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Structure and Magnetic Studies of Cobalt Nanoparticles Prepared by Modified Polyol Process

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Abstract - Cobalt nanoparticles were prepared by following the modified polyol process. The reduction of cobalt salt was carried out using hydrazine hydrate. The x-ray diffraction pattern of the as prepared cobalt sample revealed amorphous nature and annealed particles exhibited crystallinity. Crystallite sizes were determined using Debye Scherrer equation. Surface morphology has been investigated using Scanning Electron Microscopy (SEM). Average particle size estimated from SEM image was 32 nm. Magnetic properties of the as prepared particles were studied at 10K and 300K in a SQUID magnetometer. A slight decrease in saturation magnetization and appreciable decrease in coercive field has been noted as the temperature was increased from 10K to 300K. These results were discussed in view of existing literature.

Keywords— *Cobalt, nanoparticles, XRD, SQUID, magnetization*

I. INTRODUCTION

Nanosized ferromagnetic metal particles have been of great interest due to their useful electrical, optical, magnetic and mechanical properties that are mainly due to the large surface area which differentiates them from their bulk form [1]. Ferromagnetic metal nanoparticles are used in solar energy absorption and magnetic recording [2]. Particularly, the cobalt has been of special interest because of its high saturation magnetization and Curie temperature. Cobalt is also known for the allotropic forms of Hexagonal Close Packed (HCP), Face Centered Cubic (FCC), Epsilon (ε) and Body Centered Cubic (BCC) [3, 4]. Different methods have been used by the researchers to synthesize cobalt nanoparticles such as hydrothermal reduction, sodium borohydride reduction, solvothermal chemical process, high temperature thermal decomposition, vapour deposition and polyol reduction method [5-10]. Cobalt nanoparticles prepared by a facile $NaBH_4$ reduction method at room temperature showed best adsorption ability for Congo red in the waste water treatment [11]. Nano sized colloidal cobalt studied for the electrochemical potentials [12]. The liquid phase reduction method produced cobalt particles have been shown to be a potential candidate for microwave absorption applications [13]. To our knowledge, the cobalt particles prepared by modified polyol method have not been explored much for magnetic properties. Polyol process is very simple, cost effective and requires less technical apparatus.

The present work involves synthesis of cobalt nanoparticles by modified polyol process in the temperature range from 328K to 333K. The structural investigations were carried out by XRD and SEM techniques. Magnetic properties were studied using sophisticated SQUID magnetometer at low and room temperatures. Paper has been written into four distinct sections, Introduction, Materials and methods, Results and discussion and conclusions. Introduction section contains a brief review of literature survey related to the present work , motivation and scope of the work. The section on materials and methods contains sample preparation and measurements techniques. Results and discussion section deals with the results, analysis and discussion. Conclusion part narrates the major conclusions drawn from the results.

II. MATERIALS AND METHODS

AR grade sd-fine make Cobaltous chloride hexahydrate ($CoCl_2$. $6H_20$), Sodium hydroxide (NaOH), Hydrazine hydrate (N_2H_4. H_2O) 80%, 1, 2 Propandiol, acetone and double distilled water were used to prepare cobalt particles.

Cobaltous chloride hexahydrate of 3.5 g was dissolved in 60 ml of 1, Propandiol at 328K. Sodium hydroxide of 9.6 g was dissolved in 1, 2 Propandiol at 328K. The two solutions were prepared separately with magnetic stirred for 30 minutes. Then, the Sodium hydroxide solution was added to the cobaltous chloride solution. After 15 minutes of stirring, 11 ml of Hydrazine hydrate was added drop wise. Reduction was allowed to proceed for an hour in the temperature range from 328K to 333K and then the reaction was cooled to room temperature. The dark grey colour cobalt particles were collected and washed with double distilled water and acetone several times [14]. Finally powder was dried in an electric oven.

The sample so prepared was XRD studied in a X-ray powder diffractometer (model D2 PHASER). Surface morphology of the sample was probed by the Scanning Electron Microscopy (model JSM 6360). The magnetic study was performed in a SQUID magnetometer (EC MPMS XL) at 10K and 300K.

