

Optical Properties of Neodymium Pentaphosphate—A High Nd-Concentration Laser Material

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NdP₅O₁₄ shows only weak fluorescence quenching of the ⁴F_{3/2} fluorescence in spite of the high (~4 × 10²¹ per cc) Nd³⁺ concentration. Aspects of the fluorescent properties are described, and the structural basis for the reduced fluorescence quenching relative to YAG:Nd and other hosts is discussed.

Introduction

The development of optical communications systems entails a need for compact efficient optical sources. Optically pumped solid state rare earth ion lasers are attractive for this purpose, in particular those employing the ~1.06 μm ⁴F_{3/2} → ⁴I_{11/2} transition of Nd³⁺ (Fig. 1) which coincides with a low-loss wavelength region of silica based optical fibers.

Yttrium aluminum garnet (YAG) doped with 1% Nd and Nd-glass lasers have become convenient hosts for low threshold and high power applications, respectively. Both have been successfully miniaturized (1, 2) and may be pumped by conventional optical techniques or by semiconductor sources. But although appropriate techniques of pumping and light confinement permit quite low threshold (≥1 mW of absorbed power) operation, the degree of miniaturization is ultimately limited by the concentration of the active Nd³⁺ centers. In these, as in all other solid state Nd³⁺ laser hosts tested until recently, the Nd³⁺ dopant concentration must be restricted to ~1 at. % to avoid nonradiative quenching of fluorescence. The quenching is reflected in a reduction in the fluorescence lifetime of the ⁴F_{3/2} upper laser level and an increase in the absorbed power required to initiate laser action.

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Nonfluorescent decay may occur via ion-pair interactions or by a direct multiphonon process. The multiphonon process is determined by the host and the largest (⁴F_{3/2}–⁴I_{15/2}) manifold separation and is unlikely to vary greatly with the Nd³⁺ concentration. The ion-pair interactions on the other hand, which depend on the overlap of Nd³⁺ emission and absorption energies and on the separation of

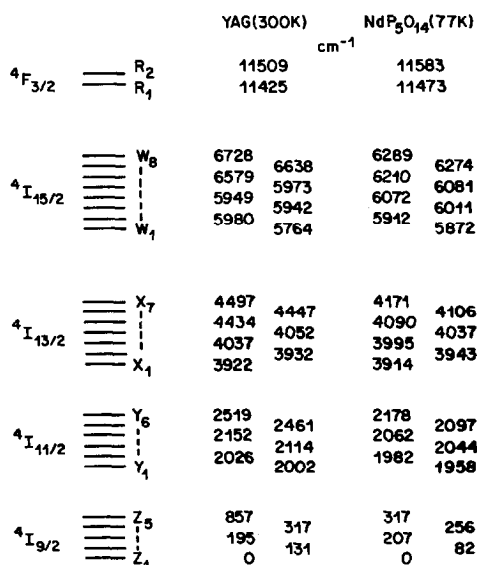


FIG. 1. Energy levels of Nd³⁺ in YAG:Nd and NdP₅O₁₄ (not to scale).

the Nd^{3+} dopant ions, are dependent on the Nd^{3+} concentration and will disappear in the dilute limit. It is these interactions which limit the useful concentration in most materials to $\sim 1\%$. The lifetime variation with Nd^{3+} concentration in $\text{Na}_{0.5}\text{Gd}_{0.5-x}\text{Nd}_x\text{WO}_4$ (3) which is typical of that shown by YAG:Nd and other hosts is shown in Fig. 2.

It is thus desirable for thin film and small-scale applications to discover materials where the Nd^{3+} pair interactions are weak and the Nd^{3+} concentration may be increased without incurring severe fluorescence quenching. A high cross section for stimulated emission and ease of preparation and manipulation into the desired device configuration are additional requirements.

Neodymium Pentaphosphate

Neodymium pentaphosphate, $\text{NdP}_5\text{O}_{14}$, an oxyacid salt rather than the usual "ionic" crystal host fulfills some of these requirements, and, in particular shows a very reduced degree of fluorescence quenching.

