Preparation and Investigation of the Magnetic Properties of Barium Hexaferrite Doped with Antimony

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Abstract

Barium hexaferrite doped with different amounts of Sb in the form $BaFe_{12-x}Sb_xO_{19}$ (x=0.0-0.6) have been prepared using ball milling method. It was found that saturation magnetization increases in the concentration range up to $x=0.3$ then saturation magnetization drops from 62.5 emu/g for $x=0.3$ to 51.5 emu/g for $x=0.6$, while a reduction in coercive field was detected for all concentration examined. Such reduction in the coercive field was attributed to the decrease in magnetic anisotropy field. It was found that $\delta m$ curves are negative for both pure and doped barium ferrite samples. Also it was found that $\delta m$ value for the pure sample is greater (in the negative direction) than for those doped with Sb, which suggests that doping with Sb leads to decrease in the process of clusters formation.

Keywords: Barium hexaferrite; Coercivity; Saturation magnetization; Anisotropy field.

Introduction

Barium hexaferrite with a chemical formula $BaFe_{12}O_{19}$ is one of the most important composition for perpendicular magnetic recording. Barium hexaferrite is suitable for magnetic recording due to its large saturation magnetization, good chemical stability, and low switching field distribution. On the other hand, barium hexaferrite can be used for high density magnetic recording if its particle size and its large anisotropy field were decreased. Large particle size and high anisotropy field cause a poor overwrite modulation [1]. In order to reduce the anisotropy field and to satisfy the dessert applications, many studies were taken out to modify the magnetic properties of barium hexaferrite by the substitution of the $Fe^{3+}$ ions with cations such as $(Sn^{4+},Ni^{2+},Ni^{3+},Co^{2+},Co^{3+},Ti^{4+},etc.)$ [2, 3, 4] or cations combinations such as (Zn-Sn, Co-Sn [5, 6], Zn-Ti [7], Co-Ti[2], etc.).

Several techniques can be used to prepare barium ferrite powders such as the sol-gel method [8-10], the glass crystallization method [11], hydrothermal technique [12], and coprecipitation method [13].
In the present work ball milling method was used to synthesize substituted barium hexaferrite powder \((BaFe_{12-x}Sb_xO_{19})\). The preparation and investigation of barium ferrite doped with Sb - to the knowledge of others - has not been performed yet. So in this work we have investigated the possibility of introducing dopants ions such as Sb by the ball milling route.

Neutron diffraction study shows that the structure of \(BaFe_{12}O_{19}\) is of the form \(RSR*S^*\), Where \(R^*\) and \(S^*\) are obtained from the blocks \(R\) and \(S\), by rotation of \(180^\circ\) around the hexagonal \(c\) axis \([14-16]\). The ferric ions are distributed among five crystallographic sites, three are octahedral sites \((12f, 4f_2,\text{ and } 2a)\), one is tetrahedral site \((4f_1)\) and one trigonal bipyramid \((2b)\) \([17-19]\).

**Experimental procedures**

The starting materials for synthesis of \(BaFe_{12-x}Sb_xO_{19}\) \((x=0, 0.1, 0.2, 0.3, 0.4, 0.5\) and \(0.6)\) were \(BaCO_3, Fe_2O_3,\) and \(Sb_2O_3\) (all are Aldrich-make). \(BaFe_{12-x}Sb_xO_{19}\) compound was prepared in a planetary ball-mill (Fritsch Pulverisette 7) with balls and vial of hardened steel. The milling experiment was carried out at 250 rpm for 16 h and the ball to powder ratio was 8:1. The as-milled powders were annealed in air atmosphere at 1100 \(^\circ\)C for 5 h. It should be noted that XRD analyses of more than 6 samples subjected to different annealing temperatures from 700 \(^\circ\)C to 1200 \(^\circ\)C revealed that the optimum annealing temperature for obtaining barium ferrite doped with Sb was 1100 \(^\circ\)C. X-ray diffraction (XRD) analysis was carried out in Philips X'Pert PRO X-ray diffractometer (PW3040/60) with CuK\(_\alpha\) radiation (45kV, 40 mA). The magnetic measurements were carried out using vibrating sample magnetometer (VSM) (MicroMag 3900, Princeton Measurements Corporation), with 10 kOe maximum applied field. All magnetic measurements were performed at room temperature.

**Results and discussion**

XRD patterns for some samples examined in this work are represented in Fig. 1. All unmarked peaks belong to hexagonal barium ferrite \((BaFe_{12}O_{19})\). XRD pattern for the sample \((x=0.0)\) shows XRD pattern which belongs to almost single phase of \(BaFe_{12}O_{19}\). The XRD patterns of doped barium ferrite contain characteristic peaks of some traces of hematite \((Fe_2O_3)\) and antimony oxide \((Sb_2O_3)\). The intensities of XRD peaks of such traces were increased with the increase of Sb content in the sample.

