

# Magnetic and atomic structure parameters of Sc-doped barium hexagonal ferrites

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(Presented on 7 November 2007; received 12 September 2007; accepted 26 November 2007; published online 13 March 2008)

Scandium-doped *M*-type barium hexagonal ferrites of the composition  $\text{BaFe}_{12-x}\text{Sc}_x\text{O}_{19}$  are well suited for low frequency microwave device applications such as isolators and circulators. A series of Sc-doped *M*-type barium hexagonal ferrite powders ( $x=0-1.2$ ) were prepared by conventional ceramic processing techniques. The resulting powders were verified to be pure phase and maintain the nominal chemical stoichiometry by x-ray diffraction and energy dispersive x-ray spectroscopy, respectively. Static magnetic measurements indicated that both saturation magnetization and uniaxial magnetocrystalline anisotropy field decreased with increasing concentration of scandium. Extended x-ray absorption fine structure measurements were carried out to clarify the correlation between the magnetic and atomic structure properties. It is found that the substituted Sc has a strong preference for the bipyramidal site. Nevertheless, the substitution did not introduce additional atomic structural disorder into the barium hexagonal structure. The structural study provided important evidence to quantitatively explain the change in dc and microwave magnetic properties due to Sc ion doping. © 2008 American Institute of Physics. [DOI: 10.1063/1.2838232]

## INTRODUCTION

During the past half century, barium hexaferrites [*M*-type  $\text{BaFe}_{12}\text{O}_{19}$  or (BaM)] has been realized as an effective material for microwave and millimeter-wave device applications such as isolators, phase shifters, and circulators.<sup>1,2</sup> However, the high anisotropy field of BaM [ $\sim 17$  kOe (Refs. 3 and 4)] restricted its device operation only to high frequencies above 30 GHz. The substitution of iron by nonmagnetic trivalent ions allows for lower frequencies, below 10 GHz, to be considered.<sup>5-7</sup>

The unit cell of BaM has hexagonal symmetry with the magnetic easy axis along the crystallographic *c* axis. The crystal structure can be built up from the spinel blocks (*S*) interposed by the hexagonal *R* block that contains the barium ions. Iron ions reside at five inequivalent crystallographical sites. Three out of five of these are octahedral sites (*B*), while the other two are tetrahedral (*A*) and fivefold tripyramidal sites (represented as “5” throughout the paper). The spin orientations of each sublattice are listed in Table I.<sup>8</sup> The magnetization of BaM results from the net moments between the magnetic ions on the five sublattices. At 0 K, BaM was predicted from the model with eight spins up and four spins down resulting in 20 bohr magnetons per formula unit. This translates to a saturation magnetization at 0 K of 6632 G.<sup>8</sup> This value is in good agreement with the experimental value of 6333 G.

The investigation of the fundamental source of magnetic anisotropy for barium ferrite remains of interest, especially for doped *M*-type ferrites. The responsible sites appear to be in the dominant magnetic sublattices.<sup>9</sup> Sc-doped BaM has a reduced anisotropy field and magnetization compared with

BaM samples. By studying the site occupancy of Sc and Fe ions within the BaM structure, we may acquire insight into the source of magnetic anisotropy from among the five sublattices. Extended x-ray absorption fine structure (EXAFS) spectroscopy is capable of supplying the element-specific structural information at atomic level. This technique was employed to investigate the relationship between the site occupancy in substituted BaM and the resulting magnetic properties.

## EXPERIMENT

A series of Sc doped *M*-type barium hexaferrite ( $\text{BaSc}_x\text{Fe}_{12-x}\text{O}_{19}$ ) samples was prepared by the general method of ceramic preparation. The samples with concentrations of scandium ions ( $x=0.4-1.2$ ) were pressed within a magnetic field of 8 kOe and sintered in air at 1150 °C for 4 h. The dc and microwave magnetic properties were characterized by vibrating sample magnetometer and ferromagnetic resonance, respectively.

