

Morphology and Magnetic Characterisation of Aluminium Substituted Yttrium-Iron Garnet Nanoparticles Prepared Using Sol Gel Technique

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Aluminum substituted yttrium iron garnet nanoparticles with compositional variation of $Y_{3.0-x}Al_xFe_5O_{12}$, where $x = 0.0, 0.5, 1.0, 1.5, 2.0, 2.5$ and 3.0 were prepared using sol gel technique. The X-ray diffraction results showed that the best garnet phase appeared when the sintering temperature was 800 °C. Nano-crystalline particles with high purity and sizes ranging from 20 to 100 nm were obtained. It was found that the aluminum substitution had resulted in a sharp fall of the d -spacing when $x = 2$, which we speculated is due to the preference of the aluminum atoms to the smaller tetrahedron and octahedron sites instead of the much larger dodecahedron site. High resolution transmission electron microscope (HRTEM) and electron diffraction (ED) patterns showed single crystal nanoparticles were obtained from this method. The magnetic measurement gave moderate values of initial permeability; the highest value of 5.3 was shown by sample $Y_3Fe_5O_{12}$ at more than 100 MHz which was attributed to the morphology of the microstructure which appeared to be homogeneous. This had resulted in an easy movement of domain walls. The substitution of aluminum for yttrium is speculated to cause a cubic to rhombodral structural change and had weakened the super-exchange interactions thus a fall of real permeability was observed. This might have created a strain in the sub-lattices and had subsequently caused a shift of resonance frequencies to more than 1.8 GHz when $x > 0.5$.

Keywords: Electron Diffraction, Super-Exchange Interactions, Real Permeability, Single Crystal, Tetrahedron.

1. INTRODUCTION

Magnetic garnet, namely, yttrium iron garnet ($Y_3Fe_5O_{12}$) that belongs to a group of magnetic oxides, is an attractive material for magneto-optical devices. They also have important applications within microwave frequencies, namely, optical isolators, oscillators, circulators and so on, due to their large Faraday rotation and high saturation magnetization.¹ For these reasons, there are ongoing interests in investigating the chemical, physical and magnetic properties of these garnet materials. The preparation techniques and the judicious choice of chemical compositions are important to arrive at the desired magnetic properties

to meet the practical utilisation mentioned as well as to study their fundamental properties.

The common method for ceramic powder synthesis of garnet is the grinding of mixed oxide starting powders followed by a solid state reaction.² This method however requires high temperature to form single phase garnet crystal. Additionally, this method also produces particles having large size, most likely more than a micrometer, and limited degree of homogeneity. This is not favorable as most researchers are currently moving towards the nano-size garnet materials. The sol gel technique seems to be one of the most popular methods since it allows the final nanocrystals to have narrow size distribution. Attempts to produce YIG using the sol gel technique have been reported extensively by many researchers.³⁻⁴

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The premise of this work focuses on vigorous and systematic investigation on the garnets having a general chemical formula of $Y_3Fe_5O_{12}$. Aluminum was used to replace yttrium having stoichiometric composition of $Y_{3-x}Al_xFe_5O_{12}$ with $x = 0.0, 0.5, 1.0, 1.5, 2.0, 2.5$ and 3.0 by sol gel preparation method. The choice of the aluminum to replace iron for YAG⁵⁻⁶ has been done quite extensively. However, using aluminum to replace yttrium has not been reported. This was carried out to see whether the magnetic properties of the garnet, due to the trivalent Fe ion (Fe^{3+}) that has a moment equivalent to five uncompensated spins,⁷ can be retained. When the iron is combined with yttrium and aluminum in a metallic crystal, the atomic moments are spontaneously held in parallel alignment over regions within each crystallite. The regions in which alignment occurs are called domains, which may extend over many thousands of unit cells.⁸ In consequence, by changing the garnet compositions with the substitution of aluminum, it is possible to alter the structural and hence the magnetic properties of the garnet system. These particles have potential application as magnetic sensor.

