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Research Article

Synthesis of Dy$_3$Fe$_{5-x}$Al$_x$O$_{12}$ garnet nanoparticles (DyIG:Al NPs) using Solgel auto-combustion method

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ABSTRACT

This study investigates the synthesis and characterization of Dysprosium iron-aluminum garnet nanoparticles (Dy$_3$Fe$_{5-x}$Al$_x$O$_{12}$ or DyIG:Al NPs), a subclass of garnet ferrites known for their remarkable magnetic, optical, and electrical properties. DyIG:Al NPs were successfully synthesized using the sol-gel method, which allows for precise control over the composition, size, and morphology of the nanoparticles. X-ray diffraction (XRD) analysis confirmed the formation of a highly crystalline cubic garnet structure, with sharp, well-defined peaks corresponding to the DyIG:Al phase. The lattice parameter remained consistent, indicating a stable crystal structure, with minor variations in some reflections suggesting only minimal structural changes. The DyIG:Al NPs exhibited excellent crystallinity and phase purity, which are essential for their superior magnetic properties, including low magnetic losses at microwave frequencies. These properties make DyIG:Al NPs highly promising for applications in high-frequency signal processing, quantum computing, and telecommunications. This study underscores the potential of garnet ferrites, particularly DyIG:Al, as advanced materials for next-generation technologies, and provides a foundation for further research and industrial optimization.

1 Introduction

Garnet ferrites, a subset of magnetic ceramics, are distinguished by their unique cubic crystal structure and intricate composition, which play a crucial role in shaping their magnetic and optical properties. Their general formula, M$_3$Fe$_5$O$_{12}$, represents compounds where M typically denotes rare-earth elements such as Yttrium (Y), Gadolinium (Gd), Dysprosium (Dy), or Terbium (Tb). This structure is derived from the natural garnet mineral, specifically the silicate Mn$_3$Al$_2$Si$_3$O$_{12}$, where silicon and manganese are replaced by aluminum and rare-earth ions to form variants like Y$_3$Al$_5$O$_{12}$ [1]. Dysprosium iron-aluminum garnet nanoparticles (DyIG:Al NPs) is a well-known material with remarkable magnetic, optical, and electrical properties [2]. The distinctive ion arrangement in garnet ferrites encompasses tetrahedral, octahedral, and dodecahedral sites, which give rise to their ferrimagnetic behavior a phenomenon where opposing magnetic moments produce a net magnetization that is weaker than that of ferromagnetic materials [3, 4]. DyIG:Al exhibits remarkable magnetic and magneto-optic properties, largely due to the incorporation of Dysprosium ions, which enhance structural stability and refine the material's magnetic characteristics. Its low magnetic losses at microwave frequencies make it particularly valuable for high-frequency signal processing, where precise and stable magnetic properties are essential. Additionally, DyIG:Al is being explored for applications in quantum computing, where its low-damping magnetic behavior could improve qubit performance, and in telecommunications, where its ability to manipulate light waves with magnetic fields offers significant advantages. Garnet ferrites, including DyIG:Al, possess a more complex cubic crystal structure compared to spinel ferrites and incorporate rare-earth elements such as Dysprosium, gadolinium, and terbium, making them highly specialized materials. They are generally represented by the formula **M$_3$Fe$_5$O$_{12}$**, where M is a rare-earth ion (e.g., Dy, Y, La, Gd). The cubic unit cell of garnet ferrites consists of 8 formula units, comprising 160 atoms arranged as 96 O^{2-} ions with interstitial cations. The garnet structure can also be expressed in a more detailed chemical format to reflect its unique composition and properties [5];

