SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE YTTRIUM IRON GARNET ($Y_3Fe_5O_{12}$) FOR MAGNETOELECTRIC APPLICATIONS

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Yttrium iron garnet ($Y_3Fe_5O_{12}$) commonly known as YIG was synthesized by sol-gel processes in the nanocrystalline form. Its phase formation was analyzed through powder X-ray diffraction and thermal analysis (TG-DTA analysis). Crystallization from amorphous phase to single phase YIG (garnet) phase was confirmed through thermal analysis and that it was confirmed that as low as 700^o C is required for combustion synthesis when compared to the solid state method. TEM measurements confirmed the coalesce nature of the garnet at nanophase level. Saturation magnetization was determined from VSM measurements. The temperature dependence of the ZFC/FC magnetization measured at applied field of 8000 Am^{-1} for the YIG was carried out for the sample in the temperature range of 20–400 K. The results in the nano-regime are discussed in detail.

(Received February 18, 2019; Accepted August 26, 2019)

Keywords: Colloidal processing, Nanocrystalline materials, Sol-gel preparation, Magnetic materials, Yttrium Iron Garnets (YIG) , Curie Temperature

1. Introduction

Ferromagnetic garnets (such as Yttrium iron garnet -$Y_3Fe_5O_{12}$ - YIG) are assigned to cubic structure (space group Ia3d) with general formula $R_3Fe_5O_{12}$. The ion distribution structure is represented by writing the garnet formula as $\{R_3\}[Fe_2](Fe_3)O_{12}$, { }, [ ], ( ) representing 24c (dodecahedral), 16a (octahedral) and 24d (tetrahedral), respectively. YIG was given much attention owing to its interesting magnetic and magneto-optical properties for data storage devices [1-4]. Yttrium iron garnets (YIG) finds wider applications as electrical insulators which are used in the microwave region and its resistivity is 10^{12} ohmcm at room temperature which are widely used as circulators, oscillators and phase shifters for microwave region, because of its controllable saturation magnetization and low dielectric loss tangent (tan d) in microwave region and small linewidth (DH) in ferromagnetic resonance [5-7].

The uniform grains can be obtained through chemical process methods rather than reducing the particle sized by ceramic methods such as ball milling and thereby agglomeration can be avoided. But this method requires very high temperatures (~1570 K); consequently, new methods of synthesis such as sol–gel method have been recently developed to obtain homogeneous fine particles [8,9]. Usually low temperature is required in this method for the synthesis of nanoparticles of rare earth iron garnets and thereby the uniformity can be achieved to synthesize high pure single phase materials. In this work, a novel simple sol–gel route to process YIG

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nanoparticles [10,11] is presented. Citrate–nitrate auto-combustion synthesis was used to prepare YIG nanoparticle by rapid phase method and the results were discussed in detail.

2. Materials and methods

Stoichiometric amount of highly purified metal nitrates of yttrium nitrate and iron nitrates were dissolved together in distilled water with required amount of citric acid was mixed with the nitrates solution in the 1:1 ratio. The mother solution was maintained at 70^{o} C using the hot plate and that the pH is maintained in acidic nature for effective combustion. The temperature of the beaker was then gradually increased which leads to the decomposed gel which gets self-ignited due to the presence of citric acid which were then calcinated at different temperature to get nanocrystalline YIG powders.

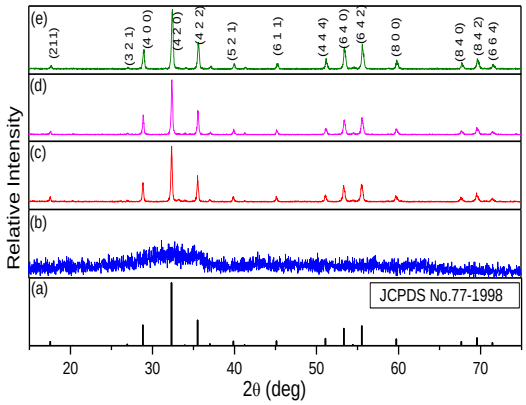
The samples calcinated at 800, 850 and 900^{o} C was used to determine the phase formation and average grain size by using a powder X-ray diffractometer (Rigaku, Cu-Kα). Thermogravimetric analysis (TGA) was performed in a EXSTAR 6000 thermal analyzer to measure simultaneous thermogravimetric Differential Thermal Analysis (TG-DTA) in the temperature range of room temperature to 1050^{o} C. Thermomagnetic analysis was performed in the same equipment by placing a small permanent magnet beneath the sample in the temperature range from ambient to 350^{o} C. The morphology was examined using a JEOL EX-2000 electron microscope to obtain the nano regime images. Tamakawa make instrument is used in the magnetic field range of 10 kOe to obtain the field versus magnetization curve at the room temperature range.

