Site preferences for cobalt and cobalt-titanium in substituted barium ferrites

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Abstract : Cobalt and cobalt-titanium substituted barium hexaferrite samples having composition $BaFe_{12-x}Co_xO_{19-x/2}$ ($0<x<1.6$) and $BaFe_{12-x}Co_xTi_xO_{19}$ ($0<x<1.0$) were prepared using an autoignition method and characterized by Mössbauer spectroscopy and magnetization measurements It is shown that the cobalt ions prefer to occupy 12k and 2b crystallographic sites of $BaFe_{12-x}Co_xO_{19-x/2}$ Mossbauer spectra of $BaFe_{12-x}Co_xTi_xO_{19}$ reveal that the magnetic cobalt and nonmagnetic titanium ions assume 12k, 2b and $4f_{iv}$ crystallographic sites preferentially with no significant involvement of other sites. The coercivity (H_c) decreases considerably with increasing substitution amount. In $BaFe_{12-x}Co_xO_{19-x/2}$, H_c decreases from 4223 Oe to 2072 Oe as x varies from 0 to 1.6, while in $BaFe_{12-x}Co_xTi_xO_{19}$, it decreases much faster and becomes 407 Oe for x = 1. It is suggested that the site preferences of substituted elements weaken the uniaxial anisotropy of the material which, in turn, leads to significant decrease in the coercivity value

1. Introduction

Magnetic recording technology in conjunction with semiconductor electronics has contributed significantly to the growth of inexpensive computer power and audio-video storage. Barium ferrite, a material for permanent magnet and microwave devices [1, 2], is also a suitable candidate for magnetic recording after a substitution of Fe^{3+} by divalent and tetravalent elements such as Co^{2+} and Ti^{4+} [3]. A number of studies have been made on Co-Ti substitution in barium ferrite prepared by different methods such as ceramic method, co-precipitation etc. It has been found that site occupancy of the substituted cation at the crystallographic sites of barium ferrite depends on the preparation methods [4-8]. For the first time we have prepared Co and Co-Ti substituted barium ferrite by autoignition combustion method [9]. The uniqueness of the process lies in the initiation of combustion at low temperature and use of the heat liberated by exothermic anionic oxidation-reduction reaction between the citrate and nitrate ions. Investigating the site preferences of cobalt and cobalt-titanium in barium ferrite, prepared by autoignition method and effect on the coercivity due to substitution, are the objectives of this work.

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The barium ferrite has magnetoplumbite structure. The unit cell consists of two spinal blocks (S and S*) and two hexagonal blocks consisting of barium (R and R*). These blocks are arranged in the sequence RSR*S*, where R* and S* can be obtained by a rotation of R and S blocks about the c axis though 180°. There are five distinct crystallographic sites $4f_{vi}$, 2b, 12k, $4f_{iv}$ and 2a for metallic cations [10]. The crystallographic properties and spins of these sites are given in Table 1.

Table 1. The crystallographic properties and spin characteristics of barium hexaferrite

Sites	Coordination	No of ions per formula unit	Block	Spin
$4f_{vi}$	octahedral	2	R	Down
3b	bipyramidal	1	R	Up
12k	octahedral	6	R-S	UP
$4f_{iv}$	tetrahedral	2	S	Down
2a	octahedral	1	S	Up

The three sites 2a, $4f_{vi}$ and 12k have octahedral symmetry whereas $4f_{iv}$ has tetrahedral symmetry and the symmetry of 2b is in between tetrahedral and octahedral. The magnetic interaction is dominated by superexchange interaction between

Fe^{3+} ions through the $180°$ bonds of $Fe^{3+} - O^2 - Fe^{3+}$. The substitution of Co^{2+} and Ti^{4+} in the cation sites alter these superexchange interactions and hence the magnetic characteristics.

The ^{57}Fe Mössbauer spectroscopy is an ideal tool to investigate the site occupancy in compounds having metal cations at different crystallographic sites. This is because the Fe nuclei having different atomic environments give rise to Mössbauer components with characteristic parameters and these components can be separated out by suitable computer programs. In this paper we present the results of Mössbauer and magnetic measurements on samples of $BaFe_{12-x}Co_xO_{19-x/2}$ and $BaFe_{12-2x}Co_xTi_xO_{19}$ with x varying from 0 to 1.6 and 0 to 1.0 respectively, in steps of 0.2.

2. Experimental

Pure barium ferrite ($BaFe_{12}O_{19}$) has been prepared by mixing stoichiometric proportions of barium and ferric nitrates with aqueous solution of citric acid (the pH is maintained by ethylenediamine at 4.0) and heating at temperature around $90°C$ to form a gel. Due to heat liberated in the exothermic reaction that follows the formation of ash, which is calcinated at $900°C - 1000°C$ for 8 to 9 hours to produce the final product.

