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 TECHNOLOGY**
**STRUCTURAL AND MICROSTRUCTURAL INVESTIGATIONS ON AL DOPED  
 $Y_3Fe_5O_{12}$  GARNET NANOPARTICLES SYNTHESIZED BY SOL-GEL AUTO  
 COMBUSTION TECHNIQUE**
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**ABSTRACT**

In the present investigation, we have successfully synthesized  $Y_3Fe_{2-x}Al_xO_{12}$  ( $x=0.00, 0.20$  and  $0.40$ ) nanoparticles by sol-gel auto combustion method. The produced phases were characterized by X-ray diffraction (XRD). Particles of uniform size around 22–30 nm were obtained in the cubic structure of the prepared samples. Various structural parameters such as lattice constant (a), X-ray density (dx) etc. were calculated from the XRD data. The variation of these structural parameters in Al composition has been studied. The lattice constant decreases while X-ray density increases with increasing Al content x. FTIR spectra show typical absorption bands indicating the formation of garnet structure of the samples. Upon aluminium substitution, absorption bands broadened and shifted towards higher wavenumber.

**KEYWORDS:** Garnet, nanoparticles, XRD, FTIR.

**I. INTRODUCTION**

Yttrium iron garnet (YIG) is a microwave ferrite and has specific characteristics in polycrystalline form. Owing to its efficient handling of microwave power with excellent magnetic and magneto-optical properties it has become a technologically significant material for making microwave frequency devices [1-3]. YIG is a soft ferrimagnetic material having cubic structure which belongs to Ia-3d space group. YIG structure consists of three sub-lattices as the octahedral (a) site occupied by two iron ions, the dodecahedral (c) site occupied by the three yttrium ions and the tetrahedral (d) site occupied by three iron ions. Both ( $Y^{3+}$  and  $Fe^{3+}$ ) the trivalent metallic ions present in these sites make YIG an exceptionally suitable material for magnetic investigations. The most important interaction is the super-exchange interaction between iron ions at octahedral and tetrahedral sites.

YIG, due to their good characteristics in Faraday rotation they are being extensively used for the magneto-optical applications like optical isolators, magnetic sensors, circulators, phase shifter, etc. The substituted YIG have found their extensive use in non-reciprocal microwave devices. It is well known fact that the microstructure of sintered materials depends very much on the characteristics of the initial powders. There are various synthesis methods which can be used for the synthesis of garnets such as coprecipitation [4, 5], sol-gel processing [6, 7], solid state sintering technique [8], modified conventional mixed oxide [9], self combustion [10], etc.

Communication systems have created the need of materials having narrow resonant linewidth and low saturation magnetization. Yttrium iron garnets are the suitable for these demands because they possess the narrow resonant linewidth, low saturation magnetization, high electrical resistivity, high radiation and chemical stability, low thermal expansion, better electromagnetic properties, low loss, etc.

The polycrystalline YIG as a function of preparative parameters viz. sintering time, temperature etc were investigated by number of researchers [11-13]. Geller et. al. [14] reported magnetic behavior of heavier rare-earth garnets. The magnetic interactions in YIG which are related to the inter sub-lattice exchanges, that is super exchange interaction between  $Fe^{3+}$  iron in octahedral and tetrahedral sites through  $O^{2-}$  ions. These sub-lattices of YIG can be tailored by substituting various cations in a structure leading to changes in magnetic properties. The

composition and homogeneity are the essential aspects of the garnets material preparation, as both strongly determine its magnetic properties.  $\text{Al}^{3+}$  element is paramagnetic and has the preference towards, the tetrahedral sites. Thus, the substitution of  $\text{Al}^{3+}$  may lead to a substantial modification in magnetic and electrical properties of YIG.

The aim of the present work was to prepare the yttrium iron garnet and aluminium substituted yttrium iron garnet ( $\text{Y}_3\text{Fe}_{5-x}\text{Al}_x\text{O}_{12}$ ) using wet chemical synthesis route and to investigate the effect of  $\text{Al}^{3+}$  ions substitution on the structural and morphological properties of YIG.

