FLUORESCENCE OF Pr3+ AND Dy3+ IN LaMgAl11O19 SINGLE CRYSTALS

B. Viana, P. Derouineau, J. Barrie, A. Lejus, B. Dunn, O. Stafsudd, D. Vivien

To cite this version:
B. Viana, P. Derouineau, J. Barrie, A. Lejus, B. Dunn, et al.. FLUORESCENCE OF Pr3+ AND Dy3+ IN LaMgAl11O19 SINGLE CRYSTALS. Journal de Physique Colloques, 1987, 48 (C7), pp.C7-509-C7-511. <10.1051/jphyscol:19877121>. <jpa-00226939>

HAL Id: jpa-00226939
https://hal.archives-ouvertes.fr/jpa-00226939
Submitted on 1 Jan 1987

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
FLUORESCENCE OF Pr$^{3+}$ AND Dy$^{3+}$ IN LaMgAl$_{11}$O$_{19}$ SINGLE CRYSTALS

B. VIANA, P. DEROUINEAU, J. BARRIE*, A.M. LEJUS, B. DUNN* 
O. STAFSUDD* and D. VIVIEN

Chimie Appliquée de l'Etat Solide, CNRS-UA 302, ENSCP, 11, Rue Pierre et Marie Curie, F-75231 Paris Cedex 05, France
*Department of Materials Science and Engineering, University of California, Los Angeles, CA 90024, U.S.A.

Abstract

LaMgAl$_{11}$O$_{19}$ doped with Pr$^{3+}$ could lead to a material lasing in the visible range. For lamp pumping it is necessary to sensitize the fluorescence (for example by Dy$^{3+}$). Optical properties have been determined by absorption, diffuse reflectance, fluorescence spectroscopies as well as fluorescence decays on 2 kinds of materials: single doped crystals La$_{1-x}$Ln$_{x}$MgAl$_{11}$O$_{19}$ (Ln = Pr, Dy) and codoped ones La$_{1-x-y}$Pr$_y$Dy$_y$MgAl$_{11}$O$_{19}$. In single doped material a strong fluorescence quenching occurs. In codoped crystals, while fluorescent levels of Dy$^{3+}$ are in resonance with Pr$^{3+}$ absorption levels, there is no sensitization of the Pr$^{3+}$ fluorescence.

Introduction

LaMgAl$_{11}$O$_{19}$ is a well known laser host for ions such as Nd$^{3+}$, Cr$^{3+}$, Ni$^{2+}$ (1, 2, 3). With Pr$^{3+}$ ions this matrix could lead to a material lasing in the visible range (4). Fluorescent levels of Pr$^{3+}$ ions are $^3P_0$ (intense) and $^1D_2$ (weak). As there is only a few levels above the fluorescent ones, laser excitation into these levels is the usual way to pump a Pr$^{3+}$ activated laser. Lamp pumping is up to now very difficult. However this pumping could be performed via a sensitization of Pr$^{3+}$ fluorescence by other ions which present U.V. and visible lines such as Dy$^{3+}$ ions. These ions reveal on the one hand strong absorptions leading to energy levels above the $^3P_0$ one, and on the other hand fluorescent levels in resonance with Pr$^{3+}$ absorption (see fig. 1):

- $^4F_9/2$ - $^6H_{15/2}$ Dy$^{3+}$ emission with $^3H_4$ - $^1D_2$ Pr$^{3+}$ absorption to sensitize the $^1D_2$ fluorescent level.
- $^4P_9/2$ - $^6H_{13/2}$ Dy$^{3+}$ emission with $^3H_4$ - $^3P_0$ - $^3P_0$ Pr$^{3+}$ absorption to sensitize the $^3P_0$ fluorescent level.
Two series of crystals have been obtained from the molten state ($T_f = 1850 \, ^\circ\text{C}$) by the flame fusion method: $\text{La}_{1-x}\text{Ln}_{x}\text{MgAl}_{11}\text{O}_{19}$ (Ln = Pr or Dy) and $\text{La}_{1-x-y}\text{Pr}_x\text{Dy}_y\text{MgAl}_{11}\text{O}_{19}$. There is a total solubility of Pr$^{3+}$ in the matrix ($0 \leq x \leq 1$) while it is limited to $y \leq 0.2$ for Dy$^{3+}$. All the crystals belong to a magnetoplumbite like structure (hexagonal symmetry, space group $P6_3/mmc$). They are rod-shaped and exhibit a cleavage along (001). Optical investigations were performed on transparent cleavage platelets.

