Structural and magnetic properties of Cu–V substituted M-type barium hexaferrites

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Abstract: In search of magnetic materials with improved magnetic characteristics for practical applications, M-type barium hexaferrites with Fe3+ ions partially substituted by a mixture of Cu and V ions were prepared by ball milling and sintering at 1200°C. The structural analyses of the prepared BaFe12-2xCu2xVxO19 samples (x = 0.1, 0.2, 0.3, 0.4) revealed the presence of BaM phase, in addition to α-Fe2O3, Ba3V2O8, and BaFe2O4 nonmagnetic phases which evolved as x increased. Scanning electron microscopy (SEM) imaging demonstrated the presence of different phases in the substituted samples, and a general trend of particle-size growth with increasing x. Energy dispersive spectroscopy was used to examine the local stoichiometry of the samples, and confirmed the different phases identified by XRD analysis. The saturation magnetization was found to be high for low substitution level (72 emu/g for the sample with x = 0.1 sintered for 2 h, and 65 emu/g for the sample sintered for 10 h), while it decreased significantly with increasing the substitution level. The coercivity (Hc) for the samples sintered for 2 h was found to decrease sharply with increasing x, even at low substitution levels (x < 0.2), where it decreased from about 3.5 kOe for the un-substituted sample down to about 1.6 kOe for the sample with x = 0.1, and down to below 0.3 kOe at higher substitution levels. The coercivity of the sample with x = 0.1 sintered for 10 h reduced further, down to about 677 Oe, demonstrating properties demanded for magnetic recording applications. Further, washing with HCl was found to remove some of the nonmagnetic phases, and increase the yield of the BaM phase.

1. Introduction

Magnetic materials are used as core components in a wide range of instruments, tools and devices we use in our everyday life [1-3]. Due to their low eddy current losses, low-cost processing, stability, and tunable magnetic properties, magnetic oxides had demonstrated superior properties compared with metallic magnetic materials for industrial and technological applications [4, 5]. Hexagonal ferrites discovered in the early 1950s [6, 7] are on the top list of important magnetic materials in use nowadays [8].

Due to their high magnetocrystalline anisotropy, hexagonal ferrites were recognized as important materials for microwave devices [2, 5, 9], and microwave absorbers [10-12]. Further, M-type barium-based hexaferrites (BaM or Ferroxdure) with chemical formula BaO.6Fe2O3 have found a wide range of applications in permanent magnet [3, 13, 14] and magnetic recording media [15-17]. M-type
hexaferrites with Ba substituted by other divalent cations such as Sr [18-21], Pb [18, 21] and Ca [22-24] were also synthesized.

The coercivity, in addition to other important magnetic properties of the magnetic material such as saturation magnetization, remanence, and permeability, should be modified to fulfill the requirements of the specific application. This was the field of intense research work growing exponentially since the development of these materials [8]. For that purpose, different techniques were adopted to fabricate hexaferrite powders such as sol-gel [25-27], coprecipitation, [26, 28, 29] hydrothermal [30-32], wet chemical mixing [33, 34], and ball milling technique [24, 35-37]. The coercivity of M-type hexaferrites was modified by the substitution of Fe$^{3+}$ ions by trivalent ions, or by combinations of divalent and tetravalent ions. The substitution of Fe$^{3+}$ by Al$^{3+}$, Ga$^{3+}$, Cr$^{3+}$ was found to enhance the coercivity of M-type hexaferrites [32, 38-40]. However, various combinations of divalent and tetravalent were found to reduce the coercivity [19, 41-44].

In a previous work conducted by our group (submitted), it was demonstrated that the substitution of Fe by V in BaM resulted in phase separation into a multicomponent powder, in which the progressive increase in V concentration resulted in a dramatic increase in the fractions of nonmagnetic phases. This led to a strong attenuation of the saturation magnetization, while the coercivity remained high. In this work, the choice of the Cu–V combination was motivated by the realization that V can assume higher valence states (V$^{4+}$ and V$^{5+}$), which can be compensated for by the lower valence states of Cu (Cu$^{1+}$ and Cu$^{2+}$) to maintain charge neutrality of the crystal when the combination replaces Fe$^{3+}$. The present work was therefore concerned with the fabrication of Cu–V substituted BaM hexaferrites and the investigation of their structural and magnetic properties, in search of new materials which could be candidates for useful applications.

