Synthesis and structural characterization of non-stoichiometric barium hexaferrite materials with Fe:Ba ratio of 11.5 – 16.16.

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Abstract: Synthesis of barium hexaferrites $\text{BaFe}_{12}\text{O}_{19}$ (BaM) is often accompanied by the presence of secondary nonmagnetic phases. The coexistence of these phases reduces the yield of the desired BaM magnetic phase and screens its intrinsic magnetic properties such as the saturation magnetization, and impacts the magnetic properties of the sample negatively. Therefore, assessment of the abundance of these phases and investigating their effect on the structural properties of the sample is of fundamental and practical importance. In this work, BaM hexaferrites were prepared by ball milling and sintering powder precursors with Fe:Ba molar ratios varying from 11.5 to 16.16. The structural properties of the phases in the samples were investigated by x-ray diffraction (XRD). The weight ratios of the different phases, as well as their refined structural parameters were determined using Rietveld analysis. XRD patterns revealed the development of $\alpha\text{-Fe}_2\text{O}_3$ (hematite) phase with increasing relative diffracted intensity as the Fe:Ba molar ratio increased. The evolution of the intensity of this phase was used to monitor the weight ratio of the secondary hematite phase in the sample, and a relation between the its weight ratio and the Fe:Ba ratio was established. The optimal Fe:Ba ratio required to synthesis a pure barium hexaferrite phase was then determined, and found to be 11.7.

1. Introduction

Magnetic materials are widely used in our everyday life, covering the range from being employed in components of electronic devices and equipment to refrigerator stickers and parts of children toys [1-3]. Ferrites existing in different forms such as cubic ferrites, hexagonal ferrites, orthoferrites and garnets, are magnetic ceramics based on iron oxides, and form a class of important magnetic materials due to their desirable magnetic and electrical properties, chemical stability, and low cost of production [1 - 7]. These materials play an important role in the technological and industrial progress, and the evolution of new applications, where for example they were efficiently used in telecommunication and radar technologies, digital storage devices, and motor industry. The demand for low-cost novel magnetic materials with properties suitable for specific needs of the various technological and industrial applications had therefore generated a great interest in the synthesis and characterization of hexagonal ferrites due to their improved and tunable properties [1-3].

M-type barium hexaferrite $\text{BaFe}_{12}\text{O}_{19}$ is the most important type of hexaferrites in terms of the annual rate of production of magnetic materials [2]. In search of new magnetic materials with modified properties, M-type hexaferrites were synthesized with Ba replaced partially or fully by different cations such as Sr, Pb, and Ca [8-13], and Fe partially substituted by trivalent metals [12, 14-17], or combinations of divalent and tetravalent cations [13, 18-24]. In many cases, the product contained undesired secondary phases which can deteriorate the properties of the synthesized samples [25-32]. One of the commonly observed nonmagnetic phases in synthesized M-type hexaferrites is $\alpha\text{-Fe}_2\text{O}_3$, which can be associated with the choice of the Fe:Ba molar ratio in the starting powder [10, 14, 29, 33-37]. Consequently, extensive research was carried out to synthesize M-type hexaferrites from
starting powders with off-stoichiometric Fe:Ba ratio [25, 33, 37-43]. In an attempt to obtain a single 
BaM phase, different research groups used a ratio of Fe:Ba below the theoretical value of 12, and 
generally, a ratio between 11 and 12 was reported to yield almost single-phase samples [30, 31, 37, 
41, 42, 44].

The presence of secondary phases together with the desired BaM phase poses difficulty in 
understanding the intrinsic properties of the synthesized samples. In addition, these phases influence 
the properties of the fabricated sample negatively, due to the reduction of the yield of the desired 
phase. Accordingly, accurate assessment of the fractions of secondary phases in the sample is of both 
fundamental and practical importance. In this paper the results of the structural refinement for the 
barium hexaferrites with Fe:Ba ratio ranging from 11.5 – 16.16 are discussed. The relative diffracted 
intensity of the evolving α-Fe₂O₃ (hematite) phase with increasing (Fe:Ba) ratio was used to 
determine the weight ratio of the secondary hematite phase in the sample. In addition, a relation 
between the weight ratio of the hematite phase and the starting Fe:Ba ratio was established, from 
which the optimal ratio required for the synthesis of a pure hexaferrite phase was determined. A 
summary of crystallographic information is also included, and the unit cell of each crystallographic 
phase is constructed from the refined crystallographic parameters.