(R3)(Fe2)(Fe3)□O3

Here, R = Y, La, Ho, Dy, Gd, Yb, Nd, Sm, Er, Eu, Sc, Ce, Tb, Tm, Pr, Lu. In the above equation, the superscripts c, a, d, refer to the lattice sites such as dodecahedral or {c} -sites, octahedral or [a]-sites, and tetrahedral or (d)-sites as shown in **Figure 1**. The prototype ferrimagnetic iron garnet is Dysprosium iron garnet:

$$\{Dy_3\}[Fe_2](Al_3)O_{12}$$

or,

Dy3Fe5-xAlxO12

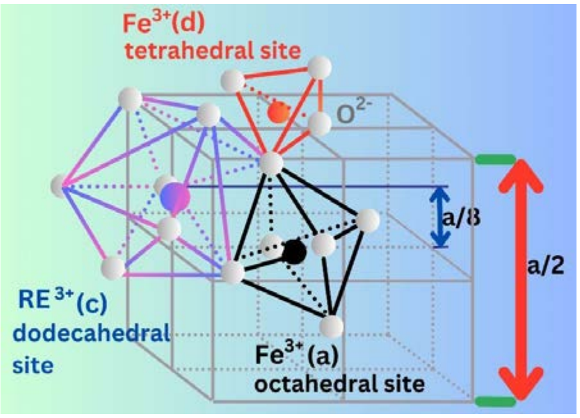

***Figure 1** Crystal structure of garnet ferrite*

DyIG:Al NPs are highly valued for their specificity and versatility across numerous applications. For example, europium, essential as a red phosphor in color cathode-ray tubes and liquid crystal displays for computer monitors and televisions, is irreplaceable due to its unique properties and limited availability. Similarly, erbium plays a pivotal role in fiber-optic telecommunications, facilitating long-distance signal transmission through erbium-doped fiber sections that function as laser amplifiers, offering significantly greater bandwidth than traditional copper cables. The sol-gel method emerges as a promising approach for synthesizing Dysprosium garnet, owing to its simplicity, cost-effectiveness, and capability to produce homogeneous, fine powders with excellent compositional precision. This method enables the production of uniform and fine particle sizes, which are crucial for enhancing material properties and ensuring superior performance in practical applications [6].