The x-ray absorption data were collected using beamline X23B at the National Synchrotron Light Source at Brookhaven National Laboratory.<sup>10</sup> The samples were evenly

TABLE I. Properties of five iron sublattices within BaM structure.

Sublattice	Coordination	Block	Number of ions per formula unit	Spin orientation
12 <i>k</i>	Octahedral	<i>S</i> + <i>R</i>	3+3	Up
4 <i>f</i>	Octahedral	<i>R</i>	2	Down
4 <i>f</i>	Tetrahedral	<i>S</i>	2	Down
2 <i>b</i>	Tripyramidal	<i>R</i>	1	Up
2 <i>a</i>	Octahedral	<i>S</i>	1	Up

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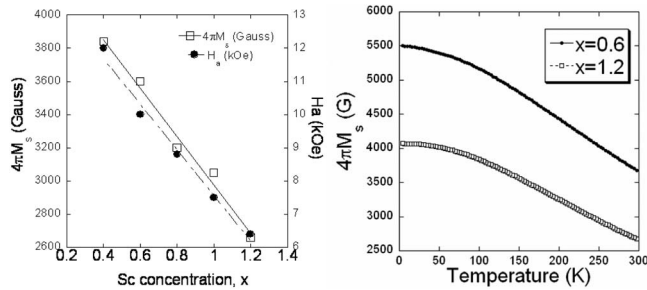


FIG. 1. (a) Magnetization and anisotropy field vs different Sc concentrations. The lines served as guidelines to readers. (b) Magnetization vs temperature curve for two Sc-doped samples,  $\text{BaSc}_x\text{Fe}_{12-x}\text{O}_{19}$ ,  $x=0.6$  and  $1.2$ .

brushed on several layers of scotch tape for data collection in transmission mode. Fe and Sc  $K$  edge EXAFS data were collected over energies ranging from 50 eV below and 14k (in wavenumber space) above the edge. The data were first converted into photoelectron wave vector ( $k$ ) space, and then Fourier transformed to radial coordinates for spectral isolation following the refinement procedures outlined by Sayers and Bunker.<sup>11</sup> We made use of the data analysis codes, Athena and Artemis, developed by Ravel and Newville<sup>12</sup> to analyze the distribution of the cations in the samples.

## RESULTS AND DISCUSSION

The substitution of iron by scandium was found to reduce the anisotropy field and saturation magnetization values. As a function of concentration of scandium ions, the anisotropy field and the saturation magnetization were found to decrease monotonically, as shown in Fig. 1. We measured the saturation magnetization of scandium doped BaM specimen as a function of temperature. The  $M$  versus  $T$  curves for  $x=0.6$  and  $x=1.2$  are shown in Fig. 1. It can be seen that the samples ( $x=0.6$  and  $1.2$ ) have magnetizations of 5502 and 4072 G at 4 K and anisotropy fields of 10 and 6.4 kOe at 300 K, respectively. The results are substantially lower than the observed value for pure barium hexaferrite [ $4\pi M_s = 6632$  G (4 K),  $H_a = 16.5$  kOe, (300 K)].

Fourier-transformed Fe EXAFS data collected from the pure BaM as a standard are presented in Fig. 2. The first peak in the Fe EXAFS data near 1.3 Å corresponds to all Fe–O nearest neighbor correlations uncorrected for electronic phase shifts. The major cation-cation features appear in the region of  $r=2-4$  Å. Two Fourier peaks are present in this region near  $r=2.6$  Å and  $r=3.1$  Å. The first peak represents the atomic correlation between two Fe ions at  $B$  sites only. The second peak consists of amplitude contributions from other Fe–Fe correlations, such as Fe(A)–Fe(A), Fe(A)–Fe(B), Fe(B)–Fe(B), Fe(5)–B, and the correlation between Fe(5) and Ba ions. The atomic pair correlations were given by the theoretical standards generated by FEFF calculations.<sup>13</sup> As a result, by observing the comparative peak amplitude changes of Fourier transformed Fe EXAFS data, a great deal of qualitative site occupancy information can be obtained.

