

## STRUCTURAL STUDY AND THE EFFECT OF IONIC SIZE OF THE SYSTEMS (Gd<sub>1-x</sub>Lu<sub>x</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> DOPED ERBIUM.

I. Lanez, B. Rekik, M. Derbal, A. Chaib

LASICOM Laboratory, Faculty of sciences, Saad Dahleb Blida1 University

Received: 26 January 2019 / Accepted: 22 April 2019 / Published online: 01 May 2019

### ABSTRACT

The structure of cubic Garnets multi-components based on Gadolinium (**GAG**) undoped or doped rare earth, stabilized by Lanthanide as Lutetium, which has weak ionic radius recently attracts much attention to obtain the phases thermodynamically stables. In this work, we have chosen to study the development of compositions of type (Gd<sub>1-x</sub>Lu<sub>x</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (x = 0, 2 - 0, 3) doped 2 and 5 at % Er<sup>3+</sup>. The polycrystalline powders were prepared by reaction solid state method. **DRX** analyses on these synthesized powders confirmed the results of the phases of GdAlO<sub>3</sub> perovskite and Gd<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> garnet due to the higher content of gadolinium stabilized by Lutetium. **FTIR** analyses have shown the active vibrations modes associated on the specifics absorption bands of M – O (M: metallic elements **Gd and Lu or Al**). The optical analyzes carried out by the photoluminescence spectroscopy which it study the transitions of Erbium (Er<sup>3+</sup>) as doping elements in elaborated samples is of great optical importance.

**Keywords:** Cubic Garnets, ionic radius, Perovskite, DRX, FTIR, Photoluminescence spectroscopy.

Author Correspondence, e-mail: [imanelanez@hotmail.com](mailto:imanelanez@hotmail.com)

doi: <http://dx.doi.org/10.4314/jfas.v11i2.20>

### 1. INTRODUCTION

(A<sub>x</sub>B<sub>1-x</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> garnet multi-components based on **A** and **B** the different rare earths elements which **A: Gadolinium** and **B: Lutetium** doped rare earth is one of particular



interest in different fields of application such as solid lasers, phosphorescence, scintillation ... according to the rare earth doping element ( $A = \text{Ho}^{+3}, \text{Er}^{+3}, \text{Nd}^{+3}, \text{Ce}^{+3}, \text{Pr}^{+3}, \text{Eu}^{+3}, \text{Tb}^{+3} \dots$ ).

### 1.1. The effect of ionic size on the structure of the cubic Garnet

Rare earth aluminates  $\text{RE}_3\text{Al}_5\text{O}_{12}$  ( $\text{RE} = \text{Lu}, \text{Gd}, \text{Er} \dots$ ) crystallize in the cubic structure with the **Ia-3d** space group. In this structural type, the **RE** ions occupy dodecahedral coordination; but the tetrahedral and octahedral sites occupied by Aluminium atoms. The occurrence and thermal stability of compounds in the  $\text{Ln}_2\text{O}_3\text{-Al}_2\text{O}_3$  system heavily depend on the ionic radius of  $\text{Ln}^{3+}$ . As results the garnet structure are thermodynamically stable[1], only for the rare-earth ions smaller than  $\text{Gd}^{3+}$  ( $\text{Lu}^{3+}\text{-Er}^{3+}$ ) and does not exist for those larger than  $\text{Gd}^{3+}$  ( $\text{La}^{3+}\text{-Eu}^{3+}$ ). So the effect of the ionic size of the substituent element is low-radius Lutetium ( $0.977\text{\AA}$ ) with respected the gadolinium ( $1.053\text{\AA}$ ), or the doping element with Erbium, also of weak ionic radius ( $1.004\text{\AA}$ ) of the coordination 8 to stabilized **Gd** which represents the objectif of this study. Therefore, the system  $\text{Er}^{3+}$  doped by  $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$  should be a new type of Phosphors to further improve the  $\text{Er}^{3+}$  emission, this new system widely used in optics.

The Gadolinium, Lutetium and Erbium concentrations were chosen in order to elaborated pure garnet phase, because the previous studies found that pure  $\text{Gd}_3\text{Al}_5\text{O}_{12}$  garnet phase can't be obtained [2] without small ions (such as  $\text{Lu}^{3+}$  and  $\text{Er}^{3+}$  ion) stabilization, because it readily decomposes to thermodynamically more stable  $\text{GdAlO}_3$  perovskite and  $\text{Al}_2\text{O}_3$ , due to it is an unstable incongruent compound [3].

### 1.2. The advantages of the Gadolinium element on the aluminate Garnet structure:

Among the best-known Garnet cubic materials that are essentially dedicated to the field of Optics is  $\text{Gd}_3\text{Al}_5\text{O}_{12}$ , which has been much explored especially because: The intrinsic  $^8\text{S}_{7/2} \rightarrow ^6\text{I}_J$  transition of  $\text{Gd}^{3+}$  can be attained via an efficient energy transfer from  $\text{Gd}^{3+}$  to the activator, also the **GAG** lattice is more covalent than **YAG** due to the lower electronegativity of  $\text{Gd}^{3+}$  ( $\chi = 1.20$ ) than  $\text{Y}^{3+}$  ( $\chi = 1.22$ )  $\text{Lu}^{3+}$  and ( $\chi = 1.27$ ), and the high theoretical density and atomic weight values of **GAG** compared with that of **YAG** [2].

The elaborated samples  $\text{Er}^{3+}$  doped  $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$  ceramic phosphors were synthesized by solid-state reaction method. One of the most effective ways is to substitute a certain

amount of  $\text{Gd}^{3+}$  by  $\text{Lu}^{3+}$  and was varied to reveal the effects of  $\text{Lu}^{3+}$  and  $\text{Er}^{3+}$  contents on characteristics of the precursor and the resultant  $\text{Ln}_3\text{Al}_5\text{O}_{12}$  powders.  $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$  powders characterizations were given to the products via X-ray diffractometer (XRD), Fourier transform infrared (FT-IR), and photoluminescence (PL) spectroscopy.