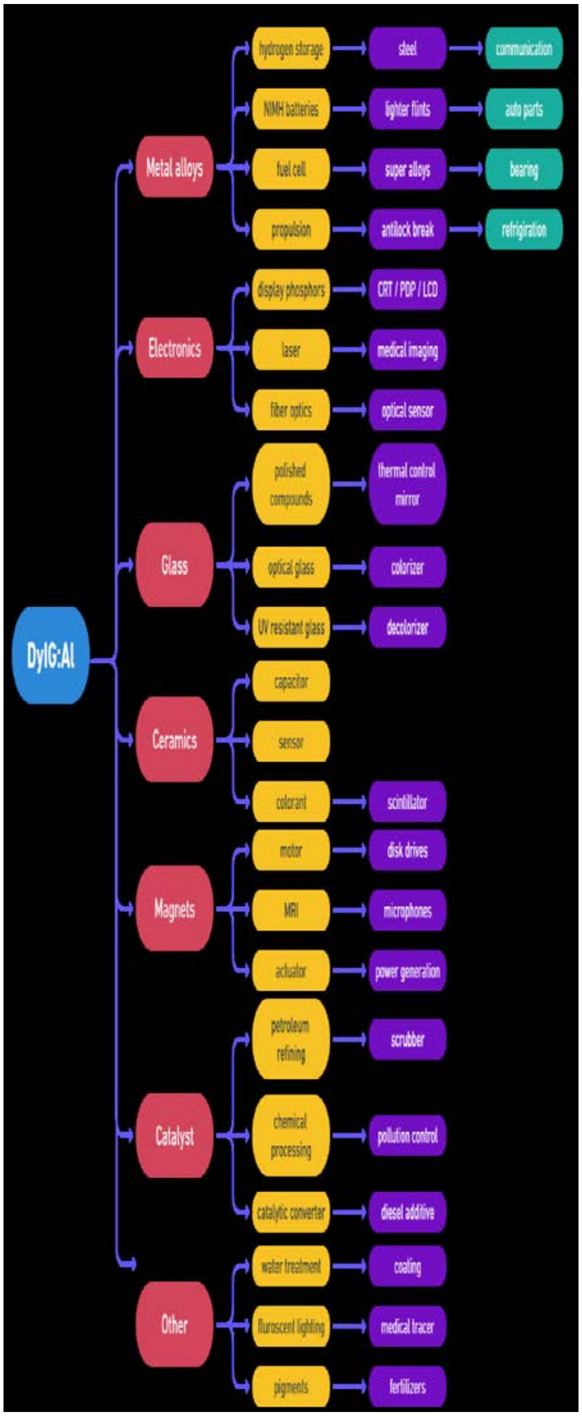

***Figure 2** Different property-based applications of DyIG:Al garnet ferrite*

DyIG:Al NPs have unique electrical and magnetic properties best suited for high-frequency applications [7]. They are used in magnetic fluids [8] and for the fabrication of magnetic core of reading and write heads of high-speed digital tapes [9]. These properties make them suitable for various applications like canting of the spins [10], tissue imaging [11], and biotechnology [12], telecommunication [13] magnetic recording heads [14], microwave devices [15], power switches, resonators, TV sets etc. [16]. Some of the important applications include medical diagnosis tools [17], memory chips [18], targeted drug delivery [15], sensor [19] etc. The exceptional properties of DyIG:Al nanoparticles, such as high saturation magnetization, high coercivity, strong anisotropy, as well as excellent mechanical hardness and chemical stability, are not typically observed in bulk samples. This study focuses on the sol-gel synthesis of DyIG:Al NPs and systematically examines their structural, magnetic, and optical properties. By investigating these properties, the research aims to uncover valuable insights into the tunability of Dysprosium garnet's characteristics, paving the way for the development of advanced materials with enhanced performance for diverse technological applications, as illustrated in **Figure 2**.

2 Experimental method

2.1 Starting Materials

DyIG:Al nanoparticles were synthesized using the sol-gel method. Stoichiometric amounts of Dysprosium nitrate hexahydrate ($Dy(NO_3)_3{\cdot}6H_2O$, 456.63 g/mol), Iron (III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$, 404.00 g/mol), and aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$, 26.98 g/mol) were dissolved in distilled water to achieve the desired composition. Citric acid ($C_6H_8O_7$, 210.14 g/mol) was added in a nitrate-to-acid ratio of 1:3 to act as a complexing agent, promoting the formation of metal-citrate complexes for homogeneous molecular-level mixing. Ammonia (NH_3) was used to adjust and maintain the pH at 7.

3 Synthesis

3.1 Solgel auto-combustion of DyIG:Al NPs

In the DyIG:Al garnet structure, Dysprosium serves as the primary cation and can be partially substituted with other elements, such as Iron (Fe), to modify the material's properties. Substitution with elements from the lanthanide series is commonly employed to fine-tune the magnetic and optical characteristics of the nanoparticles. Iron, a Group 8 element, contributes to the magnetic properties through its unpaired d-electrons, while oxygen forms the anionic framework, coordinating with metal cations to ensure structural stability. The sol-gel synthesis process, depicted in **Figure 3**, is a well-established technique for producing DyIG:Al nanoparticles at the nanoscale, offering precise control over their composition, size, and morphology. The synthesis begins with the selection of key precursors: Dysprosium nitrate hexahydrate ($Dy(NO_3)_3{\cdot}6H_2O$) provides Dysprosium ions essential for the garnet structure, while iron (III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) supplies the required iron ions.

Citric acid ($C_6H_8O_7$) acts as a complexing agent, preventing premature aggregation and ensuring a homogeneous mixture. The choice of solvent, such as ethanol or methanol, is critical as it must be miscible with the precursors and possess appropriate volatility for efficient drying. During the mixing stage, the precursors are combined to form a uniform solution, which is then aged at approximately 80°C. During this process, hydrolysis and condensation reactions occur, forming metal hydroxides that link into a three-dimensional network, resulting in gelation and the formation of a wet gel a porous metal oxide structure containing trapped solvent. The wet gel is subsequently dried to create a xerogel, with careful control to minimize cracking or shrinkage. The xerogel undergoes calcination at high temperatures (typically above 500°C), removing residual organics and facilitating the crystallization of the amorphous phase into the crystalline $Dy_3Fe_{5-x}Al_xO_{12}$ garnet. The calcination temperature and duration are critical parameters that significantly influence the final crystallinity, phase purity, and magnetic properties of the nanoparticles. By optimizing each step of the process, researchers can fine-tune the size, morphology, and performance of DyIG:Al nanoparticles for applications such as magnetic recording media and other advanced technologies.

