American J. of Engineering and Applied Sciences 2 (1): 76-79, 2009
ISSN 1941-7020

Synthesis of $Al_3Fe_5O_{12}$ Cubic Structure by Extremely Low Sintering Temperature of Sol Gel Technique

[1]Noorhana Yahya, [2]Ramadan Al Habashi Masoud, [1]Hanita Daud,
[1]Azizuddin A. Aziz and [1]Hasnah Mohd Zaid
[1]Department of Electrical and Electronic Engineering, University Teknologi PETRONAS 31750, Bandar Seri Iskandar, Tronoh, Perak, Malaysia
[2]Laboratory of Advanced Materials and Nanotechnology, Institute of Advanced Technology, University Putra Malaysia 43400 UPM, Serdang, Selangor, Malaysia

Abstract: **Problem statement:** Fabrication of nano materials particularly nano inductors at low sintering temperature remains a challenge. This study was carried out as our initial response to obtain a nano-size inductors, which is aluminium iron garnet using low sintering temperature. **Approach:** The aluminum iron garnet ($Al_3Fe_5O_{12}$) nano crystals were prepared by sol-gel technique. The starting solution is a mixture of iron nitrate $Fe(NO_3)_3.9H_2O$, yttrium nitrate $Y(NO_3)_3.6H_2O$ and aluminum nitrate $Al(NO_3)_3.9H_2O$ and were dissolved in 150 mL of citric acid, $C_6H_8O_7.H_2O$. The mixtures were stirred continuously, at about 250 r.p.m, in room temperature until the formation of a gel was observed. 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 h in air and was wet crushed using a Fritsch Planetary Micromill for 6 h to obtain fine particles powder. The sample was then characterized by X-Ray Diffraction analysis (XRD) to confirm the garnet phase. The sintered powder was characterized at different temperature by X-ray diffraction analysis and Raman Spectroscopy was used to study the vibration of atoms in a materials. Finally, Field Emission Scanning Electron Microscopy (FESEM) was used to study the surface morphology of the sample. **Results:** The XRD results showed that, the best garnet cubic phase giving [1 0 4] plane of the $Al_3Fe_5O_{12}$ crystallite appeared at 33.30 of the 2 theta. We report a clear cubic crystal structure of less than 62 nm, which was observed possible for the first time, for this type of garnet, $Al_3Fe_5O_{12}$. The much lower sintering temperature 800°C comparing to the conventional method was attributed to the sol gel method. **Conclusion:** The long stirring time (one month) that had allowed self assembly of the anions and cations to form the gelatin. In addition the small radius of aluminium prefers to occupy the tetrahedron and octahedron sites instead of the much larger dodecahedron site resulted to the clear cubic structure of the garnet.

Key words: Sol-gel, X-Ray Diffraction (XRD), cubic structure, aman spectroscopy

INTRODUCTION

Yttrium iron garnet ($Y_3Fe_5O_{12}$) belongs to a group of magnetic oxides, characterized by specific magnetic and magneto-optical properties[1]. Yttrium Iron Garnet (YIG) is one of the soft ferrites with garnet structure. It is a material widely used in microwave devices. YIG has been synthesized by sol-gel technique which produces single-phase and fine-grained microstructures that encourage good homogeneity and good purity on nano-particle size.

Some advantages of sol-gel over conventional ceramic processing[2,3] are increased chemical homogeneity in multi component systems, high surface area of the gel/powders, leading to relatively low sintering temperatures and glass formation in normal separation regions. In addition the product in the form of powder, fibers, coatings and spheres are:

Possible with simple solution controls, such as pH, temperature and aging. Relatively high chemical purity is possible due to the absence of grinding and pressing.

