

Boron Site Preference in B-Doped Barium Hexaferrite

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ABSTRACT Mössbauer studies were conducted on boron-doped barium ferrites $\text{BaFe}_{12-x}\text{B}_x\text{O}_{19}$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.6) with special attention paid to the behavior of the line widths in the Mössbauer sextets. Assuming that the broadening of the line widths in the various sextets is due to increases in the fluctuations in the hyperfine field (acting on an Fe ion in a given site) caused by the introduction of the B ions into the neighboring Fe sites, the observed broadening of the lines belonging to the different sextets indicated that the B ions are entering into the $4f_{\text{IV}}$ sites, as proposed by Ram (*J Magn Magn Mat* **82**, 129 (1989)) based on the saturation magnetization measurements.

KEYWORDS: B-doped barium ferrites, Mössbauer spectroscopy, site preferences

INTRODUCTION

As is well known, several of the magnetic properties of the ferrimagnetic ceramics, such as the M-type hexaferrites, can be modified by changing the morphology of the material. The morphology can be changed by processing the ceramics at different temperatures and maintaining the temperature for different periods of time. Sintering at high temperatures leads to large grains, while heating at low temperatures produces fine grains. The growth of the grains leads to changes in the amount of domain boundaries present in the ceramic, the larger grains having smaller boundary wall area to volume ratios than do the smaller grains. These domain boundaries directly affect the coercivity, H_c , the force required to reverse the direction of the magnetization of the ferrites. The coercivity is one of the properties which determines the usefulness of a given ferrite for certain applications. Since the presence of grain boundaries can inhibit the spin flipping, the lessening of the wall area would lead to a decrease in H_c , a desirable improvement if the ferrite is to be used as a high density recording medium.¹

One is not, however, completely free to use the sintering temperature as the only means to control the grain growth. Heating at too high a temperature can lead to destruction of the crystalline structure, while heating at too low a temperature can result in incomplete solid state reaction. The use of sintering agents such as Al_2O_3 , Bi_2O_3 , or B_2O_3 will lower the required processing

temperatures. This would be equivalent to the use of higher sintering temperatures in terms of its effect on the changes in the morphology. One should see a decrease in H_c when one either increases the sintering temperature or increases the amount of sintering aid used. This behavior has been seen by Yang *et al.*,² and Han *et al.*,³ when Co-Ti and Co-Sn were doped into barium hexaferrites (BaF), *ie*, a lowering of the coercivity.

Zheng *et al.*,⁴ found that the increased doping (keeping the sintering temperature constant) of Al_2O_3 into BaF produced larger grain sizes. They observed, however, that the coercivity increased (not decreased). To explain this behavior, Zheng *et al.* pointed out that the coercivity also depends on the anisotropy energy of the crystalline material. Since the anisotropy field, H_A , in Al-doped BaF, $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$ increases with x , the coercivity would also increase with x . Similar reasoning was used by Han *et al.*³ to help determine the site preference of impurity ions in the Co-Ti and Co-Sn doped BaF. The uniaxial crystalline anisotropy is appreciable in the M-type hexaferrites. The major contribution to the anisotropy of the BaF arises from the Fe ions in the $4f_{\text{VI}}$ and $4e$ sites (there being five types of Fe sites in the M-type hexaferrites, the others being the $2a$, $4f_{\text{IV}}$ and $12k$ sites). Replacement of the Fe ions at the $4e$ or $4f_{\text{VI}}$ sites by non Fe ions would lead to decreases in this anisotropy which in turn would lead to a decrease in H_c . This led Han *et al.* to conclude that the Co^{2+} and Ti^{4+} ions in the Co-Ti doped BaF substituted into the $4e$ and $4f_{\text{VI}}$ sites.

The site preference of Co^{2+} and Sn^{4+} for the Co-Sn doped BaF are the **4e**, **4f_{iv}** and **12k** sites. The additional site (**12k**) assignment is needed to explain the difference in the response of the magnetization to the sets of doping. In general, the assignment of the sites into which the non magnetic dopants enter is based on two considerations: (1) the behavior of M_s , e.g., if M_s decreases with the substitution, the dopants would be going into spin up sites, the **2a**, **4e** and **12k** sites, while if M_s increases, the dopants would be going into spin down sites, the **4f_{iv}** and **4f_{vi}** sites and (2) on the size of the impurity ion, the larger ions going into the octahedral sites and the smaller going into the tetrahedral sites. If the impurity ions went equally into the **4e** and **4f_{iv}**, there would be no change in M_s . This is indeed seen in the M_s of BaF when doped with Co and Ti. Doping the BaF with Co and Sn leads, however, to a linear decrease in the specific saturation magnetization, s , of the BaF. This could be explained if some of the impurity ions also went into the **12k** sites.

