

# On the Coercivity of the Bi-Doped Ba-Hexaferrite, $\text{BaFe}_{12-x}\text{Bi}_x\text{O}_{19}$

T. Osotchan and S. Thongmee

Faculty of Science, Mahidol University, Bangkok 10400, Thailand

I.M. Tang

Institute for Science & Technology for Research & Development  
Salaya Campus, Mahidol University, Nakorn Pathom 73170, Thailand

## Abstract

The changes in the coercivity and the saturation magnetization  $M_s$  of M-type Ba hexaferrites (Ba-F) due to the addition of the sintering aid  $\text{Bi}_2\text{O}_3$  are studied. It is found that the coercive force  $H_C$  of  $\text{BaFe}_{12-x}\text{Bi}_x\text{O}_{19}$  decreases monotonically up to a doping level of  $x = 0.8$  and that for a fixed  $\text{Bi}^{3+}$  content,  $H_C$  decreases as the sintering temperature  $T_a$  is increased. After an initial increase,  $M_s$  is seen to decrease with increasing Bi substitution. The decrease in the coercivity can be due to two possible causes, a decrease in the grain size or a lessening of the uniaxial anisotropy. The second explanation requires the  $\text{Bi}^{3+}$  to enter into the  $4e$  sites. This would lead to the saturation magnetization decreasing with increased Bi substitution.

Keywords: Hexaferrites, bismuth doping, coercive force

#corresponding author: email address scimt@mahidol.ac.th

## 1. Introduction

The M-type hexaferrites are some of the most commercially valuable magnets in use since they have a wide range of technological applications. The fabrication of these ceramic magnets requires the sintering at very high temperatures,  $T_a$ . However, it has been observed that Ba hexaferrites develop distortions in their structure when sintered at  $T_a > 1300^\circ \text{C}$ .<sup>1</sup> To lower the processing temperatures or reduce the distortion, sintering aids such as  $\text{Bi}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ , etc, are often added.<sup>2</sup> The addition of the sintering aids to the chemical mixtures also facilitates the crystallization of platelet-like particles. Besides activating the crystallization of the particles, the addition of sintering aids also leads to changes in the magnetic and electric properties of the ferrites. Many of the changes are due to changes in the morphology of the ceramic occurring when lower  $T_a$ 's are used. Other changes are due to the replacement of Fe ions

by the non magnetic sintering aid ions and depend on which Fe sites, the replacement takes place.



Fig. 1. Hexagonal Crystallites in M-Type Barium Ferrites Doped with Bismuth Oxides. ( x 1000 )

The M-type hexaferrite, BaFe<sub>12</sub>O<sub>19</sub> is one of the most studied and one of the most commercially valuable magnets. Ram,<sup>3</sup> found that the addition of 2.5 mole % of Bi<sub>2</sub>O<sub>3</sub> into the Ba-ferrites increased the electric permittivity by 10<sup>5</sup> times and the Curie temperature to 480° C. The saturation magnetization, M<sub>s</sub> of the 2.5 % doped ferrites were lower than those of the pure hexaferrite. The decrease in M<sub>s</sub> magnetization and the size of the Bi<sup>3+</sup> ions led Ram et al.,<sup>4</sup> to believe that the Bi<sup>3+</sup> replaced the Fe<sup>3+</sup> ions in the 2a sites. Pal et al.,<sup>5,6</sup> have also studied the effects of Bi<sub>2</sub>O<sub>3</sub> doping into the Ba-ferrites. They found M<sub>s</sub> increased initially, reaching a maximum at 0.15 molar of Bi<sub>2</sub>O<sub>3</sub> substitution and then decreasing as more Bi<sub>2</sub>O<sub>3</sub> is added. The electrical conductivity increased by three orders of magnitude with the incorporation of Bi into the ferrite. Pal et al., believed that after initially going into the 4f<sub>vi</sub> sites, the Bi<sup>3+</sup> then enters into the 12k sites, leading to M<sub>s</sub> decreasing at the higher doping levels.

