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### ARTICLE

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#### Structural and Magnetic Properties of $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$ Prepared by Milling and Calcination

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**Abstract:** Al substituted barium ferrite particles  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  with  $0 \leq x \leq 0.8$  have been prepared by ball milling method. X-ray diffraction (XRD) has shown that the average crystallite size for all samples under investigation is in the range 66 – 76 nm. Scanning electron microscopy (SEM) imaging indicates that the particle size is in the range 0.2 – 1.0  $\mu\text{m}$ , which demonstrates that the particles are polycrystalline. It was found that Al substitution does not significantly change the particle size of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$ . The magnetic properties have been investigated using a vibrating sample magnetometer, and the anisotropy field is estimated. It was found that the coercivity of the samples increases from 4.2 kOe to 6.0 kOe with increasing Al concentration from  $x = 0.0$  to 0.8 due to the increase in the anisotropy field. Interparticle interactions determined from the remnant magnetization data are found to be consistent with a reversal mechanism (demagnetizing like effect) for all samples examined.

**Keywords:** Ball milling; Barium ferrite; Coercive field; Magnetization.

### Introduction

Barium hexaferrites, briefly (BaM), have attracted considerable interest due to their potential for different applications such as in permanent magnets, microwave devices and magnetic recording devices. The magnetic properties of hexaferrites such as saturation magnetization, coercivity and anisotropy field are strongly dependent on M-type phase [1]. Hexaferrites are well-known ferrimagnetic materials with strong uniaxial anisotropy. Anisotropy field can be controlled by the substitution of  $\text{Fe}^{3+}$  ions by paramagnetic and diamagnetic cations of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$ , or cations combination such as Mn-Ti [2], Co-Sn [3, 4], Zn-Ti [5], Co-Ti [6], ... etc. These substitutions aim at developing materials with improved characteristics, which make hexaferrites suitable for technological applications. Also, the synthesis of nanocrystalline hexaferrites with particle size less than 0.1  $\mu\text{m}$  and narrow particle size

distribution leads to the production of single domain particles relevant to new applications.

Several methods have been developed to prepare barium ferrite particles including sol-gel method [7, 8], glass-ceramic method [9], glass crystallization method [10], liquid mix method [11], mechanical alloying [12], ceramic method [13], aerosol route [14] and hydrothermal technique [15, 16].

Little had been reported on the Al-substituted barium ferrites (Al-BaM). The structural and magnetic properties of these materials seem to vary with the preparation method and the Al concentration [8, 12, 16]. Moreover, the microwave absorption properties have been reported to be affected by Al-substitution [17].

In this paper, the effect of Al ions on the magnetic properties of barium hexaferrite synthesized by milling and calcination is

reported. Milling and calcination method is a technique that has been recently adopted for the preparation of barium ferrite powders, due to its simplicity of operation and handy experimental apparatus [12]. Also, this method is useful for the production of powders composed of fine particles smaller than the single domain size. The magnetic properties, X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) images have been investigated and analyzed in an attempt to explore the effect of Al substitution for Fe in BaM and to explain the magnetic behavior of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$ .

### Experimental Procedure

$\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  powders with  $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7$  and  $0.8$  were prepared by using the milling and calcination method. Metallic oxides ( $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ ) and barium carbonate ( $\text{BaCO}_3$ ) were used as starting materials. Mechanical alloying was performed in a planetary ball-mill (Fritsch Pulverisette 7) using a ball to powder ratio of 8:1. Milling was carried out for 16 h with an angular frequency of 250 rpm. After mechanical milling, the mixture was pressed at 5 tons/sq inch into disks, 1 cm in diameter. These disks were calcined in air atmosphere at  $1100^\circ\text{C}$  for 10 h. The selection of this calcination temperature was based on the analysis of XRD patterns for more than 5 samples subject to different calcination temperatures from  $800^\circ\text{C}$  to  $1200^\circ\text{C}$ , which revealed that the optimum calcination temperature for obtaining a hexagonal  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  phase was  $1100^\circ\text{C}$ . Each disk was subsequently cut into three pieces, one was finely ground for the powder X-ray diffraction study, the second was used for the grain morphology study and the last one was used for magnetic measurements.