2. EXPERIMENTAL PROCEDURE

The starting solution is a mixture of iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$, yttrium nitrate $Y(NO_3)_3 \cdot 6H_2O$ and aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$ which were dissolved in 150 mL of citric acid, $C_6H_8O_7 \cdot H_2O$. The mixtures were stirred continuously, at about 250 r.p.m, in room temperature until the formation of gel was observed. This process was carried out for one month. The gel was dried at 110 °C in an oven to remove the unneeded water. The dried powder was calcined at 600 °C, for 3 hours in air and was wet crushed using a Fritsch Planetary Micro mill for 6 hours to obtain a fine particle powder. Subsequently, they were sintered at 600 °C, 700 °C, 800 °C, and 900 °C for 3 hours in air. They were characterized by X-ray diffraction (Philips, X'pert PRO PW 3040 PAN Analytical) to confirm the best garnet phase. Field emission scanning electron microscopy (FESEM, SUPRA 35 VP), low resolution transmission electron microscope (JOEL JEM CX 200) and high resolution transmission electron microscope (FEI Tecnai F20) with 200 kV field emission gun (FEG), were used to study the morphology and the d -spacing of some of the samples. ImageJ software that runs under Linux was used to measure the length of the d -spacing. A magnetic property, real permeability, analysis was carried out using an RF Impedance Analyzer (Agilent 4291B) in the frequency range of 10 MHz–1.8 GHz.

3. RESULTS AND DISCUSSION

X-ray diffraction with $CuK\alpha$ radiation, $K\alpha = 0.89$ and wavelength $\lambda = 1.54056 \text{ \AA}$ was used to determine the crystal structure of aluminum substituted yttrium iron

garnet samples at different calcining temperatures from 600 °C to 900 °C. The unit cell size and geometry were resolved from the angular positions of the diffraction peaks, whereas arrangement of atoms within the unit cell is associated with the relative intensities of these peaks.

From the X-ray diffraction patterns of the Al-YIG sintered samples at 800 °C for 3 hours in air (Fig. 1), it was found that fully crystalline yttrium iron garnet had been formed in the $Y_3Fe_5O_{12}$ sample. The sharp peaks observed indicate high crystallinity of the samples; the highest intensity that comes from (420) plane from the yttrium iron garnet is 9515 (Fig. 1 and Table I). This peak was also previously observed by other researchers.⁶ It is obvious that the correct sintering temperature is one of the main factors affecting the formation of the garnet phase for all the samples. The highest count (4158) for aluminum iron garnet sample was also observed when the sample was sintered at 800 °C. Details on the major peaks, their intensities and the d -spacing are given in Table I. The substitution of aluminum to yttrium had resulted in a clear shift of the major peak from (420) plane to (104) plane. We speculate that it is attributed to the partial occupancy by aluminum ions of the tetrahedron and octahedron,⁸⁻¹⁰ instead of the dodecahedron sites. This is due to the fact that aluminum has a much smaller ionic radius (0.530 Å) compared to that of yttrium (0.892 Å). The larger dodecahedron sites (2.40 Å) are more suitable for the large yttrium ions. When more aluminum ions are replace the yttrium they tend to occupy the octahedron (2.01 Å) and the tetrahedron (1.87 Å) sites, instead of the dodecahedron site. Due to the smaller size of the shift from the (420) plane to (104) plane as well as the observation of two major peaks (Fig. 1) located at (420) and (104) planes for sample with $x = 1.5$ strengthens the speculations made with regard to the occupancies of these cations. It should be noted that there is a sharp fall of d -spacing (Table I) at the major peaks, when $x = 2.0$, which we attributed to the occupancy of more aluminum to the tetrahedron and octahedron sites. When lower mole fraction of yttrium occupies the dodecahedron site, there is

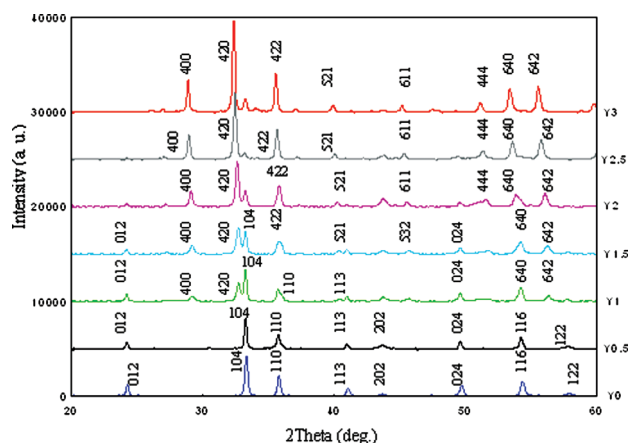


Fig. 1. XRD pattern of Al-YIG samples sintered at 800 °C.

