Effect of pH on structural and magnetic properties of nanocrystalline Y$_3$Fe$_5$O$_{12}$ by aqueous co-precipitation method

K. Praveena$^*$, K. Sadhana$^2$, S. Srinath$^3$ and S. R. Murthy$^4$

The Y$_3$Fe$_5$O$_{12}$ (YIG) nanopowders were synthesised at different pH using co-precipitation method. The effect of pH on the phase formation of YIG is characterised using XRD, TEM, FTIR and TG/DTA. From the Scherer formula, the particle sizes of the powders were found to be 13, 19 and 28 nm for pH=10, 11 and 12 respectively. It is found that as the pH of the solution increases the particle size is also increases. It is also clear from the TG/DTA curves that as the pH is increasing the weight losses were found to be small. The nanopowders were sintered at 600, 700, 800 and 900°C for 5 h using conventional sintering method. The phase formation is completed at 800°C/5 h which is correlated with TG/DTA. The average grain size of the samples is found to be $\sim$ 161 nm. The high values of $M_s$=23 emu g$^{-1}$ and $H_c$=22 Oe were recorded for the sample sintered at 900°C.

Keywords: Ceramics, Garnets, Co-precipitation, TG/DTA, Magnetic properties

Introduction

Y$_3$Fe$_5$O$_{12}$ (YIG) is useful for the fabrication of isolators, circulators, and magneto-optical devices for its excellent soft magnetic properties at microwave frequencies and optical frequencies. YIG ceramic is usually prepared by solid state method with extensively mechanical mixing and long time heat treatments above 1300°C. These processing conditions do not allow facile control over microstructure, grain size and grain size distribution in the resulting powders. The disadvantages of solid state method of preparation of YIG is that its grinding operation requires more time and yields larger particles and produces impurity phases and cannot be removed at lower sintering temperatures.1

The method of preparation strongly determines the structural and magnetic properties of YIG. There are many methods reported in the literature for the production of YIG nanopowders such as sol–gel,2 microemulsion,3 organic precursor method,4 mechanochemical,5 hydrothermal6 and co-precipitation method.7,3 Among these methods, co-precipitation is the suitable method due to its low cost, solvent free, easily scalable, mass production and chemical homogeneity.7 The co-precipitation method is versatile for preparing nanoparticles, and does not violate the laws of green chemistry.

Therefore, in the present study the nanoscale sized regular morphology particles were synthesised using co-precipitation method. In YIG nanoparticles made using this method, we notice that pH of the reaction mixture can be used to ensure significant monodispersity, and easy dispersibility. Furthermore, post-synthesis sintering can enable optimization of the magnetic properties of these materials. In addition, the aqueous synthesis method presented here results in particles that have high sinterability, making it attractive for devices such as isolators, circulators and magneto-optical devices.

It was hypothesized that the calcination temperature required for the crystallisation of these YIG nanoparticles would be lower than the temperature required for the formation of bulk phases. The novel synthesis described in this article may be directly scaled up for the production of YIG nanoparticles with high homogeneity.

Experimental

The yttrium iron garnet (YIG) nanoparticles were synthesized using yttrium nitrate [Y(NO$_3$)$_3$.6H$_2$O] and ferric nitrate [Fe(NO$_3$)$_3$.9H$_2$O] used as starting materials taken in 3:5 ratio. The powders were dissolved in hot double de-ionized water and NaOH was added dropwise with controlling of pH $\sim$ 10. The brown precipitation was constant stirred to obtain the homogeneous mixture. The powders were filtered and then washed repeatedly with hot double deionised water followed by freeze drying overnight at 80°C. The prepared powders were weighted and the percentage yields were calculated from the expected total amount based on the solution concentration and volume and the amount that was actually crystallised. Similar procedure was followed for
YIG for pH=11 and 12 by careful, dropwise addition of NaOH.