XRD analysis was carried out in Philips X'Pert PRO X-ray diffractometer (PW3040/60) with  $\text{CuK}_\alpha$  radiation (45 kV, 40 mA). The grain structure of the prepared samples was investigated using scanning electron microscope (SEM FEI Quanta 600) equipped with EDX facility for elemental analysis. The magnetic measurements were carried out using vibrating sample magnetometer (VSM MicroMag 3900, Princeton Measurements Corporation), with a

maximum applied field of 10 kOe at room temperature. The isothermal remnant magnetization (IRM) curve was obtained by the following procedure: the sample was initially demagnetized. A small positive field was applied then removed, and the remnant magnetization was recorded. The procedure was repeated with increasing the positive field to reach positive saturation remanence. Magnetic anisotropy field was estimated by differentiating the reduced IRM curve. The DC demagnetization remanence (DCD) curve was obtained by initially saturating the sample with a positive field of 10 kOe. A small negative field was applied to the sample. 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.

### Results and Discussion

XRD patterns of some samples of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  along with the standard pattern for hexagonal barium ferrite ( $\text{BaFe}_{12}\text{O}_{19}$ ) with space group  $P6_3/mmc$  are shown in Fig. 1. It can be seen from the Figure that the XRD patterns for all samples match the standard pattern 043-0002 for hexagonal barium ferrite ( $\text{BaFe}_{12}\text{O}_{19}$ ) [18]. Two peaks of  $\alpha\text{-Fe}_2\text{O}_3$  are present in all samples examined; one peak at  $33.14^\circ$  and the other at  $35.6^\circ$ , which interferes with the peak of  $\text{BaFe}_{12}\text{O}_{19}$  at the same diffraction angle. Thus, the most intense peaks between  $35^\circ$  and  $36^\circ$  (200 and 108) have reversed intensities for all samples examined. The lattice parameters  $a$  and  $c$  were calculated using the formula [19]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (1)$$

where  $d$  is the interplanar distance and  $h, k$  and  $l$  are Miller indices. The lattice parameters for this phase are shown in Table 1. These values of lattice parameters agree well with those published for the hexagonal barium ferrite [12, 20]. It should be noted that the preparation method and the  $\text{Al}^{3+}$  substitution for  $\text{Fe}^{3+}$  in the concentration range reported in this work do not affect the hexagonal structure of  $\text{BaFe}_{12}\text{O}_{19}$ . A general trend of reduction in lattice parameters, as a

result of Al substitution, can be observed from Table 1. The maximum reduction in lattice parameters is about 0.2%. In comparison, a reduction in lattice parameters

of about 0.7% was reported for Al-BaM sample prepared with  $x = 2$  using the same technique and conditions used in this work [12].

