Structural and magnetic properties of Vanadium Doped M-Type Barium Hexaferrite (BaFe$_{12-x}$V$_x$O$_{19}$)

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Abstract: Precursor powders of barium hexaferrite doped with vanadium, BaFe$_{12-x}$V$_x$O$_{19}$ with ($x = 0.1, 0.2, 0.3, 0.4, 0.5$), were prepared using the ball milling technique and then sintered at different temperatures for 2 h. The structural properties of the prepared samples were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), while the magnetic properties were examined by the vibrating sample magnetometry (VSM). XRD and SEM studies of the samples sintered at 1100°C indicated the presence of Ba$_3$V$_2$O$_8$ and α-Fe$_2$O$_3$ non-magnetic oxide phases in addition to BaM hexaferrite phase. The fractions of the non-magnetic oxide phases were found to increase with increasing $x$, and sintering the samples at temperatures higher than 1100°C was found to reduce the amounts of these non-magnetic phases only slightly. However, the addition of barium in excess of the stoichiometric ratio was found to remove the α-Fe$_2$O$_3$ oxide, and improve the saturation magnetization of the samples significantly. In addition, washing these samples with HCl was found to improve the saturation magnetization further. The effect of sintering the samples at higher temperatures was also found to reduce the coercivity due to growth of the particle size. However, the coercivity of all samples remained high enough for potential permanent magnet and magnetic recording applications.

1. Introduction

M-type hexaferrites, discovery in the early 1950s, had demonstrated to be an important class of magnetic materials. The growing interest in these ferrites is due to the suitability of their properties for a wide range of applications [1-8]. Barium-based (BaM) and strontium-based (SrM) hexaferrites are used in many technological applications such as recording media, permanent magnets, and microwave devices [9-16]. The general structural and magnetic properties of these ferrites are thoroughly discussed in the literature [1, 7, 17]. The magnetic properties of the hexaferrites are modified by different ways, such as changing the experimental conditions involved in their fabrication, substitutions of Ba or Sr by other cations, or substituting Fe by another trivalent cation or combinations of cations with different valence states [13, 18-28]. The hexaferrites were prepared using different methods such as ball milling [29-34], Sol-gel method [35-37], wet mixing method [27, 38], hydrothermal method [39-41], and coprecipitation method [42-44].
The ball milling method was used in this work to produce fine-particles powders with particle size smaller than the single domain size. The unit cell of BaM (BaFe$_{12}$O$_{19}$) is composed of the stacking sequence RSR*S* of the rhombohedral (R) and spinel (S) blocks, where the star indicates rotation by 180° around the c-axis. The small metal ions (such as the Fe ions) occupy five different interstitial sites in the hexaferrite lattice: three octahedral sites (12k, 4f$_2$, 2a), one tetrahedral site (4f$_1$), and one trigonal bipyramid site (2b) [22-24]. Eight spin-up ferric ions per formula occupy the 2a, 2b, and 12k sites, while four spin down ferric ions per formula occupy the 4f$_1$ and 4f$_2$ sites [34, 45]. According to Gorter’s collinear model [46, 47], the net magnetic moment per formula of BaM is equal to 4×5µ$_B$ = 20µ$_B$, corresponding to a magnetization of 100 emu/g at 0 K [26] and 72 emu/g at room temperature [1]. The magnetic properties of M-type hexaferrites can be modified by appropriate substitutions of Fe$^{3+}$ ions by other magnetic or non-magnetic ions. Such substitutions result in significant changes in the saturation magnetization ($M_s$) due to changes in the net magnetic moment per molecule [48-51]. Also, such substitutions could be used to tune the coercivity of the hexaferrite to fit specific applications [48, 52]. The coercivity of the hexaferrite is given by [53, 54]:

$$H_c = 0.48 \left( \frac{2K_1}{M_s} - NM_s \right)$$

(1)

Here, $K_1$ is the first magnetocrystalline anisotropy constant, $N$ (= 4π) is the demagnetizing factor along the c-axis for a uniaxial (BaM or SrM) crystal, and the number (0.48) arises from the random orientations of the c-axis. The single ion magnetocrystalline anisotropy model revealed that the contribution of Fe$^{3+}$ ion to the first anisotropy constant is largest for ions at 2b site [55].