2. Experimental

Powder precursors of BaFe$_{12-2x}$V$_x$Cu$_x$O$_{19}$ ($x = 0.1, 0.2, 0.3, 0.4$) were synthesized by ball milling the stoichiometric ratios of analytical grade BaCO$_3$, Fe$_2$O$_3$, V$_2$O$_5$, Cu$_2$O. The appropriate amounts of these material were carefully weighed, and charged into the zirconia vessels of the Fritch Pulveresette-7 ball-mill. Wet-milling of the powder by zirconia balls in an acetone bath (Powder to acetone mass ratio = 5:8) was performed for 16 h at a rotational speed of 250 rpm, with a powder to ball mass ration of 1:14. The resulting muddy mixture was dried in air, and pressed into disc-shaped pellets 1.5 cm in diameter and ~1.0 mm in thickness under a force of 5 tons. The disc was then sintered at 1200°C for 2 h.

The structural characteristics of the different samples were examined by analyzing the x-ray diffraction patterns obtained using XRD 7000-Shimadzu diffractometer with Cu-Kα radiation ($\lambda = 1.5405$ Å). The samples were scanned over the angular range $20^\circ < 2\theta < 70^\circ$ with 0.01° scanning step and speed of 0.5°/min. The XRD patterns were analyzed using X’pert HighScore 2.0.1 software for phase identification, and Rietveld refinement of the crystal structure was performed using FULLPROF software.

The grain morphology and grain size of the samples were examined by Scanning Electron Microscope (SEM) using FEI-Inspect F50/FEG electron microscope equipped with Energy dispersive X-ray spectroscopy (EDS) facility for elemental analysis. SEM images were used to investigate the general shape and mean size of the particles, while EDX analyses were used to determine the approximate compositions of the particles of the fabricated samples. Information provided by SEM analyses is essential to complement the results of the XRD structural studies, and to examine the sample homogeneity, phase separation, and the degree of crystallinity. In addition, this information is essential to
support conclusions drawn from the magnetic data, since the magnetic properties are generally sensitive to particle morphologies.

The magnetic properties determined by measurements of the magnetic parameters of the samples, such as the saturation magnetization ($M_s$), the coercivity ($H_c$), and the remnant magnetization ($M_r$), were investigated using a vibrating sample magnetometer (VSM MicroMag 3900, Princeton Measurements Corporation). Samples for VSM measurements were prepared by cutting small pieces from the sintered discs and gently polishing to the desired needle-shape. The magnetic measurements were carried out at room temperature with a magnetic field up to 10 kOe. The initial magnetization curves for the samples were obtained in a field range from 0 kOe to 10 kOe with field step of 10 Oe, while the hysteresis loops were performed in the field range from -10 kOe to +10 kOe.

3. Results and Discussion

3.1 Structural Analysis

Fig. 1 shows the refined XRD patterns for the samples sintered at 1200° C for 2h. The patterns demonstrated that the pure sample (with $x = 0$) is composed of a single hexagonal phase consistent with the standard pattern (JPCDS #: 00-043-0002) of BaM phase. The patterns of the substituted samples indicated, in addition, the presence of the vanadate (V: Ba$_3$V$_2$O$_8$) and α-Fe$_2$O$_3$ secondary phases, whose fractions increased with increasing the substitution level. In addition, small amounts of BaFe$_2$O$_4$ spinel (S) phase were detected.

To investigate the effect of the sintering time on the development of the phases, representative samples with $x = 0.1, 0.3, 0.4$ were sintered at 1200° C for 10 h, and their diffraction patterns are shown in Fig. 2. The XRD patterns for the 10 h-sintered samples showed variations which reflect changes in the fractions of the different phases, resulting from allowing enough time for reactions between the components of the powders to take place and reach the equilibrium phases.
Fig. 1: XRD diffraction patterns with Rietveld refinement for the samples BaFe_{12-2x}V_{x}Cu_{x}O_{19} sintered at 1200° C for 2 h.
Fig. 2: XRD diffraction patterns with Rietveld refinement for the samples BaFe$_{12-2x}$V$_x$Cu$_x$O$_{19}$ sintered at 1200° C for 10 h.
The structural analysis of each pattern was carried out using Rietveld refinement of, and full structural information related to cell parameters and volume, crystallite size, and weight fractions of the different phases were obtained. Rietveld analysis of the XRD pattern of a sample involved identification of the various phases, and obtaining their weight ratios in the sample, in addition to the refinement of the structural parameters of each phase. The output file resulting from the refinement process is huge, containing a large amount of structural data. In the present work, we considered only those structural characteristics relevant to the scope of this article.

