is mainly because of the longitudinal arrangement of the bits. Hence, the arrangement of bits leads to restriction of size and makes it less effective towards the application of storing data. Fig. 2 shows the instrumentation of a recording device.

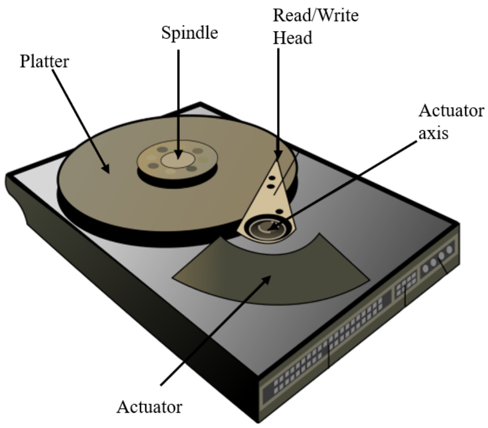

Fig. 2. Recording Device

In the Recording device, we have a magnetic surface, a reader header and a writer header. The working principle of this involves the conversion of a spin into a bit. Bit length is decided depending on the spin of the particles over the platter. Spin up implies a higher bit (Bit 1) whereas spin down implied lower bit(Bit 0), i.e., if a particle is detected in spin up state, then bit 1 is generated and for spin down, bit 0 is generated.

So, the idea is shred onto using magnets to store data and it is seen that if we use a combination of hard and soft magnets and analyze them, then the application is more effectively observed. By using nanoalloys, the magnetic properties of the particles get enhanced.

In the process of recording, an electromagnet is passed through an electric field and the change in the spins (i.e., change in signal bit) is obtained by reversing the field in the magnet i.e. by changing the direction of current through it.

There are two kinds of recording processes:

- Longitudinal recording
- Perpendicular recording

In longitudinal recording as the name suggests the bits are placed horizontally in rows. And the reader head moves across the surface and reads the magnetic signals on the storage platter. Perpendicular recording uses the space on the storage platter more effectively by adding an additional layer on the platter and now for the reader head, the bits are raised on their magnetic ends. In this way, the bits can be placed close to each other. Since the magnetization directions face each other, the magnetism gets weakened.

Hence, longitudinal magnetic recording is inadequate for high density recording. Whereas, in perpendicular magnetic recording, the interaction of the magnetic fields, next to each other is weak, making high density recording possible which leads to high data storing capacity. This increases the recording density ten times and increases the storage capacity without loss of bit quality. This can be discerned from Fig 3.

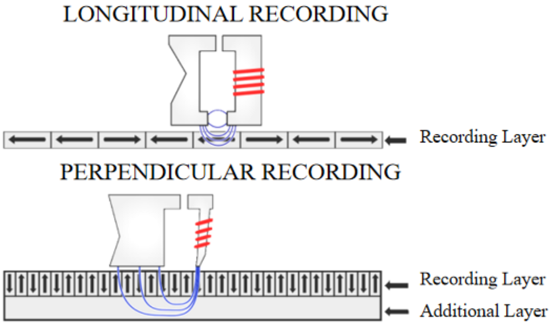

Fig. 3. Magnetic recording arrays with traditional writing mechanism *(Public Domain image by Luca Cassioli 2005)[5]*

Hence, perpendicular mode of recording is more convenient than longitudinal recording process since, a perpendicular continuous granular material exhibits higher thermal stability than longitudinal media because the demagnetizing fields are stabilizing rather than destabilizing and the grain can be larger since they can be in the form of columns, having small in-plane dimensions, which is important for short bit lengths.[6]

The goal is to obtain superparamagnetic nano-alloys for this purpose. However, for the chosen nanomaterial, an ideal device must follow:

A. Writability:

To change the signal on reversing the field, it is preferred to have a device that will do this task as fast as possible and not take much time.[7]

B. Thermal Stability:

When we are using a device, it is preferable to have a device that will do the task for a wide range of temperatures. In order to avoid superparamagnetic effects and ensure data stability, one typically compensates for the reduction in grain volume by increasing the anisotropy energy density.[8]

C. Signal to Noise Ratio:

A high Signal to Noise Ratio implies more information to be detected to the reader with minimal noise. High density media are assumed in which the transition parameter scales with in-plane grain diameter.[9]

Table 1 shows the comparison of Coercivity(Hc), Magnetization(M), and Curie Temperature(Tc) of a few superparamagnetic materials.

