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Synthesis and characterization of yttrium iron garnet (YIG) nanoparticles - Microwave material

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Magnetic Yttrium Iron Garnet (YIG) nanoparticles (NPs) were prepared by sol–gel (SG) and solid-state (SS) reaction methods to elucidate the nanoscale size on the magnetic behavior of NPs. It is found that YIG prepared by these two methods are different in many ways. The average NP sizes prepared by SG and SS methods were calculated by Scherrer formula from XRD data. SEM images show the change in grain size for both types of NPs. The sintering temperature required to form pure garnet phase is 750°C for SG and 1000°C for SS NPs. The saturation magnetizations (Ms) were 1070 Oe for SG and 1125 Oe for SS NPs, respectively. The coercivity (Hc) of SS NPs are twice larger than SG NPs. This is due to the larger crystal sizes of the SS NPs, hence more crystal boundaries. Dynamic properties were studied by ferromagnetic resonance (FMR) technique in field-sweep and frequency-sweep mode at different fixed frequencies and at different fixed magnetic fields, respectively. Resonance field (Hr) observed to increase linearly with frequency both for SS and SG NPs. The stop-band bandwidth (frequency linewidth) is narrower for SG NPs in comparison to SS NPs. Microwave absorption property make this material as a strong candidate for microwave device applications. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

I. INTRODUCTION

Ferrites have been attracting attention of microwave researchers for their possible use in miniaturized circuits and as one of the electromagnetic wave absorber. The penetration of electromagnetic (EM) waves is possible in ferrites because of their non-conducting nature. In contrast, metals are limited in this respect because of the skin effect. Due to their low eddy current losses it is treated as best material for a variety of electronic applications. The study of yttrium iron garnet (YIG) is becoming more important because of properties that can be extensively used in optical communication, 1 magneto-optical devices, and in microwave. 2 YIG is the most representative and well-known compound among the rare-earth garnets. More interestingly, various magnetizations can be achieved by substitution of normal metal ions into YIG. The recent progress in synthesis techniques of highly crystalline oxide nanoparticles such as yttrium iron garnet (YIG), Y 3 Fe 5 O 12 enables one to produce particles with size as small as in nano-meters range. 3 The nano-synthesis process also allows a very good control of the size of the nanomaterial. To make the nanoparticles useful, the fundamental understanding of magnetic behavior is essential. Nanoparticles generally have a large surface-to-volume ratio compared to the bulk material. YIG nanoparticles are observed to exhibit unique magnetic behavior due to the anisotropy and spin disorder of the surface owing to the large surface-to-volume ratio. The sol-gel synthetic method has been widely used to prepare nanostructures. YIG is one such material where the magnetic transition is much above the room temperature. It’s ferromagnetic transition is around 550K. 4 YIG has a cubic structure with space group Ia3d. 5 During the last decades

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magnetic properties especially dynamical properties of magnetic materials have attracted a lot of interest due to their application in the development of new devices for spintronics. The miniaturization and fast-time-scale applications of these devices are a new topic of research. A distinctive property of such devices is the magnetization relaxation rate (Gilbert damping) characterizing the time scale on which a system being deviated from the equilibrium returns to it, or how fast the device can be switched from one state to another. Gilbert damping can be deduced from experiment. It can be evaluated from the resonant linewidth in ferromagnetic-resonance (FMR) experiments. For microwave device applications YIG is a front runner because it can be used at room temperature. With low resonance linewidth, high quality factor, etc. it has proved to be a very useful material in microwave application. FMR is a very powerful and well-established dynamic technique to investigate magnetic materials and to determine magnetic properties. FMR absorption experiments measure either the microwave power absorbed by a specimen as a function of an applied dc magnetic field (H) or the derivative of the absorption with respect to H. In either case, the resulting curve is described by a resonance field, $H_{\text{res}}$ that corresponds to maximum power absorption, and by an absorption linewidth, $\Delta H$. This paper is motivated to gain insight into the role of nanoparticles interactions in determining the magnetic properties of YIG. Here, we investigated the magnetic behavior of YIG NPs by measuring the particle size dependence of magnetization arising due to two different synthesis techniques. We have studied the microstructure, magnetic, and microwave properties in details.

