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Dye laser excitation and crystal field calculation of the "non-garnet" site in (YGG) $Y_3Ga_5O_{12}$:Pr^{3+}

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Abstract

The luminescent properties of the trivalent praseodymium ion ($4f^2$ configuration) in $Y_3Ga_5O_{12}$ (YGG) with the garnet structure are analysed. Two different environments for the rare earth ion were found. The crystal field calculation was performed on the "non-garnet" site in the C_2 symmetry. The model, consisting of 22 parameters with 8 free ion and 14 crystal field parameters, reproduced the experimental energy level scheme of 57 electronic levels attributed to the "non-garnet" site with a root mean square (rms) deviation of 18 cm^{-1}. The real part of the crystal field parameter's values for the "non-garnet" site and the garnet site are of the same order of magnitude.

1. Introduction

The optical properties of trivalent praseodymium ion, Pr^{3+} ($4f^2$ configuration) embedded in various compounds have been extensively studied [1–4]. Except the $^1S_0$ level situated far in the UV range, all other electronic levels are situated in the visible and IR range and easily accessible by standard spectroscopic techniques. The relatively low total degeneracy of the $4f^2$ configuration [1] and several well isolated levels facilitate the interpretation of the optical data.

The garnets exhibit very broad absorption lines for all the compounds studied [1–4], crystal or powder samples, even at liquid helium temperature. Dye laser selective excitation and excitation spectra permit the separation of two (or more) distinct point sites occupied by the rare earth ion in the garnet structure.

In previous works, we underlined the very complex features concerning praseodymium spectroscopy in the garnets [1–4]. In the case of YGG:Pr^{3+}, only two distinct sites were deduced from the spectra, one of them attributed to the "garnet" site. The emission and the excitation spectra of the "non-garnet" site are consistent with a low point site, C_2 or lower. The energy level positions as well as the overall splittings of the J levels are very similar for both sites.

2. Experimental details

The $Y_{2.97}Pr_{0.03}Ga_5O_{12}$ sample was synthesised by heating a stoichiometric mixture of the corresponding oxides using the laser beam method [5]. X-Ray diffraction analysis confirmed the single garnet phase.

The visible and IR absorption spectra of the praseodymium ion was measured with a Cary 2400 spectrophotometer at 300 and 9 K, in the visible range also at 4.2 K with a 1-m Jobin-Yvon HR1000 single monochromator equipped with photomultiplier detection.The luminescence of the Pr^{3+} ion was excited either by different blue lines of 5W Spectra Physics argon ion laser at 300 and 77 K, or selectively on the $^1D_2$ level by continuous Rhodamine 6G dye laser pumped by the argon ion laser at 77 K. Alternatively, the $^3P_1$ $^3P_0$ and $^1D_2$ levels were excited by Lambda Physics FL 2001/2 dye laser pumped by a Sopra nitrogen laser at 4.2 K. The excitation spectra in the $^3P_0$–$^3P_2$ and $^1D_2$ range were monitored at liquid helium temperature.

3. Crystal structure

The rare earth gallium garnets, $RE_3Ga_5O_{12}$, form an isostructural series for RE = Pr–Lu, Y. The garnets crystallize in the cubic system with the space group $Ia3d$ (O_h^{10}) The eight-coordinated rare earth ions occupy a dodecahedral site with D_2 point symmetry. The gallium ions are situated in a six-coordinated octahedral site with S_6 point symmetry and a four-coordinated tetrahedral site with S_4 point symmetry (6).The optical studies performed on the garnets emphasized the incompability between the symmetry of the point site deduced from the luminescence spectra and the crystallographic data.

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The quantity of praseodymium ion, 1 mol%, in the YGG seems to be too small to alter the overall structure of the garnet. The gallium garnet structure is found for the praseodymium, $Pr_3Ga_5O_{12}$ (PrGG), contrary to aluminium garnet for which the pure $Pr_3Al_5O_{12}$ (PrAG) does not exist. Hence, there are no structural reasons for distortions to be created when the Pr^{3+} ion is embedded in the YGG matrix. The $Pr_{3x}Y_{3(1-x)}Ga_5O_{12}$ system studied previously with various concentrations of Pr^{3+} have shown two distinct energy level schemes for the rare earth ion [3].