Preparation and Laser Action

The rare earth pentaphosphates were prepared by Beucher (4), and three different crystalline forms are observed at room temperature depending on the size of the trivalent ion. The smaller trivalent transition metal ions do not stabilize the structure and form only triphosphates (MP_3O_9). $\text{NdP}_5\text{O}_{14}$ was

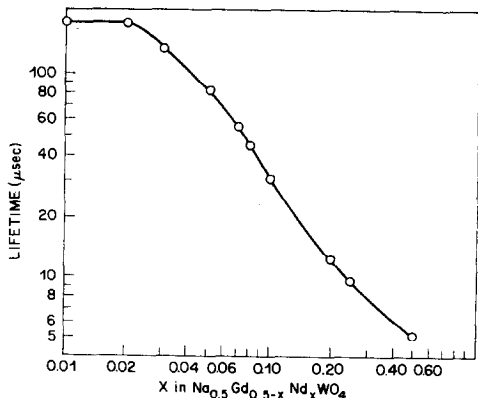


FIG. 2. The concentration variation of the fluorescent lifetime of the $\text{Nd}^{3+} \ ^4F_{3/2}$ state in $\text{Na}_{0.5}\text{Gd}_{0.5-x}\text{Nd}_x\text{WO}_4$ at room temperature (from Ref. (4)).

discovered independently by Danielmeyer and Weber (5) who observed a long fluorescence lifetime of 66 μsec indicating weak fluorescence quenching, even though the Nd^{3+} concentration is $\sim 4 \times 10^{21}$ per cc, about 30 times greater than in 1% Nd:YAG. The space group is $P2_1/c$ and the characteristic crystal shape is diamond plates with the b and c crystallographic axes along the minor and major axes, respectively (6). The crystals discussed below have been made from hot phosphoric acid solution in gold or vitreous graphite crucibles.

We first reported (7) pulsed laser action along the a -axis of a 35 μm thick platelet of $\text{NdP}_5\text{O}_{14}$ and later (8) stimulated emission from a 35 μm thick platelet of $\text{Nd}_{0.5}\text{La}_{0.5}\text{P}_5\text{O}_{14}$ (where the lifetime was increased to 150 μsec) without the aid of external mirrors and the first cw emission in this system from a 1.4 mm thick crystal of $\text{Nd}_{0.5}\text{La}_{0.5}\text{P}_5\text{O}_{14}$. Using two mirrors with transmission $T = 1.5\%$ at 1.05 μm a pump threshold of 25 mW of absorbed light at 514.5 nm (cw argon laser) was observed. All these crystals were later shown (6) to suffer from fluorescence quenching due to included hydrogen (see below). Lower thresholds (~ 1 mW) for cw operation with $\text{NdP}_5\text{O}_{14}$ where hydrogen appeared to be excluded in the growth process, have been reported (9), and we have found that low thresholds are attainable for crystals grown from H_3PO_4 if the growth temperature is high enough to avoid impurity quenching.

Fluorescence and Impurity Quenching

We have measured the fluorescence lifetime as a function of the Nd concentration in

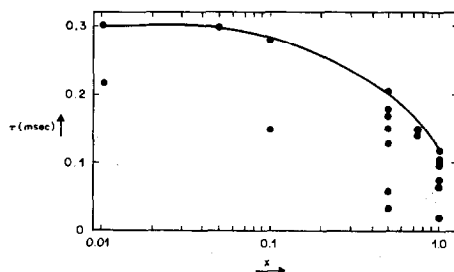


FIG. 3. The concentration variation of the $\text{Nd}^{3+} \ ^4F_{3/2}$ fluorescent lifetime in $\text{Nd}_x\text{La}_{1-x}\text{P}_5\text{O}_{14}$ at room temperature.