Material	Coercivity (Oe)	Magnetization (emu/g)	Curie Temp. (K)
$CoFe_2O_4$ [10]	620	60	789
$Co_{13}Cu_{87}$ [11]	800	160	1390
MnBi [12]	238	49	416
$SmCo_5$ [13]	30k	53	1029
Fe_3O_4 [14]	190	70	858
FeCo [15]	440	186	713
Fe_3S_4 [16]	910	59	677

Table 1. Comparison of magnetic properties of few superparamagnetic materials.

Literature studies on the structure, magnetic, and giant magneto-resistance properties of $Co_{13}Cu_{87}$ and Fe_3O_4 alloy are being carried out and we will see that the magnetic properties of these materials make them suit the best for our purpose.

- **$Co_{13}Cu_{87}$**

$Co_{13}Cu_{87}$ is a nano-alloy of Cobalt nanoparticles embedded in copper matrix. The magnetic anisotropy constant of $Co_{13}Cu_{87}$ nanoparticles is 40 times as large as the bulk value.[17,18]

When Hickey et al. carried out the study for nanoparticles containing 30 atoms of Cobalt having a diameter less than 1.5 nm, it was seen that the magnetic anisotropy goes up to 3×10^8 erg/cm^3. The magnetic properties of these nanoparticles were found to show a tremendous change in the properties (superior to those of bulk materials).[19]

Bulk cobalt has the highest Curie temperature, $T_C \approx$ 1390K. At room temperature, the saturation magnetization of bulk Cobalt, M_s=1.9T (160emu/g), and coercivity, H_c=800 A/m. Structurally, at a lower temperature (< 420ºC), cobalt is hexagonal closed packed, and at a higher temperature, it possesses face cubic crystal structure.[20]

For ferromagnetic particles with a single domain, the maximum coercive field appears. As studied by Heip et al. RF sputtering had been used to make thin films from $Co_{50}Ag_{50}$ and $Co_{15}Cu_{85}$ targets. When the films obtained in a study were annealed at 400°C, the coercivity value increased tremendously (up to 690 Oe). The results of $Co_{13}Cu_{87}$ are compared with $Co_{15}Cu_{85}$ and $Co_{17}Cu_{83}$ and summarized in Table 2.[21]

	$Co_{13}Cu_{87}$	$Co_{15}Cu_{85}$	$Co_{17}Cu_{83}$
Size	350nm	506nm	590nm
360°C	380 Oe	325 Oe	255 Oe
380°C	585 Oe	440 Oe	320 Oe
400°C	690 Oe	455 Oe	325 Oe
420°C	560 Oe	375 Oe	515 Oe

Table 2. In plane coercivity annealed in a temperature range of 360-420°C/1hr

X-ray diffraction was used to determine the structure and particle size.The X-ray diffraction patterns are shown in Fig. 4. Two peaks, one for the Co[1 1 1] FCC phase and the other for Ag[2 0 0] and Cu[2 0 0], are quite near together [2 0 0].[21]