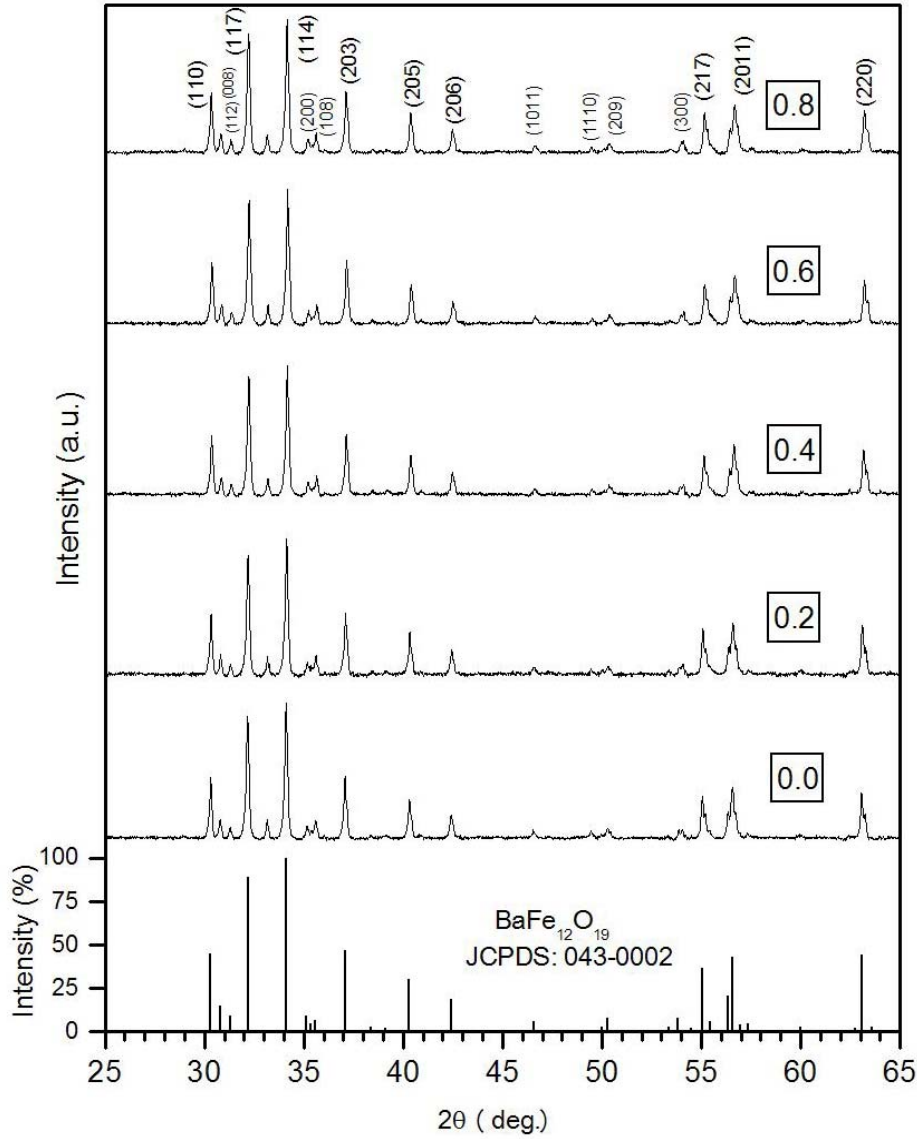


FIG. 1. XRD patterns of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  with different doping concentrations along with the standard pattern for hexagonal barium ferrite.

TABLE 1. Lattice parameters and average crystallite size of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$ .

| $x$ | $a = b$ (Å) $\pm 0.002$ | $c$ (Å) $\pm 0.007$ | Average crystallite size ( $D$ ) nm |
|-----|-------------------------|---------------------|-------------------------------------|
| 0.0 | 5.889                   | 23.194              | 76                                  |
| 0.1 | 5.889                   | 23.194              | 76                                  |
| 0.2 | 5.887                   | 23.192              | 71                                  |
| 0.3 | 5.885                   | 23.173              | 74                                  |
| 0.4 | 5.882                   | 23.164              | 70                                  |
| 0.5 | 5.880                   | 23.142              | 70                                  |
| 0.6 | 5.879                   | 23.153              | 69                                  |
| 0.7 | 5.885                   | 23.172              | 66                                  |
| 0.8 | 5.885                   | 23.171              | 72                                  |

The average  $\text{Al}^{3+}$  wt % in the particles is measured using the EDX facility in the SEM and is plotted against  $x$  in Fig. 2. The Al content in  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  is close to that of

the initial mixtures and indicates that about 90% or more of the aluminum ions enter into the lattice of barium ferrite.

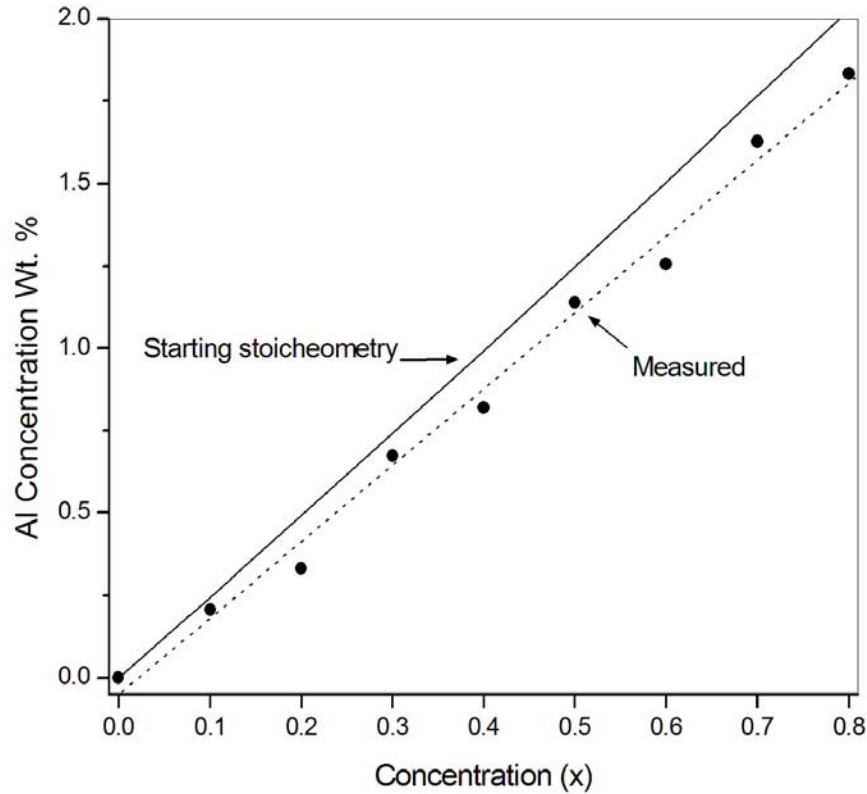


FIG. 2. Aluminum content in  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  from initial doping and measured by EDX.

