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OPTICAL DETECTION OF Eu^{3+} SITES IN $Gd_3Ga_5O_{12}:Eu^{3+}$

L. C. COURROL, L. GOMES, A. BRENIER,* C. PÉDRINI,* C. MADEJ* and G. BOULON*

*Divisão de Materiais Optoeletrônicos, IPEN/CNEN-SP; *Laboratoire de Physico-Chimie des Matériaux Luminescents, Université Claude Bernard-Lyon I*

The trivalent rare earth ions occupy the eight-coordinated (dodecahedral) sites (D_2 point symmetry) in $Gd_3Ga_5O_{12}:Eu^{3+}$ crystal. The flourescence of Eu^{3+} has been investigated using laser- excited site-selection spectroscopy. It was seen three distinct sites deduced from the spectra, one of them owing to the garnet site. The emission and excitation spectra of non-garnet site are consistent with the low symmetry point of C_{2v} site.

1 INTRODUCTION

Rare-earth doped garnets are considered very important laser materials.[1,2]

The knowledge of their structures and the determination of the rare earth multisites are essentials to the performance and the technology development of this material as laser light source in the mid-IR.

The $Gd_3Ga_5O_{12}$(GGG) type garnet has a cubic crystalline structure with eight molecules per unit cell. The Gd^{3+} ions are located in the dodecahedral D_2 site and the Ga^{3+} ions are in S_4 and S_6 sites. The rare earth Eu^{3+} ions are located generally in the Gd^{3+} positions. However, laser-excited site selection spectroscopy can give information about the different sites as well as their local symmetry. This information can be used for a complete understanding of the physical properties of this material.

The Eu^{3+} ions are appropriate for site-selection spectroscopy study, because they have absorption and emission bands in the visible range; the luminescence spectrum is particulary simple since the fundamental $^7F_0$ level is not decomposed by the crystalline field.

In this paper, laser-excited site-selection spectroscopy has been utilized to determine the Eu^{3+} occupation sites in GGG. The experimental results indicated the existence of three different sites when analysing the emission spectra. Two of them are non-garnet sites.

The GGG:Eu^{3+} sample was grown by Czochralski's technique in the Laboratoire de Physico-Chimie des Matériaux Luminescents (Lyon). The high resolution excitation and emission spectra were measured by exciting the crystal with a tunable dye laser pumped by an excimer laser. The luminescence was detected by a cooled S-20 photomultipler. The signals were recorded using an SR 400 two-channel gated photon counter and the sample was placed in a closed-cycle He cryostat for low temperature measurements.

2 EXPERIMENTAL RESULTS

We investigated the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ fluorescent transitions of Eu^{3+} at 6 K, in GGG. The first transition is forbidden because $\Delta J = 0$, but can appear in the C_n, C_{nv} and C_s symmetries.[3] The emission spectra of the $^5D_0 \rightarrow {}^7F_1$ transition at 596.3 nm at 6 K, showed the presence of an excitation band centered at 580.2 nm due to the $^7F_0 \rightarrow {}^5D_0$ transition as is shown in Figure 1. This excitation ban shows the existence of a non-garnet