The Fourier-transformed Fe  $K$  edge EXAFS data for scandium doped BaM specimen are shown in Fig. 3. The peak at around  $r=2.6$  Å, representing Fe(B)–Fe(B) correla-

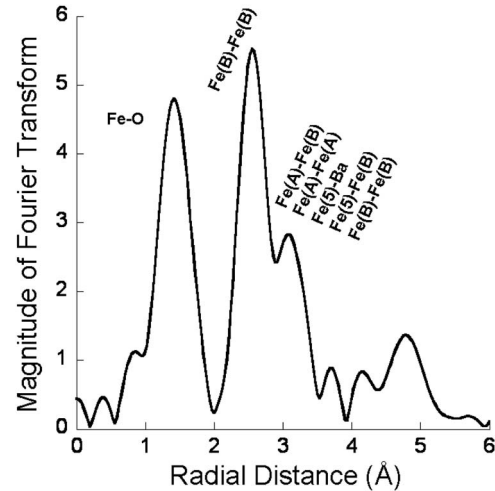


FIG. 2. Fourier transform of Fe EXAFS of  $\text{BaFe}_{12}\text{O}_{19}$  bulk sample. Fe data were transformed using  $k$  ranges of  $2.8-12 \text{ \AA}^{-1}$  with  $k^3$  weighting. The major peak features have been labeled with pairing of atomic correlations.

tions, remained about the same for  $x=0$  and  $0.4$ , but dropped a bit for  $x=0.6$ ,  $1$ , and  $1.2$ . The second peak around  $r=3.1$  Å experience reduced amplitude from  $x=0$  to  $0.4$ , increased to a maximum at  $x=0.6$ , and dropped back again as we increased further scandium concentrations to  $x=1.2$ . Based on those facts, we can tell that from  $x=0$  to  $0.4$ , the Sc ions have a strong preference for either the bipyramidal site or the tetrahedral sites. When we further increased the Sc doping, Sc ions begin to replace the Fe ions on the octahedral sites. That explains the decreased amplitude of both peaks at  $r=2.6$  Å and  $r=3.1$  Å for higher Sc doped samples.

The experimental data indicate that the magnetization values are reduced as the concentration of scandium concentration increased, as presented in Fig. 1. The scandium ion is nonmagnetic, while the  $\text{Fe}^{3+}$  ion has  $5\mu_B$ . When the scandium ions replace Fe ions at those sites with spin up orien-

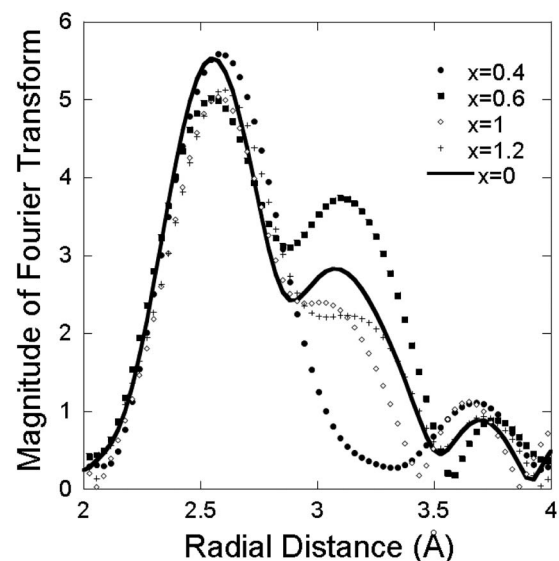


FIG. 3. Fourier transform of Fe EXAFS of  $\text{BaSc}_x\text{Fe}_{12-x}\text{O}_{19}$  samples,  $x=0$ ,  $0.4$ ,  $0.6$ ,  $1$ , and  $1.2$ . For a clear comparison, only the region of  $r=2-4$  Å was plotted here. Fe data were transformed using  $k$  ranges of  $2.8-12 \text{ \AA}^{-1}$  with  $k^3$  weighting.