3. Results and discussions

The crystallite size is increased during the high temperature calcination. The mean crystallite sizes of the calcined powders vary from 20 to 100 nm. The X-ray diffraction patterns of the samples calcinated at 800^{o} C, 850^{o} C and 900^{o} C is shown in Fig.1(a). It is evident that the annealed powders contain only the garnet phase as $Y_3Fe_5O_{12}$ [12] and it is clearly evident that all the peaks in the pattern match well with JCPDS card. No-77-1998 and thus providing a efficient method for a single step synthesis of yttrium iron garnet. The transmission electron microscope (TEM) image of the synthesized samples of yttrium iron garnet (YIG) annealed at 900 °C is shown in Fig. 1(b) and Fig. 1(c) in which the average particle size was found to be around 60 nm which is close to the values obtained from the XRD pattern. The cage like structure at 900 ^{o}C indicates the garnet nature as this phenomenon was reported earlier. [13,14] Since the cubic garnet structure has the least free energy than any other phase if exists at this thermodynamically stable state at the particular this temperature.

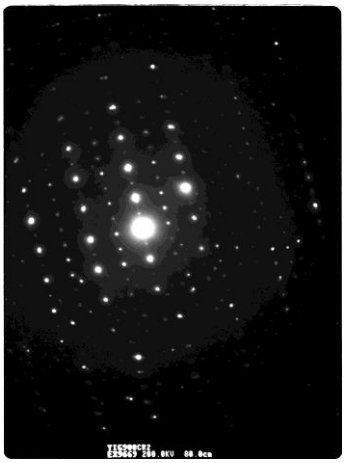
Simultaneous TG-DTA curves for the asprepared is shown in Fig. 2(a). The weight loss between 75^{o} C and 100^{o} C corresponds to the loss of water molecules. Thus there is a formation of amorphous yttrium iron hydroxide while the sample is further heated for obtaining single phase YIG. The weight loss at 210 and 390 ^{o} C corresponds to the loss of organic residues such as -NH_2 and –COOH. The carbondioxide present in the carboxylic acid group (citric acid) gets evaporated [15,16]. The broad nature of the peak indicates that the ignition takes place over a range of temperature [17].

The weight loss at 763^{o} C corresponds to the crystallization of YIG due to the oxidation of the metal–citrate complex from its amorphous state. This indicates that the YIG phase could be formed below 800^{o} C. Fig. 2(b) shows the thermomagnetization of the YIG annealed at 900^{o} C. An initial weight gain is observed followed by sharp weight loss at 276^{o} C. When the Curie temperature is reached, the magnetization is lost completely thereby resulting in thermomagnetic weight loss. The Curie temperature of the YIG is clearly observed from the thermomagnetic weight loss at 276^{o} C. This suggests that the nanocrystalline form of YIG has Curie temperature similar to that of bulk YIG [18].



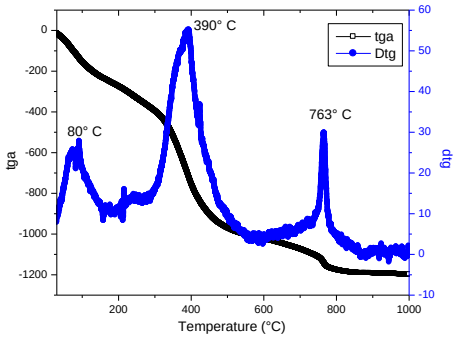
a)

b)

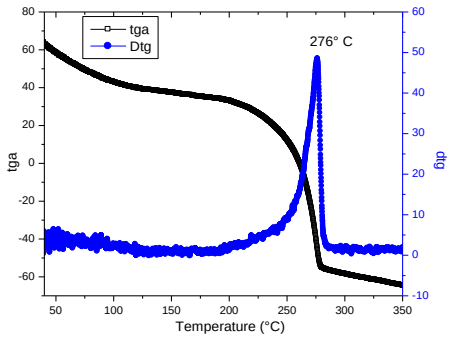


c)

Fig. 1. Powder XRD pattern of the (a) JCPDS-No for YIG – 77-1998 (b) asprepared YIG sample and the samples annealed at (c) 800, (d) 850 and (e) 900 ^{o}C and Fig. 1(b) and 1(c). TEM micrograph of YIG sample annealed at 900 ^{o}C.



a)



b)

Fig.2 (a). TG-DTG graph for the asprepared gel prepared using autocombustion method and Fig.2(b).Thermomagnetization of nanocrystalline YIG annealed at 900 ^{o}C