II. EXPERIMENTAL

Polycrystalline samples of YIG were prepared by conventional solid state reaction and sol-gel methods. In solid state synthesis, stoichiometric amounts of powders of $\text{Y}_2\text{O}_3$ (Sigma-Aldrich 99.99%) and $\text{Fe}_2\text{O}_3$ (Sigma-Aldrich 99.99%) were taken in 3:5 ratio, respectively and well ground in agate mortar pestle for overnight. The ground powder was then sintered at 1000°C in air for 24 hours. As mentioned in ref. 8 and 9 after the first heating the sample was reground and pellet pressed and then again heated at 1300°C for 24 hours. During both the heating processes the heating and cooling rate was kept 5°C/min.

The second series of sample was done by using sol-gel method. $\text{Y(NO}_3\text{)}_3\cdot6\text{H}_2\text{O}$ and $\text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$ used as precursor materials, taking in the molar ratio of (Y:Fe) (3:5), respectively, and dissolved in distilled water at room temperature. After constant stirring for 1 hour, we obtained a dark brownish sol. During the process ethylene glycol and concentrated HNO$_3$ were used for controlling the pH to ~5. Brownish sol was dried under IR heating for 12 hours and powder was calcined at 750°C for 1 hour in air to get pure phase YIG NPs.

X-ray powder diffraction was performed at room temperature using Cu-Kα Radiation ($\lambda = 1.5418\text{Å}$) in Xpert Panalytical diffractometer instrument. Zeiss table top SEM was used for analyzing nanoparticle’s morphologies. It uses an acceleration voltage of 20 kV and magnification at 30Kx. A dispersion of NPs was made in ethanol and then a drop of the nanoparticles dispersion liquid was put on the carbon tape stub and (ethanol) was allowed to dry in air. The magnetic data were taken in a Cryogenic make Physical Property Measurement System (PPMS).

The FMR experiments were done using a broad-band FMR system in transmission mode with frequency range from 1 to 20 GHz and magnetic field from 0 to 10 kOe. To do this, we have coated the nanoparticles of YIG by electrophoretic deposition (EPD) method directly on top of the coplanar waveguide. YIG NPs were dispersed in ethanol solution [2mg/10ml] for 4 hours at room temperature. 100µl of PVA solution (5mg/10ml) and 100µl of Mg$^{2+}$ ions solution (5mg/15ml) were mixed in the dispersed solution. The solution was sonicated for 2 hrs. At first, CPW was made on copper coated FR-4 substrate using photolithography with perfect 50 Ω impedance matching to the Vector Network Analyzer (VNA) system. This CPW was used as working electrode and platinum (Pt) was used as counter electrode. Electrophoresis was done at 300 volts for 5 minutes, negative potential was applied at working electrode to deposit YIG thin film on signal line of CPW. The scattering parameter ($S_{21}$) were recorded from the vector network analyzer for each field-sweep at a fixed frequency to derive resonance field ($H_{\text{res}}$) and resonance linewidth ($\Delta H$) from the absorption data.
III. RESULT AND DISCUSSION

Figure 1(a) and 1(b) shows the room temperature XRD pattern of YIG in 2θ range from 20° to 60° both for sol-gel and solid-state synthesized NPs, respectively. It is found that YIG has a cubic structure with space group $Ia3d$ and the estimated lattice parameter is $a = 12.374$ Å. The diffractograms of samples synthesized at 750 °C and 1000 °C by sol-gel and solid-state synthesis techniques, respectively, exhibit only the characteristic peaks of YIG. Using Scherrer’s equation (1), sizes of the crystallite using broadening in peaks in XRD pattern can be calculated.

$$\tau = N \frac{\lambda}{\delta \cos \theta}$$  \hspace{1cm} (1)

Where:

$N$ = shape factor,

$\lambda$ = x-ray wavelength (Cu Kα) $\lambda = 1.54181$ Å

$\delta$ = line broadening at half the maximum intensity (FWHM) in radians

$\theta$ = Bragg angle

Crystalline size was calculated by fitting of all the peaks and taking average of all the sizes obtained. The average particle size obtained for sol-gel and solid-state prepared samples are 33 nm and 65 nm, respectively.

