Evaluation of the Influence of the Substituting Cation on the Structural and Morphological Properties of the New Garnet Sm$_{3-x}$REE$_x$Fe$_5$O$_{12}$ (REE = Dy, Gd and Lu)

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Rare earth garnets (REE$_x$Fe$_{5-x}$O$_{12}$) have magnetic-electric and optical properties that can be used in transmitters, microwave and data storage devices. These properties depend mainly on partial or total substitution of the cationic sites, as well as by the synthesis method used. Therefore, in this work was studied the influence of the substituting cation on the structural and morphological properties of new garnets with formula Sm$_{3-x}$REE$_x$Fe$_5$O$_{12}$ with $x$ = 0.0 - 1.0; obtained by the solid-state reaction method. Characterization of samples was carried out by XRD, Rietveld refinement, SEM and Raman spectroscopy. The results showed that the substitution favors system stability and formation of garnets single phase with cubic structure and space group of $Ia3d$ (230) at temperatures lower than reported by other authors. The substitution generated a decrease of the lattice parameters, the crystal size and favored particle formation of the order of micrometers (from 1.3 to 3.6 $\mu$m).

Keywords: Rare earth garnets, solid state reaction.

1. Introduction

The iron-rare earth garnets REE$_x$[Fe$_y$(Fe$_{3-y}$)O$_{12}$] crystallize in the cubic system and present space group $Ia3d$ (230), the unit cell is constituted by three crystallographic sites: tetrahedral site 24d(Fe$_x$), octahedral site 16a(Fe$_y$) and dodecahedral site 24c REE$_x$. Thanks to this structural distribution, garnets can be constituted by different ions that give them remarkable magnetic-electric and optical properties.

Yttrium-iron garnet (Y$_3$Fe$_5$O$_{12}$) is the most important material in this family of oxides: it is ferrimagnetic with high Curie temperature ($T_c = 260$ °C), it has low coercive field ($H_c$) and high thermal conductivity, electrical resistivity and Verdet constant, which results in the Faraday effect or magneto-optic effect. Thanks to these properties, further investigations studied the effect of yttrium substitution by rare earth elements (REE) such as neodymium (Nd), samarium (Sm), gadolinium (Gd), holmium (Ho) and dysprosium (Dy) and cerium (Ce); this allowed to discover the existence of magnetic anisotropy, magneto-dielectric, magneto-electric and magneto optical effects associated with these new materials.

The magneto-optical and electrical properties depend on the composition, structure and morphology of the material, which are mainly influenced by the cation or substituent cations and the synthesis method, allowing its application in microwave devices, optical oscillators, phase shifters, radars and for data storages devices. The synthesis methods mainly used to obtain garnets are: the solid-state reaction method and the sol-gel method. Deka et al. synthesized the Y$_{3-x}$Sm$_x$Fe$_5$O$_{12}$ system with $x = 0.0$ to 3.0 of pure phase by the solid-state reaction method with synthesis temperatures of 1400 °C in the year 2017.

Also, in 2017 they reported the synthesis of Sm$_{3-x}$Fe$_5$O$_{12}$ with a calcination temperature of 1200 °C and a sintering temperature of 1400 °C. In the same year Jang et al. reported the synthesis of Y$_3$Fe$_5$O$_{12}$ obtained by the sol-gel method with a temperature of 1400 °C; similarly, Tholkappiyan et al. reported the same sintering temperature for dysprosium iron garnet (Dy$_3$Fe$_5$O$_{12}$), showing the formation of thick and pure phase microstructures.

The applications will not only be modified by the synthesis method used, but also by the cation that replaces the dodecahedral site of the structure, as reported by Ramesh et al. who demonstrated that the substitution of Y$_3$Fe$_5$O$_{12}$ by gadolinium allows applications in optical isolators and communication systems. Substitution with Gd improves the magnetic properties and microwave absorption, allowing its application in microwave devices and magneto-optical insulators. The substitution with Dy modifies the dielectric and magnetic properties, making it a promising material for use in radars, television screens fabrication and data storage due to the great of Faraday rotation (1x10$^4$ cm$^{-1}$). Finally, it has been established that the insertion of lutetium (Lu) does not contribute to any magnetic behavior due to the absence of unpaired electrons (4f$^3$); therefore, the net magnetic moment will be given by the unequal distribution of the octahedral and tetrahedral Fe$^{3+}$ ions. It presents important applications in telecommunications and data storage industry due to this magnetic-dielectric coupling.