2. Building Blocks of M-type Hexa Ferrites

The M-type barium hexaferrite (also known as Ferroxdue or BaM) is a ferrimagnetic material 
with chemical formula BaFe₁₂O₁₉, melting point of 1390° C, and theoretical density of 5.3 g/cm³ [2]. 
The symmetry of the barium hexaferrite crystal structure is characterized by the space group 
(P6₃/mmc) with lattice parameter \(a = b = 5.89\,\text{Å}, \quad c = 23.17\,\text{Å}, \quad \beta = \alpha = 90°, \quad \gamma = 120°\) [2].

The unit cell of M-type barium hexaferrite contains two BaFe₁₂O₁₉ molecules, and is built by 
stacking S and R structural blocks along the hexagonal \(c\)-axis in the sequence RSR*S* (the star 
indicates rotation by 180° about the \(c\)-axis) [2, 7]. The S block (Fig. 1) with chemical formula Fe₆O₈ 
consists of two close-packed oxygen layers arranged in an fcc stacking sequence, each layer 
consisting of four oxygen ions. The R block (Fig. 2) with chemical formula BaFe₆O₁₄ consists of three 
close-packed layers in an hcp stacking sequence, with Ba\(^{2+}\) ion replacing an O\(^{2-}\) ion substitutionally in 
the middle layer. The small metal cations occupy interstitial sites between the oxygen layers: one iron 
cation at (2a) octahedral site and two iron cations at (4f₁) tetrahedral sites within the S block, one iron 
cation at the (2b) trigonal bi-pyramidal site and two iron cations at the (4f₂) octahedral sites within the 
R-block, and six iron cations at (12k) octahedral sites in the R-S interfaces. (Table 1) summarizes the 
distribution of magnetic metal ions over the different sites of the M-type barium hexaferrite lattice, 
together with their coordinations, locations in the lattice, and spin orientations.
Figure 1. The S block in barium hexaferrite: (a) Top oxygen R layer viewed from above. (b) The two layers of the S-block with the oxygen ions and metal cations in the interstitial sites.

Figure 2. The R block structure in barium hexaferrite with the metal cations at the interstitial sites.

Table 1. Metallic sub-lattices of M-type hexaferrite

| Block | Sublattice | Coordination | Cations | Spin |
|-------|------------|--------------|---------|------|
| S     | 4f₁        | Tetrahedral  | 2       | ↓    |
|       | 2a         | Octahedral   | 1       | ↑    |
| R     | 4f₂        | Octahedral   | 2       | ↓    |
|       | 2b         | Bi-pyramidal | 1       | ↑    |
| S-R   | 12k        | Octahedral   | 6       | ↑    |
3. Experimental Technique

About 10 g of a mixture of the of high purity (≥ 99%) BaCO$_3$ and α-Fe$_2$O$_3$ powders with Fe:Ba molar ratio of 11.5 was prepared using high energy ball milling. Appropriate amounts of the powder precursors were weighed accurately (to five decimal places) and mixed in two zirconia cups and milled for 16 hours in an acetone bath using a (Fritsch Pulverisette-7) ball mill. Seven zirconia balls were used for the milling with a ball-to-powder mass ratio of 14. The rotational speed was 250 rpm. The milled powder was left to dry at room temperature. About one gram of the dry powder was pressed into 1.5 cm diameter disc under a 50 kN force, and sintered at 1100° C for 2 hours; this sample is labeled (0%). Then five different samples with different Fe:Ba ratios (between 11.5 and 16.16) were prepared by mixing portions of the original powder with different weight ratios of α-Fe$_2$O$_3$ (from 5% to 25%) for about an hour using an agate mortar and pestle, pressing into discs and sintering at 1100° C (Table 2).

Table 2. The iron to barium stoichiometry ratio for each sample.

| Sample name | 25%   | 20%   | 15%   | 10%   | 5%   | 0%   |
|-------------|-------|-------|-------|-------|------|------|
| Fe:Ba Ratio | 16.158| 14.993| 13.966| 13.053| 12.236| 11.500|

The structure of the samples was investigated by θ-2θ x-ray diffraction (XRD) using Shimadzu X-ray Diffraction Instrument, with Cu-K$_\alpha$ radiation (λ$_{\alpha 1}$ = 1.54056 Å and λ$_{\alpha 2}$ = 1.54439 Å). The XRD scan configuration was, (2θ = 20° – 70°) for the scan range, with step time of 1.2 s and 0.01° sampling pitch. A divergence slit of width DF = 2.4 mm, a scattering slits of width SS = 1.25 mm, and a receiving slit of width RS = 0.9 mm were used for the data collection.

XRD patterns of the samples were initially analyzed beginning with Panalytical X’Pert Highscore plus software based on PDF-2 ICDD library. This analysis revealed the phases in each sample by matching the observed pattern with those included in the library. Rietveld profile refinement was performed using the fitting parameters reported elsewhere [45-48] [50 - 53] as input parameters. A reliable fit was obtained, with a rather low Chi-Squared value, and the corresponding main structural output parameters were obtained.