All the as synthesised powders were characterised by using Phillips PANanalytical X’pert powder X-ray diffraction (XRD) with Cu Kα radiation (λ=1.5406 Å). Particle size and morphology were determined using transmission electron microscopy (TEM) JEM-2010, JEOL Inc. (Tokyo, Japan). The structural variation of the nanopowders was studied using fourier transform infrared spectroscopy (FTIR) in the range of 375 to 4000 cm⁻¹. thermogravimetry and differential thermal analysis and (TG/DTA), Rigaku Thermalplus TG 8120 were used to study the exo–endo temperature of as received YIG powders. A heating rate of 10°C min⁻¹ was used in both the TG and DTA measurements upto 1100°C in air. The obtained powders (pH=12) were mixed with an appropriate amount of 2 wt-% polyvinyl alcohol as a binder. Then the powder was uniaxially pressed at a pressure of 500 kg cm⁻² to form green pellet specimens. The compacts were sintered at different temperature 600, 700, 800 and 900°C for 5 h using conventional sintering method. The lattice parameters (Å), bulk density (d₀) were determined from the following formulae:

\[
\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}
\]

where \(d\) is the interplanar distance and \((hkl)\) are miller indices.

\[d_0 = \frac{W_{\text{air}}}{W_{\text{air}} - W_{\text{water}}}
\]

where \(W_{\text{air}}\) is weight of the sample in air and \(W_{\text{water}}\) is weight of the sample in water.

The phase and morphology of the sintered samples were studied by using XRD and scanning electron microscopy (SEM). The room temperature saturation magnetization (\(M_s\)) and coercive field (\(H_c\)) were studied using vibrating sample magnetometry (VSM) Lakeshore 7500, USA upto 5kOe.

**Results and discussion**

Figure 1 shows the XRD patterns of YIG powder prepared at different pH. The XRD shows amorphous phase below pH=10. As the pH increases the YIG phase formation appears. The XRD patterns of pH=10 and 11 shows the large amounts of YFeO₃ and Fe₂O₃ along with small amount of YIG phase is observed. The single phase YIG formation can be observed for pH=12 with small amount of YFeO₃. All the diffraction peaks were indexed and matched well with JCPDS card no. 33-693. Using the Scherer’s formula, the variations of full width at half maximum (FWHM) at different XRD peaks indicated that the average crystallite size of the nanoparticles were about 13, 19 and 28 nm corresponding to the pH of 10, 11 and 12 respectively. It was inferred that the nanoparticle sizes increased by increasing the pH of the solution. Increase in crystallite size with pH may be associated with the faster particle growth kinetics favoured by high pH. The lattice constant (Å) is found to be 12.386, 12.372 and 12.364 Å for pH=12, 11 and 10 respectively. The unit cell expansion can be attributed to the increase in the repulsive dipolar interactions at the particle surface due to the existence of unpaired electronic orbital.¹ Similar lattice expansion is reported for other nanoparticle oxide system.¹⁰

Figure 2 shows the TEM picture of as synthesised YIG powder prepared of different pH. TEM images confirm that the particles formed are indeed in the
nanoregime. It could be seen from the figure that the powders are spherical in shape and average particle size of the powders are found to be 16, 20 and 23 nm for pH 10, 11 and 12 respectively.

Figure 3 shows the FTIR spectra of as synthesised powders of pH 10, 11 and 12 recorded in the range of 375–4000 cm\(^{-1}\). The bands at 3431, 1635 and 1387 cm\(^{-1}\) were assigned to the O–H group, carboxyl group and NO\(_3\) ions respectively. The band at 1400 cm\(^{-1}\) was ascribed to splitting anti symmetrical band of carbonate having C\(_{2v}\) symmetry.\(^{11}\) The band at 853 cm\(^{-1}\) was corresponds to out of plane bending of CO\(_2\)\(^{3-}\).\(^{12}\) The three bands at 690, 558 and 455 cm\(^{-1}\) were corresponds to the asymmetric stretching (\(v_3\)) of the tetrahedron (Fe–O bond). It can be seen from the figure that the bands become narrower with an increase of pH which suggests that rate of reaction increases between the metal and oxygen atoms.