Lattice parameters \(a, c\) of \(BaFe_{12-x}Sb_xO_{19}\) were calculated according to formula 1 \([20]\), where \(d\) is interplanar distance and \(h, k,\) and \(l\) are Miller indices.

\[
\frac{1}{d^2_{hkl}} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}
\]  
(1)
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The variation of hexagonal lattice parameters $a$ and $c$ with Sb content for all doping concentration examined in this work are presented in Fig. 2. Lattice constant $a$ remains constant, whereas hexagonal lattice constant $c$ increases with increasing Sb concentration. This indicates that the change of easy magnetized $c$-axis is larger than that of $a$-axis for the substitution with Sb. The increase of $c$ might be a result of size effect, since the radius of Fe$^{3+}$ ion, 0.645 Å, is smaller than that for Sb$^{3+}$ ion, 0.76 Å. This change in lattice parameters might change the distance between magnetic ions, which leads to a disturbance in exchange interaction, thus magnetic properties can be alerted by the substitution.

Fig. 3 shows the measured hysteresis loops for some of the $BaFe_{12-x}Sb_xO_{19}$ samples as a function of applied magnetic field. The magnetization curve for the non-substituted sample belongs to hard magnetic material with high coercive field strength of 4 kOe. This value of the coercivity agree with the previous works such as sol-gel method [17], mechanical alloying method [1] and ball milling method [21] of preparing barium ferrite.
Figure 2: Lattice parameters $a$ and $c$ of $\text{BaFe}_{12-x}\text{Sb}_x\text{O}_{19}$ as a function of Sb concentration.
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Figure 3: Hysteresis loops for some of the $BaFe_{12-x}Sb_xO_{19}$ samples as a function of applied magnetic field.

The effect of Sb ions on the saturation magnetization of $BaFe_{12-x}Sb_xO_{19}$ is shown in Fig. 4. The saturation magnetization increases with the increase of Sb concentration up to $x=0.3$ recording 62.5 emu/g, while the saturation magnetization drops to 51.5 emu/g for $x=0.6$. The magnetic moment per formula for barium hexaferrite can be expressed according to the following equation [22, 23]:

$$\bar{m} = 2a + 2b + 12k + 4f_1 + 4f_2$$  \hspace{1cm} (2)

The spin-down sites ($4f_1$ and $4f_2$) are occupied by two Fe ions each, whereas the spin-up sites $2a$ and $2b$ are occupied by one Fe ion each, and $12k$ is occupied by six Fe ions [16]. Based on the above equation, the increase in the saturation magnetization in the concentration range $x=0.1$ to $x=0.3$, can be attributed to the replacement of $4f_1$ and $4f_2$ spin-down Fe$^{3+}$ ions by diamagnetic Sb$^{3+}$ ions. The observed drop in the saturation magnetization in the concentration range $x = 0.4 - 0.6$ might be associated with the replacement of Fe$^{3+}$ ions by Sb$^{3+}$ ions at the $2a$ and $2b$ spin-up sites, respectively. Furthermore, attenuation of the superexchange interaction between Fe$^{3+}$ ions at $2a$ and $2b$ spin-up sites, might be occur as a result of the excessive replacement of the magnetic
ions by non-magnetic ones (Sb^{3+}) in the concentration range $x = 0.4 - 0.6$, which is responsible for the drop in the saturation magnetization.

![Graph showing saturation magnetization as a function of Sb concentration.](image)

**Figure 4:** Saturation magnetization as a function of Sb concentration of barium ferrite samples.

Fig. 5 shows the coercive fields as a function of Sb concentration for all samples examined in this work. As one might observe the value of the coercivity for pure sample is 4000 Oe, which is in good agreement with the literature value, since the coercivity of pure BaFe$_{12}$O$_{19}$ prepared by different methods is reported in the range (3000 – 5000) Oe [3, 24]. Also it is clear from these data that doping of barium ferrites with Sb leads to significant decrease in the coercivity as a result of the Sb substitution of Fe$^{3+}$. The reduction of the coercivity may be due to the decrease in the magnetic anisotropy field ($H_a$) as a result of Sb substitution of Fe$^{3+}$. 

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Figure 5: Coercive fields as a function of Sb concentration of barium ferrite samples.

