patnawomenscollege.in/journal

Physics
Explore, 2010, Page No. 09-12
Vol. II No. 2

Low temperature Synthesis, Structural and Magnetic Studies of Rare earth, element La substituted Ba-Hexa ferrite Nanoparticles Via Citrate Precursor Method

Divya Kumari*, Rashmi Thakur*, Girija Gupta , Rakesh Kumar Singh*****
*B.Sc IIIYear (session 2007-10), Department of Physics, Patna Women's College
**Former Prof. & Head, Department of Physics, Patna Women's College, Patna University
***Lecturer, Department of Physics, Patna Women's College, Patna University
Corresponding author, E-mail : rakeshpu@yahoo.co.in

Magnetic nanoparticles of Rare earth element Lanthanum (La) substituted Barium hexaferrite nanoparticles have been synthesized by citrate precursor method using Ferric nitrate, Barium nitrate, Lanthanum nitrate and Citric acid as starting materials. The citrate precursor was annealed at temperature 650°C and 700°C for an hour. The sample was characterized using X-ray diffraction (XRD) and Vibrating sample magnetometer (VSM). Using Scherrer formula, the crystallite size was found to be 51 nm and 89nm at temperatures 650°C and 700°C respectively. The Interplanner distance(d), Coercivity, Retentivity and Magnetization of the nanoparticles were observed to be 2.6394Å, 252 Oe,1.17 emu/g and 3.53 emu/g at temperature 650°C and 2.7005 Å, 1389 Oe, 0.50 emu/g and 0.976 emu/g at temperature 700°C respectively . Insertion of La in hexa ferrite shows apperence of some additional phases.

Key Words : *Ba-hexa ferrite, Lanthanum, Nanoparticles, Citrate Precursor Method.*

Introduction : Ferrites are among the most widely used engineering materials for a broad category of technological applications in electronics industry. Ferrites first attracted attention as non-matallic ferromagnetic materials for applications at frequencies where eddy currents have undesirable consequences in the usual metallic materials (Sugemoto M., 1999). The electromagnetic properties of ferrites are affected by operating conditions such as field strength, temperature and frequency. Generally ferrites have low Curie temperature and their magnetization fluctuates in the UHF range according to temperature variations. Hence, magnetic losses, power dissipations and thermal stability in ferrites need particular attention. Ferrites include a wide range of materials with various crystal structures and composition . There are various kinds of ferrites, such as Spinel ferrites, Magnetoplumbite, Ortho ferrites, Garnet (Kojima H., 1982 and Smit J. and Wijn J.P.H., 1959) etc. Barium hexa ferrite is an example of M-type hard ferrite which has a variety of applications for permanent magnets, microwave devices and high-density perpendicular magnetic recording media (S. Chikazumi, 1997). Substitution of Rare earth element in ferrite produces changes in structural and magnetic behavior (Panda, N.R. et. al., 2003).

Materials and Method: Experimental Procedure

Samples of nanometer-sized La substituted Barium hexaferrite powder ($BaFe_{11.99}La_{0.01}O_{19}$) were prepared by using citrate precursor method. Ferric nitrate, Barium nitrate and Lathanum nitrate (purity = 99%) were taken in Stoichiometric proportions as starting materials. Aqueous solutions of these salts were prepared separately by dissolving the respective salts in a minimal amount of deionized water while stirring constantly. The solutions were then mixed together. Aqueous solution of citric acid was prepared in adequate quantity by weight and was added to the prepared salt solutions. The mixture was heated at temperature between 60°C and 80°C for two hours with continuous stirring. This solution was allowed to cool down to room temperature and was then dried overnight in oven in order to remove excess water and other impurities at temperature ranging 60°C-70°C. This was continued until it formed a brown color fluffy mass. This brown mass was taken as precursor for nanoparticle preparation. The precursor was heated at 650°C and 700°C for one hour in a muffle furnace. By this process, it decomposes to give Barium hexaferrite powder of nanometer size. Substitution of Rare earth element in Ferrite produces changes in structural and magnetic properties (Panda, N.R. et. al., 2003).

Results and Discussions:

The XRD patterns were recorded using a diffrectometer (model D/max-IIB, Rigaku, Tokyo, Japan) and Magnetic measurement were carried out at room temperature using vibrating sample magnetometer (VSM, Lakeshore 7404).

The X-ray diffraction Patterns of above mentioned synthesized samples are shown in fig.1 and fig.2 and their Magnetization curves are shown in fig. 3 and fig. 4.

