A Study of the Structural and Physical Properties of Substituted Barium Hexaferrite

PUSHPINDER GUPTA BHATIA
Guru Nanak College of Arts Science and Commerce

Abstract

Pure barium hexaferrite and its Li-Ti substituted variants are synthesized by the solid state reaction method. BaFe\textsubscript{12}O\textsubscript{19} – HXF, Ba\textsubscript{0.95}Li\textsubscript{2.85}Fe\textsubscript{8.55}Ti\textsubscript{1.90}O\textsubscript{19} – HXF\textsubscript{1}, Ba\textsubscript{1.688}Li\textsubscript{0.422}Fe\textsubscript{8.018}Ti\textsubscript{2.532}O\textsubscript{19} – HXF\textsubscript{2}, Ba\textsubscript{1.266}Li\textsubscript{0.844}Fe\textsubscript{7.596}Ti\textsubscript{2.954}O\textsubscript{19} – HXF\textsubscript{3}, Ba\textsubscript{1.688}Li\textsubscript{0.844}Fe\textsubscript{6.752}Ti\textsubscript{3.376}O\textsubscript{19} – HXF\textsubscript{4}, Ba\textsubscript{0.95}Li\textsubscript{3.8}Fe\textsubscript{5.7}Ti\textsubscript{3.8}O\textsubscript{19} – HXF\textsubscript{5}. Indexing and comparison with the JCPDS data indicate that they exist in single phase hexagonal magnetoplumbic structure with space group P6\textsubscript{3}/mmc [46]. The structural properties of all the samples are listed. Relative percentage intensity and cation occupancy show that in comparison with (114) plane, all planes get enhanced with respect to pure hexaferrite except in HXF\textsubscript{5} in which the intensity of (107) plane is maximum. It means that in all the substituted samples at least some Li has entered the 114 plane of the R block or Ba may have entered planes other than 114. This means that some lithium has entered the (114) plane. The intensity of (112) plane decreases linearly with the barium content. All substituted samples show the emergence of the (220) plane. It can be suggested that (Li + Ti) enhances material growth. On the contrary, Ba truncates material growth. The SEM images of the pellet surfaces show dense, grain structure. An elongation of grains is also observed in substituted samples as titanium content rises. Interestingly, Grain size is observed to increase considerably by substitution with Li and Ti. The grain size is largest in HXF\textsubscript{5}. It is interesting to observe that Ti content is maximum in this sample and excess Ti is known to favour Abnormal Grain Growth (AGG).

Keywords: hexaferrite, indexing, grain size, SEM

Introduction

BARIIUM hexaferrite, with its chemical formula BaFe\textsubscript{12}O\textsubscript{19} (denoted BaM), is the best-known representative of the hexaferrite family. Barium hexa-ferrite (BaFe\textsubscript{12}O\textsubscript{19}) having hexagonal symmetry belongs to the magneto-plumbite group of oxides and is classified as hard ferrite due to its high saturation magnetization and high intrinsic coercivity. The major areas in which barium hexa-ferrite finds applications include perpendicular high density recording media, microwave devices, in electric generators and in many magnetically operated devices such as magnetic levitations, telephone ringers and receivers, etc. [1, 2, 3].

The magnetic structure of hexaferrites as given by the Gorter model [4] is ferrimagnetic with five different sublattices, three parallel which are coupled by super exchange interactions through the O\textsuperscript{2-} ions. This makes it possible to improve the intrinsic magnetic properties significantly by a partial substitution of Fe ions. However, the magnetic and electrical properties of the hexaferrite are controlled also by the synthesis process involved, the chemical composition, calcination temperature and time and extent of cation substitution [5, 6].