In this work, new garnets with formula Sm$_{3-x}$REE$_x$Fe$_5$O$_{12}$ (REE = Dy, Gd and Lu) were synthesized and characterized with seven different substitution values ($x = 0.0, 0.1, 0.2, 0.4, 0.6, 0.8$ and $1.0$) by the solid state reaction method.

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The phase, the crystalline structure and the surface morphology were studied using XRD, SEM and Raman; this procedure allowed evaluating the influence the substituting cation has on the garnet’s structural and morphological properties.

2. Experimental

2.1 Synthesis of samples

The garnets Sm$_{3-x}$REE$_x$Fe$_5$O$_{12}$ (REE = Dy, Gd and Lu) with $x = 0.0, 0.1, 0.2, 0.4, 0.6, 0.8$ and $1.0$ were synthesized by the solid-state reaction method, from stoichiometric amounts of oxides: Sm$_2$O$_3$ (99.99% Sigma Aldrich), Dy$_2$O$_3$ (99.999% Sigma Aldrich), Gd$_2$O$_3$ (99.999% Sigma Aldrich), Lu$_2$O$_3$ (99.99% Sigma Aldrich) and Fe$_2$O$_3$ (99.99% Sigma Aldrich) previously calcined at 800 ºC for 2 h in order to eliminate carbon compounds and water present superficially.

Each mixture with stoichiometric amounts of oxides was subjected to grinding processes, and calcination at 800 ºC to obtain a mixture as homogeneous as possible. Then it was ground, pressed into pellets at pressure of 2.5 MPa and subjected to a sintering process at 1200 ºC for 20 h in order to favor the interdiffusion processes that allowed the obtention of the desired crystalline phase.

2.2 Characterization of samples

The mixed oxides obtained in pellet, were characterized through X-ray diffraction (XRD), in a PANalytical X Pert PRO-MPD equipment with Bragg-Brentano configuration, using the CuKα radiation ($\lambda = 1.5406$ Å) 15º and 90º 2θ. The Rietveld refinement was made using the GSAS and PCW softwares. The morphological properties of the solids were evaluated by scanning electron microscopy (SEM) in a Tescan Vega 3 SB, the analysis of the micrographs was done using the Image J program and finally the analysis by Raman spectroscopy was made an DRX Raman Microscope-Thermo Scientific equipment with a laser of 532 nm.

3. Results and Discussion

3.1 Structural analysis

Figs. 1 to 3 show the X-ray diffraction patterns taken in pellets of each of the garnet-type Sm$_{3-x}$REE$_x$Fe$_5$O$_{12}$ (REE = Gd, Dy and Lu) with $x = 0.0, 0.1, 0.2, 0.4, 0.6, 0.8$ and $1.0$ synthesized by the solid state reaction method at a temperature of 1200 ºC. The analysis allowed to determine a phase classification according to the iron-samarium garnet with reference code JCPDS 01-073-1379, of cubic structure, space group $Ia\overline{3}$d (230) and with a preferential orientation in along (4 2 0) crystal plane, which corresponds to peak with higher intensity in the theoretical XRD pattern.
Evaluation of the Influence of the Substituting Cation on the Structural and Morphological Properties of the New Garnet Sm$_{3-x}$REE$_x$Fe$_5$O$_{12}$ (REE = Dy, Gd and Lu)

Fig. 4 shows the high correlation of the experimental pattern with the theoretical one reported (Sm$_3$Fe$_5$O$_{12}$), with the presence of a signal located at 32.8° 2 Theta, which corresponds samarium orthoferrite phase (SmFeO$_3$), obtained at temperatures between 700 °C and 850 °C, it is characterized by an antiferromagnetic behavior that negatively influences the magnetic properties of the garnet$^{17}$.

The detailed XRD analysis showed a shift of the patterns to higher angles as the degree of substitution of the rare earths increases. Fig. 5 (a) shows the enlarged region of the main signal for the diffractogram of the Sm$_{3-x}$REE$_x$Fe$_5$O$_{12}$ system with $x = 0.0$, $0.8$ and $1.0$ for Gd, Dy and Lu, corresponding to the orientation in the plane (4 2 0). The similarity in each one of the signals obtained and the observed shift, reveal the contraction of the unit cell, which is attributed to the correct substitution at the dodecahedral site for each of the rare earth cations (Fig.5 (b)), at the same time related to the change in crystal size, as was been demonstrated by Muttashar et al. $^{18}$ and Wu et al. $^{19}$.