## 2. RESULTS AND DISCUSSION

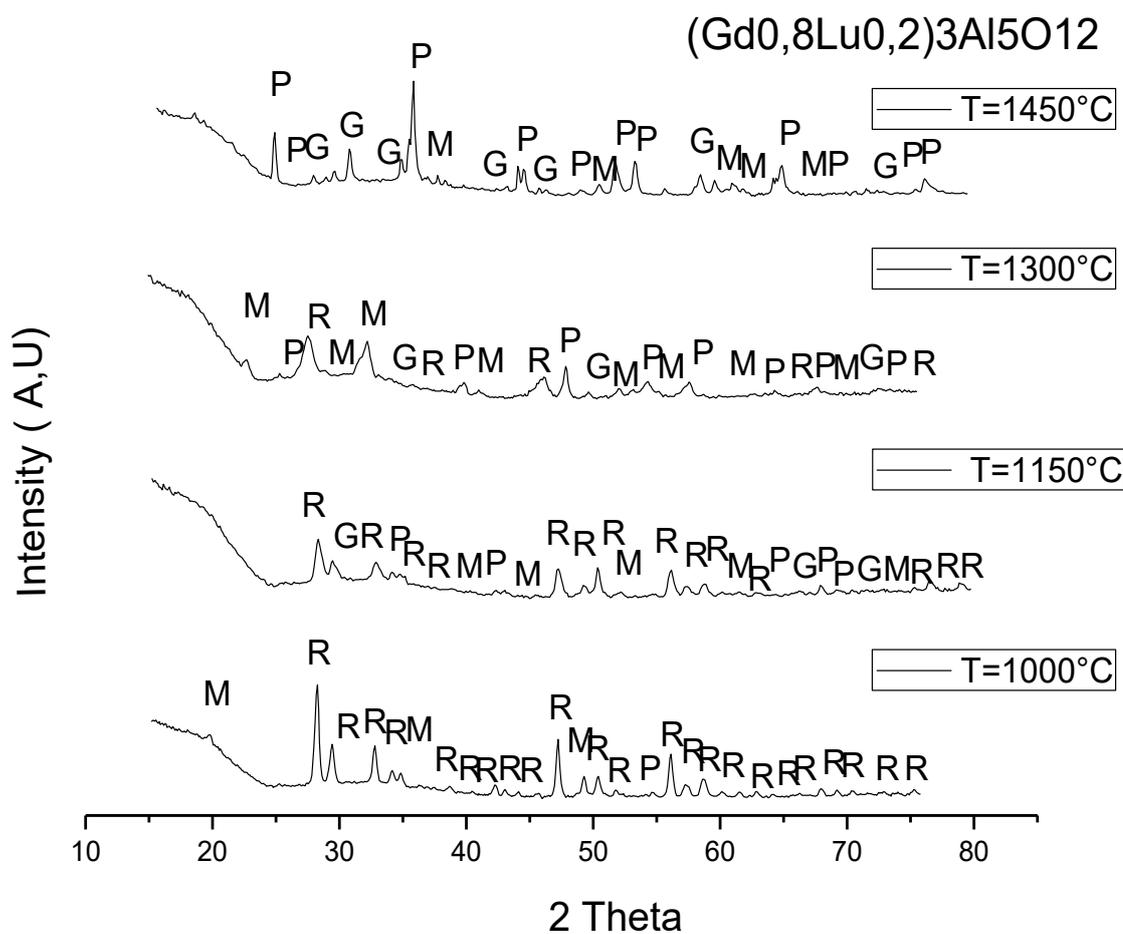
### 2.1. The structural study by XRD

#### 2.1.1: The effect of temperature

For the formation of lanthanide Aluminate Garnet (LnAG), in this work we used:  $\text{Gd}_2\text{O}_3$ ,  $\text{Lu}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$  powders as the raw materials to form  $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$  calcined at a different crystallization temperature elaborated by solid-state reaction method. The reactions leading to form the pure phase LnAG garnet with the evolution of the  $\text{Ln}_4\text{Al}_2\text{O}_9$ ,  $\text{LnAlO}_3$  and  $\text{Ln}_3\text{Al}_5\text{O}_{12}$  stable phases is function with the synthesis temperature, the reactions were identified as follows: [3]



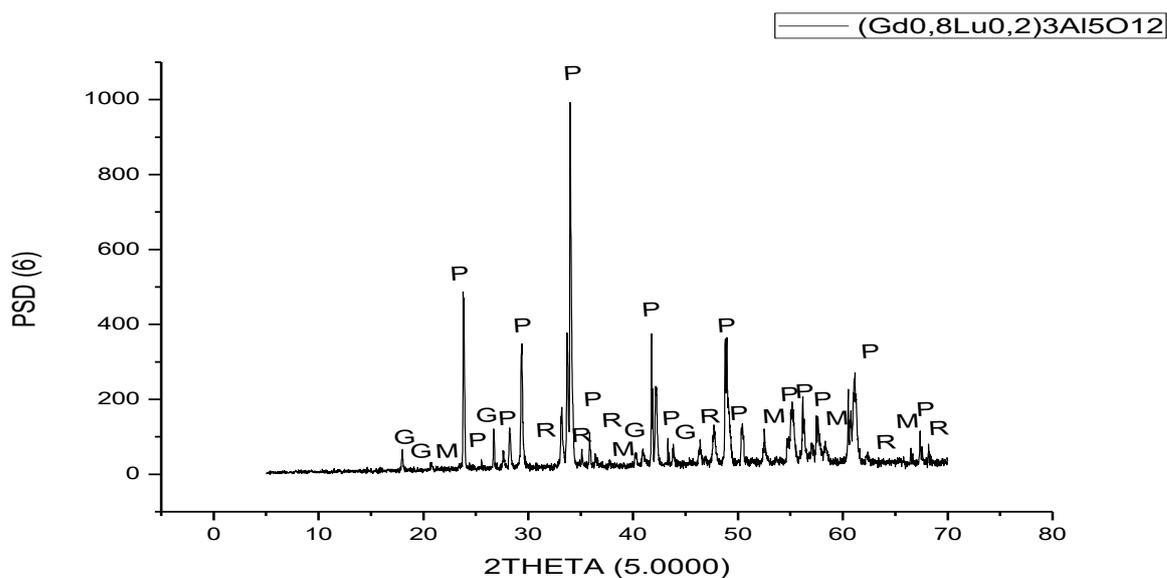
Figure 1 shows the XRD pattern of undoped  $(\text{Gd}_{0.8}\text{Lu}_{0.2})_3\text{Al}_5\text{O}_{12}$  ceramic which represent the evolution of the phases R, M, P and G, of  $\text{Ln}_2\text{O}_3$  sesquioxides, LnAM Monoclinic, LnAP Perovskite, LnAG and Garnet phases, respectively and Ln: Gd and Lu, with the rise of calcined temperature (T=1000, 1150, 1300 and 1450°C).



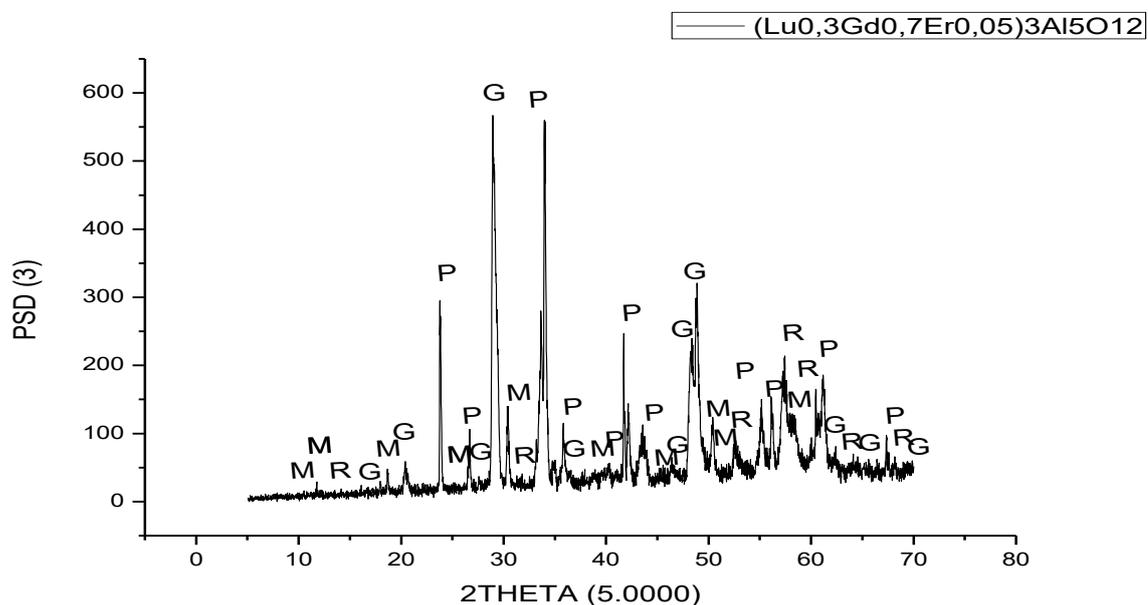
**Fig.1.** XRD pattern of undoped  $(\text{Gd}_{0.8}\text{Lu}_{0.2})_3\text{Al}_5\text{O}_{12}$  ceramic with different temperature of calcination ( $T=1000, 1150, 1300$  and  $1450^\circ\text{C}$ ).