The weight ratios of the different phases in the samples are listed in Table 1. The weight ratio of BaM phase in the samples sintered for 2 h decreased monotonically with increasing $x$, while the ratios of the $\alpha$, and V phases increased significantly (Fig. 3). The ratio of the spinel phase also generally increased, but remained relatively low in all samples. This behavior can be well explained by the consumption of Ba in the evolving Ba$_3$V$_2$O$_8$ phase, which leaves smaller fraction of Ba available for the formation of BaM phase, and consequently higher fraction of iron which remains as unreacted $\alpha$-Fe$_2$O$_3$ phase.

Sintering the samples for 10 h induced changes in the wt. % of the phases as the data of Table 1 indicated. The increase in the wt. % of the V phase indicates that the reaction involved in the formation of this phase requires prolonged sintering. The enhancement of the wt. % of the BaM phase, and the reduction in the wt. % of the $\alpha$-Fe$_2$O$_3$ and S phases in the samples with $x = 0.3$ and 0.4 is attributed to the reaction of these intermediate phases to form M-type phase.

**Table 1.** Weight % of the different phases in BaFe$_{12-2x}$V$_x$Cu$_x$O$_{19}$ samples sintered at 1200° C for 2 h and 10 h.

| $x$       | 2 h   | 10 h   |
|-----------|-------|--------|
|           | BaM   | $\alpha$ | S  | V  | BaM | $\alpha$ | S  | V  |
| 0.0       | 100   | -       | -  | -  | -   | -       | -  | -  |
| 0.1       | 95.9  | 2.70    | 0.55 | 0.85 | 93.0  | 5.34 | 0.30 | 1.36 |
| 0.2       | 76.2  | 18.2    | 0.60 | 5.00 | -   | -       | -  | -  |
| 0.3       | 59.3  | 31.4    | 1.90 | 7.4  | 64.5  | 26.1   | 0.29 | 9.07 |
| 0.4       | 48.0  | 37.4    | 1.60 | 7.4  | 50.6  | 33.9   | 1.10 | 14.4 |
| HCl Washed| 62.7  | 36.1    | 1.20 | 13.0 | -   | -       | -  | -  |
In an attempt to remove the secondary phases from the samples, the sample with $x = 0.4$ sintered for 2 h was washed with a diluted solution of HCl. XRD pattern of this sample (Fig. 4) indicated that $\text{Ba}_3\text{V}_2\text{O}_8$ phase disappeared completely, and the fractions of $\alpha\text{-Fe}_2\text{O}_3$ and $\text{S}$ phases reduced slightly with HCl washing. The weight ratio $\text{BaM}:\alpha\text{-Fe}_2\text{O}_3:S = 62.7:36.1:1.2$, which when compared with the ratios of 55.2:42.9:1.9 in the un-washed sample, one could deduce that the iron oxide and barium spinel phases partially dissolved in HCl, while BaM was not to be affected by the etching process. The rise in the fraction of the BaM is due to mass loss of the nonmagnetic $\alpha$- and S-phases. This result indicated that HCl washing is suitable for enhancing the yield of the desired BaM phase in the sample.
Fig. 4: XRD diffraction patterns with Rietveld refinement for the sample with $x = 0.4$ sintered for 2 h, with and without HCl washing.

The lattice parameters, $a$ and $c$, of the hexagonal lattice of BaM phase in the samples sintered for 2 h increased sharply up to $x = 0.2$, and then showed tendency to level up at higher concentrations as indicated by Fig 5 A. This could be evidence of the substitution of Cu$^{2+}$ ions for Fe$^{3+}$ ions at 2$h$ and 4$f$ sites, where the radius of Cu$^{2+}$ ion is larger than that of Fe$^{3+}$ ions at these sites [45]. To maintain charge neutrality of the crystal, this substitution should be accompanied by the substitution of V with higher valence states, and/or the conversion of an appropriate fraction of Fe$^{3+}$ into Fe$^{4+}$. Evidence of the presence of Fe$^{4+}$ low-spin ionic state was provided by Mössbauer results recently submitted for publication by our research group.
While the cell volume showed similar with increasing $x$, the volume did not vary significantly with increasing the sintering time up to 10 h as shown in Fig. 5 B. Also, the cell volume did not practically change with HCl washing.