Fig 1(c) shows the VSM graphs of both solid state and sol gel NPs. The hysteresis loops measured at room temperature (RT), have confirmed their ferromagnetic nature. The magnetic hysteresis loop displays a typical ferromagnetic character with the saturation magnetization (Ms), remanent magnetization (Mr) and coercive filed (Hc), which are tabulated in Table-I.

Solid-state synthesized NPs have larger Hc than sol-gel NPs, because the SS NPs have more grain boundaries and pinning sites. SG NPs with smaller grain size exhibited lower magnetization compared with SS NPs with larger grain size. The magnetic domain walls and moments played an

![Figure 1](image_url)

**TABLE I.** Experimental values observed from VSM curves.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Type of Sample</th>
<th>$4\pi$Ms (Oe)</th>
<th>Coercivity (Hc) (Oe)</th>
<th>Remanence (Mr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sol Gel</td>
<td>1070</td>
<td>31</td>
<td>150</td>
</tr>
<tr>
<td>2</td>
<td>Solid State</td>
<td>1125</td>
<td>72.5</td>
<td>64</td>
</tr>
</tbody>
</table>
important role in the variation in Ms, Mr, and Hc for SS and SG NPs. In this study, SS NPs have higher Ms and higher Hc compared with SS NPs. In this study, SS NPs have higher Ms and higher Hc compared with SS NPs.11

Fig. 1(d) and 1(e) shows the SEM images, showing morphology for both sol gel and solid state NPs, respectively. It is distinctively evident that sol gel NPs are smaller than solid state NPs. Due to larger grains solid state NPs show more crystallinity.

Room temperature FMR measurements were performed both in field sweep and frequency sweep mode. Fig (2) shows the field sweep response of YIG NPs at different frequencies ranging from 1 to 20 GHz. Fig 2(a) shows the FMR spectra for sol gel NPs. Fig. 2(b) is the ensemble of the observed resonance field (Hr) and resonance linewidth (ΔH) data from Fig. 2(a) for sol gel NPs. Similarly, Fig 2(c) shows the FMR spectra for solid state NPs and Fig. 2(d) is the ensemble of the observed resonance field (Hr) and resonance linewidth (ΔH) data from Fig. 2(c) for solid state NPs. It is clearly evident that due to larger grain size the line width for solid state NPs are somewhat higher in comparison to sol gel NPs. It is also observed that all the spectra have symmetrical and reasonably narrow linewidth, especially below 15 GHz frequency range for SG NPs. Above 15 GHz there is asymmetric behaviour of the FMR spectra giving rise to additional resonance mode at higher field side. This behavior for the magnetic NPs may be due to non-uniform modes in addition to main resonance mode, and also a random orientation of the nanoparticles. The line behavior of FMR spectra results from the random orientation of the magnetic nanoparticles having the different easy axis.

The FMR resonance field increases with the increase in operating frequency, for both type of particles synthesized via sol-gel (SG) and solid-state (SS) methods. At a fixed frequency, say 15 GHz, the SS NPs resonate at higher field than the SG-NPs. We observed linear dependency of resonance field with applied frequency. Considering spherical shape of the nanoparticles, the ferromagnetic resonance field is given by:

$$H_r = \frac{ω}{γ} - H_{eff}$$  (2)
Where, $\omega$ denotes the Larmor precession frequency, $\gamma$ is the gyromagnetic ratio and $H_{\text{eff}}$ is the effective field [$=H_D + H_K + H_{\text{int}}$], where $H_D$ is the demagnetizing field, $H_K$ is the anisotropy field and $H_{\text{int}}$ is the interaction field.

The observed FMR linewidth are a combination of intrinsic as well as extrinsic contributions to linewidths. Such linewidth responses are often interpreted in terms of a combined inhomogeneous broadening and Landau-Lifshitz or Gilbert damping model. The experimental value of Gilbert damping parameter $\alpha_{\exp}$ may be deduced from the FMR linewidth $\Delta H$ at frequency $f$ as:

$$\Delta H = \Delta H_0 + \frac{2}{\sqrt{3}} \left( \frac{4\pi f \alpha}{\gamma} \right)$$

(3)

Where $\Delta H_0$ is the linewidth at zero frequency - a measure of the inhomogeneous broadening (extrinsic linewidth) and $\alpha$ is the parameter which determines how much the linewidth changes with frequency.