### 2.1.2: The effect of solid solution and doping element

Figure 2 and 3 show the XRD pattern of the samples undoped  $(\text{Gd}_{0.8}\text{Lu}_{0.2})_3\text{Al}_5\text{O}_{12}$  calcined at  $T=1300^\circ\text{C}$  and 5 at %  $\text{Er}^{+3}$  doped  $(\text{Gd}_{0.7}\text{Lu}_{0.3})_3\text{Al}_5\text{O}_{12}$  with  $T=1450^\circ\text{C}$  as synthesis temperature.



**Fig.2.** XRD pattern of undoped  $(\text{Gd}_{0.8}\text{Lu}_{0.2})_3\text{Al}_5\text{O}_{12}$  ceramic calcined at  $T=1300^\circ\text{C}$ , with: **R**, **M**, **P** and **G** represent  $\text{Ln}_2\text{O}_3$  sesquioxides, **LnAM** Monoclinic, **LnAP** Perovskite and **LnAG** Garnet respectively and **Ln = Gd and Lu**.



**Fig.3.** XRD pattern of 5 at % Erbium doped  $(\text{Gd}_{0.7}\text{Lu}_{0.3})_3\text{Al}_5\text{O}_{12}$  ceramic calcined at  $T=1450^\circ\text{C}$ , with: **R**, **M**, **P** and **G** represent  $\text{Ln}_2\text{O}_3$  sesquioxides, **LnAM** Monoclinic, **LnAP** Perovskite and **LnAG** Garnet respectively, and **Ln = Gd, Lu and Er**

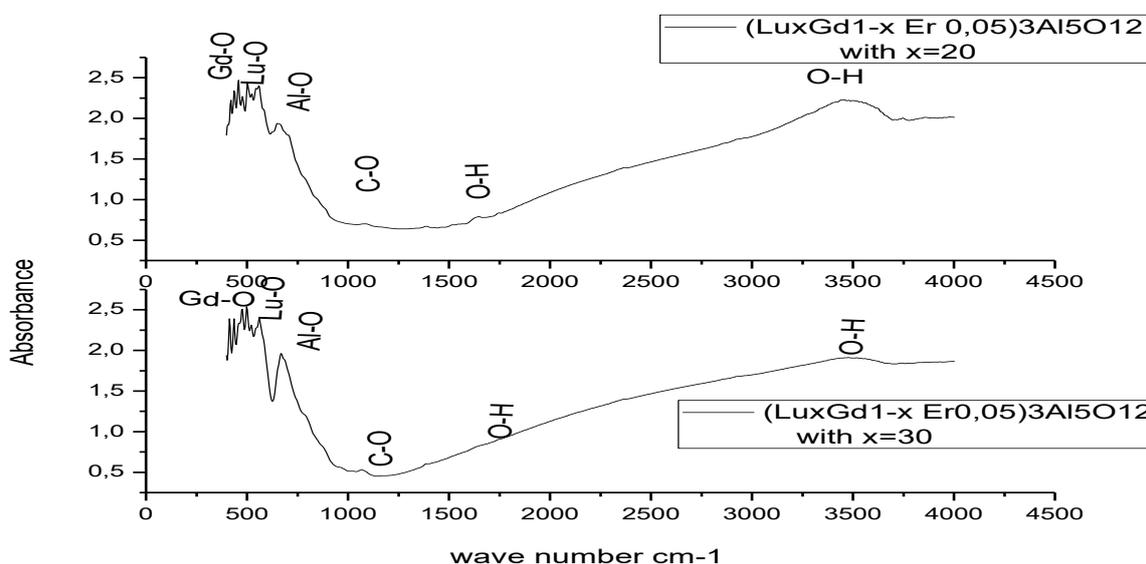
The compounds undoped and 5 at %  $\text{Er}^{+3}$  doped  $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$  ( $x = 0, 2-0, 3$ ) studied shows that high content of gadolinium compared to the content of Lutetium. **Figure 2** XRD pattern of the sample  $(\text{Gd}_{0.8}\text{Lu}_{0.2})_3\text{Al}_5\text{O}_{12}$ , the major phase formed in this cases is the Gadolinium perovskite phase ( $\text{GdAlO}_3$ ), this formation of **GAP** is due to the largest ionic radius of Gadolinium ( $R_{\text{Gadolinium}} = 1.053 \text{ \AA}$ ) compared to Lutetium ( $R_{\text{Lutetium}} = 0.977 \text{ \AA}$ ) and high concentration of Gadolinium, also  $\text{Gd}_2\text{O}_3$  does not form cubic garnet but instead forms only the perovskite structure [1] as it is illustrated in the phase diagram of binary system  $\text{Gd}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$ . The lattice parameters of  $\text{GdAlO}_3$  as major phase are calculated by high score software of this system or it is crystallized in **Pnma** a space group perovskite structure which:  $a = 5.2220 \text{ \AA}$ ,  $b = 7.3630 \text{ \AA}$  and  $c = 5.2050 \text{ \AA}$ . The systems of  $\text{Lu}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  and  $\text{Er}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  formed the garnet phase easily because it's have a weak ionic radius in the coordination 8 which ( $R_{\text{Lutetium}} = 0.977$  and  $R_{\text{Erbium}} = 1.004 \text{ \AA}$ ) [1]. However, the gadolinium element, didn't form the garnet phases as we mentioned before, thus, the stabilization of this compound to form pure garnet phases requires a substitution of a stabilizing element with a weaker ionic radius than that of gadolinium ( $R_{\text{Gadolinium}} < 1.053 \text{ \AA}$ ). When the calcination temperature increased with the increase of content of Lutetium as element stabilization of the Gadolinium Garnet structure, it exists perovskite phases but the major phases will be  $\text{Gd}_3\text{Al}_5\text{O}_{12}$  and not  $\text{GdAlO}_3$  with the appearance of intermediates phases as Monoclinic Garnet  $\text{RE}_4\text{Al}_2\text{O}_9$  (**REAM**),  $\text{RE}_2\text{O}_3$  sesquioxides with  $\text{RE} = (\text{Gd and Lu})$ . In the case of the sample  $[(\text{Gd}_{0.7}\text{Lu}_{0.3})_{0.95}\text{Er}_{0.05}]_3\text{Al}_5\text{O}_{12}$  which presented in the figure 3, which shows the increase of synthesis temperature with the augmentation of content of Lutetium, with rare earth doping element which has ionic radius weaker than that gadolinium, our choice was reported on  $\text{Er}_2\text{O}_3$  as doping element. We noted that the major phases are cubic garnet, this structure of  $\text{Gd}_3\text{Al}_5\text{O}_{12}$  with space group **Ia-3d** with the standard card (**GdAG**, JCPDS file No. **1-73-1371**), of lattice parameters  $a = b = c = 12.1130 \text{ \AA}$ . It is seen that the formation of the Garnet increases with decreased gadolinium substitution which decreases average radius of the rare earth ion to  $1.0454 \text{ \AA}$ , can effectively stabilize **GdAG** because the garnet structure is stable for the rare-earth ions with smaller ionic radius than  $\text{Gd}^{3+}$ , which presents boundary element for the garnet structure to be formed [1].

It was also noted that the diffraction peaks corresponding to  $\text{Al}_2\text{O}_3$  were absent for the two samples ( $x=0.2$  and  $0.3$ ). For the initial stoichiometry, unreacted  $\text{Al}_2\text{O}_3$  should remain in the calcined products of these samples up to  $1450^\circ\text{C}$ , because the remaining portion of  $\text{Al}_2\text{O}_3$  reacts with GAP to form pure GAG Garnet at higher temperatures ( $T > 1500^\circ\text{C}$ )[3].