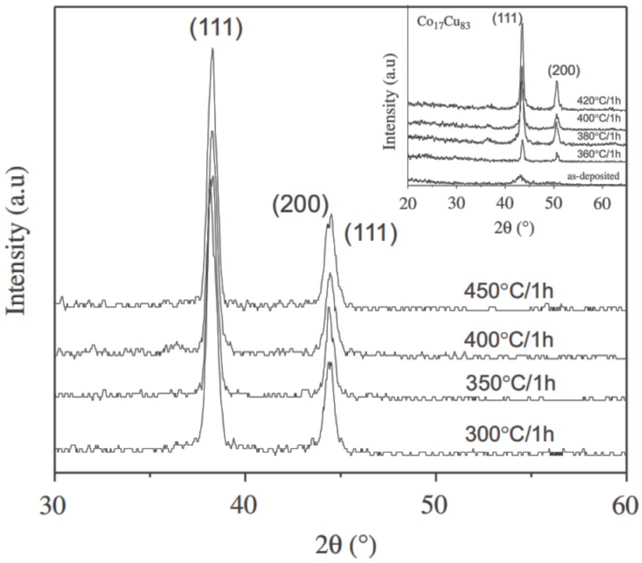

Fig. 4. XRD diagrams for 508 nm $Co_{52}Ag_{48}$ films; annealed at various temperatures. XRD for $Co_{17}Cu_{83}$ films(inset) [21]

- **Fe_3O_4**

Due to the strong coercivity, low Curie temperature, and superparamagnetic behaviour of Fe_3O_4 magnetic nanoparticles, they have undergone extensive research.[22] Fe_3O_4 usually possesses a high value of coercivity with a lower value of Curie temperature.[23,24] The average crystallite size, D, is calculated from the Debye–Scherrer equation,

$$D = \frac{K\lambda}{\beta cos\theta}$$

where K, λ, β and θ are the Debye-Scherrer constant, X-ray wavelength, peak width of half-maximum, and the Bragg diffraction angle, respectively.

Yun et al. achieved chiral magnetic nano-structured materials with a high magnetic saturation value of 28.7 emu/g. This was done for magnetite microspheres having a mean diameter of about 270nm and consisting of nanoparticles with an average size of 18nm.[25]

The study that was carried out by Wei et al. showed Fe_3O_4 nanoparticles prepared by mixing NaOH solution in FeCl3·6H2O and FeCl2·4H2O with a molar proportion of 1:2, dissolved in ethanol or deionized water with constant magnetic stirring for 30 min. the following step was carried out at different temperatures at different iron concentrations. The result is summarized in Table 3.

Samples	Temperature (°C)	Fe-concentration (molL^{-1})	Crystallite size (nm)
a	40	0.15	12.6
b	80	0.15	13.4
c	80	0.86	14.2
d	80	0.86	13.8

The average crystallite sizes noted were (a) 12.6 nm, (b) 13.4 nm, (c) 14.2 nm and (d)13.8 nm and the results were speculated by the graphs as shown below. The XRD graphs for each of these cases are shown in Fig 4. The XRD peaks are quite similar to the inverse cubic spinel structure's characteristic peaks.[26]

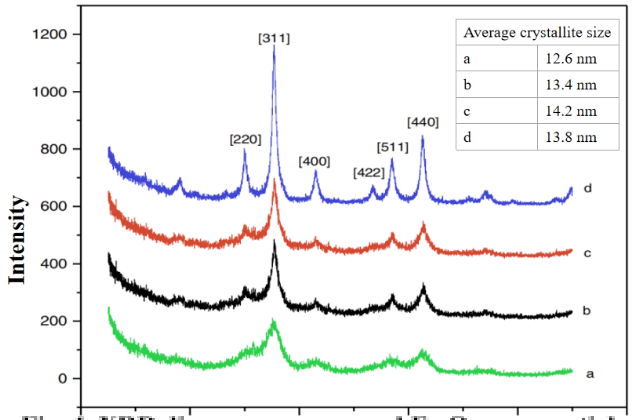

Fig. 4. XRD diagram as prepared Fe_3O_4 nanoparticles [26]

Fig. 5. shows the hysteresis curve for all the samples marked as a,b,c, and d for all the crystallite sizes as mentioned above. Symmetric hysteresis and saturation magnetization can be observed, and the prepared Fe_3O_4 magnetic nanoparticles show ferrimagnetic behaviors. Sample b has a higher saturation magnetization than Sample a, which probably could be due to the greater particle size. [27]

