Site selective optical spectroscopy of Pr$^{3+}$ in CsGd$_2$F$_7$

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Abstract

With the purpose of determining luminescence properties of lanthanide ions occupying different crystallographic sites in a same host, a new CsGd$_2$F$_7$:Pr$^{3+}$ crystal was optically characterized for the first time. Experimental data have shown that in CsGd$_2$F$_7$ doped with 2.0 at% Pr$^{3+}$, there are five Gd$^{3+}$ crystallographic sites which are substituted by Pr$^{3+}$. Under site-selective excitation at 12 K, luminescence spectra of Pr$^{3+}$ ions in the five sites are distinctly discriminated. The energies of the $^3P_0$ states for Pr$^{3+}$ in those sites are 20,889, 20,879, 20,873, 20,838 and 20,818 cm$^{-1}$. Lifetimes of Pr$^{3+}$ ion radiative levels for the different sites are also presented and analyzed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Site-selective excitation; Absorption and emission spectra; Lifetime; CsGd$_2$F$_7$:Pr$^{3+}$

1. Introduction

By now more than 70 fluoride crystals with ordered structures have been investigated as laser materials [1] and some of them present good laser performances. In particular, LiYF$_4$:Nd$^{3+}$ can rival YAG:Nd$^{3+}$ and has even got some advantages regarding, for example, the infrared laser wavelength with a better match for Nd$^{3+}$ glass amplifiers. In addition, Nd$^{3+}$ in LiYF$_4$ has a longer lifetime in the $^4F_{3/2}$ metastable state than Nd$^{3+}$ in YAG. In this context, CsGd$_2$F$_7$ and CsY$_2$F$_7$ are new potential crystal laser hosts but for the present time, only preliminary laser properties of these crystals doped with Nd$^{3+}$ have been studied [2,3]. Further spectroscopic investigations have shown that in CsGd$_2$F$_7$ structure, seven crystallographic sites can be occupied by Nd$^{3+}$ ions and some interaction may happen between Nd$^{3+}$ ions in pairs [4,5]. Hydrothermal CsGd$_2$F$_7$ crystallizes in the hexagonal crystallographic system (RbEr$_2$F$_7$ structure, space group P6$_3$22) [6,7].

With the purpose of determining the number of crystallographic sites which can be occupied by some other rare earth ions in CsGd$_2$F$_7$, a new CsGd$_2$F$_7$:Pr$^{3+}$ crystal was optically investigated. One reason for using Pr$^{3+}$ as an ion probe, is its rather simple energy level structure with a well-isolated non-degenerate $^3P_0$ state. Site-selective excitation at low temperature (12 K) has provided clear evidence that Pr$^{3+}$ occupies five crystallographic sites. Lifetimes of the radiative levels in Pr$^{3+}$ ions located in these different sites are also presented and analyzed.
2. Experiment

CsGd₂F₇ crystals doped with 2.0 at% Pr³⁺ was grown by the hydrothermal technique [4]. The synthesized crystalline phases were examined by the standard X-ray diffraction analysis which showed that Cs(Gd₀.₉₈Pr₀.₀₂)₂F₇ solid solution crystallizes in the hexagonal crystallographic system [6,7]. To benefit from the narrowness of the inhomogeneous energy transitions and to reduce the phonon effect, all the experiments were performed at 12 K. The absorption and emission spectra were recorded with a Jobin-Yvon HR-1000 monochromator. Laser selective excitation and excitation spectra were recorded using radiations from a dye laser (coumarin 480) pumped by the third harmonic of a YAG:Nd³⁺ laser (20 W Quantel). A Lecroy 9350 M oscilloscope was used for kinetics measurements.

3. Results and discussion

A part of the transmission spectrum in CsGd₂F₇:Pr³⁺ in the visible range is presented in Fig. 1. It clearly shows that there is more than one crystallographic site occupied by Pr³⁺ in this crystal structure. In particular, the maximum number of Stark levels for the ¹D₂ non-degenerate manifold is 5, but here there are at least 20 peaks for the well-isolated ³H₄–¹D₂ absorption transitions. When the terminal level is the non-degenerate ³P₀, the number of peaks in the spectrum for the ³H₄–³P₀ transition should provide the number of different crystallographic sites for Pr³⁺. In this context, there are six lines for the ³H₄–³P₀ transition. Three of them are strong and the three others are very weak or shoulders suggesting that the Pr³⁺ ions may occupy six different crystallographic sites in CsGd₂F₇.

