

Structural, Magnetic and Dielectric Properties of Sr-M Hexaferrite Nanoparticles Prepared using a Reverse Micelles Route

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Abstract: Hexaferrite materials are considered as a magnetic material, which can be used as a permanent memory storage devices. Here micro emulsion through reverse micelle route has been used in order to obtain homogeneous nano sized $\text{SrFe}_{12}\text{O}_{19}$ hexaferrite particles at very low temperature (500 °C). Synthesized sample was then characterized with using Thermo Gravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffractogram (XRD) and Scanning Electron Micrographs (SEM). A very negligible weight loss (~6%) is observed by TGA, which shows that the hexaferrite sample prepared by this route is highly thermodynamically stable. It is also observed that the particles are uniform, nano sized and homogeneous. And the calcinations temperature is very low (500° C) compared to other conventional methods.

Keywords: nano-particles, reverse micelle, CTAB.

1. Introduction

Hexaferrite possesses a "magnetoplumbite" structure. The symmetry of the magnetoplumbite structure is hexagonal. M-type hexaferrite is having a generic formula $\text{MO} \cdot 6\text{Fe}_2\text{O}_3$, where M represents a divalent ions such as Ba^{2+} , Sr^{2+} , or Pb^{2+} . A schematic *M-type* structural representation and the surroundings of five Fe^{3+} sites are shown in Fig. 1 by Collomb et al.¹. Strontium ferrite is almost identical to $\text{BaFe}_{12}\text{O}_{19}$ in its crystallographic structure and magnetic properties, except that the sintered magnets have higher coercivity. *M-type* hexaferrite has a very large saturation

magnetization, a large uniaxial magnetic anisotropy, and a high curie temperature, which have been widely used as permanent magnetic materials.

Several techniques have been used to prepare strontium hexaferrite, including the traditional sol-gel process², solid-state method³, salt melting method⁴, ball milling⁵, self-propagating high temperature synthesis⁶, chemical co-precipitation method⁷ and Microemulsion route⁸. Among the various existing methods of chemical synthesis, microemulsion route is an alternative and promising technique for preparing the ferrites, leading to highly pure, chemically homogeneous, nanometric scale particles.

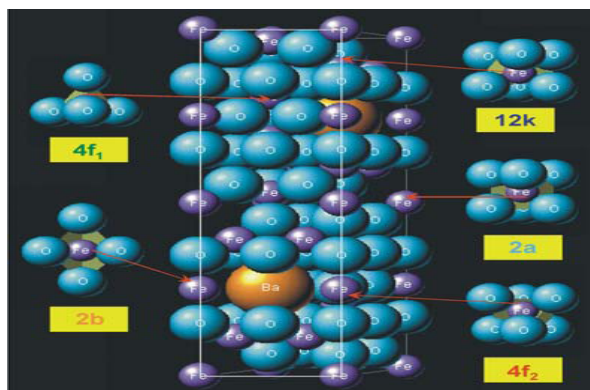


Fig. 1 M-type Hexaferrite along with five Fe sites with their surroundings

The other methods namely ceramic route, sol gel process etc. have the disadvantages like particle inhomogeneity, presence of impurity, larger grain size of the final product; requirement of high temperature sintering, etc.

2. Experimental

Strontium hexaferrite, $\text{SrFe}_{12}\text{O}_{19}$ nanoparticles have been prepared with precipitation in water-in-oil microemulsion system, using iron sulphate and strontium nitrates in molar ratio 1/12 as starting materials. The microemulsion system consisted of n-hexanol as an oil phase, n-hexadecyl trimethyl ammonium bromide (CTAB) as a surfactant and an aqueous phase of metal salts. Aqueous solution containing Fe^{2+} and Sr^{2+} ions was prepared by dissolving an appropriate amount of metal salts, 1.2M FeSO_4 (*Molychem*, GR grade) and 0.1M $\text{Sr}(\text{NO}_3)_2$ (*loba chem.*, 99 % pure) in deionized water which resemble to the ferrite stoichiometry. Aqueous solution of 6N NaOH (*Merck*, 97 % purity) served as a precipitating agent.

