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

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Magnetic nanoparticles of Rare earth element Cerium (Ce) substituted Barium hexaferrite nanoparticles have been synthesized by citrate precursor method using Ferric nitrate, Barium nitrate, Cerim nitrate and Citric acid as starting materials. The citrate precursor sample was annealed at temperature 650°C and 700°C for a hour. The sample was characterized using X-ray diffraction (XRD), Vibrating sample magnetometer (VSM). Using Scherrer formula, the crystallite size was found to be 88 nm and 71nm for the samples annealed at 650°C and 700°C respectively. The interplanner distance(d), Coercivity, Retentivity and Magnetization of the nanoparticles were observed to be 2.6995Å, 157 Oe, 0.95 emu/g and 3.73 emu/g at temperature 650°C and 2.6991Å, 716 Oe, 1.16 emu/g and 2.36 emu/g at temperature 700°C respectively . Insertion of ***Ce*** *in hexa ferrite shows apperence of some additional phase and creates stress.*

Key words : *Ba-hexa ferrite, Cerium , Nanoparticles, Citrate Precursor Method.*

Introduction : 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 compositions. 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 Ce substituted Barium hexaferrite powder ($Ba\ Ce_{0.01}Fe_{11.99}O_{19}$) were prepared by using citrate precursor method. Ferric nitrate, Cerium nitrate and Barium 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 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 650°C and 700°C for one hour in a muffle furnace. By this process, it decompose to give Cerium substituted Barium hexaferrite powder of nanometer size.

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.

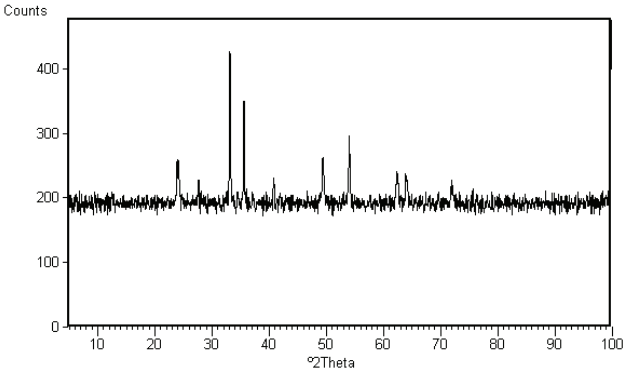

Fig. 1 - X-ray diffraction pattern for $BaCe_{0.01}Fe_{11.99}O_{19}$ observed at 650°C

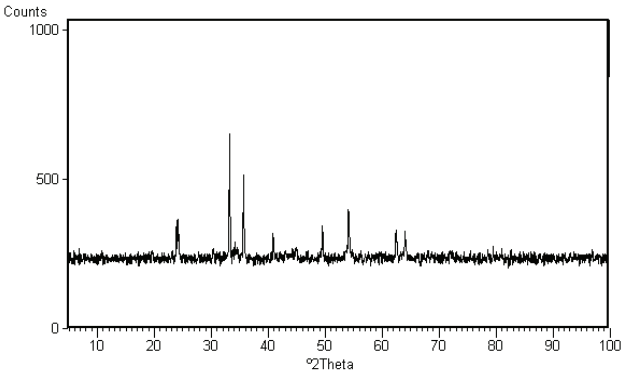

Fig. 2 – X-ray diffraction pattern $BaCe_{0.01}Fe_{11.99}O_{19}$ observed at 700°C