The average crystallite size is determined from the positions of Bragg reflections (217) (220) using the well-known Scherrer formula [19]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where  $D$  is the crystallite size,  $K$  the Scherrer constant,  $\lambda$  the wavelength of radiation (1.54056 Å),  $\beta$  the width at half peak maximum measured in radians and  $\theta$  is the peak position. The above mentioned reflections are selected for the analysis since they are strong enough and are resolved into the  $K_{\alpha 1}$  and  $K_{\alpha 2}$  components for more accuracy. The strongest reflections are not resolved into the two components, providing a wider peak and, consequently, a non-accurate smaller particle size. The results of the analysis (Table 1) indicate that the average crystallite size of all samples is in the range 66 – 76 nm and that  $\text{Al}^{3+}$  substitution for  $\text{Fe}^{3+}$  does not substantially affect the

crystallinity of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$ . On the other hand, the morphology of the grains for all samples is investigated by the direct observation via scanning electron microscopy. Fig. 3 shows a SEM photograph of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  samples with doping concentrations of 0.0 and 0.8. As  $x$  increases, the grain size practically remains constant, which indicates that the Al substitution in the concentration range reported in this work does not significantly influence the particle size distribution. The particles in all samples under investigation are close to spherical in shape with diameters extending from 200 nm to about 1  $\mu\text{m}$ . Comparing the results of the XRD analysis and SEM imaging leads to the conclusion that most of the particles in the samples are not single crystals. Also, since the critical diameter of spherical barium ferrite with single magnetic domain is reported to be 460 nm [21], we conclude that probably more than 50% of the grains in the prepared samples are single-domain ones.

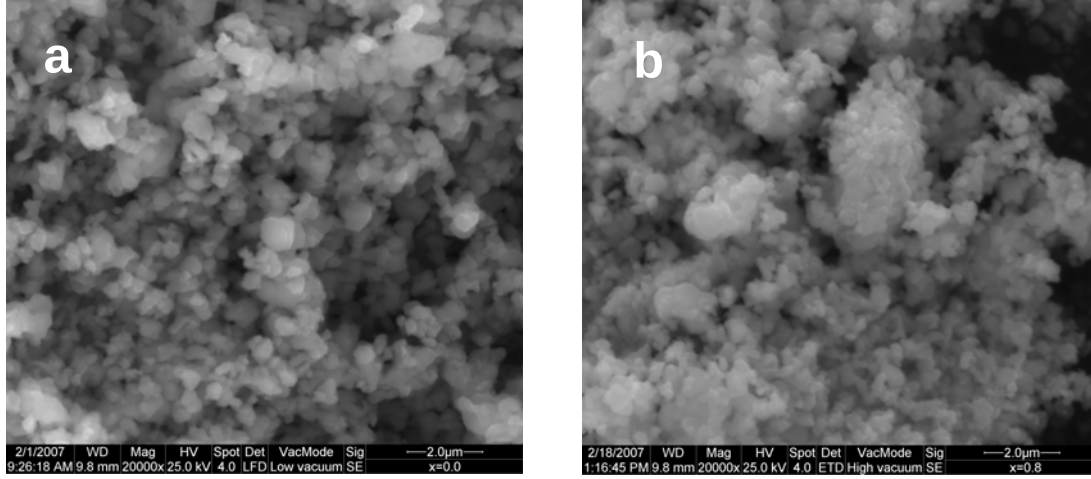


FIG. 3. SEM photograph of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$ , a)  $x = 0.0$ , b)  $x = 0.8$ .

The measured hysteresis loops for some of the  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  samples as a function of applied magnetic field are shown in Fig. 4. The magnetization curve for the non-substituted sample belongs to a hard magnetic material with high coercive field strength of about 4.2 kOe. This value of the coercivity is in good agreement with the reported results [22-24]. As one might observe, doping of barium ferrite with aluminum leads to the increase in coercive field and decrease in both remnant and saturation magnetization. The effects of Al concentration on the saturation magnetization and coercivity of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  for all samples examined are shown in

Fig. 5. The saturation magnetization decreases with increasing Al concentration, as expected, due to the weakening of the superexchange interaction of  $\text{Fe}^{3+}\text{-O-Fe}^{3+}$ . On the other hand, the coercivity increases linearly from about 4.2 kOe to 6.0 kOe as  $x$  increases from 0.0 to 0.8. This increase in coercivity can not be understood based on particle size effects, since all prepared samples have similar particle sizes. This increase in coercivity is thus attributed to the increase in anisotropy field  $H_a$ , since the coercivity is proportional to magnetic anisotropy field [25].