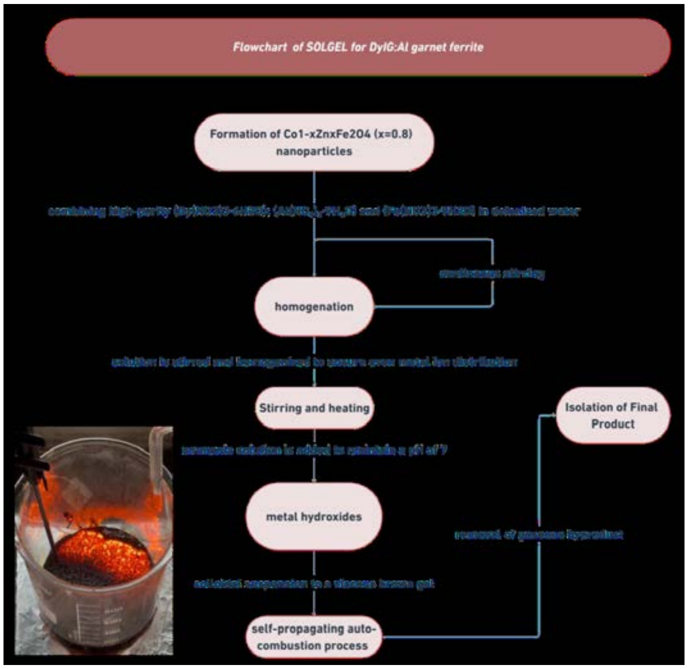

__Figure 3__ The subsequent stages involved in the sol-gel synthesis of DyIG:Al NPs

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3.2 Chemical reactions during DyIG:Al NPs formation

Dysprosium Nitrate Hexahydrate

$$(NO3)3{\cdot}6H2O \rightarrow Dy3++3NO3-+6H2O \qquad (4)$$

Iron (III) Nitrate Nonahydrate

$$(NO3)3{\cdot}6H2O{\rightarrow}Fe3++3NO3-+9H2O \qquad (5)$$

Aluminum (III) Nitrate Pentahydrate

$$(NO3)3{\cdot}5H2O{\rightarrow}Al3++3NO3-+5H2O \qquad (6)$$

$$3(NO3)3+Al(NO3)3+5Fe(NO3)3{\rightarrow} Dy3-XAlxFe(NO3)12 \qquad (7)$$

Citric acid (C6H8O7) chelates the metal ions, forming Metal-Citric Acid Complexes

$$Dy3+\ +\ Al3+\ +\ Fe3+\ +\ C6H8O7\ \rightarrow\ [Dy-Citric\ acid]\ + [Al-Citric\ acid]+[Fe-Citric\ acid] \qquad (8)$$

Gel formation involves the formation of a metal-organic network, which includes

$$[Dy-Citric\ acid]\ +\ [Al-Citric\ acid]\ +\ [Fe-Citric\ acid]\ + Ammonia\ (NH3) \rightarrow Gel\ Network\ (Dy3-xAlxFe5(OH)12) \qquad (9)$$

Obtain Xerogel

$$Gel\ Network\ (Dy3-xAlxFe5(OH)12)\ \rightarrow\ Xerogel\ (Dy3-xAlxFe5(OH)12)\ dry \qquad (10)$$