## 2.2. The vibrational study by FTIR

### 2.2.1. $(\text{Lu}_x\text{Gd}_{1-x}\text{Er}_{0.05})_3\text{Al}_5\text{O}_{12}$ ceramics which ( $x=0.2$ and $0.3$ ):

The compounds 5 at % $\text{Er}^{+3}$  doped  $[(\text{Lu}_x\text{Gd}_{1-x})_{0.95}\text{Er}_{0.05}]_3\text{Al}_5\text{O}_{12}$  elaborated in the  $T=1450^\circ\text{C}$ , the figure.3 shows FTIR spectra of these systems with the variation of the solid solution which  $x=0.2$  and  $0.3$



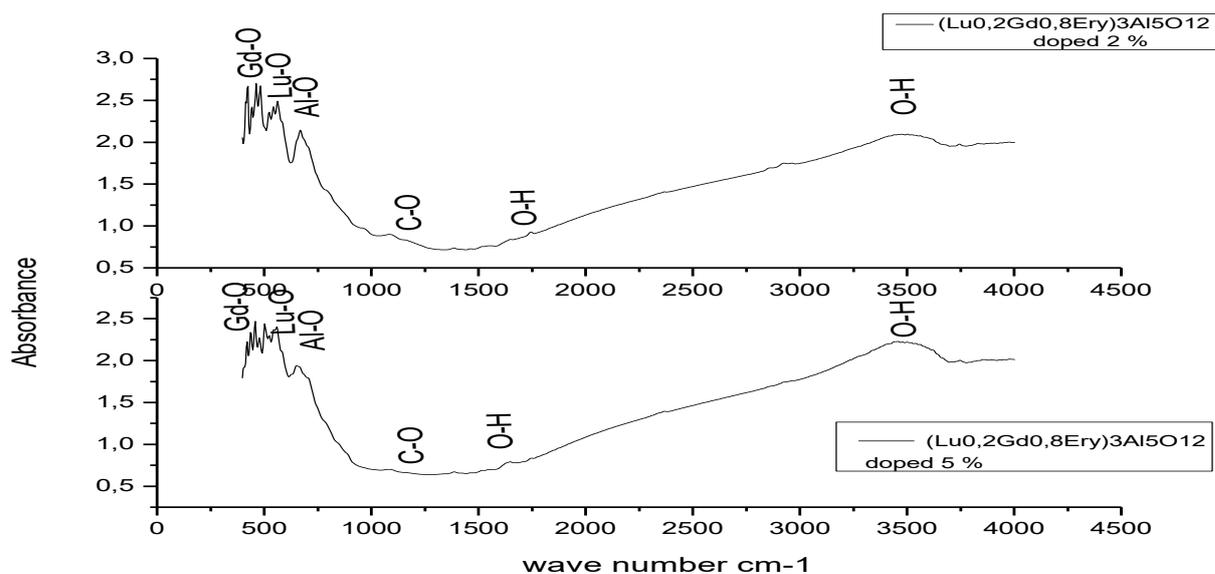
**Fig.4.** FT-IR spectra for the samples which the solide solution  $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$  ( $x = 0, 2 - 0, 3$ ) doped with 5 at % $\text{Er}_2\text{O}_3$  calcinated with  $T=1450^\circ\text{C}$

FT-IR spectra were established in the wave number range from  $400\text{-}4000\text{ cm}^{-1}$  to a different solid solution ( $x = 0.2$  and  $0.3$ ) present by actifs vibrations modes in IR of the all phases appeared in this two elaborated samples. Figure 4 and 5 present the absorption peaks near at  $3000\text{-}3710\text{ cm}^{-1}$  which are due to  $\text{H}_2\text{O}$  stretching [4], the peak  $\sim 3480\text{ cm}^{-1}$ [3] and near  $1643\text{ cm}^{-1}$  [3] provide evidence of water of hydration in the structure or surface adsorbed water and are assignable to the O-H stretching vibrations and the H-O-H bending mode, respectively. The absorption band observed in the range  $\sim 3500\text{-}3750\text{ cm}^{-1}$  is indicative of

hydroxyl (OH) groups[5], the band that appears at **1071 cm<sup>-1</sup>** can be mentioned for the **C–O** symmetric stretching vibration,[5] and the bands around **1520** and **1378 cm<sup>-1</sup>** result from the **C–O asymmetrical stretching**, on the other hand **–C=C–** bond in the synthesized compound is represented by the peak at **1564 cm<sup>-1</sup>** which is due to the absorption of atmospheric carbon, the peaks **1171** and **1387 cm<sup>-1</sup>** and **1700–1600 cm<sup>-1</sup>** domains can be assigned to vibrations of stretching-**CO-OH** groups[5]. However, a specific speaks in the **400-1000 cm<sup>-1</sup>** regions of the IR spectra which the strong and broad absorption bands may be attributed to the characteristic **M–O (M: Gd, Lu, Al)** vibrations, which the vibration modes peaks of **Gd–O** in **GdAlO<sub>3</sub>** [6] [7],[8], [9], and [10], corresponding the peaks at **415 ,420, 456 and 520 cm<sup>-1</sup>**, and the peaks about **437 , 450 and 542 cm<sup>-1</sup>** can be assigned to bond **Gd–O** stretching and bending vibrations in **Gd<sub>2</sub>O<sub>3</sub>**[4] [10] [11] and [12] also the absorption bands in the range of **477 and 583 cm<sup>-1</sup>** can be ascribed to **Lu–O** stretching modes in **Lu<sub>2</sub>O<sub>3</sub>**[13] and [14] moreover , the peaks at **465 and 650 and 669 cm<sup>-1</sup>** appeared due to stretching frequency characteristic vibration of **Al– O** in **GdAlO<sub>3</sub>** [15]. The spectrum consists the vibrations of the isolated **[AlO<sub>4</sub>]** and **[AlO<sub>6</sub>]** at **799** and **739 cm<sup>-1</sup>** in Tetrahedral and Octahedral sites respectively, which indicates that the pure and **Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>** phase was formed[16]. For the absorption peaks of Gadolinium Garnet [**(Gd<sub>0.8</sub>Lu<sub>0.2</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>**] and [**(Gd<sub>0.7</sub>Lu<sub>0.3</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>**] [3], were appeared at **600 cm<sup>-1</sup>** from **M–O** vibration[3]. This result coincides well with the **XRD** patterns.

### 2.2.2. (Lu<sub>0.2</sub>Gd<sub>0.8</sub>Er<sub>y</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> Ceramic which (y = 2 at%, 5at%)

The systems **(Lu<sub>0.2</sub>Gd<sub>0.8</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>** doped with different concentrations which **[(Lu<sub>0.2</sub>Gd<sub>0.8</sub>)<sub>0.98</sub>Er<sub>0.02</sub>]<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>** calcined with **T= 1300°C** synthesis temperature and **[(Lu<sub>0.3</sub>Gd<sub>0.7</sub>)<sub>0.95</sub>Er<sub>0.05</sub>]<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>** synthesized with **T=1450°C**. The figure 5 shows **FTIR** spectra of these systems with the variation ( **2 at%, 5at%**) of doping element.



**Fig.5.** FT-IR spectra of  $\text{Er}^{+3}$  doped  $(\text{Gd}_{0.8}\text{Lu}_{0.2})_3\text{Al}_5\text{O}_{12}$  with (2 at% calcined at  $T=1300^\circ\text{C}$  and 5 at% calcined at  $T = 1450^\circ\text{C}$ )

FT-IR spectra with a 2 at% and 5 at %  $\text{Er}^{+3}$  doped  $(\text{Gd}_{0.8}\text{Lu}_{0.2})_3\text{Al}_5\text{O}_{12}$  presented by the different modes of vibrations of all phases appeared as we mentioned before, with the modes actifs in IR, Gd-O and Al-O vibrations modes of  $\text{GdAlO}_3$  and  $\text{Gd}_3\text{Al}_5\text{O}_{12}$  which represents the most phases mentioned by DRX, in the case of the little difference between the doping element percentage (2 and 5%) of  $\text{Er}^{+3}$  doped  $(\text{Lu}_{0.2}\text{Gd}_{0.8})_3\text{Al}_5\text{O}_{12}$  also the difference between the synthesis temperature caused a different intensities of absorption vibrations and a shift in vibrations modes on the sites occupied by these samples. There is not a significant contribution with a small difference in concentration of the doping element 2 at% and 5 at %  $\text{Er}^{+3}$  doped  $(\text{Gd}_{0.8}\text{Lu}_{0.2})_3\text{Al}_5\text{O}_{12}$ .