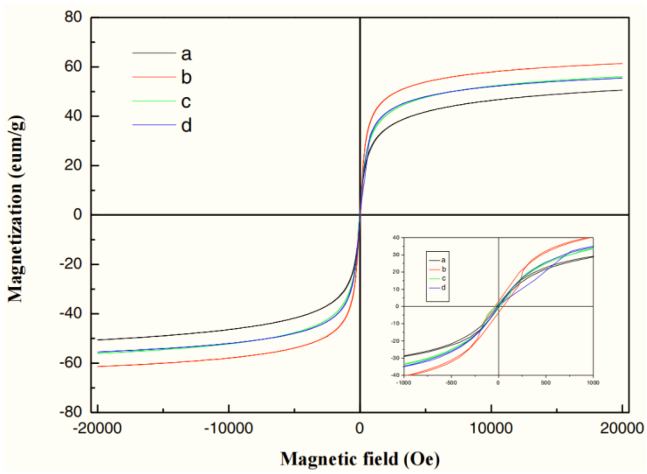

Fig. 5. Hysteresis curve of Fe_3O_4 magnetic nanoparticles[26]

Hira et al. studied the magnetic properties of Fe_3O_4 of different shapes using a Vibrating Sample Magnetometer. The superparamagnetic nature of Fe_3O_4 nanoparticles was confirmed by observing that the magnetic hysteresis was nil for all the samples. Fe_3O_4 nanoparticles in the form of spheres (216.6 nm), cubes(158.5 nm), and octahedra(4.9mm) were found to have magnetic saturation values of 87,85, and 82 emu/g respectively. SEM was used to examine the morphologies of the synthesized products. SEM images are displayed in Fig.6. [27]

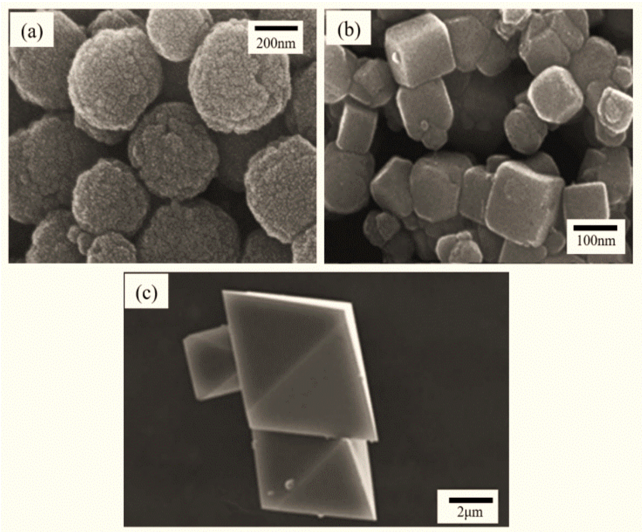

Fig. 6. SEM images of Fe_3O_4 nanoparticles (a-spherical, b-cubic, c-octahedron [27]

The results are summarized in Table 3 where the shape of these nanoparticles varies with magnetization. When the size of particles decreases, their magnetization also decreases with an increase in the coercivity value, which explains about magnetically disordered surface layer.

M_s	Shape
87	Sphere
85	Cube
82	Octahedron

Table 3. Variation of magnetization corresponding to the shape of the nanoparticle

The magnetic hysteresis curves for the examined samples are displayed in Fig. 6.

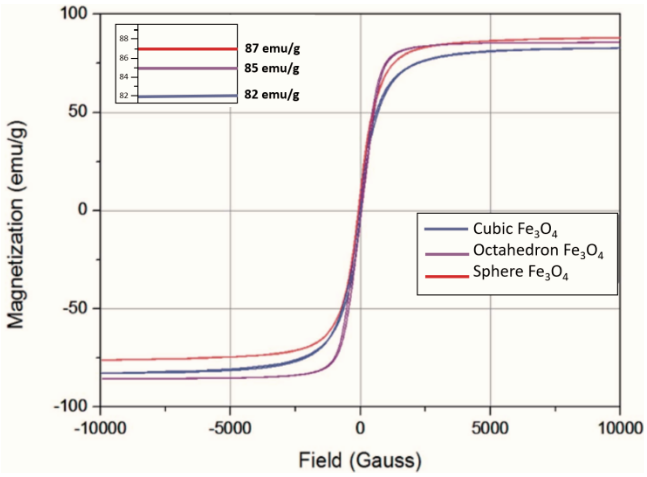

Fig. 6. Hysteresis curves for various shapes [27]