tation, the overall saturation magnetization will decrease. Those sublattices are the four octahedral ones in the spinel block, three out of five octahedral ones in the *R* block, and a bipyramidal one in the *R* block. Along with the observation in Fig. 3, it can be deduced that the scandium ions prefer the bipyramidal site in *R* blocks rather than the tetrahedral sites when the percentage of doping is small, i.e.,  $x=0.4$ . The bipyramidal site is the closest metal ion site to the Ba ion, and determines to a large degree the out-of-plane anisotropy field in *M*-type barium hexaferrite. That also explains the reduced anisotropy field measured in those Sc doped BaM samples. Quantitative information can be obtained from the least squares fitting of the EXAFS data to the theoretical standards generated by the FEFF6 code.<sup>13</sup> Due to the complexity of the BaM structure, we did a preliminary EXAFS model and fitting in which a limited range of radial coordinate,  $r=1-4$  Å, is fit using only single scattering FEFF paths with  $k$  ranges of 2.8–12 Å. The Fe *K* edge of BaM samples with  $x=0$ , 0.4, and 1.2 were studied. We found that with increasing Sc concentration from  $x=0$  to 0.4, ~97% of the Sc ions have a preference over bipyramidal sites. While Sc concentrations changed from  $x=0.4$  to 1.2, 35% of the doped Sc ions have a preference for the 12*k* sublattices among the three octahedral sites. The concentration percentage of Sc ions residing on the other two octahedral sublattices has no significant change. *R* values represent the how well the EXAFS data were fit into FEFF generated theoretical standards. In this study, *R* values were 0.039, which usually indicated good fits.

In Fig. 3, although the amplitude of Fourier peaks change from sample to sample, the spectral position of the peaks for all samples remain unchanged. That means there is little structural distortion resulting from the increased scandium doping to as high as  $x=1.2$ . One of the EXAFS fitting parameters was to define the changes in lattice parameter of the unit cell. We find that the lattice parameter changes less than 1% for samples with the highest ( $x=1.2$ ) and lowest ( $x=0.4$ ) Sc concentration. In Fig. 4, we also include a figure illustrating the Fe *K* edge near edge spectra (XANES) for the measured samples. The features of the XANES are almost identical suggesting little to no change in the local electronic properties and average valence of Fe ion due to Sc substitution.

In conclusion, we have explored the correlation between magnetic and atomic structure properties of Sc doped barium *M*-type hexaferrite samples. The doping Sc ions induced significant decreases in both magnetization and anisotropy field values. From the Fourier transform of the EXAFS spectra, it is concluded that the Sc ions have a higher preference for bipyramidal sites, which contributes the most to the anisotropy field of BaM. As the doping percentage increased, EXAFS best fitting results indicated that the Sc ions began to occupy the spin-up 12*k* octahedral sublattices. The substitution further decreased the saturation magnetization of the samples.

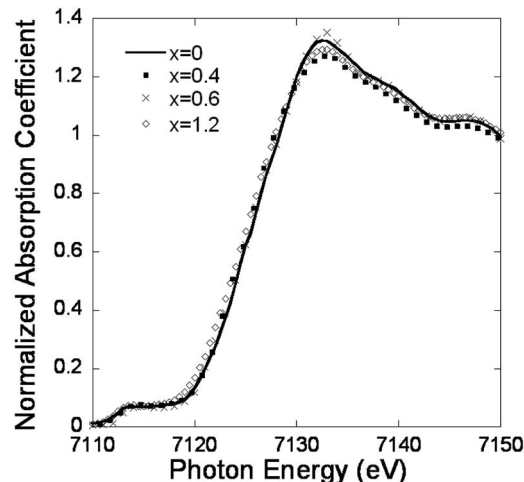


FIG. 4. Selected x-ray absorption near edge spectra for the Sc-doped BaM samples. Concentrations of Sc ions were marked in the plot.

## ACKNOWLEDGMENTS

This research was performed in part at the beamline X23B with help from Johnny Kirkland at National Synchrotron Light Source at the Brookhaven National Laboratory which is sponsored by the Department of Energy. This research was also supported by the National Science Foundation (DMR 0400676) and the Office of Naval Research (N00014-07-1-0701).

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