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Growth , Structural and Magnetic studies of Rare earth element Ce substituted Zn Ferrite Nanoparticles Via Citrate precursor method

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Ferrite magnetic nano materials having chemical formula Zn $Ce_{0.1}Fe_{1.9}$ Fe_2O_4 & Zn $Ce_{0.2}Fe_{1.8}$ Fe_2O_4 have been synthesized using chemical based Citrate precursor method at two temperatures, 650°C & 700°C. The effect of Ce content on lattice parameters, phases, crystalline size and magnetic behaviour were investigated using XRD and VSM and was observed different from without rare earth substituted Ferrite. The X-ray diffraction(XRD) analysis showed spinel phase together with some other additional phases. The average particle size was almost found same i.e 50 nm and 44nm. The maximum coercivity, retentivity and magnetization were observed 26Oe, 0.012 emu/g and 1.50 emu/g respectively.

Key words : *Rare earth Ce , Zinc ferrite, Spinel structure, Magnetic properties.*

Introduction: Ferrite having spinel structure became very pupular magnetic materials in recent year due to increasing demand in electronics industry. 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, Smit J., and Wijn H.P.H., 1959). It is interesting that desired magnetic behavior of ferrite can be tailored by controlling the different types and amount substitutes. Tillnow, many investigations have been carried out to make further improvements on the magnetic behavior of rare earth-substituted ferrite and researchers pointed out that rare earth ions drastically affected the physical properties of substituted ferrites due to their larger ionic radius and when rare earth ions entered the octahedral sites, they could replace Fe^{3+} ions at low rare earth ions contents (Jiang Jing, et. al., 2007, Cheng Fu-xiang, et. al., 2000, Panda, N.R. et. al., 2003, Sattar A.A. and Bi-Shokrofy, K.M., 1997). The properties of the ferrite particles are affected by the compositions, method of preparation and annealing temperature. Many methods have been used for synthesis of ferrite nanomaterials, such as hydrothermal, sol-gel, Citrate precursor, combusation (Pal M. and Chakravorty D., 2003, Narayan A., et. al., 2006). In the present work we have focused on the preparation, structural and magetic properties of nanocrystalline Cerium substituted Zinc ferrite using Citrate precursor method.

Materials and Method : Experimental procedure

In chemical based citrate precursor method, generally nitrate of divalent metal, nitrate of iron & Cerium and citric acid are taken in stochiometric proportions and dissolved in minimum amount of distilled water. The aqueous solution prepared above are mixed together and stirred at 60°C to 80°C temperature for two hours. Brown slurry is formed known as precursor. Then this precursor is dried in an oven at a temperature of 70°C. This dried material is the citrate precursor. This citrate precursor is annealed at pre determined temperatures 650°C and 700°C in a temperature controlled muffle furnace and the powdered sample is stored. After that, this sample is characterised through X-Ray diffraction (XRD) for its size and phases. The magnetic measurement was measured using Vibrating sample magnetometer (VSM).

Result and Discussion :