4. Result and discussion

4.1 Fitting Result:

The diffraction patterns of the samples with different Fe:Ba ratios in Fig. 3 indicated the dominance of BaM phase, and the evolution of α-Fe$_2$O$_3$ phase with increasing Fe:Ba ratio. The patterns were refined by Rietveld fitting, and the residue (blue line) was a horizontal line with small fluctuations at the positions of the peaks, indicating good fitting. The goodness of fit was also deduced from the rather low values of $\chi^2$. In what follows we present the main structural results for the two phase in the patterns of the samples. Table 3 shows the general structural characteristics of the two phases the samples, and Tables 4-9 show the main structural data including the cell parameters and cell volume, the wt.% of each phase, the ionic fractional positions in the lattice, and the symmetry of each ionic site, in addition to the indicators of the goodness of fit ($\chi^2$, Bragg R-factor, and $R_f$-factor). The ionic positions obtained in the refinement process did not change significantly
with the variations of Fe:Ba ratio, and our results are in good agreement with previously reported results [45, 46].

Figure 3. Fitted XRD pattern using Rietveld method for the samples with Fe:Ba ratio = 11.5 – 16.16.

Table 3. Barium hexaferrite and Hematite Phase data.

| Phase data          | BaFe$_{12}$O$_{19}$ | Fe$_2$O$_3$  |
|---------------------|---------------------|--------------|
| Formula sum         | Ba$_3$Fe$_{24}$O$_{38}$ | Fe$_{12}$O$_{18}$ |
| Formula weight      | 2222.96 g/mol        | 958.153 g/mol |
| Crystal system      | hexagonal            | trigonal     |
| Space-group         | $P6_3/mmc$ (194)     | $R-3c$ (167) |
| Pearson code        | hP64                 | hR10         |
| Wyckoff sequence    | k3hf3ecba            | ec           |
Table 4. Fitting factors, fractional coordinates and cell parameters for barium hexaferrite in the sample with Fe:Ba ratio = 11.5 (Sample 0%).

| Phase 1 | BaFe₁₂O₁₉ |
|-----------------|----------|
| Cell parameters | \(a = 5.8917 \text{ Å} \quad c = 23.213 \text{ Å}\) |
| Cell ratio      | \(c/a = 3.9399\) |
| Cell volume     | 697.81 Å³ |

| Atomic Parameters |
|-------------------|
| Atom             | Ox. | Wyck. | Site | S.O.F. | x/a   | y/b   | z/c   |
| Ba               | +2  | 2d    | -6m2 | 1      | 0.66667| 0.33333| 0.25000|
| Fe 1             | +3  | 2a    | -3m. | 1      | 0.00000| 0.00000| 0.00000|
| Fe 2             | +3  | 2b    | -6m2 | 1      | 0.00000| 0.00000| 0.25000|
| Fe 3             | +3  | 4f₁   | 3m.  | 1      | 0.33333| 0.66667| 0.02668|
| Fe 4             | +3  | 4f₂   | 3m.  | 1      | 0.33333| 0.66667| 0.18998|
| Fe 5             | +3  | 12k   | .m.  | 1      | 0.16883| 0.33769| 0.89142|
| O 1              | -2  | 4e    | 3m.  | 1      | 0.00000| 0.00000| 0.15270|
| O 2              | -2  | 4f    | 3m.  | 1      | 0.33333| 0.66667| 0.94377|
| O 3              | -2  | 6h    | mm₂  | 1      | 0.17887| 0.35795| 0.25000|
| O 4              | -2  | 12k   | .m.  | 1      | 0.15612| 0.31250| 0.05217|
| O 5              | -2  | 12k   | .m.  | 1      | 0.50293| 1.00585| 0.15073|

Table 5. Fitting factors, fractional coordinates and cell parameters for barium hexaferrite and hematite in the sample with Fe:Ba ratio = 12.24 (Sample 5%).

