Nanocrystalline Zirconium-Cobalt Substituted Calcium Ferrite in Data Storage Device

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Abstract:

Nano-size M-type hexaferrite $Ca(Zr-Co)_xFe_{12-2x}O_{19}$ (x=0, 0.5) powders are synthesized by the 'Microwave induced sol-gel combustion route'. Lattice parameters a=5.807-5.825Å, c=21.582-22.124Å are calculated using X-ray diffraction data confirms the hexagonal crystal structure. The Reitveld refinement of the X-ray diffraction data is done which confirms the formation of hexagonal crystal structure. TEM micrograph of the sample shows that the particles have an average particle size of 50nm. Magnetic properties of the sample saturation magnetization (Ms), the remnant magnetization (Mr) and the coercivity (Hc) are measured using vibrating sample magnetometer (VSM).The values found to decrease with increase in the degree of substitution of cations which can be attributed to different site preferences of substituted cations in parent hexaferrite.

Keywords: Calcium hexaferrites; Microwave induced; B-H curve; Coercivity heard

1. Introduction

M-type hexaferrites have large intrinsic magnetic anisotropy field and the variation of this field can be controlled by substituting Ba^{2+} and Fe^{3+} ions by extrinsic metallic cations. Darokar et. al [1] studied Lithium hexaferrites by substituting single trivalent ion Al^{3+} and Co^{3+} for Fe^{3+}. Wang et al. [2] hydrothermally synthesized Sr hexaferrites doped with suitable amount of Sm^{3+}. M. Rane et. al [3] had done comparative study of the divalent-tetravalent Co^{2+}-Zr^{4+} substituted barium hexaferrites with that of Co^{2+}-Ti^{4+} and Co^{2+}-Sn^{4+} hexaferrite systems. Teh et al. [4] synthesized the Barium Ferrite substituted with the Co^{2+}-Ti^{4+} by sol gel combustion route. According to M. R. Meshram et. al. [5] barium hexaferrites doped with stoichiometric proportion of Co^{2+}-Ti^{4+}-Mn^{2+} can act as RAM (Radar Absorbing Material). Tehrani et al [6] synthesized Mg^{2+}-Mn^{2+}-Co^{2+}-Ti^{4+} substituted Barium hexaferrite. It has been observed that $Ba^{2+}/Sr^{2+}/Pb^{2+}/La^{2+}$ M-type hexaferrite structures have been explored more as compared Ca^{2+} in parent base $AFe_{12}O_{19}$. Hence an attempt is made to synthesize and to study magnetic properties of Co^{2+}-Zr^{4+} doped calcium hexaferrites. The symmetry of magnetoplumbite structure is hexagonal. The ordering of the magnetic moments of the ferric ions and the strong super exchange interactions explain the magnetic behavior of this material.

2. Experimental procedure

The large number of preparation methods like solid state method, co-precipitation, hydro-thermal synthesis, aerosol pyrolysis, etc has been reported earlier for the synthesis of ferrites[7,8,9]. The known sol-gel combustion technique has many advantages to synthesis of substituted magnetoplumbites by virtue of simplicity in

operation, low anneal or calcine temperature, short reaction rate [10]. In addition, sol-gel combustion route gives ultra fine powder of nanoparticles with better particle size distribution, excellent chemical homogeneity and probability of forming single domain structure. The present system of calcium hexaferrite is synthesized by 'Microwave induced sol-gel combustion route' where the conventional furnace used for combustion is replaced by microwave oven which insures the uniform heating of the sample during combustion process.

M-type CaM hexaferrites with generic formula $Ca(Zr-Co)xFe_{12-2x}O_{19}$ are synthesized taking stoichiometric amounts of reactive nitrates $Ca(NO_3)_2$, $Fe(NO_3)_2.9H_2O$, $Co(NO_3)_2.6H_2O$, $ZrO(NO_3)_2.H_2O$. The nitrates are dissolved completely into 50 ml deionized distilled water at 50^oC for 15-20 min to obtain aqueous solution. Urea is used as fuel which gives required energy to initiate exothermic reaction. The viscous gel produced is then kept for an hour in the room temperature and then the combustion is carried in microwave oven for 15-20 min. The combustion takes place in self-propagating manner and the gel gets converted into reddish-brown voluminous fluffy porous product which will then crushed to get fine homogeneous powder. The powder is then sintered by giving moderate heat treatments. The sintering is done at 800^oC for 2 hours by sequentially increasing and decreasing temperature at the rate of $4^oC/min$ to remove unwanted traces if present.

