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Effect of Ho^{3+} substitutions on the structural and magnetic properties of $BaFe_{12}O_{19}$ hexaferrites

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ABSTRACT

Holmium doped barium based hexaferrites $BaFe_{12-2x}Ho_{2x}O_{19}$ with ($x = 0.0$–1.0) were synthesized by solid state reaction method. Structural and magnetic characterization of these ferrites provide significant information about their reactive physical properties. X-ray analysis reveals that in all samples M-type structure exist with few secondary phases. Scanning electron microscope revealed the grain size of the specimen. The results show that grain size decreases with the substitution degree of Holmium. Thus rare earth element Holmium Ho^{3+} acts as a grain growth inhibitor. The magnetic hysteresis loops show the variation in the values of magnetic parameters like saturation magnetization (M_s), remanent magnetization (M_r) and coercivity (H_c) were observed by changing Ho^{3+} content in $BaFe_{12-2x}Ho_{2x}O_{19}$ ferrites. Coercivity showed a maximum value of 2230 Oe for ($x = 0.4$) and then decreasing trend were observed in the values of H_c, M_r and M_s with the increasing substitution degree of rare earth element Holmium.

1. Introduction

In permanent magnetic area M-type barium hexaferrites materials possess relatively high saturation magnetization great coercive force as well as excellent chemical stability and corrosion resistance [1]. They have been widely used as traditional permanent magnets, high density magnetic and magneto-optic recording media, microwave filters, and microwave absorbing materials [2,3].

The hexaferrites have wide applications in a variety of electronic devices such as electric power generation, automotive electronics, MEMS, rotors in small DC motors microwave devices and ferrite cores [4,5]. The basic compound of barium hexaferrites has the chemical composition $BaFe_{12}O_{19}$ and a complex magneto-plumbite structure. The $BaFe_{12}O_{19}$ unit cell is a combination of two structural blocks aligned in the direction of hexagonal *c*-axis: RSR*S* (* indicates the 180° rotation of the structural block with respect to the *c*-axis). The S block has a spinel structure with cubic closed-packed 'O' ions and 'Fe' ions on its tetrahedral and octahedral sites. The 'R' block is formed of hexagonally closed-packed 'O' ions and one 'Ba' ion. Fe ions occupy the interstitial, tetrahedral, octahedral and bipyramidal sites.

The main intrinsic magnetic properties, the saturation magnetization results from the specific site occupancy of the magnetic 'Fe' ions. Magnetic properties can be varied by substituting the Fe ions with another substitution [6], to tailor the magnetic properties of the barium hexaferrites, Fe^{3+} ions are partially substituted by various di-, tri-, and tetravalent ions, aiming to occupy the spin down sites and, consequently, to increase the net magnetization [7].

In this research work solid state reaction method were used for the fabrication of barium based hexaferrites. The sites occupied by Fe ions were replaced by rare earth elements Holmium. The substitution of rare earth elements showed a variation in structural and magnetic properties. In these studies, it was observed that partial replacement of Fe ions with Ho^{3+} increases the magnetic properties.

2. Experimental

Ceramic method involves solid state reaction of metal oxides of required ferrite.

Samples of $BaFe_{12-2x}Ho_{2x}O_{19}$ with ($x = 0.0$–1.0) were synthesized using this technique. A mixture of $BaCO_3$, Fe_2O_3, Ho_2O_3 in the form of grained powder having 99.9% purity supplied by GmmH (E. MERK, Germany) were mixed. The appropriate composition of each sample was calculated in terms of weight percentage according to the following chemical reaction:

$$BaCO_3 + xHo_2O_3 + (6-x)Fe_2O_3 \rightarrow BaFe_{12-2x}Ho_{2x}O_{19} + CO_2$$