| Phase 1 | BaFe₁₂O₁₉ |
|-----------------|----------|
| Cell parameters | \(a = 5.8932 \text{ Å} \quad c = 23.223 \text{ Å}\) |
| Cell ratio      | \(c/a = 3.9407\) |
| Cell volume     | 698.48 Å³ |

| Atomic Parameters |
|-------------------|
| Atom             | Ox. | Wyck. | Site | S.O.F. | x/a   | y/b   | z/c   |
| Ba               | +2  | 2d    | -6m2 | 1      | 0.66667| 0.33333| 0.25000|
| Fe 1             | +3  | 2a    | -3m. | 1      | 0.00000| 0.00000| 0.00000|
| Fe 2             | +3  | 2b    | -6m2 | 1      | 0.00000| 0.00000| 0.25000|

| Phase 2 | Fe₂O₃ |
|-----------------|--------|
| Cell parameters | \(a = 4.9861 \text{ Å} \quad c = 13.864 \text{ Å}\) |
| Cell ratio      | \(c/a = 2.7805\) |
| Cell volume     | 298.50 Å³ |

| Atomic Parameters |
|-------------------|
| Atom             | Ox. | Wyck. | Site | S.O.F. | x/a   | y/b   | z/c   |
| Ba               | +2  | 2d    | -6m2 | 1      | 0.66667| 0.33333| 0.25000|
| Fe 1             | +3  | 2a    | -3m. | 1      | 0.00000| 0.00000| 0.00000|
| Fe 2             | +3  | 2b    | -6m2 | 1      | 0.00000| 0.00000| 0.25000|
Table 6. Fitting factors, fractional coordinates and cell parameters for barium hexaferrite and hematite in the sample with Fe:Ba ratio = 13.05 (Sample 10%).

\[ \chi^2: \quad 1.13 \]

**Phase 1**

| BaFe\(_{12}\)O\(_{19}\) | BaFe\(_{12}\)O\(_{19}\) |
|------------------------|------------------------|
| Cell parameters | \(a = 5.8949 \text{ Å} \quad c = 23.2250 \text{ Å}\) |
| Cell ratio | \(c/a = 3.9399\) |
| Cell volume | 698.93 Å\(^3\) |

**Phase 2**

| Fe\(_2\)O\(_3\) | Fe\(_2\)O\(_3\) |
|-------------------|-------------------|
| Cell parameters | \(a = 5.0364 \text{ Å} \quad c = 13.750 \text{ Å}\) |
| Cell ratio | \(c/a = 2.7301\) |
| Cell volume | 302.04 Å\(^3\) |

**Atomic Parameters**

| Atom | Ox. | Wyck. | Site | S.O.F. | \(x/a\) | \(y/b\) | \(z/c\) |
|------|-----|-------|------|--------|--------|--------|--------|
| Ba   | +2  | 2d    | -6m2 | 1      | 0.66667| 0.33333| 0.25000|
| Fe 1 | +3  | 2a    | -3m. | 1      | 0.00000| 0.00000| 0.00000|
| Fe 2 | +3  | 2b    | -6m2 | 1      | 0.00000| 0.00000| 0.25000|
| Fe 3 | +3  | 4f\(_{1}\) | 3m. | 1      | 0.33333| 0.66667| 0.02663|
| Fe 4 | +3  | 4f\(_{2}\) | 3m. | 1      | 0.33333| 0.66667| 0.19011|
| Fe 5 | +3  | 12k   | .m.  | 1      | 0.16839| 0.33637| 0.89169|
| O 1  | -2  | 4e    | 3m.  | 1      | 0.00000| 0.00000| 0.15251|
| O 2  | -2  | 4f    | 3m.  | 1      | 0.33333| 0.66667| 0.94459|
| O 3  | -2  | 6h    | mm2  | 1      | 0.17894| 0.35785| 0.25000|
| O 4  | -2  | 12k   | .m.  | 1      | 0.15878| 0.31746| 0.05133|
| O 5  | -2  | 12k   | .m.  | 1      | 0.50223| 1.00441| 0.15027|
Table 7. Fitting factors, fractional coordinates and cell parameters for barium hexaferrite and hematite in the sample with Fe:Ba ratio = 13.97 (Sample 15%).

| Atom | Ox. | Wyck. | Site | S.O.F. | x/a | y/b | z/c |
|------|-----|-------|------|--------|-----|-----|-----|
| Ba   | +2  | 2d    | -6m2 | 1      | 0.66667 | 0.33333 | 0.25000 |
| Fe 1 | +3  | 2a    | -3m. | 1      | 0.00000 | 0.00000 | 0.00000 |
| Fe 2 | +3  | 2b    | -6m2 | 1      | 0.00000 | 0.00000 | 0.25000 |
| Fe 3 | +3  | 4f1   | 3m.  | 1      | 0.33333 | 0.66667 | 0.02735 |
| Fe 4 | +3  | 4f2   | 3m.  | 1      | 0.33333 | 0.66667 | 0.18952 |
| Fe 5 | +3  | 12k   | .m.  | 1      | 0.16889 | 0.33762 | 0.89163 |
| O 1  | -2  | 4e    | 3m.  | 1      | 0.00000 | 0.00000 | 0.15173 |
| O 2  | -2  | 4f    | 3m.  | 1      | 0.33333 | 0.66667 | 0.94465 |
| O 3  | -2  | 6h    | mm2  | 1      | 0.18229 | 0.36474 | 0.25000 |
| O 4  | -2  | 12k   | .m.  | 1      | 0.15487 | 0.30965 | 0.05177 |
| O 5  | -2  | 12k   | .m.  | 1      | 0.50404 | 1.00818 | 0.14959 |