4. Spectroscopic analysis

The visible and IR absorption spectra of trivalent praseodymium ion in garnets consist of very broad lines even at liquid helium temperature (see Fig. 1 of ref. 4). This suggests some additional distortions in the rare earth neighbourhood. The selective emission and excitation spectra show the presence of various supplementary lines originating from several sites. The origin of these extra sites has been mentioned in the literature [1–4,7] but not elucidated up to now in a satisfactory manner. For the YGG host system, two definite sites were found, one being attributed to the predominent garnet site and the other to the non-garnet site.

The emission spectra originating from the respective $^3P_0$ levels are shown in Figs. 1 and 2 and the excitation spectra for the $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^3P_1$ transitions are shown in Fig. 3. The most intense bands situated on the right side of the spectra in Fig. 3 are fluorescence lines from $^3P_0$ to the first excited crystal field (cf) states

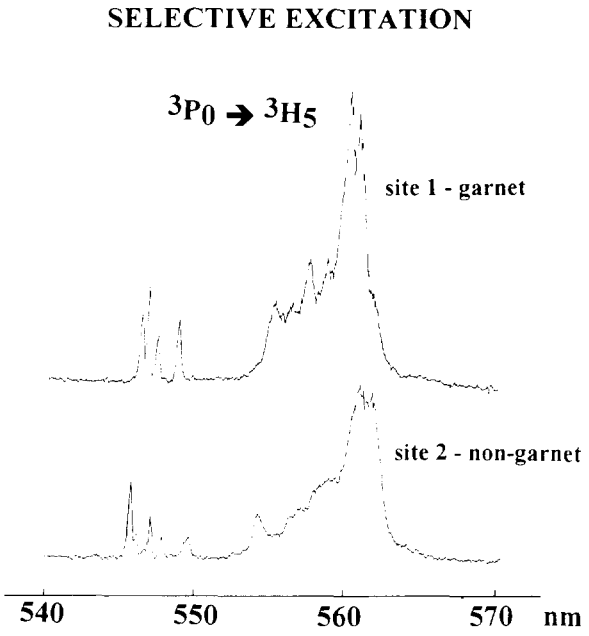

Fig. 1. A part of the emission spectra of YGG: Pr^{3+} at 4.2 K.

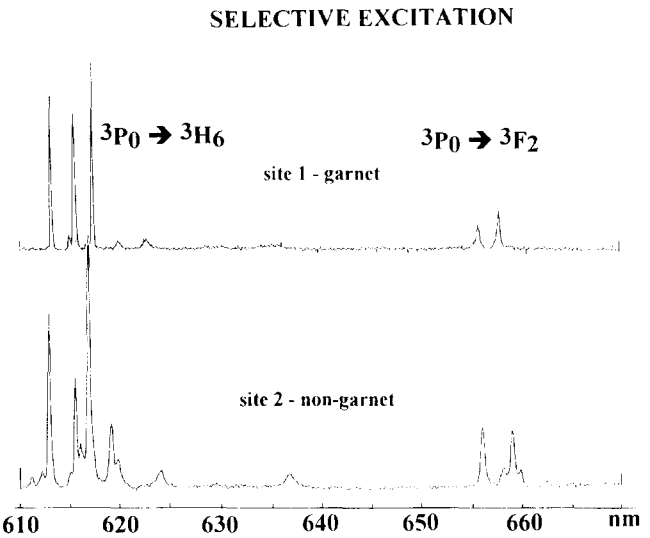

Fig. 2. A part of the emission spectra of YGG: Pr^{3+} at 4.2 K.

