

Eu-doped langasite, langatate and langanite – possible new red phosphors

S. GEORGESCU*, A. M. VOICULESCU, O. TOMA, C. TISEANU, L. GHEORGHE, A. ACHIM, C. MATEI
National Institute for Laser, Plasma and Radiation Physics, 409 Atomistilor Street, Magurele, Jud. Ilfov, 077125, Romania

We present a preliminary study concerning the luminescence properties of Eu³⁺-doped langasite (La₃Ga₅SiO₁₄ - LGS), langatate (La₃Ga_{5.5}Ta_{0.5}O₁₄ - LGT) and langanite (La₃Ga_{5.5}Nb_{0.5}O₁₄ - LGN) crystals. The luminescence, reflectance and excitation spectra are used to compare the fluorescence efficiency and determine the most efficient excitation wavelengths.

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1. Introduction

The crystals from the langasite family were initially intended as hosts for laser active media [1], but in present their main application is based on their very good piezoelectric characteristics [2, 3]. Nowadays, langasite (La₃Ga₅SiO₁₄ - LGS) tends to replace quartz in high temperature applications [4]. Also, langasite is used for electro-optic Q-switch [5], for gas sensor [6], and so on. Self-tuning of Nd³⁺ in langasite crystals was obtained [7]. Recently, interesting magnetic properties in Nd langasite crystals were put in evidence [8].

Two other members of the langasite family, langanite (La₃Ga_{5.5}Nb_{0.5}O₁₄ - LGN) and langatate (La₃Ga_{5.5}Ta_{0.5}O₁₄ - LGT) proved to have superior characteristics in some applications [9]. LGS, LGN and LGT are partially disordered crystals, i. e., one of the crystallographic positions is shared by two different ions. This results in inhomogeneously broadened absorption and fluorescence lines which was first considered an advantage for laser emission: wider absorption lines result in an efficient pumping while wider emission lines means tunability. 1.064 μm emission in Nd-doped langatate crystals was obtained [10].

LGS, LGN and LGT crystallize in the *P321* space group, symmetry class *32* and are isostructural with the calciumgallogermanate (Ca₃Ga₂Ge₄O₁₄) [11]. The general formula is *A₃BC₃D₂O₁₄* where *A* represents the dodecahedral positions (distorted Thompson cubes), *B* – octahedral positions and *C, D* – tetrahedral positions. La³⁺ occupies the position *A*. The local symmetry at this site is *C₂* [12]. In contrast with LGS where Ga³⁺ and Si⁴⁺ share with equal probability the tetrahedral positions *D*, in LGN (LGT) the octahedral positions *B* are occupied by two different ions, Ga³⁺ and Nb³⁺ (Ta⁵⁺) (also, with equal probability). Ga³⁺ occupies the remaining positions (*C* and *D*). The structural difference between LGS and LGN (or

LGT) consists in the placement of the shortest distance positions randomly occupied around the *A* site: four positions in the plane perpendicular on the *C₂* axis for LGS and two positions along the *C₂* axis in LGN and LGT. Besides, there is a larger charge difference between Nb⁵⁺ (or Ta⁵⁺) and Ga³⁺ than between Si⁴⁺ and Ga³⁺ [13, 14].

When excited in the near UV (396 nm, transition ⁷F₀ → ⁵L₆), both Eu³⁺-doped LGS and LGT crystals show bright red luminescence which suggests the possibility to use these materials as red phosphors. In this paper we compare reflectance, excitation, and emission properties of Eu-doped LGS, LGT and LGN powders to estimate their possibilities as red phosphors.

2. Experimental

Eu-doped langasite, langanite and langatate were synthesized in our laboratory from high-purity La₂O₃, Ga₂O₃, SiO₂, Nb₂O₅, Ta₂O₅, Eu₂O₃, according to (La_{0.95}Eu_{0.05})₃Ga₅SiO₁₄ and, respectively, (La_{0.97}Eu_{0.03})₃Ga_{5.5}Nb_{0.5}O₁₄ and (La_{0.97}Eu_{0.03})₃Ga_{5.5}Ta_{0.5}O₁₄ formulae. The oxides were mixed in an agate balls mill and calcinated at 1500°C for 24 h. The powder was pressed in pallets and the crystals were grown along the *C*-axis in platinum crucibles in nitrogen atmosphere, using the Czochralski method. The powders of Eu³⁺-doped LGS, LGN and LGT were obtained by milling of single crystals.

The reflectance spectra were measured using the setup in Fig. 1. A near parallel light beam from a W-halogen lamp was projected normally on the quartz cuvette containing the powder (Fig. 1). The reflected light was collected with a concave mirror and projected on the entrance slit of a Jobin-Yvon 1000M monochromator equipped with an S-20 photomultiplier. The signal was processed by a SR830 lock-in amplifier online with a

computer. A powder of BaSO_4 was used as a white etalon. The same setup was used for luminescence measurements, with appropriate filters placed between the lamp and the mirror.