Barium hexaferrite BaFe\textsubscript{12}O\textsubscript{19} belongs to the crystallographic space Group P6\textsubscript{3}/mmc of the magnetoplumbite structure and possesses hexagonal symmetry.
The unit cell of Barium hexaferrite structure contains two formula units (Figure 1), \( \text{BaFe}_{12}\text{O}_{19} \) and includes the unit block \( \text{RSR}^*\text{S}^* \), where asterisks indicate a 180° rotation with respect to the c-axis. The RS blocks are formed by the group \( \text{(BaFe}_{6}\text{O}_{11})^2 \); S block are \( \text{(Fe}_6\text{O}_{8})^{2+} \) and has no divalent cation. The close-packing arrangement of oxygen has cubic symmetry in the S units and hexagonal symmetry in the R blocks. The (111) spinel axis coincides with the hexagonal axis.

Figure 1 : Unit Cell of \( \text{BaFe}_{12}\text{O}_{19} \), show the polyhedra coordination for Fe in iv and vi sites. The common faces of two neighbouring iv and vi polyhedra are hatched (Albanese, Carbucicchio and Deriu, 1973)

**Synthesis and Characterization**

The compounds were prepared by the high temperature solid state reaction method. Five (AR) grade (99.9% purity) powders of \( \text{BaCO}_3, \text{Fe}_2\text{O}_3, \text{Li}_2\text{CO}_3, \text{TiO}_2 \) were used. The starting materials were initially dried in a furnace at 100°C to remove any traces of moisture if present. Dried powders were weighed as per the formula requirements to the nearest milligram and mixed. These powders were melted for eight hours to get homogenous mixture.

The above mixtures were calcined in steps of 8 hours each at 600°C, 800°C and 1000°C with two hours of mixing at every stage. The calcined powders finally makes in polyvinyl acetate binder and pellets of approximately 1.2 cm diameter and 1 to 2 mm thickness were prepared under high pressure of
about 5 tones applied for 10 minutes. The batches of pelletized samples were sintered at 1200°C for 24 hours to ensure the total decomposition of carbonate and homogeneous reaction. The cooling was done slowly and steadily to the room temperature. Powder XRay diffraction patterns were obtained and indexed. The surface morphology and microstructures of the obtained ceramic samples were characterized by a JSM-840 Jeol Scanning Microscope (SEM) equipped with an EDAX system.

Results

The XRay diffraction patterns for the hexaferrites indexed using JCPDS database. The physical properties are listed in table 1.

<table>
<thead>
<tr>
<th>Sample of Properties</th>
<th>a Å</th>
<th>c Å</th>
<th>c/a</th>
<th>Crystallite size Å</th>
<th>Grain size µm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HXF1</td>
<td>5.8772</td>
<td>23.196</td>
<td>3.946</td>
<td>411</td>
<td>12</td>
</tr>
<tr>
<td>HXF2</td>
<td>5.8579</td>
<td>23.006</td>
<td>3.927</td>
<td>485</td>
<td>6.85</td>
</tr>
<tr>
<td>HXF3</td>
<td>5.8671</td>
<td>23.272</td>
<td>3.966</td>
<td>585</td>
<td>2.48</td>
</tr>
<tr>
<td>HXF4</td>
<td>5.8773</td>
<td>23.288</td>
<td>3.962</td>
<td>384</td>
<td>15</td>
</tr>
<tr>
<td>HXF5</td>
<td>5.8751</td>
<td>23.232</td>
<td>3.9544</td>
<td>577</td>
<td>21</td>
</tr>
<tr>
<td>HXF</td>
<td>5.8763</td>
<td>23.196</td>
<td>3.947</td>
<td>522</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Indexing and comparison with the JCPDS data indicates that they exist in single phase hexagonal magnetoplumbic structure with space group P63/mmc [7]. Relative percentage intensity and cation occupancy (Table 2) show that, compared with (114) plane, all planes get enhanced with respect to pure hexaferrite; a maximum intensity at the (114) plane except HXF5 in which the intensity of (107) plane is
maximum. This means that some lithium has entered the (114) plane. The intensity of a plane increases significantly also if a cation having very large atomic number enters the plane. A cation of low atomic number will show a reverse impact on the intensity.

