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Crystal field and EPR studies of Nd^{3+}:YMO_4 (M=V, As, P)

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Abstract

Crystal field calculation and electron paramagnetic resonance (EPR) have been performed on zircon-type materials Nd:YMO_4 (M=V, As, P). Simulation of the energy level schemes has been carried out and the wave functions composition and *g* tensor principal values associated to the first sub-level of the $^4I_{9/2}$ manifold were calculated. A rather good correlation is obtained between crystal field calculations and the EPR measurements. Furthermore, some extra lines observed by optical spectroscopy (absorption and emission) also appear on the EPR spectra and a correlation between the two spectroscopies indicates that Nd^{3+}–Nd^{3+} exchange and dipolar interactions occur in the zircon family, even at very low doping content (less than 8×10^{19} Nd^{3+} ions cm^{-3}). Nd^{3+}–Nd^{3+} pairs at distances 3.9, 5.9 and 6.3 Å have been identified. © 1998 Elsevier Science S.A.

Keywords: Nd^{3+}; Zircon hosts; Electron paramagnetic resonance; Crystal field calculation; Optical spectra

1. Introduction

Nd:YVO_4 laser material has been extensively studied in the past years due to the very intensive absorption and emission cross-sections, one order of magnitude larger than for the Nd:YAG. The absorption bands are also very broad around 810 nm, and this property reduces the requirements on the laser diode temperature control. The very strong absorption allows a miniaturisation of the system which emits a very high quality laser beam and these small systems are called microchips lasers [1,2]. Furthermore, Nd:YVO_4 lasers are also available for higher power lasers and, with the use of an intracavity second harmonic generation, these lasers could replace the Argon ion laser, for instance in the pumping scheme of the titanium sapphire laser [3].

In this work, we present the study of zircon-type materials Nd:YMO_4 (M=V, As, P), which exhibit isomorphic structure and relatively close optical properties [4]. The crystal growth was performed in our laboratory by the flux method at a maximal temperature of 1270°C and platelets of several mm^2 were obtained. The Nd^{3+} concentration is 0.58% for YVO_4 (7.2×10^{19} ions cm^{-3}), 0.63% for $YAsO_4$ (8.1×10^{19} ions cm^{-3}) and 0.41% for YPO_4 (5.7×10^{19} ions cm^{-3}). In these hosts, Nd^{3+} ions are located on the Y^{3+} position with D_{2d} site symmetry. Some inter-atomic distances are given in Table 1, more details on the crystallographic data and the crystals preparation being reported in Ref. [5].

2. Experimental

The energy level diagrams were obtained from the low temperature absorption/emission measurements. Varian Cary 5 and Sopra SP-750 spectrophotometers were used to record the absorption and emission data, respectively. X-band EPR measurements were performed using a Bruker ER 220 D spectrometer. All these spectrometers are equipped with an Oxford Instrument liquid helium temperature device for low temperature measurements.

3. Results and discussion

From the low temperature absorption and emission spectra, it was possible to identify the Nd^{3+} energy levels in the 0–30 000 cm^{-1} range. After identification of approximately 100 levels for each host, a crystal field calculation was carried out in which the parametrized Hamiltonian includes Coulombic, spin orbit and crystal field (CF) terms in the D_{2d} symmetry [6–8]. The Hamilto-

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Table 1
Structural parameters of YMO_4 (M=V, As, P) zircon-type materials

YMO_4 compound	Unit cell parameters (Å)	O–Y distances (Å) (each ×4)	Shortest Y–Y distances (Å)
YVO_4	$a=7.118$, $c=6.289$	2.300, 2.430	3.891, 5.909, 5.935, 6.289, 7.118
$YAsO_4$	$a=7.044$, $c=6.248$	2.300, 2.412	3.853, 5.862, 5.879, 6.248, 7.044
YPO_4	$a=6.888$, $c=6.021$	2.313, 2.374	3.758, 5.679, 5.726, 6.021, 6.888

Only the Y–Y distances smaller than the unit cell parameters are considered.

nian was diagonalized for the Nd^{3+} ($4f^3$) configuration. The comparison between the experimental and calculated level positions is rather good as the mean deviation σ is 16.2, 15.4 and 15.7 cm^{-1} for Nd:YVO_4, Nd:$YAsO_4$ and Nd:YPO_4, respectively. The free ion parameters and the crystal field (CF) phenomenological B_q^k parameters were then deduced and reported in Table 2.