The crystallite size $D$ in a direction perpendicular to a given set of crystallographic planes ($hkl$) was determined for the different samples from the broadening of the corresponding peak using Stokes and Wilson formula [46]:

$$ D = \frac{\lambda}{\beta \cos \theta} \tag{1} $$

where $\beta$ is the integral breadth of the peak (defined as the integrated intensity of the peak divided by the maximum intensity), $\lambda$ is the wavelength of the radiation ($= 1.54056 \, \text{Å}$), and $\theta$ is the peak position. The crystallite size ($D_c$) along the $c$-axis normal to the hexagonal plane was determined from the (006) and (008) reflections, whereas the size ($D_p$) along the $a$-axis in the hexagonal plane was calculated from the breadth of the (200) and (300) reflections. Using the breadth obtained from the refinement process (corrected for the instrumental broadening), the average crystallite size for each sample in the different directions is listed in Table 2. Generally speaking, the crystallization improved with the Cu-V substitution in all samples. However, the crystallites grew only in the plane of the hexagonal layers in the samples with $x = 0.1$ and 0.2, indicating the evolution of platelet-like crystallites in these samples sintered for 2 h. In the meantime, the crystallites in the samples with $x = 0.3$ and 0.4 sintered for 2 h demonstrated equal growth in both the planar and normal directions, resulting in crystallites similar to those of the pure sample in shape, but larger in size. The inhibition of crystal growth along the $c$-direction in the samples with $x = 0.1$ and 0.2 could be due to crystal defects correlated with the significant shifts of ionic positions in the hexagonal lattice for these samples (not shown for brevity). On the other hand, the samples sintered for 10 h revealed general reduction in the crystallite size along the $c$-axis (with respect to those sintered for 2 h), and increase in the planar size, suggesting that prolonged heat treatment resulted in crystallization in the shape of plates. Further, the noticeable decrease of the crystallite size along the $c$-axis for the sample washed with HCl (with respect to the unwashed sample) could be indication of partial damage of the surface of the plate.
Table 2. Crystallite size in-plane ($D_p$) and normal-to-plane ($D_c$) in BaFe$_{12-2x}V_x$Cu$_x$O$_{19}$ samples sintered at 1200$^\circ$C for 2 h (calculated from the full-profile fitting breadths of XRD peaks).

| $x$      | $D_c$ (nm) | $D_p$ (nm) |
|----------|------------|------------|
|          | 2 h  | 10 h | 2 h | 10 h |
| 0.0      | 62   | 60   | 60  | 60   |
| 0.1      | 66   | 59   | 70  | 75   |
| 0.2      | 64   | 80   | 80  | 80   |
| 0.3      | 80   | 67   | 78  | 104  |
| 0.4      | 96   | 86   | 99  | 104  |
| HCl Washed | 78   | 95   |     |      |

3.2 Scanning Electron Microscopy

The morphology and particle size of the samples were examined by SEM imaging, and the sample stoichiometry was determined by EDS. The representative images for the sample with $x = 0.1$ (Fig. 6) indicated the presence of large and small hexagonal-like platelet particles, in addition to semi-circular polyhedral particles. A wide distribution of particle size with particle diameters ranging from ~220 nm up to ~3.5 $\mu$m were observed, with a characteristic distribution dominated by particles with typical diameters of ~350 to ~900 nm. The significantly larger physical particle size in comparison with the crystallite size (Table 2) indicates that the particles are not single-structural domains, possibly due to internal crystal defects.