**Optical properties**

Optical properties have been determined by absorption, diffuse reflectance, emission, excitation and fluorescence decay measurements. For example, fig. 2 shows the fluorescence spectrum of Pr$^{3+}$ under arc xenon lamp excitation. Fluorescence decays have been performed using a nitrogen pulsed laser pumping dye lasers (at 441 nm for Pr$^{3+}$ and 380 nm for Dy$^{3+}$). In the case of single doped samples, decay profiles are exponentials for both ions. Lifetimes strongly decrease when the Pr$^{3+}$ or Dy$^{3+}$ concentrations increase. For Pr$^{3+}$ in $\text{La}_{1-x}\text{Pr}_x\text{MgAl}_{11}\text{O}_{19}$, $\tau$ varies between 32 $\mu$s for $x = 0.01$ and 13 $\mu$s for $x = 0.2$. For Dy$^{3+}$ in $\text{La}_{1-x}\text{Dy}_x\text{MgAl}_{11}\text{O}_{19}$, $\tau$ decreases from 905 $\mu$s to 765 $\mu$s when $x$ increases from 0.02 to 0.2. A strong luminescence quenching occurs with the concentration. This is due to the existence of a great number of energy levels between the fluorescent levels and the ground state ones (see fig. 1), offering several paths for self quenching by energy transfer between neighbouring Pr$^{3+}$ or Dy$^{3+}$ ions.

![Fluorescence spectra of Pr$^{3+}$ in La$_{1-x}$Pr$_x$MgAl$_{11}$O$_{19}$](image)

In the case of double doped samples, decays profiles do not present any non-exponential behaviour in the same scale time. Pr$^{3+}$ lifetimes are not influenced by Dy$^{3+}$ concentration. On the contrary for high Pr$^{3+}$ concentration, Dy$^{3+}$ lifetimes decrease rapidly. For example, $\tau$ changes from 905 $\mu$s to 408 $\mu$s when Pr$^{3+}$ concentration varies from $x = 0$ to $x = 0.25$ in $\text{La}_{0.98-x}\text{Pr}_x\text{Dy}_{0.02}\text{MgAl}_{11}\text{O}_{19}$. This phenomenon is probably due to a cross-relaxation process between the two kinds of ions, this process arising because of the great number of energy levels which exist for each ion.

In conclusion neither Pr$^{3+}$ excitation spectrum nor Dy$^{3+}$ fluorescence have demonstrated that any energy transfer from Dy$^{3+}$ to $3P_0$ or $1D_2$ - Pr$^{3+}$ fluorescent levels occurs. However decay profiles of Dy$^{3+}$ reveal the existence of strong interaction with Pr$^{3+}$ involving non-fluorescent levels. Furthermore the plotting of Pr$^{3+}$ fluorescence intensity versus $\text{Ar}^+$ ($\lambda = 514.5$ nm) CW excitation power in Dy$^{3+}$ - Pr$^{3+}$ double doped samples do not show any non linear effect which could be an indication of energy transfer via two photons absorption (in 5d levels).
This work demonstrates that while fluorescent levels of Dy$^{3+}$ are in resonance with Pr$^{3+}$ absorption lines, there is no sensitization of the Pr$^{3+}$ fluorescence, neither in the $^3\!P_0$ nor in the $^1\!D_2$ energy levels. Other systems such as Tm$^{3+}$ or Sm$^{3+}$-Pr$^{3+}$ might be more efficient. This is at present under study in these laboratories.

References

(1) M. LEDUC, L.D. SCHEARER, D. VIVIEN, A.M. LEJUS, J.THERY
(2) B. VIANA, A.M. LEJUS, D. VIVIEN, V. PONCON, G. BOULON
(3) R. MONCORGE, T. BENYATTOU, D. VIVIEN, A.M. LEJUS
    J. Luminescence 35 199 (1986).
(4) R. REISFELD, C.K. JORGENSEN
    Lasers and excited states of rare earth