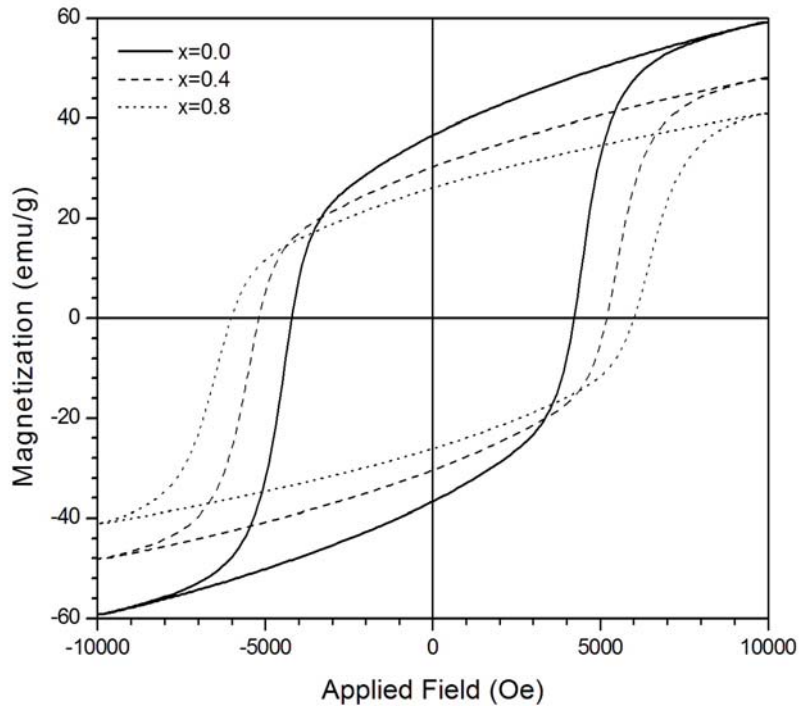


FIG. 4. Hysteresis loops for some of the  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  samples as a function of applied magnetic field.

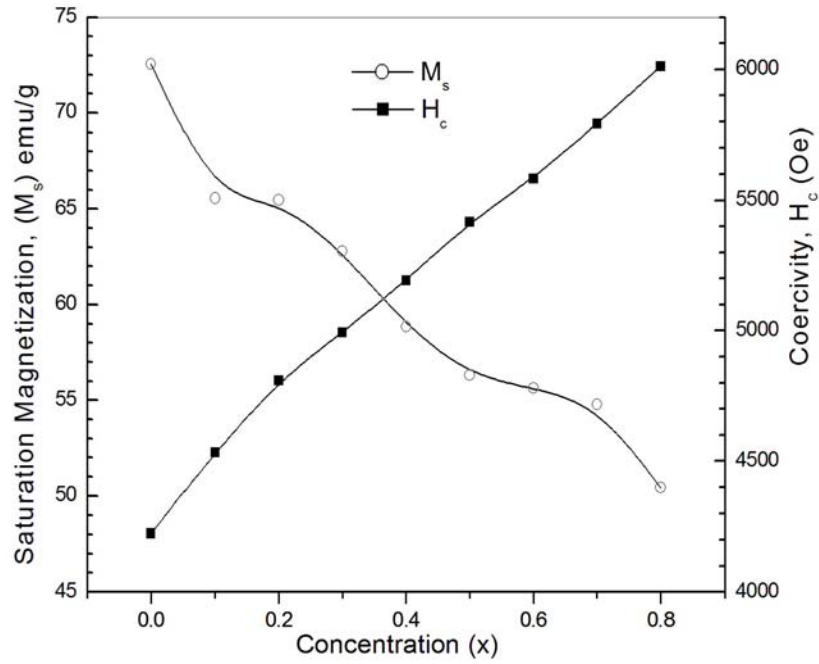


FIG. 5. Saturation magnetization and coercivity of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  as a function of Al concentration ( $x$ ).