In this article, the effects of partial substitution of iron ions by vanadium ions on the structural and magnetic properties of BaM hexaferrites were discussed. Also, the effects of different heat treatments and sample stoichiometry were addressed. Sample characterization was carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM), and vibrating sample magnetometer (VSM).

2. Experimental procedures

The appropriate molar ratios of analytical grade starting materials (BaCO$_3$, Fe$_2$O$_3$, and V$_2$O$_5$) were used to synthesize the desired samples. We used 1:11 as the ratio between Ba: Fe which is the optimal ratio to give a single phase of undoped BaFe$_{12}$O$_{19}$ [56]. The powder precursors were mixed in zirconia containers and ball-milled by zirconia balls in a Fritch Pulverissette-7 ball mill for 16 h at 250-rpm rotational speed. The wet milling was carried out in an acetone bath, with powder to ball mass ratio of 1:14, and powder to acetone ratio of 5:8. The wet powder was then left to dry in air, and then part of it was pressed into a disc of 1.2 cm in diameter and ~ 0.15 cm in thickness under a force of 5 tons. The discs were sintered in air at $T \geq 1100$ °C for 2 h. The structure of each sample was then investigated by the x-ray diffractometer with Cu-Kα radiation ($\lambda = 1.5406$ Å). The angular range of the x-ray diffraction (XRD) patterns was $2\theta \leq 70^\circ$, and the scan was performed with angular step of 0.01°. The obtained patterns were analyzed through X’pert HighScore software, and Rietveld refinement of the patterns was carried out using FULLPROF software. Scanning electron microscopy (SEM) was used to examine the particle size and morphology of the samples using the imaging mode, and the chemical composition by the energy dispersive x-ray spectrometer (EDS) facility. Room-temperature magnetic measurements were carried out using a vibrating sample magnetometer (VSM Micro Mag 3900, Princeton Measurements Corporation) with a maximum field of 10 kOe. A needle shape sample cut from each sintered disc was used for the magnetic measurements.
3. Results and Discussion

3.1. Structural Analysis

Figure 1 shows the XRD patterns of BaFe$_{12-x}$V$_x$O$_{19}$ samples with ($x = 0.0 - 0.5$) sintered at 1100$^\circ$C for 2 h in air. For $x = 0.0$, the XRD pattern shows a single phase of BaFe$_{12}$O$_{19}$ consistent with the standard pattern (JCPDS: 00-043-0002), indicating that the solid-state reaction at 1100$^\circ$C for 2 h was suitable for the production of pure BaM hexaferrite phase [57]. The diffraction pattern for the sample with $x = 0.1$ indicated the presence of BaM, in addition to very small amounts of secondary phases evidenced by very weak reflections corresponding to Ba$_3$(VO$_4$)$_2$ vanadate phase (JCPDS pattern no: 00-025-1192), and $\alpha$-Fe$_2$O$_3$ (JCPDS: 01-086-2368). As $x$ increased, a large increase in Ba$_3$(VO$_4$)$_2$ and $\alpha$-Fe$_2$O$_3$ peak intensities was observed. These results suggest that the substituted V reacts with barium to form Ba$_3$(VO$_4$)$_2$ rather than substituting Fe$^{3+}$ in the hexaferrite lattice.

The lattice parameters $a$ and $c$, and the cell volume $V$ of the BaM phase in all samples were obtained from Rietveld refinement, and the results are listed in Table 1. In addition, the X-ray densities ($\rho_x$) for the samples were calculated using the formula:

$$\rho_x = \frac{2(M_w)}{V}$$

(2)

Here $M_w$ is the molecular weight, and $V$ is the unit cell volume. The values of X-ray densities are also listed in Table 1. The lattice parameters and cell volume of the BaM phase were found to fluctuate slightly with increasing V concentration. The slight decrease in density, and increase in cell volume for $x > 0.3$ may suggest that a small amount of V ions entered the hexaferrite lattice, and indicate the low solubility of V in this case.
Figure 1. XRD patterns with Rietveld refinement for the samples BaFe$_{12-x}$V$_x$O$_{19}$ sintered at 1100$^\circ$C.