For the three hosts, it is possible to calculate the mean crystal field strength parameter N_v according to Ref. [9]

$$N_v = \left[\sum_{k\neq 0} \sum_q \frac{4\pi}{2k+1} (B_q^k)^2 \right]^{1/2}.$$

Values of 2401, 2333 and 2090 cm^{-1} are found for Nd:YVO_4, Nd:$YAsO_4$ and Nd:YPO_4 hosts, respectively. The overall splitting of the energy levels could be proportional to the N_v parameter value [9]. In our case $\Delta E(^4I_{9/2})=437$, 366 and 403 cm^{-1}, while the splitting of the $^4F_{3/2}$ level is $\Delta E(^4F_{3/2})=18$, 26 and 51 cm^{-1} for Nd:YVO_4, Nd:$YAsO_4$ and Nd:YPO_4 hosts, respectively. In that case, there is no special relation between the N_v parameter and the CF splitting of these two energy levels. However, as the $\Delta E(^4I_{9/2})$ value is lower than 470 cm^{-1} [9] (for instance this value is 859 cm^{-1} and the N_v parameter reaches 4055 cm^{-1} in Nd:YAG), the zircon family belongs to the so-called weak quenching materials [10]. The main consequence is that the concentration quenching effect is weak and it could be very interesting to consider high neodymium concentrations in these laser hosts.

Another effect of the small N_v value is that the five Stark sub-levels of the ground state are populated at room temperature. For instance, for Nd:YVO_4, the highest sub-level of the ground-state manifold, located at 437 cm^{-1}, contains around 5% of the total Nd^{3+} population. Furthermore, the weak crystal field splitting of the $^2F_{5/2}$, $^2H_{9/2}$ levels and the comparable energy difference between the sub-levels of the $^2F_{5/2}$, $^2H_{9/2}$ and $^4I_{9/2}$ manifold give rise to several optical transitions which gather around 810 nm. With this very simple analysis based on the crystal field splitting, one can account for the broad absorption bands of the zircon hosts [4].

Table 2
Free ion (E^i, α, β, γ, T^i, ξ) and crystal field parameters for Nd^{3+} in YMO_4 (M=V, P, As) single crystals

Parameter	Nd:YVO_4	Nd:$YAsO_4$	Nd:YPO_4
E^0	23 357.95	23 523.61	23 520.11
E^1	4757.07	4788.54	4780.62
E^2	23.05	23.59	23.5
E^3	478.95	486.94	484.66
α	20.91	20.69	20.38
β	−647.36	−601.49	−602.2
γ	1500	1500	1500
T^2	244.52	152.14	202.1
T^3	36.17	41.34	41.55
T^4	124.42	101.97	94.78
T^6	−278.13	−260.02	−262.65
T^7	352.72	306.31	−316.48
T^8	337.56	138.28	205.91
ξ	869.1	871.43	870.87
B_0^2	−200	−164	240
B_0^4	628	237	108
B_4^4	−1136	−1071	−1006
B_0^6	−1233	−1043	−1190
B_4^6	149	−10	−90
Number of levels	96	102	90
σ	16.2 cm^{-1}	15.4 cm^{-1}	15.7 cm^{-1}
Experimental (EPR)	$g\|\|=0.915\pm0.004$	$g\|\|=1.874\pm0.002$	$g\|\|=3.101\pm0.005$
g values	$g\perp=2.361\pm0.003$	$g\perp=1.938\pm0.001$	$g\perp1.217\pm0.007$
Calculated (CF)	$g\|\|=0.94$	$g\|\|=1.63$	$g\|\|=2.90$
g values	$g\perp=2.46$	$g\perp=2.16$	$g\perp=1.42$

Experimental and calculated g factor values for the three hosts are also reported.