### 2.3. The photoluminescence study

#### 2.3.1. $(\text{Lu}_{0.2}\text{Gd}_{0.8})_{1-y}\text{Er}_y$ and $(\text{Lu}_{0.3}\text{Gd}_{0.7})_{1-y}\text{Er}_y$ $_3\text{Al}_5\text{O}_{12}$ ceramic ( $y = 2$ and 5 at%):

The figures 6, 7 and 8 show the emission spectra of the systems  $[(\text{Gd}_{1-x}\text{Lu}_x)_{1-y}\text{Er}_y]_3\text{Al}_5\text{O}_{12}$  studied in the visible domain with an excitation 489nm for Erbium doping element. Due to the Erbium transitions as activator element and stark splitting of these compounds  $\text{Er}^{+3}$ [11], [17] doped  $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$ , all the samples were shown two types of transitions Erbium. The results are presented in Fig. 5, 6, 7. Two types of transitions were detected in this range of

this study:  $^2H_{11/2}$  to  $^4I_{15/2}$  and  $^4S_{3/2}$  to  $^4I_{15/2}$ . The emission peaks were represented by the broad peaks centered at a wavelength range (from 520 to 565 nm). Also we can divided this range into three regions: we have in the first region for the different waves lengths corresponding to the transitions  $^2H_{11/2}$ ,  $^4S_{3/2}$  to  $^4I_{15/2}$  of Erbium in the Garnet phases [18] of all the elaborated samples, and the second one corresponding to the waves lengths represent the transitions of  $^2H_{11/2}$ ,  $^4S_{3/2}$  to  $^4I_{15/2}$  of Erbium in the Perovskites phases [19]. Also, the third one represent these transitions of  $Er^{3+}$  in the sesquioxides phases [11], which implies the emission of the samples  $[(Lu_xGd_{1-x})_{1-y}Er_y]_3Al_5O_{12}$  ( $x = 0.2, 0.3$  and  $y = 2$  and  $5$  at %). **Figure 6** shows the emission spectrum of the **5 at%  $Er^{3+}$**  doped  $(Gd_{0.8}Lu_{0.2})_3Al_5O_{12}$ , it is noted that the transitions peaks of Erbium in the  $Gd_2O_3$  sesquioxides phases (**549 and 563 nm**) have disappeared completely due to quenching concentration of Erbium in this phase [18]. As well as the transitions peaks of the activator element ( $Er^{3+}$ ) in the Garnet phases and the perovskite phases tends to weaken comparing with **Figure 7** which shows the emission spectrum of the sample **5 at%  $Er^{3+}$**  doped  $(Gd_{0.7}Lu_{0.3})_3Al_5O_{12}$ , which is due to the position of the Erbium transitions in the sesquioxide phase ( $Gd_2O_3$ ) that separate  $Er^{3+}$  transitions in the Garnet and Perovskite phases in the sample **5 at%  $Er^{3+}$**  doped  $(Gd_{0.8}Lu_{0.2})_3Al_5O_{12}$ . In addition,  $Gd_2O_3$ ,  $Er_2O_3$  with  $Lu_2O_3$  and  $\alpha-Al_2O_3$  considered as raw materials to form **LnAM**, **LnAP**, then **LnAG** phases respectively with depending on the calcination temperature [3].

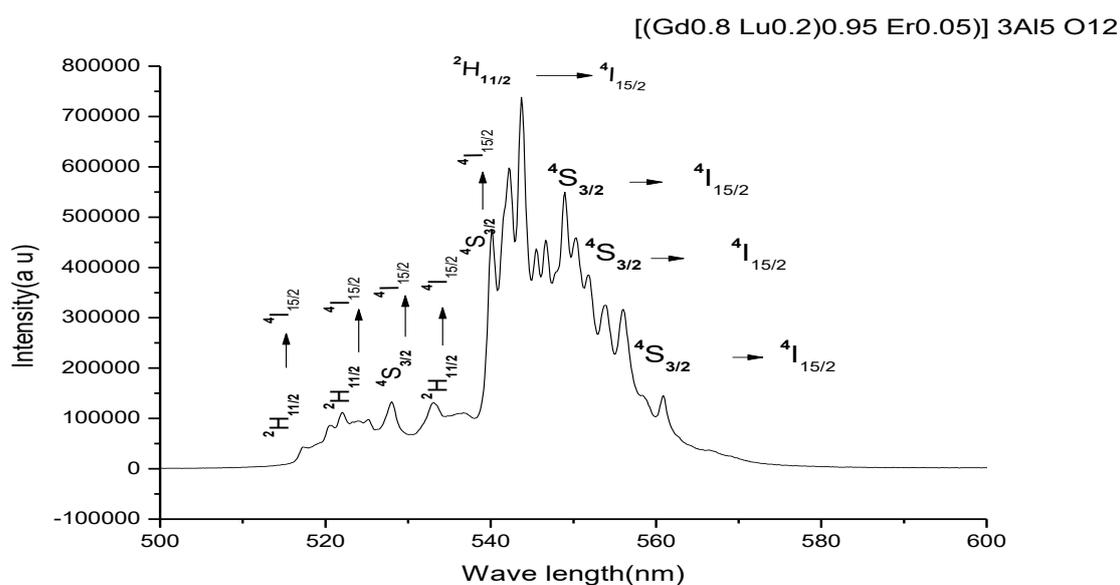
For the attribution of  $Gd^{3+}$  exhibit higher lattice covalency and charge transfer excitation band (CTB) centers owing to the lower electronegativity in the systems  $(Gd_{1-x}Lu_x)_3Al_5O_{12}$  [21] doped rare earth [2]. **Table1** shows the different values of electronegativity  $\chi$  of the elements **Gd** and **Lu** in the systems  $(Gd_{0.8}Lu_{0.2})_3Al_5O_{12}$  and  $(Gd_{0.7}Lu_{0.3})_3Al_5O_{12}$  compared with  $\chi$  of  $Ln_3Al_5O_{12}$  which **Ln: Lu, Y, and Gd**.

**Table1:** The different electronegativity  $\chi$  of the samples  $[(Lu_xGd_{1-x})_{1-y}Er_y]_3Al_5O_{12}$  ( $x=0.2, 0.3$ )

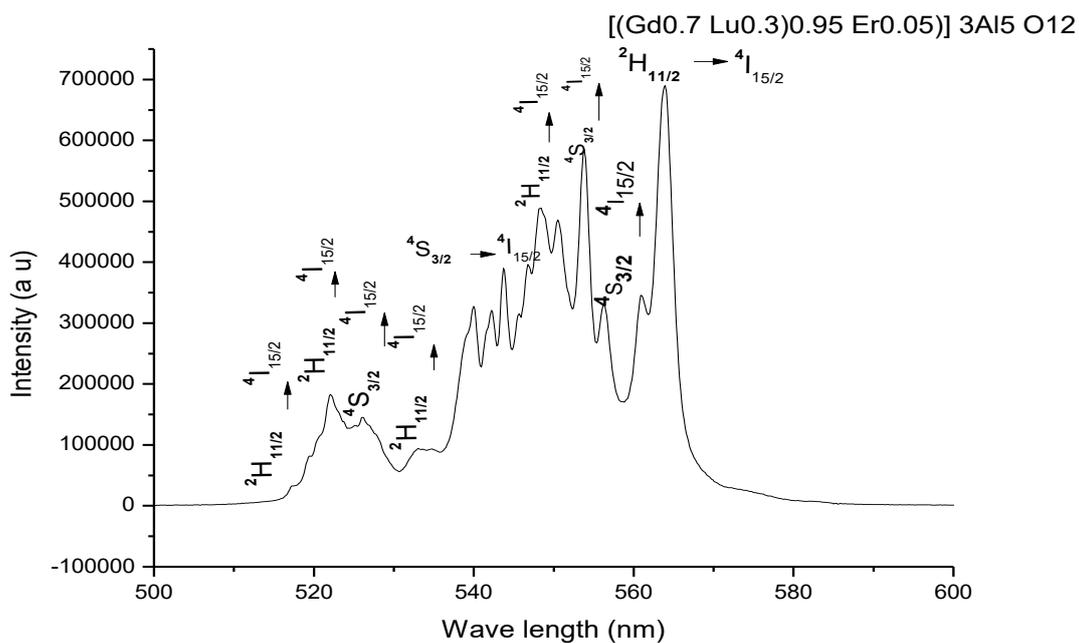
Electronegativity values of $(Gd_{0.8}Lu_{0.2})_3Al_5O_{12}$ and $(Gd_{0.7}Lu_{0.3})_3Al_5O_{12}$ [21]				
LuAG	YAG	GAG	$(Gd_{0.8}Lu_{0.2})AG$	$(Gd_{0.7}Lu_{0.3})AG$
1.27	1.22	1.2	1.214	1.221

