Structural, Magnetic and Photoluminiscent Properties of Strontium Ferrite Nanoparticles synthesized using Citrate precursor method

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Abstract

Strontium ferrite nanoparticles were synthesized using chemical based citrate precursor method. In this method, nitrates of divalent metal, trivalent metal iron and citric acid were taken in molar ratio. Citrate precursor was annealed at temperature 450 ^{0}C and 650 ^{0}C in a muffle furnace that lead to ferrite powder after crushing. The powder samples were characterized using X-ray diffraction (XRD), Vibrating sample magnetometer (VSM) and Photoluminiscence spectrometer(PL). The mean particle size observed was 15.7 nm at 450 ^{0}C and 20.3 nm at 650 ^{0}C. The lattice constant was found to increase from 10.663Å to 10.667Å . Coercivity and Retentivity are also found to increase but saturation magnetization was found to decrease.

Photoluminisence (PL) property of this sample was studied using 225nm, 250nm and 330nm excitation wavelength radiation source. The PL spectrum was obtained in visible range only by excitation through 225 nm and 250 nm radiation source.

Key words: Hexa-ferrite, Nanoparticles, Photoluminence, Magnetic behaviour

Introduction:

Strontium ferrite having general formula $SrFe_{12}O_{19}$ is a famous magnetic material which has a variety of applications in microwave devices and in permanent magnet[1,2]. The electromagnetic wave absorption property of hexaferrite with a magnetoplumbite structure in the GHz range, which includes M-, W-, Y-, Z-, U- and X-type has found demands for microwave communication, microwave dark room target camouflage, electromagnetic radiation abatement, and so on[3] .In nanocrystalline form hexaferrites are of particular interest for use as high density perpendicular magnetic recording media [4,5].

Photoluminescence (PL) is nondestructive method of probing the electronic structure of material. The intensity & spectral content of this PL is a direct measure of various important material properties. The important applications are in materials quality, impurity levels and defect detection, band gap determination and recombination mechanism[6].

Many processes have been used to prepare strontium ferrite, including the solid state method[7], Sol-gel [8,9] and coprecipitation [10] and other chemical processes[11] . Among these processes, coprecipitation and sol-gel methods are more popular for the preparation of hard ferrite nanomaterials. Recently, the nanocrystalline Sr ferrite with mean particle size below 100nm has been prepared by sol-gel process using PVA(Polyacrylic acid) as a stabilizer.[12] However such a small particles size is still difficult to achieve by simple coprecipitation method. We have prepared small particle of size found 15.7nm at annealing temperature 450 ^{0}C and 20.3nm at 650 ^{0}C. The method of preparation was used Citrate precursor method.

Materials and Methods:

Samples of nanometer-sized Strontium hexaferrite powder were prepared by using the Citrate precursor method. Ferric nitrate, Strontium nitrate and Citric acid were taken in Stoichiometric proportion 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. The mixture was heated to temperature between 60^{o}C to 80^{o}C for two hours with continuous stirring. This solution was allowed to cool to room temperature and finally it was dried overnight in oven in order to remove excess water and other impurities at 90-95^{o}C until it formed a brown color fluffy powder. The Citrate precursor was heated at temperature 450^{o}C & other sample at temperature 650^{o}C for one hour in a muffle furnace. By this process, the precursor thermally decomposed to give Strontium hexaferrite powder of nanometer size.

Result and Discussion

Ferrite powders were characterized using X-ray diffractometer (XRD) for phases and mean particles size. The X-ray diffraction spectra shown in figures 1 & 2. We have chosen maximum intensity peak for particle size calculation and particle size observed was 15.7 nm and 20.3 nm at annealing temperature 450^{o}C & 650^{o}C respectively.