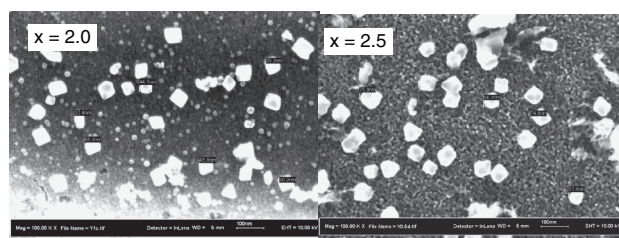
Table I. Intensity and 2-theta for Al-YIG samples sintered at 800 °C.

Mole fraction (x)	2-Theta (deg.)	Intensity (a.u.)	d-spacing (Å)	Av. d-spacing (Å)	hkl (major peak)
0.0	32.34	9515.00	2.77	2.77	420
0.5	32.45	6955.00	2.76	2.76	420
1.0	32.63	4656.00	2.74	2.74	420
1.5	32.70	2796.00	2.73	2.74	420
2.0	33.22	3300.18	2.70	2.70	104
2.5	33.24	3147.00	2.70	2.70	104
3.0	33.30	4158.00	2.69	2.70	104

a shrink of the mentioned site, and the total garnet structure. A closer look at Figure 1 reveals a slight gradual shift of the major peak to higher 2-theta at (420) plane. This indicates that a slight change of the position of some atoms in a systematic manner had caused this effect. It could be speculated that when more aluminum replaces yttrium, two major changes might had happened. First, the decrease of yttrium from the dodecahedron site had caused a slight shrink to this sub-lattice and secondly, the increment of aluminum at the smaller octahedron and tetrahedron sites might have given a slight distortion to the major (420) plane of the lattice. The slight move to the higher 2-theta angle (Fig. 1) indicates a smaller cell volume, which is in accord with the speculation made. Interesting however is the stable peak at plane (104) for $x = 2.0, 2.5$ and 3.0 , possibly due to the stable rhombohedron structure formed. It is significant to note that the sol gel technique gave excellent results of the Al-YIG samples.

FESEM micrographs of the crystalline yttrium iron garnet sample sintered at 800 °C for 3 hours in air are shown in Figure 2. From the FESEM micrographs in Figure 2, it can be observed that when more aluminum is substituting yttrium, $x = 2.0$ and 2.5 , clear cubic-like structure can be observed (Fig. 2), which we speculated to be single crystal structure of garnet. The average size of the morphology of the Al-YIG substitution can be observed in Table II.

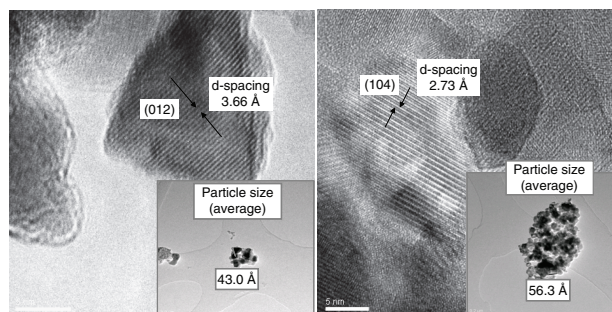
The corresponding EDX results of sample $Y_3Fe_5O_{12}$ shows that the oxygen, iron and yttrium elements are with atomic percentages of 55.21%, 25.77% and 19.02%, respectively (Table II). No impurities were observed due to the high purity starting materials of the sample composition and stringent control of the preparation procedures. The atomic% of ferum to oxygen is a constant as what

**Fig. 2.** Field emission scanning electron microscopy for samples $Y_{3-x}Al_xFe_5O_{12}$ where $x = 2.0$, and 2.5 sintered at 800 °C.**Table II.** Summary of atomic% and grain size for Al-YIG samples sintered at 800 °C.

