Review Article- Aluminium substituted Yttrium Iron Garnet Nanoparticles

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Abstract:
YIG is an important magnetic material in microwave devices such as isolators, circulators, phase shifters, filters, absorbers etc. In this paper, the structural, morphological, magnetic and dielectric results of Al-doped yttrium Iron Garnet by using XRD, SEM/TEM, FTIR, VSM, FMR techniques are reviewed. Preparation methods have great influence on structural and magnetic properties. For application purpose, one needs to select Al substituted YIG with optimum properties hence the comparative study of results is needed. The data presented in this paper would be helpful from the application point of view.

Keywords: Al-YIG, garnet, magnetic properties, YIG, Nano-garnets

Introduction

Magnetic oxides are the most promising ferromagnetic materials from the application perspective. They are generally known as ferrites and their structure was put forward by Neel in 1948. Ferrites are classified into spinels, garnet ferrites and hexaferrites. Variety of cations can be substituted in these magnetic oxides owing to their structure. This substitution results in the changes of microstructure and the magnetic properties of magnetic oxides.

Yttrium Iron Garnet is standing at the first position in the rare earth garnet family and it is a technologically important magnetic oxide. It was synthesized by researchers named Bertaut and Forrat for the first time in 1956 [1]. Geller and Gilleo studied its structure and ferrimagnetism [2]. The study of YIG is important because it has low and adjustable saturation magnetization[3], extremely narrow linewidth[4], high electrical resistivity[5] and high radiation stability[6], a low dielectric loss[13] which makes it suitable for microwave devices like oscillators, isolators, circulators, latching phase shifter, filters and so on[7-12]. It has lowest spin-wave damping and high Curie temperature so that experiments can be performed at room temperature. They are also starting to appear in low-frequency instruments such as spectrum analyzers, signal sources, sweepers, counters and synthesizers. YIG serves as best microwave material in 1 to 10 GHz frequency band [13].

In this article, we have briefly reviewed the research which has been done in the last couple of decades on structural, magnetic and dielectric properties of Al-substituted YIG nanoparticles.

Garnet structure

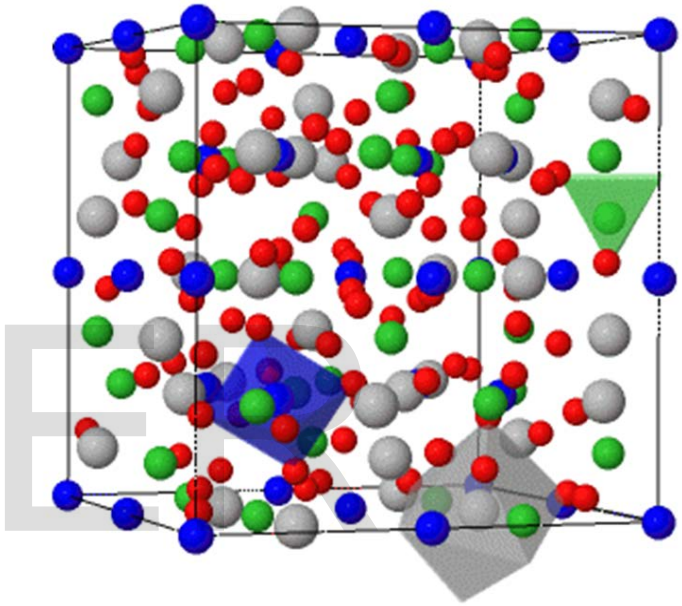

Figure 1. Unit Cell of YIG drawn using JSmol program. [colors online] [Gray- Y^{3+}, Red- O^{2-}, Blue & green Fe^{3+}ions in Octahedral & Tetrahedral sites respectively] [14-15]

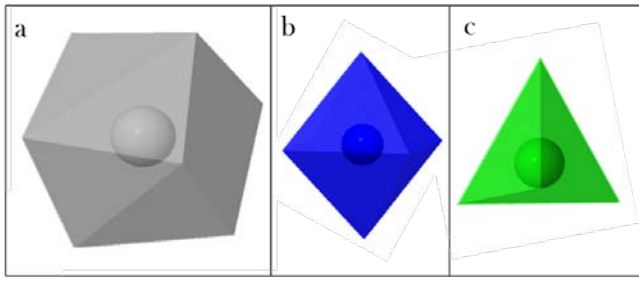

Figure 2. a) Dodecahedral site b) Octahedral site c) Tetrahedral site in YIG drawn using JSmol program [15] [colours online]