Table 1. The lattice parameters $a$ and $c$ (Å), unit cell volume $V$ (Å$^3$), and X-ray densities (g/cm$^3$) for the BaFe$_{12-x}$V$_x$O$_{19}$ samples sintered at $T = 1100^\circ$ C.

| $X$  | $a = b$ | $c$     | $V$   | $\rho_x$ | $\chi^2$ |
|------|---------|---------|-------|----------|----------|
| 0.0  | 5.89 ± 0.03 | 23.21 ± 0.03 | 697.50 | 5.29      | 1.25     |
| 0.1  | 5.89 ± 0.03 | 23.20 ± 0.03 | 697.05 | 5.28      | 1.21     |
| 0.2  | 5.89 ± 0.03 | 23.20 ± 0.03 | 697.71 | 5.29      | 1.16     |
| 0.3  | 5.89 ± 0.03 | 23.21 ± 0.03 | 697.34 | 5.29      | 1.17     |
| 0.4  | 5.89 ± 0.03 | 23.20 ± 0.03 | 697.65 | 5.28      | 1.16     |
| 0.5  | 5.90 ± 0.03 | 23.24 ± 0.03 | 699.34 | 5.27      | 1.16     |
The broadening of the diffraction peaks is mainly due to three factors [58]: instrumental effects, crystallite size \( (D) \), and lattice strain. In our system, however, the lattice strain effect was found to be very small and could be neglected. The instrumental broadening was estimated from the broadening of the peak profile of a standard silicon sample with large crystallite size (supplied by the manufacturer of the XRD instrument). The peak corresponding to a certain reflection was fitted with a Lorentzian line-shape, and integrated intensity \( (A) \) and maximum intensity \( (I_0) \) were determined from the fit. The integral breadth \( (\beta = A/I_0) \) was determined for the peak, and then corrected by subtracting from it the integral breadth of the standard silicon pattern. The crystallite sizes of the different samples were then calculated using the relation [38]:

\[
D = \frac{\lambda}{\beta \cos \theta}
\]

Here \( D \) is the crystallite size, \( \lambda \) is the wavelength of radiation (1.5406 Å), \( \beta \) is the corrected integral breadth, and \( \theta \) is the peak position. In our analysis, the (110) peak at \( 2\theta = 30.3^\circ \) was fitted to probe the crystallite size along the basal plane of the hexagonal lattice, while the approximate crystallite size along the \( c \)-direction was determined from the (107) peak at \( 2\theta = 32.2^\circ \) and (20 11) peak at \( 2\theta = 56.6^\circ \). In addition, the crystallite size in a direction perpendicular to the (114) crystallographic planes was determined from the most intense peak at \( 2\theta = 34.1^\circ \). The results shown in Table 2 indicate that the crystallite size along the basal plane is obviously larger than that along the \( c \)-axis, suggesting that the crystallites grow in platelet-like shapes.

### Table 2. The crystallite size values for the system BaFe\(_{12-x}\)V\(_x\)O\(_{19}\) calculated using different peaks.

| \( x \) | \( D \) (nm) | \( (1\ 1\ 0) \) | \( (1\ 0\ 7),\ (2\ 0\ 11) \) | \( (1\ 1\ 4) \) |
|---|---|---|---|---|
| 0.0 | 68 | 49 | 73 |
| 0.1 | 162 | 79 | 128 |
| 0.2 | 251 | 88 | 143 |
| 0.3 | 437 | 80 | 124 |
| 0.4 | 173 | 107 | 128 |
| 0.5 | 429 | 68 | 133 |

