



STRUCTURAL AND MAGNETIC PROPERTIES OF SN-ZR SUBSTITUTED CALCIUM NANO-HEXAFERRITE.

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ABSTRACT

The preparation of M-type nano hexaferrite particles with the composition $\text{Ca}(\text{SnZr})_x\text{Fe}_{12-2x}\text{O}_{19}$ ($x = 0.2, 0.4$) was prepared by sol-gel auto combustion method with urea as a fuel. The structural and magnetic characteristics have been studied by using X-ray diffractographs (XRD) and vibrating sample magnetometer (VSM). The morphological characterization was done by using transmission electron microscopy (TEM). TEM analysis revealed that the synthesized samples possess hexagonal platelet like structure with particle size much below than 100 nm and may exhibit promising magnetic properties. The XRD analysis indicated that the formation of single phase substituted M-type calcium hexagonal magnetoplumbite structure. The variation in lattice parameter and density with concentration of SnZr were studied, which showed an increasing trend while porosity showed a decreasing trend. The saturation magnetization (M_s) increases linearly with increasing doping content from 0.2 to 0.4. Coercivity slightly increases with x while Curie temperature (T_c) decreases linearly with increasing ' x '.

KEYWORDS M-type nanoferrites, auto combustion, saturation magnetization, XRD, coercivity etc.

1. INTRODUCTION

Calcium hexaferrite belongs to the family of M-type ferrites like $\text{BaFe}_{12}\text{O}_{19}$ and $\text{SrFe}_{12}\text{O}_{19}$ [1, 2]. The crystal structure and the chemistry of M-type hexaferrites are closely related to $\text{BaFe}_{18}\text{O}_{27}$ (W-type). The crystal structure of M-type hexaferrite can be described as an alternating stacking of spinel and R blocks in the direction of the hexagonal C axis. Among different ferrites such as spinel, garnet, and magnetoplumbite (M-type) ferrite, the M-type ferrite are very attractive magnetic materials due to their relatively large saturation magnetization, high coercivity and high uniaxial magnetic crystalline anisotropy, chemical stability, and corrosion resistivity. It can be therefore find wide industrial applications in electronic components, magnetic memories, magnets, and sensors [3]. Nano calcium hexaferrites are promising materials for data

storage media with high density magnetic recording applications [4]. It is well established that method of preparation, nature and concentration of dopants and their site preferences modify various magnetic properties. Extensive research is currently being carried out for new mixed valence, M-type hexagonal ferrites with desired physical and chemical properties. Substitution of Fe^{3+} ions with other ions such as Al [5], Sn [6], Cr [7], Co-Sn [8], Zn-Sn [9], Zn-Zr [10], Co-Ti [11] etc. have been studied. Besides different types of substitutions, in the present paper, structure and magnetic properties of Sn-Zr substituted CaM-type ferrite are reported with a view to study the effect of nonmagnetic substitution on the structural, electrical and magnetic behavior of ferrites.

2. EXPERIMENTAL

2.1. Synthesis of $\text{Ca}(\text{SnZr})_x\text{Fe}_{12-2x}\text{O}_{19}$ nanoparticles

The $\text{Ca}(\text{SnZr})_x\text{Fe}_{12-2x}\text{O}_{19}$ ($x = 0.2, 0.4$) particles were prepared via the sol-gel auto combustion method using nitrate salts [12]. According to the composition of $\text{Ca}(\text{SnZr})_x\text{Fe}_{12-2x}\text{O}_{19}$, the stoichiometric amounts of calcium nitrate, tin chloride, zirconyl nitrate and ferric nitrate were dissolved in the minimum amount of deionized water. Urea was used as fuel and dissolved into the solution to give a molar ratio of metal ions to urea of 1:1. Then the solution was heated on a magnetic hotplate at 70°C until a viscous gel was formed. The gel was put on the specially designed microwave oven, followed by an instantaneous gel ignition with the formation of large amount of gas. The resulting ‘‘precursor’’ powder was calcined at 800°C for 4 hrs to obtain $\text{Ca}(\text{SnZr})_x\text{Fe}_{12-2x}\text{O}_{19}$ nano-hexaferrite.

2.2. Sample's characterization

All prepared samples were identified by X-ray diffractometer (Bruker Advance X-ray diffractometer), while the lattice parameter was calculated using ‘‘XPowder-12’’ software. Morphology and particle's size of prepared nanoparticles were investigated using transmission electron microscope (TEM-CM200). The magnetic hystereses at room temperature for the compound were recorded using vibrating sample magnetometer (Lakeshore VSM 7410). Curie temperature and paramagnetic behaviour above T_c were studied using a Guoy balance.

