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Characterization of spectroscopic properties of $\text{Nd}^{3+} : \text{CaZn}_2\text{Y}_2\text{Ge}_3\text{O}_{12}$ (CAZGAR)

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Abstract

A spectroscopic investigation and Judd–Ofelt analysis of Nd^{3+} doped $\text{CaZn}_2\text{Y}_2\text{Ge}_3\text{O}_{12}$ (CAZGAR) has been performed. The broader absorption near 805 nm, longer fluorescence lifetime of 285 μs and the larger branching ratio of 40% for the $^4\text{F}_{3/2}$ to $^4\text{I}_{9/2}$ manifold are improvements over $\text{Nd}^{3+} : \text{YAG}$ as a 941 nm laser material. The effects of color centers induced by ultraviolet irradiation of CAZGAR are also discussed.

Yttrium aluminium garnet (YAG) is one of the best flash-lamp-pumped laser hosts, because it has many of the physical properties necessary to make it a good laser material. The spectroscopic and laser properties of Nd^{3+} -doped YAG, which has remained for years the most common 1 μm solid-state laser material, have been extensively studied. In an effort to find improved laser materials, many others have been investigated. Although these hosts have shown to have better spectroscopic and laser properties than $\text{Nd}^{3+} : \text{YAG}$, most were unable to tolerate the thermal stress produced by the UV radiation present in the flash lamp. This problem can be remedied by pumping the new promising materials with efficient GaAlAs diode lasers where the pump wavelength overlaps the strong Nd^{3+} absorption band around 805 nm. By directly pumping Nd^{3+} with near-infrared diode lasers, the

quantum efficiencies are $\sim 76\%$ and $\sim 86\%$ for transitions from the $^4\text{F}_{3/2}$ metastable state to $^4\text{I}_{11/2}$ and $^4\text{I}_{9/2}$ manifolds, respectively, thus reducing the thermal stress on the laser material. Important spectroscopic properties for a diode-pumped, Q-switched laser material include a long fluorescence lifetime and a broad absorption band [1].

The spectroscopic properties of a number of germanate laser hosts [1] have been found to have some improvements over $\text{Nd}^{3+} : \text{YAG}$. Being encouraged by these works, the material, calcium zinc yttrium germanium garnet, $\text{CaZn}_2\text{Y}_2\text{Ge}_3\text{O}_{12}$ (CAZGAR) doped with 2% Nd^{3+} in the melt has been chosen for investigating its spectroscopic and laser properties. The experimental measurements performed include absorption, and fluorescence spectra, fluorescence lifetime and EPR of $\text{Nd}^{3+} : \text{CAZGAR}$. The Judd–Ofelt theory was applied to predict the radiative decay rates, branching ratios, and emission cross-sections for Nd^{3+}

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transitions. These results were compared with $\text{Nd}^{3+}:\text{YAG}$ to assess the potential of the new material as a diode-pumped or flash-lamp-pumped solid-state laser. We also report here the effects of color centers on the laser characteristics of this material.

The crystals used in this study were grown by A. Linz at the MIT Crystal Physics Laboratory. $\text{CaZn}_2\text{Y}_2\text{Ge}_3\text{O}_{12}$ has the garnet structure. The density of the material is 5.11 g/cm^3 . CAZGAR is relatively hard, 7-7.5 on the Moh scale and has a thermal conductivity of $0.058 \text{ W/cm}^\circ\text{C}$. It can be inferred from the relatively high thermal conductivity that this material is quite stoichiometric and appears to be fairly well ordered, which is remarkable, considering the large number of different cations in this substance.

The crystal has the characteristic blue color when doped with Nd^{3+} . However, when the sample is irradiated with the unfiltered ultraviolet light from a Xe ILC L-268 flash lamp, it turns deep brownish purple due to the formation of color centers. A Varian E-12 x-band spectrometer was used to detect the color centers at room temperature. In these experiments, the sample was colored with a single 10 J flash lamp pulse, which was sufficient to create a strong EPR signal. The samples were bleached while in the microwave cavity by means of a tungsten lamp focused through a hole in the cavity wall. The bleaching reduced the amplitude of the EPR signal to below the EPR noise level, indicating that the observed signal was indeed due to the color centers and not an impurity in the crystal. In addition, the spectra were characterized by an isotropic g equal to 2.0065, a value close to standard g values for color centers. The strongest EPR signal was obtained when the DC magnetic field was applied along the [111] direction. This suggests the predominance of the magnetic ion in the octahedral zinc sites.

