*Bangladesh Journal of Physics, Vol. **31**, Issue 1, pp. 43 – 51, June 2024*

FACILE SOL–GEL SYNTHESIS OF CoPt NANOPOWDER IN AIR AMBIENT: A STUDY FOR SOFT MAGNETIC DEVICE APPLICATIONS

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Received on 13.07.2023, Revised received on 15.05.2024, Accepted for publication on 27.05.2024

DOI: *https://doi.org/10.3329/bjphy.v31i1.79518*

ABSTRACT

Currently, the utilization of cobalt-based soft magnetic nanocrystalline powders spans various technological domains, encompassing magnetic heads and shields, magnetic sensors, biomedical advancements, ferro-fluid technology, among other notable applications. Herein, we elucidate the impact of the presence of oxygen on CoPt magnetic nanoparticles prepared through an easy and economical sol-gel route, and annealed at 800 °C for 3 hours in an air ambient, for the first time. The structural, elemental, morphological, vibrational and magnetic properties were investigated by XRD, TEM, FTIR spectroscopy and VSM techniques. The XRD analysis yields the tetragonal unit cell dimensions of a= 3.843 Å and c= 3.754 Å. Lattice parameters are also calculated from SAED patterns which are well agreed with the value obtained from XRD peaks. The average crystalline size calculated from W-H plot was 34 nm. EDS spectra confirmed the presence of Co, Pt and oxygen without any magnetic impurities. The average size of nanoparticles, measured from TEM images of the as-prepared nanopowder, was 67 nm, which decreased to 40 nm after annealing in air atmosphere at 800 °C for 3 hours. The magnetic coercivity value of annealed nanoparticles was 204 Oe, which is considerably smaller compared to values reported in other published research. This difference can be attributed to the presence of oxygen, revealing the soft ferromagnetic nature of the nanoparticles.

Keywords: *CoPt nanoparticles, Sol-gel, XRD, TEM, Soft ferromagnetic devices.*

1. INTRODUCTION

Researchers are particularly intrigued by the distinctive characteristics of the $L1_0$ ordered face-centered tetragonal (FCT) nanopowder composed of Cobalt (Co) and Platinum (Pt) in a 50:50 ratio within bimetallic CoPt nanoparticles (NPs). Its structural, electronic, and magnetic properties have garnered significant attention among scholars in the field. It needs a very large magnetic field to demagnetize the $Co_{50}Pt_{50}$ NPs due to their hard ferromagnetic nature [1]. These permanent magnetic $Co_{50}Pt_{50}$ NPs have potential applications in different magnetic devices including magnetic storage media, biomedical application, optical science, magnetic sensors and imaging and so on [1-2]. But to obtain the desired bimetallic $L1_0$ ordered FCT $Co_{50}Pt_{50}$ nanopowder the main challenge is to remove oxygen from it in the synthesis time. Generally, gas medium such as Ar or H_2 is used in annealing time of as-prepared NPs to remove oxygen. This procedure is so difficult and also costly. Typically, during the annealing process of freshly prepared nanoparticles, a gas medium like Ar or H_2 is employed to eliminate oxygen. However, this method is often challenging and comes with significant expenses.

Y Wang *et al.* [2] synthesized $L1_0$ ordered FCT $Co_{50}Pt_{50}$ NPs at 700 ºC for 1 hour in Ar atmosphere through the sol-gel route and they achieved 11.6 nm NPs with giant value of coercivity ~5910 Oe at room temperature (T= 300 K). Y Liu *et al.* [3] reported sol-gel route to synthesis of $L1_0$ arranged FCT $Co_{50}Pt_{50}$ magnetic NPs at 800 ºC for 10 hours in Ar gas environment and they found 18.3 nm NPs with magnetic coercivity ~3200 Oe at 300 K. M Mandal *et al.* [4] synthesized $L1_0$ ordered FCT $Co_{50}Pt_{50}$ magnetic NPs by micellar technique at 900 ºC for 1 hour in Ar atmosphere and they obtained 7 nm NPs with coercivity 4400 Oe at 300 K. In our previous work [1], we successfully synthesized oxygen free $L1_0$ ordered FCT $Co_{50}Pt_{50}$ magnetic NPs annealed at 800 ºC for 3 hours in H_2 gas medium by sol-gel method and we achieved 18 nm NPs with coercivity 1800 Oe at 300 K. As far as we know, there have been no reported findings regarding the air medium annealed $L1_0$ ordered FCT CoPt magnetic nanoparticles. In this ongoing study, we delve into the synthesis of $Co_{50}Pt_{50}$ magnetic nanoparticles using the conventional and cost-effective sol-gel route. Subsequently, these nano-structured particles are subjected to annealing at 800 ºC for a duration of 3 hours in air environment for the first time. Our aim is to explore the impact of oxygen presence on the properties of the CoPt nanopowder.