For the effect of the Gadolinium ( $\text{Gd}^{3+}$ ) on the activator element, if the gadolinium content is increased, the intensities of Erbium ( $\text{Er}^{3+}$ ) emission will become higher due to the transfer of Gadolinium energy to the Erbium activator element in the  $[(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}]$  phases Garnets and  $\text{GdAlO}_3$  Perovskites appeared [2], [22], On the other hand, for the Erbium doped  $\text{Gd}_2\text{O}_3$  phase [12], [11] and [20].

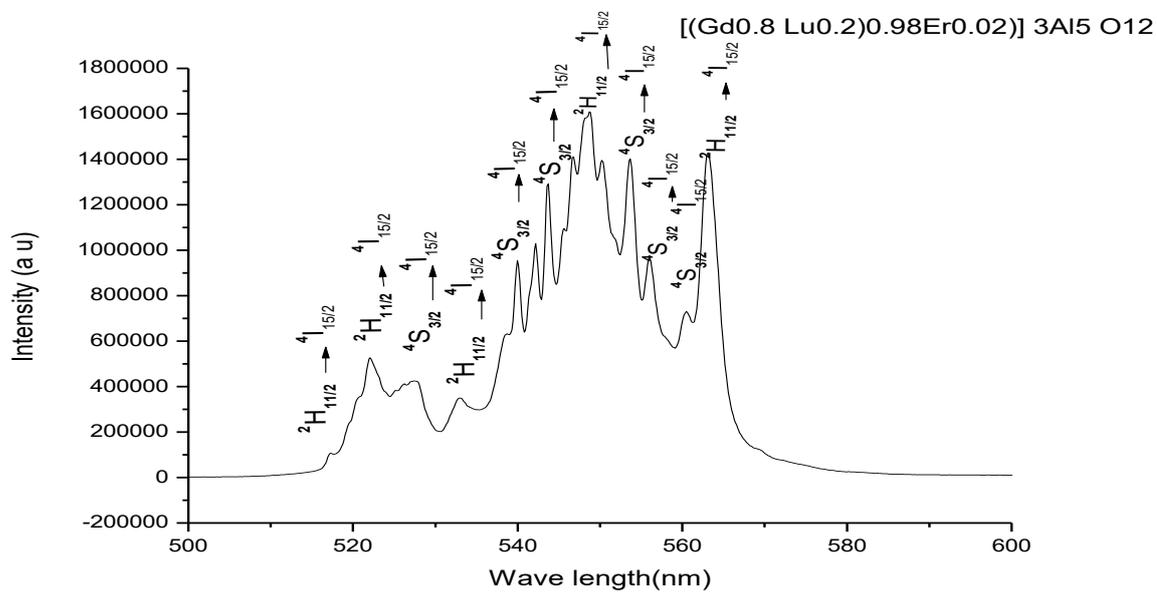
But in our case, there is the case of the sample  $(\text{Gd}_{0.8}\text{Lu}_{0.2})_{0.95}\text{Er}_{0.05}]_3\text{Al}_5\text{O}_{12}$  which have the Gadolinium content is wider, and quenching Erbium concentrations of the phase  $\text{Gd}_2\text{O}_3$ , but for the content of Gd equal to 0.7 in the sample  $(\text{Gd}_{0.7}\text{Lu}_{0.3})_{0.95}\text{Er}_{0.05}]_3\text{Al}_5\text{O}_{12}$ , has a better emission which due to the energy transfer from Gd to the Erbium activator element in the Garnet phases, Perovskites, as well as the effect of doping with Erbium in the  $\text{Gd}_2\text{O}_3$  phases in the elaborate sample  $(\text{Gd}_{0.7}\text{Lu}_{0.3})_{0.95}\text{Er}_{0.05}]_3\text{Al}_5\text{O}_{12}$ .



**Fig.6.** PL spectrum of the sample  $[(\text{Gd}_{0.8}\text{Lu}_{0.2})_{0.95}\text{Er}_{0.05}]_3\text{Al}_5\text{O}_{12}$



**Fig.7.** PL spectrum of the sample  $[(\text{Gd}_{0.7}\text{Lu}_{0.3})_{0.95}\text{Er}_{0.05}]_3\text{Al}_5\text{O}_{12}$



**Fig.8.** PL spectrum of the sample  $[(\text{Gd}_{0.8}\text{Lu}_{0.2})_{0.98}\text{Er}_{0.02}]_3\text{Al}_5\text{O}_{12}$

**Table 2:** The different relative transitions of the samples  $[(\text{Lu}_x\text{Gd}_{1-x})_{1-y}\text{Er}_y]_3\text{Al}_5\text{O}_{12}$  ( $x=0.2$ ,  $0.3$ ) and ( $y=2$  and  $5\%$ ) compared with Erbium transitions of all phases from the literature

Elaborated Samples	Wave length (nm)	Transitions	Wave length (nm) (literature)	Phases	References
$(\text{Gd}_{1-x}\text{Lu}_x)_{1-y}\text{Er}_y]_3\text{Al}_5\text{O}_{12}$ with ( $x=0.2$ and $0.3$ ) and ( $y=2$ and $5\text{at}\%$ )	516	$^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$	509, 510	$\text{Er}^{3+}$ doped $\text{GdAlO}_3$	[19]
	520-522	$^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$	523	$\text{Er}^{3+}$ doped $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$	[18]
	527	$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	525	$\text{Er}^{3+}$ doped $\text{GdAlO}_3$	[4]
	533- 537	$^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$	538	$\text{Er}^{3+}$ doped $\text{GdAlO}_3$	[19]
	542-543-546	$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	540	$\text{Er}^{3+}$ doped $\text{GdAlO}_3$	[19]
	548,549	$^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$	546	$\text{Er}^{3+}$ doped $\text{Gd}_2\text{O}_3$	[11]
	550-552-553	$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	555	$\text{Er}^{3+}$ doped $\text{GdAlO}_3$	[19]
	556	$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	556	$\text{Er}^{3+}$ doped $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$	[18]
	559	$^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$	559	$\text{Er}^{3+}$ doped $\text{GdAlO}_3$	[4]
	561	$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	560	$\text{Er}^{3+}$ doped $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$	[18]
	563	$^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$	563	$\text{Er}^{3+}$ doped $\text{Gd}_2\text{O}_3$	[11]

From the photoluminescence spectra present in the figures 6 and 8 of elaborated samples (2 and 5at % doped Erbium, and with the same solid solution  $(\text{Gd}_{0.8}\text{Lu}_{0.2})_3\text{Al}_5\text{O}_{12}$ , the sample doped with 2 at%  $\text{Er}^{3+}$  has a stronger emission than that the sample  $(\text{Gd}_{0.8}\text{Lu}_{0.2})_3\text{Al}_5\text{O}_{12}$  doped with 5 at% [17].

