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Structural and Magnetic Hysteresis Properties of Co-Zr Substituted Hexagonal Barium Ferrites

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ABSTRACT

Co-Zr substituted M-type hexagonal barium ferrites, with chemical formula $BaCo_xZr_xFe_{12-2x}O_{19}$ (where x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0), have been synthesized by double sintering ceramic method. The crystallographic properties, grain morphology and magnetic properties of these ferrites have been investigated by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Vibrating Sample Magnetometer (VSM). The XRD patterns confirm the single phase with hexagonal structure of prepared ferrites. The magnetic properties have been investigated as a function of Co and Zr ion composition at an applied field in the range of 20 KOe. These studies indicate that the saturation magnetization (M_s) in the samples increases initially up to the Co-Zr composition of x=0.6 and decreases thereafter. On the other hand, the coercivity (H_c) and Remanent magnetization (M_r) are found to decrease continuously with increasing Co-Zr content. This property is most useful in permanent magnetic recording. The observed results are explained on the basis of site occupation of Co and Zr ions in the samples.

KEYWORDS

Barium ferrites; Magnetic properties; Saturation Magnetization; and Coercivity.

1. INTRODUCTION

The M-type $BaFe_{12}O_{19}$ (BaM) is a hard ferrite with hexagonal magneto-plumbite structure belonging to space group $P6_3/mmc$. It is an important kind of permanent magnetic material due to its high saturation magnetization (M_s), great coercivity (H_c), high magneto crystalline anisotropy and excellent chemical stability [1]. In order to further improve the intrinsic magnetic properties of BaM, different cationic substitutions for Fe^{3+} ions are studied. When various combinations such as Co-Sn, Mn-Sn, Zn-Ti, Co-Ti, etc. are substituted for Fe^{3+} in M-type Ba-ferrite, the coercivity was found to reduce significantly with some small change in saturation magnetization [1,2,3]. These properties make the compounds useful in high density and perpendicular magnetic recording [4]. It is therefore important to understand the origin of property changes when these codoped type substitutions are made for iron ions in Ba-ferrite.

In the present investigation, a series of BaM hexagonal ferrite samples substituted with divalent Co^{2+} ions and tetravalent Zr^{4+} ions for Fe^{3+} ions are prepared by conventional double sintering method. The effects of these substitutions on the crystallographic and intrinsic magnetic hysteresis properties of BaM ferrites are presented in this paper.

2. STRUCTURAL STUDIES

BaM hexagonal ferrites codoped with Co^{2+} and Zr^{4+} (Ba-Co-Zr) having the compositional formula $BaCo_xZr_xFe_{12-2x}O_{19}$ (where x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) were prepared by conventional double sintering technique. The samples were pre-sintered at 1000^oC for 10 hrs and final sintering was carried out at 1250^oC for 15 hrs, the sintering atmosphere being air.

X-ray diffraction patterns for all the Ba-Co-Zr hexagonal ferrites under investigation have been obtained using Co Kα radiation with $\lambda = 1.7902$ A^0. Fig.1 shows the X-ray diffraction patterns for Ba-Co-Zr hexagonal ferrites. The diffraction patterns confirm the presence of single phase M-type hexa ferrite phase structure. The lattice parameters of the mixed ferrites were calculated from d-spacing and are given in Table 1. It can be seen from the table that the values of lattice parameters, a & c, continuously increase with the increase of Co and Zr concentrations. This can be expected in view of the fact that the ionic radii of 0.82 A^o for the Co^{2+} ions and 0.84 A^o for the Zr^{4+} ions are larger than that of 0.64 A^o for the Fe^{3+} ions.

The porosity values of the synthesized samples are calculated by using the formula $P=(1-d/d_x)x100$, where d is the bulk density and d_x is the x-ray density. The obtained porosity values are given in Table.1. The decrease in porosity indicates that the substituted ions may have causing the densification of the barium hexaferrite matrix. It can be seen that the x-ray density is increasing with increasing content of Co^{2+} and Zr^{4+} in the BaM ferrite. This may be due to the larger ionic sizes of substituents when compared to that of Fe^{3+} ion. Further, the values of bulk density are smaller than the corresponding values of x-ray density. This can be attributed to the existence of pores in the samples.