Crystal sizes are shown in Table 1, they were calculated using the Scherrer equation, replacing the values of the strongest signal with a constant of 0.9, where values between 70 and 36 nm were obtained. The smallest values were related to the system substituted with lutetium (Lu). The crystal size decreases with the percentage of substitution of samarium; these properties are explained as a function of the ionic radius of substituted rare earth$^{13}$. The ionic radii are 1.04 Å for the Sm$^{3+}$, 1.02 Å for the Gd$^{3+}$, 0.99 Å for the Dy$^{3+}$ and 0.93 Å for the Lu$^{3+}$; the difference of 10.6% in the ionic radius of the smallest cation (Lu) with the main cation favors the cohesion of the unit cell when it is substituted on the dodecahedral site of the structure, which results in lower lattice parameters$^{15}$.

![Figure 4. Diffractogram of theoretical and experimental from Sm$_3$Fe$_5$O$_{12}$](image)

![Figure 5. (a) Enlarged region of the main signal from the Sm$_{3-x}$,REE$_x$Fe$_5$O$_{12}$ system (REE= Gd, Dy and Lu) with $x = 0.0$, 0.8 and 1.0, (b) local polyhedral adopted by the Fe$^{3+}$ and RE$^{3+}$ ion.](image)
The analyses by X-ray diffraction results in tablets were carried out through the Rietveld refinement method using the GSAS and PCW software; Figs. 6 to 9 show the diffractograms refined for \( x = 0.0 \) and 1.0 of \( \text{Sm}_{3-x} \text{REE}_x \text{Fe}_5 \text{O}_{12} \) (REE = Gd, Dy and Lu). The refinement performed for the sample with \( x = 0 \) (Sm\(_3\)Fe\(_5\)O\(_{12}\)) showed the presence of a secondary phase of SmFeO\(_3\) that corresponded to 5.4%, with orthorhombic crystalline structure of space group \( Pbnm \) (62) with lattice parameters \( a = 5.40 \) (5) Å, \( b = 5.59 \) (4) Å and \( c = 7.71 \) (4) Å and cell volume of 233.29 Å\(^3\). The analyses of all the samples confirmed that the substitution with elements such as Gd, Dy and Lu in any of the established values of \( x \), favor the stability of the crystalline phase desired and the obtaining of pure phase, which is corroborated by the small values of refinement parameters (R(%) and \( \chi^2 \)) obtained and shown in Table 1, which indicate that the samples synthesized adopt the garnet-type structure.

Rietveld refinement results and the absence of secondary phases confirm that this synthesis process was optimal to favor the ions interdiffusion and the precursors reaction\(^{20}\), using a temperature 200 °C lower than reported by other authors. The insertion of rare earth elements favors crystalline-phase stability and allows to be obtained at lower temperature than reported. By the solid state reaction method, Liu et al. in 2017 synthesized iron-samarium garnet (Sm\(_3\)Fe\(_5\)O\(_{12}\)) without secondary phases at a temperature of 1400 °C\(^{9}\). Aakansha et al. synthesized a similar system of iron garnet-yttrium substituted with samarium (Y\(_{3-x}\)Sm\(_x\)Fe\(_5\)O\(_{12}\) with \( x = 0.0, 0.5, 1.0, 2.0 \) and 3.0) of pure phase, by the method of reaction of solid state, in medium of acetone and with a sintering temperature of 1400 °C\(^{8}\).

### Table 1. Rietveld refinement results obtained from the XRD patterns of the garnet-type Sm\(_{3-x} \)REE\(_x\)Fe\(_5\)O\(_{12}\)