To shed light on the evolution and temperature dependence of the stability of the Ba\(_3\)(VO\(_4\))\(_2\) phase, the BaFe\(_{12-x}\)V\(_x\)O\(_{19}\) samples were sintered at higher temperatures for 2 h, and representative XRD patterns for the sample with \( x = 0.5 \) are shown in figure 2. Comparing the diffraction patterns, a clear increase in the intensities of the peaks associated with BaM phase at the expense of Ba\(_3\)(VO\(_4\))\(_2\) and \( \alpha \)-Fe\(_2\)O\(_3\) was observed in the pattern of the sample sintered at 1300° C, while on the contrary, the vanadate Ba\(_3\)(VO\(_4\))\(_2\) phase increased upon sintering at 1200° C. This suggests that a small amount of vanadium was dissolved.
in the M-type phase of the sample sintered at 1100° C, and that a small fraction of this V-substituted BaM phases precipitates into Ba$_3$(VO$_4$)$_2$ and α-Fe$_2$O$_3$ upon sintering at 1200° C, while the vanadate and iron oxide phases react to form BaM phase at 1300° C. This result indicates that the vanadate phase stabilized at 1200° C, and the diffusion of higher amounts of V ions in the BaM lattice requires high temperatures (> 1200° C). This qualitative conclusion, however, needs to be confirmed by another technique, such as monitoring the magnetic properties of the samples with increasing sintering temperature; this will be done in a forthcoming section. The refined lattice parameters $a$ and $c$, and the cell volume $V$ (not shown) for the BaM phase in the samples sintered at different temperatures generally indicated that the samples had the same structure with a slight increase in the cell volume with increasing the sintering temperature. This can be associated with lattice relaxation and removal of lattice defects at higher sintering temperatures.

![XRD patterns with Rietveld refinement for the sample BaFe$_{1.5}$V$_{0.5}$O$_{19}$ sintered for 2 h at different temperatures.](image)

Figure 2. XRD patterns with Rietveld refinement for the sample BaFe$_{1.5}$V$_{0.5}$O$_{19}$ sintered for 2 h at different temperatures.

To examine our assumption that the vanadium has a very low solubility in BaM hexaferrite at low temperature ($T = 1100° C$), the percentage weight (wt. %) of each phase in each sample was calculated on the basis of the assumption that all vanadium is incorporated in the vanadate phase, with no solubility in the M-phase. Also, the precise values of the weight percent of the different phases were obtained from quantitative analysis by fitting of the X-ray patterns. The results in Table 3 indicate that the actual weight percent of Ba$_3$(VO$_4$)$_2$ is generally lower than the calculated value. This result supports the conclusion that vanadium ions diffused into the BaM lattice, but with a very low solubility.
In light of the previous discussion, an additional amount of 75 % molar ratio of BaCO$_3$ to the precursor powders should provide the amount of Ba required for the production of the $\text{Ba}_3(\text{VO}_4)_2$ phase in the sample with $x = 0.5$, and leave an amount which is just right for the production of BaM phase with no excess amounts of $\alpha$-$\text{Fe}_2\text{O}_3$. If no vanadium (or only a non-detectable amount of V$^{3+}$) enters the BaM lattice, then we expect that the peaks corresponding to the $\alpha$-$\text{Fe}_2\text{O}_3$ should completely disappear from the XRD pattern. If, on the other hand, a small amount of vanadium ions diffuse into the BaM lattice, the amount of Ba consumed by the vanadate phase is less, resulting in excessive amounts of Ba, which leads to the production of barium spinel phase with higher Ba:Fe ratio compared to BaM; this phase should then be detected by XRD. Accordingly, we prepared a new sample of $\text{BaFe}_{12-x}\text{V}_x\text{O}_{19}$ ($x = 0.5$) using the same procedure under the same conditions, but with 75% additional molar ratio of BaCO$_3$. The XRD pattern for this sample was compared with the original one (without extra Ba addition) as shown in figure 3. The figure shows that all peaks of $\alpha$-$\text{Fe}_2\text{O}_3$ disappeared completely, and no signature of Ba spinel was detected. This result supports our previous conclusion regarding the phases and their relative proportions in the different samples, and the low solubility level of V in the hexaferrite phase.

Table 3. Weight percent of the different phases through the different samples.

| $X$ | $\text{BaFe}_{12}\text{O}_{19}$ | $\text{Ba}_3(\text{VO}_4)_2$ | $\alpha$-$\text{Fe}_2\text{O}_3$ |
|-----|-------------------------------|-------------------------------|-----------------------------|
|     | # of moles (wt. % (calc.) | wt. % (fitted) & # of moles (wt. % (calc.)) | wt. % (fitted) & # of moles (wt. % (calc.)) | wt. % (fitted) & # of moles (wt. % (calc.)) |
| 0.1 | 0.85 91.5 97.5 | 0.05 3.1 1.6 | 0.35 5.4 9 |
| 0.2 | 0.70 75.3 82.5 | 0.10 6.2 4.9 | 1.20 18.5 12.7 |
| 0.3 | 0.55 59.1 60.3 | 0.15 9.3 9.4 | 2.05 31.6 30.3 |
| 0.4 | 0.40 42.9 50.1 | 0.20 12.4 10.9 | 2.90 44.7 39.0 |
| 0.5 | 0.25 26.8 29.5 | 0.25 15.5 14.4 | 3.75 57.7 56.1 |