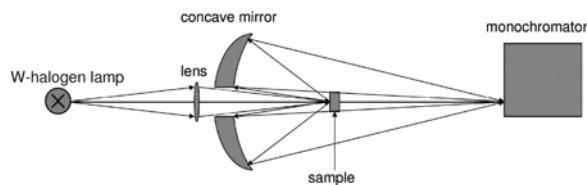


Fig. 1. Experimental setup for reflectance spectra.

Excitation spectra were measured using a FluoroMax spectrofluorometer from Horiba Jobin-Yvon, with pump wavelength in the range 250 – 600 nm and monitoring transition ${}^5D_0 \rightarrow {}^7F_2$.

3. Results

The reflectance spectra of the three samples were recorded with the setup described above and divided by the reflectance spectrum of the white etalon BaSO_4 . The results are represented in Fig. 2.

The baselines of the relative reflectance curves present three zones: first, there is an increase in the reflectance in the UV (up to about 425 nm); a nearly horizontal zone follows (425–500 nm), denoting a constant value of the reflectance; in the yellow and red, there is again an increase of the relative reflectance. This behavior of the relative reflectance baseline is in accord with the slight red coloration of the samples. The defects that lead to the red coloration of the crystals from the langasite family were studied in a series of papers [15-18].

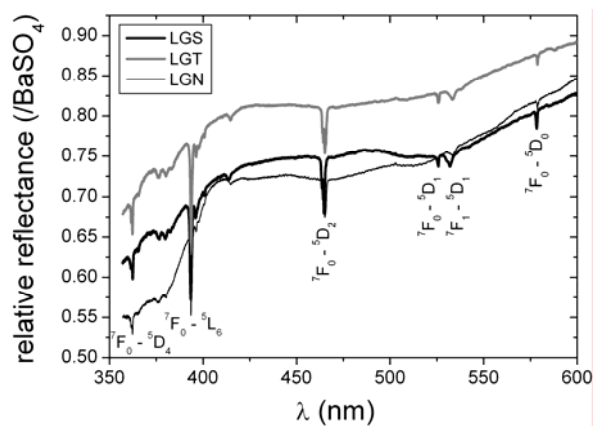


Fig. 2. Reflectance spectra of Eu-doped LGS, LGT and LGN powders. The highest reflectivity was obtained for LGT.

The coloration was found to be related to oxygen defects (vacancy, interstitial atoms) influenced by the

growth atmosphere and the composition of the crucible (iridium or platinum).

The absorption lines of Eu^{3+} (identified in Fig. 2) as well as a few emission lines of Eu^{3+} are superposed on this background. The absorption lines originate on levels 7F_0 and 7F_1 , which are significantly populated at room temperature.

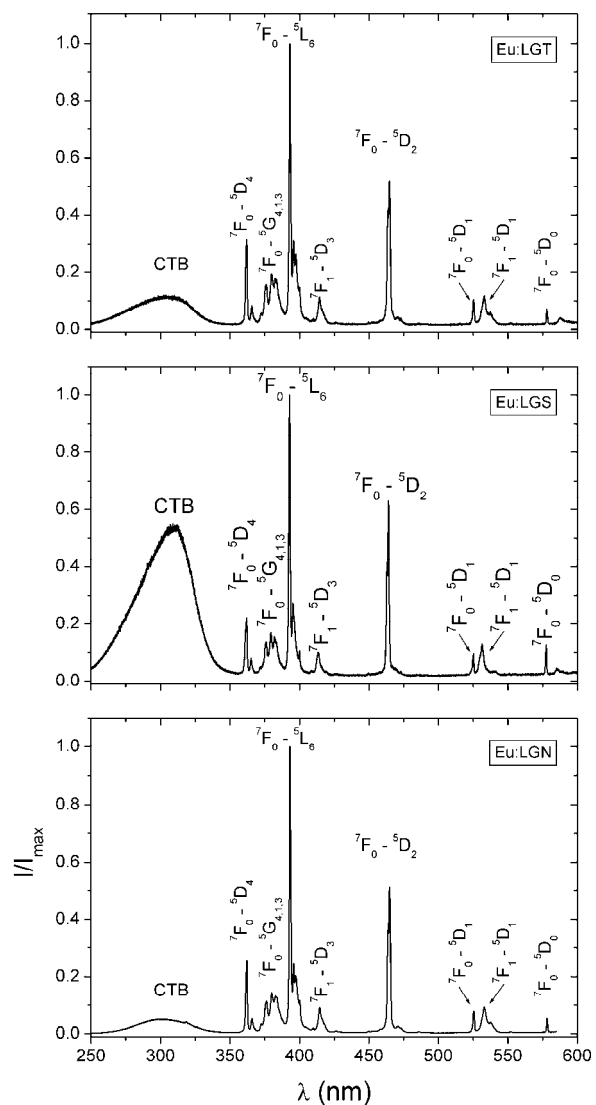


Fig. 3. Excitation spectra of Eu-doped LGS, LGT and LGN. The main absorption transitions are identified.