This mixture of corresponding metal oxides (Fe_2O_3 and Ho_2O_3) or carbonate ($BaCO_3$) in the proper ratio for each sample were crushed to fine powder in an agate mortar and pestle for about 2 h till a homogeneous mixture was obtained. The ground mixtures were left to dry for a night and again the mixture was crushed for half an hour. The homogenized mixture of each sample was calcined in air at 900 °C for an hour in digital electronic furnace that had a continuous temperature increases up to 900 °C then the furnace switched off automatically and slowly cooled down to room temperature. Then calcined powder of each sample was again ground for half an hour. The powder was cold pressed at pressure of 45 kN for 5 min in Apex Hydraulic Press. The pressed samples were initially sintered in air at 1200 °C for 2 h. They were finally sintered in air at 1275 °C for 1 h, and the temperature was kept at continued to rise till 1275 °C in one and half an hour. The furnace switched off auto-

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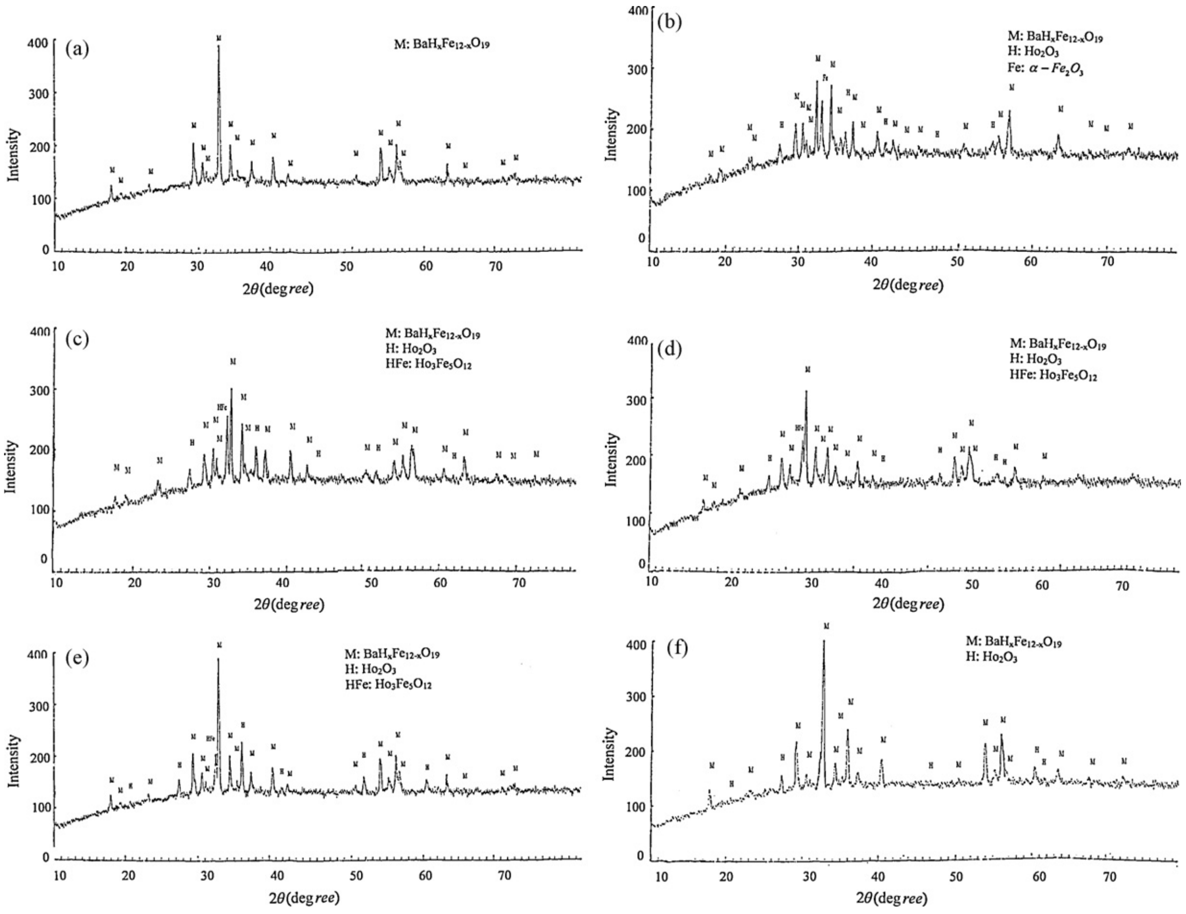