The factor $2/\sqrt{3}$ assumes Lorentzian line shape of the resonance absorption curve.

As proposed by Bastrukov et.al., considering both intrinsic and extrinsic damping torques the intrinsic and extrinsic contributions to linewidth can be expresses as:

$$\Delta H (f) = \frac{4\pi f}{\gamma |\mu_0| M_s} \left[ \alpha - \beta \left( 1 - \left( \frac{\gamma |\mu_0| M_s}{2\pi f} \right)^{1/2} \right) \right]$$

(4)

Where $\alpha$ is intrinsic damping parameter, $\beta$ is extrinsic damping parameter, $\gamma$ is gyromagnetic ratio, $M_s$ is saturation magnetization, $f$ is FMR frequency, respectively.

Fitting to eq. (3) for the FMR linewidths data given in Fig. 2(b) and 2(d), we have derived the zero-frequency offset (extrinsic part). $\Delta H_0$ increased from 0.7 to 1.4 kOe for the SG to SS NPs. The value of $\gamma$ changed from 2.4 for SG NPs to 2.65 for SS NPs. The value of Gilbert damping is 0.12 for SG NPs and increased to 0.13 for SS NPs. Similarly, fitting to eq. (4) for the FMR linewidth data, various sample parameters like $\gamma$, $\alpha$ and $\beta$ for both type of nanoparticles are derived. The intrinsic ($\alpha$) Gilbert damping constant found to increase from 0.38 to 0.5, for SG NPs to SS NPs. Whereas, the extrinsic ($\beta$) Gilbert damping constant found to increase from 0.3 to 0.4, for SG NPs to SS NPs. Hence there is an overall increase of linewidth and hence damping for solid state synthesized nanoparticles.

![FIG. 3. Frequency sweep response of (a) sol gel NPs and (c) solid state NPs. The corresponding linewidth ($\Delta f$) and resonance frequency ($f_r$) of sol-gel (b) and solid-state (d) NPs, respectively.](image-url)
as observed in the present study. Hence, the extrinsic (β) and intrinsic (α) Gilbert damping constants are dependent on the synthesis process.

To analyze the frequency tuning capability of YIG NPs we have also performed the frequency swept FMR. Fig 3 shows the frequency swept FMR both for sol-gel and solid-state NPs. Fig 3(a) and 3(b) shows the FMR spectra and the derived resonance frequency and linewidth for sol gel NPs. Similarly, Fig 3(c) and 3(d) shows the FMR spectra and the derived resonance frequency and linewidth data for solid state NPs.

The resonance frequency is observed to increase linearly with the increasing magnetic field. The frequency linewidth (bandwidth) are narrower for SG NPs in comparison to SSNPs. The EPD synthesized NPs based devices can be used as frequency tunable microwave filters with magnetic field tuning. These devices behave as frequency selective device with tunability 2.9 GHz/kOe for sol-gel and 3.12 GHz/kOe for solid-state synthesized NPs. Room temperature frequency tunability is a requirement for many high frequency devices used in radar and satellite communications.

IV. CONCLUSION

Sol gel and solid state YIG nanoparticles were successfully synthesized. The micro structural properties proved that grain size for solid state NPs were higher than sol gel NPs and this property greatly effects the characteristics of NPs. SEM study confirms its change in morphology and crystallinity. Magnetization was found to be different for these two types of NPs. The observed FMR linewidth are combination of intrinsic as well as extrinsic contributions to linewidths. There is an overall increase of linewidth and hence damping for solid state synthesized nanoparticles in comparison to sol gel synthesized nanoparticles. Frequency tunability for 2.9 GHz/kOe for sol-gel and 3.12 GHz/kOe solid-state NPs is achieved. Microwave absorption properties make this material as a strong candidate for microwave device applications. Passive microwave devices like frequency shifter, phase shifter and absorber can be designed using YIG NPs deposited EPD device.

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