This study premise deals with substitution of aluminum to replace yttrium having stoichiometric composition of $Y_{3-X}Al_XFe_5O_{12}$ with x = 3.0 using a sol gel preparation method. The choice of the aluminum to replace iron for YAG[4-8] has been done quite

Corresponding Author: Electrical and Electronic Engineering Department Universiti Teknologi PETRONAS 31750, Bandar Seri Iskandar, Tronoh ,Perak, Malaysia

extensively. However, using aluminum to replace yttrium has not been reported. We hope to observe single phase nano-structure $Al_3Fe_5O_{12}$ with good morphology.

MATERIALS AND METHODS

Stoichiometric mixtures of Y $(NO_3)_3.6H_2O$, Fe $(NO_3).9H_2O$, Al $(NO_3)_2$. $9H_2O$ were dissolved in aqueous solution of 150 mL of citric acid, $C_6H_8O_7.H_2O$. The raw materials of nitrates were stirred at about 250 rpm by using a magnetic stirrer for about a month until a gel-like solution. The resulting gelatin was then dried for 24 h in an oven at 110°C until the slurry was change to a fluffy like materials, which is brownish in color. The material was then put into a ceramic boat for calcinations process at 600, 700, 800, 850 and 900°C for 3 h in air. The green powder was then crushed using Fritsch Planetary Micromill for 6 h. The purpose for this wet milling was to ensure that the powder was crushed until very fine nano size powder is obtained. This is important to facilitate the solid state reaction in the final sintering process[2,3]. After grinding, the powder was then granulated with approximately 0.1% weight of Polyvinyl Alcohol (PVA) into powder to act as a binder, which was intended to hold the ceramic particles together as agglomerates. The sample powders were taken for X-Ray Diffraction (XRD) analysis. The intensity of the reflected radiation was recorded by using a goniometer. This data was then analyzed for the reflection angle to calculate the inner-atomic spacing (D value in Angstrom units 10^{-8} cm). The intensity (I) was measured to discriminate (using I ratio) the various D spacing and the results were to identify possible matches.

Field Emission Scanning Electron Microscopy (SUPRA 35VP version) is central to the microstructure analysis and therefore important to any investigation relating to the processing, properties and behavior of materials that involves their microstructure. Microstructure analysis was carried out to observe the sample's grain size. Raman scattering analysis was carried out using argon (514.5 nm) laser excitation source. The electron beam was accelerated using a 5 keV. The spot diameter was about 1 μm on the sample surface and the laser power was kept below 30 kW to avoid heating effect on the spectra. Olympus BX41 Horiba Jobin Yvon HR800 Raman Division was used to characterize the sample.

RESULTS AND DISCUSSION

X-ray diffraction profile of $Al_3Fe_5O_{12}$ sample calcined at different temperatures for 3 h in air is shown in Fig. 1. The structure of the sample calcined at 600°C exhibit low crystallinity. Above 600°C calcining temperature, the sample clearly showed the present of cubic single phase of pure aluminum iron garnet. Above 800°C calcining temperature, we could observe some unknown peaks. In addition, we also observe a fall of counts at the major peak of the hkl plane. The peaks for (012), (104), (110), (113), (202), (024), (116) and (122) planes located at the 2θ(°) values are 24.2546, 33.3052, 35.7729, 41.0220, 43.6886, 49.6756, 54.3299 and 57.9588, which correspond to the d-spacing [Å] values of 3.66, 2.69, 2.51, 2.20, 2.07, 1.83, 1.68 and 1.59 respectively. It is very clear that the sample completely changed to aluminum iron garnet phase due to the absence of the 2θ(°) 32.7591 peak corresponding to (420) plane for the major peak of YIG samples[2,3].

The XRD profile reveals a single phase garnet phase structure and the crystallization had completely occurred at 800°C. This is much lower than the temperature used[10] in the conventional ceramic method, 1450°C. The lower crystallization temperature could be related to the long stirring time which resulted to good homogeneity during the gel preparation of the sol-gel technique.

