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Variation in structural and dielectric properties of co-precipitated nanoparticles strontium ferrites due to value of pH

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ABSTRACT

Nanoparticles of strontium ferrites with nominal composition $SrFe_{12}O_{19}$ were prepared by co-precipitation method, by decreasing pH from 13 to 8 with a regular step of 1. The secondary phase of α-Fe_2O_3 was increased with the decrease in pH. The crystallite size estimated from X-rays diffraction data was in the range 52–70 nm, which is much smaller than that already reported. Most of the particles formed had hexagonal structure, as observed by the scanning electron microscopy. Particle size and dielectric loss were increased where as dc electrical resistivity and dielectric constant were decreased with decrease in pH. The results show that the material synthesized with higher pH is phase pure and is potentially more suitable for high frequency applications.

1. Introduction

Ferrites are ferrimagnetic ceramic materials that can be magnetized to produce large magnetic flux densities in response to small applied magnetic forces. They are considered better than other magnetic materials because they have high electrical resistivity and low eddy current losses [1]. These are one of the most significant dielectric materials whose properties depend upon synthesis conditions, composition, sintering temperature and grain size [2–4]. Among these materials, M-type hexa-ferrites $MFe_{12}O_{19}$ (M = Ba, Sr, Pb) have been a subject of continuous interest for several decades due to the fact that these compounds have been the work horse of the permanent magnet market [5,6]. Prepared $SrFe_{12}O_{19}$ can be used as magnetic fillers in microwave absorber components [7–9]. These materials can also find their applications in magnetic recording media, electronic devices, medicine and magneto-optical recording [10–14].

For microwave applications, the dielectric properties such as dielectric constant and dielectric loss are very important as the dielectric constant affects the thickness of microwave absorbing layer and the dielectric loss factor ($\tan\delta$) of a material determines dissipation of the electrical energy. This dissipation may be due to electrical conduction, dielectric relaxation, dielectric resonance and loss from non-linear processes [15]. High performance devices require low dielectric loss ($\tan\delta$) because the lower it is the higher the efficiency and lower the noise. The porosity of the material also increases the dielectric loss ($\tan\delta$) and that may be due to absorption of humidity by the pores of that material [16].

M-type hexa-ferrites are highly resistive. The electronic conduction at high temperature in ferrites is mainly due to hopping of electrons between ions of the same element present in more than one valence state, distributed randomly over crystallographic equivalent lattice sites [17]. The wet chemical method provides better control on particle size distribution and chemical homogeneity [18–20]. In co-precipitation method, pH plays very important role. In the present work a comparative study of effect of pH on structural and dielectric properties of strontium hexa-ferrites synthesized by co-precipitation method is given.

2. Experimental

Strontium hexa-ferrite nano particles with different pH values were prepared by co-precipitation method. It provides better control on structural parameters at nano scale. The chemicals used for the synthesis of samples were $Sr(NO_3)_2$ and $Fe(NO_3)_3{\cdot}9H_2O$. The salts were dissolved in de-ionized water. The solution of both of these precursors with molar ratio (Fe/Sr = 11) was prepared. This solution was heated along with continuous stirring on hot plate. When temperature of solution was reached to 70 °C, solution of NaOH was added until required pH was achieved. pH of the samples was varied from 13 to 08. The aqueous solution was stirred for 1 h to get fine homogeneity. The solution was washed for four times with de-ionized water and then dried in an oven at 105 °C. The dry precursors were ground well and then their pellets were formed using a pressure of 75 kg m^{-2}. These pellets were sintered in a box furnace for 1 h at 925 °C. The phase formation was studied by powder X-rays diffraction (XRD) using Cu-Kα (λ = 1.5406 Å). Structural morphology was studied by scanning electron microscope (SEM). Effect of temperature on resistance

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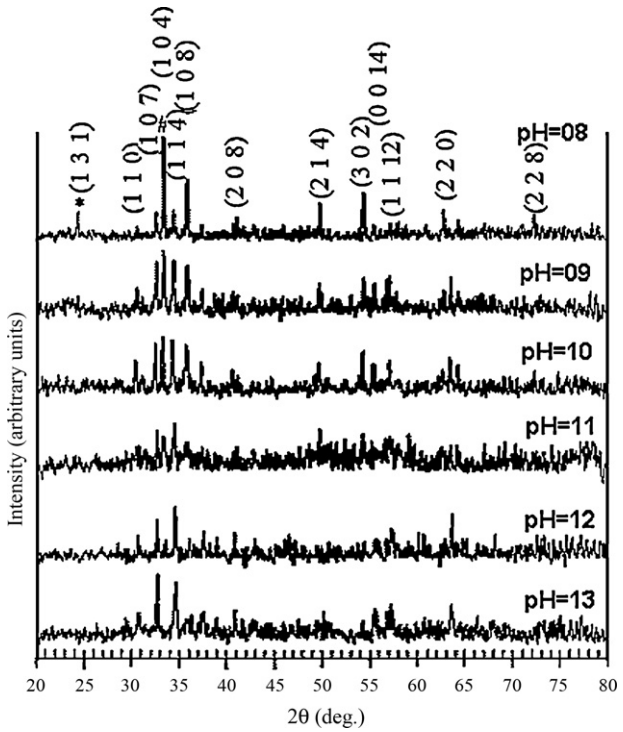

Fig. 1. Indexed patterns of XRD of samples of $SrFe_{12}O_{19}$ for different values of pH (* - $SrFe_2O_4$, # - α-Fe_2O_3).

and drift mobility of charge carriers were investigated. Apparatus to study the effect of temperature on resistance was designed and assembled in the laboratory. The dielectric constant (ε') and dielectric loss ($\tan\delta$) were measured in the frequency range of 1 kHz to 3 MHz using precision component analyzer.

