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Laser demonstration of neodymium-doped strontium chlorovanadate

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Nd:Sr₅(VO₄)₃Cl has been successfully lased using a Ti:sapphire pump laser operating at 810 nm. A slope efficiency of 52% for the 1.065 μ m laser line and a lasing threshold of only a few tens of milliwatts have been measured. These favorable results are comparable to another Nd-doped vanadate apatite, Sr₅(VO₄)₃F. A brief survey of the spectroscopy of Nd³⁺ in Sr₅(VO₄)₃Cl, Sr₅(VO₄)₃F, and Ca₅(VO₄)₃F reveals properties which suggest the vanadate-based apatite crystals as a whole may represent a useful new class of Nd-laser hosts.

In the late 1960s, Nd-doped Ca₅(PO₄)₃F, known as fluorapatite (FAP), emerged as a high gain laser medium that was suitable for flash-lamp pumping.^{1,2} The contemporaneously developed Nd:YAG (Y₃Al₅O₁₂) laser material, possessing an emission cross section of only about one-half that of FAP, eventually came to dominate laser technology due to its superior thermal and mechanical properties.³ The Nd:YAG emission did in fact have adequate transition strength for most laser requirements, and therefore the greater mechanical strength proved to be a more significant factor. More recently, diode lasers have developed into viable pump sources for applications requiring high efficiency and compact laser designs. Some applications in particular require systems with low threshold powers in order to minimize the pump power consumption. These criteria are generally satisfied by laser crystals with a large product of the emission cross section and emission lifetime, and a strong absorption peak with adequate bandwidth at the output wavelength of the diode. While Nd:YAG and Nd:YLF (LiYF₄) are presently the most commonly employed Nd lasers,⁴ considerable effort has gone into developing Nd:YVO₄ as an alternative, low threshold diode-pumped laser medium. Nd:YVO₄ offers attractive performance parameters as well as higher Nd-doping levels, which can serve to minimize the required thickness of the gain medium.^{5,6} Nevertheless, Nd:YVO₄ has crystal growth problems which although showing recent and dramatic improvement, have greatly limited the size of high quality single crystals available. It is interesting that now, as a result of the reduced thermal loading associated with diode pumping (compared to flash-lamp pumping), Nd:FAP is again a favorable candidate for lasers requiring a low laser threshold, in spite of its inferior thermal properties.^{7,8}

The use of the apatite hosts for laser ions has steadily evolved over the last few decades. Westinghouse scientists initially investigated the phosphate and silicate apatite analogs and found that the structure provided a favorable site for the Nd³⁺ and Ho³⁺ activator ions.^{1,9} More recently, our group has explored the potential of the Yb³⁺ ion in the phosphate apatites and discovered that Yb-doped Ca₅(PO₄)₃F and Sr₅(PO₄)₃F exhibit excellent laser performance.^{10–12} We have subsequently expanded our research to include several apa-

tite crystals based on the vanadate species. Thus far, we have reported the laser results of two promising new vanadate-based apatites: Yb:Sr₅(VO₄)₃F and Nd:Sr₅(VO₄)₃F.^{13,14} The Nd:Sr₅(VO₄)₃F demonstrates excellent spectroscopic features and laser performance. It also offers the advantage that high quality boules of several cubic centimeters are readily grown by conventional Czochralski crystal growth. We believe this new apatite crystal will become a major contender for low-threshold diode-pumped Nd laser systems. In this letter, we describe the spectroscopic properties of Nd-doped Ca₅(VO₄)₃F, Sr₅(VO₄)₃F, and Sr₅(VO₄)₃Cl. We also report Nd:Sr₅(VO₄)₃Cl has been grown and lased successfully for the first time.