Figure 3. XRD patterns with Rietveld refinement for samples $\text{BaFe}_{12-x}\text{V}_x\text{O}_{19}$ ($x = 0.5$) sintered at 1200$^\circ$ C with (upper panel) and without (lower panel) extra Ba.
In order to remove the $\text{Ba}_3(\text{VO}_4)_2$ phase, the sample with $x = 0.5$ added with $\text{BaCo}_3$ and sintered at 1200° C was washed with diluted HCl solution (diluted in distilled water with HCl: $\text{H}_2\text{O}$ equals 2:10), and figure 4 shows the XRD pattern of this sample, together with that of the un-washed sample. It is clear that the vanadate phase was completely dissolved in HCl, leading to a single BaM phase in the sample.

Figure 4. XRD patterns with Rietveld refinement for the samples $\text{BaFe}_{12-x}\text{V}_x\text{O}_{19}$ ($x = 0.5$) added with $\text{BaCo}_3$ and sintered at 1200° C for 2 h. Upper panel: washed with HCl, and lower panel: unwashed.

3.2. Electron microscopy

Figure 5 shows the SEM image for the un-doped $\text{BaFe}_{12}\text{O}_{19}$ sample, and that with $x = 0.1$, sintered at $T = 1100°$ C for 2 h. The image of the pure sample shows evidence of hexagonal platelets with diameters ranging from 200 to 750 nm. The size distribution is, however, dominated by grains with typical diameters in the range of 400 to 500 nm. The image of the sample with $x = 0.1$ also shows evidence of hexagonal platelets with a more regular and narrower grain size distribution and grain diameters in the range from about 170 to about 500 nm. This distribution is dominated by grains with diameters in the range ~350 to 400 nm. The porosity in this sample is clearly lower than that in the pure sample.
Figure 5. SEM images for BaFe$_{12-x}$V$_x$O$_{19}$ with (a) $x = 0$, and (b) $x = 0.1$ samples sintered at $T = 1100^\circ$ C.

Typical SEM images for the sample with $x = 0.2$ are shown in figure 6. Evidence of platelet-like hexagonal grains is provided by image (a). The grain diameters range from ~170 to 600 nm, and the size distribution is dominated by grains with typical diameters of 350 to 400 nm. Image (b) (in the EDS mode) demonstrated the presence of lighter and darker particles in the powder, which can be associated with different phases. The chemical composition of the light particles was examined by EDS, where the observed Ba:Fe:V atomic ratios were found to be 1:6.2:0.36. The Ba:(Fe+V) ratio of 1:6.56 indicate a Ba-rich region with stoichiometry much different from the stoichiometric ratio of 1:12 for V-substituted BaM. The Ba-rich phase confirmed by XRD was the vanadate phase, and EDS measurements on the light particle, therefore, suggest that the measured region contained both Ba$_3$(VO$_4$)$_2$ and BaM phases. On the other hand, EDS measurements on a typical “dark” particle revealed that the Ba:V:Fe atomic ratios in this particle were 1:0.09:10.13, which is close to the BaM stoichiometric ratio. Although the difference of about 15% between the observed and theoretical Ba:Fe ratio of BaM is within experimental uncertainty of the technique, the observed higher concentration of Ba makes one believe that the possibility of the presence of small amounts of the Ba-rich vanadate phase in the measured region should not be excluded. The results, however, indicate clearly that while the darker particles consist mainly of barium hexaferrite phase, the lighter particles contain Ba-rich vanadate as a major phase.