YIG has BCC cubic structure with a lattice parameter a = 12.3738 Å and it comes under cubic crystal space group "Ia$\bar{3}$d" or "Oh10"[16]. Each unit cell of YIG contains 8 formula unit ($Y_3^{3+}Fe_5^{3+}O_{12}^{2-}$) and total 160 atoms which occupy a proper location in the unit cell [17]. There is

no site inversion problem in garnets. YIG has three different sites and ion distribution in these sites is given by formula $\{Y_3\}[Fe_2](Fe_3)O_{12}$ where the curly bracket { } indicates largest 24c dodecahedral sites, the round bracket ( ) indicates smallest 24d tetrahedral site and a square bracket [ ] is used for 16a octahedral sites. A schematic of the unit cell and different sites generated using JSmol software [14-15] is shown in Figure. 1 and Figure. 2. The magnetic moments of Fe^{3+} ions in a-site are antiparallel to the magnetic moments of Fe^{3+} ions in d-site due to dominant superexchange interactions. This gives YIG ferrimagnetism. The magnetic moment of YIG is 5 μ_B per formula unit at 0 K [4].

$$\{Y_3\}[Fe_2\downarrow](Fe_3\uparrow)O_{12}$$

$$0 + \downarrow\downarrow + \uparrow\uparrow\uparrow = \uparrow$$

The three different sites of YIG can be substituted by various cations depending upon the ionic radius of the cation [25]. As plenty of cations can be substituted in various sites structural, magnetic and magneto-optic and dielectric properties of YIG can be adjusted as per the need and application basis.

Synthesis methods

YIG nanoparticles can be fabricated by using synthesis methods like mechanical alloying [18], co-precipitation [19], solid state sintering technique [20], spray pyrolysis, microwave hydrothermal [24], sol-gel, modified conventional mixed oxide etc. Out of these various methods, the sol-gel technique is reliable and comparatively cheaper as inexpensive precursor usually metal nitrates and fuels like glycine, citric acid, urea, oxalyl dihydrazide (ODH), sucrose, glucose are used. Sol-gel method provides high homogeneity and high purity. This method is useful to synthesize garnets with controlled composition and grain size [20-23]. It is observed that sol-gel technique has the best results of Al-substituted YIG. The Figure 3 shows unmagnetized and magnetized nano powder of Aluminium substituted YIG synthesized using sol-gel technique.

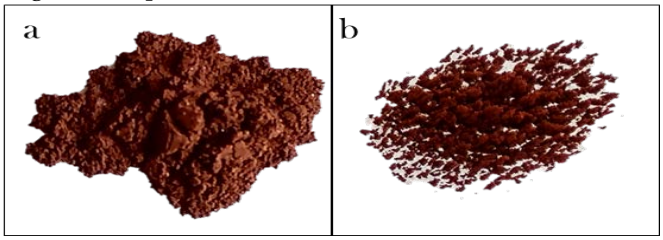

Figure 3. Al substituted YIG nanopowder a) without magnetic field b) with the magnetic field

Result and analysis

I. Structure and Morphology

XRD Analysis: Substitution of Al in tetrahedral and octahedral sites is common but few researchers also have studied substitution of Al in dodecahedral site. XRD studies of various samples of $Y_3Fe_{5-x}Al_xO_{12}$ confirmed cubic structure. XRD studies of $Y_{3-x}Al_xFe_5O_{12}$ confirmed cubic structure for low concentration of Al and stable rhombohedral structure with increasing Al content (x > 1.5) [26]. A garnet phase is obtained by researchers only after calcination and it was seen that the calcination temperature decreased with increasing Al content [27].

The decrease in lattice constant on increasing the Al content in different sites of YIG is observed by the researchers. This decrease is obvious as ionic radius of Al^{3+} (0.530 Å) is less than Fe^{3+} (0.61 Å). In figure 4 and figure 5, the shift of diffraction lines to higher diffraction angles clearly indicates this decrease in lattice constant on increasing the Al concentration.

