

Site Selective Spectroscopy of Nd³⁺ in Strontium Fluorovanadate

R. E. Peale, P. L. Summers, and H. Weidner

Department of Physics, University of Central Florida, Orlando, Florida 32816

P. Hong and B. H. T. Chai

Center for Research and Education in Optics and Lasers (CREOL),
University of Central Florida, Orlando, Florida 32826

Abstract

High resolution site-selective photoluminescence spectroscopy reveals that Nd³⁺ ions occupy more than forty different crystal-field environments in Sr₅(VO₄)₃F. Preferential energy transfer to the lasing site occurs but becomes less complete with increasing temperature.

Spectroscopy and laser performance studies show that Nd³⁺:Sr₅(VO₄)₃F (Nd:SVAP) is a promising new crystal for certain diode-pumped lasing applications[1]. It can be grown in large sizes with low scattering loss and has high emission cross section, an adequate lifetime, low threshold, and high slope efficiency. SVAP is generally interesting as a host, because the similar crystal SFAP [Sr₅(PO₄)₃F] doped with Yb has recently been identified as having the best combination of properties for the solid-state-laser driver of an inertial confinement fusion power reactor[2]. We report our spectroscopic characterization of high quality Nd:SVAP crystals grown by the conventional Czochralski technique at CREOL. Nominal concentrations were 0.2, 1, 1.5, 2, and 4%. Actual concentrations (microprobe analysis) were 0.05, 0.26, 0.38, 0.48, and 0.71%, respectively[3]. Absorption and photoluminescence spectra were collected with a Fourier-spectrometer at 1 cm⁻¹ resolution. Site-selective cw excitation was achieved with an Ar-laser-pumped jet-dye laser. Samples were cooled to 2 K by immersion in superfluid helium or to 80 K with a liquid-nitrogen cold-finger cryostat.

The ⁴I_{9/2} → ⁴F_{9/2} transmission spectrum at 1.7 K is presented in Figure 1. The presence of at least 30 lines indicates at least 6 different crystal-field

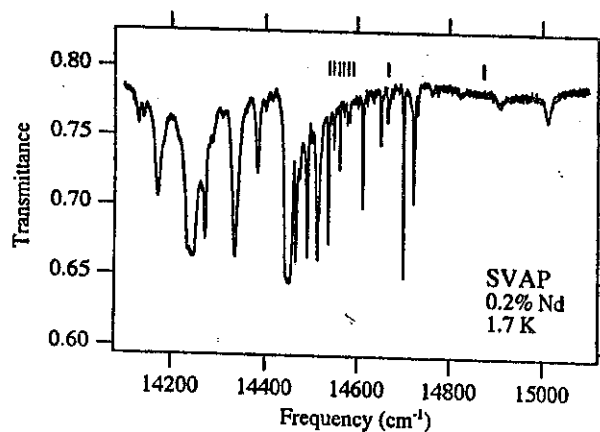


Figure 1. ⁴I_{9/2} → ⁴F_{9/2} transmittance spectrum of Nd:SVAP. Marks indicate excitation frequencies for the photoluminescence spectra plotted in Fig. 2

environments for Nd³⁺ in SVAP. Figure 2 presents a portion of the ⁴F_{3/2} → ⁴I_{11/2} emission spectrum at 2 K for the excitation frequencies given and indicated in Fig. 1 by markers. Evidently, tuning the laser over even a small portion of the ⁴F_{9/2} band produces a tremendous variety of photoluminescence peaks. All of the various peaks in Fig. 2 change strength independently with changes in excitation frequency. Therefore, each line arises from a unique crystal-field environment. The fifteen prominent lines in Fig. 2 imply at least 15 significantly occupied environments in SVAP. Analysis of weak features for a larger number of excitation frequencies than presented in Fig. 2 shows that in fact *more than forty* different crystal-field environments exist. Each independent emission spectrum is remarkable in that it consists primarily of a