The composition of water : CTAB : oil was taken as 15 : 30 : 55 wt % by mixing of an appropriate amount of water solution of metal salts with proper amounts of CTAB (*Spectrochem*, AR grade) and n-hexanol (*s. d. fine chem.*, LR grade). During mixing, the microemulsion was heated and kept at temperature between 50 and 60° C. When an alkaline solution of 6N NaOH was added to the starting microemulsion, the pH value rose to about 11 and green coloured intermediate precipitate was formed. As oxidation with H₂O₂ took place; intermediate precipitate was changed into the brownish precipitate of the final phase. A 30% solution of hydrogen peroxide, H₂O₂ was used as the oxidizing reagent. The resulting microemulsion was then mixed with an equal volume of water-methanol (1:1) solution to break up the micelles by washing the particles. The samples were centrifuged with ethanol for 20 min. followed by further washing the particles several times using distilled water and dried at 100° C. The dried precursors sintered at 500°C in a muffle furnace for 2 hrs. Also one part of the powder is heated inside a microwave oven for 30 minutes at frequency 2.45 GHz, power 300 W. Schematic of the experimental procedure is shown in Fig. 2.

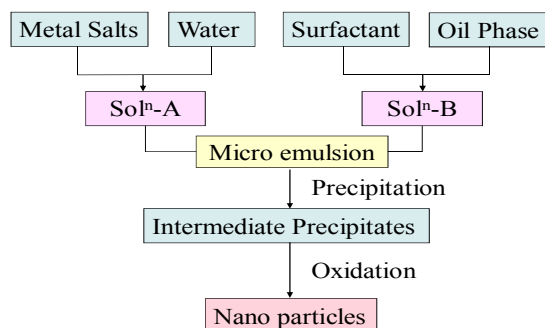


Fig. 2. Schematic Representation for Preparation of Nano Particles via Micro Emulsion Route

Samples prepared are labelled as follows

Sample code	Heating condition	Heating Time
ME-r	without heating	-
ME-MW	Microwave heating	30 minutes
ME-500	Heating at 500° C in Furnace	2 hours

3. Results and Discussion

3.1 Fourier Transform Infrared Spectroscopy: FTIR spectra for synthesized samples were recorded at room temperature over the wavenumber ranges from 4000 to 400 cm⁻¹.

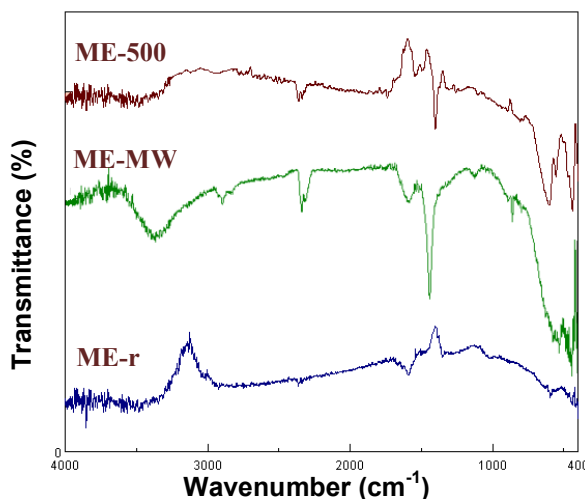


Fig. 3 FTIR spectra for sample ME-r, ME-MW & ME-500

Fig. 3 represents the FTIR spectra for the sample prepared via microemulsion route. As shown in figure, there is no confirmation of ferrite formed for precursor ME-r sample. As the sample heated in microwave oven, a broad band around 3400 cm^{-1} appears which is due to the O-H stretching⁹. The peak near 1450 cm^{-1} is assigned to the H-O-H bending vibration. Intensity of these peaks decreases with heating the sample at 500°C because of the evaporation of water. For samples ME-MW and ME-500, the broadening band $1000\text{--}600\text{ cm}^{-1}$ indicates a band of metal-oxygen¹⁰.