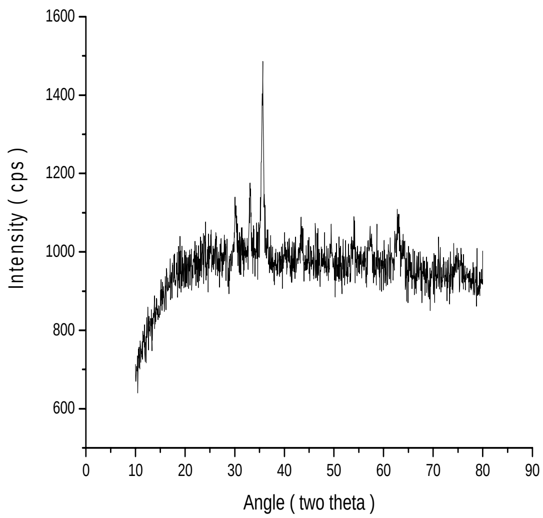


Figure1: X-raydiffraction pattern for $SrFe_{12}O_{19}$ annealed at $450\,^{0}C$

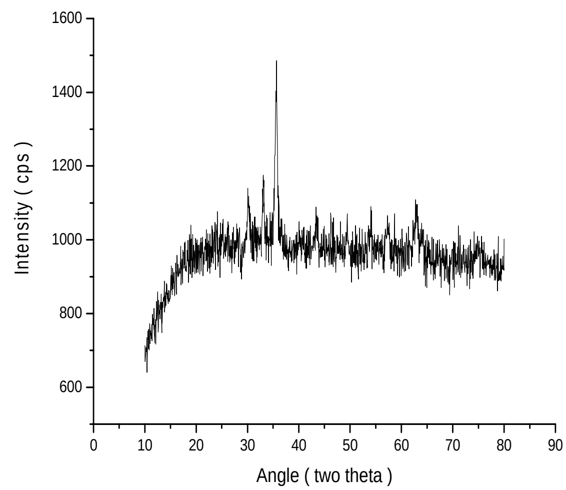
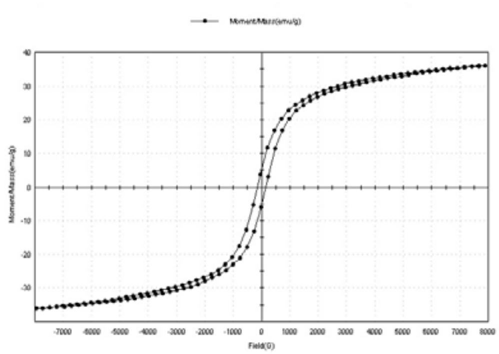


Figure2: X-raydiffraction pattern for $SrFe_{12}O_{19}$ annealed at $650\,^{0}C$.

The magnetic measurement of these nanometric particles was done using vibrating sample magnetometer. The magnetization curve are shown in figures 3 & 4. The magnetic parameters are tabulated in table 1.



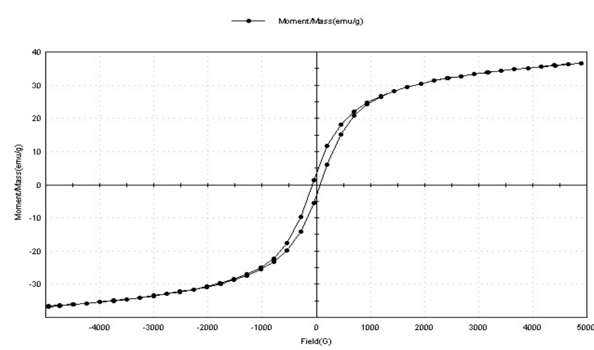


Fig 3: Hysteresis curve for Sr ferrite nanoparticles annealed at 450 ^{0}C. **Fig 4:** Hysteresis curve for Sr ferrite nanoparticles annealed at 650 ^{0}C

Table 1: Observed data for Sr ferrite nanoparticles.

Annealing temperature	Mean particle size	Lattice constant	FWHM	Coercivity H_c	Retentivity M_r	Saturation magnetization M_s
450^{0}C	15.7nm	10.663 Å	0.539	75.539 G	3.321 emu/g	36.615 emu/g
650^{0}C	20.3 nm	10.667 Å	0.423	157.04 G	5.665 emu/g	36.149 emu/g

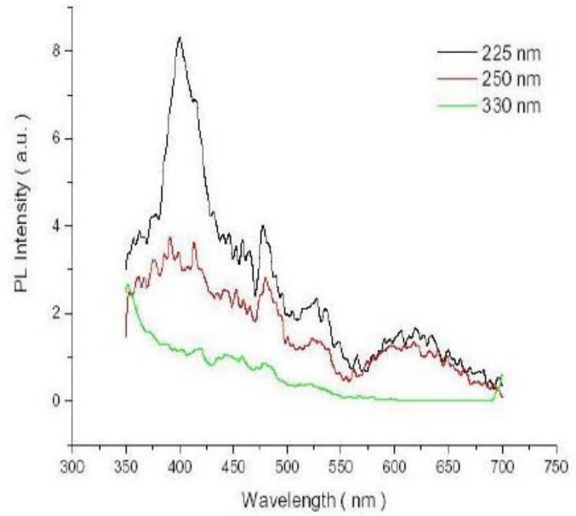


Figure 5: Photoluminescence spectrum of Strontium ferrite nanoparticles (annealed at 450 ^{0}C) under 225, 250 and 330 nm excitation.

