OPTIMIZATION OF SYNTHESIS RELATED PARAMETERS SINTERING TEMPERATURE AND TIME FOR Ba-HEXAFERRITE BY CO-PRECIPITATION METHOD.

A. Haq.

Physics Department, Govt. Post Graduate College (B) \ S. Town, Rawalpindi -Pakistan

Email: awarulhaq876@gmail.com

ABSTRACT: BaFe₁₂O₁₉ was synthesized by Co-precipitation method at room temperature. Basic ingredients used were BaCO₃, HNO₃, Di-H₂O water and Fe(NO₃)₃·9H₂O. Molar solution M=5 of NaOH was used as fertilization, pH maintained was 13. Fe³⁺/Ba²⁺ ratio used to be 12. Each sample was sintered at 600±5°C, 800±5°C, 900±5°C, 950±5°C, 1000±5°C and 1050±5°C for four hours in a furnace for phase development. Samples sintered at 950±5°C, 1000±5°C were further used for structural, electrical and magnetic properties. X-ray Diffractometry (XRD) and Scanning Electron Microscopy(SEM) were used for structural analysis. For dc electrical properties, dc current was measured as a function of temperature, then resistivity, activation energy and mobility were studied. For ac properties, capacitance “C” and energy dissipation factor “D” were measured as a function of frequency then dielectric constant and dielectric loss were studied. Synthesized composition is useful for recording media head. This study is guideline for newly entered researchers that how different synthesis parameters were optimized necessary for further research and for development of device fabrication.

Key words: BaFe₁₂O₁₉, Parameters Optimizations techniques, recording media heads

1-INTRODUCTION

Material Science and material engineering are the most attractive area of research in the development of the advancement of today’s technological world. Researchers developed new methodologies and techniques for engineers to use them to design and fabricate new devices. So the research combination of physicists and engineers means development of technology. The research combination of material scientists and material engineers makes new devices.

In materials, magnetic materials are the most important material used from toys level technology to high level technology like stealth, satellite /space. Magnetism in a material occurs because of spin and orbital motions. Whenever a material placed in a magnetic field, its response to the applied field differentiates the nature of magnetic material. Susceptibility “χ” defines the nature of material. According to Mathew [1] following figure is sufficient to differentiate the nature of magnetic material.

![Diagram of magnetic material classification](image)

Figure 1.1: Classification of magnetic material [1]

- Ferromagnetism: Moments of individual atoms aligned
- Antiferromagnetism: Moments alternating from atom to atom
- Ferrimagnetism: Unequal moments alternate
- Paramagnetism: No long-range order; alignment with applied field
- Diamagnetism: No long-range order; alignment opposes field

Figure 1.1 has explained the magnetic material in terms of magnetic moments. Those materials in which magnetic moments of equal magnitude arranged in antiparallel form are called anti-ferromagnetism. Ferrimagnetism property exhibits by those materials whose magnetic moments are not equal in magnitude but directed oppositely in the absence of an applied field under Neel temperature. In normal behavior, within magnetic domain, the net magnetization comes from antiparallel alignment of nonequivalent sub-lattices. Macroscopic behavior is similar to ferromagnetic materials. The cooperative interactions (sum of magnetic moments) between a large number of atoms if become unidirectional, then that particular region has given name domain. In 1930, Dr. Yogoro Kato and Dr. Takeshi Takei in Tokyo institute of technology invented ferrites. It was an oxide of iron, oxygen and other elements. It was given name ferrites, a ceramic ferromagnetic material [2].