The present work reports the synthesis of  $\text{Y}_3\text{Fe}_{5-x}\text{Al}_x\text{O}_{12}$  ( $x = 0.00, 0.20$  and  $0.40$ ) by sol-gel auto combustion technique and experimental results obtained of the crystallographic and morphological properties of  $\text{Y}_3\text{Fe}_{5-x}\text{Al}_x\text{O}_{12}$ .

## II. MATERIALS AND METHODS

### Materials

Yttrium nitrate ( $\text{Y}_3(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ ), Iron nitrate ( $(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), Aluminium nitrate ( $\text{Al}_3(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) and Citric acid ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ).

### Synthesis

The YIG and Al substituted YIG nanoparticles of the chemical formula  $\text{Y}_3\text{Fe}_{2-x}\text{Al}_x\text{O}_{12}$  ( $x=0.00, 0.20$  and  $0.40$ ) were prepared by sol-gel auto combustion synthesis route. The metal nitrates were used as oxidants while the citric acid was selected as fuel. Following raw materials purchased by Merck with purity 99.99% were used without further purification during the synthesis of the YIG and Al substituted YIG samples.

The starting materials were weighed according to the chemical formula for each composition and dissolved in minimum amount of distilled water. In particular, each metal nitrate and citric acid were dissolved in 100ml distilled water and mixed together. The mixed solution of all nitrates was continuously stirred at  $50^\circ\text{C}$  on magnetic stirrer with hot plate until a completely dissolved solution was obtained. Then the solution of citric acid was added as a fuel to the mixed solution of metal nitrates and heated at  $90^\circ\text{C}$ . Upon continuous heating, the sol converted to gel, very viscous gel and combustion took place and formed a powder. Various stages of the synthesis using sol-gel auto combustion are presented in the flowchart as shown in Fig. 4.1. The combusted powder was ground using agate pestle mortar. The obtained fine powder was annealed at  $950^\circ\text{C}$  for 24 h. The annealed powder was used for the structural and morphological characterizations.

### Characterizations

The structural characterizations of YIG and Al substituted YIG nanoparticles were carried out by X-ray diffraction (XRD) of Rigaku in  $2\theta$  range of 20-80 degrees with  $\text{Cu-K}\alpha$  radiation at room temperature. The nature and phase purity of the prepared YIG and Al substituted YIG samples were checked by XRD patterns. Other structural parameters were also determined from XRD data. Fourier transform infrared (FTIR) spectrometer was employed for the extraction of the characteristics bands of metal-oxygen environment in frequency range of  $400\text{-}4000\text{ cm}^{-1}$ .

## III. RESULTS AND DISCUSSION

The results X-ray diffraction (XRD) patterns of YIG and Al substituted YIG samples prepared by sol-gel auto combustion technique are shown in Fig. 1. It is revealed from XRD patterns (Fig. 1) that the diffraction peaks relevant to garnet structure are present. The peaks (400), (420), (422), etc which belongs to garnet structure are sharply reflected and are matched to ICSD reference code 980021229 for YIG and 980064818 to Al substituted YIG. The observed XRD patterns revealed the presence of cubic phase structure of YIG and Al substituted YIG samples along with secondary phase of  $\text{YFeO}_3$ . However, the intensity of the secondary phase peak decreases with Al concentration. This indicates that the substitution of aluminium has reduced the temperature for YIG single phase formation. Similar result was reported by Ozturk *et al.* (2013) in which the secondary phases were observed.