Particularly, the figures 7 and 8 compare the PL spectra of the samples  $[(\text{Gd}_{0.7}\text{Lu}_{0.3})_{0.95}\text{Er}_{0.05}]_3\text{Al}_5\text{O}_{12}$  and  $[(\text{Gd}_{0.8}\text{Lu}_{0.2})_{0.98}\text{Er}_{0.02}]_3\text{Al}_5\text{O}_{12}$  calcined at different temperature 1450 and 1300°C respectively. The green light intensity of the emission increase with the increase of the  $\text{Er}^{3+}$  concentration, and with calcination temperature [2].

The emission tends to deteriorate with increasing Lu incorporation, which can be due to the lattice distortion of the large size between  $\text{Gd}^{3+}$  and  $\text{Lu}^{3+}$  [21], it is also seen from Table 1 that the electronegativity tends to be bigger with more Lu in these studied systems. The better luminescence of the  $x=0.3$  than  $x=0.2$  sample could be due to its higher crystallinity of the  $[(\text{Gd}_{0.7}\text{Lu}_{0.3})_{0.95}\text{Er}_{0.05}]_3\text{Al}_5\text{O}_{12}$ , since it has already crystallized in garnet phase at the low temperature compared with the system  $[(\text{Gd}_{0.8}\text{Lu}_{0.2})_{0.98}\text{Er}_{0.02}]_3\text{Al}_5\text{O}_{12}$  [21]. It should be noted that a small shift of variation of the position and the value of the wavelength in the samples  $[(\text{Gd}_{0.8}\text{Lu}_{0.2})_{0.98}\text{Er}_{0.02}]_3\text{Al}_5\text{O}_{12}$  and  $[(\text{Gd}_{0.7}\text{Lu}_{0.3})_{0.95}\text{Er}_{0.05}]_3\text{Al}_5\text{O}_{12}$

$\text{O}_{12}$  it can be due to the amount of Gadolinium substituted with Lutetium in the solid solution which  $x = 0.2$  and  $0.3$  with the difference of Erbium doping element concentrations well the effect of synthesis temperature [18], but in general does not change the spectrum feature.

### 3. EXPERIMENTAL

$(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$  ( $x = 0, 2 - 0, 3$ ) undoped or doped 2 and 5 at %  $\text{Er}_2\text{O}_3$  ceramics were fabricated by a solid state reaction method. Alfa  $-\text{Al}_2\text{O}_3$  (99.99%),  $\text{Lu}_2\text{O}_3$  (99.99%),  $\text{Gd}_2\text{O}_3$ (99.99%) and  $\text{Er}_2\text{O}_3$  (99.99%) powders were mixed very well in agate mortar and calcined at different temperature  $T = 1000, 1150, 1300$  and  $1450^\circ\text{C}$  during long time. also a synthesis was carried out for the samples doped 2% Erbium  $(\text{Gd}_{0.8}\text{Lu}_{0.2})_3\text{Al}_5\text{O}_{12}$  at  $T = 1300^\circ\text{C}$  during 24 h and 5% Erbium  $(\text{Gd}_{0.7}\text{Lu}_{0.3})_3\text{Al}_5\text{O}_{12}$  at  $T = 1450^\circ\text{C}$  during 72 h with heating rate was  $5^\circ\text{C}/\text{min}$ . The samples  $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$  were synthesized by the solid state reaction accordingly to the following chemicals equations:



After the elaboration of powders ceramics, undoped and doped with 2 and 5 at%  $\text{Er}_2\text{O}_3$ , the phases of the samples were identified by X-ray diffraction which they were obtained with a Bragg-Brentano Bruker D8 Advance diffractometer working with the Cu K $\alpha$  radiation, thanks to a backward monochromator, then we also detailed the vibrational studies of characterization by the Infrared spectroscopy using a JASCO-4100 FTIR Fourier Transform Spectrometer as KBr pellets in the  $4000\text{-}400\text{ cm}^{-1}$  region. The photoluminescence (PL), with an excitation by Laser used for the visible luminescence analysis was performed with an Ekspla NT342 optical parametric oscillator (OPO), with a resolution of 0.2 nm using 1200 lines/mm, and analyzed with an iSTAR CCD.

#### 4. CONCLUSION

The elaborated samples undoped and  $\text{Er}^{+3}$  doped  $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$  prepared by the solid state reaction method. The substitution of Gadolinium by Lutetium can be stabilize the phase Garnet, with the increase of temperature of synthesis. Structural **XRD** analysis of undoped or Erbium doped  $[(\text{Gd}_{1-x}\text{Lu}_x)]_3\text{Al}_5\text{O}_{12}$  with the rise of calcination temperature which  $T=1000,1150,1300$  and  $1450^\circ\text{C}$  show the appearance of the phases  **$\text{Ln}_2\text{O}_3$ ,  $\text{LnAM}$ ,  $\text{LnAP}$**  than  **$\text{LnAG}$**  respectively. Also, presence of the Perovskite ( **$\text{GdAlO}_3$** ) as major phase in high proportion (**0.8**), with calcination temperature equal to  **$1300^\circ\text{C}$** , but if we increase the temperature to  **$1450^\circ\text{C}$**  with the decrease of the content of Gadolinium and increase the content of Lutetium with Erbium as activator doping element which has a smaller ionic radius compared with Gd, the major phase is Garnet of Gadolinium ( **$\text{Gd}_3\text{Al}_5\text{O}_{12}$** ), with others phases as **sesquioxides, monoclinic Garnet, and perovskites**, due to the lower synthesis temperature. We have also refined the lattice parameters of our materials with X'pert High score software. **XRD** analysis shows an orthorhombic perovskite network of  **$\text{Pnma}$**  space group of lattice parameters  **$a = 5.2220 \text{ \AA}$ ,  $b = 7.3630 \text{ \AA}$  and  $c = 5.2050 \text{ \AA}$**  for Lutetium concentration  **$x=0.2$** , and a cubic garnet phase of space group  **$\text{Ia-3d}$**  of lattice parameters  **$a = b = c = 12.1130 \text{ \AA}$**  for concentration  **$x= 0.3$**  with Erbium doping element that has a lower ionic radius than gadolinium with concentrations chosen in this study **2 and 5 at%**.

The vibrational study by **FT-IR** spectroscopy was an essential step to determine the bands characterizing the **Gd-O, Lu-O and Al-O**, the specific modes of vibration of the phases appeared in our compounds with others vibrational modes as **O-H, C-O, C-C CO-OH ....**The photoluminescence spectra of  $\text{Er}^{+3}$  doped  $(\text{Lu}_x\text{Gd}_{1-x})_3\text{Al}_5\text{O}_{12}$  show the appearance of the others peaks due to the existence of the differents phases with the major  **$\text{GdAlO}_3$**  and  **$\text{Gd}_3\text{Al}_5\text{O}_{12}$**  as majorities phases appeared with concentrations  **$x=0.2$  and  $x =0.3$** . The concentration **5 at%** of the Erbium of the sample  $[(\text{Gd}_{0.8}\text{Lu}_{0.2})]_3\text{Al}_5\text{O}_{12}$  presents the case of quenching for the  **$\text{Gd}_2\text{O}_3$**  phase, and the **PL** spectrum of this sample is lower than the samples **2 and 5 at%**  $[(\text{Gd}_{0.8}\text{Lu}_{0.2})]_3\text{Al}_5\text{O}_{12}$  and  $[(\text{Gd}_{0.7}\text{Lu}_{0.3})]_3\text{Al}_5\text{O}_{12}$  respectively. The emission intensities of  $[(\text{Gd}_{0.7}\text{Lu}_{0.3})_{0.95}\text{Er}_{0.05}]_3\text{Al}_5\text{O}_{12}$  and  $[(\text{Gd}_{0.8}\text{Lu}_{0.2})_{0.98}\text{Er}_{0.02}]_3\text{Al}_5\text{O}_{12}$  increase

with the increase of synthesis temperature and Erbium doping element concentration.