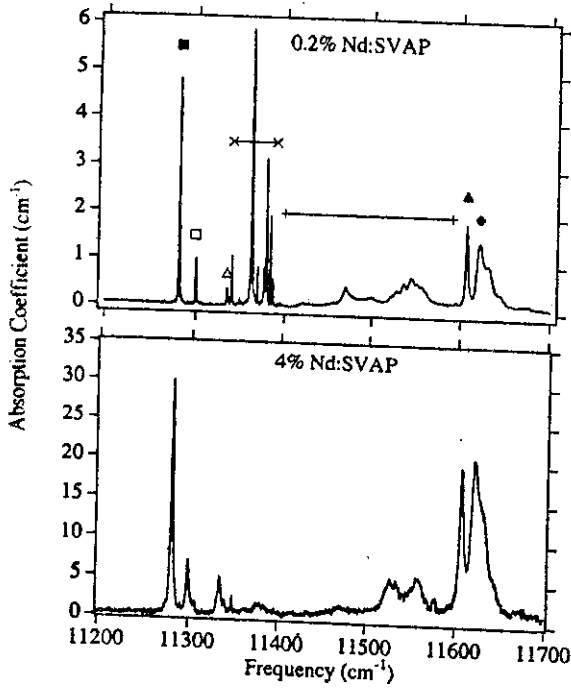


Figure 3. $4I_{9/2} \rightarrow 4F_{3/2}$ absorption coefficient for two concentrations of Nd^{3+} in SVAP. The sample temperature was 1.7 K. Markers indicate the lines or bands integrated for analysis in Fig. 4.

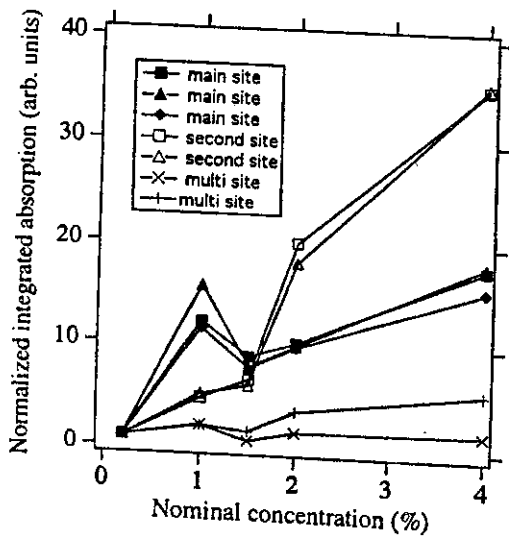


Figure 4. Integrated absorption vs. nominal concentration for lines or bands indicated in Fig. 3. To aid comparison, all curves are scaled to give the value unity at lowest concentration.

correlated with that of the main site. Significant unanswered questions remain for either interpretation, so this problem merits further study. The line indicated by the solid diamond is taken to give the frequency of the main-site upper $4F_{3/2}$ level[3]. This value is listed in Table 1.

Those features indicated by open symbols, referred to in Fig. 4 as "second site", increase together more rapidly with nominal concentration than do the main site lines. That the open-symbol features are sharp and distinct at all concentrations suggests that the crystal-field environment they belong to is also distinct, i.e. a distinct crystallographic site within the crystal, rather than just the main site perturbed by charge compensating defects. Luminescence transitions at the frequencies of the two second-site lines indicated are never clearly observed. Rather, at these two frequencies, sharp dips are observed in the broad luminescence profiles of other sites, presumably caused by second site absorption of multisite emission.

The two groups of features indicated by x and + in Fig. 3 each have integrated strengths which are relatively constant. The apparent decrease in the peak heights of these lines with increasing concentration is due to broadening. Comparison with the site selective emission data identify these bands with many of the luminescence lines which appear in addition to main site emission. We refer to these as "multi-site" bands. In addition to the total multisite concentration, the multiplicity of crystal-field environments is also independent of [Nd], as determined by 2 K site-selective experiments in the 4% sample. These observations contradict the first of the above postulated explanations for good lasing in high concentration SVAP.

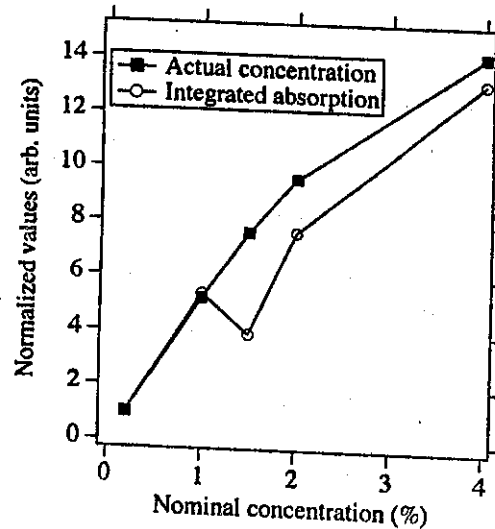


Figure 5. Actual Nd concentration and total integrated $4I_{9/2} \rightarrow 4F_{3/2}$ absorption vs. nominal concentration. Both curves are scaled to give unity at $[Nd]=0.2\%$.