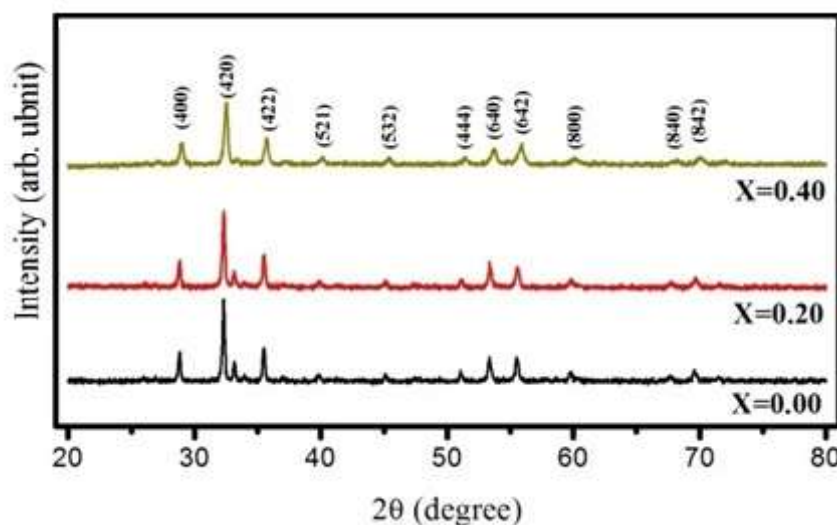


Fig. 1. XRD patterns of  $Y_3Fe_{5-x}Al_xO_{12}$  ( $x=0.00, 0.20$  and  $0.40$ )

Furthermore, the values of Miller indices (h k l), Bragg's angle ( $\theta$ ), interplanar spacing (d) and intensity (I) obtained from XRD data. The lattice parameter (a) values of YIG and Al substituted YIG samples were calculated using standard relation,

$$a = d\sqrt{(h^2+k^2+l^2)} \quad \text{\AA} \quad \dots 1$$

where, (d) is interplanar spacing and (h k l) is Miller Indices.

The obtained values of the lattice parameter (a) are tabulated in table 1. It was found that the lattice parameter decreases with increase in Al concentration. The decrease in lattice parameter with aluminium content 'x' is according to Vegard's law and can be interpreted on the basis of the smaller ionic radii of the constituent Al ion. In the present system larger  $Fe^{3+}$  ions are replaced by smaller  $Al^{3+}$  ions. This decreases the d-spacing which leads to the decrease in lattice parameter. The variation of lattice parameter with aluminium content 'x' is similar to that reported in the literature [Motlagh].

The unit cell volume (V) was calculated by using the following equation;

$$V = a^3 \quad \text{\AA}^3 \quad \dots 2$$

where, V is the unit cell volume and a is the lattice constant.

The unit cell volume (V) shows gradual decrease with the substitution of aluminium. The decrease in unit cell volume is attributed to decrease in lattice parameter of the system under investigation.

The X-ray density ( $d_x$ ) was calculated by using the relation and values are summarized in table 1;

$$d_x = \frac{Z \times M}{V \times N_A} \quad \text{gm/cm}^3 \quad \dots 3$$

where, Z is the number of molecules per formula unit, M is molecular mass of the sample,  $V = a^3$  is the unit cell volume and  $N_A$  is the Avogadro's number.

It can be observed from table 1 that X-ray density increases as aluminium content x. The increase in X-ray density may be due to the fact that the increase in molecular weight / mass as well as the decrease in volume.

The bulk density of the present sample was obtained through Archimedes principle using toluene as an immersion liquid. The values of bulk density are reported in table 1. It is evident from table 1 that bulk density also increases with aluminium content x.

The crystallite size of the YIG and Al substituted YIG was calculated by using the most intense peak (420) and using the Debye-Scherrer's relation for small and uniform sized cubic crystals,

$$t = \frac{0.9\lambda}{\beta \cos\theta} \quad \text{nm} \quad \dots 4$$

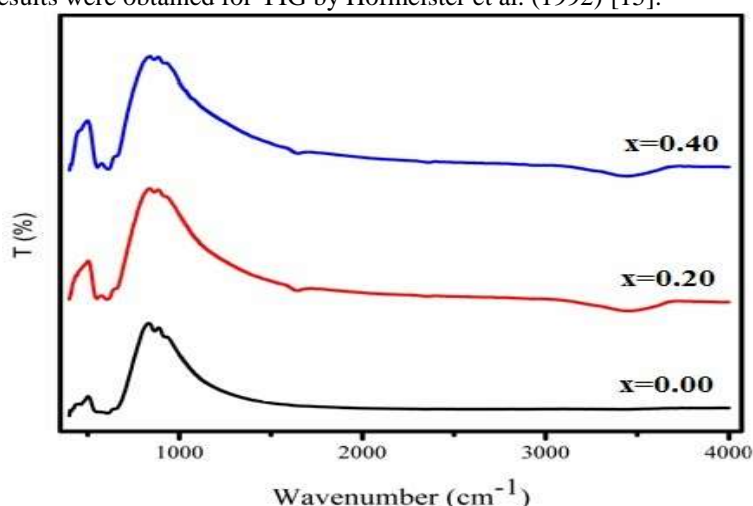
where,  $\lambda$  is wavelength of the Cu-K $\alpha$  radiation,  $\beta$  is the full width of the half maximum,  $\theta$  is Bragg's angle.