3.2 X-ray Diffraction: X-ray Diffraction patterns for all the sample are recorded at room temperature using Cu-K α radiation ($\lambda=1.5406\text{ \AA}$) in a 2θ range from 20° to 80° , with a step of $0.05^{\circ}/\text{min}$. **Fig. 4** represents XRD of samples ME-r, ME-500 and ME-MW. Peaks are identified with powder-X software and compared with standard JCPDS data cards. For sample ME-r, figure shows a flat diffractogram indicating that no oxide crystallization occurs for as-precipitated samples. For calcinations at microwave frequency and 500°C , almost all the peaks are assigned with M-phase. It reveals that even at low sintering temperature at 500°C , M-phase formation is possible with microemulsion method. Particles size is measured with debye scherrer formula which comes in the nano-scale range, which will also be confirmed by SEM images. It is observed from figure that the broadness of the major peak $[1\ 1\ 4]$ is maximum for microwave heated sample, which means that the resultant samples with microwave heating are having smaller grain size.

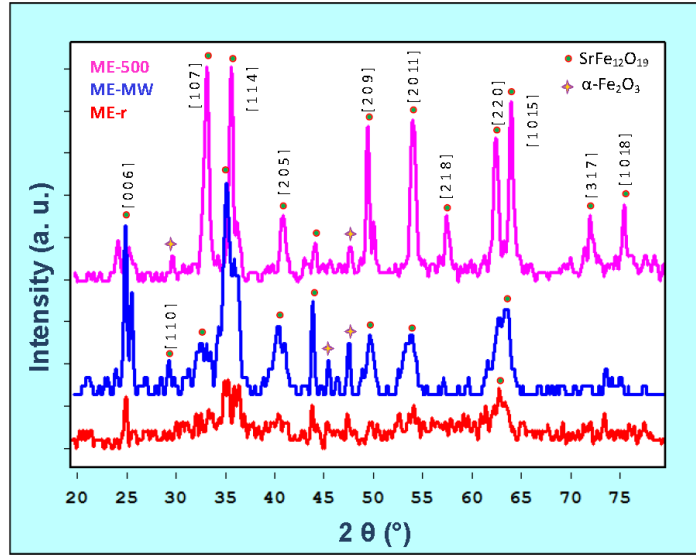


Fig. 4 XRD Pattern for Sample ME with Different Calcination Conditions

Table 3.1 comprises the details of lattice parameters a , c and value of unit cell volume, V for the samples ME heated at different calcinations conditions.

Table 3.1 Lattice Parameters Derived from XRD Patterns of $\text{SrFe}_{12}\text{O}_{19}$ Hexaferrites Samples

Sr. No.	Sample Code	Lattice parameters		Unit cell Volume $V (\text{\AA}^3)$
		$a (\text{\AA})$	$c (\text{\AA})$	
1	ME-r	5.76	23.02	661.43
2	ME-MW	5.58	22.85	616.15
3	ME-500	5.79	22.94	666.01

3.3 Dielectric properties of ME-MW and ME-500 samples: Fig. 5(a) and 5(b) show the frequency dependent dielectric constant (complex, ϵ'') and ac conductivity (σ_{ac}) behavior of $\text{SrFe}_{12}\text{O}_{19}$ hexagonal ferrite samples prepared using a microemulsion route respectively. There is a rapid decrease in dielectric constant at lower frequency and attain constant value at higher frequencies (for ME-MW sample, while it is increase up to 200k for the sample heated in a furnace at 500°C). This decrease in dielectric behavior indicates dispersion due to Maxwell-Wagner¹¹ type of interfacial polarization in well agreement with Koop's phenomenological theory¹². The higher values of dielectric constant (ϵ'') at lower frequencies are explained by using the concept of space charge polarization and due to heterogeneity

in the sample¹³. There is an increase in dielectric constant in the microwave heat treated ME-MW sample until reaching a peak (200k) after which it displays the traditional relaxation; this behavior can be explained on the basis of Rezlescu and Rezlescu assumption¹⁴.