Figure 6. SEM images for BaFe$_{11.8}$V$_{0.2}$O$_{19}$ sample sintered at $T = 1100^\circ$ C: (a) in the imaging mode, and (b) in the EDS mode.
Figure 7 shows representative SEM images for BaFe$_{12-x}$V$_x$O$_{19}$ ($x = 0.3, 0.4, 0.5$) samples sintered at $T = 1100^\circ$C for 2 h. The image of the sample with $x = 0.3$ indicates that the particle size distribution is similar to that for the samples with $x = 0.1$ and $x = 0.2$, with a particle size ranging from about 200 nm up to 650 nm. For $x = 0.4$, however, the image indicates the presence of larger particles with diameters ~ 1000 nm, while the size distribution is still dominated by particles with diameters in the range between 350 and 400 nm. In addition, SEM image for the sample with $x = 0.5$ demonstrate similar grain size distribution with no large-grain growth.

**Figure 7.** SEM images for the samples of BaFe$_{12-x}$V$_x$O$_{19}$ ($x = 0.3, 0.4, 0.5$) sintered at $T = 1100^\circ$C.

### 3.3. VSM results

#### 3.3.1. The system BaFe$_{12-x}$V$_x$O$_{19}$

Hysteresis loops (HL) for all samples sintered at 1100° C are shown in figure 8, and the remanence magnetization and the coercive fields were determined directly from the loops. The hysteresis loops showed a behavior characteristic of hard magnetic material for all samples. The curves did not saturate up to the upper limit of the applied field (10 kOe), so the law of approach to saturation (LAS) was used to obtain the saturation magnetization [59, 60]:

$$
\text{magnetization} = \text{saturation magnetization} \times \left(1 - \frac{H}{H_{sat}}\right)^{1/2}
$$
where $M_s$ is the spontaneous saturation magnetization of the domain per unit volume, $A$ is a constant representing the contributions of inclusions and/or micro-stress, $B$ is a constant representing the contribution of magnetocrystalline anisotropy, and $\chi H$ is the forced magnetization term. A plot of $M_s$ vs. $1/H^2$ in the high field region ($8.5\text{kOe} < H < 10\text{kOe}$) for each sample gave a perfect straight line as shown in figure 9, indicating that the contributions of the forced magnetization terms and the inclusions/micro-stress are negligible. The intercept of this straight line with the $M$-axis gave the saturation magnetization of the sample.

The saturation magnetization $M_s$ of the pure sample was found to be 69.0 emu/g, which is consistent with the reported value for bulk BaM at room temperature [1, 7, 59]. The remanence ($M_r$) was found to be 37.4 emu/g, and the squareness ratio ($S = M_r/M_s$) was 0.54, which is close to that of random, single domain particles. This result is consistent with SEM images which showed that the particle size distribution for this sample is dominated by particles with sizes of the order or below the critical single domain size of 460 nm for hexaferrites. The saturation magnetization, remanence, and the squareness ratio for each sample are tabulated in Table 4.
Figure 9. $M$ vs. $1/H^2$ relation with the straight line fit from which the saturation magnetization and the magnetocrystalline anisotropy parameters were derived.
The dependence of $M_s$ and $H_c$ on the concentration of vanadium is shown in figure 10. The saturation magnetization decreased monotonically with increasing vanadium concentration, recording a reduction of 68% in the sample with $x = 0.5$. The monotonic decreases in saturation magnetization is associated mainly with the progressive increase of the amounts of Ba$_3$(VO$_4$)$_2$ and $\alpha$-Fe$_2$O$_3$ non-magnetic phases with increasing $x$ as confirmed by the XRD analysis.

**Table 4.** The saturation magnetization, remanence, the normalized remnant magnetization, coercive field, anisotropy field, and first anisotropy constant for the system BaFe$_{12-x}$V$_x$O$_{19}$ measured at room temperature.

| $x$ | $M_s$ (emu/g) | $M_r$ (emu/g) | $S$  | $H_c$ (kOe) | $H_a$ (kOe) | $K_1$ ($10^6$ erg/cm$^3$) |
|-----|--------------|--------------|------|-------------|-------------|--------------------------|
| 0.0 | 69.0         | 37.3         | 0.54 | 3.5         | 12.1        | 2.2                      |
| 0.1 | 68.6         | 37.4         | 0.54 | 4.1         | 12.1        | 2.2                      |
| 0.2 | 56.8         | 30.8         | 0.54 | 4.4         | 12.3        | 1.8                      |
| 0.3 | 49.3         | 26.7         | 0.54 | 4.1         | 12.1        | 1.6                      |
| 0.4 | 38.0         | 20.8         | 0.55 | 3.8         | 12.0        | 1.2                      |
| 0.5 | 21.8         | 11.4         | 0.52 | 4.0         | 12.3        | 0.7                      |