2. SAMPLE PREPARATION AND TECHNIQUES

CoPt nanoparticles were fabricated through the utilization of inexpensive sol-gel methodology, employing $CoCl_2.6H_2O$ and $H_2PtCl_6.6H_2O$ as the initial reactants. Non-toxic cobalt chloride hexahydrate ($CoCl_2.6H_2O$, 97% pure; Merck) and chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$; SIGMA ALDRICH) are used as the precursors. Citric acid ($C_6H_8O_7.H_2O$, 99% pure; Merck) serves a crucial role as a chelating agent. Additionally, hydrochloric acid (HCl) is provided in solution form to act as a reacting agent. The detailed experimental procedures to obtain the as-prepared dried sample have been described in our previous work [1]. Subsequent to this, the cultivated sample underwent extensive grinding until it reached a fine nanopowder state, employing a unique agate mortar and pestle. Following that, the nanopowdered sample underwent an additional process of annealing at 800 ºC for a duration of 3 hours in air atmosphere. This step was crucial in yielding the desired low-cost CoPt nanoparticles, which were subsequently utilized in various characterization experiments. Figure 1 illustrates the step-by-step procedure of the sol-gel synthesis method.

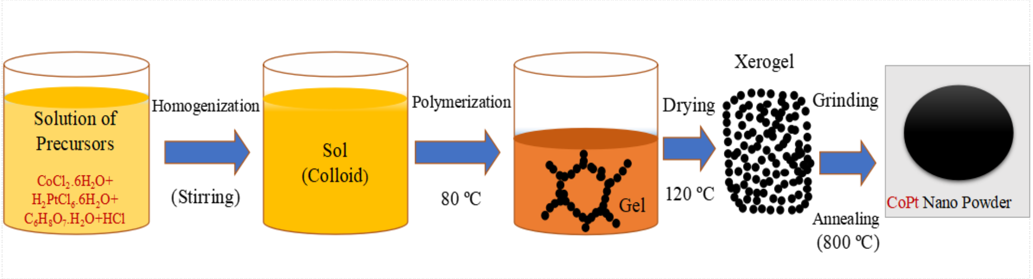

Fig. 1. Different steps of CoPt NPs fabrication in sol-gel synthesis method.

The structural analysis of nano-powdered CoPt was completed by x-ray diffractometer (XRD, RINT-V, Rigaku Company) using Cu-K_α radiation (λ = 1.5406 Å). The CoPt sample under examination underwent analysis using Fourier Transform Infrared Radiation (FTIR) spectroscopy, conducted with a Perkin Elmer 100 instrument, to identify its inherent vibrational modes. The transmission electron microscope (TEM, JEOL-200CX), functioning at 200 kV, was utilized to observe the surface morphology. Energy dispersive spectroscopy (EDS) was employed to analyze the elemental compositions within the experimental sample. Furthermore, the magnetic coercivity and saturation magnetization of the nanopowdered sample were determined using a vibrating sample magnetometer (VSM).