Figure 2 a reveals the XRD profile for the $Al_3Fe_5O_{12}$ sample calcined at 800°C. The major diffraction peaks occur at 33.30 of the 2 theta and at 104 khl plane (Table 1). As mentioned above, the $Al_3Fe_5O_{12}$ crystallite sample that was sintered at 700°C exhibit less counts (3990) indicating the degree of crystalinity as compared with the $Al_3Fe_5O_{12}$ sample that was sintered at 800°C (that has 4160).

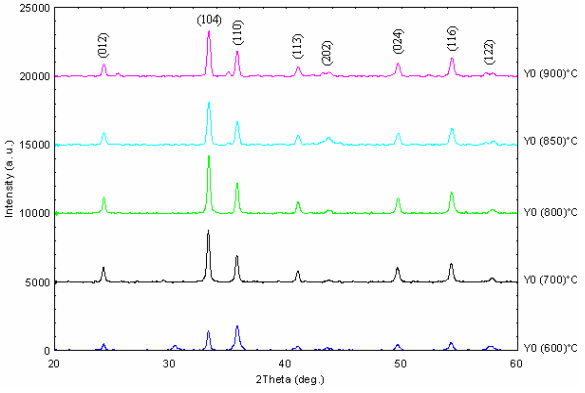

Fig .1: X-Ray Diffraction profile of $Al_3Fe_5O_{12}$ samples calcined at different temperatures

Table 1: Average grain size, 2 theta, intensity (a.u), hkl and the structure for the $Al_3Fe_5O_{12}$ samples calcined at 700, 800 and 900°C

Sintering temperature	Avg. Grain size (nm)	2θ (deg.)	Intesity (a.u)	hkl (major peak)	Structure
700°C	62 nm	33.30	3990	104	Cubic
800°C	320 nm	33.30	4160	104	Cubic
900°C	530 nm	33.20	3100	104	Cubic

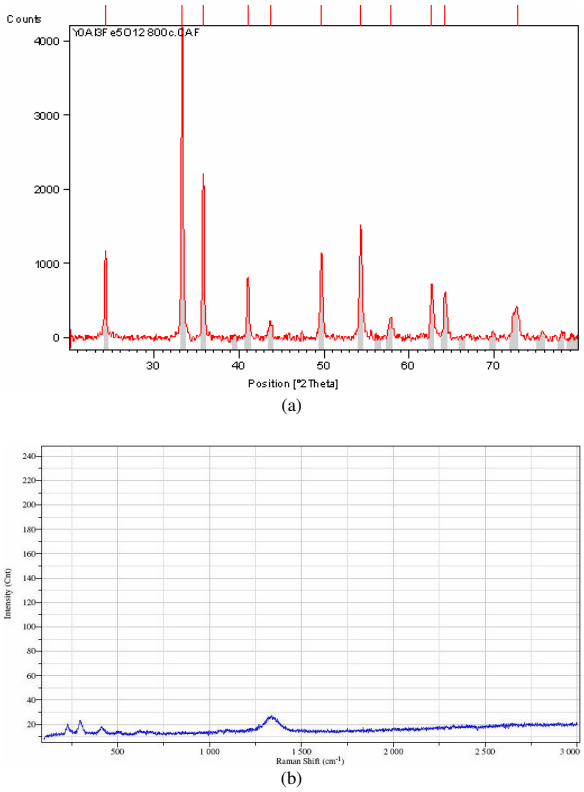

Fig. 2: (a): X-ray diffraction profile of $Al_3Fe_5O_{12}$ sample calcined at 800°C; (b): Raman spectroscopy profile of $Al_3Fe_5O_{12}$ sample calcined at 800°C

The Raman spectroscopy profile which is a fingerprint of the $Al_3Fe_5O_{12}$ is shown in Fig. 2 b. It could be observed that there are four bands which are clearly observable at 200, 300, 400 and 1300 cm^{-1}. The first three bands are vibrations of Y ions while the vibration of Fe ions occurs at 1300 cm^{-1} band. This result is similar to the results obtain by other researchers[11]. Observing the FESEM images (Fig. 3) it is obvious that the $Al_3Fe_5O_{12}$ sample reveals a cubic structure. However, when the garnet sample was sintered at high temperature (900°C) the cubic structure cannot be observed and the grain size grew to about 500 nm.