$\text{Nd}_{1-x}\text{La}_x\text{P}_5\text{O}_{14}$ (6) (Fig. 3). The maximum lifetimes given by the solid curve show that quenching is present, although small, the lifetime dropping only from $\sim 300 \mu\text{sec}$ to $120 \mu\text{sec}$ for $x \sim 0.99$ to $x = 0$. The lower lifetimes indicated are observed for crystals prepared at temperatures below $\sim 550^\circ\text{C}$ and this effect is not related to crystal quality or composition. Infrared absorption measurements (6) indicate the effect to be due to included hydrogen, probably as P-O-H or bound water (Fig. 4). O-H stretching vibrations can allow an efficient two-phonon ${}^4F_{3/2} \rightarrow {}^4I_{15/2}$ nonradiative decay. The lifetimes of low lifetime crystals may be raised to the characteristic values by annealing in a P_2O_5 atmosphere although not all the hydrogen is removed (6). Alternatively, hydrogen seems to be prevented from entering the crystal by growth (10) in the presence of an excess of a smaller ion such as Sc^{3+} which does not significantly enter the pentaphosphate lattice. Hydrogen-free preparative routes might also be used.

Multiphonon Decay

The multiphonon decay rate W_m , observed for several rare earth ions in various hosts, may be approximated by (11)

$$W_m = \Gamma(1 - e^{-hv/kT})^{-n} e^{-\gamma\Delta E}, \quad (1)$$

where ΔE is the energy gap (${}^4F_{3/2} \rightarrow {}^4I_{15/2}$ for Nd^{3+}), v is the phonon frequency, $n = \Delta E/hv$ is the number of phonons needed to cause decay and Γ and γ are initially unknown characteristics of the system. The presence of the PO_4 tetrahedra with available high energy ($\sim 1300 \text{ cm}^{-1}$ (6)) vibrational quanta (P-O stretching) might be expected to facilitate direct multiphonon quenching relative to YAG:Nd where the phonon cutoff is 850 cm^{-1} (12). There is still some uncertainty over the actual multiphonon quenching efficiencies (η_q) in YAG , and values of 0.44 ± 0.11 (13) and $0.0-0.2$ (14) have recently been quoted. The value of η_q of $0.0-0.2$ recently determined by us for $\text{NdP}_5\text{O}_{14}$ (15) indicates, however, that the multiphonon decay rate in this compound does not compare unfavorably with that in YAG:Nd , in spite of the high phonon cutoff.

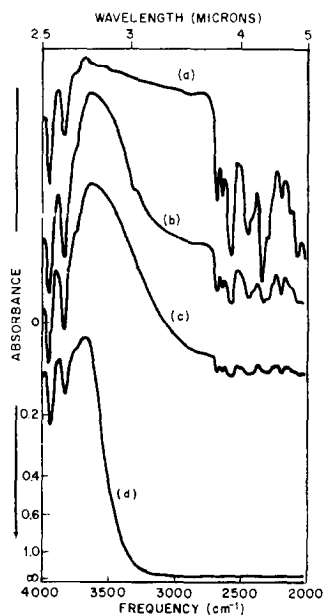


FIG. 4. The near ir absorption spectra (2.5–5 μm) of pentaphosphate crystals showing the increasing absorption at $\approx 2800 \text{ cm}^{-1}$ and $\approx 3300 \text{ cm}^{-1}$ due to hydrogen incorporation as the growth temperature is lowered. (a) $\text{Nd}_{0.5}\text{La}_{0.5}\text{P}_5\text{O}_{14}$ crystal prepared at 650°C (unpolished, thickness 0.8 mm); (b) $\text{NdP}_5\text{O}_{14}$ crystals prepared at 500°C (unpolished, thickness 0.8 mm); (c) crystals of (b) after annealing in a P_2O_5 atmosphere at 650°C for 48 hr; (d) $\text{NdP}_5\text{O}_{14}$ crystals prepared at 300°C (parallel polished faces, thickness 0.35 mm). The absorption scale for all the spectra is the same as that indicated for (d). The bands at 3830 cm^{-1} and 3950 cm^{-1} are part of the $\text{Nd}^{3+} {}^4I_{9/2} \rightarrow {}^4I_{13/2}$ absorption and that at 2185 cm^{-1} is the highest energy ${}^4I_{9/2} \rightarrow {}^4I_{11/2}$ absorption. The bands from $2230-2670 \text{ cm}^{-1}$ are overtones of P-O stretch fundamentals.