## 5. REFERENCES

- [1] Jinkai Li, Ji-Guang Li, Jing Li, Shaohong Liu, Xiaodong Li, Xudong Sun, Yoshio Sakka, Development of  $\text{Eu}^{3+}$  activated monoclinic, perovskite, and garnet compounds in the  $\text{Gd}_2\text{O}_3$ – $\text{Al}_2\text{O}_3$  phase diagram as efficient red-emitting phosphors. *Journal of Solid State Chemistry* 206 (2013) 104–112.
- [2] Ji-Guang Li and Yoshio Sakka, , 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan. Doi:10.1088/1468-6996/16/1/014902.
- [3] Jinkai Li, Ji-Guang Li, Zhongjie Zhang, Xiaoli Wu, Shaohong Liu, Xiaodong Li, Xudong Sun, and Yoshio Sakka. *J. Am. Ceram. Soc.*, 95 [3] 931-936 (2012). Doi: 10.1111/j.1551-2916.2011.04991.x
- [4] Raunak kumar Tamrakar, Kanchan Upadhyay, Manjulata Sahu, Spectral characterization of  $\text{Er}^{3+}$ ,  $\text{Yb}^{3+}$  co doped  $\text{GdAlO}_3$  phosphor prepared by solid state reaction method, *Journal of Alloys and Compounds* 689 (2016) 702-712.
- [5] BOUKERIKA ALLAOUA, thèse du doctorat, Elaboration par voie sol-gel et caractérisation des matériaux inorganiques de type grenats (Y, Lu)  $_3\text{Al}_5\text{O}_{12}$  activés aux ions cérium, Université de Jijel, Faculté des Sciences exactes et informatique. Département de Physique en 2014.
- [6] Higor Henrique de Souza Oliveira, Marco Aurélio Cebim, Alison Abreu da Silva, and Marian Rosaly Davolos, Structural and Spectroscopic Studies of  $\text{Pr}^{+3}$  Doped  $\text{GdAlO}_3$ , *IEEE TRANSACTIONS ON NUCLEAR SCIENCE*, VOL. 57, NO. 3, JUNE 2010.
- [7] S. Cizauskaite, V. Reichlova, G. Nenartaviciene, A. Beganskiene, J. Pinkas, A. Kareiva, Sol-gel preparation and characterization of gadolinium aluminate, *Materials Chemistry and Physics* 102 (2007) 105–110.
- [8] GIRISH H. N, BASAVALINGU B, SHAO G.-Q, SAJAN C. P., S. K. VERMA, *Materials Science-Poland*, 33(2), 2015, pp. 301-305 <http://www.materialsscience.pwr.wroc.pl/Doi:10.1515/msp-2015-0045>.

- [9] S.K. Saji , R. Vinodkumar , Shibu M. Eappen , P.R. SobhanaWariar ,Optical and dielectric characterization of gadolinium aluminate ceramic nanoparticles synthesized by combustion technique, *Materials Chemistry and Physics* 193 (2017) 189-195.
- [10] N. Dhananjaya H. Nagabhushana , B.M. Nagabhushana , R.P.S Chakradhar , C. Shivakumara , B. Rudraswamy , Synthesis, characterization and photoluminescence properties of  $Gd_2O_3:Eu^{3+}$  nanophosphors prepared by solution combustion method, *Physica B* 405 (2010) 3795–3799.
- [11] LI Yanhong, HONG Guangyan, ZHANG Yongming, DAI Caiyun, DAI Shuping, Vol.23 No.4. Doi 10.1007/s11595-007-4448-0.
- [12] Guodong Xia, Sumei Wang<sup>1</sup>, Shengming Zhou<sup>1</sup>, 4 and Jun Xu. *Nanotechnology* 21 (2010) 345601 (5pp). Doi:10.1088/0957-4484/21/34/345601.
- [13] LiLi, Xingli Zhang, Xiantao Wei, Guangchuan Wang, and Changxin Guo, Near-Infrared to Visible Up-conversion in  $Tm^{3+}$  and  $Yb^{3+}$ Codoped  $Lu_2O_3$ Nanocrystals Synthesized by Hydrothermal Method, *Journal of Nanoscience and Nanotechnology*, Vol. 14, 4313–4319, 2014 .
- [14] HaiGuo , Min Yin, Ning Dong, Mei Xu, Liren Lou, Weiping Zhang, Effect of heat-treatment temperature on the luminescent properties of  $Lu_2O_3:Eu$  film prepared by Pechini sol–gel method, *Applied Surface Science* 243 (2005) 245–250.
- [15] N. Dubnikova, E. Garskaite, J. Pinkas , P. Bezdicka , A. Beganskiene , A. Kareiva. *J Sol-Gel Sci Technol* (2010) 55:213–219. Doi: 10.1007/s10971-010-2235-4.
- [16] R. Praveena, Luminescence Properties of  $Lu_3Al_5O_{12}:Tb^{3+}$  Nano-garnet, *Journal of the Korean Physical Society*, Vol. 64, No. 12, June 2014, pp. 1859~1865.
- [17] H. Xu, S. Kröll, Up-conversion dynamics in  $Er^{3+}$  -doped YAG, *Journal of Luminescence* 111 (2005) 191-198.
- [18] Jinkai Li, Ji-Guang Li, Xiaodong Li, Xudong Sun, Up-conversion luminescence of new Phosphors of  $Gd_3Al_5O_{12}: Yb/Er$  stabilized with  $Lu^{3+}$ , *Ceramics International* 42 (2016)3268-3274.
- [19] A. Brenier, A.M. Jurdyc, H. Verweij, M.T. Cohen-Adad, G. Boulon, Up-conversion dynamics in  $GdAlO_3: Er^{3+}$  single crystal fibre, *Optical Materials* 5 (I 996) 233-238, May

1996.

[20] M. BUIJS, A. MEYERINK and G. BLASSE, ENERGY TRANSFER BETWEEN  $\text{Eu}^{3+}$  IONS IN A LATTICE WITH TWO DIFFERENT CRYSTALLOGRAPHIC SITES:  $\text{Y}_2\text{O}_3 : \text{Eu}^{3+}$ ,  $\text{Gd}_2\text{O}_3 : \text{Eu}^{3+}$  and  $\text{Eu}_2\text{O}_3$ . Journal of Luminescence 37 (1987)9-20.

[21] Ji-Guang Li, Jinkai Li, Qi Zhu, Xuejiao Wang, Xiaodong Li, Xudong Sun, and Yoshio Sakka, Photoluminescent and cathodoluminescent performances of  $\text{Tb}^{3+}$  in the  $\text{Lu}^{3+}$ -stabilized gadolinium aluminate garnet solid-solutions of  $[(\text{Gd}_{1-x}\text{Lu}_x)_{1-y}\text{Tb}_y]_3 \text{Al}_5\text{O}_{12}$ , RSC Advances, DOI: 10.1039/C5RA06564J.

[22] Jinkai Li, Ji-Guang Li, and Yoshio Sakka, Investigation of New Red Phosphors of  $\text{Eu}^{3+}$  Activated  $(\text{Gd}, \text{Lu})_3\text{Al}_5\text{O}_{12}$  Garnet, International Journal of Materials Science and Engineering vol.1, No.1 June 2013.

**How to cite this article:**

Lanez I, Rekik B, Derbal M, Chaib A. Structural study and the effect of ionic size of the systems  $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$  doped erbium. J. Fundam. Appl. Sci., 2019, 11(2), 857-874.