The properties of this newly discovered material were encouraging and fascinating one. Due to this achievement, Professor Takei was honored and was praised as “Father of ferrites”, by American Ceramic Society (ACS) Dallas, Texas. Ferrite got peoples attraction after 1950s. Its applications include radio, TV, communications, computers, microwave devices and other high technological devices. Its two main types are soft ferrites and hard ferrites [2]. Soft ferrites possess narrow hysteresis loop, moderate saturation and low coercivity (< 1kA/m). These materials are commonly used in core transformers as well as switch-mode power supply. Spinel and garnets are examples of soft ferrite. Hard ferrites are also known as permanent magnetic materials. They have high coercivity (>10kA/m). These ferrites are used in different applications like communication devices and various tunable devices like circulator and phase shifter. They provide energy to maintain the field strength for particular application. Permanent magnet or hard ferrite is a big family. Cobalt rare earth alloys, neodymium-iron-boron, iron-platinum, cobalt-platinum and Hexagonal family. Hexagonal ferrite is a big family which depends upon composition, structure and applications. Neel has defined the net magnetic moment of unpaired electrons (with spin ↑ and ↓) of atoms present on interstitial sites of composition (ferrite). According to him, net magnetic moments appear due to difference in magnetic ions present on two types of interstitial sites [3].
Barium hexaferrite (M-type) is ferrimagnetic in nature. It is named as Hexaferrite because of its six fold symmetrical and uniaxial crystallographic structure. It has similarity with spinel ferrite (structure) with the fact that both possess same ratio of octahedral and tetrahedral sites. Major difference is because of trigonal bipyramidal 2b site which has one big divalent Ba or Sr or Pb ions. Due to this inclusion spinel symmetry breaks which transform this material to become hexagonal. It also contain Fe\(^{3+}\) ion which is responsible for strong uniaxial or planar anisotropy of M-type materials. Hexagonal structure forms because of alternate blocks of spinel ‘SRS*R*R*’ blocks aligned along c-axis. R and R’ and S and S’ are similar in structure with a rotation of 180° along c-axis, thus six fold symmetry obtained [4]. A large group of ferrimagnetic oxides with hexagonal structure was discovered in 50s. Scientists and researchers called them hexagonal ferrites only in order to distinguish them from other ferrimagnetics with spinel and garnet in terms of structure. This group of ferrite became popular as permanent magnet materials. According to figure 1.2 M, U, W, X, Y and Z are the member of this family. By substituting or replacing divalent or trivalent or combination of both it is possible to obtain large number of new materials with distinguished properties and applications [5].

In present work, we have first tried to obtain pure BaFe\(_{12}\)O\(_{19}\) at relatively low sintering temperature and time. In this study efforts were made to make synthesis parameters and route simple in order to improve the properties. It was also important for industrial use of these parameters. Scientists are trying hard to simplify its synthesis route especially from industrial point of view i.e. low cost commercial production.

2- EXPERIMENTAL METHODOLOGY

BaCO\(_3\) and Fe (NO\(_3\))\(_3\)·9H\(_2\)O in solid form were dissolved in HNO\(_3\) and DI-H\(_2\)O. A series of experiment were performed to optimize different synthesis parameters and influencing factors like quantitates of different precursors (solute and solvent) their mixing and stirring speed and time, technique of their addition or mixing along with volume rate addition of alkaline solution. It was NaOH solution. Stoichiometric combinations of different molar solution were also optimized. Similarly M=5, quantity of Di water for NaOH solution was also optimized. The solution of NaOH used for fertization was formed slightly in higher quantity. It was necessary for final solution because synthesis was at room temperature. It was noted that if energy involved during reaction kinetics cannot optimized in one time or in phase than chances of imitating impurity phases become maximum. We have to minimize them. In this way the basic stoichiometric combinations for different solutions were finalized. Magnetic stirrers and their time were also optimized through different experiments. In co-precipitation method, washing is one of the most important parameter plays an effective role to minimize the impurity elements/ions for improvement in homogeneity of final product. About 95% of NaOH solution was added at once so that small particles could be obtained. It was also necessary for almost uniform growth, better homogenization and particle distribution. All these synthesis parameters used in co-precipitation method were optimized by performing different experiments. During these experiments different parameters like solute and solvent quantities, molar ratio, molarity, pH, volume of rate addition, stirring speed and time were optimized and finalized. These optimized parameters were used to synthesize the optimize composition BaFe\(_{12}\)O\(_{19}\). For this composition main parameters finalized were Fe\(^{3+}\)/Ba\(^{2+}\)=12, pH=13 and M=5 for NaOH solution. The pH of the solution was monitored by pH meter. Magnetic stirring was also carefully monitored then applied for further experiments. Speed and time of magnetic stirring was carefully monitored and noted. All these factors were carefully applied when solution of BaCO\(_3\) and Fe(NO\(_3\))\(_3\)·9H\(_2\)O were mixed together along alkaline NaOH solution. Stirring at this stage was important. Different factors like removal of impurity, grain growth mechanism and their homogeneity were carefully applied which were observed in different experiments. Finally paste like product obtained which was dried out in an oven at 110±2°C for overnight. Dry material obtained was used for further processing.

2.1-Pellets formation

The dried material obtained was crushed into powder form through grinding. This powder was converted into pellets by applying hydraulic pressure of 1000 lbs/in\(^2\) for five minutes. These pellets after sintering were used for different processes.
characterizations. These pellets were sintered at different temperatures to study phase development process. Basic idea behind this sintering scheme was to get the possible temperature of phase purity along with better and improved morphology.