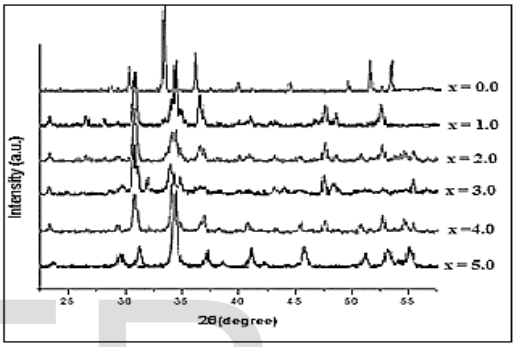

Figure 4 XRD patterns of $Y_3Fe_{5-x}Al_xO_{12}$ samples[32]

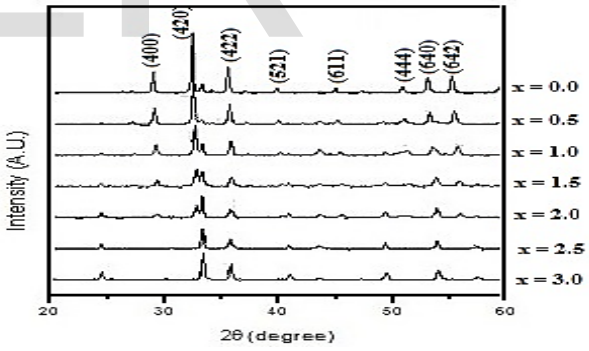

Figure 5 XRD patterns of $Y_{3-x}Al_xFe_5O_{12}$ samples sintered at 800 ℃[26].

In $Y_{3-x}Al_xFe_5O_{12}$, Al (0.530 Å) substitution in the largest dodecahedron site (2.40 Å) resulted in a small shrinkage to this site and the increase of Al content in tetrahedral (1.87 Å) and octahedral (2.01 Å) sites gave the shift of the main peak from (420) plane to (140) plane for higher concentration of Al (x > 1.5). The stable (140) peak is said to indicate rhombohedral structure [26].

The X-ray density is found to be higher than bulk density [28]. The decrease in X-ray density can be mainly because of the higher decrease in mass than the rate of decrease of the lattice constant [29, 30].

SEM -

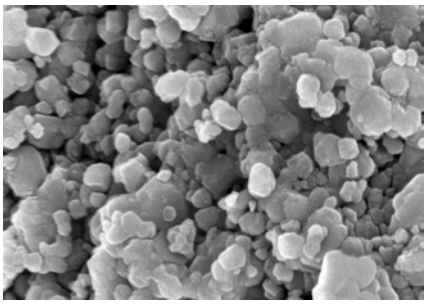

Figure 6 SEM image of Al-substituted Yttrium Iron Garnet[33]

Notable alterations in the microstructure of YIG and Al-doped YIG were observed. With the decrease of Fe/ Al ratio, the agglomeration of the particles was increased [31]. Enhanced temperature and prolonged calcination time resulted in an aggregation of the particles in Al substituted YIG samples. [32] On increasing sintering temperature, the average grain size of the powder was increased and the shape of crystallite changed from irregular to regular. [31,32]. We can observe the spherical shape of particles in figure 6 which is a typical SEM image. [33] The Al substitution resulted in a small reduction of the particle size, regular particle shape and narrow particle size.[29]

FTIR spectroscopy: Garnet phase formation can be confirmed using FTIR spectroscopy. The Stretching and bending vibrations of O-H bonds and C-O bonds in carbonates and carboxylates were observed. [31,33,28]. Three bands corresponding to Stretching mode of Fe-O in tetrahedral of YIG were observed. In Al-YIG, these three bands are widened and shifted to higher wavenumbers. [31] This is due to the smaller atomic number of Al as compared to iron ions. The absorption modes shift to lower wavenumbers with the higher molar mass substituent and shift to higher wave number with a lower molar mass substituent [34].