3. RESULTS AND DISCUSSION

3.1 Structural analysis

In Fig. 2, we present the x-ray diffraction (XRD) profiles depicting the structural characteristics of the CoPt nanopowder sample after undergoing a thermal treatment at 800 ºC in air atmosphere for a duration of 3 hours. As a result of subjecting the specimen material to high-temperature heat treatment, the peaks undergo sharpening, while the intensity experiences a noticeable increase owing to the enlarged growth of particles. In XRD peaks (1 1 0), (1 1 1), (2 0 0), (0 0 2), (2 0 1), (1 1 2), (2 2 0), (2 0 2) and (2 2 1) planes indicate the formation of FCT crystalline structured CoPt (space group P4/mmm) [1], in which (1 1 0), (1 1 1), (2 0 0) and (0 0 2) planes confirm the $L1_0$ ordered state [1, 4]. A negligible impurity peak is observed for Co_3O_4 which is antiferromagnetic in nature [5].

The dimensions of the tetragonal lattice can be determined through x-ray diffraction (XRD) data analysis, employing the equation provided in reference [1]:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Where, d_{hkl} denotes the interplaner spacing of the crystalline structure. The experimental lattice constants obtained from the XRD peaks are: a = 3.843 Å and c = 3.754 Å, these values are higher than the values obtained by other researchers [1-4]. This is because we synthesized CoPt NPs in air ambient instead of any gas medium. The c/a tetragonality ratio stands at 0.976, just a tad greater than 0.973 as reported in previously published literature [1, 3]. The order parameter, denoted as S, for the $L1_0$ FCT CoPt NPs can be determined using the equation provided in [2]:

$$\mathrm{S} = \frac{1 - (\mathrm{c/a})}{1 - (\mathrm{c/a})_{\mathrm{th}}}$$

In the equation provided, (c/a) represents the observed value of the CoPt NPs sample under study, while $(c/a)_{th}$ stands for the theoretical value expected for fully ordered CoPt NPs, which is 0.972 as cited [1]. The order parameter of the investigated CoPt NPs registers at 0.888, slightly lower than the 0.929 reported by Y. Wang *et al.* [2]. This diminution in value is attributed to the oxygen content within the CoPt crystalline nanopowder. Nevertheless, this value aligns closely with the theoretical calculation proposed by S. Karoui *et al.* [6].

Lattice parameters can also be calculated from selected area electron diffraction (SAED) patterns (Fig. 3(b)) using the *ImageJ* software. The SAED pattern exhibits diffraction rings corresponding to crystallographic planes indexed as (0 0 1), (1 1 0), (1 1 1), (2 0 0), (2 0 1), (1 1 2), (2 2 0), and (2 2 1), providing compelling evidence for the emergence of the $L1_0$ ordered FCT phase of CoPt [1]. The measured values of cell constants from SAED patterns are a= 3.822 Å and c= 3.741 Å, consistent with the experimental value obtained from XRD data. Table 1 presents the calculated values of the structural parameters.

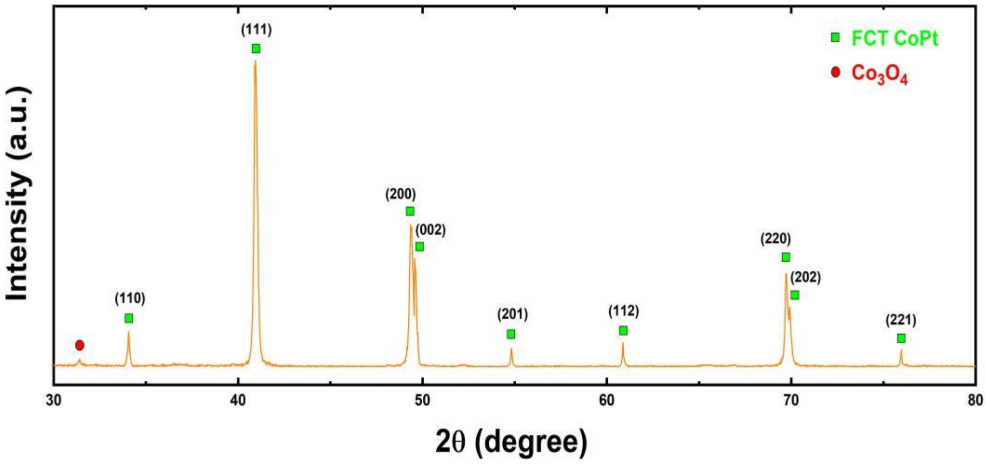

Fig. 2. The powder x-ray diffraction (XRD) pattern obtained from the CoPt nanoparticles sample following annealing at 800 ºC in ambient air environment.