In this study, electron paramagnetic resonance (EPR) was used firstly as a probe of the crystal field calculations. As seen in Table 1, less than 17% discrepancy is found between calculated and observed Nd^{3+} g values for the three zircon hosts. Secondly, EPR spectroscopy appears to be a powerful tool for the site occupancy determination [11], since it allows us to understand the origin of the satellites observed in the optical spectra beside the main bands attributed to Nd^{3+} ions in the regular sites (see Fig. 1). In Fig. 1 the 4.4 K absorption spectra in the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ range are reported for the three hosts. At this temperature, and according to the energy level schemes previously determined, only the first sub-level of the $^4I_{9/2}$ manifold is populated and only two bands due to the CF splitting of the $^4F_{3/2}$ level are expected. Other lines appear which were not accounted for by the previously reported crystal field calculation. Their origin can be more specifically studied by considering the EPR spectra, repeated in Fig. 2.

The main EPR lines are due to Nd^{3+} ions in Y^{3+} sites (with D_{2d} point symmetry) in the 180–450 mT range and consist of a hyperfine structure of eight lines for each of the two odd neodymium isotopes (see Fig. 2). Besides the main EPR signals several pairs of satellites appear on each side of the central line with their intensity increasing with doping concentration. This doublet structure can be attributed to Nd^{3+}–Nd^{3+} pairs in dipole–dipole magnetic interaction. By measuring the distance between the two lines of each pair, it is possible to calculate the distance between

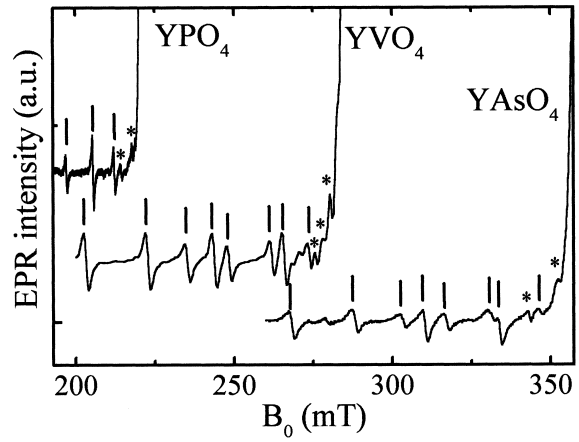

Fig. 2. Low field part of the EPR spectra of the Nd:YMO_4 (M=Y, As, P). The gain of the EPR signal is adapted to visualise the satellites for the three compounds. Satellites marked with a star are related to Nd^{3+}–Nd^{3+} pairs and vertical marks indicate the hyperfine lines.