The switching field distribution can be obtained by differentiating the reduced 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 a representative sample with  $x = 0.4$ . The effective magnetic anisotropy field for each sample examined in this work is obtained

from the maximum of the switching field distribution [26]

$$f(H)_{\max} = \left[ \frac{dm_r}{dH} \right]_{H=H_a/2} \quad (3)$$

(i.e.,  $H_a = 2H_{\max}$ , where  $H_{\max}$  is the value of the field at the maximum of the switching field distribution).

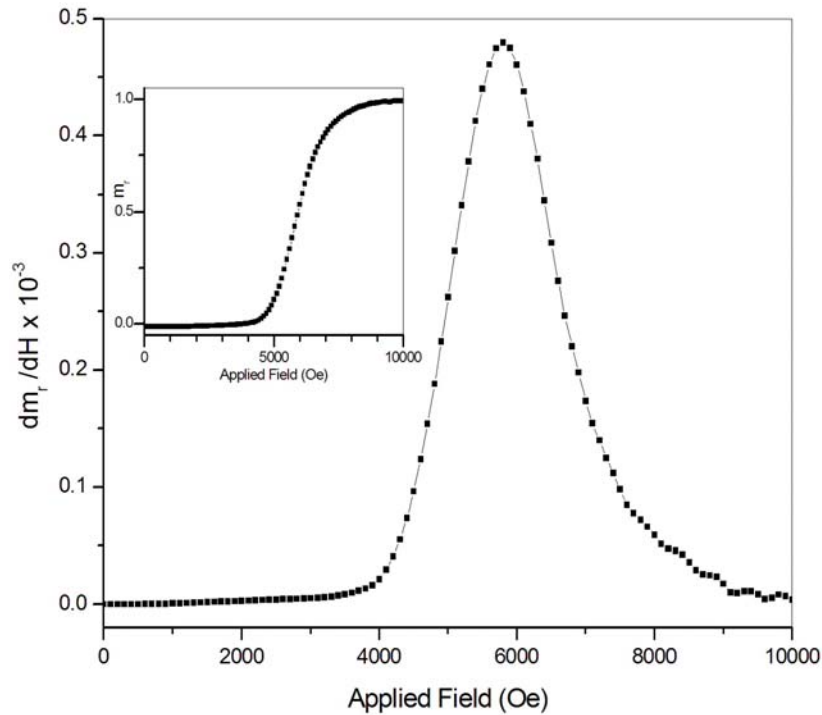


FIG. 6. Switching field distribution for a sample with  $x = 0.4$ . Inset: reduced IRM curve for a sample with  $x = 0.4$ .

Fig. 7 shows the variation of magnetic anisotropy field with Al concentration for all samples examined. It is clear that  $H_a$  increases with increasing Al concentration. The ratio  $H_c / H_a$  for all samples is about 0.44, which is close to Stoner-Wohlfarth [27] value of 0.48 for single-domain noninteracting

randomly oriented particles. The ratio observed in our samples is higher than that observed by Görnert *et al.* [25] for samples with particle diameters of 110 nm and 420 nm. The deviation from the theoretical value could be due to interparticle interactions.

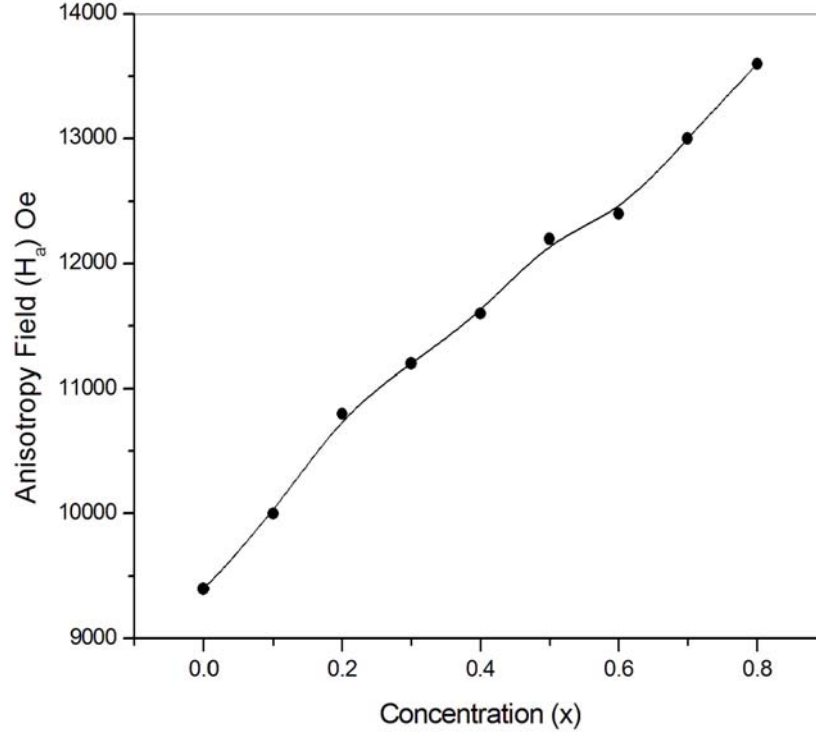


FIG. 7. Anisotropy field of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  as a function of Al concentration (x).