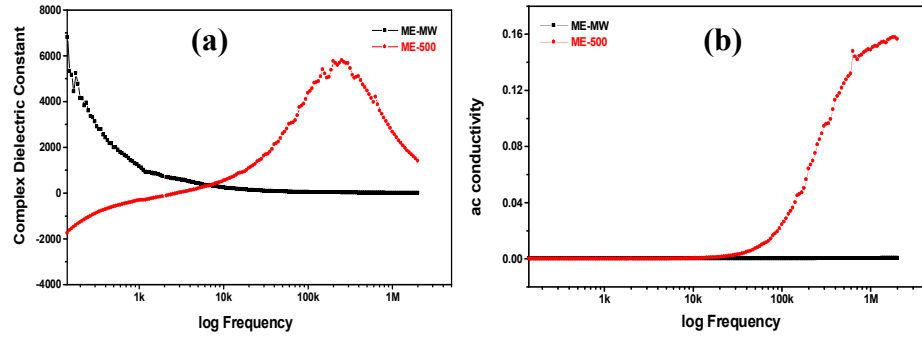


Fig. 5 (a) Dielectric constant and (b) ac conductivity versus log F for samples ME-MW and ME-500

Table 3.2 Dielectric parameters for samples ME-MW and ME-500

Sr. No	Frequency	ME-MW			ME-500		
		Dielectric Constant ϵ''	Dielectric loss $\tan \delta$	ac conductivity σ_{ac}	Dielectric Constant ϵ''	Dielectric loss $\tan \delta$	ac conductivity σ_{ac}
1	100 Hz	3738	4.62	2.08 E-05	-3218	2.54	-1.79 E-05
2	1 kHz	1157	3.90	6.51 E-05	-317.11	0.45	-1.76 E-05
3	10 kHz	237	3.55	1.32 E-04	540.12	-0.82	3.01 E-04
4	100 kHz	35.57	1.53	1.98 E-04	4368	-5.79	2.43 E-02
5	1 MHz	6.87	0.52	3.83 E-04	2669	14.85	1.48 E-01
6	2 MHz	4.67	0.39	5.19 E-04	1407	9.00	1.56 E-01

It can be observed from Fig. 5(a) and Table 3.2 that the value of the dielectric constant (ϵ'') for sample ME-MW is high particularly at lower frequencies can be attributed to the interfacial polarization known to occur in the heterogeneous structures^{12, 15}.

3.4 SEM analysis: Micro-structural and surface morphology was investigated through SEM micrographs. Fig. 6 corresponds to the SEM images of $\text{SrFe}_{12}\text{O}_{19}$ hexaferrite sample prepared via different

microemulsion route and calcined with different heat conditions: conventional heating and microwave heating. It is clear from figure that the products are composed of agglomerated spherical particles. With microwave treated samples, almost all the particles are uniform and nano meter scale range. It is well in agreement with the XRD results.

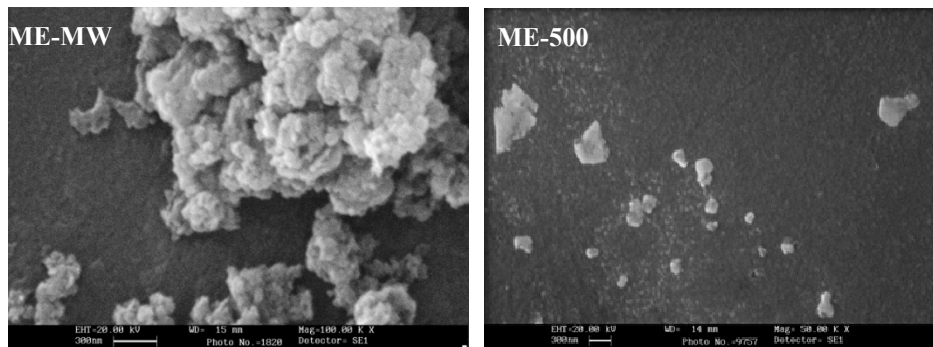


Fig.6 SEM images for samples ME calcined at microwave frequency and 500° C

4. Conclusions

It is observed that the particles prepared by this route are uniform, nano sized and separated particle achieved. Also the calcinations temperature is very low (500° C) compared to other conventional methods.

The effect of particle size in sintering is related to the concept of total surface energy of the product. The driving force, in sintering being the total surface energy, is increased by decreasing the particle size. As the particle size of the powder is decreased a higher surface area to volume ratio is obtained. Therefore the total surface energy per unit mass is increased. Due to the promoted driving force, the peak temperature required for sintering process can be lowered. Structural integrity and structural perfection can be preserved more easily when the hexaferrite is fired at low temperature. In addition, the possibility of the occurrence of discontinuous grain growth may also diminish at lower sintering temperature.

Powder synthesis methods play a crucial role in defining the particle size of final product.

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