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High Saturation Induction for Bi-Substituted Yttrium Iron Garnet Prepared Via Sol Gel Technique

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Abstract: $Y_{3.0-x}Bi_xFe_5O_{12}$ samples (x = 0.2 and 0.4) were prepared via novel sol-gel and conventional solid-state techniques. The effect of bismuth in both techniques was investigated in terms of shrinkage, density, hysteresis and initial permeability. Sharp and clear diffraction XRD lines with highest peak appear at about 32° of the 2θ, for all the powders sintered at 900°C and 1250°C for both techniques. In evaluating the magnetic properties, it was observed that the saturation induction (1.1902kG) of sample prepared via sol-gel technique ($Y_{2.8}Bi_{0.2}Fe_5O_{12}$) is more than 200% higher than sample with the same formula prepared via conventional technique. Fine grained microstructure with average grain size of about 5 μm and higher shrinkage, about 11% were observed from the samples prepared via sol gel technique. It is concluded that samples prepared via sol gel technique appear to be an attractive route due to the possible reduction of cost of production and the enhanced magnetic and structural properties of the sample.

Key words: Conventional solid state, hysteresis, initial permeability, sol gel technique, C (conventional) S (sol-gel)

INTRODUCTION

Ferrites may be defined as magnetic materials composed of oxide containing ferric ions as the main constituent. The term is often restricted to such materials having mineral spinel cubic crystal structure, but it is also loosely applied to magnetic oxides in general irrespective of their crystallic structure. Yttrium iron garnet (YIG) has been studied intensively by researchers for decades now. It prides itself as being one of the most well known soft ferrites hitherto. Its grandeur can be justified by its application in microwave devices such as spatial light modulators, guided wave optical isolators[1], optical Faraday rotator[2], phase shifters, switches and sensors[3,4]. Doped YIG were also subjected to scrutiny. The magnetic and electric properties of these YIG compounds changed slightly or drastically based on the type and quantity of dopant as well as substituent employed. Recent studies involved the work of Marysko[5], who studied the properties of cobalt doped YIG films and the work of Xhang *et al.* that focused on the magneto-optical properties of Nd substituted YIG[6]. This work however deals with preparation of Bi-$Y_3Fe_5O_{12}$ samples using conventional, solid-state and novel, sol-gel techniques. The magnetic and structural properties of all the samples were investigated and compared.

MATERIALS AND METHODS

The raw materials used for the conventional technique in this project are bismuth oxide (purity: 99.98%), yttrium oxide (purity: 99.9%) and iron oxide (purity: 99.99%). For conventional technique, raw materials were wet mixed in milling machine for 16 hours to get a homogeneous mixture and subsequently, filtering, drying and pre-sintering were done at 1150°C in air. On the other hand, stoichiometric mixtures of nitrates, comprise of iron (III) nitrate, $Fe(NO_3)_3.9H_2O$, bismuth (III) nitrate, $Bi(NO_3)_3.9H_2O$ and yttrium nitrate, $Y(NO_3)_3.6H_2O$ were weight and dissolve in an aqueous solution of citric acid for the sol-gel technique. The nitrates were dissolved by stirring them with a magnetic stirrer at 300 r.p.m at room temperature for three days. The solution was then heated up to 80°C with the same stirring rate until the gel was obtained. The gel was then dried at 110°C in an oven for another 24 hours. The dried powders were then sent for x-ray diffraction measurements to discern the reaction pathway and to study the gel to crystalline transformation. The samples were then pre-sintered at 1150°C (solid-state) and 800°C (sol-gel) in air for 5 hours. All the pre-sintered green powders were wet crushed for 6 hours using Planetary Micromill to obtain fine particles granules. The green powders were moulded to a toroidal shape using hydraulic machine at 60kN. 1.5% of PVA acted as binder and 1.5% of zinc

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stearate acted as lubricant were added into the powders. All the toroids were then sintered at 1250°C for 10 hours and 900°C for 5 hours in air, for the conventional and novel techniques, respectively. Samples that were prepared via solid state technique are denoted as C1 ($Y_{2.8}Bi_{0.2}Fe_5O_{12}$) and C2 ($Y_{2.6}Bi_{0.4}Fe_5O_{12}$). On the other hand, samples that were prepared via sol gel technique are denoted as S1 ($Y_{2.8}Bi_{0.2}Fe_5O_{12}$) and S2 ($Y_{2.6}Bi_{0.4}Fe_5O_{12}$). For the hysteresis measurements (AMH-Hysteresis Graph, Walker Scientific), the samples were wounded 20 turns of 0.3mm diameter insulating copper wire as its primary turns and 40 turns as the secondary turns. All the four ends of the copper wire were scraped with grade 1000 sand paper and were then soldered with silver to ensure contact during measurements. Value of coercive force (H_c), remanence (B_r), saturation induction (B_{max}) and core loss (W_h) can be obtained from this measurements. To obtain these values, the effective area, A and path length, P of the toroidal sample had to be calculated from the formulae below:

Effective area,

$$A = \frac{(Do - Di)t}{2} \qquad (1)$$

Path length,

$$P = \frac{(Do + Di)\pi}{2} \qquad (2)$$

Inductance (L_S) measurements were essential as values of the initial permeability had to be obtained by this measurement. The samples were connected to a Hewlett Packard model 4195A Network/spectrum analyzer. Series inductance values, Ls, were taken from 1MGz to 50 MHz. Initial permeability values can be obtained automatically from the analyzer.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the Bi substitute YIG particles for samples C1 and S1 after pre-sintering and sintering. A clear diffraction line with highest peak appears at about 32° of the 2θ, for all the powders. Sharp and clear diffraction lines could be observed for all the powders sintered at 900°C and 1250°C for both the techniques.

Interesting however is the disappearance of the unknown peak mentioned above for C1 after sintering process was done. This corresponded to the progression of crystal growth of the entire particles.

The density of sample would increase with the increase of Bi^{3+} ions concentration. It is because Bi^{3+} ion is placed in group 5 in the periodic table, with the atomic weight of 208.98 a.m.u (atomic mass unit) comparing to Y^{3+} ion with atomic weight of just 88.91 a.m.u. Referring to Table 1, the increase of Bi^{3+} ions concentration has increased the total atomic weight of the sample and as a result the density increases[8].

However, the density of samples prepared via sol-gel technique is greater than those prepared via conventional technique. Samples prepared via sol-gel technique are speculated to have finer grains and therefore would have higher density. The difference in density is due to the mixing of solution in atomic molecular form, which resulted in large surface area.

The shrinkage during firing depends on the reactivity of the milled powder, the binder content and the firing conditions (temperature, time and atmosphere). Improper preparation may result in extensive shrinkage and as a result micro-cracks could occur. Linear shrinkage during firing may vary from 10-20%[9]. In this experiment, the shrinkage is less then 12% for all the samples. It could also be observed that the shrinkage increases with the increase Bi^{3+} concentration for both the techniques. The melting point of bismuth oxide is 825°C[8]. Since the samples were sintered at high temperature (900°C and 1250°C via both techniques), we anticipate the bismuth oxide to be in liquid form. During sintering process we speculate that Bi_2O_3 may soften to liquid phase providing attractive capillary forces for neighbouring particles to come closer and react.

This process, commonly known as liquid phase sintering[9], causes the enhancement of reactivity of the powder to form the garnet phase when the Bi^{3+} ions concentration was increase. In consequence, the shrinkage will also increase. We observed fine grained and traces of some melting regions (Fig. 4). Larger grain size (Fig. 3) for the S1 sample, with almost poreless microstructure, prepared via sol gel were observed even though we speculated them to be in nano size and smaller than those prepared via sol gel technique[7]. However, for the sol gel technique, since the starting materials are nitrates that dissolve in citric acids, we anticipate the melting point to be much lower. The reactivity during sintering is enhanced and as such the 900°C is found to be too high that causes the grains to grow much more than we expected, approximately 14 μm. The shrinkage of samples prepared via sol-gel technique was greater than those prepared via conventional technique (Table 1).

Observing Fig 2, the saturation induction, B_{max}, for samples prepared via sol gel technique are higher then those prepared via conventional technique. The B_{max} for $Y_{2.8}Bi_{0.2}Fe_5O_{12}$ sample prepared via sol gel technique is 1.1902 kG, 200% higher than the sample of the same formula prepared via conventional technique. We speculate the better formation of microstructure in samples prepared via sol gel technique gave the higher B_{max} value. Substituting Bi^{2+} to Y^{3+}, as a result increases the net magnetic moment of the garnet system. From Fig. 3 and Table 1, the B_{max} for sample C1 and sample C2 is 0.3673 kG and 0.4979 kG, respectively. This is in accord with the above statement. Sample S1 gave higher B_{max} (1.1902 kG) as compared to sample S2 (0.8635 kG). As mentioned, bismuth is a sintering aid. Too much bismuth content resulted in formation of pores.

