JOURNAL OF MATERIALS SCIENCE 27 (1992) 813–816

Energy transfers in the potential laser materials LMA:Ce, Nd and LMA:Cr, Ce, Nd (LMA = $LaMgAl_{11}O_{19}$)

B. VIANA, A. M. LEJUS, D. VIVIEN
Laboratoire de Chimie Appliquée de l'Etat Solide, URA302 (CNRS), ENSCP 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

C. GARAPON
Laboratoire de Physico-chimie des Matériaux Luminescents, URA442 (CNRS) Université de Lyon 1, 43 Bd du 11 Nov. 1918, 69622 Villeurbanne Cedex, France

Single crystals of $LaMgAl_{11}O_{19}$ (LMA) coactivated with Ce^{3+}, Nd^{3+} or Ce^{3+}, Cr^{3+}, Nd^{3+}, have been grown by the Verneuil (flame-fusion) method. In LMA:Ce, Nd the Ce → Nd energy transfer occurs both radiatively and non-radiatively. The efficiency of the non-radiative Ce → Nd transfer reaches ~47%, as deduced from Ce^{3+} fluorescence lifetime measurements. In LMA:Ce, Cr, Nd, besides the Ce → Nd energy transfer, Ce → Cr and Cr → Nd transfers occur. The Ce → Cr energy transfer is highly efficient. This results from the good resonance between Ce emission and Cr absorption, and also from the short Ce–Cr distance compared to the longer Ce–Nd one.

1. Introduction

One way to increase the pumping efficiency of a neodymium solid state laser is to incorporate a second doping ion, such as Cr^{3+}, whose efficiency in the gallium garnets, for instance, is well established [1–4]. Ce^{3+} is also often used as a sensitizer for Nd^{3+} or for other ions such as Sm^{3+}, Dy^{3+}, Tb^{3+}, Ho^{3+}, Er^{3+}, etc. [5–7]. Cr^{3+} absorbs mainly in the visible range while Ce^{3+} absorbs in the ultraviolet spectral range. Incorporated simultaneously into neodymium-doped solid state lasers, these ions greatly increase the absorption of the pump light in the ultraviolet and visible ranges. For example, in $YAlO_3$ and $Y_3Al_5O_{12}$ (YAG) matrix [8, 9] attempts have been made to increase the laser gain in this way. Lanthanide hexaaluminate with the formula $LnMgAl_{11}O_{19}$ ($Ln = La_{1-x}Nd_x$ for LMA:Nd) has proved to be an interesting laser material [10]. It has the hexagonal magnetoplumbite-like structure (hexagonal symmetry, space group $P6_3/mmc$ [11]). Its unit cell is composed of compact spinel blocks separated by mirror planes which contain the rare-earth ions. Other ions such as Ce^{3+} [12] and Cr^{3+} [13] can also be incorporated into LMA. In this matrix, Ce^{3+} substitutes for La^{3+} and occupies two kinds of site in the mirror plane. Conversely Cr^{3+} ions, substitute for Al^{3+} and are distributed among the three octahedral sites in the compact spinel blocks, with a preferential occupancy of the 4f site close to the mirror plane.

The aims of this work were firstly to determine whether cerium to neodymium energy transfer occurs in LMA:Ce, Nd crystals and secondly to analyse the opportunity of adding Cr^{3+} as a second sensitizer, leading to LMA:Ce, Cr, Nd. The interactions between Cr^{3+} and Nd^{3+} in LMA have been studied previously [14]. They could be complementary to the Ce–Nd ones in hexaaluminate matrix.

2. Experimental procedure

Two series of doped hexaaluminate single crystals: $La_{1-x-y}Ce_xNd_yMgAl_{11}O_{19}$ and $La_{1-x-y}Ce_xNd_yMgAl_{11-z}Cr_zO_{19}$ with the composition range: $x = [0, 0.05]$, $y = [0, 0.35]$ and $z = [0, 0.11]$ have been obtained from the molten state ($T_f = 1850$–$1900\,°C$) by the flame fusion method (Verneuil process). In the LMA matrix there is a total solubility of Ce^{3+} and Nd^{3+} while it is limited to about $z = 1$ for Cr^{3+} [13], but our maximum z value (0.11) is well below the chromium solubility limit. During crystal growth, the Verneuil torch must work with a reducing flame ($H_2/O_2 \approx 3$) to ensure that cerium is in the trivalent state.