Another property that was studied was the coercivity of the ferrite. Coercivity is a measure of the field H<sub>C</sub> needed to reduce the induction **B** to zero. Different ranges of values are needed for different applications. High coercivity is required of materials used for permanent magnetic application while low coercivity is required of materials used for magnetic recording applications. Ram et al., found that the addition of sintering aid Bi<sub>2</sub>O<sub>3</sub> to the BaF decreased the H<sub>C</sub>'s of these ferrites. Pal et al., found the coercive force decreased initially from a value of 3400 kOe down to 2966 kOe and then began to increase as more Bi was added. Brahma et al.,<sup>7,8</sup> found that doping with Sb<sub>2</sub>O<sub>3</sub> lowered the coercive force while doping with As<sub>2</sub>O<sub>3</sub> produced an initial increase with initial doping, but decreased upon additional doping. Ram<sup>1</sup> found that doping with the sintering aid B<sub>2</sub>O<sub>3</sub> also decreased H<sub>C</sub> initially. Further doping caused the decrease to plateau out. H<sub>C</sub>, then remained constant or began to

increase depending on the fabrication conditions. Zheng et al.,<sup>9</sup> found that the substitution of Al into the BaF lead to a monotonic increase in the coercive force as the Al<sup>3+</sup> content increased. Han et al.,<sup>10</sup> and Yang et al.,<sup>11</sup> have studied the effects of Co-Sn substitution on H<sub>C</sub> of the Ba-ferrites. Both groups observed that H<sub>C</sub> decreases monotonically with increasing Co-Sn substitution. Yang et al., also looked at the effects of Co-Ti substitution on the coercivity. This substitution into BaF also leads to drastic drops in the H<sub>C</sub>'s.

Changes in the coercivity are usually attributed to changes in the particle (or grain) sizes. Muller et al.,<sup>12</sup> and Yang et al., both found that the coercivity of Co-Ti substituted Ba-ferrites decreased as the particle size increased. The increase in particle size was achieved by annealing the substituted Ba-F at higher T<sub>a</sub>. Saha and Yetter<sup>13</sup> found similar dependences in the coercivity of Sr-hexaferrites. The increase in particle sizes was again achieved by annealing at higher T<sub>a</sub>. Kurtz and Carpay<sup>14</sup> developed a theory to describe the particle growth in ferrimagnetic ceramics. They showed that particle growth depends on both the duration of the heat treatment and the temperature used. In general, the particle size increases monotonically with longer annealing times and use of higher temperatures. Yang et al., noted that the particle size of the Ba-ferrites decreased with increasing impurity substitution (Co-Ti in their case). Ram<sup>1</sup> reported for the case of B-doped Ba-F, that the particle sizes increase with increasing B content.

Most of the studies do not however report any systematic variation of the particles sizes with the amount of sintering aid substitution. The lack of any correlation between the amount of substitution and the particle ( or grain ) size forced the above investigators to come up with new reasons for the behavior of the coercivity. Ram attributed the dependence of H<sub>C</sub> to B substitution to the increasing stress induced by the introduction of B into the structure. Yang et al., attributes the increase in H<sub>C</sub> of the Al-substituted Ba-F to the

increase in the anisotropic field caused by the Al substitution. Han et al., and Yang et al., attribute the decreases in  $H_C$  to decreases in the uniaxial crystalline anisotropy. Based in part on this reason for the decrease, Han et al., believed that in the Co-Sn substituted Ba-F and in the Co-Ti substituted Ba-F, the  $Co^{2+}$  and  $Sn^{4+}$  ions and the  $Co^{2+}$  and  $Ti^{4+}$  ions substitute preferentially into the  $4e$  and  $4f_{vi}$  sites in the two respective substituted Ba-ferrites. The replacement of the  $Fe^{3+}$  ions on these sites will reduce the uniaxial crystalline anisotropy since the  $Fe^{3+}$  ions on these sites is a main contributor to the uniaxial anisotropy in the BaF. To account for the decrease in the saturation magnetization of the Co-Sn substituted Ba-F with increasing doping, Han et al., also have some of the Co and Sn ions going into the  $12k$  sites. Han et al., do not believe that any Co or Ti ions substitute into the  $12k$  sites of the Co-Ti substituted Ba-F since  $M_S$  of this Ba-F changes with additional Co-Ti substitution. We wish to report our study of the coercivity of bismuth substituted barium ferrites,  $BaFe_{12-x}Bi_xO_{19}$ .