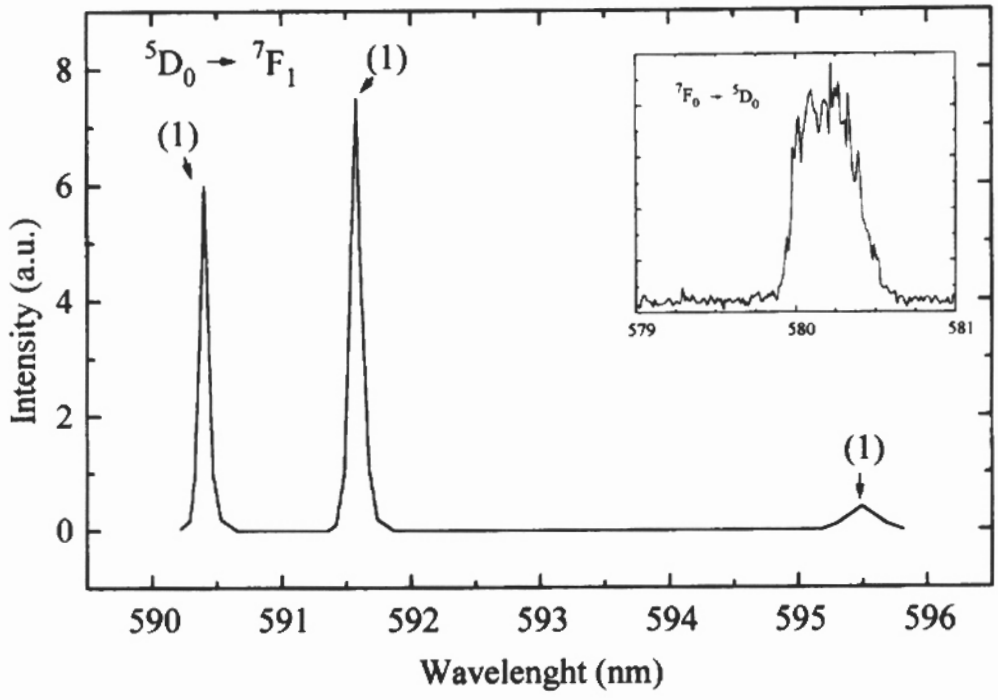

FIGURE 1 Emission spectra of the transition $^5D_0 \rightarrow {}^7F_1$ with excitation fixed at 580.2 nm at 12 K. The excitation spectra of the fundamental transition $^7F_0 \rightarrow {}^5D_0$ with emission fixed at 596.3 nm at 6 K is shown too.

site probably with a C_{2v} symmetry. The excitation of this transition at 580.2 nm ($^7F_0 \rightarrow {}^5D_0$) shows the presence of emission bands corresponding to the $^5D_0 \rightarrow {}^7F_1$ transition composed of three sharp lines centered at 590.4, 591.6 and 595.5 nm (1 site) (see Figure 1).

This ion when excited at 527.5 nm shows the emission band due to $^5D_0 \rightarrow {}^7F_1$ transition which is exhibited in Figure 2. In this spectrum we observe the presence of 6 more lines beside the 3 already identified lines. These lines have peaks at 591, 591.2, 592.2, 592.5, 594.2 and 594.5 nm corresponding to different site symmetries. The identification of these lines with their symmetries could be obtained by specific excitation at different positions, Figure 3. For example, the excitation at 526.86 nm contributes with the lines: 591.2, 592.2 and 594.5 nm (site 3). The excitation at 527.6 nm exhibited lines peaking at 591.0, 592.5 and 594.2 nm (site 2).

The (3) site is the D_2 site, expected for Eu^{3+}, the most abundant site in the lattice.

The (2) site must have the D_{2h} symmetry, showing also 3 lines. It can not be the Ga^{3+} site which has S_4 or S_6 symmetry.

By using second order approximation in the crystalline field effects, it was possible to calculate the A_2^0 and A_2^2 parameters for the $^5D_0 \rightarrow {}^7F_1$ transition. We found for the (1) site: 224.28 and 88.9 cm^{-1}; for the (3) site: 142.03 and 60.28 cm^{-1} and for the (2) site: 126.15 and 54.48 cm^{-1}.

It was observed that the (1) site have the ligand ions closest that the (2) and (3) sites, due to the fact that $A_2^2(1) > A_2^2$ (2 and 3).