For cobalt substitution, cobalt nitrate was added to the citric acid solution and for cobalt-titanium substitution, cobalt nitrate and titanium oxide have been used.

Magnetic measurements were carried out using a vibrating sample magnetometer. Mössbauer spectra were recorded using a constant acceleration Mössbauer spectrometer with a 5-mCi ^{57}Co source in rhodium matrix. All spectra were recorded at room temperature and analyzed using least squares fitting programms.

3. Result and discussion

3.1 Interpretation of Mössbauer spectra :

Mössbauer spectra for $BaFe_{12-2x}Co_xTi_xO_{19}$ with different amounts of substitution recorded at room temperature were fitted with discrete sextet subpatterns corresponding to the five crystallographic cation sites $4f_{vi}$, $4f_{vi}$, $2a$, $2b$ and $12k$ of pure barium ferrite. Adding a small contribution from a sixth sextet in the spectra of substituted samples improves the fitting. Some of the typical Mössbauer spectra are given in Figure 1. The solid circles denote the experimental data points and the line corresponds to the computer-generated data according to the Mössbauer parameters obtained. The relative spectral areas of sextets corresponding to the crystallographic sites $12k$, $4f_{iv}$ and $2b$ are found to decrease, whereas those for $4f_{vi}$ and $2a$ sites remain almost constant with increase in Co-Ti substitution. The area of a sextet corresponds to the number of iron ions present at the respective crystallographic site. The decrease in the area of the sextets denotes the substitution of Co and Ti ions to $12k$ and $4f_{iv}$ sites with a slight involvement of $2b$ site for small x. The

hyperfine magnetic field (HMF) at a given site can change because of nonmagnetic substitution at neighboring sites as well as because of any change in the bond angle due to crystal
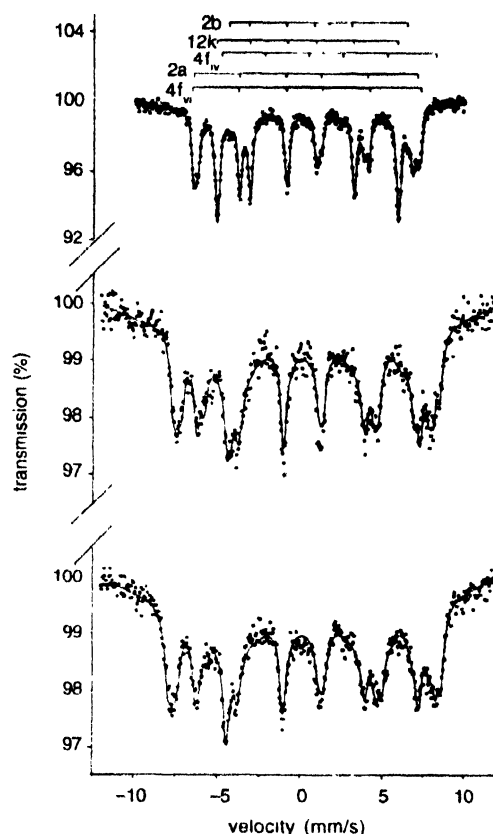

Figure 1. Mössbauer spectra of $BaFe_{12-2x}Co_xTi_xO_{19}$ samples at room temperature. (a) $x = 0.0$, (b) $x = 0.6$, (c) $x = 1.0$

strains. The HMF at different crystallographic sites varies slightly as a function of amount of Co-Ti substitution. The variation is shown in Figure 2. The significant decrease in hyperfine fields at $4f_{vi}$, $2a$ and $4f_{iv}$ sites indicate that the surroundings of Fe^{3+} ions in these sites have changed and possibly contain non-magnetic ion Ti^{4+}. This provides further evidence for substitution of Fe^{3+} ions at $12k$ and $2b$ sites. As stated earlier, addition of a sixth sextet with much reduced and
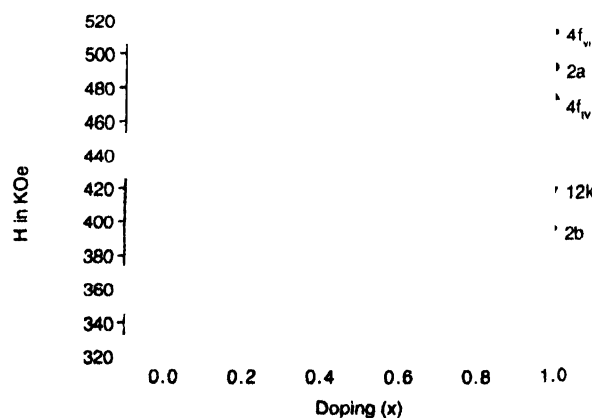

Figure 2. Variation of hyperfine field H with doping x for different crystallographic sites for $BaFe_{12-2x}Co_xTi_xO_{19}$.

broad lines improves the fitting significantly. Such new HMF may come from the statistical probability of several nonmagnetic Ti^{4+} ions occupying the neighboring sites of particular iron sites. This results, in reduction of hyperfine field of that site significantly. Zhou *et al* [4] have also reported new HMFs on Co-Ti substitution and interpreted as coming of due to changes in the environment of iron ions at $12k$ site when substitution takes place in R blocks.

