ELSEVIER
Journal of Alloys and Compounds 275–277 (1998) 304–306
Journal of ALLOYS AND COMPOUNDS

Optical spectra and analysis of Pr^{3+} in β-$NaYF_4$

N. Martin[a,*], P. Boutinaud[a], M. Malinowski[b], R. Mahiou[a], J.C. Cousseins[a]

[a] *Laboratoire des Matériaux Inorganiques, ESA-6002, Université Blaise Pascal and ENSCCF, F-63177 Aubière Cedex, France*
[b] *Institute of Microelectronics and Optoelectronics, ul. Koszykowa 75, PL-00-662 Warsaw, Poland*

Abstract

We report a spectroscopic investigation of β-$NaYF_4$:Pr^{3+}. In order to study the upconversion properties of this system we determined the Stark energy level of different multiplets from luminescence spectra using polycrystalline samples with several concentrations at temperatures between 15 and 300 K. We correlate the luminescence and structural description and confirm the presence of three sites for the rare-earth ions in this material. Selective excitation is used to assign the self energy levels for each Pr^{3+} ion in the three sites.

Keywords: Fluoride; Luminescence; Praseodymium

1. Introduction

Interest in the spectroscopy of rare-earth ions in fluoride compounds is continuously increasing, especially in connection with laser research and related applications. Resistance to short wavelength radiation, relatively high optical damage threshold, low nonlinear refractive indices, and a number of other properties distinguish fluorides from numerous other materials. Among the fluorides usable for solid-state lasers, $LiYF_4$ is widely known as an efficient host for several rare-earth ions, especially for Pr^{3+} (Refs. [1,2] and references therein). This ion is very attractive since its emission spectrum ranges from the ultraviolet to the near infrared.

Moreover, recent studies have evidenced efficient upconversion processes of IR photons to blue emission in Pr^{3+}-doped $LiYF_4$ crystals [3]. Such processes have also been observed in Pr^{3+}-doped β-$NaYF_4$ (NYF) powdered samples [4].

The high efficiency of the mechanism could be ascribed to the multisite character of this matrix. Indeed, the latter contributes to the broadening of the absorption and emission lines and therefore improves the resonances between levels involved in the upconversion process. In order to investigate in detail the processes within the $4f^2$ configuration, we performed a laser spectroscopy study of NYF:Pr^{3+}. Of special interest are transitions in which the $^3P_0$ level is involved. This level is nondegenerate, so that splitting of lines must be due to Pr^{3+} in different crystal field sites.

2. Experimental

The luminescence measurements were performed on polycrystalline samples. $NaY_{1-x}Pr_xF_4$ ($x=0.1$–2%) powders were obtained in the solid state by reacting stoichiometric mixtures of the starting fluorides NaF, YF_3 and PrF_3. The reaction was carried out for 72 h at 600–680°C, depending on the composition, in sealed Ni tubes. The samples were mounted in a Cryomech GB15 cryorefrigerator allowing us to work between 300 and 15 K. The excitation was provided by a pulsed dye laser (Continuum ND60) pumped by a Continuum Surelite I-SL10 doubled Nd:YAG laser. The dye solution was a mixture of Rhodamines (610+640) allowing lasing in the 599–629 nm range. The output wavelength passed through a 0.6 m Raman Cell filled with hydrogen at 30 atm. The first anti-Stokes beam generated by the stimulated Raman scattering effect allows excitation in the 479–499 nm range and was selected by two Pellin–Brocca prisms and appropriate filters.

3. Results and discussion

The first complete characterisation of the NaF–LnF_3 system (for Ln=Y, La–Lu) was conducted by Thoma et al.

---

[*] Corresponding author.

0925-8388/98/$19.00
PII: S0925-8388(98)00323-5

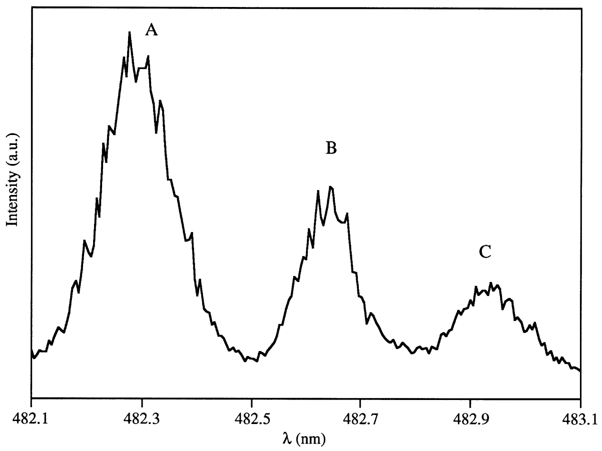

Fig. 1. $^3H_4 \rightarrow {}^3P_0$ time-resolved excitation spectra of β-NYF:0.1% Pr^{3+} for the 538.7 nm $^3P_0 \rightarrow {}^3H_5$ emission at 15 K (delay time 6.4 μs, gate width 50 ns).