Mole fraction (x)	Atomic%				Grain size (nm)
	Oxygen (K)	Aluminium (K)	Ferum (L)	Yttrium (L)	
0.0	55.21	0.00	25.77	19.02	82.1
0.5	57.69	2.02	29.39	10.90	57.8
1.0	55.28	4.99	27.80	11.92	55.9
1.5	57.47	6.95	27.29	8.29	25.2
2.0	59.30	7.06	27.22	6.42	46.5
2.5	56.88	8.98	32.13	2.01	64.2
3.0	59.37	13.06	27.57	0.00	55.3

we expected. Compared to oxygen, the higher peak oxygen in the spectrum indicated more concentration of oxygen comparing to the ferum element as in the formula, $Y_{3-x}Al_xFe_5O_{12}$. Table II shows the atomic% of yttrium versus mole fraction for the Al-YIG samples sintered at 800 °C which was extracted from the EDX data. There is a gradual fall of yttrium and a consistent rise of atomic% of yttrium. On the other hand, since we did not change the mole fraction of the ferum and the oxygen of the Al-YIG, there is a constant atomic% of both these elements.

The FESEM (Fig. 2) images for samples with $x = 2.0$ and $x = 2.5$ that exhibit a cubic-like single crystal structures had attracted our interest. Further analysis was done using high resolution transmission electron microscopy (HRTEM). Observing Figure 3 for $x = 2.0$, the size of the particles show an average d -spacing of 3.66 Å. Extracting the data of d -spacing from the XRD data (Fig.1), we correspond this to the (012) plane. The average particle size of sample with $x = 2.0$ and $x = 2.5$, is 43.0 Å and 46.5 Å obtained from HRTEM and FESEM, respectively. The difference between the particle size obtained from those of the HRTEM and FESEM micrographs is just about 8%. On the other hand, sample with $x = 2.5$, showed an average d -spacing of about 2.73 Å. The average particle size of sample with $x = 2.5$, is 56.3 Å and 64.2 Å obtained from HRTEM and FESEM, respectively. This is about 14% difference obtained between those of the FESEM to the HRTEM micrographs. It should be noted that average d -spacing obtained from the HRTEM image

**Fig. 3.** Particle size and d -spacing of samples $Y_{3-x}Al_xFe_5O_{12}$ where $x = 2.0$ and 2.5 taken by HRTEM.

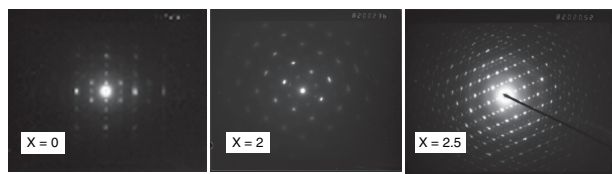


Fig. 4. Electron Diffraction of samples $Y_{3-x}Al_xFe_5O_{12}$ where $x = 0.0, 2.0$ and 2.5 taken by Transmission Electron Microscope.

comparing with that of the XRD data is in good agreement with about 1% of difference. Figure 4 shows the electron diffraction pattern of the samples with $x = 0.0, 2.0$ and 2.5 . This result is consistent with the aforementioned fact, the formation of single crystal of the samples that were prepared via sol gel technique.

An RF Impedance analyzer (Agilent 4291B) measurement was used to study the magnetic properties of aluminium substituted yttrium iron garnet samples at sintered at $800\text{ }^\circ\text{C}$ for 3 hours in air. The measurements of the real permeability as a function of frequency for all the Al-YIG samples were done at room temperature using toroid shape samples.

The real permeability (μ') increases monotonically with frequency for sample $Y_3Fe_5O_{12}$. Obvious resonance peak due to nature resonance phenomena can be observed in the spectrum at about 300 MHz. However, beyond 300 MHz the real permeability starts to decrease rapidly. Above this point, the magnetic moments tend to absorb the energy from the external wave anticipating occurrence of spin-spin interactions as well as spin lattice interactions. The higher magnetic permeability compared to all the other samples is due to the easy movement of domain walls as a result of the large grain size. This is in good agreement with FESEM results of the samples. The substitution of aluminum to yttrium when $x = 0.5$ shows a fall of real permeability but an increase of resonance frequency. As we expected, the substitution of non magnetic ions such as aluminum will result in a weakening of super-exchange interactions which resulted to the fall of the real permeability values. For sample $Y_{2.5}Al_{0.5}Fe_5O_{12}$, the real permeability values, μ' , increases monotonically with frequency and when resonance occurred at about 300 MHz, it tends to fall abruptly. Real permeability falls and resonance frequencies are shifted towards higher values for the rest of the Al-YIG samples. It has to be noted that the resonance frequencies of samples with mole fraction >0.5 cannot be observed due to the limitation of the Impedance Analyzer. The extremely high resonance is speculated to be due to the fact that aluminum ions are occupying the smaller tetrahedron and octahedron sub-lattices, as mentioned previously (see X-ray results, Fig. 1). This is speculated to result a strain and lattice distortion in both the tetrahedron and the octahedron sub-lattices.