![Figure 10. Saturation magnetization and coercive field as a function of V concentration.](image)

The coercivity is known to depend on the magnetocrystalline anisotropy and saturation magnetization in accordance with equation (1). The anisotropy field ($H_a$) and the first anisotropy constant ($K_1$) were
calculated from the slope of the $M - 1/H^2$ straight line, where according to equation (4), the slope = $-M_B B$, and the constant $B$ in the LAS for the hexagonal ferrite is given by [20, 27]:

$$B = \frac{H_a^2}{15} = \frac{1}{15} \left( \frac{2K}{M_s} \right)^2$$

(5)

The magnetic anisotropy field as well as the first anisotropy constant for each sample is listed in Table 4, and the variations of these parameters with $x$ are shown in figure 11. It should be mentioned here that while the anisotropy field is characteristic of the BaM phase (since it is the only magnetic phase in the sample), the anisotropy constant does not have much meaning in multi-phase samples. Therefore, only the anisotropy constant in the pure, single phase sample represents magnetocrystalline anisotropy of BaM hexaferrite, whereas the constants of the other samples should be normalized by the volume fraction of the magnetic phase in the sample.

![Figure 11. The magnetic anisotropy field and the first anisotropy constant as a function of V concentration.](image)

The experimental value of $H_c$ for the single BaM phase in the sample with $x = 0$ is 3.5 kOe (from the HL). When the first anisotropy constant ($2.2 \times 10^6$ erg/cm$^3$) and saturation magnetization (69.0 emu/g = 365 emu/cm$^3$) for this sample are substituted in equation (1), the calculated coercivity is found to be 3585 Oe, in very good agreement with the experimental value. This result supports the conclusion that this sample consists of a random assembly of single domain particles, in agreement with the size distribution concluded from SEM imaging. Similar calculations cannot be carried out for the remaining samples, since these samples do not contain a single magnetic phase with well-defined saturation magnetization and first anisotropy constant. If, however, the value of the anisotropy field is used in equation (1), and the saturation magnetization is assumed to be equal to that of the pure sample (since the coercivity is characteristic of the magnetic phase only), the calculated coercivity of the samples would range between
3560 Oe and 3700 Oe. The observed variations in the experimental coercivity are significantly larger than the calculated variations, which could be attributed to differences in the microstructure of the samples. The porosity was reported to result in a decrease in the coercivity of the sample [54], which explains the lower coercivity for the pure sample, which has the highest porosity as confirmed by SEM images.

3.4.2 Effect of extra barium addition

VSM measurements were performed for the sample with \( x = 0.5 \) added with 75% extra barium and sintered at 1200°C with and without washing by HCl. As discussed previously, the additional barium reacted with the unreacted \( \alpha\text{-Fe}_{2}\text{O}_3 \) phase to form BaM and remove residual hematite phase, while washing with HCl removed the vanadate phase. Figure 12 shows the HL of the un-washed and washed sample, together with that of the samples with no barium addition sintered at 1100°C and 1300°C for comparison.

The saturation magnetizations of the samples were calculated from the law of approach to saturation (equation (4)) by plotting \( M \) vs. \( 1/H^2 \). In addition, the remnant magnetization and coercivity were found directly from the HL. The values of the magnetic parameters for these samples are listed in Table 5. The saturation magnetization increased significantly from 21.8 to 56.3 emu/g with Ba addition due to the reaction of the residual \( \alpha\text{-Fe}_{2}\text{O}_3 \) phase with the extra added barium, resulting in an increase in the fraction of magnetic BaM phase. The coercivity of this decreased by 48% with respect to that with no extra Ba added and sintered at 1100°C. However, this comparison should not be made since the two samples were sintered at different temperatures, and comparison between their coercivity should be addressed in the context of discussing the effect of heat treatment on the magnetic properties. The sample washed by HCl showed higher saturation magnetization due to removal of the non-magnetic vanadate phase from the sample. The coercivity of the washed sample did not change with respect to the un-washed one, which indicates that HCl did not attack the magnetic particles which provided the magnetic coercivity.