III. RESULTS AND DISCUSSION

i) *XRD*: A trace of X-ray diffractogram of the present cobalt powder is shown in the Figure 1. In the figure, we see no peaks even up to 90° of 2θ. Absence of characteristic diffraction peaks suggests that as prepared Cobalt sample is amorphous in nature. Cobalt nanoparticles synthesized using $NaBH_4$ as reducing reagent were reported to have shown amorphous nature [11, 15, 16]. Cobalt nanoparticles prepared at temperature near boiling point of the solvent by polyol method have shown HCP and FCC crystal structures [10, 16, 17]. The amorphous nature of the present cobalt powder may be attributed to the preparation temperature and the concentration of the reducing agent used.

A part of as prepared cobalt sample was annealed at 773 K and the XRD characterization was done again. XRD pattern of this annealed sample is shown in Figure 2. The peaks found at 2θ values are matching with HCP and FCC structure. But intensity of FCC peaks is very weak compared to HCP peaks. Cobalt oxide peaks are also seen in the pattern [18]. Crystallinity of the annealed powder has been reported earlier in [15, 16]. Cobalt FCC structure was preferred thermodynamically above 723K [3, 4]. In the present case we found coexistence of the FCC and HCP phases at 773K. The existence of the HCP along with FCC structure after annealing at 873K was observed in [3]. Annealing the sample still at higher temperature may lead to FCC structure. Using Debye-Scherrer formula, average crystallite sizes were estimated to be 28 nm for HCP phase and 10 nm for FCC phase.