Our interest in this paper is the site assignment or preference of the B^{3+} ions in boron-doped BaF. To account for the increase in M_s observed when B_2O_3 is used as a sintering aid, Ram⁵ has the B^{3+} ions going into the **4f_{iv}** sites. The **4f_{iv}** sites were chosen over the **4f_{vi}** sites based on the relatively small size of the boron ions. Being small should not, however, prevent the ions from going into the larger octahedral **4f_{vi}** sites. We are interested in applying our recently introduced method for determining the site preferences of impurity ions in doped ferrimagnetic ceramics^{6,7}, which is based on the observation of changes in the line widths in the Mössbauer sextets associated with the Fe ions in the layers adjacent to the layers into which the impurity ions substitute.

Following the steps given in ref. 6, we find that the fluctuating part in the hyperfine fields acting on the Fe ions in the **2a**, **4e** (**2b**), **4f_{iv}**, **4f_{vi}** and **12k** sites in the M-type hexaferrites are:

$$\delta H_f(2a) = (P_2((2-x_3)/2)(1/N_3)\Sigma_k |J_{13}(\mathbf{k})\langle\langle S_3 \rangle\rangle|^2)^{1/2} \quad (1a)$$

$$\delta H_f(4e) = (P_2((2-x_4)/2)(1/N_4)\Sigma_k |J_{24}(\mathbf{k})\langle\langle S_4 \rangle\rangle|^2)^{1/2} \quad (1b)$$

$$\delta H_f(4f_{iv}) = (P_2(1-x_1)(1/N_1)\Sigma_k |J_{13}(\mathbf{k})\langle\langle S_1 \rangle\rangle|^2 + P_c((2x_3)/2)(1/N_3)\Sigma_k |J_{33}(\mathbf{k})\langle\langle S_3 \rangle\rangle|^2 + P_2((6-x_6)/6)(1/N_5)\Sigma_k |J_{35}(\mathbf{k})\langle\langle S_5 \rangle\rangle|^2)^{1/2} \quad (1c)$$

$$\delta H_f(4f_{vi}) = (P_2(1-x_2)(1/N_2)\Sigma_k |J_{24}(\mathbf{k})\langle\langle S_2 \rangle\rangle|^2 + P_2((6-x_6)/6)(1/N_5)\Sigma_k |J_{45}(\mathbf{k})\langle\langle S_5 \rangle\rangle|^2 + P_2((2-x_4)/2)(1/N_4)\Sigma_k |J_{44}(\mathbf{k})\langle\langle S_4 \rangle\rangle|^2)^{1/2} \quad (1d)$$

and

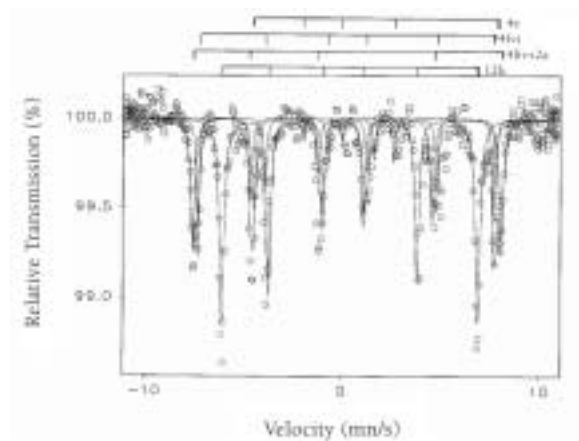
$$\delta H_f(12k) = (P_2((2-x_3)/2)(1/N_3)\Sigma_k |J_{35}(\mathbf{k})\langle\langle S_3 \rangle\rangle|^2 + P_2((2-x_4)/2)(1/N_4)\Sigma_k |J_{45}(\mathbf{k})\langle\langle S_4 \rangle\rangle|^2)^{1/2} \quad (1e)$$

where $P_2(x) = (x - x^2)$ is the second cumulant function; x_i , the concentration of non magnetic impurity ions in the i -th layer; $J_{ij}(\mathbf{k})$, the Fourier transform of the superexchange interaction J_{ij} and N_i , twice the number of sites in the i -th layer.