A 300 W xenon lamp excitation was used to obtain the fluorescence spectra. The detector was a PMT (Hamamatsu R928) in the visible range and a PbS cell in the infrared one. The Ce^{3+} fluorescence decays were obtained using a 285 nm excitation from a doubled frequency R590 dye laser pumped by an XeCl excimer laser from Lumonics. The signal was detected by a cooled fast GaAs PMT (RCA 31084), connected to a digital oscilloscope HP 1980B. The pulse width of the system was 10–15 ns.

0022–2461/92 $03.00 + .12

3. LMA:Ce, Nd

3.1. Analysis of the LMA:Nd and LMA:Ce, Nd fluorescence with pass-band filters

The absorption spectrum of trivalent cerium in LMA covers the ultraviolet emission range of the xenon (or mercury) arc-lamps well. Furthermore there is a good overlap between the Ce^{3+} emission band and the Nd^{3+} absorption bands corresponding to the $^4I_{9/2} \rightarrow {}^4D_{3/2,5/2}$ transitions. This good resonance is the first condition to be fulfilled for an eventual transfer, but as the $^4D_{3/2,5/2}$ levels are far above the $^4F_{3/2}$ fluorescent one and separated from it by a large number of other electronic levels, it appears first necessary to evaluate the contribution of the higher levels ($\lambda < 400$ nm) to the $^4F_{3/2} \rightarrow {}^4I_J$ transitions. Both $^4F_{3/2} \rightarrow {}^4I_{13/2}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ fluorescence, around 1.35 and 1.055 μm, respectively, have been investigated and the results are very similar for the two transitions. The crystals are pumped with a xenon arc lamp fitted with glass filters passing either the ultraviolet range ($\lambda < 400$ nm) or the visible plus infrared range ($\lambda > 400$ nm). The fluorescence intensity under unfiltered excitation is taken to be equal to 100%. For $La_{0.9}Nd_{0.1}MgAl_{11}O_{19}$, when the only levels to be excited are the ultraviolet ones, the fluorescence intensity value is 8% while it is approximately 90% with the second filter, $\lambda > 400$ nm. The occurrence of strong bands in the visible and infrared spectral range explain the relatively low efficiency of the ultraviolet range excitation for the Nd^{3+} fluorescence. However, the possibility of non-radiative de-excitation of the high levels via energy migration to defect centres or cross-relaxation, cannot be completely ruled out.

Our purpose was to increase this efficiency by adding Ce^{3+} ions. Indeed when the Ce^{3+} concentration increases, the ultraviolet contribution increases up to a maximum value of about 12% for the $La_{0.9}Ce_{0.02}$-$Nd_{0.08}MgAl_{11}O_{19}$ crystal. The variation, around 50%, is significant but the value of the ultraviolet contribution remains very small. A similar investigation has been previously performed on LMA:Cr, Nd single crystals, for which the Cr^{3+} fluorescent levels are closer to the $Nd^{3+}(^4F_{3/2})$ one. For comparison, the efficiency of the visible part of the xenon lamp emission increases from around 15% in LMA:Nd to more than 55% in the LMA:Cr, Nd crystals [14]. In this case the sensitization process appears much more interesting than for the LMA:Ce, Nd compounds.

3.2. Ce^{3+} emission spectrum

Radiative energy transfer between Ce^{3+} and Nd^{3+} is clearly demonstrated by looking at the Ce^{3+} emission spectrum of LMA:Ce, Nd single crystals (Fig. 1). The appearance of minima at wavelengths corresponding to Nd^{3+} absorption bands ($^4I_{9/2} \rightarrow {}^4D_{3/2,5/2}$) indicates that photons emitted by Ce^{3+} are trapped in the matrix and reabsorbed by Nd^{3+}. Furthermore the total intensity of the Ce^{3+} emission decreases in the presence of Nd^{3+} indicating that both radiative and non-radiative energy transfer processes occur.