RAMAN spectroscopy: Al substitution in YIG changes YIG vibrational modes towards YAG RAMAN spectrum. The substitution of Al in tetrahedral and octahedral sites makes these sites heavier and thus weakens the vibration and decreases the relative intensities of the peaks [31]

Mössbaur study: The preferential site occupation of different ions in YIG can be investigated by using this technique. For YIG, two magnetic sextets can be observed. The intensity ratios of these two magnetic component were observed to be 2:3, which implies 2 Fe^{3+} ions in octahedral and 3 Fe^{3+} ions in tetrahedral site[29]. As the content of paramagnetic Al in YIG increases, the magnetic hyperfine fields decrease for octahedral and tetrahedral site as well. The decrease in the magnetic hyperfine field is attributed to the reduction in the superexchange interactions[36]. A smaller broadening in the linewidth is also reported in the literature. For small concentration Al preferentially occupies the tetrahedral site and for higher concentration, it occupies the octahedral site. [36]

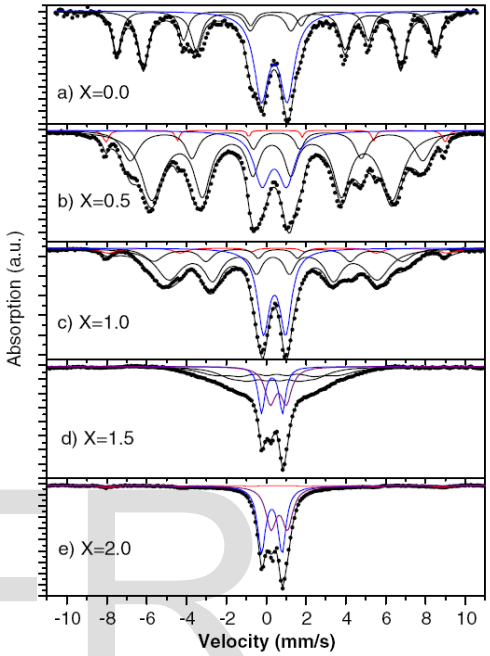

Figure 7 Mössbauer spectra for Al-YIG [4]

II. Magnetic Properties

Curie temperature: For nonmagnetic Al substituted YIG, Curie temperature can be given by

$$\frac{Tc(x,y)}{Tc(YIG)} = \frac{n(x,y)}{\frac{24}{5}}$$

where n(x,y) is the number of interactions per magnetic cations in a and d site. Curie temperature goes on decreasing with increasing Al content. This is because of the reduction in the total number of main magnetic interactions n(x,y) per magnetic cation per formula unit.[31]. Curie temperature is found to be greater than room temperature for few studies [27]

Saturation Magnetization: J_{ad} interaction is dominant over J_{aa} interaction and J_{dd} interaction. [31]. Saturation magnetization is found to decrease with increasing Al content. Nonmagnetic Al substitution weakens the super-exchange interactions between a and d site.[29] For small concentration, Al preferentially enters in the tetrahedral site due to its smaller ionic radius. For large concentration, it enters in octahedral site. [8,27,31-32]

Coercivity: On decreasing particle size of nanoparticles, Hc increases toward single domain size and then decreases toward the superparamagnetic size. [27]. Because of this Coercivity shows decreasing and increasing trend [34].

Remnant Magnetization: The substitution of paramagnetic Al ion instead of ferromagnetic Fe ion leads to decrease in residual magnetization (Mr) value up to zero.[35] The paramagnetic properties suppress the ferromagnetic properties with increasing Al content.. [34]

FMR Linewidth: A non-magnetic ion substitution in YIG is the best way to narrow the FMR linewidth. The FMR linewidth for Al Mn substituted YIG was measured to be 38.6Oe at 3.2 GHz. [37] The resonance linewidth is dependent on grain size. The resonance linewidth decreases with a decrease in grain size.[20]

Permeability The substitution of non-magnetic Al weakens the superexchange interactions which results to the fall of the real permeability. Operating frequency range is dependent on the particle size. With decreasing particle size operating frequency shifts towards higher frequency value. [26]

III. Dielectric Properties:

Dielectric permittivity increases with increase in temperature up to Curie temperature and then it decreases [31]. It is seen that the maximum dielectric permittivity is dependent on the composition. The higher the Al content is the lower is the Curie temperature and hence lower values of maximum dielectric permittivity [31].

Conclusion:

YIG is technologically very important and most extensively studied microwave material. The substitution of Al in YIG improved the physical, magnetic and dielectric properties of YIG. Al substituted YIG can be used in S-band latching phase shifter. From the present review, it is concluded that if one chooses the proper substitution, proper synthesis method and proper sintering temperature, YIG with superior properties can be obtained.

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