| REE | X Value | \( X^2 \) | R(%) | \( a = b = c \) (Å) | \( U_{iso} \) | Crystallite size (nm) | Link angle Fe(a)-O-Fe(d) | Particle size μm |
|-----|---------|---------|------|-----------------|-------|-------------------|---------------------|-----------------|
| Gd  | 0.0     | 1.61    | 8.85 | 12.53(7)        | 0.025 | 70                | 128.89(7)          | 1.35(4)         |
|     | 0.1     | 1.60    | 11.89| 12.55(1)        | 0.025 | 61                | 128.14(7)          | 3.20(8)         |
|     | 0.2     | 1.84    | 16.69| 12.52(8)        | 0.025 | 65                | 128.56(9)          | 3.43(4)         |
|     | 0.4     | 1.84    | 16.15| 12.53(2)        | 0.025 | 56                | 125.76(9)          | 3.61(1)         |
|     | 0.6     | 1.01    | 9.21 | 12.51(3)        | 0.025 | 58                | 128.44(2)          | 3.33(6)         |
|     | 0.8     | 2.65    | 13.07| 12.52(8)        | 0.025 | 58                | 128.84(2)          | 3.21(8)         |
|     | 1.0     | 1.89    | 11.82| 12.49(4)        | 0.025 | 56                | 129.71(2)          | 3.26(8)         |
| Dy  | 0.1     | 2.86    | 10.54| 12.53(6)        | 0.025 | 66                | 129.03(5)          | 2.89(7)         |
|     | 0.2     | 2.74    | 14.16| 12.52(5)        | 0.025 | 67                | 129.03(5)          | 3.08(5)         |
|     | 0.4     | 1.52    | 16.62| 12.52(9)        | 0.025 | 36                | 130.42(9)          | 2.53(7)         |
|     | 0.6     | 1.01    | 10.17| 12.49(2)        | 0.025 | 53                | 132.94(0)          | 2.38(7)         |
|     | 0.8     | 1.75    | 8.57 | 12.49(7)        | 0.025 | 51                | 128.56(1)          | 2.21(8)         |
|     | 1.0     | 1.12    | 9.71 | 12.49(5)        | 0.025 | 51                | 125.77(8)          | 2.01(6)         |
| Lu  | 0.1     | 1.83    | 16.29| 12.51(7)        | 0.025 | 66                | 131.27(1)          | 3.57(9)         |
|     | 0.2     | 1.26    | 13.08| 12.51(1)        | 0.025 | 42                | 131.67(6)          | 3.65(2)         |
|     | 0.4     | 1.24    | 9.30 | 12.49(4)        | 0.025 | 36                | 129.00(1)          | 3.04(4)         |
|     | 0.6     | 1.31    | 14.81| 12.48(5)        | 0.025 | 36                | 128.85(8)          | 2.53(3)         |
|     | 0.8     | 1.44    | 13.56| 12.46(9)        | 0.025 | 40                | 127.90(1)          | 3.02(4)         |
|     | 1.0     | 1.17    | 9.95 | 12.45(1)        | 0.025 | 44                | 125.65(9)          | 2.28(1)         |
Evaluation of the Influence of the Substituting Cation on the Structural and Morphological Properties of the New Garnet Sm$_{3-x}$REE$_x$Fe$_5$O$_{12}$ (REE = Dy, Gd and Lu)

The synthesis method used in comparison to chemical methods, does not generate polluting gases or any type of by-product, due to it does not require the use of solvents. Also, the method allows to obtain materials with higher crystallinity.

From the results obtained by Rietveld refinement, it was determined that as the concentrations of Gd$^{3+}$, Dy$^{3+}$ and Lu$^{3+}$ ions increase, the binding angle of Fe(a) -O- Fe(d) is modified (Table 1), indicating that the distortion of local polyhedral causes a modification in the lattice parameters. Fig. 10 (a) shows the trends of the lattice parameters obtained from the Rietveld refinement for each one of the systems synthesized; the inclusion of rare earth elements with smaller ionic radius causes a modification in the local polyhedral (Fig. 10) (b), which is represented by smaller lattice parameters.

In order to verify different distortions of the local polyhedral, Raman spectroscopy was performed, in which the cubic symmetry presents $3A_{1g} + 8E_g + T_{2g}$ as active translational and rotational modes. The spectra are shown in Fig. 11 - 13; these results are characteristic of garnet-type materials, which indicate that the Gd$^{3+}$, Dy$^{3+}$ and Lu$^{3+}$ ions were properly integrated in the structure. The signals located on 150 cm$^{-1}$, 250 cm$^{-1}$ and 325 cm$^{-1}$ are attributed to vibrational modes of Sm$^{3+}$ and other REE$^{3+}$ in the dodecahedron and vibrational modes of Fe-O in the tetrahedron and octahedron; all this is in concordance with what was previously reported by Wu et al. In addition, the signals located from 350 to 800 cm$^{-1}$ are result from stretching and reflection of the tetrahedron (FeO$_4$).

The analysis by Rietveld refinement allowed to calculate the Fe(d)-O bond distance of 1.89 Å for Sm$_2$DyFe$_5$O$_{12}$, 1.88 Å for Sm$_2$LuFe$_5$O$_{12}$, 1.84 Å for Sm$_2$GdFe$_5$O$_{12}$ and 1.81 Å for Sm$_3$Fe$_5$O$_{12}$.