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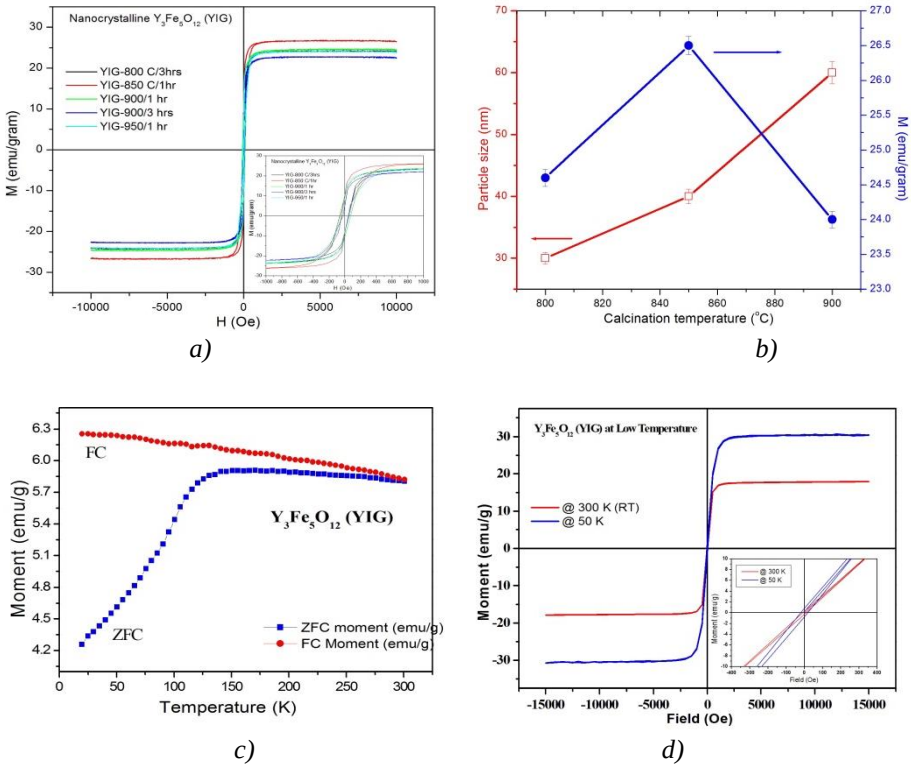

Fig. 3(a). Magnetic hysteresis of synthesized nanocrystalline YIG and Fig.3(b). Calcination temperature Vs Particle size and saturation magnetization Fig. 3(c). ZFC-FC curves and Fig.3(d). LT-VSM of YIG sample calcined at 700^{o} C.

The magnetization curve for various annealed samples of 800, 850 and 900^{o} C is shown in the below Fig. 3(a) which shows that the magnetization varies between 28 to 20 emu/g for various calcinations temperatures. The difference in this magnetization is due to the crystallization percentage with respect to the thermal stress induced in the samples at the nano regime [19,20].The avera ge particle size with respect to the calcination temperature and the saturation magnetization are shown in Fig. 3(b) and it agrees well with the ones reported earlier [21]. Saturation magnetization (Ms) increases as the calcinations is increased and decreases on further calcinations. The increase in magnetization indicates diminishing surface effects and single phase formation further leads to decrease indicating the increase in particle size.

The above Fig.3(c)shows the temperature dependence of ZFC/FC magnetization for the applied field of 8000 Am^{-1} in the temperature range of 20 – 400 K and it can be seen that the Curie temperature TC for YIG is higher than 400 K [22], the following features can be observed: (1) if we could increase the temperature, both curves will probably collapse above TS ≥ 400 K; (2) irreversibility is observed below TS, with MZFC < MFC; (3) the maximum value of the ZFC magnetization is observed at TM < TS (~ 260 K). Hysteresis loops shown in Fig.3(d) at the temperature of 50 K and 300 K indicate that with increasing of the sintering temperature, the saturation magnetization rises with increasing amount of the $Y_3Fe_5O_{12}$ (YIG) phase. The profile of the magnetization for the YIG sample suggest obtaining of a soft ferromagnetic material, because sample is very sensitive to an external magnetic field, reaches its saturation at relatively small field and the coercivity is small (< 1600 Am-1) [23,24].

4. Conclusions

Nanocrystalline form of yttrium iron garnet $Y_3Fe_5O_{12}$ (YIG) was synthesized by citrate gel method at low temperature. Single phase formation was achieved through single step combustion synthesis. The phase analysis and the particle size were confirmed from powder X-ray diffraction analysis. Cage like morphology was visualized through TEM analysis. The saturation magnetization was in good coherence with the reported values.

Acknowledgments

One of the author Jasper Goldwin wishes to thank the management of Agni College of Technology, Thalambur, Chennai – 600130 for permitting to carry out the research and providing the necessary lab and infrastructure facilities.

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