To test our analysis of Fig. 3, we compare the sum of all integrations (the integral of the entire ${}^4I_{9/2} \rightarrow {}^4F_{3/2}$ band) to the actual concentration. Both quantities are plotted versus nominal concentration in Figure 5, where each curve has been scaled to give unity at $[Nd]=0.2\%$. For low concentration, the two curves are nearly identical, as they should be. That the absorption curve eventually drops below the concentration curve suggests that at high concentration some Nd is optically inactive. Nonetheless, the total integrated absorption is always roughly proportional to actual concentration, which affirms our method of analysis above.

Our second postulate, preferential energy transfer to the main-site, is explored next. Figure 6 presents ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ photoluminescence at 80 K for three concentrations and fixed excitation frequency. Solid symbols designate the five main-site lines. The remainder are multisite bands. As a measure of main site emission strength, we integrate the lowest main-site line, since this line is far from any multi-site band.

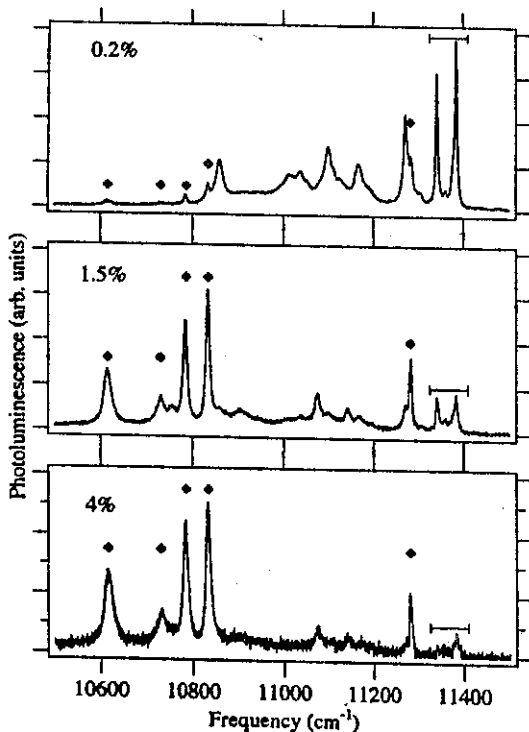


Figure 6. SVAP photoluminescence at 80 K for three Nd concentrations and fixed excitation frequency. Solid symbols designate the main-site lines. The bracket indicates multisite lines integrated for analysis.

For multi-site emission, we integrate the group of lines indicated by the bracket. From Table 1, it is clear that this group can contain no emission from the thermally populated upper ${}^4F_{3/2}$ level of the main site. Neither does it contain emission corresponding to the second-site transitions labeled by open symbols in Fig. 3.

The main-site:multi-site luminescence ratio is compared with the main-site:multi-site integrated absorption ratio as a function of nominal concentration in Fig. 7. Clearly, the main:multi emission ratio grows faster than the main:multi concentration ratio, which argues for energy transfer to the main site. For other excitation frequencies and choices of multi-site lines, this difference in the rates of increase for the two ratios varies between a factor of 3 and 9. Such transfer was already suggested by Fig. 2, in which the main site line appears for all excitation frequencies.

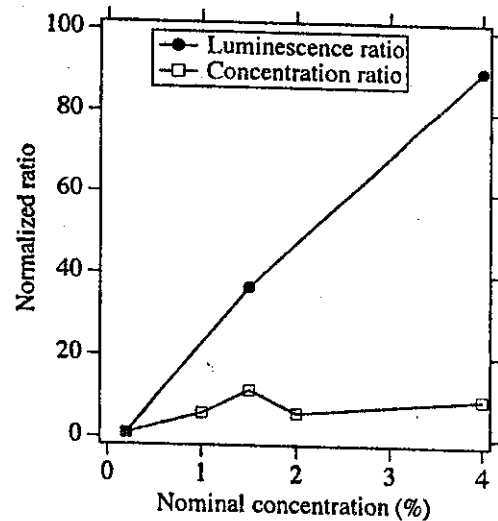


Figure 7. Main:multi luminescence and integrated absorption ratios vs nominal concentration. Both curves are scaled to give unity at $[Nd]=0.2\%$.

Since the lowest main site ${}^4F_{3/2}$ level is below that for any other site, the transfer is down hill. Preferential transfer to the laser active site has been observed[4] also in the similar system Nd:fluorapatite $[Nd:Ca_5(PO_4)_3F]$, allowing the absorption of two extra sites to contribute to the population buildup in the main-site upper laser level. This favorable situation evidently holds also for Nd:SVAP, even with its considerably larger site multiplicity.