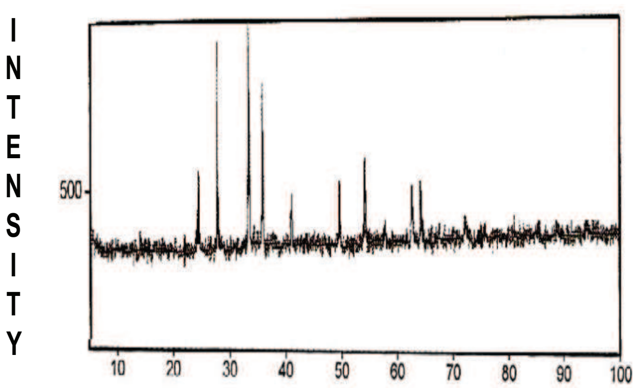

Fig. 1 – X-ray diffraction pattern for $BaFe_{11.99}$ $La_{0.01}O_{19}$ at 650°C

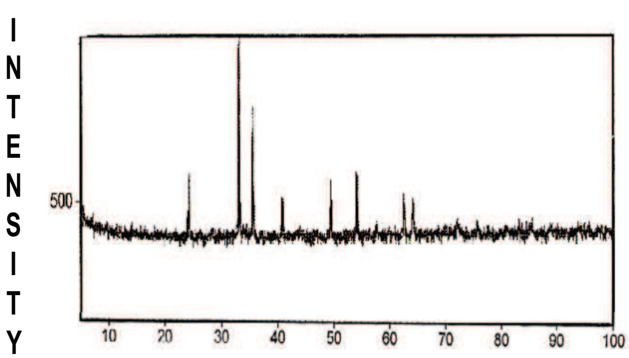

Fig. 2 – X-ray diffraction pattern for $BaFe_{11.99}$ $La_{0.01}O_{19}$ nanoparticle annealed at 700°C

Results from VSM readings Magnetization Studies :

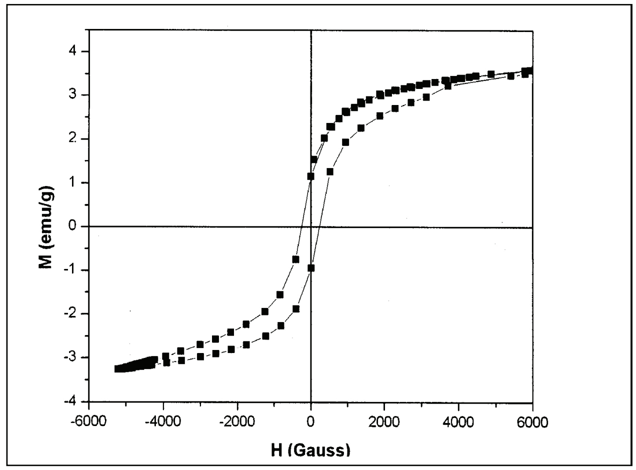

Fig. 3 – Hysteresis curve for $BaFe_{11.99}$ $La_{0.01}O_{19}$ annealed at 650°C.

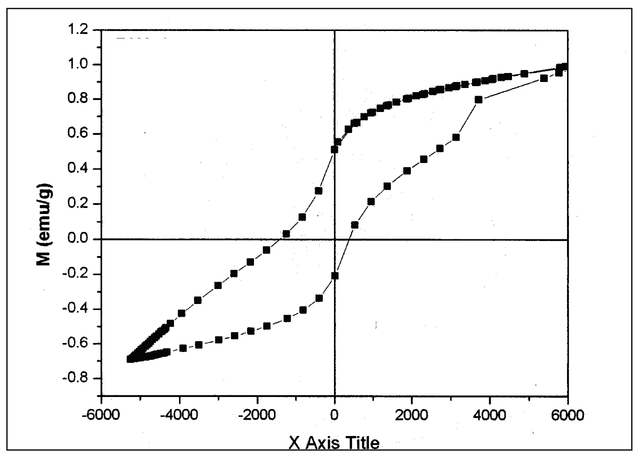

Fig. 4 – Hysteresis curve for $BaFe_{11.99}$ $La_{0.01}O_{19}$ annealed at 700°C.

Table 1: Observed data from XRD and VSM for Ba $La_{0.01}$ $Fe_{11.99}$ O_{19}

Annealing Temperature	Particle Size(nm)	Interplanner distance(d)	Coercivity (Oe)	Retentivity (emu/g)	Magnetization (emu/g)
650°C	51nm	2.6394Å	252 Oe	1.17	3.53
700°C	89 nm	2.7005 Å	1389 Oe	0.5	0.97

The X-ray diffraction pattern shows hexaferrite phase together with some additional peaks (JCPDS diffraction file, Card No.39-1433 and Panda, N.R. et. al., 2003). The crystalline size calculated using Scherrer formula (Culity B.D., 1978 and West, 2009) was found 51nm and 89nm. As the annealing temperature increases from

650°C to700°C, particle size and coercivity increases while retentivity and magnetization decrease. Larger particles have larger coercivity (Table 1). Hysteresis loop of sample annealed at 700°C shows some special magnetic behavior as compared to the sample annealed at 650°C. Further study is needed to understand this phenomenon. This may provide a lot to learn about the intrinsic property. It may be incorporated that a variety of low temperature methods are used the synthesis of hexa ferrite nanomaterials but in all these methods excepting the citrate precursor method, the formation of single-phase hexa ferrite take place at or above 900°C and the particles obtained are of relatively large size (> 50 nm) (Sankar Narayan K.V. et. al., 1996).