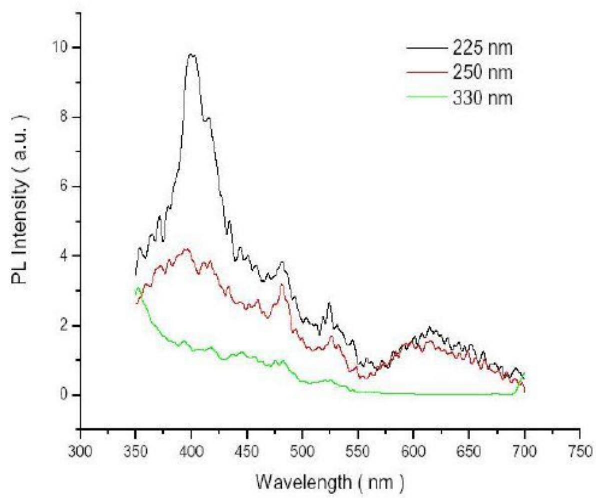


Figure 6: Photoluminescence spectrum of Strontium ferrite nanoparticles (annealed at 650 ^{0}C) under 225, 250 and 330 nm excitation.

The magnetic parameters such as coercivity, saturation magnetization, and retentivity of sample Strontium ferrite nanoparticles were obtained using VSM as 75.539G, 36.615emu/g, and 3.321emu/g at annealing temperature 450^{0}C while 157.04 G, 36.149 emu/g and 5.665 emu/g at annealing temperature 650^{0}C respectively. In the preparation of hexaferrite, a high annealing temperature is required to obtain pure phase . This results in significant increases of particle size together with improvement of ion occupancy[13]. Jun Wang et al. have reported that the Barium hexaferrite nanoparticles formed at 140^{o}C in presence of 0.25T magnetic field exhibited a higher saturation magnetisation i.e. 6.1emu/g at room temperature as compared with 1.1 emu/g obtained for sample prepared in zero magnetic field. V. K. Sankaranarayanan and D.C. Khan have reported in their work[13] that magnetization first decreases with increasing annealing temperature, reaches a minimum for annealing temperature 690K(417^{0}C), and then increases to reach a maximum for annealing temperature 720K(447^{0}C), before decreasing again sharply to approach zero[14]. W. A. Kaczmarek et al[14] found that annealing in air promotes slightly higher H_c value. They assume that different particle morphology, it directly responsible for fluctuations in magnetic parameters value. The value of coercivity increases over six times and reaches a value 445.6 kA/m. This value is typical of chemically coprecipited fine hexa-ferrite powders, where perfect crystal structure assures a defect and stress-free spin arrangement with high magnetocrystalline anisotropy energy[12]

Photoluminescence is the emission of light from a material under optical excitation. When the light of sufficient energy is incident on a material, photons are absorbed and electronic excitations are created, after that these excitations relax and the electrons return to the ground state. If radiative relaxation occurs, the emitted light is called photoluminescence. The choice of excitation light is critical in any photoluminescence study of material. The excitation wavelength may influence the photoluminescence of any material as the absorption of a material depends strongly on the energy of the incident light. The excitation wavelength controls the density of photoexcited electrons and holes, which governs the behavior of these carriers. Figure 5 and 6 show the photoluminescence spectrum of strontium ferrite nanoparticles annealed at temperature 450 ^{o}C and 650 ^{o}C, respectively, at different excitation 225 nm, 250 nm and 330 nm. The photoluminescence spectrum consists of emission peaks at 400 nm (3.09 eV) , 480 nm (2.57 eV) , 530 nm (2.33 eV) and 650 nm (1.89 eV). These emission peaks seem due to different defects in Strontium ferrite nanoparticles. It is also observed that the emission intensity of the peaks depend on the excitation wavelength. Regarding the mechanism of PL, it may be due to quantum confinement. This confinement explain in terms of shortening of the superexchange interaction bond length in the nanocrystalline ferrite materials, which modifies the electronic structure of hexaferrite or by the presence of fast nonradiative relaxation channels in nanocrystals taking part at the surface[16]. PL around 3eV is indeed mainly due to the quantum confinement, because the peak value approximately agress with band gap of ferrite nanomaterials[17]. The analysis of the PL spectrum also should include the effect of the surface oxide and nonhomogenous sizes generally if there is a difference in the energies, which is associated with the stokes shift between the absorption- surface defects or surface oxide. The mechanism of charge transfer between the trivalent ion appears to involve a nonradiative, superexchange process via the intervening oxide ions, that support the ferromagnetic ordering[18]. As follows from the above discussion, the situation with the PL mechanism is very complex and is difficult to draw a definite conclusion about the PL mechanism at this stage. Further studies are needed in order to elucidate the correct mechanism of PL in hexa ferrite Nanoparticles.

Conclusion

We have prepared small particle size using Citrate precursor method. The annealing temperature 450^0C & 650^0C are also low in this method. The Coercivity and retentivity both increase with temperature while saturation magnetization slightly decreases. PL spectra in visible region shows only by excitation through 225 nm and 250nm radiation source. PL spectrum shows different colours in visible region and their intensities also found to decrease.

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