Next, we investigate the role of Al substitution on the interparticle magnetic interactions in  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  using the difference  $\delta m$  defined by Kelly [28]:

$$\delta m(H) = m_d(H) - [1 - 2m_r(H)] \quad (4)$$

where  $m_r(H) = M_r(H) / M_r(\infty)$  is the reduced IRM and  $m_d(H) = M_d(H) / M_r(\infty)$  is the reduced DCD. Usually,  $\delta m$  is used to clarify the sign and strength of the interaction between magnetic particles. Positive  $\delta m$  is attributed to magnetizing exchange interactions (magnetizing-like effect), whereas negative  $\delta m$  is associated with demagnetizing interactions (demagnetizing-like effect), i.e. negative  $\delta m$  indicates that the interparticle interactions assist magnetic reversal mechanisms. Fig. 8 shows the  $\delta m$  curves as a function of the applied field for samples of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  with different doping concentrations. The Figure illustrates

that  $\delta m$  is negative for all samples at all applied fields, exhibiting a maximum negative value at a field that increases with increasing the Al concentration due to the consequent increase in magnetic anisotropy. The maximum of  $\delta m$  fluctuates around the value of 0.35 for all Al concentrations investigated, which indicates that doping barium ferrite with Al in the range investigated does not systematically and significantly affect the demagnetizing effect in  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$ .

## Conclusions

Nano-size particles of diameters smaller than 100 nm of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  have been prepared using a very simple method of milling and calcination. It was found that doping of barium ferrite with Al leads to a decrease in saturation magnetization and to a significant increase in the coercive field due

to the increase of magnetic anisotropy field. Interparticle interactions are found to assist the reversal mechanisms (demagnetizing-like

effect), which is not significantly affected by Al concentration in the sample.

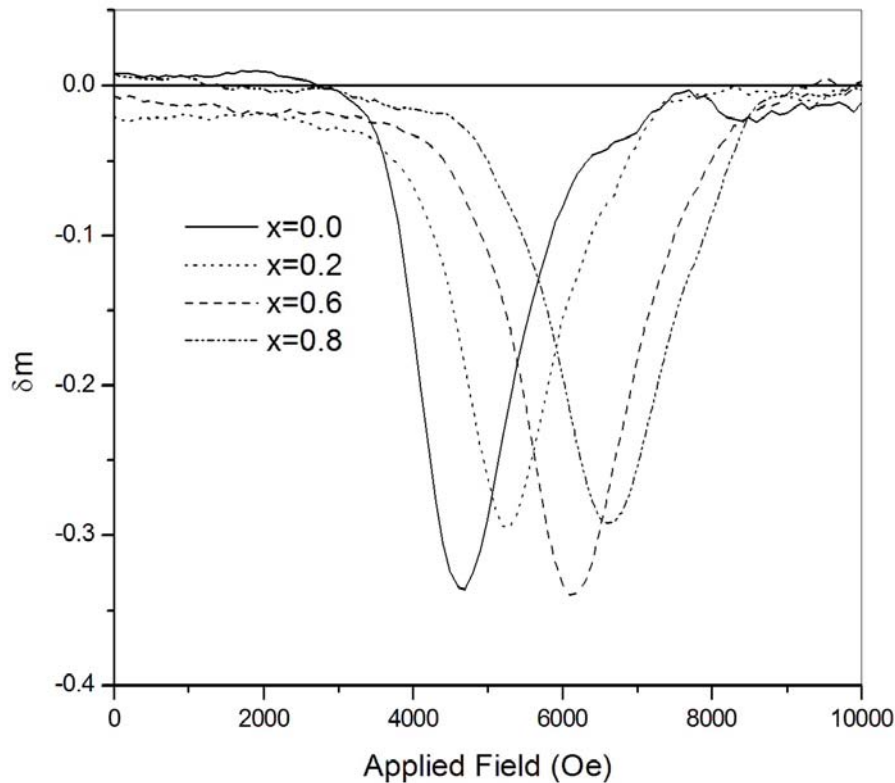


FIG. 8.  $\delta M$  curves of  $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$  for some of the concentrations examined.