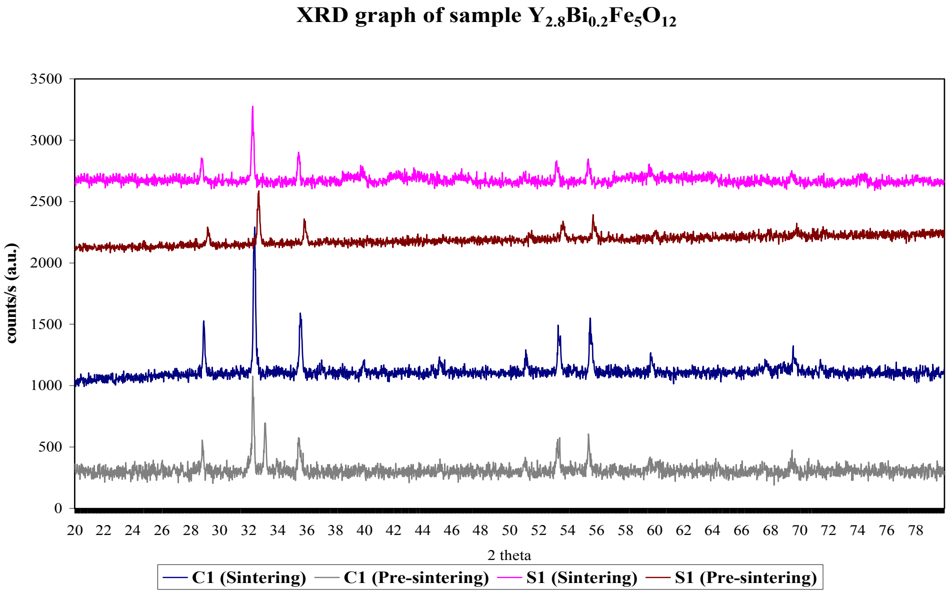

Fig. 1: X-ray diffraction profile for sample C1 and S1 for pre-sintering and sintering

Table 1: Results of Density, Shrinkage, Saturation Induction (B_{max}) and Initial Permeability and XRD before and after sintering for samples C1, C2, S1 and S2

Sample	Conventional Technique		Sol-Gel Technique	
	$Y_{2.8}Bi_{0.2}Fe_5O_{12}$ C1	$Y_{2.6}Bi_{0.4}Fe_5O_{12}$ C2	$Y_{2.8}Bi_{0.2}Fe_5O_{12}$ S1	$Y_{2.6}Bi_{0.4}Fe_5O_{12}$ S2
Density (g/cm^3)	4.2378	4.5262	4.8493	5.1238
Shrinkage (%)	5.3047	7.1270	10.9103	11.3720
B_{max} (kG)	0.3673	0.4979	1.1902	0.8635
Initial Permeability, (μ_i') at 10 MHz	54.4105	38.8799	40.0393	30.1530
XRD Pre-sintering (2ϑ)	32.2900	32.7100	32.2700	32.1900
XRD Sintering (2θ)	32.4100	32.2900	32.4100	32.1900

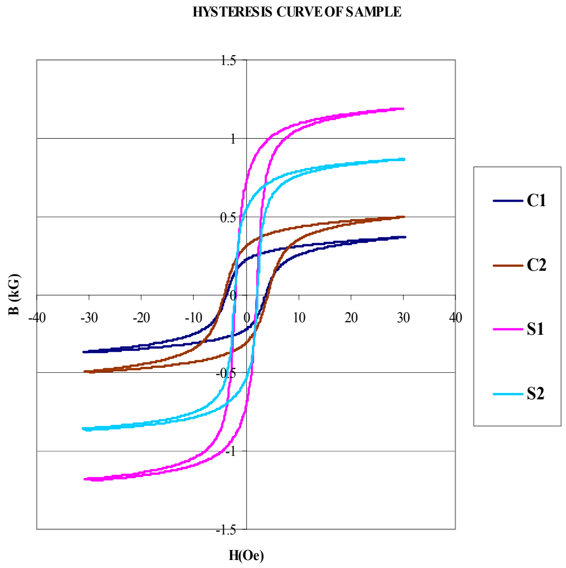

Fig. 2: Hysteresis graphs of samples C1, S1, C2 and S2 measured at room temperature

The microstructure of sample S1 and sample S2 will have a large impact on the magnetic properties. The microstructure of S1 (Fig. 3) is large, almost poreless and homogenous. On the other hand, the microstructure of sample S2 is porous and there are some traces of liquid phase sintering due to the melting of the structures. This had weakened the super-exchange interaction and thus reduced the saturation induction, B_{max}.

