Effect of annealing temperature and substitution of Zr-Cu on magnetic properties of strontium hexaferrite nanoparticles

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Abstract: ZnTe and ZnTe:Cr films were prepared onto glass substrates using the thermal evaporation method. Structural properties of the prepared samples were analyzed using X-ray diffractometry, and the presence of a ZnCrTe phase was identified along with poor crystallinity. Composition analysis was done using XPS and the Cr content in the film was found to be 0.05 atomic percent. Transmittance spectra were recorded using UV-Vis spectrophotometry. The valence state of Cr in ZnTe:Cr film is determined to be +2 using electron spin resonance (ESR) spectroscopy. Magnetic moment data as a function of magnetic field were recorded using a Superconducting Quantum Interference Device (SQUID) magnetometer at temperatures of 5, 77 and 300 K. The results showed minority ferromagnetic behavior even at room temperature. Magnetic domains were observed using Magnetic Force Microscopy and the average domain size is 3.7 nm.

Keywords: Nanomaterials; Sr-hexaferrite; Saturation magnetization; Coercivity; Zr-Cu substitution

1. Introduction
Nano-materials have become a very active research area in the field of material chemistry. The surface effect is mainly responsible for deviation of the properties of nano-materials from that of the bulk [1-2]. Recently, attention has been drawn toward ferrite nanomaterials because of their great scientific and technological importance. Fine particles of strontium hexaferrites are suitable for use in high density magnetic recording media. One factor that limits the performance of high density recording media is media noise which results from coupling between magnetic grains. It is generally believed that the grain interaction is less significant when the grain size becomes small. In high density recording media, magnetic grains of the size of <50 nm are desirable for obtaining a suitable signal-to-noise ratio [3]. The fine particles of ferrites sintered at low temperature are also required for multilayer chip inductors [4]. It also has applications in the field of telecommunication, microwave devices and as permanent magnets due to its perfect chemical stability and high uniaxial magnetocrystalline anisotropy [5-7].
The solid state reaction method is commonly used for the fabrication of strontium hexaferrites but it requires high annealing temperature of ~ 1200 °C and it is also not easy to obtain very fine and mono-dispersed particles [8]. Recently, several techniques such as glass crystallization [9], sol-gel [10], microemulsion [11], aerosol pyrolysis [12], hydrothermal [13] and chemical co-precipitation [14] have been developed to synthesize nanosized and mono-dispersed particles of strontium hexagonal ferrites for utilization in recording and microwave devices. Some of these methods are complex and expensive. Sol-gel and microemulsion methods use low annealing temperatures, yet a much longer annealing time (~5-10) hours is generally required [11,15]. The chemical co-precipitation method [14] ensures a proper distribution of various metal ions to produce stoichiometric and smaller size particles as compared to the others. It also requires an annealing time of only one hour in order to obtain a single phase.

Requisites for application of materials in the high density recording media are high values of saturation magnetization and remanence but low coercivity (600 Oe) [16]. The physical, electrical and magnetic properties of the M-type hexaferrites depend upon the occupation of the substituted cations at five different sites [17]. In M-type hexaferrites, 12 ferric ions are distributed over five distinct sites i.e. 2a, 2b, 4f1, 4f2 and 12 k: Out of these, 2a, 4f1 and 12k are octahedral, 4f2 is tetrahedral and 2b is a trigonal bi-pyramid [18]. It has been reported that the substitution of Ti4+ along with Ni2+ and Co2+ at octahedral sites occupied by Fe3+ ions results in an improvement of its magnetic properties for application in the magnetic recording media [19-21]. Unfortunately, the annealing temperature required for single phase formation by substitution of these elements is higher than that of the unsubstituted hexaferrite[22]. Zr4+ has a similar electronic configuration and is in the same group of the periodic table in the present study it has been chosen to replace Ti4+. Zirconium salts are relatively cheaper than those of titanium. In addition the Cu2+ has been selected to maintain the overall electroneutrality.

The aim of the present study is to synthesize nano-materials with large saturation magnetization and remanence and low coercivity. This paper presents the effect of the substitution of Zr-Cu and annealing temperature on the saturation magnetization (Ms), remanence (Mr) and coercivity (Hc) of Sr-hexaferrites.

