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Growth and Characterization of Rare earth elements Ce and La substituted Sn Fe_2O_4 Nanoparticles Via Citrate Precursor Method

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Magnetic nanoparticles of Rare earth element Cerium (Ce) and Lanthanum (La) substituted Sn ferrite nanoparticles have been synthesized by citrate precursor method using Ferric nitrate, Cerium nitrate, Lanthanum nitrate and Citric acid as starting materials. The citrate precursor was annealed at temperature 650°C for an hour. The sample was characterized using X-ray diffraction (XRD), Vibrating sample magnetometer (VSM). Using Scherrer formula, the crystallite size was found to be 63nm and 76nm. The interplanner distance(d), coercivity, retentivity and magnetization of the nanoparticles was observed to be 3.3362Å, 183Oe, 0.31 emu/g and 1.309 emu/g for $SnLa_{0.01}Fe_{1.99}O_4$ and 3.3361 Å, 205 Oe, 0.39 emu/g and 1.386 emu/g for Sn $Ce_{0.01}Fe_{1.99}O_4$ at annealing temperature 650°C . Insertion of La & Ce in Tin ferrite shows apperence of some additional phase and creates some distortion in lattice

Key words : *Sn ferrite, Ce and La, Nanoparticles, Citrate Precursor Method.*

Introduction : Synthesis and study of spinel nanoscale ferrite materials have been intensively persued because of their increasing possibilities in material science and technology. Ferrites are mixed oxides with iron is the main component having the general formula (MO) (Fe_2O_3)where M stands for some divalent metal like Zinc, Cobalt, Nickel, etc. Ferrites have been receiving growing attention because of their various commercial and technological applications (Sugimoto Mitsuo, 1999 and F. Mazaleyrat et al., 2000). The spinel structure of ferrites was first proposed in 1909 by Hilpert and has been investigated since then in quite detail (Hilpert S., 1909, Hilpert S. and Wille A., 1932, Hilpert S. and Lindner A., 1933, Hilpert S. and Schweinhagen R., 1935). Ferrites were prepared in nanocrystalline state for the first time in late eighties (Yoshizawa Y. et. al., 1988). In the nanocrystalline phase, ferrites have exhibited properties that are notably different from their bulk phase properties and are strongly dependent on the conditions and method of preparation (Fresh D.L., 1956 and Chandan Rath, et al., 2000). This dependence has not been adequately investigated and we still lack standardized procedures for obtaining ferrites with desired properties. Thus, it appears relevant to study and understand the behaviour of ferrite samples prepared under varied conditions. There are several routes for preparation of nanocrystalline samples. One technique that has been widely used is by powdering. Ball Mills are normally employed for this. Fine powders have also been obtained using chemical precipitation and annealing. Electrolytic techniques have also been used. Several other methods exist besides these. A review of the different preparation techniques has been given by M. Pal and D. Chakravorty (Pal M. and Chakravorty D., 2003). Each of these techniques has its own advantage and disadvantage. The chemical route has a number of attractive features like simplicity and low cost of preparation so that it becomes an attractive alternative for preparation of nanocrystalline phase ferrite. **We have used chemical based Citrate Precursor method to synthesized La and Ce substituted Tin ferrite Nanoparticles**. Polycrystalline ferrite materials have been attractive for microwave applications, radio frequency circuits, transformer cores, rod antennas, read/ write heads for high speed digital tapes, sensors due to their high resistivity, low magnetic coercivity, low eddy current losses, high Curie temperature and chemical stability etc. (Sugimoto Mitsuo, 1999, F. Mazaleyrat et al., 2000 and Hilpert S. and Lindner A., 1933).

Materials and Methods: Experimental Procedure

Magnetic nanoparticles of Rare earth element Cerium (Ce) and Lanthanum(La) substituted Sn ferrite nanoparticles having formula $SnLa_{0.01}Fe_{1.99}O_4$ and $SnCe_{0.01}Fe_{1.99}O_4$ have been synthesized using the Citrate precursor method. Ferric nitrate Cerium nitrate, Lathanum nitrate and nitrate of divalent metal, Sn (purity 99%) were taken in Stoichiometric proportions as starting materials. Aqueous solutions of these salts were prepared separately by dissolving the salt in minimum 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 about 60°C to 80°C for two hours with continuous stirring. This solution was allowed to cool at room temperature and finally it was dried at 60°C-65°C temperature in an oven until it formed a brown color fluffy mass. The gels were annealed at temperature 650°C for one hour in a muffle furnace. By this process, the precursor thermally decomposed to give ferrite powder that were later proved to be nanometer size particles.

Results and Discussions :