| Atom | Ox. | Wyck. | Site | S.O.F. | x/a | y/b | z/c |
|------|-----|-------|------|--------|-----|-----|-----|
| Fe   | 3   | 12c   | 3    | 1      | 0.00000 | 0.00000 | 0.35570 |
| O    | -2  | 18e   | 0.2  | 1      | 0.30620 | 0.00000 | 0.25000 |
Table 8. Fitting factors, fractional coordinates and cell parameters for barium hexaferrite and hematite in the sample with Fe:Ba ratio = 14.99 (Sample 20%).

| Phase 1 | BaFe$_{12}$O$_{19}$ |
|---------|---------------------|
| $\chi^2$: | \textbf{1.15} |
| Cell parameters | $a = 5.8929$ Å, $c = 23.217$ Å |
| Cell ratio | $c/a = 3.9398$ |
| Cell volume | 698.23 Å$^3$ |
| B.R.-factor | 2.65 |
| $R_F$-factor | 2.77 |
| Wt. % | 81.6 |

| Phase 2 | Fe$_2$O$_3$ |
|---------|-------------|
| Cell parameters | $a = 5.0352$ Å, $c = 13.747$ Å |
| Cell ratio | $c/a = 2.7304$ |
| Cell volume | 301.86 Å$^3$ |
| B.R.-factor | 3.16 |
| $R_F$-factor | 2.65 |
| Wt. % | 18.4 |

**Atomic Parameters**

| Atom | Ox. | Wyck. | Site | S.O.F. | $x/a$ | $y/b$ | $z/c$ |
|------|-----|-------|------|--------|-------|-------|-------|
| Ba | +2 | 2d | -6m 2 | 1 | 0.6667 | 0.3333 | 0.2500 |
| Fe 1 | +3 | 2a | -3m | 1 | 0.0000 | 0.0000 | 0.0000 |
| Fe 2 | +3 | 2b | -6m 2 | 1 | 0.0000 | 0.0000 | 0.2500 |
| Fe 3 | +3 | 4f$_1$ | 3m | 1 | 0.3333 | 0.6667 | 0.0266 |
| Fe 4 | +3 | 4f$_2$ | 3m | 1 | 0.3333 | 0.6667 | 0.1895 |
| Fe 5 | +3 | 12k | .m | 1 | 0.1694 | 0.3377 | 0.8919 |
| O 1 | -2 | 4e | 3m | 1 | 0.0000 | 0.0000 | 0.1534 |
| O 2 | -2 | 4f | 3m | 1 | 0.3333 | 0.6667 | 0.9444 |
| O 3 | -2 | 6h | mm 2 | 1 | 0.1814 | 0.3629 | 0.2500 |
| O 4 | -2 | 12k | .m | 1 | 0.1573 | 0.3146 | 0.0526 |
| O 5 | -2 | 12k | .m | 1 | 0.5047 | 1.0095 | 0.1506 |

| Fe$_2$O$_3$ |
|-------------|
| Atom | Ox. | Wyck. | Site | S.O.F. | $x/a$ | $y/b$ | $z/c$ |
|--------|-----|-------|------|--------|-------|-------|-------|
| Fe | 3 | 12c | 3 | 1 | 0.0000 | 0.0000 | 0.3556 |
| O | -2 | 18e | 0.2 | 1 | 0.3113 | 0.0000 | 0.2500 |

Table 9. Fitting factors, fractional coordinates and cell parameters for barium hexaferrite and hematite in the sample with Fe:Ba ratio = 16.16 (Sample 25%).

| Phase 1 | BaFe$_{12}$O$_{19}$ |
|---------|---------------------|
| $\chi^2$: | \textbf{1.17} |
| Cell parameters | $a = 5.8936$ Å, $c = 23.220$ Å |
| Cell ratio | $c/a = 3.9399$ |
| Cell volume | 698.49 Å$^3$ |
| B.R.-factor | 3.02 |
| $R_F$-factor | 3.10 |
| Wt. % | 75.1 |
Phase 2 Fe₂O₃

Cell parameters  
\( a = 5.0356 \text{ Å} \)  \( c = 13.747 \text{ Å} \)  
\( B.R \)-factor: 2.27