The color centers' absorption band peaks at 500 nm and extends to $\sim 720 \text{ nm}$. The color center should have minimal effects on an optically pumped $\text{Nd}^{3+}:\text{CAZGAR}$ laser. In the case of a diode-pumped $\text{Nd}^{3+}:\text{CAZGAR}$ laser, the absorption band near 805 nm and the laser wavelengths from 900 to 1100 nm are not in the region of the color

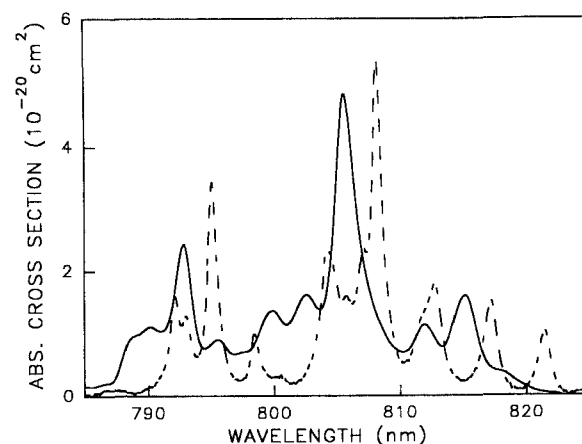


Fig. 1. The room temperature absorption spectra of $\text{Nd}^{3+}:\text{CAZGAR}$ (solid) and $\text{Nd}^{3+}:\text{YAG}$ (dashed) covering GaAlAs diode-pump wavelengths.

centers absorption band. For flash-lamp-pumped laser applications the coloration can be avoided by using UV absorbing cooling jackets between the flash lamp and the laser rod.

The room temperature absorption spectra of $\text{Nd}^{3+}:\text{CAZGAR}$ were taken using a Cary 17 and a Perkin-Elmer Lambda-19 Spectrophotometers. Figure 1 shows the room temperature absorption spectra of $\text{Nd}^{3+}:\text{CAZGAR}$ (solid line) and $\text{Nd}^{3+}:\text{YAG}$ (dashed line) covering the emitting region of GaAlAs laser diodes. The $\text{Nd}^{3+}:\text{CAZGAR}$ absorptions are significantly broader than those of $\text{Nd}^{3+}:\text{YAG}$. The $\text{Nd}^{3+}:\text{CAZGAR}$ line strength for the $^4\text{F}_{5/2}$ and $^2\text{H}_{9/2}$ transitions was measured to be $2.8 \times 10^{-20} \text{ cm}^2$. For $\text{Nd}^{3+}:\text{YAG}$ the line strength is $3.5 \times 10^{-20} \text{ cm}^2$ [2].

The room temperature fluorescence spectrum of the irradiated and bleached sample is shown in Fig. 2, which indicates that the relative fluorescence output of $\text{Nd}^{3+} \ ^4\text{F}_{3/2} \rightarrow \ ^4\text{I}_{9/2}$ transition is reduced by about 10% when the crystal is in the colored state and excited in the visible region. The fluorescence lifetime of the $^4\text{F}_{3/2}$ level was measured using a N_2 -laser-pumped tunable dye laser (Rhodamine 6G), Spex model 1911F photomultiplier tube, Spex model 340E monochromator, and an EG&G boxcar integrator triggered by the N_2 -laser. The value at room temperature was measured to be

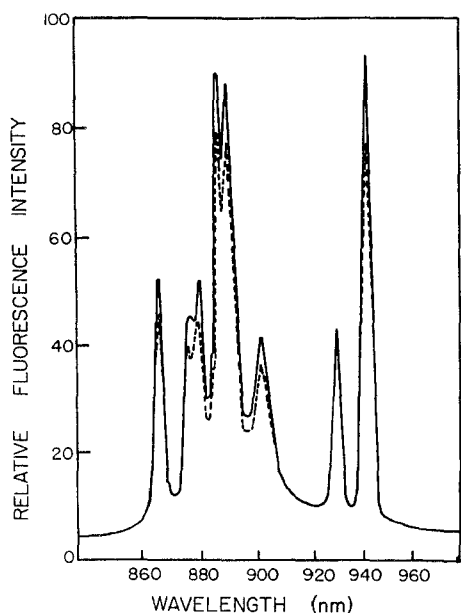


Fig. 2. The irradiated (dashed) and bleached (solid) fluorescence spectrum of the $\text{Nd}^{3+} \ ^4\text{F}_{3/2} \rightarrow \ ^4\text{I}_{9/2}$ transition in CAZGAR at room temperature.