In the excitation spectrum of the luminescence at 604.52 nm (Fig. 2(a)) six lines attributed to ³H₄–³P₀ transition are also observed. In order to index accurately the six peaks, a selected emission wavelength was monitored where all the six Pr³⁺ centers can contribute. It turned out that the energies of the ³P₀ state for Pr³⁺ in the different sites are 20,889 cm⁻¹ (478.71 nm), 20,879 cm⁻¹ (478.95 nm), 20,873 cm⁻¹ (479.08 nm), 20,854 cm⁻¹ (479.52 nm), 20,838 cm⁻¹ (479.88 nm) and 20,818 cm⁻¹ (480.36 nm) and these sites are labeled as Site 1, 2, 3, 3', 4 and 5, respectively. Accordingly, under selective excitation to these levels at 12 K, five different emission spectra are observed (Fig. 3). It should be noted that the emission spectrum induced under 479.52 nm excitation (Site 3') being almost identical to Fig. 3(c) except its very weak intensity, it is not reproduced here for clarity. The fact that excitation at 479.08 nm (Site 3) and 479.52 nm (Site 3') gives the same spectrum is not surprising when Fig. 2 is taken into account. Obviously, the intensity ratios between the lines at 479.08 and 479.52 nm always remains constant. Secondly, when the line at 479.08 nm disappears or is very weak, one cannot record the 479.52 nm line (Fig. 2(b), (e) and (f)). On the contrary, when the 479.08 nm absorption transition for Site 3 is strong...
enough, the line at 479.52 nm can clearly be observed (Fig. 2(a), (c) and (d), especially (d)). From these results, we can draw the conclusion that Sites 3 and 3’ are not distinct and accordingly, the satellite lines at 479.08 and 479.52 nm originate from the same luminescent center.

The excitation spectra of Pr\(^{3+}\) luminescence ions in the five sites of CsGd\(_2\)F\(_7\) crystal doped with 2.0 at\% Pr\(^{3+}\) at 12 K are presented in Fig. 2. The corresponding emission wavelengths are also shown in the figure. In this case, the monitoring wavelengths have been selected on the basis of spectral intensity and in order to avoid overlapping in the emission spectra. In Fig. 2(b), since the monitored wavelength at 603.56 nm belongs only to Site 1, without any contribution from other sites (see Fig. 3), a single absorption line attributed to Site 1 can be recorded. In a similar way, when 605.42 and 606.34 nm emission wavelengths are monitored, the excitation peaks mainly due to Pr\(^{3+}\) in Sites 4 and 5 are very strong whereas the others are very weak (Fig. 2(e) and (f)). The spectra labeled (c) and (d) are slightly different owing to the overlapping of emissions from Pr\(^{3+}\) in different sites. All the six peaks are observed but the peaks characteristic of Pr\(^{3+}\) in either Sites 2 or 3 dominate, respectively.

The symmetry of the rare earth environment can be deduced from the electronic structure of the emission spectrum. In Fig. 3, the spectrum of Pr\(^{3+}\) in Site 5 has the simplest structure, which suggests that this site should have the highest symmetry among the five sites. On the other hand, Pr\(^{3+}\) in Sites 1 and 2 give the most complicated spectra, implying that these sites have the lowest symmetry. Besides, it should be noted that under excitation...
into the $^3P_0$ level of Pr$^{3+}$ in CsGd$_2$F$_7$, the emission from only this level is observed. This is a peculiarity of fluoride crystals in general and the CsGd$_2$F$_7$ crystal in particular in comparison with oxygen-containing crystals, for example with YPO$_4$:Pr$^{3+}$ in which the emission from the $^1D_2$ Pr$^{3+}$ level occurs from a very efficient energy relaxation from the $^3P_0$ to the $^1D_2$ level owing to higher phonon energies in this crystal [8].

The fluorescence decays of the $^3P_0$ levels for the Pr$^{3+}$ ions in all the five sites are purely exponential. In particular, experimental results show that within experimental uncertainties, the Pr$^{3+}$ ions in Sites 4 and 5, as well as in Sites 1 and 3 display the same kinetics behavior (Fig. 4). The lifetimes of the $^3P_0$ state are 38 and 33 μs for the former ones and the latter ones, respectively. Obviously, the $^3P_0$ state for the Pr$^{3+}$ ions in Site 2 has the shortest lifetime of 29 μs. These results are consistent with the above discussion regarding the site symmetry. All the lifetimes given here are much longer than those determined for the same level in YPO$_4$:Pr$^{3+}$ (0.66 μs) [9], where the effective non-radiative energy relaxation from the $^3P_0$ to the $^1D_2$ level results in shorter lifetime. The very straight lines in Fig. 4 indicate that energy migration or energy transfer between Pr$^{3+}$ in the different sites can be neglected in the CsGd$_2$F$_7$ crystal doped with 2.0 at% Pr$^{3+}$.

4. Conclusion

Low-temperature absorption, excitation and emission spectra of CsGd$_2$F$_7$ crystal doped with 2.0 at% Pr$^{3+}$ have been investigated. In the CsGd$_2$F$_7$ structure, there are five different crystallographic sites which are occupied by the Pr$^{3+}$ ions. The $^3P_0$ state energies for Pr$^{3+}$ in these sites are 20,889, 20,879, 20,873, 20,838 and 20,818 cm$^{-1}$. Under site selective excitation at 12 K, emission spectra from Pr$^{3+}$ ions were clearly detected and the $^3P_0$ luminescence decay curves in all the sites show a single exponential decay with lifetimes equal to 33 μs (Sites 1 and 3), 29 μs (Site 2) and 38 μs (Sites 4 and 5).

References