Figure 4 shows the TG/DTA curves for as synthesised YIG powders prepared at different pH using co-precipitation method. The DTA curve shows four exothermic peaks. The exothermic peak in the range of 60–80, 320–340, 450–510 and 680–715°C is due to removal of any absorbed/adsorbed moisture from the sample surface, evaporation of residual nitrate, decomposition of the hydroxides of yttrium and iron into their corresponding metal oxides and the last exothermic peak corresponds to the crystallization of YFeO\(_3\) and YIG respectively. The results of DTA curves can be correlated to the XRD patterns (Fig. 1). The reaction of formation takes place in the range of 680–715°C. The endothermic peak in the range of 740–810°C shows the formation of YIG phase. It can be seen from the figure that as the pH is increasing the peaks are becoming narrower and shifting towards the lower temperature side. For pH=12, the YIG formation temperature is found to be 790°C.

It could be seen from the Fig. 4b that for pH=10 and 11 the variation of weight loss (%) is similar but for pH=12 it is significantly varied. The weight loss corresponds to the temperatures 60–80, 320–340, 450–510, 680–715 and 740–810°C for pH=11 were 0.97, 3.12, 1.51, 2.54 and 0.22% respectively. Similarly for pH=12, 10.79%, 3.34%, 1.25%, 0.25% and 0.20%, respectively. It is concluded that the weight loss (%) decreases with increasing pH. A very small percentage of weight loss is observed in the range of 740–810°C, which shows the formation of YIG phase.

Figure 5 shows the XRD patterns of YIG samples sintered at different temperatures. All the XRD peaks were indexed. It could be seen from the figure that at 600°C, it has the phase of YFeO\(_3\) and Fe\(_2\)O\(_3\) along with YIG phase is formed. As the sintering temperature increases the reaction between Fe\(_2\)O\(_3\) and YFeO\(_3\) increases and which leads to the formation of single phase YIG at 800°C. The formed phases were compared with the JCPDS no. 43-0507 and matches well. No impurity phases were observed. From the XRD results, the garnet formation can be described as following.

4 a and b DTA and TG curves of as synthesised powders of pH=10, 11 and 12
Polydispersity in the sintered samples is measured using an index of dispersion called Fano factor. In this case, it is the ratio of the variance \( \sigma^2 \) to the mean size \( d \). Samples with relatively low Fano factors are less polydisperse when compared to those with larger Fano factors. Both the variance and the mean size is obtained using image analysis (performed using ImageJ software) on SEM images. Particles synthesized at pH 12 show the best dispersability (5-1). Increase in sintering temperature results in particle size distributions with lower Fano factors, which implies that sintering promotes monodispersity.

Figure 6 shows the microstructure of the YIG samples sintered at different temperatures. The morphology of the grains is found to be in spherical shape. For the samples sintered at 600 and 700°C, over the spherical grains some small sized grains were observed which are attributed to the YFeO\(_3\) phase which can be clearly observed in XRD patterns. The value of grain sizes at different sintering temperature is listed in Table 1. It shows that as the sintering temperature increases from 600 to 900°C, the grain size also increases due to the grain growth kinetics. The large grain size indicates decrease of grain boundary and surface energy. The average grain sizes of the sintered samples were found to be in the range of 125 to 186 nm.

Figure 7 shows the temperature dependence of magnetisation for 900°C sample in the temperature range of 300–600 K. It can be seen that the sharp ferromagnetic to paramagnetic transition which is also known as Curie temperature \( T_C \) and it is found to be 528 K. This value is slightly lower than the literature value.\(^{13}\) The sharp fall of temperature indicates the homogeneous nature of the sample.

Figure 8a shows the magnetisation curves (M–H loops) of YIG samples prepared at different pH. A room temperature M–H loops clearly shows that the samples are magnetic in nature. As the pH increases the magnetisation values are also increasing. The saturation magnetisation was found to be 3, 6 and 7 emu g\(^{-1}\) corresponding to pH=10, 11 and 12 respectively. It clearly shows that the magnetisation values depend on pH. Figure 8b shows the magnetisation curves of YIG samples sintered at different temperatures.