Fig. 1. (a–f) X-ray diffraction patterns of $BaHo_{2x}Fe_{12-2x}O_{19}$ M-type hexagonal ferrites with ($x = 0.0$–1.0) concentrations, prepared by solid state reaction method.

matically and slowly cooled down to room temperature. X-ray powder diffraction is performed on a Rigaku Geigerflex D-MAX/A Diffractometer using Cu Kα radiation.

A Hitachi S-3400N scanning electron microscope was employed to examine microstructural features such as grain size. Magnetic properties like saturation magnetization (M_s), remnant magnetization (M_r) and coercivity (H_c) for a given samples were calculated from the M–H loops, measured by using VSM at a maximum applied field (±8000 Oe) manufactured by Lake Shore's new 7404 series. The measurements were taken at 300 K beginning at zero applied magnetic fields.

3. Results and discussion

3.1. X-ray analysis

The X-ray diffraction analysis reveals that, in all the patterns, the main peaks correspond to hexagonal M-type phase. It was done by using JCPDS file 27-1029.

Formation of single phase material has been achieved for the unsubstituted sample at ($x = 0.0$) while in the substituted samples secondary phases are present as shown in Fig. 1(a)–(f). It has been reported [8] that phase formation is affected by the concentration of rare earth element Ho^{3+} in substituted samples of barium hexaferrites. The most important reason for the phase formation in the substituted samples is electronic configuration and ionic radii of the rare earth element Ho^{3+}. The Ho^{3+} ion has the larger radius of about 1.041 Å to occupy the tetrahedral (4f1) or the octahedral (12k, 2a, 4f2) sites [9] of Fe^{3+} whose ionic radius is 0.69 Å. So if the concentration of Ho^{3+} is high, this lead to the formation of secondary phases on the grain boundaries.

For the substituted sample at ($x = 0.2$) composition, hematite α-Fe_2O_3 and holmium oxide (Ho_2O_3) phases were identified by using JCPDS files 03-0800 and 10-0194, respectively. The presence of α-Fe_2O_3 is in accordance with the literature [10]. The presence of Ho_2O_3 phase at ($x = 0.2$) composition shows that Ho^{3+} only partly enters the M-lattice forming simultaneously secondary Ho^{3+} phases [11].

At ($x = 0.4$) with small traces of Ho_2O_3, the formation of spinel holmium ferrites ($Ho_3Fe_5O_{12}$) peak was observed by using JCPDS card 23-0282 [12]. The amount of α-Fe_2O_3 phases vanished with the increase of Ho^{3+} concentration up to $x = 1.0$ composition. At ($x = 0.6$ and 0.8) compositions traces of Ho_2O_3 were also detected and they increased with the substitution degree of rare earth element Ho^{3+} in barium hexaferrites as given in literature [10]. While at ($x = 0.6$ and 0.8) the intensity of a spinel holmium ferrite ($Ho_3Fe_5O_{12}$) decreases with the substitution degree of Ho^{3+}. At ($x = 1.0$) only traces of Holmium oxide were observed what is in agreement with the literature [11]. The solubility of rare earth element shows an increment in the lattice parameters as shown in Fig. 2, which is also in agreement with literature [12]. But it is not remain constant for the higher substitution due to the difference in ionic radii of the Iron Fe and Ho^{3+} as discussed in this section.

3.2. SEM analysis

SEM observation shows in Fig. 3(a)–(f) a majority of relatively well defined hexagonal like grains. For ($x = 0.0$) composition, when there is no substitution of rare earth element Ho^{3+} in barium hexaferrite, the observed value of grain size is 2.71 μm is given in Table 1.