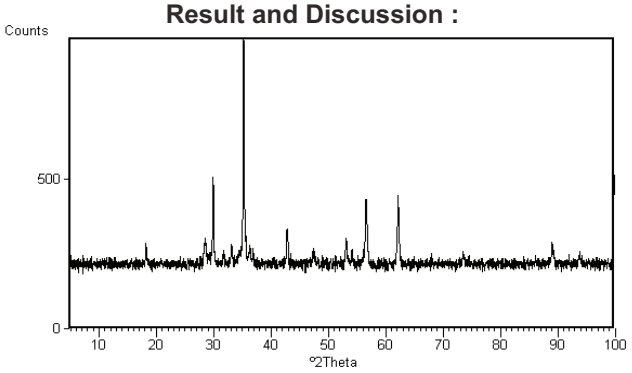

Fig. 1 – X-ray diffraction pattern of $ZnFe_{1.9}Ce_{0.1}O_4$ annealed at 650°C

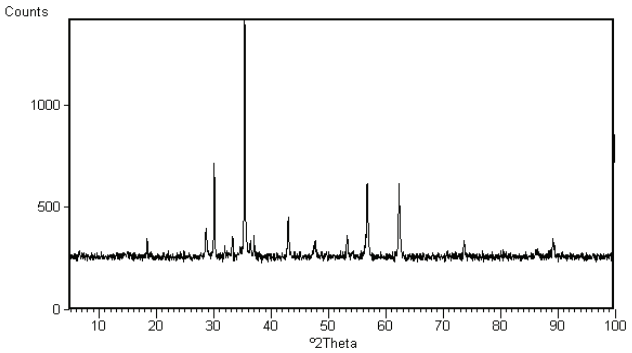

Fig. 2 – X-ray diffraction pattern of $ZnFe_{1.9}Ce_{0.1}O_4$ annealed at 700°C

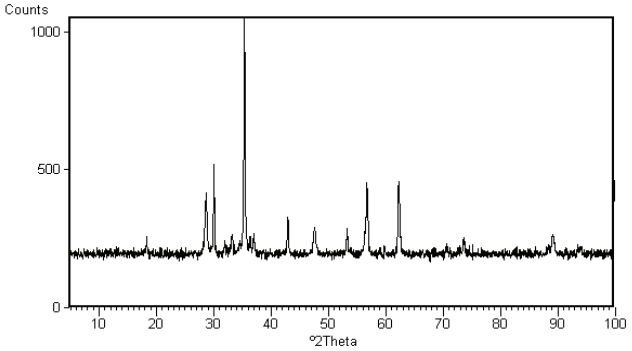

Fig. 3 – X-ray diffraction pattern of $ZnFe_{1.8}Ce_{0.2}O_4$ annealed at 650°C

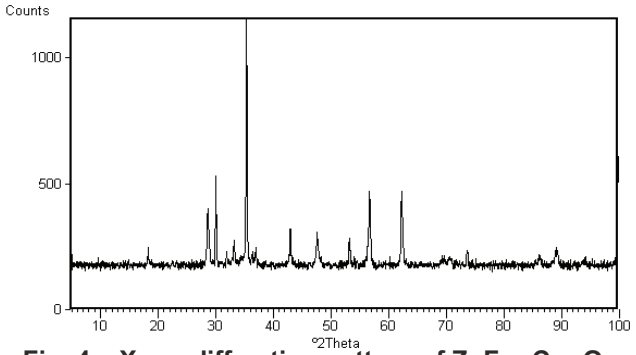

Fig. 4 – X-ray diffraction pattern of $ZnFe_{1.8}Ce_{0.2}O_4$ annealed at 700°C

Table 1: Structural parameters observed

Sample	Annealing Tempe-rature	Interplanner distance	Lattice Constant	Particle Size
$ZnFe_{1.9}Ce_{0.1}O_4$	650°C	2.549Å	8.452Å	50 nm
	700°C	2.535Å	8.406Å	50 nm
$ZnFe_{1.8}Ce_{0.2}O_4$	650°C	2.537Å	8.412Å	49nm
	700°C	2.538Å	8.416Å	43 nm

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 pattern of the synthesized samples are shown in figures 1 to 4. 0.1 mole of Ce composition substituted zinc ferrite have almost same particle size and d (interplanner distance) value at annealing temperatures 650°C and 700°C. But when concentration of Ce composition was increased from 0.1 mole to 0.2, the particle size was found 49 nm at 650°C where as when annealed at temperature 700°C; the size was found to be 43nm. The synthesized materials belongs to spinel ferrite together with some other phases i.e. Fe_2O_3 but their intensity is very low. The crystalinity of the synthesized materials was observed good at annealing temperature 700°C (Fig.2 & Fig.4).

Lattice constant was found to decrease in $ZnFe_{1.9}Ce_{0.1}O_4$($Ce_{0.1}$ substituted zinc ferrite; 8.452 Å to 8.406 Å) while when Ce composition was increased from 0.1 mole to 0.2 mole, the lattice constant was observed to increase (8.412 Å to 8.416 Å) and the crystallinity size was found to decreased (49nm to 43nm).

The size of the Cerium (Ce^{3+}) 1.034 Å is greater than Fe^{3+}(0.67 Å). When Fe^{3+} ions are substituted by Ce^{3+} ions, they create stress in the lattice and lattice constant must increases. But in sample $ZnFe_{1.9}Ce_{0.1}O_4$ particle size does not change and the lattice constant was found to decrease while annealing temperature was increased. This may be due to the some morphological effect in the form appearance of some additional phases together with spinel phase. In sample $ZnFe_{1.8}Ce_{0.2}O_4$ lattice constant was found to increase, while crystalline size decreases. Generally, the lattice constant is found to increase with the increase of particle size, but here the result is reverse. This is due to more Ce^{3+} ions in the spinal lattices (Said Z.M. et al., 2007).