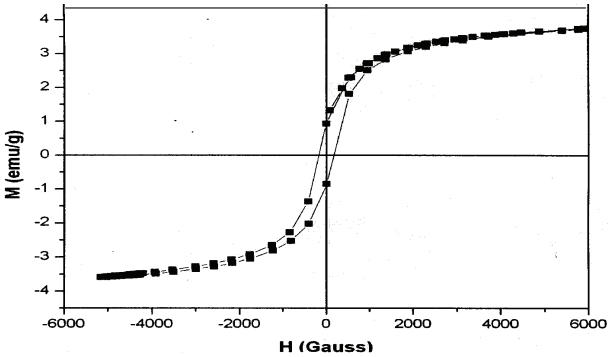

Fig. 3 - Magnetization curve observed at 650°C

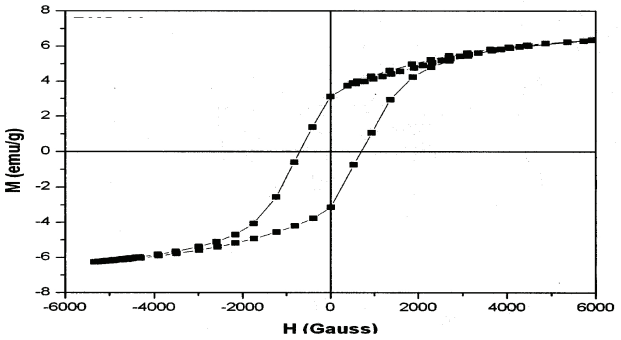

Fig. 4 – Magnetization curve observed at 700°C

Table 1: Data observed from XRD and VSM for $BaCe_{0.01}Fe_{11.99}O_{19}$

Annealing Temperature	Particle Size (nm)	Inter-planner distance (d)	Co-ercivity (Oe)	Reten-tivity (emu/g)	Magne-tization (emu/g)
650°C	88nm	2.6995Å	157 Oe	0.95	3.73
700°C	71 nm	2.6991Å	716 Oe	3.01	6.46

The X-ray diffraction pattern shows hexaferrite together with some additional phase of very small inensity (JCPDS diffraction file, Card No.39-1433 and Vidyawathi S.S. et. al., 2002). The crystalline size calculated using Scherrer formula (Culity B.D., 1978 and West., 2009) was found to be 88nm and 71nm at annealing temperature 650°C and 700°C. This also decreases particle size, interplanner distance(d). Crystallinity and particle size variation with annealing temperature does not show systemic change in other rare earth elements such as Gd, and Pr substituted soft ferrite materials (Panda, N.R. et. al., 2003 and Said Z.M. et. al., 2007). Many researchers have observed the

particle size of rare earth substituted ferrite to decrease with the decrease of annealing temperature. The size of the Ce^{3+}ion is larger than Fe^{3+} ion. In this work, 0.01 mole cerium has been substituted and these structural and magnetic behavior were observed. Ce^{3+}ion creates magnetic anisotropy. Therefore coercivity was found to increase. Additional phase exerts a presser and hence grain growth was not found to increase with increase in annealing temperature. 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.

The magnetic properties were measured with vibrating sample magnetometer (VSM). The coercivity and retentivity increase (157 Oe to 716Oe and 0.95 emu/g to 3.06 emu/g) whereas magnetization increases (3.73 emu/g to 6.46 emu/g) (Table 1). This may be partly due to particle size dependent properties or partly due to rare earth substitution. 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 (Said Z.M. et. al., 2007). Due to the large bond energy of Ce^{3+} - O^{2-} as compared to that of Fe^{3+} – O^{2-}, more energy is needed to make Ce^{3+} ions enter into lattice and form the bond of Ce^{3+}– O^{2-}. Hence, Ce^{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 our work, at annealing temperature 700°C, we have observed 71 nm particles (anneald 700°C) with large area hysteresis loop compared to sample having particle size 88 nm anneald at 650°C. 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).

Conclusion:

We have used Citrate precursor method to prepare nanosized small particles of Ce substituted Ba- hexa ferrite having crystallite size 88 nm and 71nm annealed at temperatures 650°C and 700°C. For this low annealing temperature we obtained a relatively high coercivity of 716 Oe. With increase in annealing temperature only particle size decrease, while retentivity, magnetization and coercivity increase. Due to large size of Cerium ion in comparison to iron ion, some other additional phase was observed. This additional phase prevents the grain growth.

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