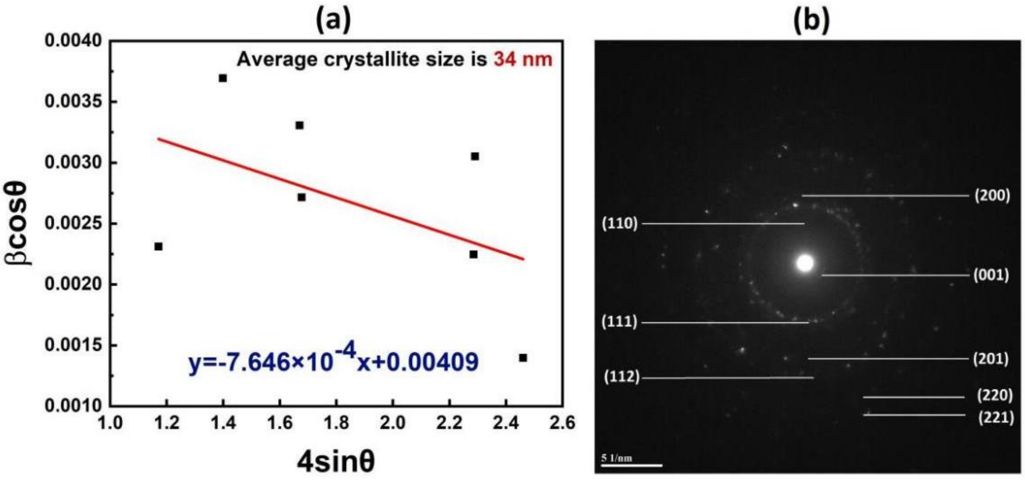

Fig. 3. (a) W-H plot and (b) SAED pattern of CoPt NPs annealed at 800 ºC for 3 hours in air.

The annealed CoPt nanoparticles were analyzed for their average crystallite size via the Williamson-Hall plot derived from x-ray diffraction peaks (Fig. 3(a)). The resultant calculation yielded a size of 34 nm.

Table 1. Structural parameters of $L1_0$ ordered FCT structured CoPt NPs.

Lattice constants (Å)				**Order parameter**	***c/a* value**	**Average particle size (nm)**	**Annealing medium**	**Remarks**
From XRD		**From SAED**						
a	***c***	***a***	***c***					
3.843	3.754	3.822	3.741	0.888	0.976 0.978*	40.0	Air	Present work
3.798	3.694	-	-	0.964	0.973	18.0	H_2	[1]$^{expt.}$
3.789	3.692	-	-	0.929	0.974	11.6	Ar	[2]$^{expt.}$
3.797	3.694	-	-	0.964	0.973	18.3	Ar	[3]$^{expt.}$
3.810	3.720	-	-	0.888	0.976	-	-	[6]$^{theor.}$