The trend of relative spectral area and HMF are not so well defined when only Co is substituted. We have studied $BaFe_{12-x}Co_xTi_xO_{19-x}$ for $x = 0$ to 1.6 in step of 0.2. For large amount of substitution ($x > 1.0$) the relative spectral area of $12k$ and $2b$ sites decreases, showing that Co alone also prefer these sites.

3 2 Effect on coercivity :

The variation of coercivity as a function of cobalt-titanium content is showm in Figure 3 we see that there is a large decrease in the coercivity value from 4223 Oe for $x = 0.0$ to 407 Oe for $x = 1.0$. The variation seems to follow the exponential equation $H_c = H_{co} \exp(-\alpha x)$ where H_{co} is the coercivity value for $x = 0$ and α is found to be 2.27 ± 0.06.
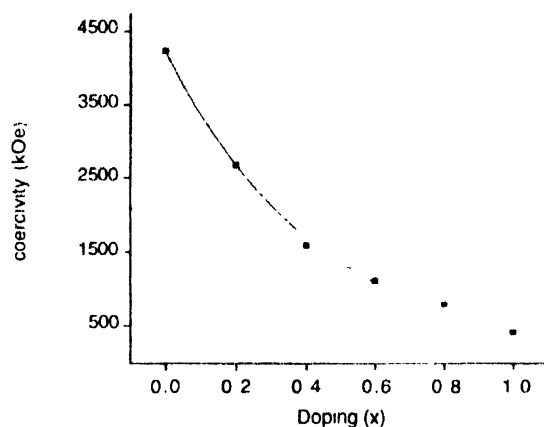

Figure 3. Variation of coercivity with doping x for $BaFe_{12-x}Co_xTi_xO_{19}$

According to Albanese [5] the origin of uniaxial magnetocrystalline anisotropy in $BaFe_{12}O_{19}$ lies in the iron ions of bipyramidal (2b) and octahedral ($4f_{VI}$, $2a$ and $12k$) sites belonging to R block. In the present case, we find cobalt-titanium prefers $12k$, $2b$ and $4f_{IV}$ sites. The replacement of iron in $12k$ and $2b$ sites will therefore give rise to decrease in anisotropy and hence coercivity. In Co substituted samples also the coercivity has decreased from 4223 for $x = 0$ to 2082 for $x = 1.6$ but not so rapidly as in the Co-Ti substituted ferrite. This may be due to the fact that the Co itself is magnetic ion and replacement of Fe by Co may not be as effective in reducing the coercivity as the nonmagnetic Ti substitution.

3 3 Comparison with samples prepared through other routes :

The sites occupancy and variation of coercivity of $BaFe_{12-2x}Co_xTi_xO_{19}$ studied in the present work agrees by and large with

those prepared by other methods Turilli *et al* [6] explained the changes in magnetic order in Mn-Ti substituted barium ferrite by ceramic method, assuming preferential occupation of the crystallographic site $12k$ by both the Mn^{2+} and non-magnetic Ti^{4+} ions.

Agresti *et al* [7] introduced a low-temperature, ambient pressure coprecipitation method to prepare $BaFe_{12-2x}Mo_xTi_xO_{19}$. The saturation magnetization was found to be indepenent of local crystalline order and coercivity in the range of 500-1400 Oe. These workers also found a monotonic decrease in the relative intensity of the $12k$ sites in Mossbauer spectra of Co-Mo substituted samples suggesting preferential occupancy of this very location with little distortion in the crystal structure.

Rane *et al* [8] in their recent study on Ni-Zr doped system have also shown that substitution of Zr^{4+} occurs at $4f_{VI}$ and $2b$ crystallographic sites and Ni^{2+} substitute $4f_{IV}$ site for small values of doping but for larger doping it substitute the $12k$ site.

Zhou *et al* [4] studied the Mössbauer spectra of Co, Ti substituted systems synthesized by ceramic method. They have suggested that Co^{2+} and Ti^{4+} cations preferably occupy the $4f_{IV}$ and $2b$ crystallographic sites, in variance with our interpretation that substantial substitution takes place in $12k$ site. These authors also observed new HMFs with much reduced value, which they assign to $12k$ sites with modified environment. Additional experiments are needed to support this assertion.

4. Conclusion

Barium ferrite samples doped with Co, Ti using autoignition method have the same crystal structure as the undoped system. The samples prepared by autoignition method shows that the substituted elements prefer site occupancy in $12k$, $4f_{IV}$ and $2b$. The substitution gives controls to vary coercivity over a long range making these systems attractive for magnetic application.

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