Cell ratio  
\( c/a = 2.7301 \)  
\( R_F \)-factor: 1.30

Cell volume  
301.90 Å³  
Wt. % 24.9

### Atomic Parameters

**BaFe₁₂O₁₉**

| Atom | Ox. | Wyck. | Site | S.O.F. | \( x/a \) | \( y/b \) | \( z/c \) |
|------|-----|-------|------|--------|----------|----------|----------|
| Ba   | +2  | 2d    | -6m2 | 1      | 0.66667  | 0.33333  | 0.25000  |
| Fe 1 | +3  | 2a    | -3m. | 1      | 0.00000  | 0.00000  | 0.00000  |
| Fe 2 | +3  | 2b    | -6m2 | 1      | 0.00000  | 0.00000  | 0.25000  |
| Fe 3 | +3  | 4f₁1  | 3m.  | 1      | 0.33333  | 0.66667  | 0.02645  |
| Fe 4 | +3  | 4f₂3  | 3m.  | 1      | 0.33333  | 0.66667  | 0.18976  |
| Fe 5 | +3  | 12k   | .m.  | 1      | 0.16847  | 0.33684  | 0.89173  |
| O 1  | -2  | 4e    | 3m.  | 1      | 0.00000  | 0.00000  | 0.15381  |
| O 2  | -2  | 4f    | 3m.  | 1      | 0.33333  | 0.66667  | 0.94369  |
| O 3  | -2  | 6h    | mm2  | 1      | 0.17753  | 0.35526  | 0.25000  |
| O 4  | -2  | 12k   | .m.  | 1      | 0.16050  | 0.32090  | 0.05198  |
| O 5  | -2  | 12k   | .m.  | 1      | 0.50541  | 1.01093  | 0.15105  |

**Fe₂O₃**

| Atom | Ox. | Wyck. | Site | S.O.F. | \( x/a \) | \( y/b \) | \( z/c \) |
|------|-----|-------|------|--------|----------|----------|----------|
| Fe   | 3   | 12c   | 3    | 1      | 0.00000  | 0.00000  | 0.35550  |
| O    | -2  | 18e   | 0.2  | 1      | 0.31098  | 0.00000  | 0.25000  |

### 3.2 Discussion:

The process of Rietveld refinement revealed full structural information and the relative proportions of iron oxide (α-Fe₂O₃) and BaM phases in each sample. Fig. 4 shows the diffraction patterns of all samples added with different amounts of α-Fe₂O₃. The figure demonstrated the evolution of the structural peaks corresponding to α-Fe₂O₃ (shaded in yellow) as a function of the weight ratio of hematite added to the original powder (Fe:Ba = 11.5). The integrated intensities \( I_{α} \) and \( I_{BaM} \) of all structural peaks of α-Fe₂O₃ and BaFe₁₂O₁₉ phases, respectively, and the ratio of these intensities for each sample are summarized in (Table 10).

(Fig. 5) demonstrated a linear variation of the relative integrated intensity of α-Fe₂O₃ with increasing Fe:Ba ratio. The linear fit to the data gave a slope of 5.2088 and an intercept of –62.701. These values were used to determine an approximate value (based on integrated intensity) of the optimal Fe:Ba ratio for fabricating single BaM phase with no additional iron oxide phase. The results indicates that the optimal value of Fe:Ba ratio is 12.039.
Figure 4. XRD patterns of all samples added with different amounts of $\alpha$-Fe$_2$O$_3$. The main structural peaks of iron oxide phase are shaded in yellow.

Table 10. The integrated intensity of all structural peaks of BaM ($I_{\text{BaM}}$) and of $\alpha$-Fe$_2$O$_3$ ($I_{\alpha}$), and the ratio ($I_{\alpha}/I_{\text{BaM}}$) for the samples with different Fe:Ba ratio. The percentage ratio associated with the Fe:Ba ratio represents the wt. % of $\alpha$-Fe$_2$O$_3$ added to the original powder.

| Fe:Ba ratio (sample) | $I_{\text{BaM}}$ | $I_{\alpha}$ | $I_{\alpha}/I_{\text{BaM}}$ (%) |
|----------------------|------------------|--------------|-------------------------------|
| 16.158 (25%)         | 1234.7           | 265.80       | 21.530                        |
| 14.993 (20%)         | 1368.9           | 209.20       | 15.280                        |
| 13.966 (15%)         | 1408.9           | 146.00       | 10.360                        |
| 13.053 (10%)         | 1727.3           | 80.700       | 4.6700                        |
| 12.236 (5%)          | 1626.3           | 37.100       | 2.2800                        |
| 11.500 (0%)          | 1661.8           | 0.0000       | 0.0000                        |
The ratio of the secondary iron oxide phase in each sample can also be determined by investigating the integrated intensities of the main peaks of the phases. (Table 11) shows the integrated intensity of the main peak of BaM at 34.1° (I_{MB}) and that of α-Fe₂O₃ located at 33.15° (I_{Mα}), as well as the ratio of the intensities of these peaks. Fig. 6 shows the relative intensity of the main peak of α-Fe₂O₃ as a function of Fe:Ba ratio. Linear fit to the data gave a slope of 9.0535 and an intercept of -109.565. From these values the optimal Fe:Ba ratio for a single BaM phase was found to be 12.102. This value is close to that obtained from the whole-pattern integrated intensity analysis, and to the stoichiometric composition of 12.0 for M-type hexaferrite. Further, Fig. 6 can be used to determine the weight ratio of α-Fe₂O₃ phase in any hexaferrite sample by evaluating the relative intensity of the main peak and determining the corresponding Fe:Ba ratio, which can be subsequently converted into wt% of the α-Fe₂O₃ phase using the molecular weights of the phases and standard calculations.