The Crystal Structure, Fluorescence Quenching, and Energy Diffusion

The crystal structure of $\text{NdP}_5\text{O}_{14}$ has been described recently (16, 17). $(\text{P}_5\text{O}_{14}^{3-})_\infty$ ribbons composed of repeating $\text{P}_{10}\text{O}_{28}$ units lie in the ac plane and are stacked along the b axis (Fig. 5). The ribbons extend along the a -axis. A ribbon at $y = 0$ is parallel to those at $y = \frac{1}{2}$ but is displaced along the c -axis so that it overlaps two ribbons at the next level (Fig. 6). Adjacent ribbons are joined only by Nd-O bonds and the structure explains the easy cleavage plane perpendicular to the b -axis.

Concentration quenching of fluorescence

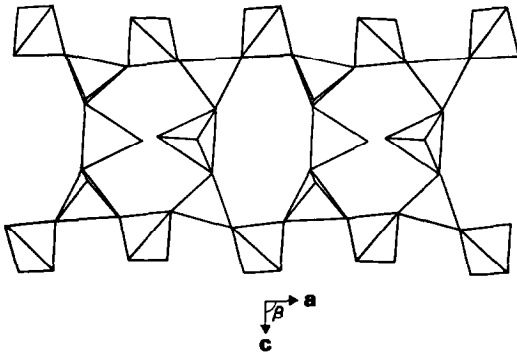


FIG. 5. The $(P_5O_{14}^{3-})_\infty$ ribbon in the NdP_5O_{14} structure (from Ref. (17)).

results from Nd^{3+} pair interactions. If one Nd^{3+} ion is in the ${}^4F_{3/2}$ upper laser state and its neighbor is in the ${}^4I_{9/2}$ ground state a nonradiative redistribution of energy may take place leaving both Nd^{3+} ions in intermediate 4I manifolds from which rapid phonon decay to the ground state may take place. Resonant electronic deexcitation via the ${}^4I_{15/2}$ levels was suggested as a likely mechanism for this process several years ago (18).

For NdP_5O_{14} it has been suggested (19) that the reduced fluorescence quenching relative to the YAG:Nd system is due to the less efficient overlap of the ${}^4F_{3/2} \rightarrow {}^4I_{15/2}$ emission lines with the ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$ absorption. However, in NdP_5O_{14} there are still four overlapping transitions within 6 cm^{-1} (20) which is much less than the peak width at room temp-

erature. Thus, the much weaker ${}^4F_{3/2} \rightarrow {}^4I_{15/2}$ fluorescence in NdP_5O_{14} ($<10^{-4}$ of total at room temperature (19)) compared to YAG:Nd ($\sim 10^{-2}$ of total at room temperature (21)) may be the more relevant factor. Singh et al. (20) have suggested that the observed quenching may occur via a one-phonon-assisted process involving ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ fluorescence and ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$ absorption. This mechanism would be consistent with the temperature independence of the fluorescence lifetime below room temperature (15).

The principal distinguishing characteristic of NdP_5O_{14} compared to all previously studied laser hosts, however, is the isolation of the NdO_8 polyhedra (slightly distorted square antiprism (16)). No two Nd ions share the same oxygen atom and the nearest Nd-Nd distance is 5.194 \AA (16). This isolation must significantly reduce the ion-pair interactions leading to fluorescence quenching and we confidently predict that such isolation will be a feature of other systems which may show reduced concentration quenching of fluorescence. We have demonstrated this to be the case, for example, in $Cs_2NaNd_{1-x}Y_xCl_6$ where the $NdCl_6^{2-}$ octahedra are isolated from one another and the closest Nd-Nd distance is 7.7 \AA (22).

The Nd^{3+} ions form chains along the a -axis with alternating distances of 5.194 \AA and 5.945 \AA —the shortest Nd-Nd distances in the structure. These links have been proposed as the principal pathway for energy diffusion in NdP_5O_{14} and an average diffusion distance of $\approx 5000\text{ \AA}$ was predicted (19). This is considerably larger than a quarter wavelength of the $1.05\text{ }\mu\text{m}$ laser line and it was predicted (19) that single transverse mode NdP_5O_{14} lasers should spontaneously oscillate in a single frequency for cw operation between threshold and approximately twice threshold. Preliminary experiments on NdP_5O_{14} and $Nd_{0.5}La_{0.5}P_5O_{14}$ did not appear to confirm this effect (23). Single frequency cw operation in $Nd_{0.5}La_{0.5}P_5O_{14}$ was, however, achieved by intracavity mode selection and pumping at five times threshold with only 20% reduction of output power compared to operation without mode selection. We have recently directly measured (24) the energy diffusion