When sintered at various temperatures 5 h, the magnetic moment clearly shows a swift increase from temperatures between 600 and 900°C. On the other hand, we have observed in the XRD data that at 600°C the crystal phase of the nanoparticles transforms from an amorphous phase to the garnet phase. Hence the onset of the magnetic moment occurs at a temperature slightly higher than that for the formation of the garnet phase. It is speculated that the difference between the magnetic and crystallographic onset temperatures could be associated with some change in the local ionic...

Table 1: Grains size, lattice constant, bulk density and variation of dispersity (measured in the form of Fano factor \( \sigma/d \)) with respect to sintering temperature\(^*\)

<table>
<thead>
<tr>
<th>Sintering temperature/ C/5 h</th>
<th>Lattice constant (Å) ± 0.001</th>
<th>Bulk density (g cm(^{-3})) ± 0.04</th>
<th>Grain size/nm</th>
<th>d/nm</th>
<th>( \sigma/nm ) (( \sigma^2/d ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>600(YIG1)</td>
<td>12.390 ± 0.001</td>
<td>5.03</td>
<td>125</td>
<td>130</td>
<td>33</td>
</tr>
<tr>
<td>700(YIG2)</td>
<td>12.392 ± 0.001</td>
<td>5.11</td>
<td>156</td>
<td>162</td>
<td>33.5</td>
</tr>
<tr>
<td>800(YIG3)</td>
<td>12.395 ± 0.015</td>
<td>5.15</td>
<td>178</td>
<td>182</td>
<td>34.2</td>
</tr>
<tr>
<td>900(YIG4)</td>
<td>12.398 ± 0.023</td>
<td>5.23</td>
<td>196</td>
<td>190</td>
<td>34.9</td>
</tr>
</tbody>
</table>

\*Sintering reduces the polydispersity of YIG particles, synthesised at pH 12.
coordination around the ferric ions. In general, Fe$^{3+}$ and O$^{2-}$ ions in the garnet form tetrahedrally and octahedrally coordinated ionic clusters. If a deficiency of ions or a local disorder exists in the garnet clusters, the change in the ionic coordination could sensitively alter the superexchange coupling. In the nanoparticle sample, the garnet phase is formed at 600°C but some clusters may still contain some oxygen deficiency. On the other hand, at temperatures higher than 700°C, Fe–O bondings in the clusters could be nearly completed to establish the Fe–O–Fe superexchange couplings which results in the observed onset of magnetization.\(^\text{14}\) The curves clearly show that all the sintered samples are magnetically ordered. The data of magnetic properties such as saturation magnetisation ($M_s$) and coercive field ($H_c$) are given in Table 2. It can be seen from the table that as the sintering temperature increases the values of $M_s$ increases due to the increase in grain size. The magnetisation values depend upon the grain size.

According to the relation

$$M_s(D) = M_s(\text{bulk}) \left(1 - \frac{\beta}{D}\right)$$

where $M_s(D)$ is the saturation magnetisation of sample with a grain size $D$, $M_s(\text{bulk})$ is the bulk saturation magnetisation value, and $\beta$ is a constant.\(^\text{15}\) The experiment result of Fig. 8b is in accord with the formula on the whole. The values of $M_s$ are found to be low as compared with the bulk ferrite\(^\text{6}\) which is due to the surface anisotropy of the samples.\(^\text{16}\)

The squareness factor ($M_r/M_s$) also monotonically increases with calcination temperatures, suggesting an increase in magnetocrystalline anisotropy (Table 2). We believe that this increase in magnetocrystalline anisotropy is most likely due to improvement in crystal order and structure, expected in samples sintered at high temperatures.