2. Experimental Details

The chemicals used in the synthesis of samples were Fe(NO3)3·9H2O(Panreac Quimica SA, 98%), Sr(NO3)2 (Fluka, ≥ 99%), Cu(CH3COO)2·H2O (Merck, 99%), ZrOCl2·4H2O (BDH, 96%) and NaOH (Fluka, ≥ 97%). The strontium hexaferrites substituted with Zr–Cu and having nominal composition of SrZrₓCuₓFe₁₂₋₂ₓO₁₉ (where x = 0.0–0.8) were prepared by a chemical coprecipitation method [14]. The metallic salt solutions of required molarities were prepared in distilled water and mixed together. The solution mixture was heated up to 70 °C with continuous stirring. When the temperature of the solution reached 70 °C, the 2M NaOH was added drop wise to form a precipitate. The pH of the solution was kept in the range 12.5–13 during precipitation. All the samples were stirred for 3 hours in order to control the crystallite size and homogeneity of the samples. The precipitates were washed with distilled water, dried at 100 °C and annealed at an optimized temperature of 920 °C for 1h in a temperature-programmed tube furnace at a heating rate of 5 °C min⁻¹.

Transmission electron microscopy (TEM) analysis was carried out with a Jeol JEM-1200EX microscope. The hysteresis loops of the samples were recorded by the standard AC induction method [23] where the magnetic field H and the magnetic induction B were both measured through two coils placed near the sample. The values of the saturation magnetization (Ms), remanence (Mr) and coercivity (Hc) were calculated from the loops. The magnetic moments of all the samples were also calculated from the saturation magnetization data.
3. Results and discussion

XRD data show that the synthesized materials are in the magnetoplumbite hexagonal phase as already reported [24]. Figure 1a shows the particles in the TEM micrograph of the sample annealed at 920 °C for one hour are in the range of 40-70 nm. The particle sizes increase to 150-250 nm as the annealing temperature is increased to 1120 °C as shown in figure 1b.

![Fig. 1a](image1.png)  ![Fig. 1b](image2.png)

**Figure 1.** Transmission electron micrographs (TEM) of SrZr_{0.4}Cu_{0.4}Fe_{11.2}O_{19} annealed at (a) 920 °C and (b) 1120 °C.

Figure 2 shows the effect of annealing temperature on the saturation magnetization (M_s), remanence (M_r) and coercivity (H_c) of SrZr_{0.4}Cu_{0.4}Fe_{11.2}O_{19}. Higher values of saturation magnetization and remanence are obtained at the annealing temperature of 1393K while the value of coercivity decreases continuously with temperature. It is well known that particle size has a significant effect on the magnetic properties of the ferrite materials [7]. As the annealing temperature is increased, the particle size is increased to reach the critical single domain size and as a result the remanence (M_r) and saturation magnetization (M_s) increase reaching eventually a maximum value at the single domain size because of the coherent rotation of spins. As the particles become larger than the single domain size at higher temperature, the values of M_r and M_s decrease. The coercivity of the samples decreases with increasing annealing temperature due to an increase in their particle size. This is also complemented by the TEM micrograph (fig. 1b). The sample of larger particle size has low coercivity and vice versa.
Figure 2. Effect of annealing temperature on the saturation magnetization ($M_s$), remanence ($M_r$) and coercivity ($H_c$) of SrZr$_{0.4}$Cu$_{0.4}$Fe$_{11.2}$O$_{19}$.