3. RESULTS & DISCUSSION

The synthesized polycrystalline samples has been studied by the X-ray diffraction powder method and found to exhibit a hexagonal M-type symmetry (space group $P63/mmc$) with lattice parameters found to be within the range of $a = 5\text{-}6 \text{ \AA}$ and $c = 23\text{-}24 \text{ \AA}$. Typical X-ray diffraction pattern of the compound is shown in figure 1. All the reflections could be indexed well with the crystal cell of hexagonal ferrite. The structural data, viz. X-ray density, bulk density, porosity and particle size are included in table 1.

Table No. 1: The structural parameters of $\text{Ca}(\text{SnZr})_x\text{Fe}_{12-2x}\text{O}_{19}$ sample.

Co nc. (x)	a (Å)	c (Å)	Volum e (Å ³)	X-ray density (gm/cm ³)	Bulk densi ty (gm/cm ³)	Poro sity P(%)	c/a rati o
x = 0.2	5.8337	22.2126	655.767	5.236	3.397	35.12	3.81
x = 0.4	5.8492	22.2834	660.225	5.299	3.509	33.77	3.81

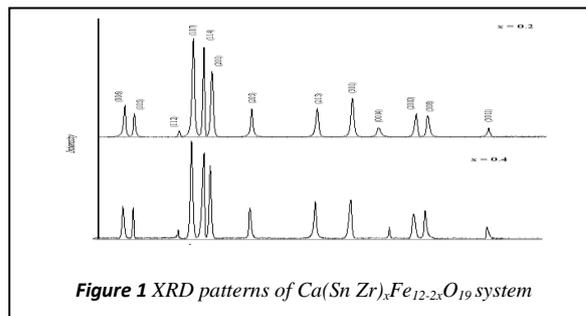


Figure 1 XRD patterns of $\text{Ca}(\text{SnZr})_x\text{Fe}_{12-2x}\text{O}_{19}$ system

However, the change in parameter ‘a’ is much less significant than in ‘c’ [Table 1]. The parameter ‘c’ increases by 1.328% from 22.2126 to 23.2834 Å. Nevertheless the $P63/mmc$ space group is maintained. The cell volume increases monotonically with increasing ‘x’ which may be due to the substitution of large Zr^{4+} (0.72 Å) and Sn^{2+} (0.69 Å) ions for Fe^{3+} ions (0.64 Å) [14, 15]. As reported earlier an examination of c/a parameters may be used to quantify the structure type [16]. The M-type hexagonal structure can be assumed if the observed ratio is lower than 3.98. In all our compounds this ratio falls below 3.98.

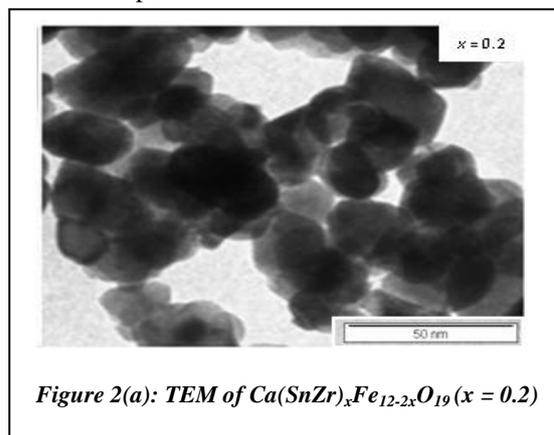


Figure 2(a): TEM of $\text{Ca}(\text{SnZr})_x\text{Fe}_{12-2x}\text{O}_{19}$ ($x = 0.2$)

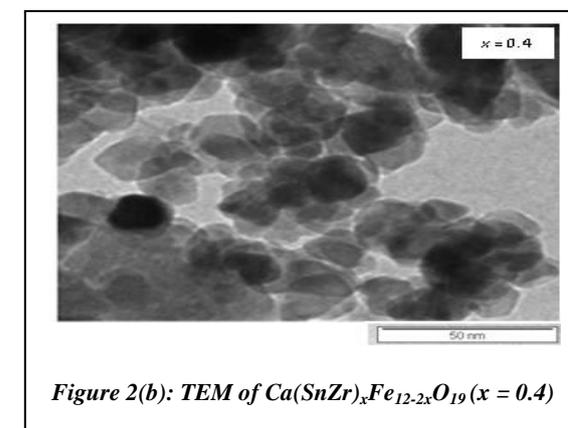


Figure 2(b): TEM of $\text{Ca}(\text{SnZr})_x\text{Fe}_{12-2x}\text{O}_{19}$ ($x = 0.4$)

The microstructure and morphology of the samples in sintered powder form were carried out using a Transmission Electron Microscopy (TEM).