Figure 9 shows the dependence of coercive field $H_c$ on grain size $D$. It is observed that $H_c$ increases with an increase of $D$ and further increase of grain size, $H_c$ decreases. The transition from single domain to multidomain particles will lead to decrease in $H_c$. The boundary between single domain and multidomain particle is given by critical diameter of the particle $D_c$. The critical diameter of the particle is estimated from the formula\(^\text{17}\)

6 a–d images (SEM) of YIG samples sintered at different temperatures

7 Temperature dependence of magnetisation of YIG\(_4\) (900°C)
where \( \sigma_s \) is specific wall energy, \( K \) is magnetocrystalline anisotropy constant, \( T_c \) is Curie temperature, \( M_s \) is saturation magnetisation, \( k_B \) is boltzman constant and \( a \) is lattice constant. The critical diameter is found to be \( \sim 171 \text{ nm} \) which is in good agreement with the reported value \( 190 \text{ nm} \). The particles sizes below \( D_c \) are single domain particles and \( D > D_c \) are multi-domain. Therefore, above \( 800^\circ \text{C} \) the coercivity field decreases with increasing crystallite size due to multi-domain formation and the easy movement of the domain walls.

**Conclusions**

\( \text{Y}_3\text{Fe}_5\text{O}_{12} \) nanoparticles with high \( H_c \), large \( M_s \), easy dispersibility (at pH 12) and easy sinterability (with sintering temperature as low as \( 800^\circ \text{C} \)) was synthesised by a rapid, low temperature chemical co-precipitation method. The simplicity and cost effectiveness of the method ensures easy scaleability. The high yield (96%) of synthesis and the monodispersity of the resulting particles makes it a viable method for making \( \text{Y}_3\text{Fe}_5\text{O}_{12} \) nanoparticles for commercial applications (e.g. isolators, magneto-optical devices, etc). The grains observed in as synthesised powder are \( \text{Y}_3\text{Fe}_5\text{O}_{12} \) single nanocrystallites.

The average grain sizes, as well as the magnetic properties depend on the sintering temperature. The \( M_s \) of 23 emu g\(^{-1}\) and \( H_c \) of 22 Oe were obtained for the samples annealed at 900°C/5 h. The Curie temperature is 528 K. The critical diameter of the particle is found to be 171 nm. The simplicity of the technique makes it promising for obtaining related ferrite materials, including doped systems.

### Table 2

<table>
<thead>
<tr>
<th>Sintering temperature (°C/5 h)</th>
<th>( M_s )/emu gm(^{-1})</th>
<th>( M_r )/emu gm(^{-1})</th>
<th>( M_r/M_s )</th>
<th>( H_c )/Oe</th>
</tr>
</thead>
<tbody>
<tr>
<td>600(YIG1)</td>
<td>15</td>
<td>0.5</td>
<td>0.033</td>
<td>20</td>
</tr>
<tr>
<td>700(YIG2)</td>
<td>17</td>
<td>1.98</td>
<td>0.116</td>
<td>51</td>
</tr>
<tr>
<td>800(YIG3)</td>
<td>20</td>
<td>2.0</td>
<td>0.1</td>
<td>76</td>
</tr>
<tr>
<td>900(YIG4)</td>
<td>23</td>
<td>1.1</td>
<td>0.047</td>
<td>22</td>
</tr>
</tbody>
</table>

**Figure 8** Magnetisation curves (M–H loops) of YIG samples \( a \) prepared at different pH and \( b \) sintered at different temperatures.

**Figure 9** Coercive field of YIG increases with respect to grain size and sintering temperature: it reaches maximum at 171 nm; after which \( H_c \) decreases; this trend is most likely due to single domain to multidomain transition, beyond this grain size.
Acknowledgement

One of the authors (Dr K. Praveena) is thankful to UGC, New Delhi for Dr D. S. Kothari Post-Doctoral Scheme.

References

Authors Queries

Journal: Materials Research Innovations
Paper: 574
Title: Effect of pH on structural and magnetic properties of nanocrystalline Y\textsubscript{3}Fe\textsubscript{5}O\textsubscript{12} by aqueous co-precipitation method

Dear Author

During the preparation of your manuscript for publication, the questions listed below have arisen. Please attend to these matters and return this form with your proof. Many thanks for your assistance

<table>
<thead>
<tr>
<th>Query Reference</th>
<th>Query</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Please confirm the running head is correct.</td>
<td></td>
</tr>
</tbody>
</table>