## 2. Experimental Details and Results.

Stoichiometric amounts of Purum grade (Fukla, Switzerland) of  $BaCO_3$ ,  $Bi_2O_3$  and  $Fe_2O_3$  were weighed and mixed to yield the nominal compositions  $BaFe_{12-x}Bi_xO_{19}$  ( $x = 0.0, 0.1, 0.2, 0.3, 0.4,$  and  $0.8$ ). The mixtures were ball milled for ten hours before they were pre-fired for two hrs. at  $1300^\circ C$  in an oxygen atmosphere in a Lindberg (USA)  $1700^\circ C$  crucible furnace. The calcinated mixtures were ball milled again for 7 hrs., after which they were pressed into pellets of 9 mm diameter under a pressure of about 1500 psi. Pellets of each composition were sintered at  $1100^\circ C$ ,  $1200^\circ C$  and  $1300^\circ C$  in an oxygen atmosphere for twenty four hours. As was pointed out earlier, the addition of sintering aids facilitates the growth of hexagonal platelet-crystals. This can be seen in Fig. 1.

The magnetic hysteresis loops were obtained using a Walker Scientific (USA)

Hysteresisgraph with special coils. The upper halves of the magnetic hysteresis loops at room temperature of  $BaFe_{12-x}Bi_xO_{19}$  annealed at  $1200^\circ C$  are shown in Fig. 2.

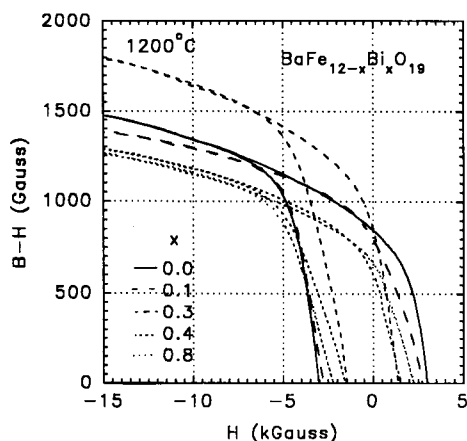


Fig. 2. Upper Half of the Hysteresis Loops for  $BaFe_{12-x}Bi_xO_{19}$ . The intercepts of the loops with the Horizontal axis give the values of the coercive force.

The intercepts of the hysteresis loops for the different Bi-doped BaF with the horizontal axis shows the coercivity decreasing as more  $Bi_2O_3$  is added. This is different from the results obtained by Pal et al., for  $Bi_2O_3$  substitution and by Ram<sup>1</sup> for  $B_2O_3$  substitution. Ram found the coercive forces decreased initially with the impurity doping, but then increased or remained the same as more impurity is added. The results obtained by Pal et al., are for pellets sintered at  $1100^\circ C$  for two hrs. In Ram's study of Bi doped ferrites,<sup>3</sup> it was found that  $Bi_2O_3$  was not completely incorporated into the ferrite core when heated at  $1100^\circ C$ . We show the hysteresis loops of  $BaFe_{11.2}Bi_{0.8}O_{19}$  annealed at  $1100^\circ C$ ,  $1200^\circ C$  and  $1300^\circ C$  on Fig. 3. We see that the coercivity of the  $1100^\circ C$  specimen is higher than that of the  $1200^\circ C$  specimen which in turn is higher than that of the  $1300^\circ C$  specimen. Since higher sintering temperatures promote particle growth and since the coercivity depends inversely on the particle size, the decrease in the

coercivity accompanying the use of higher sintering temperature is not unexpected.