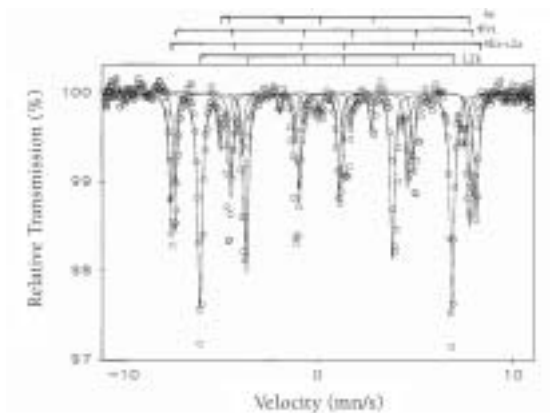
Looking at the expressions for the five dH_f , we find that the broadening of any of the Mössbauer sextets is dependent on the value of one or more of the x_i 's. The absence of systematic broadening of a sextet means that the x_i 's appearing in the expression for that dH_f would be equal to zero. In the analysis presented in ref. 6 on the determination of Al sites in the substituted $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$, the existence of a broadening in the sextets for the **4f_{iv}** + **2a** sites, the absence of the broadening in the sextets for the **4e**, **4f_{vi}** and **12k** sites, and the decrease in the saturation magnetization accompany the Al doping clearly pointed to the Al^{3+} ions going into the **2a** sites.

We should mention that Simsa *et al.*⁸ have proposed a much simpler method for determining the cation distribution from the Mössbauer measurements. They believe that the distribution can be inferred from an analysis of the areas under the sextets associated with the different sites. They applied the method to the determination of the cation distribution of the Co-Ti ions in the $\text{BaFe}_{1-2x}\text{Co}_x\text{Ti}_x\text{O}_{19}$ ferrites, along with data from optical and magneto-optical measurements. They concluded that the cobalt ions go into the **4f_{iv}** and **4f_{vi}** sites, with very little going into **2a** sites and that the Ti ions go into the **12k** site with small amounts going into the **4e** and the **4f_{iv}** sites. These assignments are somewhat different from those given by Han *et al.*,³ and those given by Batlle *et al.*⁹ The latter has the Ti ions showing preference for the **4f_{vi}** and **12k** sites and the Co ions for the **4f_{vi}** sites (with none going into the **12k** sites) at low impurity levels. Batlle *et al.* site assignments are based on neutron diffraction studies and are probably the definitive assignment.

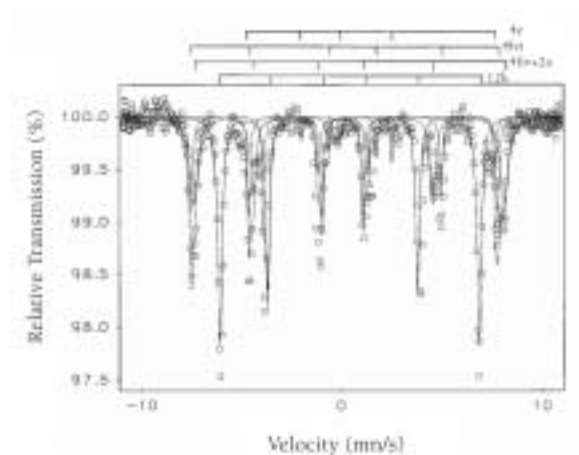
The discrepancy between the site assignments in the Co-Ti doped BaF gained from neutron diffraction studies and the method used by Simsa *et al.*, clearly demonstrates one of the drawbacks of the latter method. The relative intensities of the different sextets in the Mössbauer spectrum of the BaF do not depend only on the relative amounts of Fe atoms in the different sites. They also depend on other factors. This is clearly seen in a Mössbauer study on single crystal and powdered $\text{PbFe}_{12}\text{O}_{19}$ by Evans and Thompson.¹⁰ They report that the relative intensity of the **4e** (**2b**) pattern of a single crystal specimen aligned parallel to the c-axis is 8.2%, close to the theoretical value, the percentage of Fe at **4e** sites in the total BaF structure, 8.33. The relative intensity of the **4e** pattern of a polycrystalline specimen is reduced to only 6.7%.