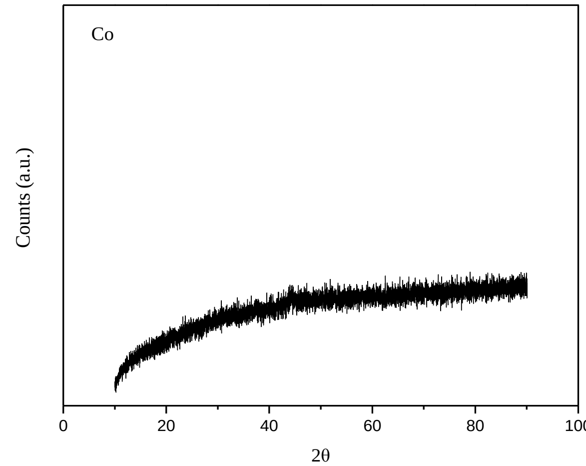


Figure 1. X-ray diffraction of as prepared cobalt powder

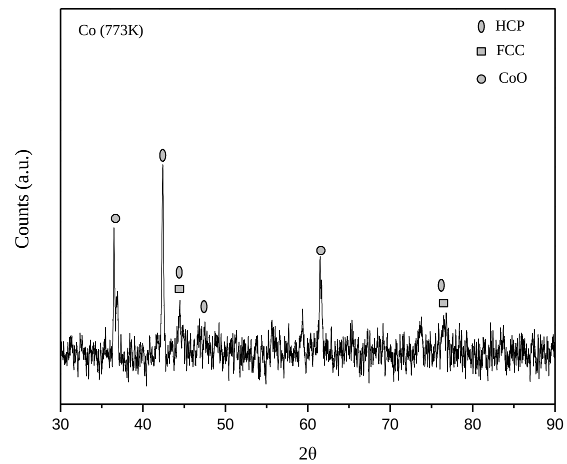


Figure 2. XRD pattern of Cobalt powder annealed at 773 K

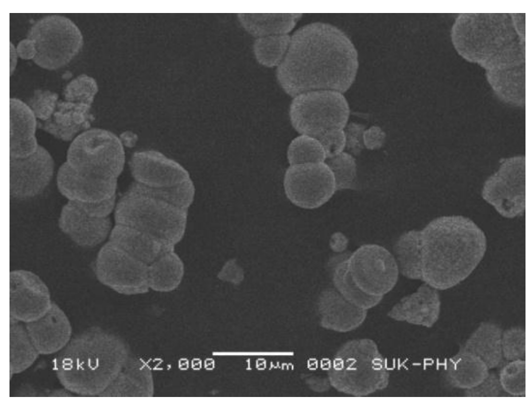
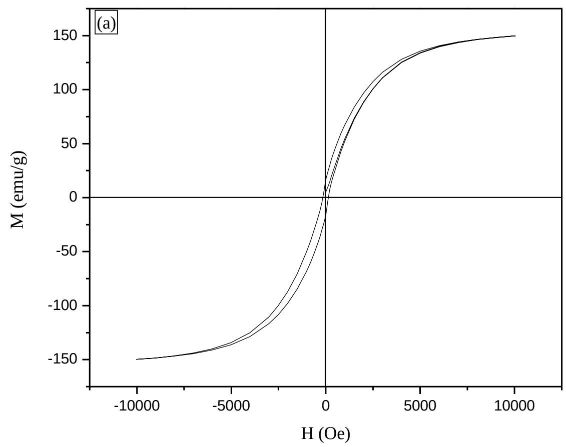


Figure 3. SEM image of as prepared Cobalt powder

ii) *SEM*: Figure 3. shows the Scanning electron Microscopy image of as prepared cobalt sample. Heavy agglomeration of the particles taking globular shape is noticeable in the figure. Average particle size calculated from SEM image is 32 nm.



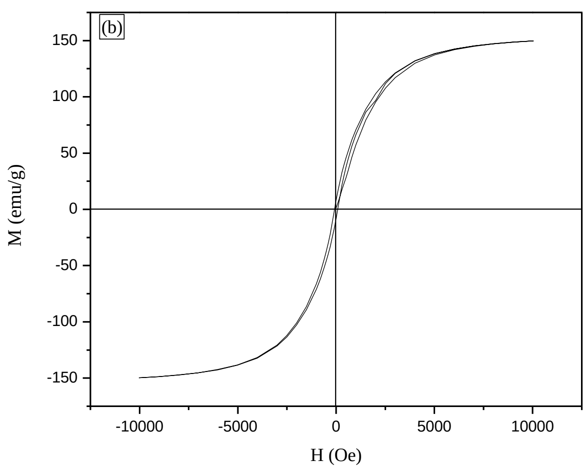


Figure 4. Hysteresis loops of as prepared cobalt powder at (a) 10K and (b) 300K.

iii) *Magnetic properties*: The magnetic properties of the as prepared cobalt particles have been investigated at two different temperatures in a Superconducting Quantum Interference Device (SQUID) magnetometer. Hysteresis loops recorded at 10K and 300K are shown in Figure 4(a) and 4(b) respectively. These loops reveal perfect ferromagnetism of the particles. Magnetic parameters obtained from the loops are tabulated in Table 1. A slight decrease in M_s value was noted when the temperature increased from sizable 10K to 300K. But fall in M_s compared to bulk cobalt material (M_s=168 emug^{-1}) can be observed. The decrease in saturation magnetization can be attributed to the smaller particle size, high surface energy and possible partial surface oxidation of the cobalt nanoparticles [17]. The coercive field H_c of the sample is decreased remarkably from 149.908 Oe to 82.932 Oe on increasing the temperature from 10K to 300K. However, the H_c value observed at 300K is much higher than that measured for bulk sample (H_c = 10 Oe) [11]. Enhanced coercive field is in agreement with reports for ultrafine ferromagnetic material [3, 11, 17, 19]. Remnant magnetization also decreased from 17.339 emug^{-1} to 8.119 emug^{-1} when the temperature was increased from 10K to 300K.

Table1: Magnetic parameters of the as prepared Cobalt particles.

Temperature (K)	**Saturation magnetization (M_s) in emug^{-1}**	**Remnant magnetization (M_r) in emug^{-1}**	**Coercive field (H_c) in Oe**	**M_r/M_s**
10	149.942	17.339	149.908	0.116
300	149.542	8.119	82.932	0.054

IV. CONCLUSIONS

Cobalt nanoparticles were prepared by modified polyol process. Absence of characteristic peaks in the XRD pattern confirmed amorphous nature of the as prepared cobalt nanoparticles. These particles exhibited crystallinity upon annealing at 773K. The globular shapes were seen in SEM image, which were the result of strong agglomeration of the particles. Magnetic properties were studied for as prepared sample at two different temperatures. Saturation magnetization decreased slightly and Coercive field decreased appreciably on increasing the temperature from 10K to 300K. From this it is learnt that cobalt particles become magnetically soft as the temperature is increased. Based on this we propose these nanoparticles for magnetic recording media.