3.3. Ce^{3+} fluorescence decays

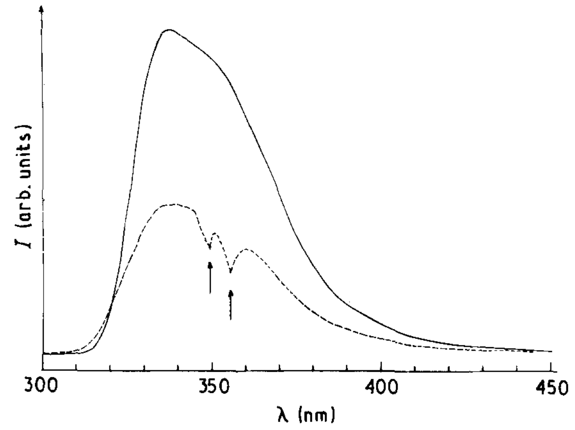

Figure 1 Emission spectra under xenon lamp excitation of Ce^{3+} in: (a) $La_{0.98}Ce_{0.02}MgAl_{11}O_{19}$, (b) $La_{0.90}Ce_{0.02}Nd_{0.08}MgAl_{11}O_{19}$. Arrows show the $^4I_{9/2} \rightarrow {}^4D_{3/2,5/2}Nd^{3+}$ absorption bands in resonance with the Ce^{3+} emission.

The measurement of the Ce^{3+} fluorescence decay curves gives another indication of the interactions between Ce^{3+} and Nd^{3+} in the matrix. For LMA:Ce the decay profiles are exponential at room temperature and independent of the cerium concentration [12]. The decay times, τ, depend on the emission wavelength indicating a multisite character of Ce^{3+} in this matrix. For example, in crystals containing $6.7 \times 10^{19} Ce^{3+}\ cm^{-3}$, $\tau = 26$ and 35 ns, at 365 and 394 nm, respectively.

An estimation of the $Ce^{3+} \rightarrow Nd^{3+}$ energy transfer efficiency can be deduced from the shortening of the Ce^{3+} lifetime for different Nd^{3+} concentrations in the matrix. If interactions between the two ions occur, Ce^{3+} excited states will find a new way of de-excitation via Nd^{3+} ions and this will decrease the Ce^{3+} luminescence lifetime. Therefore, the evolution of the Ce^{3+} decay profiles with the Nd^{3+} concentration allows us to determine the non-radiative transfer efficiency. In our case the decays are too fast to be fitted with a high accuracy, as was done in YAG:Ce, Nd crystals where the Ce^{3+} lifetimes are much longer [9]. The average value of 25 ns for the Ce^{3+} lifetime must be compared to the width of the laser pulse: around 10–15 ns. Furthermore, our decays are weak and have only a decade and half of amplitude.

The equation [15]

$$\mu = 1 - \tau/\tau_0 \qquad (1)$$

gives an indication of the non-radiative efficiency, μ, where τ and τ_0 are the Ce^{3+} luminescent decay times with and without the presence of Nd^{3+}, respectively. In both cases, the decay curves are exponential. The values of the transfer efficiency at 365 and 394 nm wavelength, each corresponding to one kind of Ce^{3+} site [12], are reported in Table I. The results are quite similar for the two wavelengths at low Nd^{3+} concentration, but when the Nd^{3+} concentration is increased, the Ce^{3+} lifetime for the 365 nm emission approaches the bandwidth of the laser pulse. The two types of Ce^{3+} site transfer their energy to Nd^{3+} ions with similar efficiency.

The large increase in the value of the non-radiative transfer efficiency with neodymium concentration is

TABLE I Measured lifetime and non-radiative energy transfer efficiencies

Starting composition	τ_{365} (ns)	$\mu_{\iota 365}$ (%)	τ_{393} (ns)	$\mu_{\iota 365}$ (%)
$La_{0.98}Ce_{0.02}MgAl_{11}O_{19}$	26	/	35	/
$La_{0.9}Nd_{0.08}Ce_{0.02}MgAl_{11}O_{19}$	21	19	29	17
$La_{0.78}Nd_{0.2}Ce_{0.02}MgAl_{11}O_{19}$	17	35	22	37
$La_{0.63}Nd_{0.35}Ce_{0.02}MgAl_{11}O_{19}$	15	42	19	46