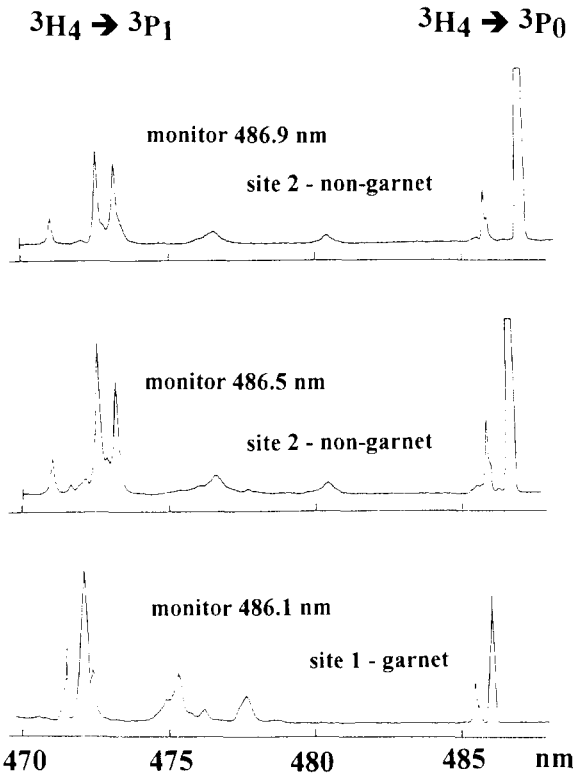

Fig. 3. Excitation spectra of YGG: Pr^{3+} at 4.2 K.

of $^3H_4$. The interpretation of the optical data, emission and excitation spectra, could be carried out reliably. The sites are characterized by similar cf splittings as well as by very similar decay times, 17 and 19 μs, for the non-garnet and the garnet sites, respectively. The overall splittings of the $^1D_2$ level for the two sites are given in Fig. 4. For the garnet site, four of the five possible Stark components were observed at liquid helium temperature; the fifth component (marked by an * on the figure) has been deduced from the absorption

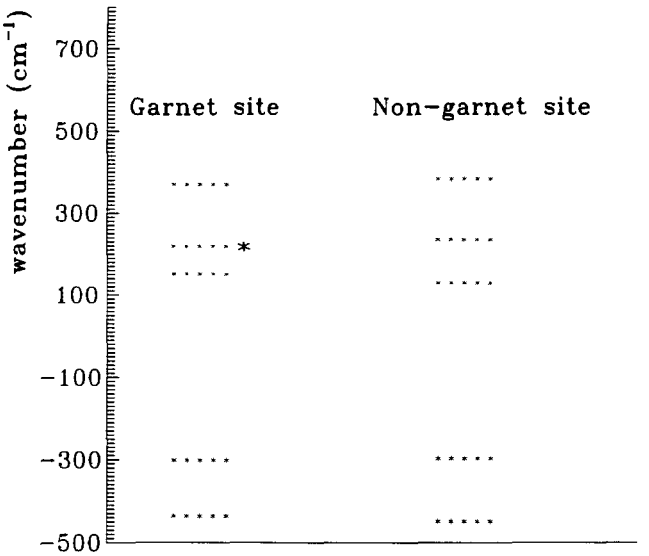

Fig. 4. The experimental $^1D_2$ level crystal field splittings for two observed sites for Pr^{3+} in YGG host.

TABLE 1. The phenomenological free ion and B_q^k (S_q^k) crystal field parameter values for the Pr^{3+} ion in YGG host (in cm^{-1})

	Non-garnet site C_2	Garnet site from ref. 4 D_2
E_0	9732	9723
E_1	4461	4491
E_2	21.55	21.47
E_3	455.33	457.50
α	20.21	21.94
β	−562	−692
γ	[1386]	[1470]
ζ	740	745
B_0^2	−115	139
B_2^2	181	−67
B_0^4	79	−227
B_2^4	−1995	−2202
S_2^4	228	–
B_4^4	−1540	−1089
S_4^4	111	–
B_0^6	−1729	−1784
B_2^6	−442	−730
S_2^6	213	–
B_4^6	956	747
S_4^6	−162	–
B_6^6	−325	−164
S_6^6	−107	–
Levels	57	68
rms	18	17

spectra at higher temperature between Stark levels using group theory selection rules. The application of the group theory confirms D_2 point symmetry for the garnet site. For the non-garnet site, all components