Figure 8. Rietveld refinement results for sample Sm$_2$DyFe$_5$O$_{12}$.

Figure 9. Rietveld refinement results for sample Sm$_2$LuFe$_5$O$_{12}$.

Figure 10. (a) Lattice parameter vs x value for garnet-system Sm$_{3-x}$REE$_x$Fe$_5$O$_{12}$ (REE = Gd, Dy and Lu) and (b) distortion angle experienced by local polyhedral.
These values explain why the Raman spectrum of $\text{Sm}_3\text{Fe}_5\text{O}_{12}$ is located at higher wave numbers and that of $\text{Sm}_2\text{DyFe}_5\text{O}_{12}$ is displaced to lower wave numbers; this is attributed to the fact that for a harmonic oscillator, the frequency of vibration is proportional to the square root of the binding force$^{22}$, the frequency is affected by the angular distribution of the adjacent oxygens. The increasing in the size of substituent cation causes repulsion effects what generates the tetrahedron contraction, this demonstrates that the substitution by elements of rare earths in the garnets has been performed in an accurate way, modifying the bond distances and angles between atoms but not the type of crystal structure$^{24,25}$.

### 3.2 Morphological analysis

The Fig. 15 show the micrographs obtained with secondary electrons for the garnets $\text{Sm}_3-x\text{REE}_x\text{Fe}_5\text{O}_{12}$ ($\text{REE}=\text{Gd, Dy}$ and $\text{Lu}$ with $x=0.0$ and $1.0$), the formation of particles with well-defined edges are observed, these characteristics are due to sintering process and the rare earth substituted which modify the arrangement of the particles. When samarium is substituted by gadolinium, the particle size is greater (Fig. 15 b), the characteristics of these particles depend on the nucleation process and growth rate, which can be highly influenced by the substitution with REE, affecting their alignment sizes and shapes$^{26}$.

Using the Image J software, the particle size was determined using image taken at 10000x, the average particle size was determined for each of the synthesized garnets. Table 1 shows the particle size values obtained, the larger particles are associated with the substitution with the Gd$^{3+}$ ion, which is in accordance with the larger crystal size obtained by XRD, the substitution of Sm$^{3+}$ promotes the formation of larger particles$^{27}$, this is in accordance with the results obtained by Liu et al. who studied the dependence of optical and thermochromic properties respect particle size of $\text{Sm}_3\text{Fe}_5\text{O}_{12}$.

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**Figure 11.** Raman spectra of garnet-system $\text{Sm}_3-x\text{GdFe}_5\text{O}_{12}$ with $x=0.0, 0.1, 0.2, 0.4, 0.6, 0.8$ and $1.0$.

**Figure 12.** Raman spectra of garnet-system $\text{Sm}_3-x\text{DyFe}_5\text{O}_{12}$ with $x=0.0, 0.1, 0.2, 0.4, 0.6, 0.8$ and $1.0$.

**Figure 13.** Raman spectra of garnet-system $\text{Sm}_3-x\text{LuFe}_5\text{O}_{12}$ with $x=0.0, 0.1, 0.2, 0.4, 0.6, 0.8$ and $1.0$.

**Figure 14.** Amplified region Raman spectrum of the garnet-system $\text{Sm}_3-x\text{REEFe}_5\text{O}_{12}$ ($\text{REE}=\text{Gd, Dy}$ and $\text{Lu}$) with $x=0.0$ and $1.0$. 

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4. Conclusion

New garnets $\text{Sm}_{3-x}\text{REE}_x\text{Fe}_5\text{O}_{12}$ (REE = Gd, Dy and Lu, $x = 0.0 - 1.0$) were synthetized by the solid-state reaction method at lower temperature than previously reported by other authors. The Rietveld refinement showed the presence of 5.4% of SmFeO$_3$ phase in the garnet ($\text{Sm}_3\text{Fe}_5\text{O}_{12}$). The substitution with rare earth cations in dodecahedral site favors the stability of single phase with cubic structure and space group $Ia\overline{3}d$ (230), and crystal size between 36 and 70 nm, the smallest values were related to Lu$^{3+}$ cation, which is explained according to the ionic radius for the structural cohesion. The characterization confirmed that the rare earth ions substituents were integrated into the garnet structure. The samarium substitution caused a modification of angles and bond lengths in the garnet structure and an increase in the particle sizes.

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