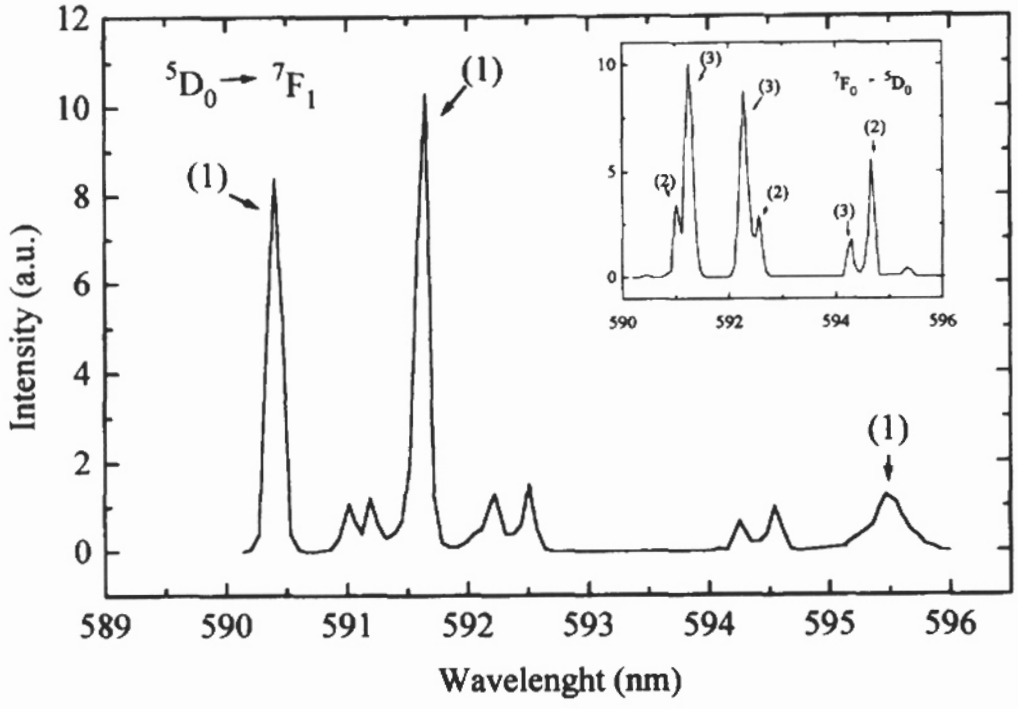

FIGURE 2 Emission spectra of the $^5D_0 \rightarrow {}^7F_1$ transition with excitation at 527.5 nm at 12 K. Emission spectra of the $^5D_0 \rightarrow {}^7F_1$ transition with excitation at 527.6 nm at 12 K (inserted figure).

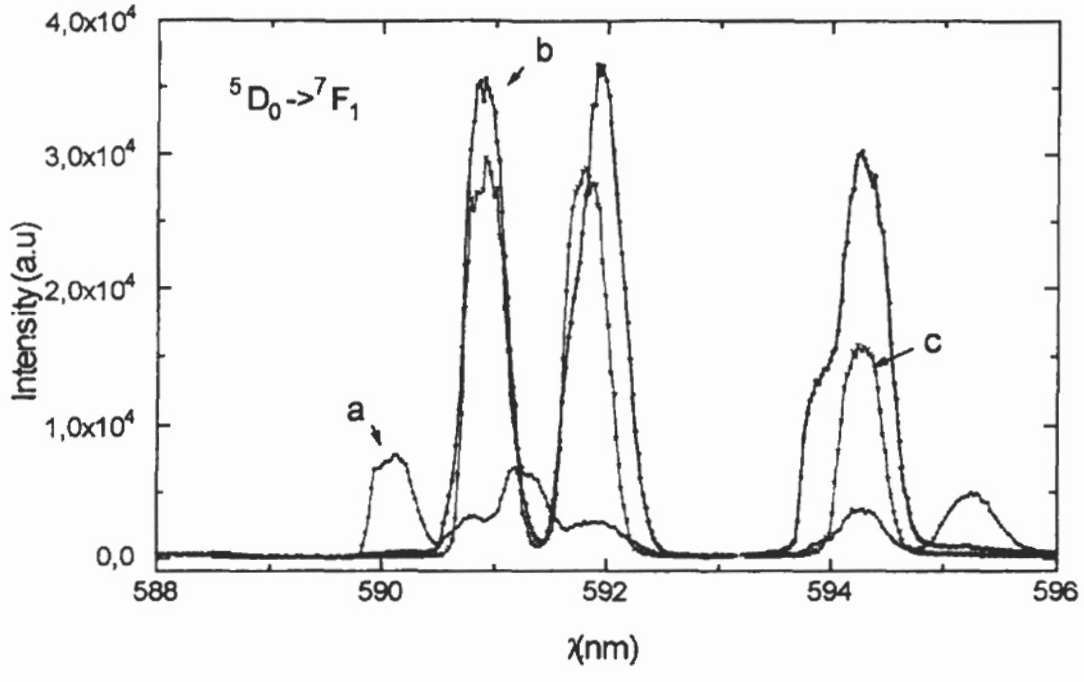

FIGURE 3 Emission spectra of the $^5D_0 \rightarrow {}^7F_1$ transition with excitation at a) 527.36 nm, b) 527.45 nm and c) 526.86 nm, at 6 K.

3 CONCLUSION

The experimental results showed the presence of 3 non equivalent crystalline sites in GGG:Eu^{3+} crystal. These different sites were named (1), (2) and (3) sites could be identified by their group of emission lines of $^5D_0 \rightarrow {}^7F_1$ transition when selectively excited at 580.2 nm and 527.6 nm respectively.

By the observation of fundamental transition $^7F_0 \rightarrow {}^5D_0$, we could verify that the (1) site must have one of the C_2, C_{2v}, or C_s symmetry (most probably, C_{2v} symmetry).

The predominant site D_2 has symmetry that corresponds to site type (3). The (2) site must have D_{2h} symmetry.

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