The obtained values of the crystallite size are presented in table 1. The average crystallite size calculated by using Debye Scherrer's formula is varying from 22 - 30 nm.

**Table 1. Lattice parameter (a), Unit cell volume (V), X-ray density ( $d_x$ ), Bulk density ( $d_B$ ), Porosity (P %) and Crystallite size (t) of  $Y_3Fe_{5-x}Al_xO_{12}$  where  $x = 0.00, 0.20$  and  $0.40$**

'x'	a (Å)	V (Å <sup>3</sup> )	$d_x$ (gm/cm <sup>3</sup> )	$d_B$ (gm/cm <sup>3</sup> )	P (%)	t (nm)
0.00	12.3851	1895.1	4.958	3.638	29.6717	30.051
0.20	12.3762	1872.8	4.969	3.617	30.3522	26.672
0.40	12.3586	1873.9	4.990	3.587	30.3500	22.114

In understanding the garnet phase formation, a comprehensive study of Fourier transform infrared spectra is essential. It can provide the necessary information regarding the structure, bond strength, imperfection and impurities. In the infrared region, the molecular vibration gives rise to absorption bands, which identify the vibration modes associated with the tetrahedral metal-oxygen. Fig. 2 shows FTIR spectra of annealed powder of the typical samples ( $x = 0.00, 0.20$  and  $0.40$ ) of YIG and Al substituted YIG nanoparticles. The band positions of YIG and Al substituted YIG obtained from FTIR spectra are given in table 2. The vibrational frequency depends upon the cation mass, cation oxygen bonding force, distance etc. FTIR spectrum for YIG ( $x=0.00$ ) exhibits three bands at around  $542\text{cm}^{-1}$  and  $602\text{cm}^{-1}$  which can be assigned to the stretching mode of the tetrahedral site in the YIG structure. This observation indicates that the crystallization of YIG sample is completed. Similar results were obtained for YIG by Hofmeister *et al.* (1992) [15].



**Fig. 2. FTIR spectra of  $Y_3Fe_{5-x}Al_xO_{12}$  ( $x=0.00, 0.20,$  and  $0.40$ )**

**Table 2. Vibrational bands of  $Y_3Fe_{5-x}Al_xO_{12}$  where  $x = 0.00, 0.20$  and  $0.40$**

'x'	Vibrational absorption bands (cm <sup>-1</sup> )				
0.00	542	602	863	-	3437
0.20	546	604	860	1645	3446
0.40	552	612	861	1649	3436

The modes ranging from  $860\text{cm}^{-1}$ - $863\text{cm}^{-1}$  can be assigned to the stretching of C=O in carbonates. Moreover, the vibration bands ranging from  $1645\text{cm}^{-1}$ - $1649\text{cm}^{-1}$  can be associated to the deformation of O-H bonds which can be attributed to the adsorbed water molecules. Furthermore, the absorption peaks at  $3437\text{cm}^{-1}$ ,  $3446\text{cm}^{-1}$  and

3436cm<sup>-1</sup> are corresponding to the stretching vibrations of O-H due to absorption of water molecules. In case of Al substitution, the absorption bands are found to slightly broadened and shifted towards higher wavenumber. Our results on FTIR studies of YIG and Al substituted YIG are in good agreement with the literature reports [16].

#### IV. CONCLUSION

The nanocrystalline yttrium iron garnet and aluminium substituted yttrium iron garnet was prepared by sol-gel auto combustion synthesis route. The required garnet phase formation was confirmed from the investigated samples. The lattice parameter decreased with Al substitution due to its smaller ionic radius. X-ray density of YIG was found to decrease with Al substitution. FTIR spectra show typical absorption bands indicating the formation of garnet structure of the samples. Upon aluminium substitution, absorption bands broadened and shifted towards higher wavenumber.

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