2.2- Sintering temperature and Time

It is one of the most important parameters to be optimized. These samples were sintered at 600±5°C, 800±5°C, 900±5°C, 950±5°C, 1000±5°C and 1050±5°C for four hours in a furnace. Figure 2.1 shows the effect of sintering process on phase purity of samples.

![Figure 2.1: Phase development process as a function of Temperature for BaFe_{12}O_{19}](image)

This graph figure 2.1 shows that phase purity still need some modification/optimization in terms of sintering temperature. At 950±5°C phase purity obtained was 92% (maximum). It dropped to 90% for sample sintered at 1000±5°C. So another composition with same parameters was synthesized and passed through sintering range (from 600 to 1000) but 950°C was incremented to 960°C. Sintering time was same as above i.e. four hours. Same furnace and technique was used and applied.

![Figure 2.2: Phase development for optimized composition BaFe_{12}O_{19} sintered at different temperature for four hours.](image)

Experimentally it was noted that mixing of different solutions, speed of volume rate addition of precipitating agent and stirring speed were important factors. They played an effective role in phase purity, cation distribution grain growth and their homogeneity. Phase purity achieved at 960±5°C was 97% (improved from 92% for sample sintered at 950±5°C). Optimized parameters were sintering temperature and time. From above graph (Figure 2.2), sintering temperature optimized was 965±5°C while sintering time was reduced to 3 hours from four hours. It was necessary to restrict the grain growth. It also depends upon the choice of dopant. The dopant own properties like melting point, volatile nature and moving ability are important for this optimization.

These characteristics were important during phase development and crystallization process. BaFe_{12}O_{19} composition was synthesized by co-precipitation method. Above different discussed optimized synthesis parameters and related conditions were used and applied in further experiments. They were molar ratio, pH, quantity of different solvents and solute, stirring speed and time, mixing and addition rates, sintering temperature and time etc. Volume rate additions of precipitating agent, pH value being chosen were also important for phase purity, homogenization and grain growth. All these parameters were optimized and finally two samples with same composition sintered at 960±5°C and 1000±5°C of BaFe_{12}O_{19} were characterized and studied. Structural, electrical and magnetic properties of these two pellets (960 ± 5°C and 1000 ± 5°C) were studied and reported here.

3-Structural Analysis

XRD and SEM were used to investigate the structure and morphology of prepared material. This analysis helped us to relate structural parameters to electrical and magnetic properties.

3.1-XRD analysis

CuKα was used as a source of emission for X-ray beam. The wavelength λ = 1.5406 Å was used. The range obtained for (2θ) was from 20 to 80°. The sample sintered at 960±5°C showed that purity obtained was ~97% while same composition when sintered at 1000±5°C, purity was 93%. Sintering at 1000±5°C was responsible of improving magnetic properties to some extent. Sintering at higher temperature for four hours was responsible of improving crystallinity [10]. X-ray diffraction patterns are shown in figure 3.1. Preferential growth along particular crystallographic axis can be seen in SEM micrographs figure 3.2. Increasing the temperature from 960±5°C to 1000±5°C diffraction peaks of different intensities improved which could be linked with grain coarsening process and better crystallinity. During this process new structures were developed. Different ions after gaining energy during sintering begin to move and occupied new crystallographic sites/positions. Thus new phases started to appear. Continued growth (removal and occupancy from settled positions) generated internal stresses and distortions. This mechanism was responsible of initiated impurity phases.

![Figure 3.1: XRD of the BaFe_{12}O_{19} sintered at two different temperatures](image)
Table 1: Calculated structural parameters of BaFe$_{12}$O$_{19}$ sintered at two different temperatures

<table>
<thead>
<tr>
<th>Samples sintered at</th>
<th>Lattice parameter (a) (Å)</th>
<th>Lattice parameter (c) (Å)</th>
<th>Volume (V) (Å$^3$)</th>
<th>Crystallite Size (D) (nm)</th>
<th>Phase purity (%)</th>
<th>Porosity (P) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>960±5°C</td>
<td>5.90(±0.15)</td>
<td>22.36(±0.21)</td>
<td>674</td>
<td>30(±2)</td>
<td>97%</td>
<td>38</td>
</tr>
<tr>
<td>1000±5°C</td>
<td>5.93(±0.25)</td>
<td>23.40(±0.45)</td>
<td>713</td>
<td>34(±3)</td>
<td>93%</td>
<td>42</td>
</tr>
</tbody>
</table>