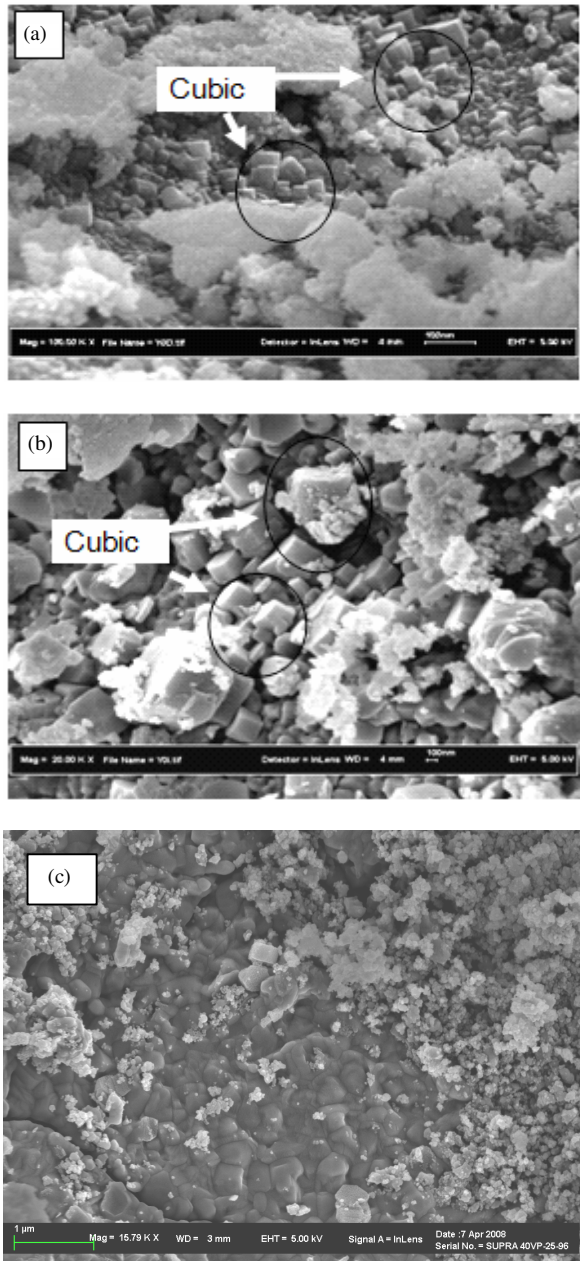

Fig. 3: FESEM images of $Al_3Fe_5O_{12}$ crystallite sample treated. (a): 700°C; (b): 800°C; (c): 900°C

Both the intrinsic and the extrinsic properties play a role in the observation of the cubic structure. We speculate that intrinsically, it is attributed to the partial occupancy by aluminum ions of the tetrahedron and octahedron[2,7,9,11], 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. All the aluminum ions tend to occupy the octahedron (2.01 Å) and the tetrahedron (1.87 Å) sites, instead of the dodecahedron site as what we expected. Due to the smaller size of aluminium, comparing to the slightly larger ionic radius of the ferum (0.65 Å) and yttrium, there are high tendency of the aluminium to occupy the smaller tetrahedral site. On the other hand extrinsically, the much lower sintering temperature comparing to the conventional ceramic method resulted to the cubic structure.

We attribute to the long stirring h, which allow the self assembly of cations and anions during the formation of gelatin. Interesting however is the $Al_3Fe_5O_{12}$ sample that was sintered at 800°C (only 100°C higher) had resulted to a much larger grain size 320 nm compared to the much smaller grain size, 62 nm (Table 1).