It is clearly demonstrated that the operating frequency range strongly depends on the particle size. As the particle size decrease, the operating frequency is shifted to higher

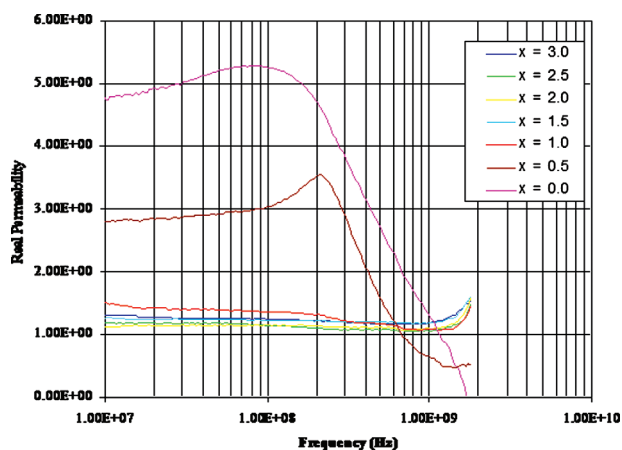


Fig. 5. Real permeability versus frequency (Hz) for Al-YIG samples.

value (Fig. 5). This strengthens the speculations made with regard to the occupancies of the aluminum ions. Hence the desired operating frequency range can be achieved by tailoring the size of the particles in the materials due to the choice of the preparation method, namely the sol-gel technique. Choosing the desired substitution material such as aluminum to replace yttrium in the YIG samples will result in high operating frequencies. We intend to use the nano-particle as magnetic sensors for deep water oil and gas exploration.

4. CONCLUSION

We had successfully prepared single crystal yttrium iron garnet and aluminium-yttrium iron garnet using a sol gel technique. The long stirring time allows the formation of single crystal garnet structure. The substitution of aluminium to yttrium in the YIG system had resulted to a change of structure, from cubic to rhombohedral and a fall of the d -spacing indicating the occupancies of aluminium to tetrahedral and octahedral instead of the larger dodecahedral site. This created strain and possibly lattice distortion and are strongly speculated to have caused the shift of operating frequencies. Substitution of non magnetic aluminium had also weakened the super-exchange interaction and thus a fall of real permeability. The preparation technique had resulted in single crystal nanoparticles and had greatly affected the range of the operating frequencies.

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References and Notes

1. M. Ristić, I. Nowik, S. Popović, I. Felner, and S. Musić, *Mate. Lett.* 57, 2584 (2003).
2. H. Zhou, J. Zhou, Y. Bai, Z. Ejai, and L. Li, *J. Magn. Magn. Mater.* 280, 208 (2004).

3. P. Vaqueiro and M. A. Ropez-Quintela, *Chemical Mater.* 9, 2836 (1997).
4. A. Leleckaite and A. Kareiva, *Optical Materials* 26, 123 (2004).
5. S. Saxena, *Mater. Lett.* 60, 1315 (2006).
6. M. Rajendran, S. Deka, P. A. Joy, and A. K. Bhattacharya, *J. Magn. Mater.* 301, 212 (2006).
7. A. Potdevin, G. Chadeyron, D. Boyer, and R. Mahiou, *J. Non-Cryst. Solids* 352, 2510 (2006).
8. E. P. Wohlfarth, *Ferromagnetic Materials*, North-Holland Publishing Company, North Holland (1980).
9. E. Gamaliy, H. Štěpánková, J. Kohout, A. Snezhko, M. Kučera, and K. Nitsch, *J. Magn. Mater.* 242–245, 766 (2002).
10. W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, John Wiley and Sons, New York (1976), p. 470.
11. N. Yahya and G. K. Hean, *American J. Appl. Sci.* 4, 80 (2007).

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