Calcination to Form Garnet

$$Xerogel\ (Dy3-xAlxFe5(OH)12){\rightarrow}(Dy3-xAlxFe5(OH)12)+H2O \qquad (11)$$

4. Structural property of DyIG:Al NPs

DyIG:Al nanoparticles ($Dy_3Fe_{5-x}Al_xO_{12}$, CAS number 12063-56-8) are composed of elements from specific groups of the periodic table: Dysprosium from Group 3, Iron from Group 8, and Oxygen from Group 16. The garnet structure, which is a type of cubic crystal system, follows the general formula $AB_3C_2O_{12}$, where the cations occupy distinct sites within the crystal lattice. Dysprosium iron-aluminum garnet ($Dy_3Fe_{5-x}Al_xO_{12}$) adopts a cubic crystal structure associated with the Space Group: I4-3d, which is characteristic of the garnet family. In this structure, Dysprosium (Dy^{3+}) ions occupy the 8-coordinate dodecahedral (A) sites, while Iron (Fe^{3+}) ions are situated in the 6-coordinate octahedral (B) sites. The Oxygen ions form a three-dimensional network that stabilizes and enhances the material's functionality. The highly ordered crystal lattice of DyIG:Al NPs, with oxygen ions creating a tetrahedral network linking the metal ions, ensures a stable and robust structure. This arrangement is key to the material's superior magnetic and optical properties. The presence of Dysprosium (Dy) ions introduces magnetic anisotropy and alters the Curie temperature, while also contributing to distinctive optical absorption and emission behaviors due to their 4f-4f electronic transitions. The well-defined structure of DyIG:Al NPs makes them ideal for advanced applications, including optical isolators, microwave devices, and magnetic sensors [20-23].

4.1 X-ray diffraction pattern of DyIG:Al NPs

The X-ray diffraction (XRD) pattern of DyIG:Al NPs, shown in Figure 4, reveals sharp and well-defined peaks, indicating the formation of a highly crystalline phase. The prominent peaks are indexed to specific crystal planes, including (211), (400), (420), (422), (521), (532), (444), (640), (642), (800), (840), (842), (664), and (868), confirming the cubic garnet structure of DyIG:Al. The absence of additional peaks indicates high phase purity, with no detectable impurities or secondary phases such as $DyFeO_3$ or α-Fe_2O_3.

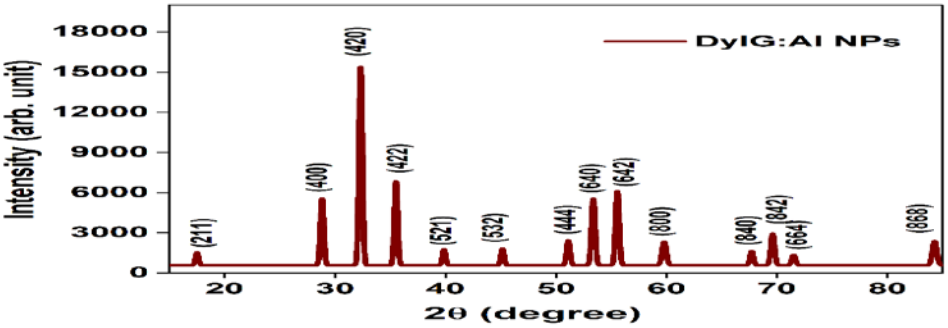

Figure 4 X-ray diffraction pattern of DyIG:Al NP

The sharpness and intensity of the peaks further emphasize the excellent crystallinity of the nanoparticles, which is essential for their magnetic and optical properties. The highest intensity peak at the (420) plane suggests a preferred crystallographic orientation along this direction, potentially affecting the anisotropic behavior of the material. The diffraction pattern is consistent with standard JCPDS data (e.g., PDF card 43-0507), confirming the successful synthesis of the DyIG:Al phase. Additionally, the crystallite size can be estimated using the Scherrer equation for further structural analysis [24].

5. Conclusion

The synthesis and characterization of Dysprosium iron-aluminum garnet nanoparticles (DyIG:Al NPs) using the sol-gel method have provided valuable insights into the material's structural, magnetic, and optical properties. X-ray diffraction (XRD) analysis confirmed the successful formation of the cubic garnet structure, demonstrating high phase purity and excellent crystallinity, both critical for the material's superior magnetic performance. The consistent lattice parameter observed in the diffraction data suggests a stable crystal structure, with minor variations indicating subtle structural changes. The DyIG:Al NPs exhibit remarkable magnetic properties, including low magnetic losses at microwave frequencies,

making them promising candidates for high-frequency signal processing, quantum computing, and telecommunications. The ability to fine-tune their properties through controlled synthesis and elemental substitution enhances their versatility for a wide range of technological applications. This research underscores the potential of garnet ferrites, especially DyIG:Al, as advanced materials for cutting-edge applications in electronics and quantum technologies.

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