Table No. 2: The magnetic parameters of Ca (Sn Zr)_xFe_{12-2x}O₁₉ sample.

Conc. (x)	Saturation magnetization M _s × 10 ⁻³ (emu/g)	Coercivity H _c (Gauss)	Curie Temperature (T _c)
x = 0.2	10.135	324.68	597 K
x = 0.4	12.298	598.37	588 K

Figures 2(a-b) show the TEM micrographs of calcium nano-hexaferrite Ca(SnZr)_xFe_{12-2x}O₁₉ samples for x = (0.2, 0.4). TEM images given in Fig. 2(a-b) show that Sn and Zr, Ca-doped nano-hexaferrites for x = (0.2, 0.4) resulted in the formation of hexagonal platelet structure with average size of 24 and 21 nm respectively. The grain size for x = 0.2 sample appears to be larger than that of the x = 0.4 sample as shown in figure. The grain size of the substituted samples was reduced with increase in Sn-Zr doping. The surface of the samples exhibits a mixture of individual nanoparticles. The aggregates of small size formed due to agglomeration of these particles.

The magnetization curves of different powders of Sn-Zr doped Ca hexaferrites were measured on a VSM at room temperature under an applied field of 15 KG. Hysteresis loops in Fig. 3(a) and (b) show that substituted samples exhibit increase in magnetization at low applied field which slows down at high field. It becomes clear that saturation magnetization increases with Sn-Zr ions substitution. The increase in coercivity because of reduction in the grain size with Sn-Zr substitution as the doping results in inhibiting of the grain growth and would give rise to the enhancement of magneto-crystalline anisotropy [17]. The increase in coercivity with calcium (Ca²⁺) substitution could be an intrinsic effect associated with an increase in the magnetocrystalline anisotropy or an extrinsic effect associated with the microstructure or a combination of both. The increase in coercivity (H_c) might be attributed to an enhancement of the magnetocrystalline anisotropy due to reduction of particle size. The higher coercivity values in this study may be because of the low calcination temperature, which kept the grain size small [19]. The longitudinal magnetic recording media requires high enough

coercivity (600 G). Hence, the synthesized nanomaterials may be suitable for applications in the recording media. The Curie temperature (T_c) was found to be decreasing with increase in the concentration of Sn-Zr in calcium hexaferrite. The dip observed is in the vicinity of the Curie temperature, contributed to the change in spin arrangement in ferrimagnetic compound at the Curie temperature below which magnetic ordering sets in.

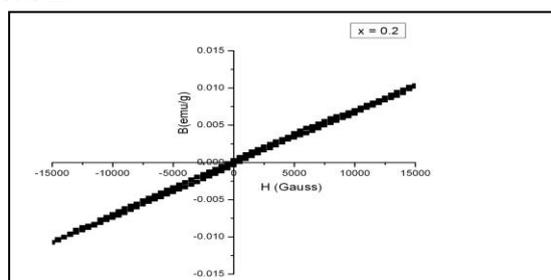


Figure 3(a): Hysteresis loops of Ca(SnZr)_xFe_{12-2x}O₁₉ (x = 0.2)

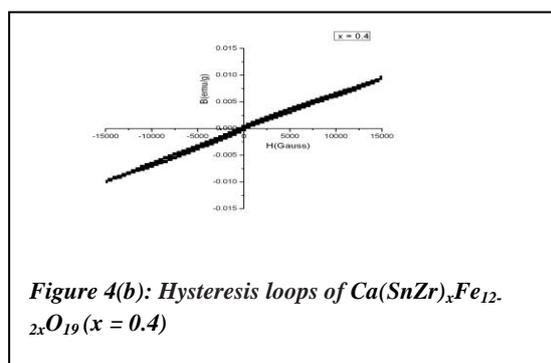


Figure 4(b): Hysteresis loops of Ca(SnZr)_xFe_{12-2x}O₁₉ (x = 0.4)

4. CONCLUSIONS

A series of morphologically pure Sn-Zr doped nanoscale ferrites of the composition Ca(SnZr)_xFe_{12-2x}O₁₉ have been successfully synthesized by applying sol-gel method at a temperature of 800^oC. The TEM of the sample shows average particle size is found to be in nanorange. The reduction of particle size of hexaferrites to nanorange helps to improve many magnetic properties. The magnetization increases with increasing the concentration of Sn-Zr content, and hence the superexchange interaction between Fe³⁺ and O²⁻ ions also increases. The coercivity of the samples is found to be in the range of 328 G to 598 G, and the enhancement in coercivity is because of increase in the magnetocrystalline anisotropy. These materials can be useful for the applications in high-density recording media.

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