Figure 3 shows the variation of the saturation magnetization, coercivity and remanence with the Zr-Cu contents. The saturation magnetization increases from a value of 71 kAm$^{-1}$ to 84 kAm$^{-1}$ when Zr-Cu contents, $x = 0.0$-0.4 (table 1). However, the coercivity decreases regularly from 137 kAm$^{-1}$ to 49 kAm$^{-1}$ (table 1) in the entire concentration range. The value of remanence remains almost constant up to the Zr-Cu concentration of $x = 0.4$ but decreases above this concentration. The variation in the magnetic properties can be explained on the basis of occupancy by the substituted ions at different sites in the hexagonal structure. It has been reported that the Cu$^{2+}$ occupies the 4f$^2$ (octahedral site) which has spin in the downward direction [25] and Zr$^{4+}$ occupies the site having spin in downward direction (4f$^1$) [26]. Both of these sites may contribute negatively to the total saturation magnetization of M-type hexaferrites. When both of the substituted ions replace the Fe$^{3+}$ ions in a site having downward spin, the total number of spin in the upward direction increases and as a result the total magnitude of the magnetic moment increases. Consequently, the saturation magnetization increases and the abrupt fall in the value saturation magnetization and remanence (above $x = 0.4$) may be due to the following reasons: 1) the presence of a number of nonmagnetic Zr$^{4+}$ ions and less magnetic Cu$^{2+}$ ions probably decreases the superexchange interaction between 4f$^1$-12k, 4f$^2$-12k and 4f$^1$-2a leading to a decrease in the saturation magnetization. 2) This abrupt fall in both the properties is due to the loss of magnetic collinearity leading to the spin canting. The observed decrease in coercivity is owing to a reduction in magnetocrystalline anisotropy.
In M-type hexaferrites the 12k, 4f$_2$ (octahedral) and 2b (trigonal bipyramidal) sites are known as major contributors to the magnetocrystalline anisotropy [27]. As mentioned above, Cu$^{2+}$ occupies the 4f$_2$ and has a negative impact on the magnetocrystalline anisotropy, so consequently the coercivity decreases. This is one of the few examples in which the saturation magnetization increases and at the same time the coercivity decreases. The decrease in coercivity and increase in saturation magnetization suggest that the synthesized materials are promising materials for application to high density recording media.

Table 1 Saturation magnetization ($M_s$), remanence ($M_r$), coercivity ($H_c$) and magnetic moment ($n_B$) for the SrZr$_x$Cu$_x$Fe$_{12-2x}$O$_{19}$ ($x = 0.0-0.8$).

| Parameters                  | $X = 0.0$ | $X = 0.2$ | $X = 0.4$ | $X = 0.6$ | $X = 0.8$ |
|-----------------------------|-----------|-----------|-----------|-----------|-----------|
| Saturation magnetization ($M_s$) kAm$^{-1}$ | 71        | 80        | 84        | 61        | 58        |
| Remanence ($M_r$) kAm$^{-1}$            | 56        | 54        | 55        | 38        | 32        |
| Coercivity ($H_c$) kAm$^{-1}$            | 137       | 109       | 101       | 61        | 49        |
| Magnetic moment ($n_B$) $\mu_B$          | 11.2      | 12.9      | 13.2      | 11.6      | 11.3      |
The magnetic moment ($n_B$) for all the samples has been calculated using the following equation.

$$n_B = \frac{M \cdot M_s}{5.585}$$  \hspace{1cm} (1)

where ‘M’ is the molar mass of the sample, ‘$M_s$’ the saturation magnetization and $d_b$ is the measured density of the sample. The magnetic moment increases with the substitution of Zr-Cu content up to a value of $x = 0.4$ as shown in figure 4. The variations of magnetic moment can be explained on the basis of saturation magnetization which also increases up to this substitution level. From equation 1, it is clear that the saturation magnetization is directly proportional to the magnetic moment.

4. Conclusion
We have used an economic and simple method for the synthesis of nano-sized strontium hexaferrites doped with Zr-Cu. The particle sizes are in the range 40-70 nm and 150-250 nm for the samples annealed for one hour at 920 °C and 1120 °C, respectively. The observed particle size is small enough to be used in the high density recording media to minimize the signal to noise ratio. The maximum saturation magnetization and remanence are observed at the annealing temperature of 1120 °C. Up to a substitution level of $x = 0.4$ the saturation magnetization increases while the remanence remains almost constant, but the coercivity decreases from 137 to 49 KAm$^{-1}$. This improvement in both properties suggests that the synthesized material is quite significant, and makes the synthesized materials suitable for application in the high density recording media.

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