Barium hexaferrite nanoparticles formed at 140°C in presence of 0.25T magnetic field exhibited a higher saturation magnetization i.e. 6.1 emu/g at room temperature as compared with 1.1 emu/g obtained for samples prepared in zero magnetic field (Wang Jun, et. al., 2004). The magnetization first decreases as we increase the annealing temperature, reaches a minimum for annealing temperature 690K, and then increases to reach a maximum for annealing temperature 720K, before decreasing again sharply to approach zero (Sankarnarayan et. al., (1993). Annealing effect in air promotes slightly higher H_c value. They assume that different particle morphology, is directly responsible for fluctuations in magnetic parameteric values (Kackzorek and Ninham. W.B., 1994). The value of coercivity increases over six times and reaches a value 445.6 kA/m. This value is typical of chemically coprecipited fine Ba-ferrite powders, where perfect crystal structure assures a defect and stress-free spin arrangement with high magnetocrystalline anisotropy energy. Due to the large bond energy of La^{3+} - O^{2-} as compared to that of Fe^{3+} – O^{2-}, more energy is needed to make La^{3+} ions enter into lattice and form the bond of La^{3+}– O^{2-}. Hence, La^{3+} substituted Ferrites have higher thermal stability relative to without rare earth substituted samples to complete crystallization and grow grain (Said Z.M. et. al., 2007 and Jiang Jing, et. al., 2007). In this work 450°C and 650°C annealing temperature are very low and we observed, increase in the annealing temperature particle size and coercivity increased, while magnetization and retentivity decreases. This is due to anisotropic nature of Ba^{2+} and Ce^{3+} XRD investigations revealed the presence of hexaferrite and the Fe_2O_3 phase of sample annealed at 650°C. This indicates that the formation of hexa ferrite is not complete and some unreacted iron oxide phases were found, probably needs high annealing temperature or longer duration annealing.

Conclusion :

We have used Citrate precursor method to prepare nanosized particles of La substituted Ba- hexa ferrite having crystallite size 51 nm and 89 nm annealed at low temperatures 650°C and 700°C respectively. Largest coercivity and magnetization was observed 1389 Oe, 3.53 emu/g respectively. This hysteresis loop at 700°C is broaden with some characteristic feature. Particle size, Coercivity, Interplanner distance were found to increase with annealing temperature. Insertion of La^{3+}ion in hexa ferrite shows appearance of additional phase and also create stress.

Acknowledgement :

The authors are thankful to Prof. H.C.Verma and his group at I.I.T Kanpur, Dr. Amarendra Narayan, Dept. of Physics, Patna University for constant encouragement.

References :

1. *Culity B.D. (1978). Elements of X-ray diffraction, second edition, Addison-Wiley Pub, pp. 101-102.*

2. *JCPDS diffraction file, completed by the international centre for diffraction data, 1601 Park Lone, Pennsylvania, U.S.A., Card No.39-1433.*

3. *Jiang Jing, Yang Tan-Min, Li Liang-ehao. (2007). Synthesis and magnetic properties of La substituted Li-Ni ferrite via soft chemistry route. Physica, B, Vol. 399, 105-108.*

4. *Kackzorek and Ninham. W.B. (1994). Preparation of high-coercivity fine barium ferrite powder, J. Appl. Phys. 76(40), 6065-6067.*

5. *Kojima H. (1982). Ferro magnetic materials, North-Holend Publishing, Tokyo, Vol. 3, 305-385.*

6. *Panda, N.R. Shih J.C., Chin S.T. (2003). Magnetic properties of nano-crystalline Gd or Pr-substituted $CoFe_2O_4$ synthesized by citrate precursor technique, J. Magn. Mag. Mater, Vol. 257, 75-86.*

7. *Sankar Narayan V.K., Khan C.D., (1993). J. Magn. Mater, Vol 125, 199-203.*

8. *S. Chikazumi. (1997). Physics of ferromagnetism, University press Oxford, pp. 601-613.*

9. *Said Z.M. Hemeda M.D., Kader Abdel S., Rarag Z.G. (2007). Structural, Electrical and Infrared Studies of* $Ni_{0.7}Cd_{0.3}Sm_xFe_{2-x}O_4$ *ferrite, Turk. J. Phys., 41-50.*

10. *Smit J. and Wijn J.P.H. (1959). Ferrites, Physical properties of ferromagnetic oxide in relation to their technical applications, pp. 177-196.*

11. *Sugemoto M. (1999). The Past, Present and Future of Ferrites, J. Am. Ceram-Soc, Vol. 82, No. 82, 269-280.*

12. *Vidyawathi S.S. Amaresh R and Satapathy NL. (2002). Effect of boric acid sintering aid on densification of barium ferrite, Bull. Mater. Science, Vol. 25, No. 6, 569-572.*

13. *Wang Jun, Chen Qianwang, Che shah. (2004). Magnetic properties in* $BaFe_{12}O_{19}$ *nanoparticles prepared under a magnetic field, J. Magn. Mag. Mater, Vol. 280, 281-286.*

14. *West. (2009). Solid state Chemistry, Wiley publishing. pp. 174-175*