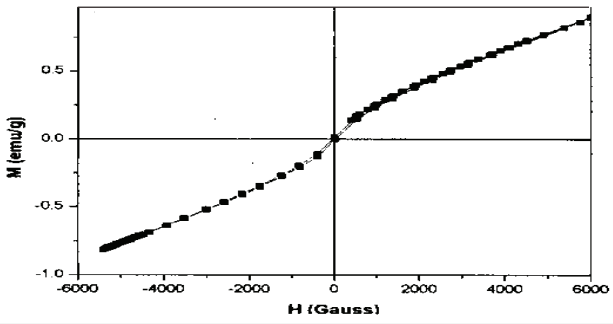

Fig. 5 – Magnetization curve loop for $ZnFe_{1.9}Ce_{0.1}O_4$ annealed at 650°C

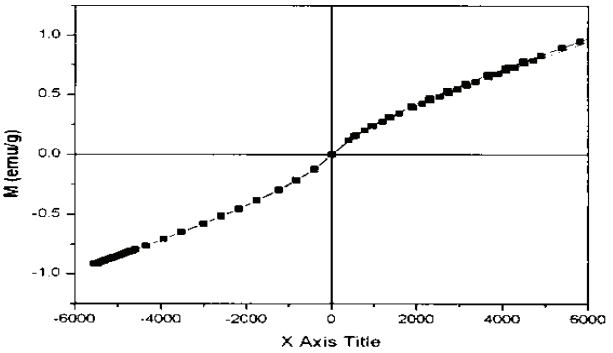

Fig. 6 – Magnetization curve for $ZnFe_{1.9}Ce_{0.1}O_4$ annealed at 700°C

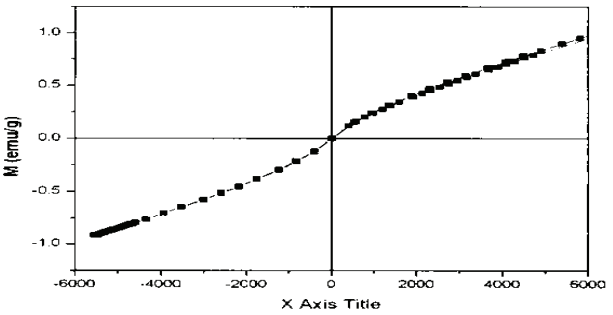

Fig. 7 – Magnetization curve for $ZnFe_{1.8}Ce_{0.2}O_4$ annealed at 650°C

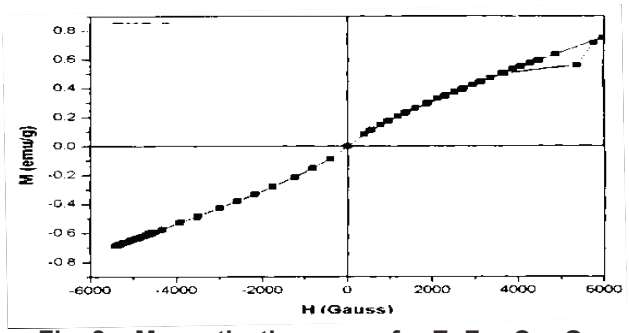

Fig. 8 – Magnetization curve for $ZnFe_{1.8}Ce_{0.2}O_4$ annealed at 700°C

Table 2 : Observation of Magnetic parameteric values

Sample	Annealing Temperature (°C)	Coercivity (Oersted) (Hc) Oe	Retentivity (Mr), emu/g	Magn-etization (M), emu/g
$ZnFe_{1.9}Ce_{0.1}O_4$	650°C	10	0.005	1.50
	700°C	26	0.012	0.86
$ZnFe_{1.8}Ce_{0.2}O_4$	650°C	10	0.004	0.95
	700°C	10	0.002	0.72

The hystersis curve observed using vibrating sample magnetometer are shown in fig. 5 – 8 and magnetic parameters are tabulated in Table 2. It is noteworthy that the crystalline size decreases with increase of the Rare earth Ce content. Due to large bond angle of Ce^{3+}-O^{2-} as compared to that Fe^{3+}- O^{2-}, more energy is needed to make Ce^{3+} ions enter into lattice. So thermal stability increases and more energy is needed for the complete crystallization and to grow grains.

When Ce concentration was 0.1 mole and annealing temperature is increased from 650°C to 700°C, coercivity was found to increase from 10 Oe to 26 Oe while Retentivity increases from 0.005 to 0.012 emu/g but magnetization decreases from 1.50 to 0.86 emu/g. From this observed data we conclude that only Coercivity increases 10 Oe to 26 Oe with the rise of annealing temperature by 50°C and same Rare earth element was substituted in all samples. Other Researchers reported in their work that rare earth substituted ferrite changes structural and magnetic properties drastically (Jiang Jing, et. al., 2007 and Panda, N.R. et. al., 2003). When concentration of Ce was increased from 0.1 mole to 0.2 mole and annealing temperature was in the same increasing order, there is no change in coercivity while Retentivity and magnetization decreases.

The size of Ce^{3+} ion is larger than Fe^{3+}, therefore, when Fe^{3+} ion is replaced from octahedral site the distortion in the crystal affect the X-ray diffraction pattern and magnetic behaviour of synthesized Nanomaterials (fig.1 & fig.2) to some extent.

Zn is a diamagnetic material, Ce has electronic configuration $4f^2 6s^2$ whereas the configuration of Fe is $3d^6 4s^2$. The net magnetization of this nanomaterial is the net magnetic moment of octahedral and tetrahedral sites (Said Z.M., 2007 and Li S.F., et. al., 2003). Therefore, no drastic change in magnetic properties was observed.

Conclusion :

The X-ray diffraction studies show that the Ce^{3+} ion addition is not soluble in the spinel phase but forms another additional phase, which exerts pressure on the spinel and prevents its expansion. Lattice constants and interplanner distance (d) values are not linear function of annealing temperature. The largest coercivity was observed 26 Oe. Substitution of rare earth element (Ce) in Zinc ferrite alters the grain growth and magnetic parameteric values to a very small extent.

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