Fig. 6: Representative SEM images for BaFe$_{12-2x}V_x$Cu$_x$O$_{19}$ ($x = 0.1$) sample sintered at $T = 1200^\circ$C for 2 h.
Fig. 7 shows SEM images for \( \text{BaFe}_{12-2x}\text{V}_x\text{Cu}_x\text{O}_{19} \) (\( x = 0.2 \)). The images showed hexagonal platelet-like, in addition to polyhedral particles. A general growth in particle size was observed, indicating an improvement of crystallization. Some particles had a large size (> 12 \( \mu \)m) as indicated by Fig. 7 (a), while the majority of the particles have a smaller diameter ranging from 350 nm up to 1100 nm. The image in the EDS mode (b) showed, in addition to the regular particles, light particles with no particular shape which could be associated with different phases in the sample. The difference in particle shape is another evidence of the multi-phase nature of the sample. EDS spectrum collected on a typical “dark” particle indicated a Ba: Fe atomic ratio 1: 12.3 which is close the BaM stoichiometric ratio, indicating that the barium hexaferrite form the majority of the sample. In addition, small amounts of Cu and V were detected. The small difference between the observed and stoichiometric Ba:Fe ratio in this sample is due to experimental uncertainty of the technique.

![SEM images for BaFe_{12-2x}V_xCu_xO_{19} (x = 0.2) sample sintered for 2 h: (a) imaging mode, and (b) EDS mode.](image)

The SEM images for the sample \( \text{BaFe}_{12-2x}\text{V}_x\text{Cu}_x\text{O}_{19} \) (\( x = 0.3 \)) is shown in Fig. 8. The images indicated further particle growth, with particle size ranging from \( \sim 1 \) – 10 \( \mu \)m or larger. Also, particles which clearly crystallized in different shapes were observed, indication that the sample may contain different phases. For brevity, in-depth analysis of the stoichiometry of the particles with different shapes will be discussed below, in the context of examining the phases in the sample with \( x = 0.4 \).
Fig. 8: SEM images for BaFe$_{12-2x}$V$_x$Cu$_x$O$_{19}$ ($x = 0.3$) sample sintered for 2 h.

Fig. 9 shows SEM images for the sample BaFe$_{12-2x}$V$_x$Cu$_x$O$_{19}$ ($x = 0.4$) in the imaging mode (a) and the EDS mode (b). The particle size is obviously very large in this sample, where the size of the majority of the particles is $\sim 10 \, \mu m$ or larger. The image in the EDS mode indicated the presence of large light regions in the sample, with no particular shape.

Fig. 9: SEM images for BaFe$_{12-2x}$V$_x$Cu$_x$O$_{19}$ ($x = 0.4$) sample sintered for 2 h. (a) imaging mode, and (b) EDS mode.

To check the chemical composition of these light region, EDS spectra were collected and a typical spectrum is shown in Fig. 10. The spectrum indicated dominance of the Ba and V spectral lines with very small signature of other elements, indication that this region is mainly composed of the V-
phase. On the other hand, the spectrum from an octahedral-like particle (Fig. 11) revealed the presence of Fe (in addition to oxygen) as a major element, which is an indication that this type of particles correspond to the α-Fe₂O₃ oxide. Further, EDS spectrum on hexagonal plated (Fig. 12) indicated an atomic ratio of Fe in the range 11 – 12 (with respect to Ba), and of ~ 0.5 for Cu; these stoichiometries are consistent with the expected ratios for Cu-doped BaM phase. These results confirmed the multi-phase nature of the samples as indicated by XRD results.

Fig. 10: EDS spectrum on the light region in the sample with \(x = 0.4\).
Fig. 11: EDS spectrum on the octahedral-like particle in the sample with $x = 0.4$. 
Fig. 12: EDS spectrum on the hexagonal-like particle in the sample with $x = 0.4$.

SEM images (Fig. 13) for the sample with $x = 0.4$ sintered for 10 h showed an improvement in the crystallization of the particles as indicated by the sharp-edged particles. However, well-crystallized particles with size smaller than the typical size observed in the sample sintered for 2 h seem to develop in this sample. The presence of particles with distinctly different shapes (hexagonal and irregular polyhedral particles, in addition to regions with no particular shape) is an indication of the multi-phase nature of the sample. Step-like formations in large and thick hexagonal plates similar to that reported in other multi-phase hexaferrites was also observed in this sample [8].
3.3 Magnetic Measurements

Fig. 14 shows the hysteresis loops of the samples sintered at 1200°C for 2 h, while Fig. 15 shows the hysteresis loops of the samples sintered for 10 h in air. The coercive field and remanence magnetization were determined directly from the hysteresis loops. However, since the magnetization did not saturate up to the maximum applied field of 10 kOe, the saturation magnetization was obtained from the law of approach to saturation (LAS) [34, 35, 47, 48]:

Fig. 13: SEM images for BaFe$_{12-2x}$V$_x$Cu$_x$O$_{19}$ ($x = 0.4$) sample sintered for 10 h.
\[ M = M_s \left(1 - \frac{A}{H} - \frac{B}{H^2}\right) + \chi H \]  

(2)

where the constant \( A \) is due to microstress/inclusions in the sample, \( B \) arises from the magnetocrystalline anisotropy, and \( \chi H \) is the forced magnetization term. A plot of \( M \) vs. \( 1/H^2 \) gave very good straight lines, indicating the dominance of the magnetocrystalline contribution in this field range (8.5 – 10.0 kOe) [34, 35, 38, 48]. The saturation magnetization is obtained from the intercept of the straight line, while the slope is used to determine the magnetocrystalline anisotropy field (\( H_a \)) and the first magnetocrystalline anisotropy constant (\( K_1 \)) according to the following equations:

\[ \text{slope} = -M_s B \]  

(4)

\[ B = \frac{H_a^2}{15}; \quad H_a = \frac{2K_1}{M_s} \]  

(3)

The magnetic parameters resulting from the straight-line fit to the high-field region of the magnetization curves are tabulated in Table. 3.

Fig. 14: Hysteresis loops for the samples BaFe\(_{12-x}V_xCu_x\)O\(_{19}\) sintered for 2 h.
The saturation magnetization for the sample with $x = 0.1$ is larger than that of the pure sample by ~5%, which could be due to substitution of non-magnetic ions for iron at spin-down sites. However, the XRD pattern for this sample showed the presence of the vanadate phase which is evidence that the increase of $M_s$ is due to the copper substitution. Sintering the sample for 10 h at the same temperature leads to a decrease of the saturation magnetization by 11%. This could be due to the increase in the fractions of the non-magnetic $\text{Ba}_9(\text{VO}_4)_2$ and $\alpha$-$\text{Fe}_2\text{O}_3$ phases with increasing the sintering time as evidenced by the XRD analysis. At higher substitution levels, the saturation magnetization of the samples sintered for 2 h

### Table 3

The saturation magnetization ($M_s$ in emu/g), remanence ($M_r$ in emu/g), the squareness ratio ($S = M_r/M_s$), coercivity ($H_c$ in Oe), anisotropy field ($H_a$ in Oe), and first anisotropy constant ($K_1$ in units of $10^6$ erg/cm$^3$) for the systems BaFe$_{12-2x}$V$_x$Cu$_x$O$_{19}$ samples sintered for 2 h and 10 h.

|          | $x = 0.0$ | $x = 0.1$ | $x = 0.2$ | $x = 0.3$ | $x = 0.4$ |
|----------|-----------|-----------|-----------|-----------|-----------|
|          | 2 h       | 10 h      | 2 h       | 10 h      | 2 h       | 10 h      | 2 h       | 10 h      | 2 h       | 10 h      |
| $M_s$    | 69.0      | -         | 72.6      | 64.9      | 52.5      | -         | 42.4      | 39.6      | 30.6      | 33.4      |
| $M_r$    | 37.3      | -         | 34.3      | 20.1      | 9.2       | -         | 3.7       | 3.7       | 1.8       | 2.3       |
| $S$      | 0.54      | -         | 0.47      | 0.31      | 0.17      | -         | 0.09      | 0.09      | 0.06      | 0.07      |
| $H_c$    | 3455.6    | -         | 1634.8    | 676.5     | 281.9     | -         | 121.5     | 151.9     | 76.6      | 92.5      |
| $H_a$    | 12.1      | -         | 10.3      | 8.8       | 6.6       | -         | 5.5       | 6.7       | 5.4       | 5.1       |
| $K_1$    | 2.20      | -         | 1.98      | 1.51      | 0.92      | -         | 0.61      | 0.70      | 0.43      | 0.45      |
decreased monotonically down to 30.6 emu/g at \( x = 0.4 \). This decrease is also associated with the progressive increase of the fractions of the non-magnetic phases. Also, this decrease could be partially due to the onset of Cu substitution for Fe at spin-up sites at this level of substitution. In addition, the general decrease in saturation magnetization for the samples sintered for 10 h (compared to the respective values in the samples sintered for 2 h) could be associated with the enhancement of the substitution in the hexaferrite lattice promoted by the prolonged sintering process.