Coercive force (H_c) is expected to be the most sensitive of all properties, with respect to density[10].

Observing the H_c (Fig. 2), it is notable that both samples that were prepared via sol gel technique gives lower H_c. We attribute this to the speculation made; higher density (Table 1), which is associated with the homogeneous and poreless microstructure (Fig. 3). Comparing the coercive force between the two techniques, it is obvious that samples prepared via conventional method showed higher coercive force. Most likely, smaller grain size gives greater number of grain boundaries. When a moving domain wall

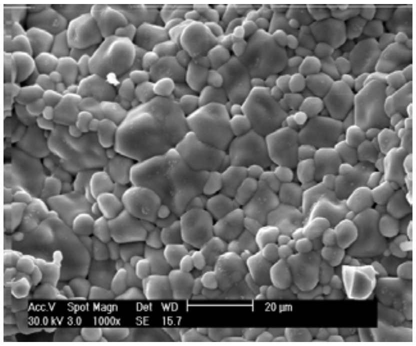

Fig. 3: Scanning electron microscopy image of sample S1 prepared via sol-gel technique

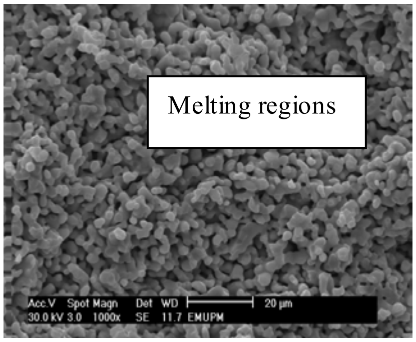

Fig. 4: Scanning electron microscopy image of sample C1 prepared via solid state technique

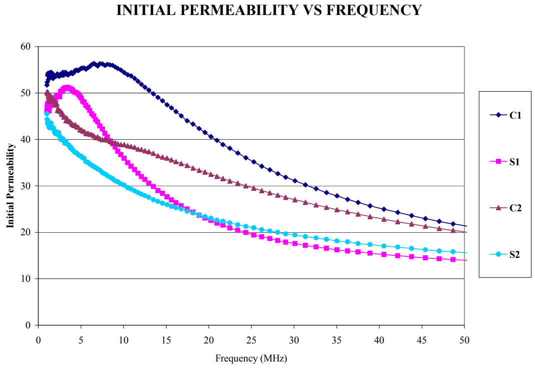

Fig. 5: Initial permeability vs. frequency of samples C1, S1, C2 and S2 measured at room temperature

encounters a grain boundary, the wall area is reduced and the total energy is lowered in proportion to the wall-surface energy density. As a result, additional energy in the form of an increased applied field is required to overcome the decrease in wall energy and free it from the pore. This resulted in an increase of coercive force. The result obtained in this work is in accord with the general theories of coercivities.

Table 1 gives the initial permeability over at 50 MHz. Samples that were prepared via conventional technique gave higher initial permeability, 54.41 and 38.88 for samples C1 and C2 respectively. However, the initial permeability of those prepared via sol gel technique showed slightly lower, 40.04 and 30.15 for samples S1 and S2, respectively (Fig. 5). However, the resonance frequency for the S1 and S2 samples are higher than those prepared conventional technique. Additional of Bi^{3+} ions would result in increase of unwanted pores as well of melting points, this may be the cause of the lower initial permeability of the samples prepared via both the techniques.

Internal stress, σ, is another factor that could have affected the initial permeabilty. When internal stress, σ, decreased, initial permeability, μ_i' would increase. We speculate, less internal stress for samples prepared via conventional technique resulted to the higher permeability.

From the result, there was an increase of initial permeability, μ_i' starting from 1 MHz to 15 MHz for all the samples. A decline in the initial permeability are seen in all the samples at higher frequencies, above 20 MHz. This is due to the non-magnetic effect of the bismuth that had weakened the super-exchange interaction.

CONCLUSION

Each of the methods presented here enables the production of single phase yttrium iron garnet which have excellent magnetic properties. This study shows that rigorous control of preparation technique gives different magnetic properties, such as B_{max} and initial permeability. The density and shrinkage for samples prepared via sol gel technique are higher then those prepared via conventional route. Substituting bismuth to yttrium in the garnet system enhanced the density and shrinkage for both techniques due to it's role as a sintering aid. In conclusion, the sol gel technique appears to be the favourable technique; the 40 and 50% reduction of sintering temperature and of sintering time, respectively, is an attractive route for the preparation of single phase bi-substituted yttrium iron garnet. This is due to the possible reduction of cost of production and the enhanced magnetic and structural properties of the samples.

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