## References

- [1] Lechevallier, L., Le Breton, J.M., Wang, J.F. and Harris, I.R., *J. Magn. Magn. Mater.*, 269 (2004) 192.
- [2] Turilli, G., Licci, F., Rinaldi, S. and Deriu, A., *J. Magn. Magn. Mater.*, 59(1-2) (1986) 127.
- [3] Yang, Z., Zeng, H.X., Han, D., Liu, J.Z. and Geng, S.L., *J. Magn. Magn. Mater.*, 115 (1992) 77.
- [4] Han, D.H., Yang, Z., Zheng, H.X., Zhou, X.Z. and Morrish, A.H., *J. Magn. Magn. Mater.*, 137 (1994) 191.
- [5] Wartewig, P., Krause, M.K., Esquinazi, P., Rosler, S., Sonntag, R., *J. Magn. Magn. Mater.*, 192 (1999) 83.
- [6] Gruskova, A., Slama, J., Dosudil, R., Kevicka, D., Jancarik, V. and Toth, I., *J. Magn. Magn. Mater.*, 242–245 (2002) 423.
- [7] Zhong, W., Ding, W., Zhang, N., Hong, J., Yan, Q. and Du, Y., *J. Magn. Magn. Mater.*, 168 (1997) 196.
- [8] Yue, Z., Zhong, M., Ma, H. and Gue, G., *J. Shanghai Univ.*, 12 (2008) 216.
- [9] Shirk, B.T. and Buessem, W.R., *J. Am. Ceram. Soc.*, 53 (1970) 192.
- [10] El-Hilo, M., Pfeiffer, H., O'Grady, K., Schüppel, W., Sinn, E., Görnert, P., Rösler, M., Dickson, D.P.E. and Chantrell, R.W., *J. Magn. Magn. Mater.*, 129 (1994) 339.
- [11] Pernet, M., Obradors, X., Vallet, M., Hernandez, T. and Germa, P., *IEEE Trans. Magn.*, MAG-24 (1988) 1898.
- [12] Wang, S., Ding, J., Shi, Y. and Chen, Y.J., *J. Magn. Magn. Mater.*, 219 (2000) 206.

- [13]Albanese, G., J. Magn. Magn. Mater., 147 (1995) 421.
- [14]Singhal, S., Garg, A.N. and Chandra, K., J. Magn. Magn. Mater., 285 (2005) 193.
- [15]Liu, X., Wang, J., Gan, L.M. and Ng, S.C., J. Magn. Magn. Mater., 195 (1999) 452.
- [16]Mishra, D., Anand, S., Panda, R.K. and Das, R.P., Mater. Lett., 58 (2004) 1147.
- [17]Qui, J., Zhang, Q. and Gu, M., J. Appl. Phys., 98 (2005) 103905.
- [18]International Centre for Diffraction Data (ICDD), JCPDS File 27-1029.
- [19]Warren, B.E., X-Ray Diffraction, (Addison-Wesley, Reading, Massachusetts, 1969).
- [20]Mallick, K.K., Shepherd, P. and Green, R.J., J. Magn. Magn. Mater., 312 (2007) 418.
- [21]Rezlescu, L., Reslescu, E. and Popa, P.D., J. Magn. Magn. Mater., 193 (1999) 288.
- [22]An, S.Y., Shim, I.B., Kim, C.S., J. Appl. Phys., 91(10) (2002) 8465.
- [23]Sharma, P., Rocha, R.A., de Medeiros, S.N. and Paesano, A.Jr, J. Alloys and Compounds, 443(1-2) (2007) 42.
- [24]Babu, V. and Padaikathan, P., J. Magn. Magn. Mater., 241 (2002) 85.
- [25]Görnert, P., Schüppel, W., Sinn, E., Schumacher, F., Hempel, K.A., Turilli, G., Paoluzi, A. and Rösler, M., J. Magn. Magn. Mater., 114 (1992) 193.
- [26]Pfeiffer, H. and Schüppel, W., Phys. Stat. Sol. (a), 119 (1990) 259.
- [27]Stoner, E.C., Wohlfarth, E.P., Phil. Trans. Roy. Soc., 240A (1948) 599.
- [28]Kelly, P.E., O'Grady, K., Mayo, P.I. and Chantrell, R.W., IEEE Transactions on Magnetics, 25(5) (1989) 3881.