Down-hill transfer may be incomplete under practical lasing conditions since level differences between the main site and most of the multi-sites are less than kT at room temperature. The temperature dependence of the transfer is revealed in Figure 8, which presents the main:multi luminescence ratio with fixed-frequency excitation at 1.7 and 80 K. Line broadening,

and the appearance of additional lines from thermally populated multisite levels, prevent straightforward integrations at 300 K. A decrease in the relative main-site emission with increasing temperature is clear. Evidently, thermally activated back transfer competes with transfer to the main site. This suggests that in thermodynamic equilibrium at room temperature significant multisite population exists in excited $^4F_{3/2}$ levels.

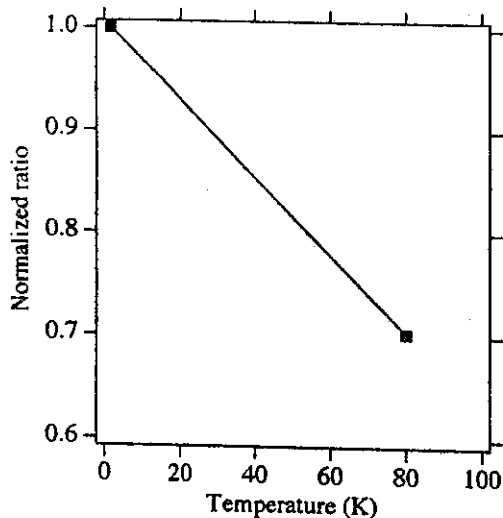


Figure 8. Temperature dependence of the main:multi luminescence ratio for the multi-site band indicated in Fig. 6. The points are scaled to give unity at 2 K. Nominal [Nd] = 0.2%.

Our visible absorption spectrum presented in Figure 9 shows that no level is available for excited state absorption (ESA) of laser emission (9386 cm^{-1}) from the upper laser level (11278 cm^{-1} at 300K), for otherwise an absorption line would appear at the position of the arrow. On the other hand, Fig. 9 reveals the existence of absorption lines at the necessary energy above multisite $^4F_{3/2}$ levels. Hence, absorption which originates in populated multisite $^4F_{3/2}$ levels is possible at the laser frequency, especially since such transitions tend to be broad at high concentration.

To summarize, Fourier-transform photoluminescence spectroscopy with selective excitation reveals a large number of crystal-field environments for Nd^{3+} ions in $\text{Sr}_5(\text{VO}_4)_3\text{F}$. Preferential energy transfer to the lasing site has been observed, but this is incomplete at room temperature.

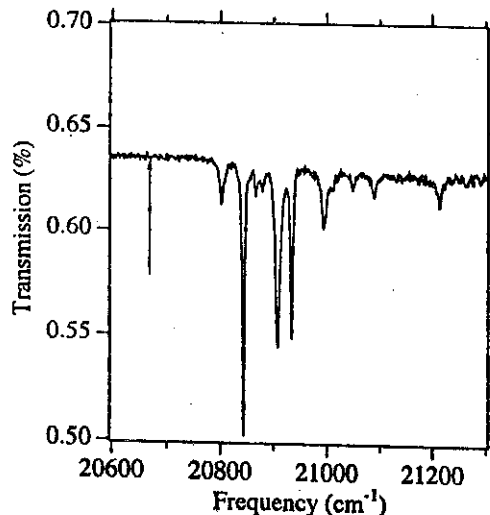


Figure 9. Transmission spectrum of 2% Nd:SVAP at 80 K. The arrow shows the level position necessary for main site excited state absorption of the laser emission.

The experimental methods used in this work, Fourier-transform photoluminescence spectroscopy with selective excitation, are generally applicable to other transfer problems in multisite, as well as frequency-converting, laser crystals.

References

1. S. A. Payne, B. H. T. Chai, W. L. Kway, L. D. DeLoach, L. K. Smith, G. Lutts, R. Peale, X. Zhang, G. D. Wilke, and W. F. Krupke, Conf. on Lasers and ElectroOptics (CLEO), Baltimore, (1993), postdeadline paper.
2. W. F. Krupke, S. A. Payne, and C. Orth, in Abstracts for Fall Meeting of the Materials Research Society, Symp. R (Materials Research Society, Pittsburgh, 1993), paper R4.1.
3. P. Hong, X. X. Zhang, G. Lutts, R. E. Peale, H. Weidner, M. Bass, B. Chai, S. A. Payne, L. D. DeLoach, L. K. Smith, and W. F. Krupke, this conference.
4. K. B. Steinbruegge, T. Henningsen, R. H. Hopkins, R. Mazelsky, N. T. Melamed, E. P. Riedel, and G. W. Roland, *Appl. Optics* **11**, 999 (1972).