[5], who identified three types of equilibrium phases, among them the hexagonal phase of 1:1 composition (β-$NaLnF_4$). This phase exists for Ln=Y, La–Lu.

Following the structural description [6] there are 1.5 formula units per unit cell so the formula is sometimes written as $NaLn(Na_{0.5}Ln_{0.5})F_6$ to indicate that there are three cation sites; one occupied to 100% by the rare earth (site 1a), one occupied randomly by both the rare earth and Na^+ (site 1f), and the third occupied to 100% by Na^+ (site 2h).

Recently, one of the present authors has shown through a careful analysis of the low temperature luminescence spectra of β-NYF:Eu^{3+} that the dopant is embedded in three sites, the third cationic site corresponding to the site 2h [7]. Such a result does not contradict the structural description if we assume a very low occupancy rate of this site by the rare earth. This result prompted us to investigate carefully the luminescence spectra of Pr^{3+}-doped β-NYF.

Fig. 1 shows the excitation spectrum of the Pr^{3+} blue emission in the area of the $^3H_4 \rightarrow {}^3P_0$ transition at 15 K. The spectrum consists of three broad bands labelled A, B and C located at 482.32 nm (20 733 cm^{-1}), 482.67 nm (20 718 cm^{-1}) and 482.97 nm (20 705 cm^{-1}), respectively. The more intense excitation band is band A, whereas bands B and C are weaker. To examine details of the site distribution, low temperature $^3P_0 \rightarrow {}^3H_{4-6}$ emission spectra were recorded upon excitation in the A, B and C bands. These three excitations result in blue and red luminescence, the blue being the more intense. The results displayed in Fig. 2 clearly show three distinctly different Pr^{3+} spectra; an observation which confirms that Pr^{3+} are distributed over the three cationic sites.

An interesting fact is the observation of blue upconverted spectra under orange $^3H_4 \rightarrow {}^1D_2$ pumping. The spectral distribution of this luminescence differs notably with respect to the Pr^{3+} concentration in the sample. Especially, in the 2% doped sample the $^3P_0 \rightarrow {}^3H_4$ emission spectrum shows only the features related to the A excited emission, while the low doped sample, viz. 0.1% Pr^{3+},