The crystal growth and preparation of the starting materials for the fluorovanadates and fluorophosphates have been previously described in Refs. 14–17. In this study, crystals were doped with 1–2 wt % Nd in the melt. We give a summary of the melting points and the Nd distribution coefficients we have determined in Table I with general comments about their crystal quality and growth. Generally, the fluorovanadates melt at lower temperatures than the fluorophosphates, and the Nd distribution coefficient tends to be smaller for the larger host metal ions and for the chlorides versus the fluorides. The most favorable hosts for crystal growth are Ca₅(PO₄)₃F, Sr₅(PO₄)₃F, and Sr₅(VO₄)₃F, while Ca₅(VO₄)₃F and Ba₅(PO₄)₃F growth runs produce only low quality samples. Apparently, Sr₅(VO₄)₃Cl can be grown from a melt (with substantial vaporization of SrCl₂), while Ca₅(PO₄)₃Cl must be obtained from a CaCl₂ flux. The attempts to grow Ba₅(VO₄)₃F single crystals have been unsuccessful.

We have collected room-temperature absorption and emission data of the new Nd-doped vanadate apatites from which adequate single crystals were obtained for spectroscopic study: Ca₅(VO₄)₃F, Sr₅(VO₄)₃F, and Sr₅(VO₄)₃Cl. The absorption spectra were obtained using a Perkin Elmer Lambda 9 spectrophotometer and are plotted in Fig. 1. Both Sr₅(VO₄)₃F and Sr₅(VO₄)₃Cl were oriented and scanned with polarized light (since apatite crystals are optically anisotropic), whereas the lack of higher optical quality for Ca₅(VO₄)₃F prevented us from specifying its orientation. The polarized spectra in Fig. 1 correspond to the favorable pump and ex-

TABLE I. Selected crystal growth properties of apatite crystals (CZ=Czochralski).

Crystal	Melting point (°C)	Nd distribution coefficient	Comments
$\text{Ca}_5(\text{VO}_4)_3\text{F}$	1510	0.44	CZ; not single phase; high scatter losses prevent optically orienting bulk crystal
$\text{Sr}_5(\text{VO}_4)_3\text{F}$	1650	0.25	CZ; low-loss crystals; $\sim 3 \times 15$ cm boules
$\text{Ba}_5(\text{VO}_4)_3\text{F}$	(1570)	...	Decomposes to $\text{Ba}_5(\text{VO}_4)_2$ and BaCl_2
$\text{Sr}_5(\text{VO}_4)_3\text{Cl}$	1550	0.05	CZ; high vaporization of SrCl_2 component; boule cracking limited size of oriented crystal to $5 \times 5 \times 15$ mm ³
$\text{Ca}_5(\text{PO}_4)_3\text{F}$	1700	0.52	CZ; low-loss crystal; $\sim 3 \times 15$ cm boules
$\text{Sr}_5(\text{PO}_4)_3\text{F}$	1810	0.33	CZ; low-loss crystal; $\sim 3 \times 15$ cm boules
$\text{Ba}_5(\text{PO}_4)_3\text{F}$	1730	...	CZ; small, partially opaque boule; clear regions of a few cubic millimeters
$\text{Ca}_5(\text{PO}_4)_3\text{Cl}$	1200(flux)	...	CaCl_2 flux; incongruently melting; millimeter-sized, low-quality crystals

traction orientation of the apatite laser crystal, $E \parallel c$, which is the unique symmetry axis for these structures. Normal to the c axis the absorption pump band, ~ 810 nm, is reduced by a factor of 1.9 in the fluorovanadate and by 1.6 in the chlorovanadate. The unpolarized emission spectra of these Nd-doped apatites were obtained by exciting the samples near 575 nm with a Nd:YAG pumped dye laser and measuring the

dispersed signal with a grating monochromator and an S-1 photomultiplier tube. These spectra are plotted in Fig. 2 in the region of the prominent 1065 nm emission peak. Also, the emission decay rate which has been measured for these hosts with a transient digitizing oscilloscope is indicated on each spectral plot. Employing the Füchtbauer-Ladenburg formula which requires an emission spectrum and radiative lifetime (we assume the measured emission lifetime), we

FIG. 1. The absorption spectra of the Nd-doped vanadate apatites. For comparison, the absorbance at the 810 nm peak height and the thickness for each sample are as follows: $\text{Ca}_5(\text{VO}_4)_3\text{F}$ $A=0.26$, $t=0.07$ cm; $\text{Sr}_5(\text{VO}_4)_3\text{F}$ $A=1.56$, $t=0.38$ cm; $\text{Sr}_5(\text{VO}_4)_3\text{Cl}$ $A=0.67$, $t=0.19$ cm.