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REFERENCES

[1]. D. Hongzhen, L. Xiangyang, L. Guanpeng, X. Lei, L. Fengsheng, *"Synthesis of Co Nanoparticles and Their Catalytic Effect on the Decomposition of Ammonium Perchlorate"*, Chinese Journal of Chemical Engineering, Vol.16, Issue. 2, pp.325-328, 2008.

[2]. F. Guo, H. Zheng, Z. Yang, Y. Qian, *"Synthesis Of Cobalt Nanoparticles In Ethanol Hydrazine Alkaline System (EHAS) At Room Temperature"*, Materials Letters, Vol.56, pp.906–909, 2002.

[3]. S. L. Wen, Y. Liu, X. C. Zhao, *"Effect Of Annealing On Electromagnetic Performance And Microwave Absorption Of Spherical Cobalt Particles"*, Journal of Physics D: Applied Physics, 48: 405001. doi:10.1088/0022-3727/48/40/405001. 2015.

[4]. S. Hui, M. Wu, S. Ge, D. Yan, Y. D. Zhang, T.D. Xiao, M. J. Yacaman, M. Miki-Yoshida, W. A. Hines, J. I. Budnick, *"Synthesis and Characterization of Structure Controlled Nano-cobalt Particles"*, Mat. Res. Soc. Symp. Proc. 755, 2003.

[5]. B. Q. Xie, Y. T. Qian, S. Y. Zhang, S. Q. Fu, W. C. Yu, *"A Hydrothermal Reduction Route to Single-Crys- talline*

Hexagonal Cobalt Nanowires", European Journal of Inorganic Chemistry, Vol.12, Issue.2, pp.2454- 2459, 2006.
[6]. G. N. Glavee, K. J. Klabunde, C. M. Sorensen, G. C. Hadjipanayis, *"Sodium Borohydride Reduction of Cobalt Ions in Nonaqueous Media. Formation of ultrafine Particles (Nanoscale) of Cobalt Metal"*, Inorganic Chemistry, Vol.32, issue.4, pp.474-477, 1993.
[7]. K. Gandha, K. Elkins, N. Poudyal, X. Liu, J. P. Liu, *"High Energy Product Developed from Cobalt Nanowires"*, Scientific Reports, 4: 5345. doi: 10.1038/srep05345, 2014.
[8]. H. T. Yang, Y. K. Su, C. M. Shen, T. Z. Yang, H. J. Gao, *"Synthesis And Magnetic Properties Of e-Cobalt Nanoparticles"*, Surface and Interface Analysis, Vol.36, pp.155-160, 2004.
[9]. S. Gangopadhyay, G. C. Hadjipanayis, C. M. Sorensen, K. J. Klabunde, *"Magnetic Properties of Ultrafine Co Particles"*, IEEE Transactions on Magnetics, Vol.28, Isuue.5, pp.3174-3176, 1992.
[10]. L. Biao, G. Jian-guo, W. Qi, Z. Qing-jie, *"Preparation of Nanometer Cobalt Particles by Polyol Reduction Process and Mechanism Research"*, Materials Transactions, Vol.46, issue.8, pp.1865-1867, 2005.
[11]. X. Liang, L. Zhao, *"Room-Temperature Synthesis of Air-Stable Cobalt Nanoparticles And Their Highly Efficient Adsorption Ability For Congo Red"*, RSC Advances, Vol.2, pp.5485–5487, 2012.
[12]. B. G. Ershov, N. L. Sukhov, E. Janata, *"Formation, Absorption Spectrum, and Chemical Reactions of Nanosized Colloidal Cobalt in Aqueous Solution"*. J. Phys.Chem. B Vol.104, pp.6138-6142, 2000.
[13]. S. Wen, X. Zhao, Y. Liu, J. Cheng, H. Li, *"Synthesis of Hierarchical Sword-Like Cobalt Particles and Their Microwave Absorption Properties"*, RSC Adv, Vol.4, pp.40456–40463, 2014.
[14]. T. G. Altınçekiç, I. Boz, A. C. Basaran, B. Aktas, S. Kazan, *"Synthesis and Characterization of Ferromagnetic Nickel Nanoparticles"*, J Supercond Nov Magn. doi.10.1007/s10948-011-1261-y, 2011.
[15]. Y. W. Zhao, R. K. Zheng, X. X. Zhang, J. Q. Xiao, *"A Simple Method to Prepare Uniform Co Nanoparticles"*, IEEE Transactions on Magnetics, Vol.39, Issue.5, pp.2764-2766, 2003.
[16]. M. G. Montiel, P. Santiago-Jacinto, J. A. I. D. G´ongora, E. Reguera, G. Rodr´ıguez-Gattorno, *"Synthesis and Thermal Behavior of Metallic Cobalt Micro and Nanostructures"*. Nano-Micro Letters, Vol.3, Issue.1, pp.12-19, 2011.
[17]. S. S. K. Kamal, P.K. Sahoo, M. Premkumar, N. V. R. Rao, T. J. Kumar, B. Sreedhar, A. K. Singh, S. Ram, K. Chandra Sekhar, *"Synthesis Of Cobalt Nanoparticles By A Modified Polyol Process Using Cobalt Hydrazine Complex"*, Journal of Alloys and Compounds, Vol.474, pp.214–218, 2009.
[18]. M. Th. Makhlouf, B. M. Abu-Zied, T. H. Mansoure, *"Direct Fabrication of Cobalt Oxide Nanoparticles Employing Sucrose as a Combustion Fuel*", Journal of nanoparticles, doi: 10.1155/2013/384350.
[19]. Y. Zhang, Q. Yao, Y. Zhang, T. Cui, D. Li, W. Liu, W. Lawrence, Z. Zhang, *"Solvothermal Synthesis of Magnetic Chains Self-Assembled by Flowerlike Cobalt Submicrospheres"*, Crystal Growth & Design, Vol.8, Issue.9, pp.3206-3212, 2008.