CONCLUSION

A cubic structure of $Al_3Fe_5O_{12}$ sample that was prepared by sol gel technique and calcined at 800°C and 700°C was observed. We speculate the small radius of aluminum prefers to occupy the tetrahedron and octahedron sites instead of the much large dodecahedron site. We also attribute the structure to the self assembly of anion and cation formation of gelatin during the long stirring time (30 days). This novel cubic structure has promising usage as a nano-inductor.

ACKNOWLEDGMENT

We would like to thank Ministry Of Science, Technology and Innovation (MOSTI) in Malaysia for research grant under Intensification of Research in Experimental Applied (IRPA) program grant number IRPA (09-02-0955-EA001) Vot. 54430 and Academy Science of Malaysia (ASM) under the Science Advancement Grant Allocation (SAGA).

REFERENCES

1. Ristic, M., I. Nowik, S. Popovic, I. Felner and S. Music, 2003. Influence of synthesis procedure on the YIG formation. Mater. Lett., 57: 2584-2590. DOI: 10.1016/S0167-577x(02)01315-0
2. Vaqueiro, P., M.P. Crosnier-Lopez and M.A. Lopez-Quintela, 1996. Synthesis and characterization of yttrium iron garnet nanoparticals. J. Solid State Chem., 126: 161-168. DOI: 10.1006/JSSC.1996.0324
3. Rehspringer, J.L., J. Bursik, D. Niznansky and A. Klarikova, 2000. Caracterisiation bismuth-doped yttrium iron garnet layers prepared by sol-gel process. J. Magnet. Magnet. Mater., 211: 291-295. DOI: 10.1016/S0304-8853(99)00749-0
4. Saxena, S., 2006. Sol-gel preparation and optical characterization of $Tb_xY_{3-x}Al_5O_{12.}$ Maters Lett., 60: 1315-1318. DOI: 10.1016/J.MATLET.2005.11.006
5. Xia, G., S. Zhou, J. Zhang and J. Xu, 2005. Structural and optical properties of YAG: Ce^{3+} phosphors by sol-gel combustion method. J. Cryst. Growth, 279: 357-362. DOI: 10.1016/j.jcrysgro.2005.01.072
6. Ruan, S.K., J.G. Zhou, A.M. Zhong, J.F. Duan, X.B. Yang and M.Z. Su, 1998. Synthesis of $Y_3Al_5O_{12}$: Eu^{3+} phosphor by sol-gel method and its luminescence behavior. J. Alloy Compound, 275-277: 72-75. DOI: 10.1016/S0925-8388(98)00276-X
7. Potdevin, A., G. Chadeyron, D. Boyer and R. Mahiou, 2006. Production and shaping of high performance of phosphors by using the sol-gel process: Yttrium Aluminum Garnet ($Y_3Al_5O_{12}$). J. Non-Cryst. Solids, 352: 2510-2514. DOI: 10.1016/j.jnoncrysol.2006.03.046
8. Pereira, P.F.S., J.M.A. Caiut, S.J.L. Ribeiro, Y. Messaddeq, K.J. Ciuffi, L.A. Rocha, E.F. Molina and E.J. Nassar, 2007. Microwave synthesis of YAG: Eu by sol-gel methodology. J. Luminescence, 126: 378-382. DOI: 10.1016/j.jlumin.2006.08.085
9. McCurrie, R.A., 1994. Ferromagnetic Materials: Structure and Properties. Academic Pr. University of Michigan, ISBN: 10: 0124824951, pp: 352.
10. Chien-Yih, T., L. Chu-Yu, L. Kuo-Shung, L. I-Nan, H. Long-Jang and Y. Tung-Sheng, 2003. Low temperature sintering of microwave magnetic garnet materials. J. Mater. Chem. Phys., 79: 138-142. DOI: 10.1016/S0254-0584(02)00273-0
11. Chen, Y.F., K.T. Wu, Y.D. Yao, C.H. Peng, K.L. You and W.S. Tse, 2005. The influence of Fe concentration on $Y_3Al_{5-X}Fe_XO_{12}$ garnets. Microelect. Eng., 81: 329-335. DOI: 10.1016/j.mee.2005.03.028