This value of the grain size for M-type barium hexaferrite what is in accordance with the literature [14,7]. While by introducing rare earth element Ho^{3+} into the iron Fe^{3+} sites, it has been observed

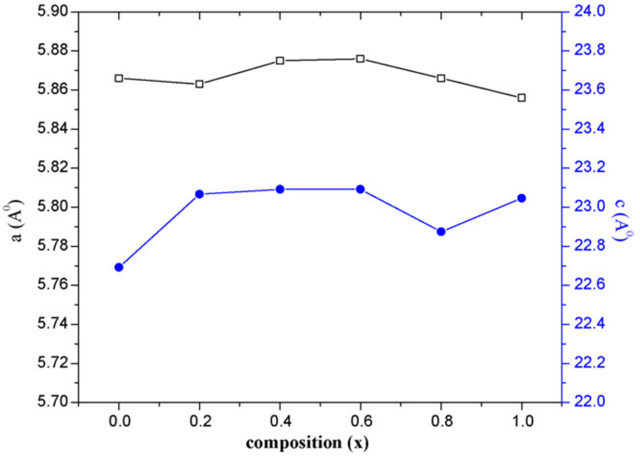

Fig. 2. Variation of lattice parameters for $BaHo_{2x}Fe_{12-2x}O_{19}$ M-type hexagonal ferrites prepared by ceramic method, vs. concentration 'x'.

Table 1
Calculated values of average grain size of $BaHo_xFe_{12-x}O_{19}$ ferrites with (x = 0.0–1.0) prepared by solid state reaction method.

Composition	Grain size (μm)
0.0	2.71
0.2	2.60
0.4	1.81
0.6	1.67
0.8	1.21
1.0	2.14

that the grain size continuously decreases up to 1.21 μm, with the increasing concentration of Ho^{3+}.

The decreasing trend of the grain size with increasing rare earth element Ho^{3+} concentration shows that Ho^{3+} acts as a grain growth inhibitor, which is in accordance with the literature [15,13]. When x = 1.0, it has been observed that this trend is reversed and grain size increases up to 2.14 μm. This shows that further increases of Ho^{3+} content does not take part as a grain growth inhibitor as shown in Fig. 4.