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Ms. G. Chandraprabha has pursed M.Sc and M.Phil from Gulbarga University Currently she is pursuing Ph.D. Physic (Condensed Matter Physics) in the Department of Physics, Gulbarga University. Because of her merit and research ability she has been awarded UGC-BSR fellowship for her PhD studies. She has also taught Physics for few years for Engineering and B.Sc students in different colleges. She is four years into the PhD programme and will commence shortly to write her Ph.D thesis for submission to the University.

Mr. T.Sankarappa has completed M.Sc and M.Phil degrees in physics from the Gulbarga University. He acquired Ph.D in Physics from the famous H.H.Wills Physics laboratory, University of Bristol, United Kingdom. For his Ph.D studies he was awarded Government of India's National overseas Scholarship. For his PhD degree he worked on 'Quantum oscillations in a superconductor'. These experimental studies were conducted using high intense magnetic fields of the order of 20 Teslas and ultra low temperature down to few milli-Kelvins. He has been working (Lecturer, Reader and Professor) with Department of Physics, Gulbarga University for 27 years. He is 9 years into the Professor Cadre. He has vast experience of research in variety of fields both theoretical and experimental, such as Magnetohydrodynamics, Low Temperature Physics, Supercondutivity, Oxide glasses, Conducting polymers, Solid thin films etc. He has more than 80 research publications to his credit and has successfully executed research projects (DST and UGC) of worth more 1.3 crores of INR.

Mrs.T.Sujatha has completed her B.Sc from Gulbarga university. She acquire M.Sc Physics degree from Kuvempu University in the Distance mode and secured first rank to the University. She pursed Ph.D (Physics) studies in Gulbarga university and obtained the degree in 2016. Her Ph.D thesis was related to electrical studies on oxide glasses. She has more than 25 research papers to her credit. She worked for more than 12 years as a teacher for Physics and mathematics for high school students. Presently she is continuing in her teacher job waiting for assignment at higher level institutions.