*Calculated from SAED analysis

3.2 Vibrational property

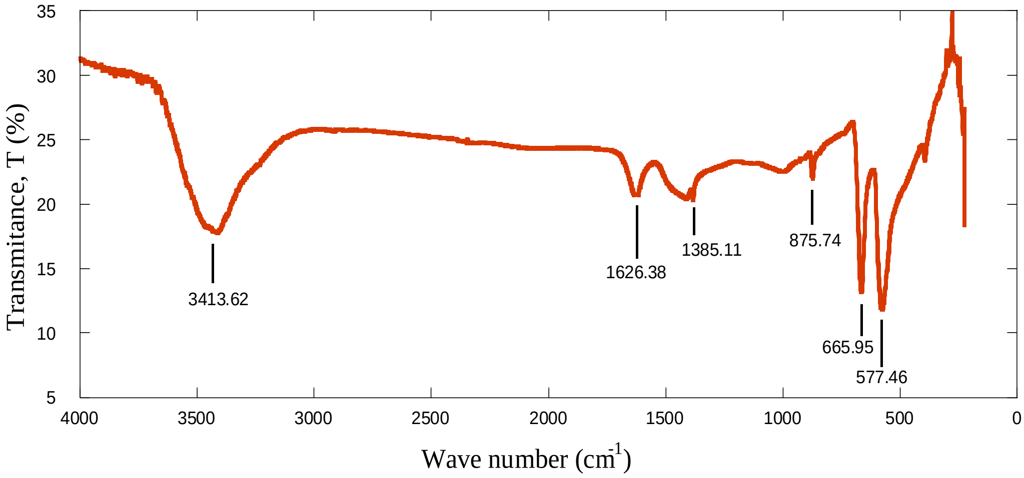

Fig. 4. FTIR spectra of the studied CoPt NPs specimen.

The analyzed nanoparticles demonstrated molecular bonds, which were confirmed through FTIR spectroscopy with remarkable precision, detecting the presence of functional groups along with their associated molecular vibrations. Figure 4 depicts the FTIR spectra captured within the 225-4000 cm^{-1} range, depicting the molecular interactions in a CoPt nanopowder sample annealed at 800 ºC under atmospheric conditions. The intense peak at 577.46 cm^{-1} in the FTIR spectra is attributed to the metal oxide vibration such as Co-O (stretching) vibration [7]. The intense peak at 665.95 cm^{-1} indicates the metal oxide vibration such as and Pt-O (stretching) vibration [8]. The peak at 1626.38 cm^{-1} represents the N-H bonding vibration. The peak 1385.11 cm^{-1} is due to bending vibration of C-H group. The peak 875.74 cm^{-1} shows the N-H stretching vibration. The absence of peaks from 1700 to 3100 cm^{-1} indicates CoPt alloy formation. The peak 3413.62 cm^{-1} is due to the stretching and bending vibration of O-H group which is an indication of the presence of moisture in the molecule.

3.3 Morphology

Figure 5 shows the TEM images and the EDS spectra of as-prepared and annealed NPs. Particle size was measured using *ImageJ* software. From the TEM image of the as-synthesized CoPt nano-powder sample (Fig. 5 (a)), the average particle size is found about 67 nm and the particle size after annealing at 800 ºC in air atmosphere is 40 nm (Fig. 5 (b)). That means the nanoparticle size is decreased after annealing due to the reduction of oxygen in CoPt NPs. During annealing at 800 ºC, the removal of oxygen from the CoPt nanoparticles occurs due to the high temperature and the reactivity of the oxygen with the nanoparticle surface. This process is more pronounced during annealing compared to the as-synthesized nanoparticles because the elevated temperature facilitates the diffusion of oxygen atoms out of the nanoparticle structure, leading to a reduction in oxygen content. Specifically, at this elevated temperature, more metal-oxygen bonds break, allowing oxygen atoms to diffuse to the surface and escape into the air. Additionally, high temperatures enhance atomic mobility and stabilize metallic phases of the alloy that incorporate less oxygen. These processes collectively result in a significant reduction of oxygen content in the annealed CoPt nanoparticles. The average particle size observed in this study is larger than those reported by Y. Wang *et al.* [2] and Y. Liu *et al.* [3]. This increase in nanoparticle size is attributed to the presence of oxygen in the CoPt.

The EDS spectra of the as-synthesized and annealed CoPt NPs samples in the Fig. 5(a) and 5(b), respectively, show the existence of Co, Pt and O. The indexed peaks correspond to those of Co, Pt, O, C and Cu and no magnetic impurity is detected in the sample. The C and Cu peaks are originated from the copper grid of TEM [2]. Analysis indicates that the atomic ratio of Co:Pt:O in the as-prepared NPs is 13.21:11.41:75.38 and the atomic ratio of Co:Pt:O in the annealed NPs is 33.09:37.13:29.78. The EDS spectra analyses verified that air medium annealing of the experimental nanopowdered sample resulted in a reduction in the number of oxygen atoms.