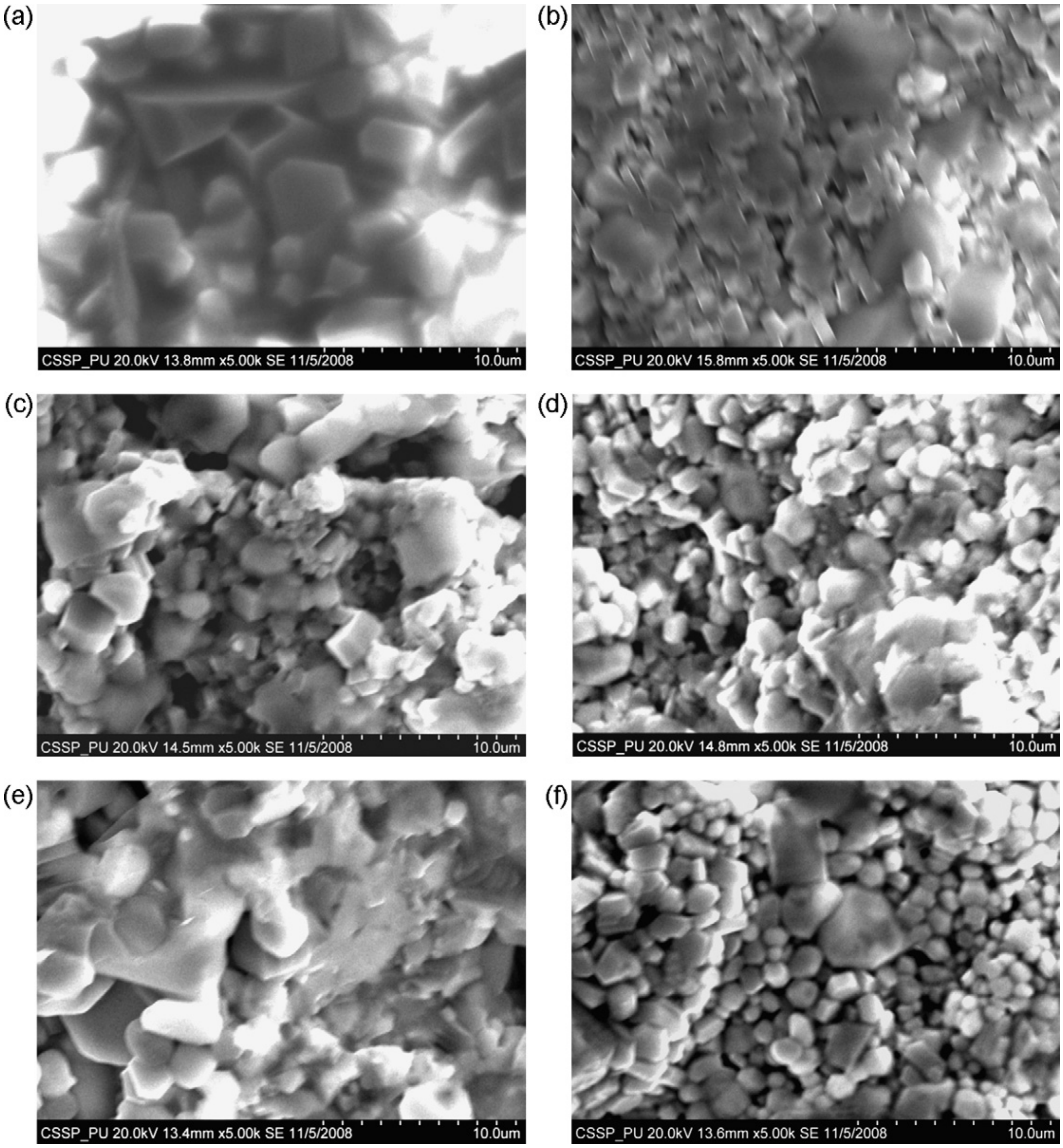

Fig. 3. (a–f) SEM micrographs of $BaHo_{2x}Fe_{12-2x}O_{19}$ M-type hexagonal ferrites with (x = 0.0–1.0) concentrations, prepared by solid state reaction method.

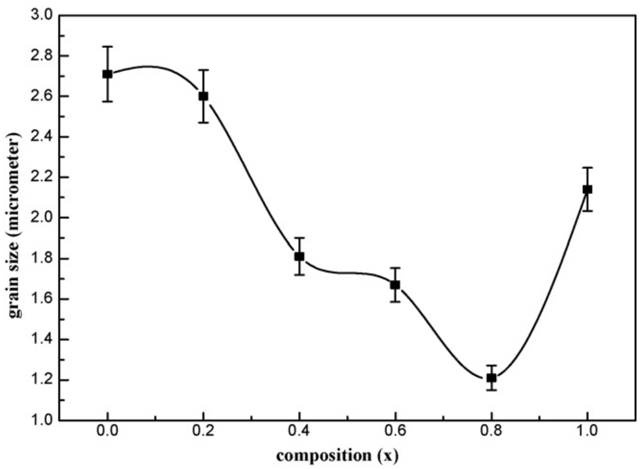

Fig. 4. Grain size, for $BaHo_{2x}Fe_{12-2x}O_{19}$ M-type hexagonal ferrites prepared by ceramic method, vs. concentration '*x*'.

Table 2
Calculated values of M_s, M_r and H_c at ($x=0.0$–1.0).