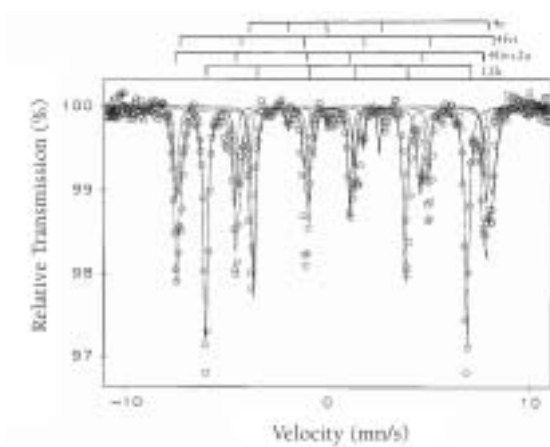
a. Spectrum of an undoped specimen ($x = 0.0$)



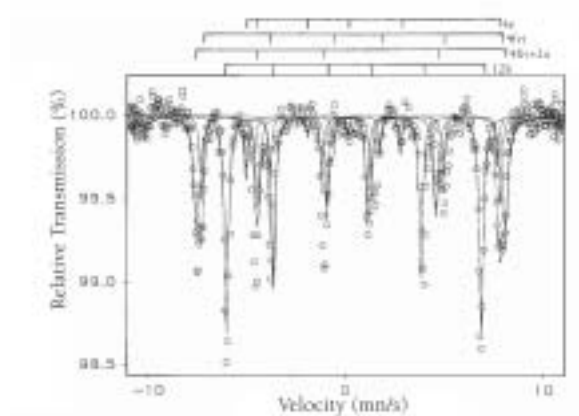
b. Spectrum of $x = 0.1$ specimen



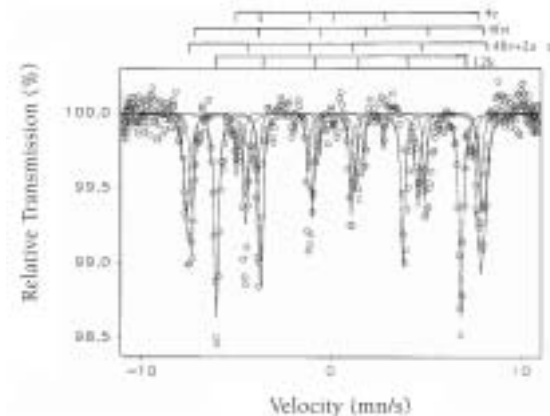
c. Spectrum of $x = 0.2$ specimen



d. Spectrum of $x = 0.3$ specimen



f. Spectrum of $x = 0.4$ specimen



g. Spectrum of $x = 0.6$ specimen

Fig 1. Mössbauer spectra of the boron doped Ba-hexaferrite, $\text{BaFe}_{12-x}\text{B}_x\text{O}_{19}$.

EXPERIMENTAL DETAILS AND RESULTS

The boron doped BaF was fabricated using the standard solid state reaction. In such a method, stoichiometric amounts of high purity grades (99-99.5%) of B_2O_3 and $BaCO_3$ and Fe_2O_3 powders (Fluka, Switzerland) were weighed and mixed to yield the nominal compositions $BaFe_{12-x}B_xO_{19}$ ($x=0.0, 0.1, 0.2, 0.3, 0.4$ and 0.6). The mixtures were mixed together in an agate mortar and then pre-fired for one hour in O_2 at $1100^\circ C$. The calcinated lumps were reground and pressed into pellets of 9 mm in diameter and 2-3 mm in thickness, under an uniaxial pressure of 2000 psi. The pressed pellets were then sintered for twelve hours⁶ in a flowing O_2 atmosphere at $1200^\circ C$. The Mössbauer spectra were obtained at room temperature using a constant acceleration spectrometer (CMTE, Germany). The source was 50 mCi of ^{57}Co in a Rh matrix. The Mössbauer spectra were analyzed using the NSeXT program supplied by CMTE.