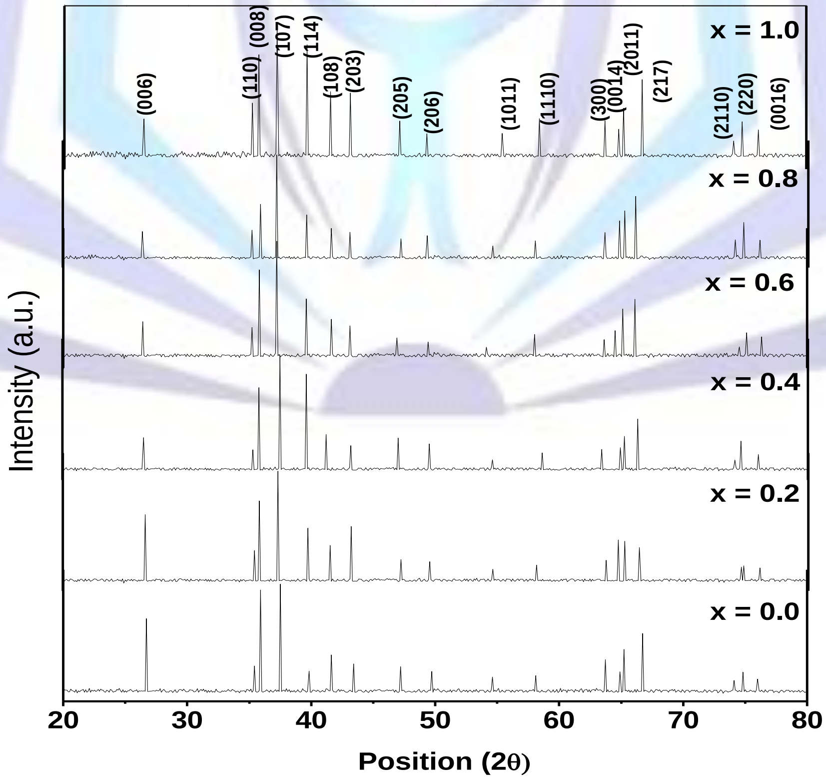


Fig. 1: X-ray diffraction patterns of BaCo$_x$Zr$_x$Fe$_{12-}$2xO19 hexaferrites

(with x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0).

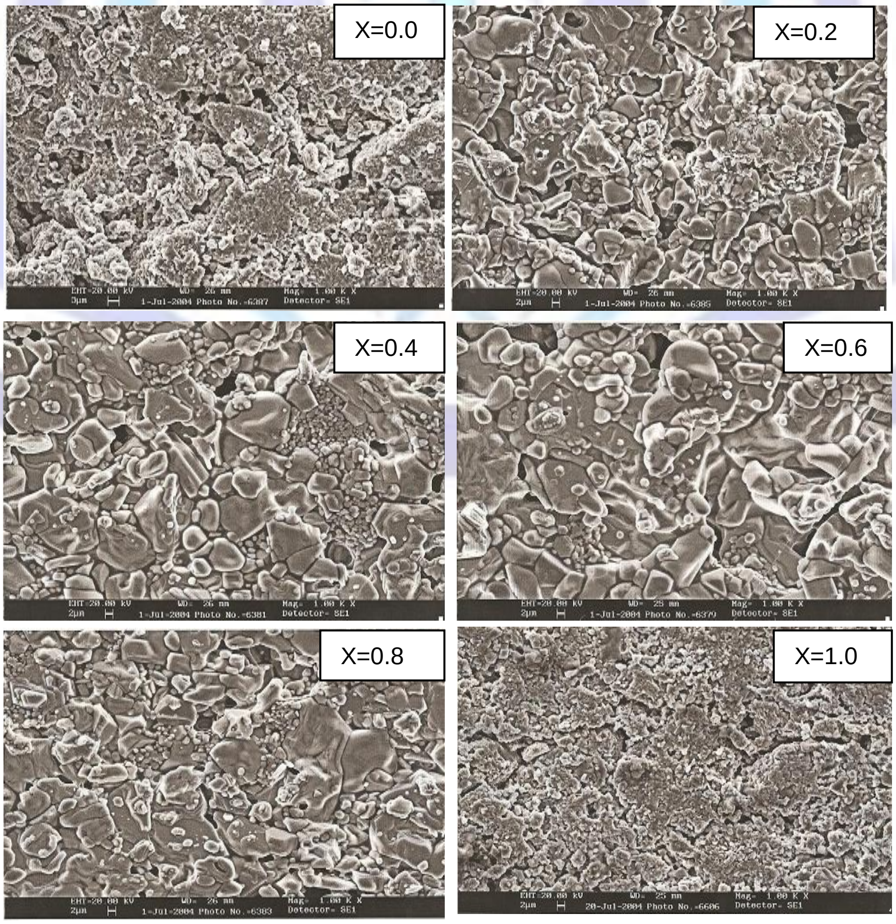
Table 1: Lattice parameters, porosity values, etc. of Ba-Co-Zr hexagonal ferrites