In the present case, atomic number of barium is > Fe ≈ Ti >> Li. Thus it means that in all the substituted samples at least some Li has entered the 114 plane of the R block or Ba may have entered planes other than 114. The situation becomes complex due to the tendency of lithium to occupy the regular octahedral site, the affinity of lithium towards the spinel block and its intercalating habit. The stabilization energy makes Ti to occupy regular octahedral site in particular. Ba has a tendency to occupy vacant spaces and voids. In this connection, it is interesting to note that the intensity of (112) plane decreases linearly with the barium content. Further all substituted samples show the emergence of (220) plane.

This comparative study of XRD intensities of all the substituted samples reveals that all low intensity reflections become stronger in the doped samples. An appreciable enhancement is visible in the (112), (206), (2011) planes with respect to (114) plane in HXF5 which contains Ba^{2+} < 1 in the formula unit and maximum (Ti+Li) content. The increase in Li in HXF5 could be the reason behind this strengthening. Li^+, due to its small ionic radius, has an affinity for the spinel structure and its octahedral sites.

**SEM Studies**

The SEM images of the pellet surfaces, in Figure 2 show dense, grain structure. An elongation of grains is also observed in subst. Samples as titanium content rises. Interestingly, Grain size is observed to increase considerably by substitution with Li and Ti. The grain size is largest in HXF5.

<table>
<thead>
<tr>
<th>Samples</th>
<th>SURFACE</th>
<th>BULK</th>
<th>STOICHIOMETRIC RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe/Ti</td>
<td>Ba/Ti</td>
<td>Fe/Ti</td>
</tr>
<tr>
<td>HXF1</td>
<td>1.46</td>
<td>0.602</td>
<td>4.74</td>
</tr>
<tr>
<td>HXF2</td>
<td>2.42</td>
<td>0.7</td>
<td>2.5</td>
</tr>
<tr>
<td>HXF3</td>
<td>1.72</td>
<td>0.4056</td>
<td>1.12</td>
</tr>
<tr>
<td>HXF4</td>
<td>1.57</td>
<td>0.458</td>
<td>1.11</td>
</tr>
<tr>
<td>HXF5</td>
<td>2.32</td>
<td>0.2</td>
<td>1.61</td>
</tr>
<tr>
<td>HXF0</td>
<td>0.00</td>
<td>11.61</td>
<td>00</td>
</tr>
</tbody>
</table>

It is interesting to observe that Ti content is maximum in this sample and excess Ti is known to favour Abnormal Grain Growth (AGG). AGG is associated with the formation of a liquid phase. HXF5 has considerable amount of lithium even as the barium content falls below 1 in the formula unit. This lowers the melting point of the sample leading to a liquid phase and AGG. [8]. In Ti – rich samples, the excess of titanium would induce Ba vacancies with larger grain size in the samples [9]. This could be the
cause of the large grain in HXF5. Further, an agglomeration is evident in the sem images. Due to this, a change from single domain to multidomain structure occurs which deteriorates the magnetic properties in the substituted samples [10].

The EDAX of the samples (Table 3) indicates grain and grain boundary compositions. It is observed that on the surface of the pellets, the Fe content reduces as Fe in the sample reduces. However, an optimization of the Fe values is seen. As Fe content further reduces from HXF4 to HXF5, Fe content on surface rises sharply. The Fe seems to be marginalised as is the tendency of iron in a ferrite.

![SEM images of all samples](image1.jpg)

**Figure 6.13:** SEM for all the Samples

**Conclusion**

All hexaferrites show an enhancement in grain size with the additives lithium and titanium. Crystallite size is affected by the titanium content and all magnetic properties could show a strong dependence on titanium whereas lithium could affect resistivity.
Acknowledgement: The author thanks Dr S V Salvi for his guidance and support in this work.

References