All Mössbauer spectra taken at room temperature are shown in Figs 1a, 1b, 1c, 1d, 1f and 1g, corresponding to $x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.6 , respectively. These spectra show the presence of the four sextets associated with the Fe ions located in the **12k**, **4f_{iv}**, **4f_{iv} + 2a** and **4e** sites. In Table I, we list the values of the hyperfine fields at the different sites for the sintered pellets. In Figure 2 and Figure 3, we present the values of the broadening of the widths of the outer lines and the area under each of the sextets in the spectra for each of the sintered specimens, respectively. The values of the hyperfine fields listed in Table 1 are within the range of values of the hyperfine fields given in the literature. Looking at Fig 2, we see that there is a systematic broadening in the line widths (G) in the sextets of the Fe ions in the **4e** sites as the boron content x increases from 0.1 @ 0.4, a broadening of G of the lines in the sextets of the Fe ions in the **12k** sites as x increases from 0.1 @ 0.3, and a broadening of G of the lines in the **4f_{iv}** as x increases from 0.1 @ 0.3. There does not appear to be any systematic changes in the areas under any of the sextets as more boron is doped into the BaF.

TABLE 1. Hyperfine Field Strength (kOe) in Boron Doped M-Type Barium Hexaferrite.

$BaFe_{12-x}B_xO_{19}$				
Boron Content	12k	4f _{iv} + 2a	4f _{iv}	4e
$x = 0.0$	403	486	466	387
$x = 0.1$	402	486	472	383
$x = 0.2$	403	482	476	382
$x = 0.3$	402	482	476	382
$x = 0.4$	401	485	470	396
$x = 0.6$	401	486	472	394

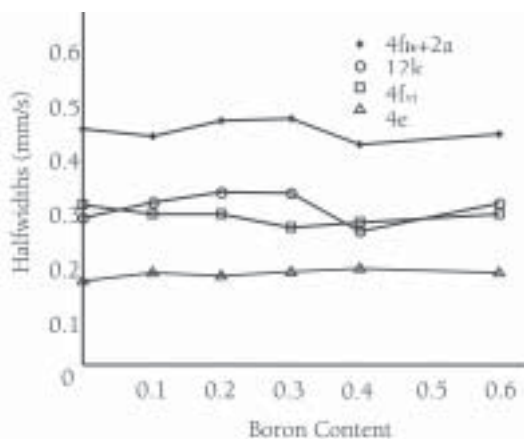


Fig 2. Halfwidths, G, (mm/s) of outer lines of the Mössbauer sextets.

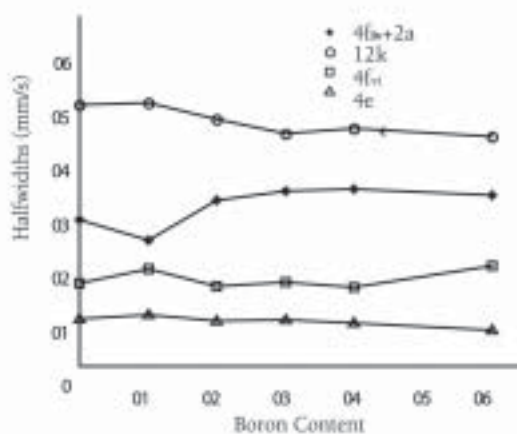


Fig 3. Relative intensities of the different sextets in Mössbauer spectra.

DISCUSSION

If Ram⁵ is correct, *ie*, that the B^{3+} ions replace the Fe ions located in the **4f_{iv}** sites only, then $x_4 = x$ and $x_1 = x_2 = x_3 = x_5 = 0$. Substituting these values of x_i 's into the expressions for the fluctuating parts of the hyperfine field, eqns. (1a)-(1e), the equations predict increases in the G's of the lines in the **4e**, **4f_{iv}** and **12k** sextets. No increases in the broadening are predicted for the lines of **2a** and **4f_{iv}**. As we mentioned in the previous section, there are systematic increases in the line widths of the **4e**, **4f_{iv}** and **12k** patterns. No increases in the line widths of the other patterns are observed. Looking at Figure 3, we do not see any systematic decreases in the intensities of any patterns as the boron doping is increased. Our results on the line broadening are consistent with the boron ions in the B-doped BaF entering into the **4f_{iv}** sites, and can be viewed as being supportive of Ram's conclusion.⁵

All specimens were prefired in oxygen at 1100°C for one hour. After being pressed into pellets, they were sintered in a flowing oxygen atmosphere at 1200°C for twelve hours. The spectra were resolved in four sextets arising from a hyperfine field splitting of the levels of the ^{57}Fe ions located on the $4f_{\text{VI}}$, $4f_{\text{IV}}+2a$, $12k$ and $4e$ sites respectively.

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