Structural characterization is carried out by X-ray diffraction (XRD) using , Philips X'pert Diffractometer and Cu Kα radiation with wavelength λ=1.542 Å. Lattice Parameters a,c are calculated. Transmission Electron Microscope (TEM), Philips CM200 used to observe the particle size and particle shape of the synthesized powders.

The magnetic properties of the series $Ca(Zr-Co)_xFe_{12-2x}O_{19}$ are carried out at room temperature using vibrating sample magnetometer (VSM) Lakeshore 665. From the obtained B-H hysteresis curves, the saturation magnetization (M_s), remnant magnetization (M_r) and coercivity (H_c) are determined.

3. Result and Discussion

3.1 X-ray Diffraction:

Fig. 1 shows the Reitveld analyzed X-ray powder diffraction patterns for the ferrites synthesized $CaFe_{12-2x}(ZrCo)_xO_{19}$ with (x = 0,0.5). Prominent sharp peaks indicate the crystalline nature. By comparing the patterns with JCPDS the space group for the samples is observed to be P63/mmc (No. 194). Matching of the peaks confirms the formation of single phase magnetoplumbite which can also be attributed to the replacement of Fe^{3+} ions by cations Co^{2+} and Zr^{4+}. These observations are attributed to the occupation of crystallographic sites of Fe^{3+} ions by substituted ions [6]. Lattice parameters *a* and *c* are calculated by indexing these patterns. The value of *a* is found to vary between 5.807Å to 5.825Å and that of *c* in between 21.582 Å to 22.124Å, which confirms the formation of hexagonal unit cell. The value of lattice parameter *c* changes significantly by 22.124-21.582 =0.542Å as compared to the value of *a* 5.825-5.807= 0.018Å , which indicates that the *c-axis* may be the easy axis of magnetization [11].
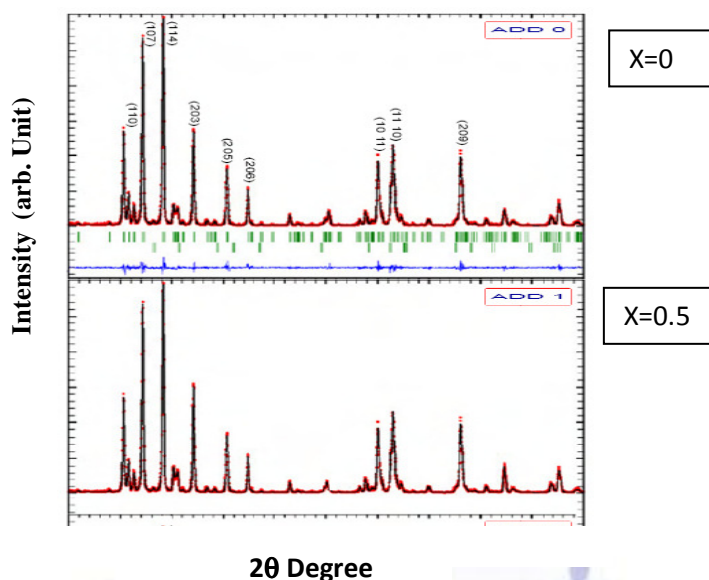
2θ Degree

Fig. 1 : Reitveld analysized X-ray diffraction pattern of Zr –Co substituted calcium hexaferrite.

3.2 TEM analysis: Fig. 2 shows the TEM image of the samples. Micrograph shows morphological homogeneity showing hexagonal platelet like structure with prominent grain boundaries. TEM image of the samples are taken at 50nm which gives an idea about the particle size, which confirms the nanosize formation of calcium hexaferrite particles.
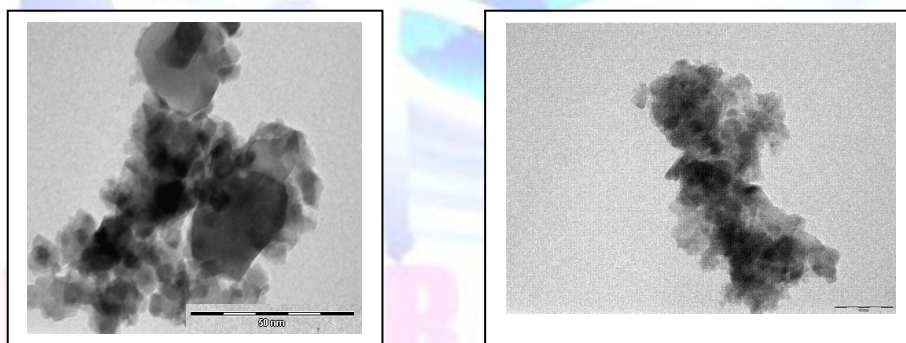