Composition	Magnetization, M_s (emu/g)	Retentivity, M_r (emu/g)	Coercivity, H_c (Oe)
0.0	15.734	8.195	1942
0.2	15.0176	8.7047	2201
0.4	52.593	29.077	2230
0.6	23.044	12.543	1889
0.8	16.953	9.100	1910
1.0	13.3459	7.061	1951

3.3. Magnetic measurements

The saturation magnetization (M_s), remanent magnetization (M_r) and coercive force (H_c) of the prepared samples were measured by means of VSM at a maximum applied field of 8000 Oe at room temperature. The effect of different doping amounts of Ho^{3+} on magnetic properties of barium ferrite powders are shown in Table 2 and Fig. 5.

The hexagonal structure of barium hexaferrite is built up of a cubic block S, having the spinel structure and a hexagonal block R, containing Ba^{2+} ion. Five oxygen layers make one molecule and two molecules make one unit cell. In the unit cell, Fe^{3+} ions occupy five different crystallographic sites, i.e., tetrahedral (4f1), octahedral (12k, 2a, 4f2), and hexahedral (2b) site of oxygen lattice. In the magnetically ordered state of $BaFe_{12-2x}Ho_{2x}O_{19}$, the 12k, 2a, and 2b sites have their spins parallel to the crystallographic *c*-axis, where as those of 4f1 and 4f2 points are anti-parallel [16]. In present work to tailor the magnetic properties of the barium hexaferrites, Fe^{3+} ions are partially substituted by tetravalent ions of rare earth element Ho^{3+}, aiming to occupy the spin down sites and, consequently, to increase the net magnetization. Recent investigations revealed that in some ferrimagnetic oxides, including barium hexaferrites, Holmium retains the trivalent state [17]. Therefore, it could be assumed that Holmium substitution does not require any charge balance.

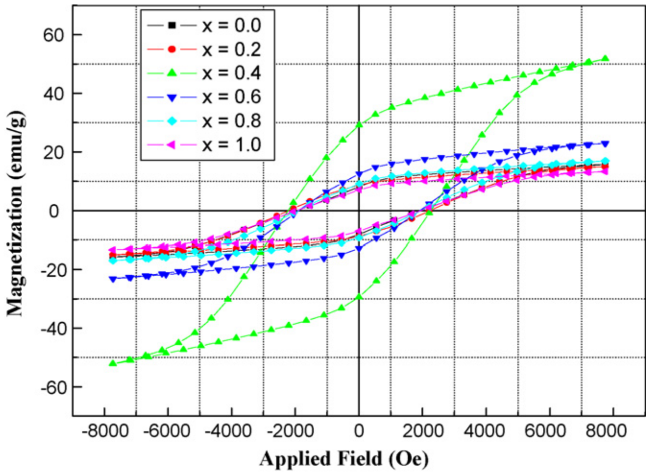

Fig. 5. The hysteresis loops of $BaHo_{2x}Fe_{12-2x}O_{19}$ at ($x=0.0$–1.0) M-type hexagonal ferrites prepared by solid state reaction method at room temperature.

The effect of rare earth element Ho^{3+} substitution on the magnetic properties of the material is in general a positive one. The magnetic patterns of the unsubstituted $BaFe_{12}O_{19}$ and substituted $BaFe_{12-2x}Ho_{2x}O_{19}$ samples for ($x=0.0$, 0.2, 0.4, 0.6, 0.8 and 1.0) are given in Fig. 3. All the substituted magnetic patterns of the samples show that values of coercive force (H_c), saturation magnetization (M_s) and remanent magnetization (M_r) increase up to a certain concentration of rare earth element Ho^{3+}. After the certain concentration of Ho^{3+} was reached, a considerable decrease in H_c, M_r and M_s values for all the substituted samples has been observed.