Sl. No.	Ferrite composition	$a(A^0)$	$c(A^0)$	X-ray density (g/cm^3)	Bulk density (g/cm^3)	Porosity (%)	Grain Size (μm)
1	$BaFe_{12}O_{19}$	5.890	23.208	5.271	4.544	14	5
2	$BaCo_{0.2}Zr_{0.2}Fe_{11.6}O_{19}$	5.891	23.213	5.285	4.653	12	6
3	$BaCo_{0.4}Zr_{0.4}Fe_{11.2}O_{19}$	5.893	23.224	5.322	4.896	8	8
4	$BaCo_{0.6}Zr_{0.6}Fe_{10.8}O_{19}$	5.897	23.243	5.336	4.962	7	10
5	$BaCo_{0.8}Zr_{0.8}Fe_{10.4}O_{19}$	5.903	23.267	5.348	5.012	6	7
6	$BaCo_{1.0}Zr_{1.0}Fe_{10}O_{19}$	5.905	23.271	5.426	5.127	5	4

Fig.2 shows the SEM micrographs of Ba-Co-Zr hexa ferrites. These micrographs are obtained by using LEO-440I model Scanning Electron Microscope instrument. It can be seen from the micrographs that the morphology of particles is similar and they are largely agglomerated. The average grain sizes of the samples calculated from line intercept method from SEM micrographs is in the range of 4 to 10 μm (Table 1). It can be seen that with the increase of Co-Zr doping up to x=0.6, the average grain size for all the samples increases and with further increase of x, the grain size decreased.

3. MAGNETIC HYSTERESIS STUDIES

The magnetic measurements were carried out by using vibrating sample magnetometer (VSM) with an applied field in the range of 20 kOe. From vibrating sample magnetometer data, M-H hysteresis loops are drawn which are shown in the Figs.3. The observed saturation magnetization (M_s), remanent magnetization (M_r) and coercive field (H_c) are tabulated in Table 2. It is observed that saturation magnetization increased gradually from 57.57 emu/gm to 63.84 emu/gm as Co-Zr composition is increased from x = 0.0 to 0.6 and then decreased from 63.84 emu/gm to 47.00 emu/gm for x=0.6 to x=1.0. The magnetization value for pure hexaferrite is 57.57 emu/gm which is lower than the theoretical value of 72 emu/gm, calculated for single crystal of $BaFe_{12}O_{19}$ [5]. This difference may be attributed to the sintering conditions and large grain sizes [6].