Figure 5. A plot of I_{α/Lo} vs Fe:Ba ratio for all samples

The ratio of the secondary iron oxide phase in each sample can also be determined by investigating the integrated intensities of the main peaks of the phases. (Table 11) shows the integrated intensity of the main peak of BaM at 34.1° (I_{MB}) and that of α-Fe₂O₃ located at 33.15° (I_{Mα}), as well as the ratio of the intensities of these peaks. Fig. 6 shows the relative intensity of the main peak of α-Fe₂O₃ as a function of Fe:Ba ratio. Linear fit to the data gave a slope of 9.0535 and an intercept of -109.565. From these values the optimal Fe:Ba ratio for a single BaM phase was found to be 12.102. This value is close to that obtained from the whole-pattern integrated intensity analysis, and to the stoichiometric composition of 12.0 for M-type hexaferrite. Further, Fig. 6 can be used to determine the weight ratio of α-Fe₂O₃ phase in any hexaferrite sample by evaluating the relative intensity of the main peak and determining the corresponding Fe:Ba ratio, which can be subsequently converted into wt% of the α-Fe₂O₃ phase using the molecular weights of the phases and standard calculations.
Table 11. The integrated intensities of the main peaks of BaM ($I_{MB}$), $\alpha$-Fe$_2$O$_3$ ($I_{M\alpha}$), and the peak ratios of the two phases for all samples. The percentage ratio associated with the Fe:Ba ratio represents the wt. % of $\alpha$-Fe$_2$O$_3$ added to the original powder.

| Fe:Ba ratio | 16.158 | 14.993 | 13.966 | 13.053 | 12.236 | 11.500 |
|-------------|--------|--------|--------|--------|--------|--------|
| $I_{MB}$ at 2θ of 34.10 | 187.1  | 208.9  | 212.00 | 266.2  | 248.6  | 267.9  |
| $I_{M\alpha}$ at 2θ of 33.15 | 69.20  | 53.50  | 37.10  | 21.00  | 4.000  | 0.000  |
| $I_{M\alpha}/I_{MB}$ (%) | 37.00  | 25.60  | 17.50  | 7.900  | 1.600  | 0.000  |

Figure 6. A plot of $I_{M\alpha}/I_{MB}$ (%) vs Fe:Ba ratio for all samples

The weight ratios of the different structural phases in a given sample can be evaluated using Rietveld fitting of the corresponding diffraction pattern. The wt% of $\alpha$-Fe$_2$O$_3$ phase for each sample as determined by the fitting routine is listed in Table 12. These values are generally lower than the wt. % of $\alpha$-Fe$_2$O$_3$ added to the original powder (with Fe:Ba = 11.5), which indicates that the Fe:Ba ratio required for the synthesis of a single BaM phase is higher than 11.5, a result consistent with the optimal ratio determined by the analyses associated with Fig. 5. Fig. 7 shows the variation of the relative main peak intensity of $\alpha$-Fe$_2$O$_3$ with the wt. % of this phase determined from Rietveld refinement of the corresponding diffraction pattern.
Table 12. α-Fe$_2$O$_3$ wt. % determined from Rietveld refinement of the diffraction patterns and the corresponding relative main peak integrated intensity.

| Sample | 25%  | 20%  | 15%  | 10%  | 5%   | 0%   |
|--------|------|------|------|------|------|------|
| α-Fe$_2$O$_3$ wt% | 24.88 | 18.37 | 13.05 | 6.500 | 3.530 | 0.000 |
| $I_{M\alpha}/I_{MB}$ (%) | 37.00 | 25.60 | 17.50 | 7.900 | 1.600 | 0.000 |

Figure 7. A plot of $I_{M\alpha}/I_{MB}$ (%) as a function of α-Fe$_2$O$_3$ wt. % evaluated from the refinement of the patterns of all samples.