As a result, phase purity dropped from 97% to 93%. Such type of process has also reported in literature [11,12]. Different kinetics of S and R blocks, different reaction times of $\alpha$-Fe$_3$O$_4$, $\gamma$Fe$_3$O$_4$ and BaFe$_2$O$_4$ were the reasons for impurity phases. In fact molar ratio 12 was another reason for occurrence of impurity phases. This area still needs some work [13]. Different structural parameters like lattice parameters (a) and (c) were calculated by using appropriate formula and then volume of unit cell was calculated. By using XRD data, bulk density and crystallite size were also calculated. These parameters are shown in table 1 above.

### 3.2- SEM analysis

In order to investigate the surface morphology and grain growth mechanism and their interconnectivity, Scanning Electron Microscopy was used. These micrographs clearly indicated that morphology and distribution of particles and change with increase in sintering temperature. Platelets like structures in figure 3.2(a) transformed into angular form as shown in Figure 3.2(b). Their size modified themselves dimensionally and increased (2.2 µm to 2.6 µm), but it did not affect the properties at large. This is the estimated size of SEM micrographs. Size of the particles is still useful for magnetic recording media applications [14, 15].

![SEM micrographs of BaFe$_{12}$O$_{19}$ sintered at two different temperatures by co-precipitation method.](image1)

![BH and MH loops for both samples sintered at two different temperature synthesized by Co-precipitation method.](image2)
Conclusions from above discussion say that if sintering time (4 hours) is reduced then the growth of particles, their distribution as well as morphology can be modified. Due to sintering for four hours, preferential grain growth (c-axis) obtained. Sharp edges with platelet like structures were developed. Some grains stick to each other while others did not. Because of sharp edges and corners, porosity was slightly changed.

4- Magnetic characterizations

Magnetic properties of both sintered samples were investigated by magnetometer. \((BH)\) and \((MH)\) loops as measured are shown in figure 4.1. The figure shows that preferential growth slight have changed different magnetic parameters. \((MH)\) loops showed that increase in growth structure helped the domains to saturate up to maximum. It was observed that modification in particle size and distribution and morphology did not significantly affect the magnetic properties like coercivity. However difference in remanance (increased from 1.47kG to 1.59kG) obtained. It was because of incremental increase in grains along c-axis (as c-axis increased from 22.36 Å to 23.40Å). Another reason for this was increase in the net alignment of magnetized grains under the effect of strong inter grain-exchange interactions [16].

This increase in remanance was responsible for increase of maximum energy product \((BH)_{max}\). Different magnetic parameters as measured by magnetometer are given in Table 2 below. The obtained magnetic properties are useful in recording media heads and for other recording media applications[17].

Overall increase in magnetic properties (remanance and maximum energy product) with increase of sintering temperature has already been reported by Wang et. al. [10], Ren et. al. [18], and Ogasawara et. al. [19]. According to these researchers, sintering of samples for long time probably enhanced the preferential crystal growth and the generated oxygen vacancies. As a result magnetic properties increased. It happened in sample sintered at 1000±5˚C. Coercivity almost maintained same value. It confirmed that with these synthesized parameters and applied conditions, variation in particles and their morphology did not affect the coercivity at large. Its obtained value is better than already reported by above researchers. Maximum energy product almost attained the same range as reported by Ogasawara et. al. [19] at higher temperature as compared to be presented value of \((BH)_{max}\).

![Figure 5.1: Temperature dependent dc resistivity and mobility.](image1.png)

![Figure 5.2: Dielectric constant (lnε) and Dielectric loss (tan δ) as a function of frequency lnf.](image2.png)
The obtained coercivity for pure Ba-hexaferrite is useful to achieve recording density of 10Gbits/in². It is also helpful for the fabrication of read/write heads for recording media [15]. Morphology obtained for pure Ba-hexaferrite is acceptable for recording media applications [20].

5- Electrical Properties
Ferrites are high resistive materials so they are useful for high frequency applications. Role of difference in sintering temperature in terms of conduction mechanism was studied and reported here.

5.1- Temperature dependent dc and ac Properties
Ferrites are highly resistive material than metals like iron [21]. DC measurements provide information about their conduction mechanism. Two probe method was used to study these properties. \( \mu \) was measured as a function of temperature from room temperature to 700K. Different dc parameters were also calculated and measured and reported here.