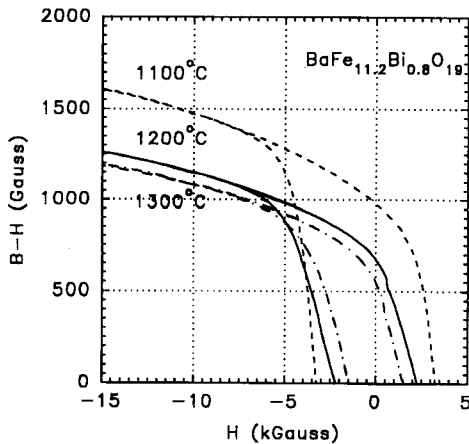


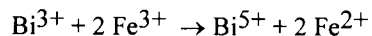
Fig. 3. Upper Half of the Hysteresis Loops for  $\text{BaFe}_{12.6}\text{Bi}_{0.4}\text{O}_{19}$  Sintered at  $1100^\circ\text{C}$ ,  $1200^\circ\text{C}$  and  $1300^\circ\text{C}$ .

### 3. Discussion.

Ram<sup>1</sup> believes the upturn of  $H_C$  of the B doped ferrites for  $x > 0.2$  is due to the stress induced by the structural distortion which he believes occurs as boron is added above this doping level. An alternative explanation is needed to explain the upturn in the  $H_C$ 's of the boron doped ferrites since it is observed that the average grain size in these doped ferrites increased as more boron was added, which in turn would lead to a monotonic decrease of  $H_C$ . As we have mentioned, the decrease in the coercivity of the Bi-doped BaF could also be due to the lessening of the uniaxial crystal-line anisotropy. If this were true, the Bi ions would be replacing the Fe ions in either the  $4e$  or  $4f_{vi}$  sites. Substitution of non magnetic ions into the  $4e$  sites ( a spin up layer ) should result in  $M_S$  decreasing while substitution into the  $4f_{vi}$  sites ( a spin down layer ) results in an increasing  $M_S$ . Looking at Fig. 2, we see  $M_S$  is initially increasing (the intercept of the  $x = 0.1$   $M_S$  curve with the vertical axis being higher than that of the pure BaF ) and then decreasing with further Bi substitution. The implication of this

behavior is that the Bi ions first enter into the  $4f_{vi}$  sites and then into the  $4e$  sites. The decrease in  $M_S$  at other than the lowest doping level could also be due to the Bi ion entering into the  $2a$  or  $12k$  sites ( both belonging to spin up layers and both large enough to accommodate the rather large  $\text{Bi}^{3+}$  ion ). The substitution in these two sites would not lead to the observed behavior of the coercivity.

To be able to explain the behaviors of both the saturation magnetization and the coercivity to Bi substitution, the Bi ions should be substituting into the  $4e$  sites. The placement of the  $\text{Bi}^{3+}$  ions into the octahedral  $\text{Fe}^{3+}$  site in the S block by Ram and his coworkers is based on the behavior of the saturation magnetization and the sizes of the  $\text{Bi}^{3+}$  ions and of the  $2a$  sites. The placement of the bismuth ions into the  $12k$  sites in the R+S block and the  $4f_{vi}$  sites in the R block by Pal and his coworkers is based on their assumption that the  $\text{Bi}^{3+}$  would not be stable at the  $\text{Fe}^{3+}$  sites and would undergo the following reaction



Due to the increased sizes of the  $\text{Bi}^{5+}$  and  $\text{Fe}^{2+}$  ions ( both being larger than the  $\text{Fe}^{3+}$  ion ), the chemical reaction occurs at the  $12k$  and  $4f_{vi}$  sites. Through an analysis of the saturation magnetization, Pal et al., estimated the ratio  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in each of their Bi-doped specimens. For the  $\text{BaFe}_{11.8}\text{Bi}_{0.2}\text{O}_{19}$  ferrite, they estimated the ratio to be 1/13.5. Ram et al., questions this conversion of  $\text{Fe}^{3+}$  ions to  $\text{Fe}^{2+}$  ions. They report that a chemical analysis of their Bi-doped ( 2.5 mol. % ) Ba-F contains  $\text{Fe}^{2+}$  of less than  $10^{-5}$  %. We hope to carry out Mossbauer studies on the Bi-doped Ba-F. This will give us addition clues to the site locations of the Bi ions.

### 4. Acknowledgement.

T. Osotchan, one of the authors, would like to thank the Faculty of Science, Mahidol University for a Young Scientist Grant.