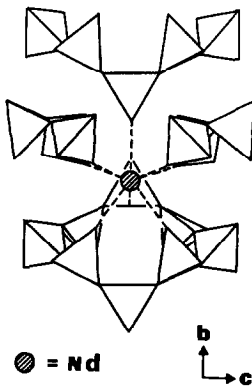


FIG. 6. The stacking of $(P_5O_{14}^{3-})_\infty$ ribbons in NdP_5O_{14} . The coordination of an Nd^{3+} ion is indicated (from Ref. (17)).

distance in $\text{NdP}_5\text{O}_{14}$ ($\tau = 120 \mu\text{sec}$) to be only 320 \AA , which is indeed far smaller than suggested (19) and not nearly large enough to support spontaneous single-frequency laser operation.

Interesting features of the small monoclinic distortion ($\beta \approx 90.5^\circ$) of the lighter rare earth pentaphosphates (La-Tb) are the presence of a second order phase transition at slightly elevated temperatures to an orthorhombic unit cell, and the ferroelastic properties of the monoclinic crystals. The shear stress required to induce ferroelastic reorganization via twin boundary motion is two orders of magnitude lower than that reported to induce ferroelastic reorganization in other crystals (25).

Emission Cross Sections

Room temperature emission cross sections for the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions have been measured (15). The maximum ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ cross section ($R_1 \rightarrow Y_2$) is $\sigma = 1.7 \times 10^{-19} \text{ cm}^2$, 0.35 times the largest peak emission cross section for YAG:Nd (13). The $1.051 \mu\text{m}$ laser line has contributions from two transitions $R_1 \rightarrow Y_1$ and $R_2 \rightarrow Y_4$ with an effective cross-section of $1.2 \times 10^{-19} \text{ cm}^2$. This is two-thirds the peak effective cross section in YAG:Nd of $1.8 \times 10^{-19} \text{ cm}^2$, resulting in a slightly lower laser gain per Nd ion in $\text{NdP}_5\text{O}_{14}$. The polarization dependence of the cross sections has also been studied (20).

In the end-pumped configuration the lower cross section of $\text{NdP}_5\text{O}_{14}$ relative to YAG:Nd does not give the former material any advantage in pump threshold power for equivalent nonresonant losses in the cavity, although the threshold of 1 mW reported (9) for such operation in $\text{NdP}_5\text{O}_{14}$ is lower than any so far reported for YAG:Nd. But the high Nd concentration in the pentaphosphate results in a much smaller absorption length ($\sim 1:30$ (20)), which is a great advantage in producing a crystal of low nonresonant loss.

For transverse pumping of thin films or fibers, however, we may anticipate that the greater absorption coefficient of $\text{NdP}_5\text{O}_{14}$ can potentially endow significant advantages relative to YAG:Nd or other hosts.

Conclusions

Neodymium pentaphosphate is the first material to be discovered which combines a high neodymium concentration with low fluorescence quenching. Laser quality crystals have all been grown so far from phosphoric acid solution and the problems of hydrogen incorporation have been identified. In the absence of hydrogen, highly perfect crystals may be grown which show cw operation at room temperature with very low threshold power. The formation of $\text{NdP}_5\text{O}_{14}$ into thin films or configurations other than "as-grown" crystals has not yet been demonstrated, however. $\text{NdP}_5\text{O}_{14}$ may be melted into a glass in sealed Pt tubes, and pulsed laser action in the glass was observed (7), but the decomposition to lower phosphates in the absence of encapsulation precludes the formation of fibers by normal means or crystal growth from the melt. The stimulated emission cross section, although somewhat less than in YAG:Nd is fairly high.

Clearly, the study of $\text{NdP}_5\text{O}_{14}$ has marked a major advance, both in the understanding of fluorescence quenching and in the preparation of miniaturized solid state laser hosts. The room for improvement which still exists will ensure continuing research, both towards perfecting $\text{NdP}_5\text{O}_{14}$ and towards the synthesis of alternative high concentration neodymium laser hosts.

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