The coercivity dropped sharply with increasing \( x \) as shown in Fig. 16, where it was reduced from about 3.5 kOe for the sample with \( x = 0 \) down to about 1.6 kOe for the sample with \( x = 0.1 \). The coercivity was reported to proportional to the magnetocrystalline anisotropy [15], and to decrease with increasing particle size beyond the single domain critical size [15, 49]. Since the squareness ratio of 0.47 for the sample with \( x = 0.1 \) sintered for 2 h is very close to the theoretical ratio of 0.5 for a random assembly of single domain particles, the observed reduction in the coercivity of this particle could be mainly ascribed to the reduction in magnetocrystalline anisotropy. The further reduction of the coercivity of this sample down to about 0.68 kOe upon sintering for 10 h could, however, be associated with the increase in particle size beyond the single domain critical size as evidenced by the significant drop in squareness ratio down to 0.31. This range of coercivity, coupled with the relatively high saturation and remanent magnetization, indicate this sample could be a good candidate for high density magnetic recording.

The reduction in squareness ratio down to below 0.2 with increasing \( x \) beyond 0.1 is a clear indication of particle growth, and the multi-domain nature of particles in these samples. The coercivity in these samples dropped down to below 300 Oe, possibly as a result of the combined effect of the increased particle size and reduction in magnetocrystalline anisotropy. The values of coercivity and remanent magnetization in these samples are not suitable for magnetic recording applications. However, these samples could be promising in other applications, which call for extended studies on these samples involving the dielectric and microwave properties, which are beyond the scope of this article.

![Saturation magnetization and coercivity as a function of x for the samples BaFe_{12-2x}V_xCu_0O_{19} sintered for 2 h.](image)

**Fig. 16**: Saturation magnetization and coercivity as a function of \( x \) for the samples \( \text{BaFe}_{12-2x}V_x\text{Cu}_0\text{O}_{19} \) sintered for 2 h.

The behavior of the coercivity with increasing \( x \) could be attributed to the behavior of the magnetocrystalline anisotropy as mentioned in the above discussion. The anisotropy field and first
anisotropy constant (Fig. 17) were found to decrease with increasing the substitution level. The large drop in $H_a$ indicates that the material is transforming into a soft magnetic material with increasing $x$, and this decrease in magnetic anisotropy could be responsible for the major part of the observed reduction in coercivity. The faster rate of decrease in $K_1$ compared to the rate of decrease of $H_a$ is ascribed to the fact that $K_1$ is proportional to both $H_a$ and $M_s$, both of which decrease with increasing $x$. At this point, it is worth mentioning that since the decrease in saturation magnetization is not completely due to changes in the intrinsic properties of the material, but partially due to the development of nonmagnetic phases, the obtained values of $K_1$ for the substituted samples cannot be accepted as characteristic parameter of BaM phase. However, since $H_a$ is determined from the approach to saturation which is not influenced by nonmagnetic phases, the behavior of the magnetocrystalline anisotropy of the substituted BaM phase can only be deduced from the behavior of $H_a$ in the present study.

![Fig. 17. The magnetic anisotropy field and the first anisotropy constant as a function of concentration for the samples BaFe$_{12-2x}$V$_x$Cu$_x$O$_{19}$ ($x = 0.0 - 0.4$) sintered at 1200° C for 2 h.](image)

4. Conclusions

Cu-V substituted M-type hexaferrites prepared by ball milling and sintering at 1200° C for 2 h and 10 h revealed the presence of secondary nonmagnetic phases, and the different phases existed in the form of separate particles with different sizes and shapes. The particle size was found to increase with increasing $x$, and sintering for 10 h was found to improve crystallization. The substitution was found to have a dramatic effect on the coercivity, even at low concentrations. The sample with $x = 0.1$ demonstrated properties promising for high density magnetic materials. The sharp decrease in the coercivity of the substituted hexaferrites resulted from a combination of the growth of the particle size, and the attenuation of the magnetocrystalline anisotropy as a result of substituting Fe$^{3+}$ ions by nonmagnetic ions. The fast deterioration of the saturation magnetization, remanent magnetization and squareness ratio for $x > 0.1$
indicate that these samples are not good candidates for magnetic recording. Consideration of these materials for other applications requires further investigation beyond the scope of this work.

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