Number of ferrous ions \( (Fe^{2+}) \) ions on octahedral sites play an active role in conduction as well as in polarization [22]. Band theory and hopping model explained this mechanism. In terms of band theory, change of temperature is responsible of variation in charge concentration \( (n) \) thus current generates. Other parameters which played a dominant role here were temperature, grain morphology, heterogeneity of material and activation energy.

Sintering temperature was responsible of generation of \( Fe^{2+} \) ions. If temperature increases, generation of \( Fe^{2+} \) ions from \( Fe^{3+} \) ions also increases. In normal situation, \( Fe^{2+} \) ions on octahedral sites will gain energy and will hop from one octahedral site (lattice site) to next. Hexaferrite structure consists of heterogeneous elements \( (Ba, Fe \) and \( O) \). \( Fe^{3+} \) ions occupy different crystallographic sites inside the structure. Exchange interaction with oxygen ions \( Fe^{3+} \leftrightarrow O^{2-} \leftrightarrow Fe^{3+} \) also affected from temperature [21,23]. These factors affected the hopping probability. Distortions, dislocations, impurity, moisture and grain boundaries were the factors providing hindrance in generation and hopping and polarization mechanisms at different levels. Sintering up to 1000±5°C slightly changed the morphology which resulted in slight increase in resistivity, decrease in mobility and increase in activation energy supported it. Any \( Fe^{3+} \) ions generated during processing \( (oxidation \ of \ Fe^{3+}) \) preferentially occupy B (octahedral) sites only. Hopping probability depends upon the distance involved between ions and the activation energy [23,24].

A decreasing trend in these graphs was because of the prominent role of heterogeneity, morphology and grains orientation. This mechanism has explained by the Maxwell – Wagner Model [26]. According to this model increase in frequency decreases the dielectric constant and dielectric loss which is a normal and usual behavior of all ferrites. At lower frequency, space charge polarization started to play its effective role, thus a linear and slow decaying trend in dielectric constant and loss was observed. Trend in both samples have same reasons i.e. relatively high at low frequency than low at high frequency. Difference in values of dielectric constant and dielectric loss is due to the difference in morphology of both sintered samples. It is basically a dispersion phenomenon. According to Koops theory ferrite-

\[ \text{BaFe}_{12}O_{19} \text{ consists of heterogenous medium (two-layer model) conducting layer – grains and resistive layer – grain boundaries; grains have high conductivity (low resistivity) while grain boundaries have high resistivity (low conductivity). At lower frequency, grain boundaries are effective, hopping charge piles up there as a result dielectric constant becomes high. The decreasing phenomenon slightly speed up as the applied frequency increases. As the applied frequency increases hopping slightly speeds up. In other words, electron exchange between ferrous and ferric ions was unable to follow the frequency of the applied electric field [27, 28]. Fall in dielectric loss (tanδ) was more rapid and become almost equal at higher frequency for both sintered samples.} \]

**Table 4: Dielectric constant (ε) and dielectric loss factor (tanδ) of BaFe₁₂O₁₉**

<table>
<thead>
<tr>
<th>Sample sintered at</th>
<th>Dielectric constant (ε) at 3MHz</th>
<th>dielectric loss(tanδ) at 3MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>960±5°C</td>
<td>48±4</td>
<td>0.55±0.12</td>
</tr>
<tr>
<td>1000±5°C</td>
<td>44±3</td>
<td>0.54±0.22</td>
</tr>
</tbody>
</table>

The measured values of both parameters at 3MHz have been reported above. No big difference in dielectric properties was observed. Thus the synthesized material is useful for high frequency applications.

6-CONCLUSIONS
Optimized \( \text{BaFe}_{12}O_{19} \) was synthesized by co-precipitation method. This composition was synthesized only to test and verify different optimized parameters necessary for further work. Newly research can start work by observing such effective parameters. They are molar ratio, pH, stirring rate and time, sintering temperature and time. All these parameters were optimized. Morphology of composition changed due to difference in sintering temperature. The effect of sintering temperature was also observed by sintering by keeping temperature fixed for four hours. Structural, electrical and magnetic properties were investigated and reported here. Magnetic properties of pure \( \text{BaFe}_{12}O_{19} \) are useful for magnetic recording media applications, read /write heads fabrication and other devices like smart switch power supplies. Effect of small difference in sintering temperature was also important for morphology and grain growth understanding.

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