$285 \pm 10 \mu\text{s}$, which is significantly larger than 1% $\text{Nd}^{3+}:\text{YAG}$ value of $237 \mu\text{s}$. The longer lifetime suggests that $\text{Nd}^{3+}:\text{CAZGAR}$ is capable of storing higher energy than $\text{Nd}^{3+}:\text{YAG}$.

The Judd–Ofelt (J–O) analysis has been employed to the room temperature absorption data to calculate the radiative decay rates for various transitions from the $\text{Nd}^{3+} \ ^4\text{F}_{3/2}$ to $^4\text{I}_J$ manifolds. The detailed theory and its applications can be found in the literature [3,4]. Nine absorption bands were chosen to determine the J–O parameters, Ω_2 , Ω_4 and Ω_6 . A least-square fitting of the measured and the calculated line strengths provides the three J–O parameters for $\text{Nd}^{3+}:\text{CAZGAR}$ and are tabulated in Table 1. These parameters were used to calculate the radiative decay rates and branching ratios from the metastable $^4\text{F}_{3/2}$ to the lower $^4\text{I}_J$ ($J = \frac{15}{2}, \frac{13}{2}, \frac{11}{2}, \frac{9}{2}$) manifolds which appear in Table 1. In these calculations, the radiative lifetime of the $^4\text{F}_{3/2}$ level was set at $285 \mu\text{s}$. The spectroscopic quality factor, $X = \Omega_4/\Omega_6$, of this sample is approximately 0.88, which is larger than $\text{Nd}^{3+}:\text{YAG}$'s value of 0.3 [5]. This yields a greater

Table 1
Judd–Ofelt parameters and predicted spectroscopic properties of $\text{Nd}^{3+}:\text{CAZGAR}$

Characteristics	Values
Judd–Ofelt parameters	$\Omega_2 = 0.94 \times 10^{-20} \text{ cm}^2$ $\Omega_4 = 3.25 \times 10^{-20} \text{ cm}^2$ $\Omega_6 = 3.68 \times 10^{-20} \text{ cm}^2$
$^4\text{F}_{3/2}$ fluorescence and radiative lifetime	285 μs
Radiative decay rates	
$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$	1404 s^{-1}
$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$	1754 s^{-1}
$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$	327 s^{-1}
$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{15/2}$	17 s^{-1}
Branching ratios	
$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$	0.401
$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$	0.501
$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$	0.093
$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{15/2}$	0.005

branching ratio for the $^4\text{I}_{9/2}$ transitions, at the expense of the $^4\text{I}_{11/2}$ manifold.

The peak emission cross-section for the $\text{Nd}^{3+} \ ^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ transition has been determined from the following expression for a Gaussian line shape [4]:

$$\sigma_p(R_1 \rightarrow X_5) = \frac{\lambda_p^2}{4\pi c n^2 \Delta\nu} \left(\frac{\ln 2}{\pi} \right)^{1/2} A(R_1 \rightarrow X_5), \quad (1)$$

where $A(R_1 \rightarrow X_5)$ is the radiative transition rate from the lower Stark level of the $^4\text{F}_{3/2}$ manifold (R_1) to the upper Stark level of the $^4\text{I}_{9/2}$ manifold (X_5), λ_p is the wavelength at the peak position of the emission band, n is the index of refraction, c is the speed of light, and $\Delta\nu$ is the FWHM line-width. From Fig. 2, we obtain $\lambda_p = 941 \text{ nm}$, $\Delta\nu = 42 \text{ cm}^{-1}$, a $^4\text{F}_{3/2}$ Stark splitting of 126 cm^{-1} and a branching ratio of 0.193 for the $R_1 \rightarrow X_5$ inter-Stark transition. Using these values, $n = 1.83$, and the values appearing in Table 1, we obtain from Eq. (1), $\sigma_p(R_1 \rightarrow X_5) = 3.3 \times 10^{-20} \text{ cm}^2$ at room temperature. This cross section is smaller than that of $\text{Nd}^{3+}:\text{YAG}$ ($\sigma_p(R_1 \rightarrow X_5) = 8.0 \times 10^{-20} \text{ cm}^2$) [2].

In summary, the spectroscopic properties of $\text{Nd}^{3+}:\text{CAZGAR}$ warrant a laser characterization of the material. Owing to its broad absorption at

about 805 nm, good energy storage capability and large branching ratio for the $^4I_{9/2}$ manifold, Nd^{3+} :CAZGAR can be an excellent candidate as a 0.94 μm , GaAlAs diode-pumped laser material.

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