3.4 Magnetic property

In Fig. 6, we observe the magnetic hysteresis loop (M-H curve) of CoPt nanoparticles, which were subjected to annealing at 800 °C for 3 hours in air ambient environment. This plot illustrates the characteristic ferromagnetic behavior of the studied material at room temperature (T= 300 K). It is worth noting that the magnetic attributes of nanoparticles are intricately linked with their microstructural features. Consequently, the incorporation of oxygen during the annealing process in the ambient air significantly impacts the magnetic properties of $L1_0$ ordered FCT structured CoPt NPs. The calculated magnetic coercivity value from M-H loop is $H_c = 204$ Oe and the squareness ratio at 300 K is 0.26. The squareness ratio is lesser compared to Y. Wang *et al.* (0.54) [2].

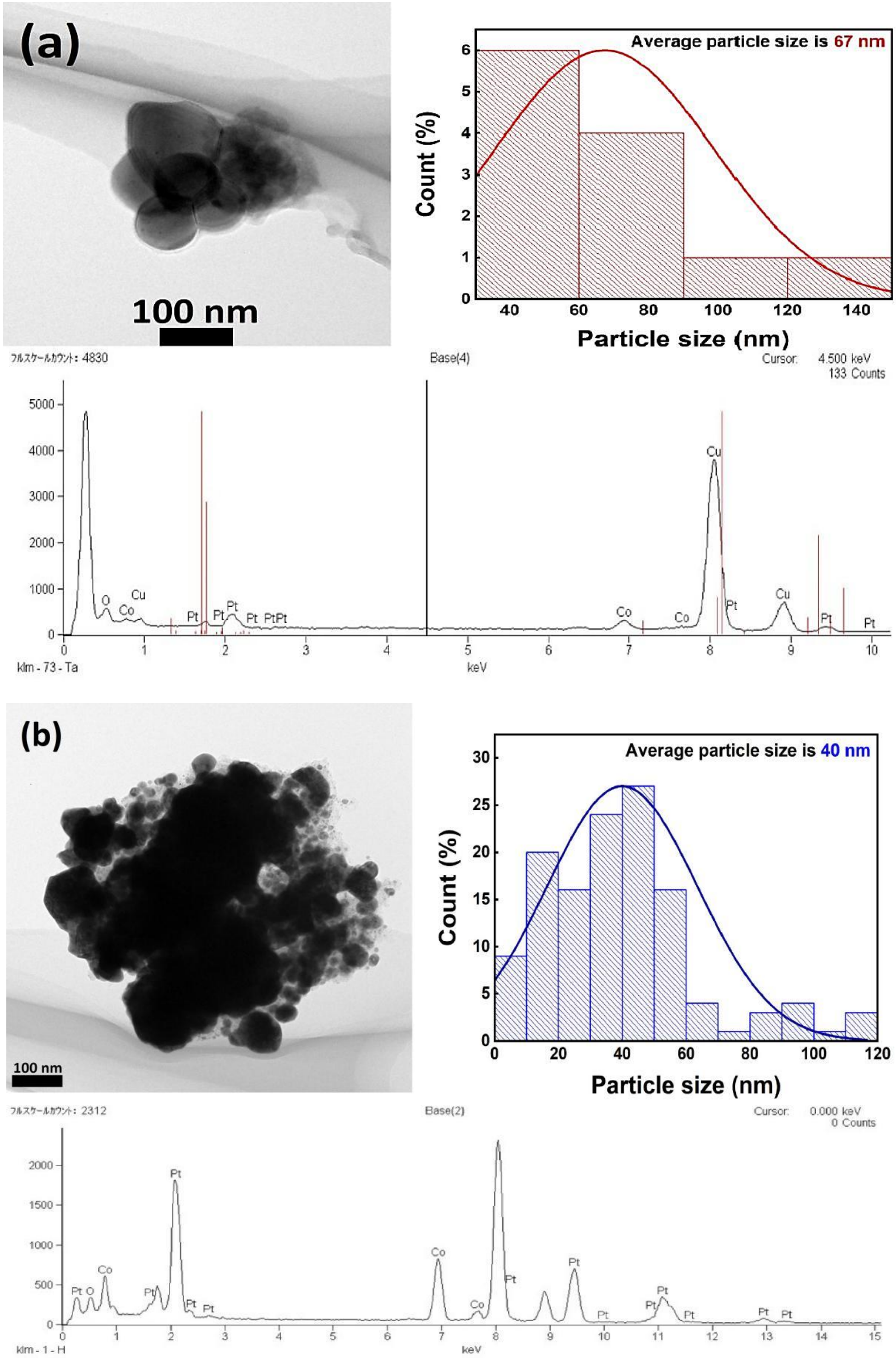

Fig. 5. TEM images and EDS spectra of the (a) as-prepared and (b) annealed CoPt NPs.

The magnetic coercivity value is notably lower when juxtaposed with the findings of Y. Liu et al. [3] and M. Mandal et al. [4]. This discrepancy arises from the decreased order parameter (0.888) and heightened tetragonality ratio (0.976) observed in the annealed NPs sample, distinguishing it from the outcomes reported in earlier publications [1-3]. The low coercivity value indicates the soft ferromagnetic nature of the NPs. All the calculated magnetic parameters are listed in Table 2. The potential utilization of these soft ferromagnetic NPs in diverse soft magnetic device applications holds great promise.