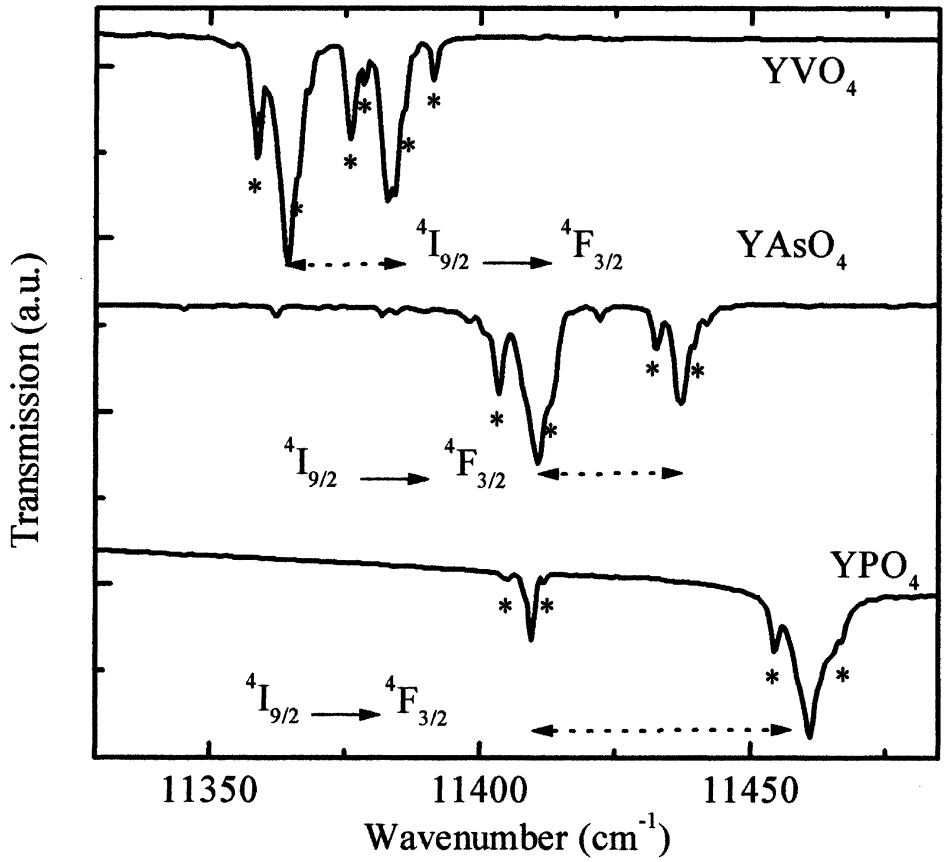

Fig. 1. Visualisation of satellites on the low-temperature absorption spectra of Nd^{3+} ions in YMO_4 (M=V, P, As). The Nd^{3+} concentration is 0.58% for YVO_4 (7.2×10^{19} ions cm^{-3}), 0.63% for $YAsO_4$ (8.1×10^{19} ions cm^{-3}) and 0.41% for YPO_4 (5.7×10^{19} ions cm^{-3}). Comparable features have been obtained on the emission spectra [12]. Satellites marked with * are due to Nd^{3+}–Nd^{3+} pairs.

the two Nd^{3+} ions which is correlated to the Y–Y distances of the zircon structure [13]. In the Nd:YVO_4 host, the calculated distances between Nd^{3+} pairs are 3.89, 5.9 and 6.3 Å, while only one value, 3.9 Å, is obtained for the $YAsO_4$ matrix. These distances are in very good agreement with the Y^{3+}–Y^{3+} distances in the zircon structure presented in the Table 1. This indicates that Nd^{3+} ions exhibit a tendency to associate in pairs even at relatively low Nd^{3+} concentration (around 7×10^{19} cm^{-3}). An intensity measurement indicates that about 15% of the Nd^{3+} are associated in Nd^{3+}–Nd^{3+} pairs, and this effect could strongly affect the optical properties of these zircon materials. The magnetic dipolar interaction between Nd^{3+} in pairs is too small ($\sim10^{-2}$ cm^{-1}) to account for the additional satellites observed in the optical spectra. However, these satellites can be accurately explained by an isotropic exchange splitting of the two $^4I_{9/2}\rightarrow{}^4F_{3/2}$ transitions. In that case, the splitting is the result of a weak ferromagnetic exchange interaction between the fictitious $S=1/2$ spins of two neighbouring Nd^{3+} ions, giving two spin states $S=1$ and $S=0$ split by the exchange interaction J.

4. Conclusion

In this study, after identification of the absorption and emission spectral lines and crystal field calculations, it was possible to estimate the crystal field strength for neodymium in the three zircon hosts YMO_4 (M=V, As, P). The overall splitting values of the $^4I_{9/2}$ manifold are 437, 366 and 403 cm^{-1} for the Nd:YVO_4, Nd:$YAsO_4$ and Nd:YPO_4 compounds, respectively. These values are characteristic of a low crystal field strength and, in particular, the degeneracy of the $^4F_{3/2}$ level is lifted by only 18 cm^{-1} by the crystal field in Nd:YVO_4. This characteristic can account for the broad absorption bands around 810 nm observed in the zircon hosts.

By using EPR spectroscopy, it was possible to correlate the extra lines observed on the absorption and emission spectra to Nd^{3+}–Nd^{3+} pairs formation even at low doping concentration (7×10^{-19} Nd^{3+} ions cm^{-1}). This ion-pairing effect will appear as a strong limitation for increasing the concentration even if these hosts could be considered as weak concentration quenching compounds on the basis on the small overall splitting of the $^4I_{9/2}$ Nd^{3+} level.

Further investigations are now in progress in our laboratories. We are considering the investigation of zircon compounds doped with different Nd^{3+} doping concentrations. For crystal field calculations, the next step will be to try to explain the unusual strengths of the optical transitions in these hosts by modelling the transition intensities using odd rank crystal field parameters.

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