Figs. 2: SEM micrographs of $BaCo_xZr_xFe_{12-2x}O_{19}$ hexaferrite samples

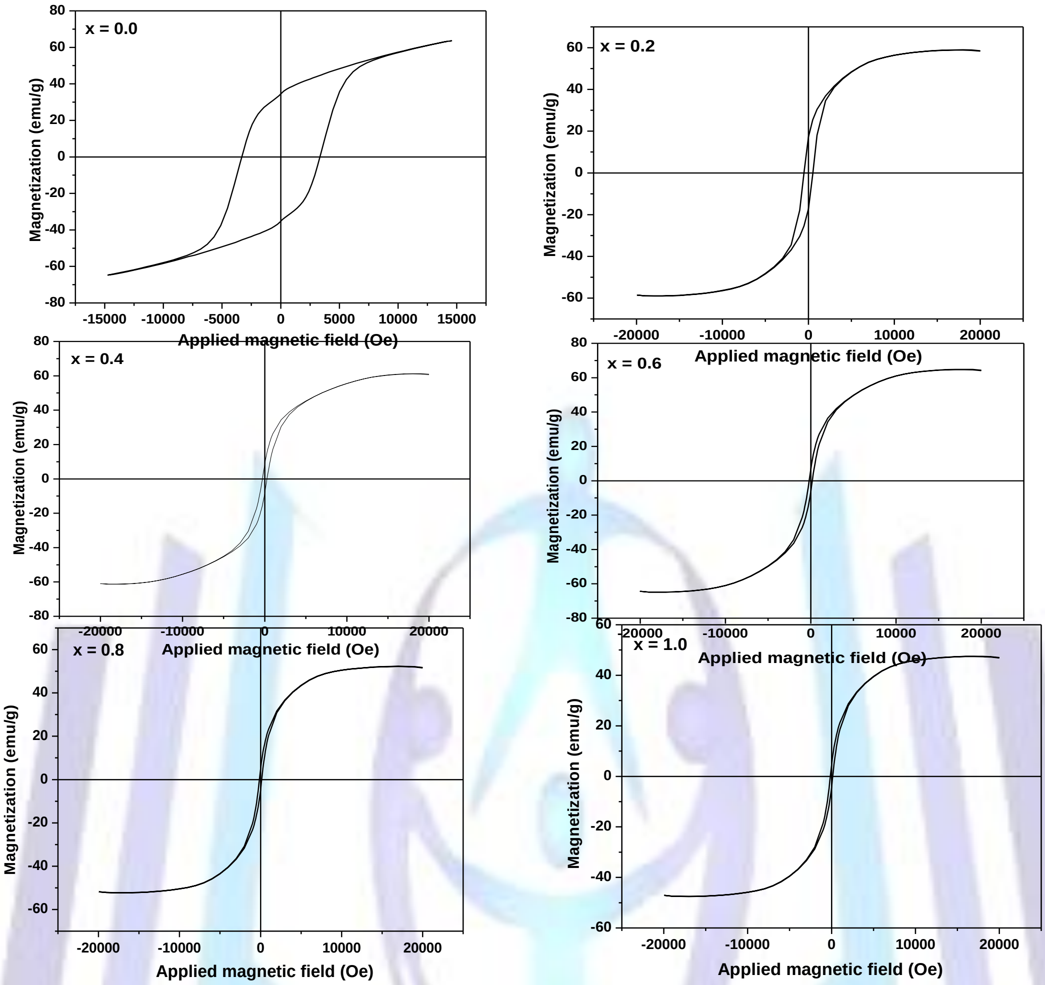


Fig.3: Hysteresis loops of $BaCo_xZr_xFe_{12-2x}O_{19}$ hexaferrite samples

Table 2: Magnetic parameters of $BaCo_xZr_xFe_{12-2x}O_{19}$ hexaferrites.

S.No.	Composition (x%)	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
1	0.0	57.57	34.43	3250
2	0.2	57.59	17.76	540
3	0.4	59.54	13.65	313
4	0.6	63.84	10.51	227
5	0.8	52.09	4.86	140
6	1.0	47.00	4.05	133

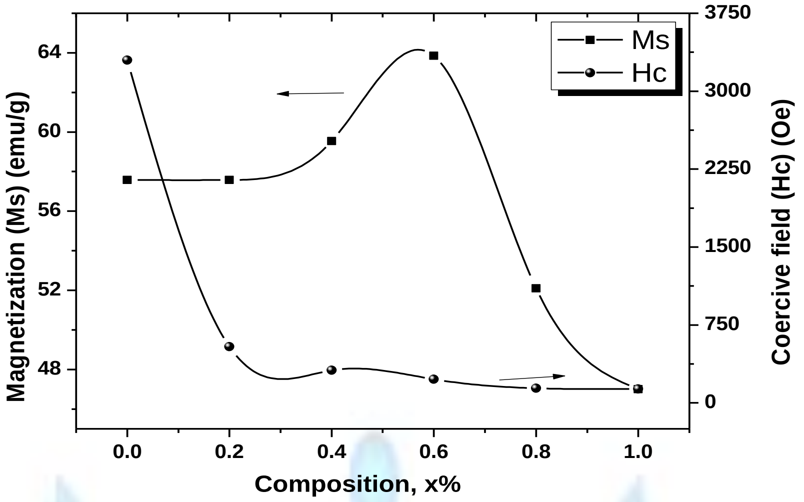


Fig.4: The variation of M_s and H_c of $BaCo_xZr_xFe_{12-2x}O_{19}$ hexaferrites as a function of Co-Zr composition.

There are two $BaFe_{12}O_{19}$ units in M-type barium hexa ferrite unit cell and in this 24 Fe^{3+} ions are distributed over five different types of 24 interstitial sites. These interstitial sites are 2a, 12k and $4f_2$, which are octahedral type; $4f_1$, which is tetrahedral type and 2b, which is trigonal bipyramidal type. Super exchange interactions through O^{2-} ions make the magnetic spins of Fe^{3+} at $4f_1$ and $4f_2$ opposite to those at 2b, 2a and 12k [1]. The total magnetic moment of each $BaFe_{12}O_{19}$ unit comes from the contribution of one each Fe^{3+} ion at 2a and 2b sites and six Fe^{3+} ions at 12k sites, thus making total eight magnetic spins in one direction; and two each Fe^{3+} ions at $4f_1$ and $4f_2$ sites, thus giving four in the opposite direction. Therefore the total magnetic moment of one unit of $BaFe_{12}O_{19}$ becomes (8-4) x $5\mu_B$ = 20 μ_B, wherein 5 μ_B is the magnetic moment of each Fe^{3+} ion.