Excitation spectra of all samples are represented in Fig. 3 and the transitions corresponding to various lines are identified. The Charge Transfer Band (CTB) $\text{O}^{2-} - \text{Eu}^{3+}$ is centered at ~ 300 nm. The most efficient pump band is the line corresponding to $f-f$ transition ${}^7F_0 \rightarrow {}^5L_6$ (at 393 nm). Another interesting line is that corresponding to $f-f$ transition ${}^7F_0 \rightarrow {}^5D_2$, at 464 nm, which can be used for pumping with blue light-emitting diodes. The intensities of the CTB at the three crystals cannot be compared due to various growth defects in these crystals, that can induce an

increased absorption in the blue and UV regions of the spectrum (as evidenced by the reflectance spectra).

Luminescence spectra of Eu(5%):LGS, Eu(3%):LGT and Eu(3%):LGN, measured in the same conditions at room temperature, are represented in Fig. 4. The spectra of Eu:LGT and Eu:LGN have greater areas than the spectrum of Eu:LGS, denoting a greater luminescence efficiency for Eu:LGT and Eu:LGN than for Eu:LGS. The transitions taken into account were ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0, \dots, 4$), whose contribution to the spectrum area is dominant.

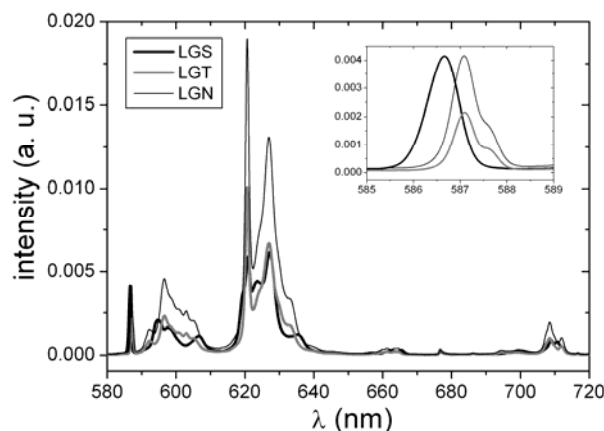


Fig. 4. Fluorescence spectra of Eu-doped LGS, LGT and LGN. Inset: transition ${}^5D_0 \rightarrow {}^7F_0$.

In order to characterize the potential of these powders as red phosphors, we compared the areas of the luminescence spectra in Fig. 4 to that of an efficient Eu-based red phosphor – $\text{YVO}_4:\text{Eu}$. The luminescence spectrum of $\text{YVO}_4:\text{Eu}$ is not shown in Fig. 4 for clarity's sake. The $\text{YVO}_4:\text{Eu}$ sample was synthesized in our laboratory by a precipitation method and annealed at 800°C [19]. For an easier comparison, the areas of the luminescence spectra of the Eu:LGX ($X = \text{S}, \text{T}, \text{N}$) samples were divided by the Eu atomic concentration of each sample and by the area of the luminescence spectrum of $\text{Eu}:\text{YVO}_4$ (which was also normalized at its atomic concentration). The resulting relative efficiencies of the luminescence are listed in Table 1.

Table 1. Relative efficiency (in rapport with $\text{YVO}_4:\text{Eu}$) values for the three samples investigated.

Sample	Ratio LGX/ YVO_4
Eu:LGS	0.28
Eu:LGT	0.35
Eu:LGN	0.66

The shift of the ${}^5D_0 \rightarrow {}^7F_0$ line towards red in Eu:LGT and Eu:LGN (as seen in the inset in Fig. 4) denotes a greater covalence of Eu – O bonding in LGT and LGN [13, 14].

4. Conclusions

Powders of Eu-doped crystals LGS, LGT and LGN were studied by various spectroscopic methods in order to estimate their possibilities as red phosphors.

From the excitation spectra, the main pump bands are the charge transfer band (~ 300 nm), ${}^7F_0 \rightarrow {}^5L_6$ (393 nm), ${}^7F_0 \rightarrow {}^5D_2$ (464 nm); the last two can be used for pumping with light-emitting diodes.

The reflection spectra put into evidence, besides the absorption lines of Eu^{3+} , the effect of the point defects of the hosts, that induce their red coloration.

The areas of the fluorescence spectra of the three samples were used for a comparison between these samples and an efficient red phosphor – $\text{Eu}:\text{YVO}_4$. The above-estimated efficiency of langasite-family samples (Table 1) is quite good, especially for the LGN:Eu sample. Although the performances of the Eu:LGX crystals can be influenced by the synthesis conditions, the good efficiency obtained for Eu:LGN indicates this crystal as a promising red phosphor. Its efficiency can be improved by careful selection of the synthesis conditions.

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*Corresponding author: serban.georgescu@inflpr.ro