This magnetic behavior of the substituted samples may depend upon the following factors. The ionic radii of Holmium Ho^{3+} and Iron Fe^{3+} is not comparable, so this difference in ionic radius introduces local strain which may cause the disorder and modifications of local electronic states. Various Ho^{3+} concentrations have different influences on the super exchange interactions between magnetic cations and hence, on the magnetization [18]. One might consider that the Ho^{3+} substitutions weaken the super exchange interactions between Fe sites (Fe^{3+} possesses five different crystal locations 2a, $4f_2$, 12k, 4f1, 2b in the crystal structure of magnetoplumbite type barium ferrite) [2]. The considerable decrease in M_r and M_s values for all substituted samples may be due to the presence of unreacted α-Fe_2O_3 and Ho_2O_3 traces and this is in agreement with the findings of an early work [10].

According to literature [19] the rare earth element Ho^{3+} has slow diffusion rate and posses low solubility in the M-type structure, so the dissolution of Ho^{3+} ions into the hexagonal structure will result in a reduction of total magnetic moment.

The coercivity H_c for sample at ($x=0.0$) is 1942 Oe, when there is no replacement of iron with Holmium. The coercivity of samples increases with small replacement of iron with Holmium, at ($x=0.2$) the value of H_c is 2201 Oe and at ($x=0.4$) sample H_c increases to maximum value which is 2230 Oe. H_c for the ($x=0.6$, 0.8 and 1.0) samples decreases with the further increase of Holmium to replace iron. For ($x=0.6$) coercivity of the sample decreases to 1889 Oe, at ($x=0.8$) $H_c=1910$ Oe and at ($x=1.0$) $H_c=1951$ Oe, as all these values are smaller than the maximum value of H_c for ($x=0.4$) as shown in Fig. 6 and Table 2.

At ($x=0.0$), when there is no substitution of Holmium the value of M_s is 15.734 emu/g as given in Table 1. A small decrease of the saturation magnetization for ($x=0.0$–0.2) with the substitution of holmium have been observed. For further increase of Holmium substitution there is a drastic increase of the saturation magnetization up to 52.593 emu/g for ($x=0.4$). As we go on increasing the Holmium content, a steady decrease for M_s is consequently observed for ($x=0.6$) the value of $M_s=23.044$ emu/g, for ($x=0.8$) the value of $M_s=16.953$ emu/g and for ($x=1.0$) the value of $M_s=13.346$ emu/g as shown in Fig. 7 and Table 2.

The values of retentivity M_r as given in Table 2 and shown in Fig. 7 display that at ($x=0.0$) the value of $M_r=8.195$ emu/g. There is a small increase in retentivity is observed as we make the substitution of Holmium in barium hexaferrite so at ($x=0.2$) the value of M_r increases to 8.705 emu/g. Further increase of Holmium at ($x=0.4$) composition, the drastic increase in retentivity is observed and the value of M_r increases up to 29.077 emu/g. As we go on increas-

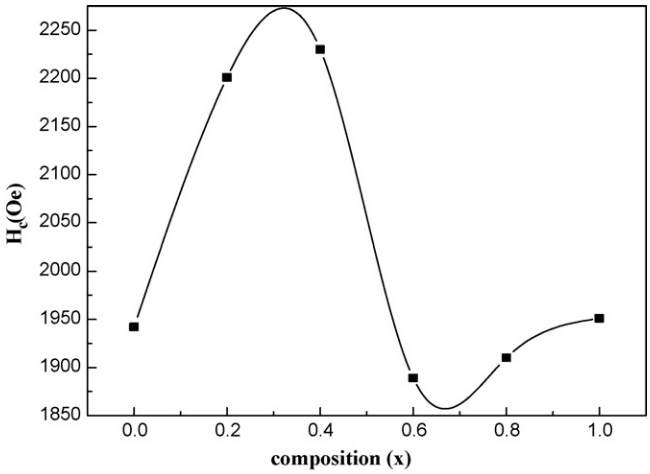

Fig. 6. Coercive field H_c, for $BaHo_{2x}Fe_{12-2x}O_{19}$ M-type hexagonal ferrites prepared by solid state reaction method, vs. composition (x).