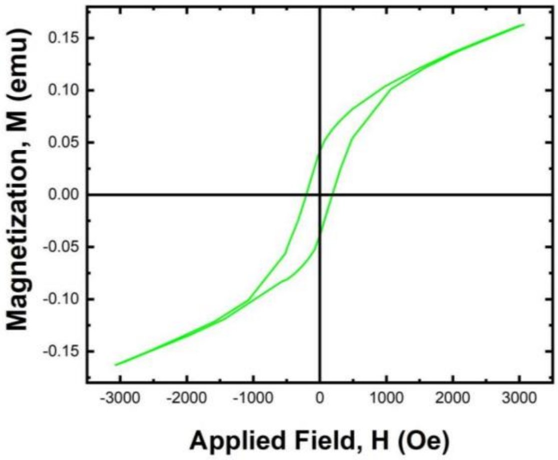

Fig. 6. Magnetization curve (M-H loop) of CoPt NPs showing coercivity at 300K.

Table 2. Magnetic parameters of L1$_0$ ordered FCT structured CoPt NPs.

Compound	Coercivity, H_c (Oe)	Squareness ratio	Annealing medium	Remarks
CoPt	204	0.26	Air	Present work
	1800	0.45	H_2	[1]$^{expt.}$
	5910	0.54	Ar	[2]$^{expt.}$
	3200	-	Ar	[3]$^{expt.}$

4. CONCLUSIONS

CoPt magnetic NPs have successfully been synthesized in low-cost air ambient using a citrate assisted inexpensive sol-gel route from metal chloride precursors. The structural analyses from XRD peaks and SAED patterns confirmed the formation of FCT structured and L1$_0$ ordered CoPt NPs. The average crystallite size is 34 nm. The coercivity value from room temperature magnetization curve of 40 nm sized NPs is 204 Oe, revealed the soft ferromagnetic nature. The order parameter and squareness ratio are small in value due to the effect of oxygen in crystalline nanopowder. These soft ferromagnetic nano-sized CoPt particles synthesized through easy and low-cost way can be suitably applied in magnetic heads and shields, magnetic sensors, biomedical technology and other soft magnetic devices.

ACKNOWLEDGEMENTS

There was no significant financial support for this research. The authors are thankful to the Materials Science Division, Atomic Energy Center, Dhaka-1000, Bangladesh for providing some experimental facilities.

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