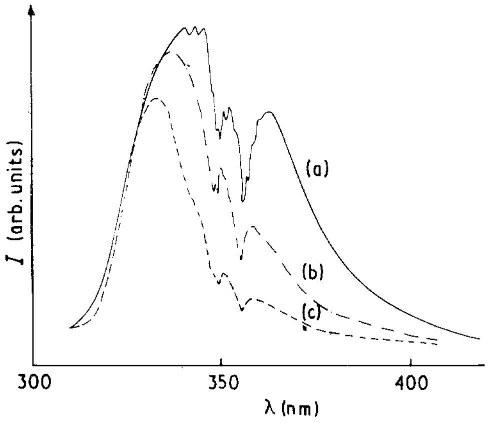

Figure 2 Emission spectra under xenon lamp excitation of Ce^{3+} in $La_{0.9}Ce_{0.02}Nd_{0.08}MgAl_{11-x}Cr_xO_{19}$ for x = (a) 0, (b) 0.055, (c) 0.11.

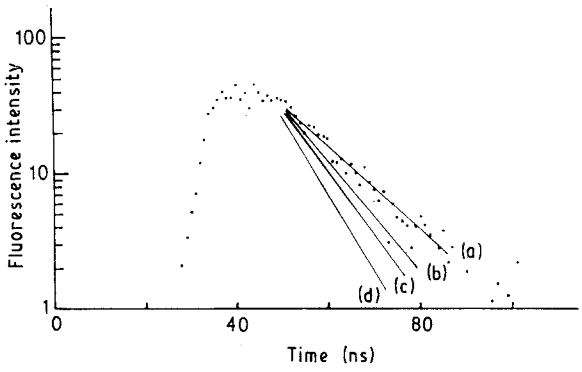

Figure 3 Decay curves of the Ce^{3+} fluorescence at room temperature in $La_{0.9}Ce_{0.02}Nd_{0.08}MgAl_{11-x}Cr_xO_{19}$. Excitation wavelength: 285 nm, emission: 393 nm. (a) $x = 0$, $\tau = 30$ ns; (b) $x = 0.011$, $\tau = 27$ ns; (c) $x = 0.055$, $\tau = 23$ ns; (d) $x = 0.11$, $\tau = 19$ ns. The experimental points (corrected from the dark current) are shown only for (a) for the sake of clarity.

related to a shortening of the $Nd^{3+} - Ce^{3+}$ distances which may be equal at least to the unit cell parameter, i.e. 0.56 nm.

In the hexaaluminates the non-radiative process leads to a maximum efficiency of about 47% for the highest Nd^{3+} concentration studied. This value is comparable to that obtained for β″-alumina crystals exchanged simultaneously with Ce^{3+} and Nd^{3+} in which the distance between the donor and the activator ions is very similar to ours [16]. Nevertheless this value is not very high compared to these obtained for Cr → Nd non-radiative energy transfer in LMA [14].

4. LMA:Cr, Ce, Nd

Preliminary results have also been obtained on the double sensitizer system which could combine the excitation of Ce^{3+} in the ultraviolet range and of Cr^{3+} in the visible range to produce emission of Nd^{3+} in the LMA hexaaluminate matrix. In the $La_{1-x-y}Ce_xNd_y MgAl_{11-z}Cr_zO_{19}$ single crystals, besides the Ce → Nd and the Cr → Nd energy transfer, one can also observe a strong interaction between the Ce^{3+} and Cr^{3+} ions. This interaction is demonstrated in Fig. 2 where it can be seen that the Ce^{3+}; emission strongly decreases, mainly at the long wavelengths ($\lambda > 350$ nm), when the Cr^{3+} concentration increases in the matrix. There is a good overlapping between the Cr^{3+} absorption spectrum [13] and the Ce^{3+} emission spectrum [14] and energy transfers occur between these two ions.

In Fig. 3, the fluorescence decay curves of the Ce^{3+} at 393 nm are depicted for several Cr^{3+} contents. At this wavelength the fluorescence intensity is smaller than for a wavelength of 365 nm but it is easier to follow the variation of the Ce^{3+} lifetime because its initial value is higher. From qualitative point of view, according to the uncertainties of the absolute values of these very short lifetimes, one finds that when the Cr^{3+} concentration increases, these Ce^{3+} lifetimes decrease from 30 ns in $La_{0.9}Ce_{0.02}Nd_{0.08}MgAl_{11}O_{19}$ to 19 ns in $La_{0.9}Ce_{0.02}Nd_{0.08}MgAl_{10.89}Cr_{0.11}O_{19}$. The efficiency of the Ce → Nd, Cr transfer evaluated from Equation 1 increases from 17% to 47% between the two compounds. The Cr → Nd, Cr non-radiative transfer efficiency is three times that of the non-radiative Ce → Nd, transfer when the concentration of Nd^{3+} and Cr^{3+} ions are both equal to 2×10^{20} ions cm^{-3}.