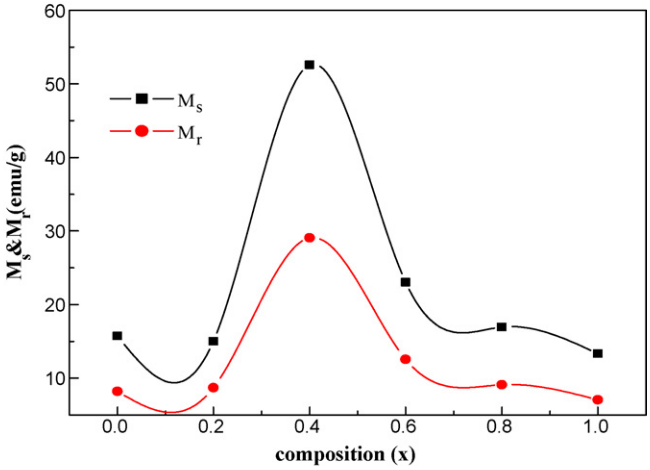

Fig. 7. Saturation magnetization M_s and remanent magnetization M_r, for $BaHo_{2x}Fe_{12-2x}O_{19}$ M-type hexagonal ferrites prepared by solid state reaction method, vs. concentration 'x'.

ing the Holmium content in barium hexaferrite, a steady decrease in the retentivity is consequently observed for ($x = 0.6$) value of $M_r = 12.544$, for ($x = 0.8$) value of $M_r = 9.100$ and for ($x = 1.0$) value of $M_r = 7.061$ emu/g, respectively.

4. Conclusion

Structural and Magnetic properties of Ho^{3+} substituted $BaFe_{12-2x}Ho_{2x}O_{19}$ M-type hexagonal ferrite for different compositions ($x = 0.0–1.0$) prepared by solid state reaction method have been investigated. The following conclusion can be drawn from this effort. Single phase with M-type hexagonal structure was observed for the sample at ($x = 0.0$). The substitution of Ho^{3+} with Fe^{3+}, dominant phases were of M-type structure in all the samples. The Ho_2O_3 secondary phases in the substituted samples increased with the content rare earth element holmium. Magnetic measurements of the ferrites show that the substitution of Ho^{3+} with Fe^{3+} in $BaFe_{12-2x}Ho_{2x}O_{19}$ ferrites lead to the increase in coercivity at ($x > 0$). The coercivity increased up to 2230 Oe for ($x = 0.4$). After attaining the maximum value, the coercivity decreased with the substitution degree of Ho^{3+}. Micrographs of ferrites $BaFe_{12-2x}Ho_{2x}O_{19}$ relatively well defined hexagonal like grains. With the addition of Ho^{3+} contents for Fe^{3+} in $BaFe_{12-2x}Ho_{2x}O_{19}$ compound grain size decreased with the substitution degree of Ho^{3+}. Thus the rare earth element holmium acts as a grain growth inhibitor.

Magnetic measurements of the ferrites show that the substitution of Ho^{3+} for Fe^{3+} in $BaFe_{12-2x}Ho_{2x}O_{19}$ ferrites leads to the increase in saturation magnetization M_s at ($x > 0$). The M_s increased up to 52.593 emu/g for ($x = 0.4$). After attaining the maximum value, the saturation magnetization decreased with the substitution degree of Ho^{3+}. Magnetic measurements of the ferrites shows that the substitution of Ho^{3+} with Fe^{3+} in $BaFe_{12-2x}Ho_{2x}O_{19}$ ferrites leads to the increase in remnant magnetization M_r at ($x > 0$). The M_r increased up to 29.077 emu/g for ($x = 0.4$). After attaining the maximum value, the remnant magnetization decreased with the substitution degree of Ho^{3+}. The maximum value of coercivity obtained for rare earth element Holmium substituted M-type barium hexaferrite is 2230 Oe. Hence rare earth element Ho^{3+} substituted ferrite can be used as a high density data storage device.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2010.01.133.

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