In the refinement process of the sample added with 5 wt% α-Fe$_2$O$_3$, the parameters belonging to the α-Fe$_2$O$_3$ phase were left to be generated automatically in order to obtain reliable results with no constraints. This is because the phase peaks are weak in this sample, approaching the background fluctuations, so that the X-Ray absorption contrast cannot play a significant role in this calculation.

The optimum ratio for synthesizing pure sample of barium hexaferrite (BaFe$_{12}$O$_{19}$) can be obtained from the experimental result by linearly fitting the Fe:Ba ratio of the prepared samples with the α-Fe$_2$O$_3$ wt% obtained from Rietveld refinement (Fig. 8). The best straight line representing the data intercepts the Fe:Ba ratio axis at 11.7, which is the refined optimum ratio for a single barium hexaferrite phase. This value is somewhat lower than the theoretical stoichiometric ratio of 12, and lower than the value obtained from analysis of the integrated intensities. These results indicate the sensitivity of the resulting optimal Fe:Ba ratio to the analytical method used for evaluating this ratio. However, the results are close, although Rietveld analysis indicated that the optimal ratio is somewhat lower than the theoretical value.
Figure 8. Linear fit of Fe:Ba ratio vs $\alpha$-Fe$_2$O$_3$ wt. % obtained from the refinement of the diffraction patterns.

The refined patterns with rather low Chi-square values gave valuable information on the crystal structure and relative proportions of $\alpha$-Fe$_2$O$_3$ $\alpha$-Fe$_2$O$_3$ secondary phase. Fig. 9 shows the calculated pattern of our hexaferrite sample with Fe:Ba = 11.5, together with standard patterns available in the ICDD library.

Figure 9. The calculated XRD stick pattern for BaFe$_{12}$O$_{19}$ phase compared with other standard patterns in ICDD library.

All the data needed to build up the structural model of the unit cell were obtained by the structural refinement of the diffraction patterns. Since no significant differences were observed in the crystallographic structure of the phases in samples prepared with different stoichiometries as can be
clearly seen from the results of the refinement, the structural data of the sample with Fe:Ba = 11.5 was used to construct the unit cell. (Fig. 10 and 11) show the unit cell from different angles as can be noted from the direction of the unit cell vectors in each snapshot.

Figure 10. The crystal structure of BaFe$_{12}$O$_{19}$ unit cell in 3D.

Figure 11. The crystal structure of Fe$_2$O$_3$ unit cell in a 3D.

The structural analysis shows that there are no actual structural differences in the two extreme samples (Fe:Ba = 11.5 and 16.16). Table 13 and figures 12-14 show that there are no significant differences between the two samples.
Table 13. The calculated polyhedral volume, average bond length and distortion index for each site polyhedron for the samples of Fe:Ba (11.5, 16.16).

|       | 2a site | 2b site | 4f₁ site | 4f₂ site | 12k site |
|-------|---------|---------|----------|----------|----------|
| Fe:Ba |         |         |          |          |          |
| 11.5  | 1.9830  | 1.9357  | 1.9112   | 2.0611   | 2.0207   |
|       | 10.362  | 6.5575  | 3.5760   | 11.193   | 10.974   |
|       | 0.0000  | 0.0912  | 0.0007   | 0.0292   | 0.0382   |
| 16.16 | 2.0346  | 1.9183  | 1.8767   | 2.0455   | 2.0127   |
|       | 11.217  | 6.3665  | 3.3912   | 11.198   | 11.225   |
|       | 0.0000  | 0.0822  | 0.0120   | 0.0351   | 0.0368   |

Figure 12. Compression of two octahedron structures in the 2a site, for the samples of Fe:Ba (11.5 and 16.16).
In addition, our refined chemical composition Ba Fe$_{12.18}$O$_{18.75}$ is in good agreement with the theoretical formula and with the previous reported formula Ba Fe$_{11.80}$O$_{19.46}$ by Sozeri et al. [36].

Conclusions

The structural analysis of the samples consisting of a mixture of M-type barium hexaferrite (with Fe/Ba ratio of 11.5) and α-Fe$_2$O$_3$ iron oxide revealed the presence of pure M-type phase and α-Fe$_2$O$_3$ phase, with no other secondary phases. Also, the structural properties of the M-type barium hexaferrite phase were found to be independent of the α-Fe$_2$O$_3$ mass ratio in the mixture. The quantitative analysis using Rietveld refinement for these samples had shown that the optimum iron-to-barium ratio required to prepare a pure M-type barium hexaferrite phase is in the range of 11.7 – 12. This work established a reference scheme for the determination of the mass ratio of iron oxide (α-Fe$_2$O$_3$) impurity phase in hexaferrite samples.
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