FIG. 2. Unpolarized emission spectra of the $^4F_{3/2}$ to $^4F_{11/2}$ transition of Nd^{3+} in the vanadate apatites.

FIG. 3. The laser efficiency data for Nd:Sr₅(VO₄)₃F and Nd:Sr₅(VO₄)₃Cl.

have determined the effective emission cross section, σ_{em} , of the 1065 nm band within $\pm 15\%$ to be $5.0 \times 10^{-19} \text{ cm}^2$ in Nd:Sr₅(VO₄)₃F. We observe that the lifetimes of Nd³⁺ in Sr₅(VO₄)₃F and in Sr₅(VO₄)₃Cl are similar, $\sim 220 \mu\text{s}$, while Nd³⁺ in Ca₅(VO₄)₃F is $159 \mu\text{s}$. The bandwidth of the laser line feature in these hosts is also indicated and is between 1 and 2 nm for each apatite. Using the σ_{em} of Nd in Sr₅(VO₄)₃F, we have estimated a value for Sr₅(VO₄)₃Cl using the ratio of the emission linewidths at 1065 and the ratio of the squared refractive indices, and we obtain $2.8 \times 10^{-19} \text{ cm}^2$.

Crystals of both Nd:Sr₅(VO₄)₃F and Nd:Sr₅(VO₄)₃Cl have been lased in a standard experimental arrangement which has been described in detail previously.¹⁰ The 2–4-mm-thick laser crystal is centrally situated in a 10 cm concentric cavity employing an output coupling of 16% and a Ti:sapphire laser at 810 nm as the pump source. By comparing the output power to the absorbed input power [fraction adsorbed is 99% for an antireflection-coated Sr₅(VO₄)₃F and 74% for an uncoated Sr₅(VO₄)₃Cl], we obtain the slope efficiency data which are plotted in Fig. 3. The lower slope efficiency of 52% in Nd:Sr₅(VO₄)₃Cl compared to 66% in Sr₅(VO₄)₃F may be a reflection of higher scattering losses. Scattering losses of only 0.3%/cm have been measured in Sr₅(VO₄)₃F,¹⁴ and although no determinations have been made for the chlorovanadate the optical quality appears to be lower. Some parasitic absorption loss from impurities may be present in both laser crystals.

A comparison of the spectroscopic and laser properties for the Nd-doped vanadate apatites shows a marked similarity to the favorable properties generally arising from the apatite structure crystals. These include highly polarized spectra with strong absorption and emission bands for light polarized along the *c* axis, which provide an effective means for both pumping and extracting energy. Among these vanadate analogs, the positions and widths of the emission lines vary from one host to another. The calcium fluorovanadate has an emission peak at 1070 nm and a bandwidth (FWHM) of 1.5 nm. The strontium analogs both peak at 1065 nm, with the chlorovanadate having a greater bandwidth of 2.1 nm compared

with 1.2 nm in the strontium fluorovanadate. The greater bandwidth of the chlorovanadate is estimated to produce a lower effective emission cross section of $2.8 \times 10^{-19} \text{ cm}^2$ compared to the measured value of $5.0 \times 10^{-19} \text{ cm}^2$ in the strontium fluorovanadate. The laser performance data in Fig. 3 indicate that the Nd:Sr₅(VO₄)₃F has a slope efficiency of 66% with a 16% output coupling, compared to a lower slope efficiency of 52% for Nd:Sr₅(VO₄)₃Cl. This difference may be due to inferior quality of the Sr₅(VO₄)₃Cl crystal compared to the Sr₅(VO₄)₃F sample that was lased.

In conclusion, we find that the vanadate-based apatites define a new class of Nd lasers which should serve usefully in diode-pumped systems. The crystals we have studied include the calcium and strontium fluorovanadates and the strontium chlorovanadate. Of these, the two strontium analogs were of adequate crystal quality for characterization of the laser performance. We have measured the slope efficiencies in Nd:Sr₅(VO₄)₃F and Nd:Sr₅(VO₄)₃Cl to be 66% and 52%, respectively. The best laser candidate from this class appears to be the strontium fluorovanadate, but the strontium chlorovanadate may prove to be of similar value with the availability of higher quality crystals.

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