![Figure 12. Hysteresis loops of the sample BaFe\(_{11.5}\)V\(_{0.5}\)O\(_{19}\) prepared with different experimental conditions.](image-url)
The first anisotropy constant of the sample added with extra barium increased significantly with respect to that of the sample with no barium addition, which is due to the conversion of the relatively large fraction of the \( \alpha-Fe_2O_3 \) non-magnetic phase into BaM and the consequent significant increase in saturation magnetization. When this sample was washed with HCl, the magnetization increased slightly (~4%) due to removal of the extra non-magnetic vanadate phase. However, XRD analysis confirmed that the sample added with extra Ba and washed by HCl was composed of a pure BaM phase, and should have a saturation magnetization similar to that of the pure sample. Therefore, the observed decrease of \( M_s \) from ~69 emu/g for the sample (with \( x = 0.0 \)) to \( M_s = 59.6 \) emu/g for this sample could be evidence of partial limited substitution of vanadium for iron in the BaM lattice; such a substitution should take place at spin-up sites.

### Table 5. The magnetic parameters of BaFe\(_{12-x}V_x\)O\(_{19}\) (\( x = 0.5 \)) samples prepared under different experimental conditions: heat treatment, addition of extra Ba, and washing by HCl.

| \( x = 0.5 \) | \( M_s \) (emu/g) | \( M_r \) (emu/g) | \( S \) | \( H_c \) (kOe) | \( H_a \) (kOe) | \( K_1 \) (10\(^6\) erg/cm\(^3\)) |
|--------------|-----------------|-----------------|------|-------------|-------------|-----------------|
| (Sintered at 1100° C) (1) | 21.8 | 11.4 | 0.52 | 4.0 | 12.3 | 0.7 |
| (Sintered at 1300° C) (4) | 26.6 | 11.9 | 0.45 | 1.6 | 13.0 | 0.9 |
| (Sintered at 1200° C) (2) (Extra Ba)-unwashed | 56.3 | 29.3 | 0.52 | 2.1 | 11.9 | 1.8 |
| (Sintered at 1200° C) (3) (Extra Ba)-washed by HCl | 59.6 | 32.8 | 0.55 | 2.1 | 11.7 | 1.8 |

### 3.4.3 Effect of sintering temperature

To examine the temperature effect on the magnetic properties, room-temperature magnetic measurements for the samples with \( x = 0.5 \) sintered at 1100° C, 1200° C, and 1300° C were compared in figure 12 (curves (1), (2), and (4), respectively). The saturation magnetization of the sample sintered at 1300° C increased by 22% with respect to that sintered at 1100° C. This could be signature of partial substitution of vanadium for iron in the BaM phase, resulting in the reduction of the fraction of Ba consumed by the vanadate phase, and providing more Ba for the production of the magnetic phase. On the other hand, the coercivity decreased significantly with increasing sintering temperature, an effect that could be associated with particle growth instigated by the higher sintering temperatures. The observed coercivity for the sample sintered at 1200° C is almost identical to the 2000 Oe coercivity reported for BaM prepared by sintering at this temperature [54]. In addition, the sample sintered at 1300° C exhibited a further decrease in coercivity (down to 1600 Oe), apparently due to further particle growth. These values of the coercivity, together with the relatively high saturation magnetization, make these materials promising for high-density magnetic recording applications.

The highest anisotropy field exhibited by the sample sintered at 1300° C could be associated with better crystallization and lower levels of crystal defects at higher sintering temperatures [54], and the lower values of the anisotropy field of the sample added with extra Ba could be indicative of the presence of more crystal defects in this sample.
4. Conclusions
Vanadium substituted BaM hexaferrites prepared by ball-milling and sintering at temperatures $\geq$ 1100° C were found to be multi-phase samples, consisting of the magnetic BaM phase in addition to vanadate and iron oxide non-magnetic phases. The magnetic properties of the samples sintered at 1100° C were consistent with a system of randomly-oriented single-domain magnetic particles as confirmed by SEM measurements. These samples demonstrated typical hard magnet properties with coercivity $\geq$ 3500 Oe. The magnetic properties of the samples improved by sintering at higher temperatures, and by addition of extra Ba and washing by diluted HCl solution.

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