Figure 6: Reduced IRM curves and switching field distributions for the samples with $x = 0.0$ and $x = 0.4$. 
In order to investigate the correlation between the coercivity and the magnetic anisotropy field in our system, we determine the effective magnetic anisotropy field for each sample examined in this work from the switching field distribution (SFD). The switching field distribution can be obtained by differentiating the reduced isothermal remanent magnetization (IRM) curve \( m_r(H) = M_r(H)/M_r(\infty) \). Fig. 6 shows the reduced IRM curve and the corresponding switching field distribution for the samples with \( x = 0.0 \) and 0.4. The effective magnetic anisotropy field for each sample examined in this work is obtained from the maximum of the switching field distribution according to the formula [25]:

\[
\left[ \frac{d m_r}{dH} \right]_{H = H_{a}/2} = \frac{1}{2} \left[ \frac{d m_r}{dH} \right]_{H = H_{a}/2} \tag{3}
\]

Here \( H_a = 2H_{max} \), where \( H_{max} \) is the value of the field at the maximum of the SFD. Fig. 7 shows the variation of magnetic anisotropy field with Sb concentration for all samples examined. It is clear that \( H_a \) decreases monotonically with increasing Sb concentration up to \( x = 0.6 \), which might be the reason of suppressing the coercivity (Fig. 5). It could be noted that, the decrease in anisotropy field might leads to decrease in energy barriers, as a result a smaller field is required to reverse the magnetization, which suppress the coercivity.

![Figure 7](image.png)

Figure 7: Anisotropy field as a function of Sb concentration of barium ferrite samples.
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In order to investigate the role of doping with Sb on the interaction effects we use $\delta m$ relationship given by Kelly [26]:

$$\delta m (H) = m_d (H) - [1 - 2m_r (H)]$$

(4)

where $m_r (H)$ is the reduced isothermal remanent magnetization (IRM) and $m_d (H)$ is the reduced dc demagnetization (DCD). The IRM curve was obtained by the following procedure: first the sample was demagnetized, second applying positive field, third measuring the remanence magnetization after removing the applied field. The procedure was repeated with increasing the positive field to reach positive saturation remanence. The DCD curve was obtained by, first, the sample was saturated with a positive field of 10 kOe, second a negative field was applied to the sample, third remanence magnetization was recorded after removing the negative field and at last this procedure was repeated with increasing the negative field until negative saturation remanence was reached. $\delta m$ curves give the strength and the sign of the interaction in the prepared samples. For non interacting systems $\delta m$ plots will show a horizontal line, any deviation from linearity in $\delta m$ is a sign for the existence of interparticle interactions. Positive $\delta m$ values indicates the existence of interparticle interactions that contribute constructively to the magnetization (magnetizing like effect), while negative $\delta m$ values suggest that the existing interactions are demagnetizing (demagnetizing like effect), i.e. negative $\delta m$ means interactions that assists the reversal mechanisms. Fig. 8 shows the $\delta m$ plots for barium ferrite samples at different doping concentration of Sb. These curves show the magnitude of particle interaction in each sample. The curves show negative $\delta m$ which according to equation (4) result from the interaction making it difficult to magnetize the sample from the demagnetized state (demagnetizing-like effect), or from $m_d$ being easy to demagnetize. These data suggest that the interaction fields in these samples have a negative values and interaction effects decrease in magnitude with the increase of Sb concentration. Thus it seems that the particles tend to form clusters rather than a column of stacked platelets, i.e. the cluster growth in the doped samples seems to be less than for the pure one.
Conclusion

Our data suggest that doping of barium ferrite with Sb (BaFe$_{12-x}$Sb$_x$O$_{19}$) leads to increase in c lattice parameter, and to significant reduction in the coercivity as a result of suppression of the anisotropy field. Also it was found that Sb doping enhances the saturation magnetization at low concentrations and reduces it for concentration higher than x=0.3. It was found that $\delta m$ curves are negative for both pure and doped barium ferrite samples. Also it was found that $\delta m$ value for the pure sample is more negative than for those doped with Sb, which suggests that doping with Sb reduce the process of clusters formation.
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تحضير ودراسة الخصائص المغناطيسية للباريوم فراイト السداسي المشاب بالانتيمون

ملخص

تم تحضير مركبات الباريوم فرايت السداسي المشاب بالانتيموني 
$BaFe_{12-x}Sb_xO_{19}$ بقيم $0 \leq x \leq 0.6$ بطريقة الطحن بالكرات. تبين من القياسات المغناطيسية أن قيمة مغلفة الابجا زادت مع $x=0.6$. بعد ذلك تنخفض قيمة مغلفة الابجا في المدى من $x=0.3$ إلى $x=0.6$. بينما تبين أن المجال القسري يتناقص مع زيادة نسبة الانتيموني لكافة التراكيز التي تمت دراستها وتتبان التنافل في مجال القسري مرده إلى التنافل في مجال التباين الناتج عن عملية التضيي بالانتيمون. تنافل مدرسة في مجال القسري مع تغير بالتنافل $\delta m$ سالب لجميع العينات الممضية، مما يدل على وجود تفاعلات داخليّة تساهم في عمليات عكس المغلفة. وقد تبين أيضاً أن عملية الإشابة بالانتيمون تعمل على التقليل من شدة التفاعلات المساعدة في عملية عكس المغلفة وتكوين الكليسترات.

References

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