Fig. 2: TEM micrograph of Zr –Co substituted calcium hexaferrite

3.3 Magnetic Properties:

The method of synthesis of the samples and substitution level decides the occupancy of the sites [12]. Magnetic behavior of the samples is strongly governed by the site occupancy by the substituted ions in the parent hexaferite. The magnetic hysteresis loop measurements of the series $Ca(ZrCo)_xFe_{12-2x}O_{19}$ with (x = 0,0.5) is shown in Fig. 3. Figure shows the magnetization of the material in the presence of external applied magnetic field. Table 1 depicts the values of magnetic parameters of these compounds obtained from the data of Fig. 3. Values of saturation magnetization M_s, remnant magnetization M_r and coercivity H_c are found to decrease with the increasing degree of substitution of cations. Decrease in the values of M_s, M_r with increase in values of x is attributed to the substitution of diamagnetic Co^{2+} ions not only into the spin-down

sublattices $4f_1$ of Fe^{3+} ions but also into other octahedral spin-up sublattices 12k, 2a and 2b. The decrease in the value of coercivity, H_c with increase in the value of x is due to lowering of magneto crystalline anisotropy. Tetravalent Zr^{4+} has strong preference for octahedral spin-up sites whereas divalent Co^{2+} prefers tetrahedral spin-down sites [13]. From Fig. 3 the area under magnetic hysteresis loop observe to decrease with increase in substitution level which indicates that the ferrites become soft with increasing degree of substitution, such nature of the material is more suitable information storage recording media.
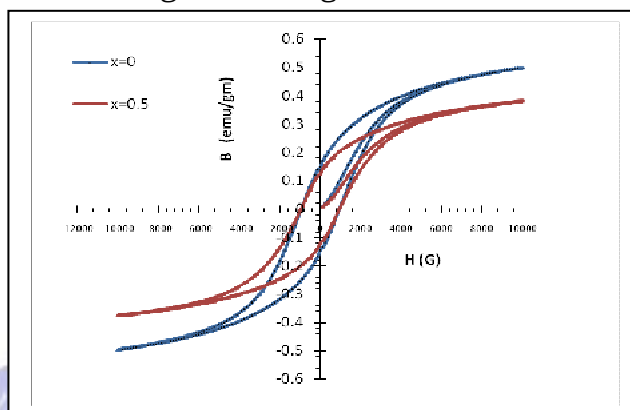

Fig. 3: B-H curves of Zr –Co substituted calcium hexaferrite at 300K

Conclusions

Microwave induced sol-gel combustion route is found to be useful to synthesis Co^{2+} and Zr^{4+} substituted nanosize calcium hexaferrites. The X-ray diffraction studies confirm the formation of hexaferrites. The values of lattice parameters a and c supports this. Reitveld analysis studies have confirmed the space group of samples to be $P6_3/mmc$. From TEM images of the sample, average particle size is found to be in nanorange. Decrease of area under magnetic hysteresis loop indicates the ferrites become soft with substitution. Hysteresis curves of the samples depicts that with small value of coercivity and comparatively good values of saturation magnetization indicating these samples are more useful as storage devices , particularly information storage recording media. Also the system of $Ca(Zr-Co)_xFe_{12-2x}O_{19}$ with small incremental substitution value between x=0 to x=0.5 should further be studied to obtain hexaferrites with low coercivity accompanied with better value of saturation magnetization.

Table 1: Lattice parameters (a, c), saturation magnetization (M_s), remenance (M_r) and coercivity (H_c) of the samples

Crystallographic parameters			Magnetic parameters		
Sample	a (Å)	c (Å)	M_s (emu/gm)	M_r (emu/gm)	H_c (G)
$CaFe_{12}O_{19}$	5.807	21.582	0.4975	0.1495	875
$Ca(Zr-Co)_{0.5}Fe_{11}O_{19}$	5.825	22.124	0.3805	0.1245	742

4. References

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