3. Results and discussion

3.1. Structural analysis

Structural analysis was done by using XRD patterns and SEM. Fig. 1 shows indexed XRD patterns of the strontium hexa-ferrite samples for the different pH values, synthesized by the co-precipitation method. All the peaks were indexed by comparing with ICSD 01-080-1197, 00-048-0156 and 00-002-0919. Indexed XRD patterns showed that as pH was decreased from 13, extra phase of α-Fe_2O_3 started appearing and increased with the further decrease in pH. Parameters such as crystallite size (D), lattice parameters a (Å) and c (Å), cell volume (V) and X-ray density (ρ_x) were calculated from indexed XRD patterns and are given in Table 1. The crystallite size (D) was calculated by using Scherer's formula [21]. The crystallite size was in range 52–70 nm which is much smaller than that already reported [22]. This may be due to difference in molarities of solution. X-ray density (ρ_x) and bulk density (ρ_m) were calculated by using Eqs. (1) and (2) respectively.

$$\rho_x = \frac{\text{Number of formula units/unit cell} \times M_m}{VN_A} \quad (1)$$

where M_m is molecular mass, V is volume of unit cell, N_A is Avogadro's number.

$$\rho_m = \frac{m}{v} \quad (2)$$

where m is mass of pellet and v is volume of pellet.

Structural morphology was studied by SEM and is given in Fig. 2. The micrographs of pH varying samples of strontium hexa-ferrite showed that the particle size increased with the decrease in pH and most of the particles had hexagonal structure with diameter in the range of 0.4–3.5 μm. As the pH increased, the rate of nucleation sites formation increased which resulted in decrease in agglomeration. Distribution in particle size was also increased with the decrease in pH. This behavior is different as reported by Hessien et al. [21].

3.2. Electrical properties

The electrical properties of the ferrites depend upon particle size, chemical composition, synthesis technique and sintering temperature. Octahedral sites of hexa-ferrites are mainly responsible for electrical conduction. It is the number of ferrous ions on the octahedral sites that play a dominant role in the process of conduction as well as dielectric polarization [23]. According to the band theory, the temperature dependence of conductivity is mainly due to the variation in the charge carrier concentration with temperature. According to the hopping model, the change in their mobility with temperature is considered to lead to the conduction current by jumping or hopping from one iron ion to the next [24]. The conduction at room temperature is because of impurities and at high temperature it is due to polaron hopping explained by Verwey's hopping mechanism. According to Verwey, the electronic conduction in ferrites is mainly due to hopping of electrons between ions of the same element present in more than one valence state, distributed randomly over crystallographic equivalent lattice sites [17]. The crystal structure of ferrites shows that the cations either in tetrahedral or octahedral sites are surrounded by oxygen anions and to a first approximation can be treated as isolated from each other. Thus the localized electron model is more appropriate to discuss the conduction mechanism in ferrite rather than the band model [23]. M-type hexa-ferrites belong to $P6_3/mmc$ space group and crystallize in a hexagonal structure containing 64 ions per unit cell on 11 different symmetry sites. The 24 Fe atoms are distributed over five distinct sites: three octahedral (B) sites (12k, 2a, and $4f_2$), one tetrahedral (A) ($4f_1$) site and one bipyramidal (C) site (2b). The magnetic structure is ferrimagnetic with five different sublattices: three parallel (12k, 2a, and 2b) and two antiparallel ($4f_1$ and $4f_2$) [15,16]. Two tetrahedral sites are adjacent to each other and for these two only one metal ion is available. This metal ion now occupies position halfway between them, amidst the three oxygen ions. The distance between two metal ions at (B) site is smaller than

Table 1
Lattice constants a (Å) and c (Å), crystallite size (D), cell volume (V), X-ray density (ρ_x), bulk density (ρ_m), % age α-Fe_2O_3 and particle size. Standard deviations are also mentioned.

	pH = 13	pH = 12	pH = 11	pH = 10	pH = 09	pH = 08
Lattice constant a (Å) c (Å)	5.82(5)23.12(4)	5.88(2)23.00(6)	5.86(3)22.84(9)	5.87(2)23.03(4)	5.89(2)23.04(2)	5.86(3)23.06(4)
Crystallite size, D_{av} (nm)	62	68	65	59	69	59
Volume, V (Å^3)	678(6)	688(7)	685(9)	686(7)	689(5)	686(9)
X-ray density, ρ_x (g/cm^3)	5.20	5.13	5.15	5.13	5.12	5.15
Bulk density, ρ_m (g/cm^3)	3.27	3.18	3.39	3.53	3.29	3.63
% age of α-Fe_2O_3	0	5	10	16	20	24
Particle size (μm)	0.6–0.9	0.5–1.2	0.5–1.5	0.5–2.0	0.8–3.0	0.4–3.5