The variation of shape anisotropy of variously shaped nanoparticles as reported by Zhao et al. is as follows: spheres < cubes < modified particles < octahedrons. [27]

4. Conclusion

To sum up the entire work, after doing the literature study and shortlisting a few nanoparticles, it comes to notice that $Co_{13}Cu_{87}$ and Fe_3O_4 show extraordinary behavior at their nanosize. $Co_{13}Cu_{87}$ has a magnetic anisotropy constant which is 40 times greater than the bulk value. Fe_3O_4 is one of the lowest coercive materials. It has an advantage because of the several shapes it possesses. Since each shape shows extraordinary behaviour. Hence, $Co_{13}Cu_{87}$ and Fe_3O_4 can be promising materials for magnetic data storage.

5. Future Directions

The main motivation of this study is to discover more effective nanoalloys for the purpose of magnetic recording. The research can be extended to discovering more particles having a combination of hard and soft nanoparticles for varied values of sizes and also diversity in shapes.[28]

6. Acknowledgment

I would like to express my deep and sincere gratitude to my research supervisor Dr. Bheemalingam Chittari for the constant support and encouragement. My completion of this work could not have been accomplished without their assistance.

I sincerely thank IISER Kolkata for giving me the opportunity to carry out my summer internship.

7. References

[1] "Indian IT & BPM Industry Analysis"

[2] Chittari, Bheema Lingam, and Vijay Kumar. "Ab Initio Studies of Segregation, Ordering, and Magnetic Behavior in (Fe–Pt) n , n = 55 and 147: Design of $Fe_{75}Pt_{72}$ Nanoparticle.", *J. Phys. Chem. C*, **2015**;119;20:11062–71.

[3] Areef Billah, "Investigation of multiferroic and photocatalytic properties of Li doped BiFeO3 nanoparticles prepared by ultrasonication", Yamagata University, **2016**,54

[4] Roger Wood. "Future hard disk drive systems",*J Magn Magn Mate.,* **2009**;321:555–561

[5] Cassioli (26781 bytes), Scheme of perpendicular recording technology, **2005**

[6] Weller, D., and A. Moser. "Thermal Effect Limits in Ultrahigh-Density Magnetic Recording." *IEEE Trans. Magn.* **1999**, *35*, 4423–4439. .

[7] S. N. Piramanayagam et al., "Writability Improvement in Perpendicular Recording Media Using Crystalline Soft Underlayer Materials," *IEEE Trans. Magn.* **2013**, *49*, 758–764.

[8] S. H. Charap, P.-L. Lu, Y. He, "Thermal stability of recorded information at high densities," *IEEE Trans. Magn.*, **1997**, vol. 33, p. 978.

[9] H. N. Bertram, H. Zhou, and R. Gustafson, "Signal to noise ratio scaling and density limit estimates in longitudinal magnetic recording," *IEEE Trans. Magn.*, **1998**, vol. 34, p. 1845

[10] A. Hossain, M. S. I. Sarker, M. K. R. Khan, F. A. Khan, M. Kamruzzaman and M. M. Rahman "Study of Magnetic Properties of $CoFe_2O_4$ Nanoparticles", *Applied Physics A*, **2018**; 124; 608.

[11] Khalyapin, D.L., J. Kim, S.V. Stolyar, I.A. Turpanov, P.D. Kim, and I. Kim. "Formation of 4H-Closely Packed Structure in Thin Films of Metastable Nanocrystalline $Co_{13}Cu_{87}$ Alloy." *Solid State Commun.,* **2003**;128; 6–7:209–12.