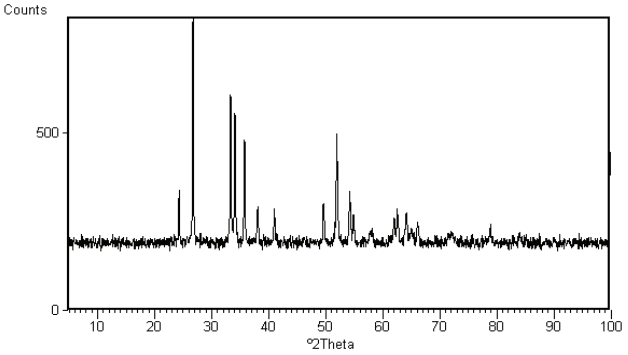

Fig. 1 – X-ray diffraction pattern of $SnFe_{1.99}La_{0.01}O_4$ at 650°C

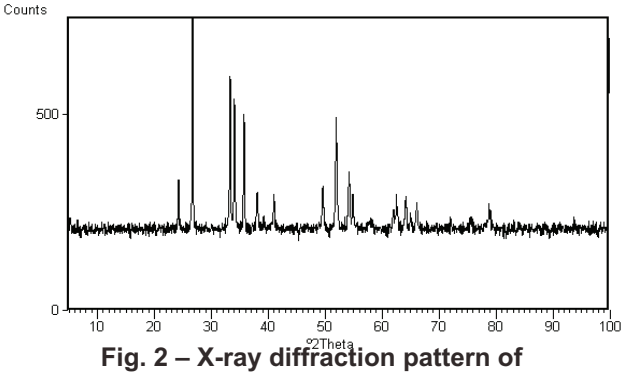

Fig. 2 – X-ray diffraction pattern of $SnFe_{1.99}Ce_{0.01}O_4$ at 650°C

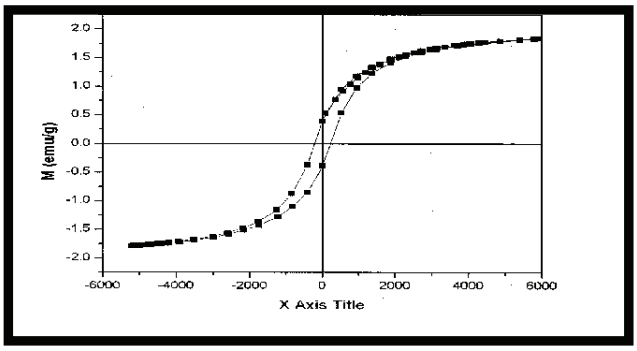

Fig. 3 – Magnetisation curve for sample $SnFe_{1.99}La_{0.01}O_4$ annealed at 650°C

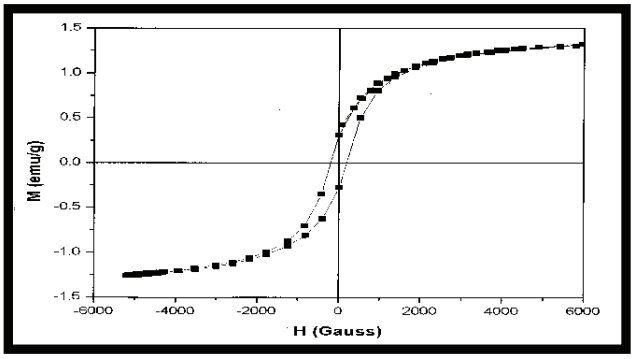

Fig. 4 – Magnetisation curve for sample $SnFe_{1.99}Ce_{0.01}O_4$ annealed at 650°C

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.

Table 1: Data observed from XRD and VSM for $Sn\ La_{0.01}Fe_{1.99}O_4$ and $SnCe_{0.01}Fe_{1.99}O_4$ at annealing Temperature 650°C

Sample	Particle Size (nm)	Inter-planner distance (d)	Co-ercivity (Oe)	Reten-tivity (emu/g)	Magne-tization (emu/g)
$Sn\ La_{0.01}\ Fe_{1.99}\ O_4$	63 nm	3.3362Å	183 Oe	0.31	1.31
$Sn\ Ce_{0.01}\ Fe_{1.99}\ O_4$	76 nm	3.3361Å	205 Oe	0.39	1.39

The average particle size of synthesized samples was found to be 63 nm and 76 nm using Scherrer equation (Culity B.D.,1978 and West., 2009) and samples correspond to spinel structure together with presence of some other phases (Zhoo L. et. al., 2004, Said Z.M., et. al., 2007 and Liu Fangxin, 2004). It was observed that at

the same annealing temperature (Table 1), particle size was found to be different even when same composition of Rare earth elements, Lanthanum (La) and Cerium (Ce) were substituted and were annealed at the same temperature. As a conclusion we get that the substitution of cerium increases the particle size. XRD investigations revealed the presence of the Fe_2O_3 phase was observed in sample annealed at 650°C. This indicates that the formation of ferrite is not complete and some unreacted iron oxide phases were found, probably needs high annealing temperature or longer duration annealing. The size of Ce^{3+} ion is grater than La^{3+} and this difference in ionic radii causes changed structural and magnetic properties. Many researchers have found that Rare earth element substitution alters a lot in structural and magnetic behavior of ferrite magnetic materials (Zhoo L. et. al., 2004, Said Z.M., et. al., 2007, Jiang Jing, et. al., 2007 and Cheng Fu-xiang, 2000). Interplanar distance is almost same with the substitution of lanthanum and cerium. Lanthanum substitution in $SnFe_2O_4$ hinders the domain growth. From the above data of magnetic parameters (Table-1), it was found that at the same annealing temperature all observed values increases for the sample substituted with cerium. Cerium substitution increases magnetic anisotropy. Hence, Coercivity was found to increase. At this same annealing temperature coercivity, retentivity and magnetization were larger for Ce substitution while La substitution have lower coercivity, retentivity and magnetization (Table-1).

Conclusion :

The X-ray diffraction studies shows that the Ce^{3+} ion and La^{3+} ion addition is not soluble in the spinel phase but instead forms another additional phase, which exerts pressure on the spinel. Substitution of rare earth alters the grain growth and magnetic parameters values. At the same annealing temperature 650°C, the Ce substitution Sn ferrite have large particle size and coercivity comparative to La substituted Sn-Ferrite. The magnetic properties of Sn-Ferrite depend upon the particle size and ionic radii of Ce^{3+} and La^{3+}.

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