Fig.4 shows the variation of saturation magnetization and coercivity with Co-Zr composition in $BaCo_xZr_xFe_{12-2x}O_{19}$ ferrites. The saturation magnetization shows a maximum value of 63.84 emu/gm for the Co-Zr concentration of x=0.6 and decreased thereafter. However, the coercivity is found to decrease regularly from 3250 Oe to 133 Oe as Co-Zr composition is increased. From this, it can be concluded that the hard ferrite is becoming softer as more and more Fe^{3+} in BaM ferrite is replaced by relatively less magnetic Co^{2+} and Zr^{4+} ions [7]. The variation in the magnetic properties can be explained on the basis of occupancy by the substituted ions at different sites in the M-type hexagonal structure of BaM ferrite. It has been reported earlier that Co^{2+} ions have preferential occupancy of $4f_1$ and $4f_2$ sites [8] and Zr^{4+} shows preference to occupy both tetrahedral and octahedral sites for lower concentrations and octahedral sites for higher substitutions [9]. Thus when both the substituted ions replace the Fe^{3+} ions in a site having the spin in downward direction, the total number of spins in the upward direction increase, since the magnetic moment of Co^{2+} ion with d^7 configuration is 3 μ_B and that of Zr^{4+} with p^6 configuration is 0 μ_B, whereas that of Fe^{3+} is 5 μ_B. As a result of this, the total magnitude of the magnetic moment increases initially. The decrease in saturation magnetization above the composition of x=0.6 may be due to the following reasons: i) The presence of a number of non-magnetic Zr^{4+} ions and less magnetic Co^{2+} ions probably decreases the super exchange interaction between various sites leading to a decrease in the saturation magnetization, and ii) there will be a loss of magnetic collinearity leading to spin canting [10].

It can be seen from Fig.4 that the coercive field (H_c) decreased continuously with Co-Zr composition. According to Stoner-Wohlfarth theory [11], the magnetic anisotropy constant (K) can be determined from saturation magnetization (M_s), coercive field (H_c) and permeability of free space, μ_0 (4π X 10^{-7} H/m) as $K = \mu_0 M_s H_c/2$. As per this, to obtain a high coercivity the sample should possess a large K values. In M-type hexaferrites, the 12k, $4f_2$ (octahedral) and 2b (trigonal bipyramidal) sites are known as major contributors to the magnetocrystalline anisotropy [12]. As mentioned earlier, the Co^{2+} and Zr^{4+} ions have preference to occupy these sites resulting in a negative impact on the magnetocrystalline anisotropy. It has also been reported earlier that Co-Ti and Co-Ir substitution can modify the anisotropy from uniaxial to planar for M-type ferrites [13, 14]. In the present case, it seems reasonable to assume that the substitution of Co^{2+} and Zr^{4+} ions in BaM ferrites contribute preferentially to planar anisotropy, which results in the decrease of H_c values as x increases. Another reason for the reduction in coercivity is extrinsic effect which is associated with intergranular pores. The SEM micrographs show the existence of these pores in the samples substituted with different compositions of Co^{2+} and Zr^{4+} ions. These pores act as non-magnetic inclusions and offer hindrance to the flow of applied field across the grains [15]. As can be seen from Table.1, the porosity is decreasing with increasing content of Co^{2+} and Zr^{4+} ions in BaM ferrite. When the porosity decreases, the applied field required to demagnetize the ferrite also decreases and therefore, the coercivity decreases. This affirms that porosity strongly affects coercivity [16].

Remanent magnetization (M_r) or residual magnetization is the remaining magnetic field M of a magnetic material, when the magnetizing force is reduced to zero after the material is saturated. It can be seen that the remanent magnetization decreased continuously from 34.43 emu/gm to 4.05 emu/gm as Zr^{+4} and Co^{2+} composition increased from x = 0.0 to x = 1.0. This can again be attributed to the substitution of less magnetic Co and Zr ions for relatively more magnetic Fe ions in BaM ferrite. Similar variation is reported elsewhere for Zr-Cu substitution in SrM ferrites [10].

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