The coupling between Ce^{3+} and Cr^{3+} ions appears more favourable than between Ce^{3+} and Nd^{3+}. This is probably related to the fact that the spectral overlap is better. Furthermore, the shortest Ce–Cr distance is ~ 0.35 nm [14] while the Ce–Nd one is much longer (0.56 nm).

5. Conclusion

This preliminary study indicates that Ce^{3+} ions in the LMA matrix appear not only interesting as a preventative for the polarization process of the material [12], but also as a sensitizer for energy transfer to Cr^{3+} and Nd^{3+} codoping ions. In LMA:Ce, Nd crystals, Ce → Nd energy transfer occurs by both radiative and non-radiative processes, both with significant contributions. In the LMA:Cr, Ce, Nd crystals both Ce → Nd and Cr → Nd energy transfers occur, but at different transfer times: approximately 40 ns for the Ce → Nd interaction and 250 μs for the Cr → Nd interaction [14].

There is also a strong Ce → Cr interaction in these crystals because of the short distance between these two ions. The new scheme of sensitization via Cr^{3+} ions, Ce → Cr → Nd, is governed by the slow transfer time between Cr^{3+} and Nd^{3+} ions. Further investigations of these systems will need more precise lifetime measurements and the growth of large crystals by the Czochralski process to make laser tests. This will be undertaken in the near future.

References

1. S. E. STOKOWSKI, M. H. RANDLES and R. C. MORRIS, *IEEE J. Quant. Electron.* **24** (1988) 934.
2. V. A. SMIRNOV and I. A. SHCHERBAKOV, *ibid.* **24** (1988) 949.
3. D. S. SUMIDA, D. A. ROCKWELL and M. S. MANGIR, *ibid.* **24** (1988) 985.
4. C. GARAPON, A. MONTEIL and G. BOULON, *J. Phys. (Paris)* **48-C7** (1987) 493.
5. G. BLASSE and A. BRIL, *J. Chem. Phys.* **51** (1969) 3252.
6. J. M. P. J. VERSTEGEN, J. L. SOMMERDIJK and J. G. VERRIET, *J. Lumin.* **6** (1973) 425.
7. J. L. SOMMERDIJK and J. M. P. J. VERSTEGEN, *ibid.* **9** (1974) 415.
8. J. KVAPIL, Jos. KVAPIL, B. PERNER and K. HAMAL, *Czech. J. Phys.* **B37** (1987) 1277.
9. J. MARES, B. JACQUIER, C. PEDRINI and G. BOULON, *Rev. Phys. Appl.* **22** (1987) 145.
10. L. D. SCHEARER, M. LEDUC, D. VIVIEN, A. M. LEJUS and J. THERY, *IEEE J. Quant. Electron.* **QE22** (1986) 713.
11. A. KAHN, A. M. LEJUS, M. MADSAC, J. THERY, D. VIVIEN and J. C. BERNIER, *J. Appl. Phys.* **52** (1981) 6864.
12. B. VIANA, G. AKA, D. VIVIEN, A. M. LEJUS, T. THERY, A. DERORY, J. C. BERNIER, C. GARAPON and G. BOULON, *ibid.* **64** (1988) 1398.
13. B. VIANA, A. M. LEJUS, D. VIVIEN, V. PONCON and G. BOULON, *J. Solid State Chem.* **71** (1987) 77.
14. B. VIANA, C. GARAPON, A. M. LEJUS and D. VIVIEN, *J. Lumin.* **47** (1990) 73.
15. R. REISFELD, in "Energy Transfer Processes in Condensed Matter", edited by Di Bartolo (Plenum Press, New York and London, 1983) p. 521.
16. L. A. MOMODA, J. D. BARRIE, B. DUNN and O. M. STAFSUDD, in "Proceedings of the Conference on Luminescence Science and Technology", edited by B. Di Bartolo and Y. M. Yen, The Electrochemical Society, **88-24** (1989) p. 235.

Received 11 October 1990
and accepted 25 February 1991