[12] J. Zamora, I. Betancourt, and I.A. Figueroa, "Coercivity mechanism of rare-earth free MnBi hard magnetic alloys",*Revista Mexicana de F´ısica* ,**2018** ;64: 141–144

[13] HaoTang, MohammadAref Hasen Mamakhel & Mogens Christensen, "High coercivity $SmCo_5$ synthesized with assistance of colloidal SiO2",*Nature Portfolio*, **2021**; 11:4682

[14] McMichael RD, Shull RD, Swartzendruber LJ, Bennett LH, Watson RE. "Magnetocaloric effect in superparamagnets." *J Magn Magn Mate.*, **1992**;111:29-33.

[15] Karipoth, P.; Thirumurugan, A.; Velaga, S.; Greneche, J.-M.; Joseyphus, R. J. Magnetic Properties of FeCo Alloy Nanoparticles Synthesized through Instant Chemical Reduction"Journal of Applied Physics. *Journal of Applied Physics* **2016**, *120.*

[16] Andrew P. Roberts. "Magnetic properties of sedimentary greigite(Fe_3S_4)" *Earth and Planetary Science Letters*,**1995**;134:227-236

[17] Gubin, S P, Y I Spichkin, G Yu Yurkov, and A M Tishin. "Nanomaterial for High-Density Magnetic Data Storage" **2002**;47; 37.

[18] Gubin, S. P., and Yu. A. Koksharov. "Preparation, Structure, and Properties of Magnetic Materials Based on Co-Containing Nanoparticles." *ChemInform*, **2003**; 34, 20

[19] Hickey, B.J., Howson, M.A., Greig, D., and Wiser, N., Enhanced Magnetic Anisotropy Energy Density for Superparamagnetic Particles of Cobalt, *Phys. Rev. B: Condens. Matter,* **1996**; 53,32–33.

[20] Peña O′Shea, Víctor A. de la, Pilar Ramírez de la Piscina, Narcis Homs, Guillem Aromí, and José L. G. Fierro. "Development of Hexagonal Closed-Packed Cobalt Nanoparticles Stable at High Temperature." *Chemistry of Materials* 21, **2009**, 23 , 5637–43.

[21] Hiep, V.V., N. Chau, D.M. Hong, and N.H. Luong."High Coercivity and Giant Magnetoresistance of CoAg, CoCu Granular Films." *J Magn Magn Mate.*, **2007**;310; 2: 2524–26.

[22] Beydoun D, Amal R, Low GKC, McEvoy S. "Novel photocatalyst: titania-coated magnetite. Activity and photodissolution." *J. Phys Chem B*, **2000**;104:4387-4396.

[23] McMichael RD, Shull RD, Swartzendruber LJ, Bennett LH, Watson RE. "Magnetocaloric effect in superparamagnets." *J Magn Magn Mate.*, **1992**;111:29-33.

[24] Zhao, Guoping , Z. Xuefang, F. Morvan , " Theory for the coercivity and its mechanism in nanostructured permanent magnetic materials", *American Scientific Publishers* , **2015**;4;1:25

[25] Wei, Yun, Ailin Tian, Yan Li, Xiong Wang, and Bo Cao. "A General Chiral Selector Immobilized on Silica Magnetic Microspheres for Direct Separation of Racemates." *J. Mater. Chem.*, **2012**, 22, 17, 8499

[26] Wei, Yan, Bing Han, Xiaoyang Hu, Yuanhua Lin, Xinzhi Wang, and Xuliang Deng. "Synthesis of Fe_3O_4 Nanoparticles and Their Magnetic Properties." *Procedia Eng.* 27, **2012**, 632–37

[27] Hira Fatima, Dae-Won Lee, Hyun Joong Yun and Kyo-Seon Kim"Shape-controlled synthesis of magnetic Fe_3O_4 nanoparticles with difffferent iron precursors and capping agents" RSC Adv.,**2018**;8:22917–22923

[28] L. Zhao, et al., Morphology-controlled synthesis of magnetites with nanoporous structures and excellent magnetic properties, *Chem. Mater.*, **2007**, 20:198–204.

[29] Coey, J.M.D., Magnetism in Future, *J. Magn. Magn Mater.*, **2001**; 226–230:2107-2112