## 5. References

- [1] Ram, S. (1989), *Crystallization of BaFe<sub>12</sub>O<sub>19</sub> Hexagonal Ferrite with an Aid of B<sub>2</sub>O<sub>3</sub> and the Effects on Microstructure and Magnetic Properties Useful for Permanent Magnets and Magnetic Recording Devices*, J. Magn. Magn. Mat., Vol. 82, pp. 129-150.
- [2] Smit, J. and Wijn, H.P.J. (1959), **Ferrites**, John Wiley, New York .
- [3] Ram, S. (1989), *Observation of Enhanced Dielectric Permittivity in Bi<sup>3+</sup> Doped BaFe<sub>12</sub>O<sub>19</sub> Ferrite*, J. Magn. Magn. Mat., Vol. 80, pp. 241-245.
- [4] Ram, S., Krishnan, H., Rai, K.N. and Narayan, K.A. (1989), *Magnetic and Electrical Properties of Bi<sub>2</sub>O<sub>3</sub> Modified BaFe<sub>12</sub>O<sub>19</sub> Hexagonal Ferrite.*, Jpn. J. Appl. Phys., Vol. 28, pp. 604-608.
- [5] Pal, M., Brahma, P., Chakravorty, D. and Agrawal, D.C. (1995), *Magnetic Properties of Ba Hexaferrites Doped with Bismuth Oxide*, J. Magn. Magn. Mat., Vol. 147, pp. 208-212.
- [6] Pal, P., Brahma, P., Chakravorty, B.R., and Chakravorty, D. (1997), *DC Conductivity in Barium Hexaferrites Doped with Bismuth Oxide.*, Jpn. J. Appl. Phys., Vol. 36, pp. 2163-2166.
- [7] Brahma, P., Giri, A.K., Chakravorty, Tiwari, M., and Bahadur, D. (1991), *Magnetic Properties of Sb<sub>2</sub>O<sub>3</sub>-Doped Ba-M Hexagonal Ferrites.*, J. Magn. Magn. Mat., Vol. 102, pp. 109-115.
- [8] Brahma, P., Giri, A.K., Chakravorty, D., Roy, M., and Bahadur, D. (1992), *Magnetic Properties of As<sub>2</sub>O<sub>3</sub>- and Sb<sub>2</sub>O<sub>3</sub>-Doped Ba-M Hexagonal Ferrites Prepared by the Sol-Gel Method.*, J. Magn. Magn. Mat., Vol. 117, pp. 163-168.
- [9] Zheng, Z.Y., Feng, J., Mei, X.M., Guo, B.J., and Zhang, Y.G. (1990), *The Influence of Al<sup>3+</sup> Substitution for Fe<sup>3+</sup> in M-type Ba Ferrite Powder on the Intrinsic Coercivity H<sub>CJ</sub>*, Jpn. J. Appl. Phys., Vol. 29, pp. 856.
- [10] Han, D.H., Yang, Z., Zeng, H.X., Zhou, X.Z., and Morrish, A.H. (1994), *Cation Site Preference and Magnetic Properties of Co-Sn Substituted Ba Ferrite Particles*, J. Magn. Magn. Mat., Vol. 137, pp. 191-196.
- [11] Yang, Z., Zeng, H.X., Han, D.H., Liu, J.Z., and Geng, S.L. (1992), *Morphological, Structural and Magnetic Characteristics of Co-Ti and Co-Sn Substituted Ba-Ferrite Particles for Magnetic Recording.*, J. Magn. Magn. Mat., Vol. 115, pp. 77-86.
- [12] Mueller, R., Pfeiffer, H., and Schuppel, W. (1991), *Variation of the Magnetic Properties of Barium Ferrite Powders by Heat Treatment.*, J. Magn. Magn. Mat., Vol. 101, pp. 237-238.
- [13] Saha, B., and Yetter, W. (1993), *On the Magnetic Properties and Domain Structure of Strontium Ferrite Particles.*, J. Appl. Phys., Vol. 73, pp. 6260-6262.
- [14] Kurtz, S.K., and Carpay, F.M.A. (1980), *Microstructure and Normal Grain Growth in Metals and Ceramics. Part I. Theory.*, J. Appl. Phys., Vol. 51, pp. 5725-5744.