TABLE 2. The experimental and calculated energy levels of the Pr^{3+} ion in the "non-garnet" site in YGG host (cm^{-1})

$^{2S+1}L_J$ state	Experimental	Calculated C_2
$^3H_4$	0	−4
	38	22
	54	52
	475	461
	512	544
	572	586
	616	614
	704	704
	–	750
$^3H_5$	2269	2247
	2279	2290
	2312	2312
	2338	2316
	2397	2396
	2548	2531
	2612	2626
	2642	2655
	2691	2696
	2760	2767
	2788	2796
$^3H_6$	4274	4270
	–	4313
	4346	4333
	4381	4401
	4442	4427
	4457	4467
	4568	4570
	–	4785
	–	4845
	–	4851
	4884	4886
	–	4989
	–	5076
$^3F_2$	5348	5352
	–	5356
	5393	5406
	5416	5410
	5433	5437
$^3F_3$	6492	6470
	6510	6514
	6531	6535
	–	6735
	–	6755
	–	6781
	–	6967
$^3F_4$	–	7014
	–	7050
	7099	7078
	7109	7122
	7248	7262
	7297	7299
	–	7318
	–	7347
	–	7433

(continued)

TABLE 2. (*continued*)

$^{2S+1}L_J$ state	Experimental	Calculated C_2
$^1G_4$	–	9600
	–	9642
	–	9749
	–	9755
	–	9928
	–	10176
	–	10321
	–	10324
	–	10888
$^1D_2$	16399	16434
	16551	16538
	16977	16964
	17083	17095
	17231	17201
$^3P_0$	20593	20557
$^1I_6$	20821	20383
	–	20852
	–	20929
	20940	20948
	–	20973
	20987	20986
$^3P_1$	21135	21150
	21162	21161
	21231	21249
$^1I_6$	–	21653
	21785	21781
	21852	21844
	–	21913
	22006	22012
	22046	22062
	22215	22200
$^3P_2$	22330	22328
	–	22363
	22469	22482
	–	22573
	22604	22593
$^1S_0$	–	46086

are observed for the $^1D_2$ level as well as for the $^3P_1$ level (instead of two for the garnet site) at liquid helium temperature. This suggests a lower point symmetry for the non-garnet site. All the J level degeneracy seems to be lifted and there are no selection rules valid for electric dipole transitions. The point site symmetry is hence very low, probably C_2 or lower. Owing to the similarities between the two energy level schemes, one might suppose that the second site results from the real garnet site by local distortions introduced by lattice defects or impurities.

5. Simulation

The simulation of the experimental energy level scheme was performed according to Wybourne's classical formalism [8]. For the non-garnet site, 57 of the 91 theoretical J levels for the $4f^2$ configuration were deduced from the experimental data. Some lines attributed previously to $^3F_{3,4}$ levels [3] are not used in the simulation here. The coincidence with the $^1D_2 \rightarrow {}^3H_5$ transition of the garnet site is the reason (lines at 6485 and 6562 cm^{-1}) as well as a doubt about the assignment of lines at 7100 cm^{-1}. Table 1 lists a set of 17 and 22 phenomenological free ion and crystal field parameters (cfp) for the D_2 and the C_2 point symmetries, which reproduce well the energy level scheme of the garnet and the non-garnet sites of the trivalent praseodymium ion in the YGG matrix. The rms standard deviation, taken as a figure of merit of the simulation, is low.

The experimental and calculated energy level values are gathered in Table 2. The simulation of the "extra site" energy level scheme is relatively easy to perform because the two spectra are close to each other. The final cfp values for the "non-garnet" site are not so different from those of the "garnet" site.

Acknowledgments

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