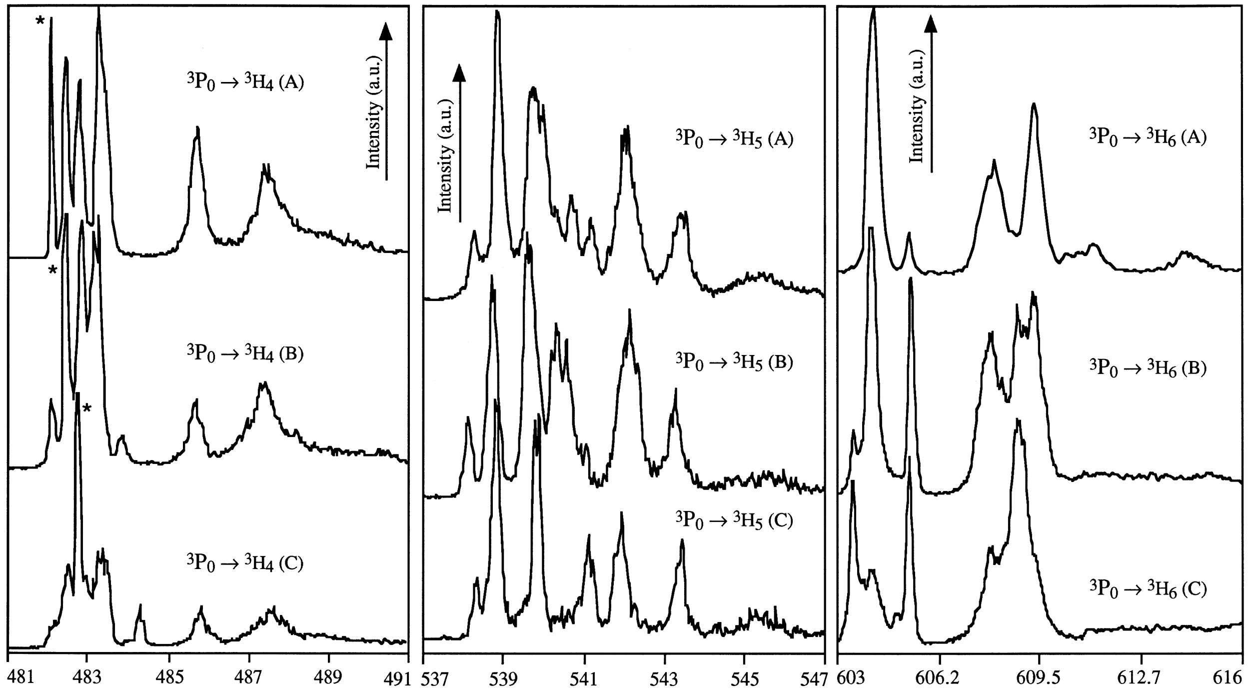

Fig. 2. $^3P_0 \rightarrow {}^3H_{4-6}$ time-resolved emission spectra of β-NYF:2% Pr^{3+} at 15 K under selective excitation into the $^3H_4 \rightarrow {}^3P_0$ absorption (delay time 20 μs, gate width 50 ns); *laser.

Table 1
Stark components of some energy levels of trivalent praseodymium in β-$NaYF_4$. Energy values given in cm^{-1}

	Site A	Site B	Site C
$^3H_4$	0, 20, 31, 56, 149, 226, 288	0, 33, 59, 130, 211	0, 28, 53, 67, 124, 198
$^3H_5$	2148, 2155, 2171, 2198, 2209, 2236, 2253, 2283, 2283, 2328, 2392	2133, 2171, 2185, 2205, 2219, 2265	2127, 2182, 2196, 2223, 2250, 2264, 2367
$^3H_6$	4183, 4213, 4273, 4284, 4289, 4321, 4351, 4375, 4452	4147, 4163, 4199, 4278, 4291, 4304, 4315	4138, 4146, 4154, 4176, 4187, 4258, 4282, 4301
$^1D_2$	16 705	16 689	16 679
$^3P_0$	20 733	20 718	20 705

shows in addition the features characteristic for the B and C excited emissions. Moreover, the emission peaks are always more numerous under the A excitation than under the B or C excitation; the spectra obtained under these latter two excitations exhibit approximately the same characteristics. It is clear that the B and C sites have similar environments, which differ from that of site A. An interpretation of these results can be made within the crystal structure considered.

The β-NYF structure contains two types of sites clearly identified for cation substitution, namely 1a and 1f, both showing C_{3h} symmetry, and a third site with C_3 symmetry, which is nominally exclusively devoted to Na^+. In the related material NYF:Eu^{3+}, the europium ion is found to occupy both the C_{3h} and C_3 positions [7]. Thus, by considering both the *J* splittings and the number of recorded emission peaks, we can assign the A excited spectrum to the low symmetry 2h site and the B and C excited spectra to the 1a and 1f sites, respectively.

Differentiation between these two sites can be made on the basis of the relative luminescence intensity. The B emission intensities always appear stronger than the C intensities, in agreement with the occupancy of site 1a which is twice that of site 1f. Moreover, it appears clearly from Table 1 that the splitting of the energy levels is always greater for Pr^{3+} in site 1a than for Pr^{3+} in site 1f, in agreement with the fact that the latter ions have an average distance to the ligand larger than that of the former. For all the $^3H_4 \rightarrow {}^3P_0$ pump wavelengths, the three $^3P_0$ emissions decay exponentially with a lifetime of 22 μs at 15 K. This value is considered as the radiative lifetime of the Pr $^3P_0$ levels in the investigated compounds, since it is constant in the experimented concentration range, and is similar to the lifetime of the $^3P_0$ level found in $LiYF_4$:Pr^{3+} (i.e. 38 μs) [8].

In conclusion, it is shown that Pr^{3+} in β-NYF exhibits efficient emissions. The spectral features are consistent with the existence of three cationic sites over which the dopant is distributed. Furthermore, selective excitation measurements allow a precise assignment of the spectral distribution to each of the three sites and are in agreement with the structural description.

References

[1] L. Esterowitz, R. Allen, M. Kruer, F. Bartoli, L.S. Goldberg, H.P. Jenssen, A. Linz, V.O. Nicolai, J. Appl. Phys. 48 (1977) 650.

[2] M. Malinowski, M.F. Joubert, R. Mahiou, B. Jacquier, J. Phys. C 7 III-4 (1994) 541.

[3] M. Malinowski, M.F. Joubert, B. Jacquier, Phys. Rev. B 50 (1994) 12367.

[4] N. Martin, private communication.

[5] R.E. Thoma, G.M. Hebert, H. Insley, C.F. Weaver, Inorg. Chem. 2 (1963) 1005.

[6] J.H. Burns, Inorg. Chem. 4 (1965) 881.

[7] D. Zakaria, R. Mahiou, D. Avignant, M. Zahir, J. Alloys Comp. (accepted).

[8] M. Malinowski, M.F. Joubert, B. Jacquier, J. Lumin. 60–61 (1997) 179.