Spectroscopic analysis and the effects of color centers on the laser performance of Nd$^{3+}$:CaZn$_2$Y$_2$Ge$_3$O$_{12}$

Dhiraj K. Sardar $^a$, Santiago Vizcarra $^a$, Mohammad A. Islam $^a$, Toomas H. Allik $^b$, Edward J. Sharp $^c$, Albert A. Pinto $^c$

$^a$ Division of Earth and Physical Sciences, The University of Texas at San Antonio, San Antonio, TX 78249, USA
$^b$ Science Applications International Corporation, 1710 Goodridge Drive, McLean, VA 22102, USA
$^c$ Army Research Laboratory, Fort Belvoir, VA 22060, USA

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Abstract

Spectroscopic and EPR investigations of Nd$^{3+}$-doped CaZn$_2$Y$_2$Ge$_3$O$_{12}$ (CAZGAR) have been performed. The absorption, fluorescence, excitation spectra and fluorescence lifetime have been measured at room temperature. The Judd-Ofelt theory has been applied to the measured optical absorption intensities to predict the radiative decay rates, branching ratios, and peak stimulated emission cross section from the metastable $^4F_{3/2}$ state to the $^4I_{5/2}$ manifold. The fluorescence lifetime of the $^4F_{3/2}$ level of Nd$^{3+}$ at low concentration in this host was measured to be $285 \pm 10$ µs, which is longer than that for Nd$^{3+}$:YAG. Color centers located at zinc octahedral sites have been produced in these crystals by ultraviolet irradiation and have been detected by EPR techniques. The effects of the color centers on the potential laser characteristics of this material are discussed.

1. Introduction

Advances in high-power diode arrays and flashlamp technology, coupled with the generation of novel laser wavelengths have renewed interest in the research of trivalent rare-earth-doped materials. From these newly developed diode-pumped solid-state lasers, it is possible to obtain high wall-plug laser efficiencies and good laser beam quality since the thermal stress on the gain medium is reduced. Although the flashlamp-pump Nd lasers tend to be two to five times less efficient than the diode-pump analogs, the cost-to-performance ratio favors flashlamp-pumping. This is due to the fact that laser diode arrays are considerably more expensive than flashlamp-pump technology. To date, diode pumping has not become cost competitive in the 0.1–1.0 J Q-switch laser marketplace. For these reasons, the evaluation of new solid state materials should still address both the diode and flashlamp-pump characteristics.

A number of germanate laser hosts [1–5] have proved to possess superior spectroscopic properties over the most common diode-pumped solid state laser material, Nd$^{3+}$:YAG. Due to the potential of these materials as lasers, Nd$^{3+}$-doped CaZn$_2$Y$_2$Ge$_3$O$_{12}$ (CAZGAR) has been chosen to investigate its spectroscopic and laser properties. The absorption, emission, excitation and the fluorescence lifetime of Nd$^{3+}$:CAZGAR have been measured. The Judd-Ofelt theory has been used to predict the radiative decay rates and branching ratios for Nd$^{3+}$ transitions. This material is compared with Nd$^{3+}$:YAG to assess its potential as a diode-pumped solid state laser.

Color center formation has been noticed in Nd$^{3+}$:CAZGAR crystals when exposed to unfiltered UV flashlamp radiation. In the past, little work has
been done on color centers in optically pumped solid-state laser materials. Some exceptions are the early work of Piper et al. [6] on fluorapatite, Stickley et al. [7] on ruby; Forester and Sampson [8], O’Connor and Chen [9], and O’Connor and Bostick [10] on Sm$^{3+}$:CaF$_2$; and Snitzer and Woodcock [11] on Nd$^{3+}$ and Yb$^{3+}$ laser glass. Similar centers were seen in other garnet-structured germanate crystals Nd$^{3+}$:BaMg$_2$Y$_2$Ge$_5$O$_{12}$ (BAMGAR) [12]. We report on the nature of the color centers produced by flashlamp pumping and their effect on the laser characteristics of this material.

2. Crystal preparation

CAZGAR samples were grown by A. Linz at the MIT Crystal Physics Laboratory using a top-seeded solution technique [13]. The samples used in our study were doped with a nominal 2% Nd in the melt. For some crystal growth runs, a small amount of Mg was added. The optical quality of the material was only fair and the index of refraction was found to be 1.83 at 632.8 nm. Additional properties of this material can be found in Ref. [14].

Nd$^{3+}$:CAZGAR has a characteristic light blue Nd$^{3+}$ color in the undamaged state. Upon irradiation with a single 200 μs long pulse of unfiltered light from a xenon ILC L-268 flashlamp (2.5 cm arc length and 3 mm bore diameter), a deep brownish-purple coloration was observed to a depth of approximately 1 mm in the sample. The sample was placed ≤3 cm from the lamp. The energy stored in the capacitor was 10 J and the total lamp radiation efficiency between 250 and 1000 nm is approximately 50%. Repeated flashes would color the entire sample nearly uniformly, with the surface of the crystal always remaining slightly more discolored than the bulk. The samples were prepared for the optical spectra by exposing them to 10 flashes of 10 J pulses every 30 minutes to insure a uniform density of centers.

Bleaching of the centers was obtained in two ways: thermally and optically. Thermal bleaching was accomplished by heating the crystals in an air atmosphere for 30 minutes at 300°C and then let cool to room temperature before removal from the oven. In all cases, complete thermal bleaching was observed. Further experiments showed that 30 minutes of un-filtered, unfocused irradiation from a 1200 W tungsten lamp is sufficient to completely bleach the material from a heavily colored state.

A series of bleaching experiments were carried out in which several filters were used to determine the most effective wavelength region for optical bleaching. A 10 cm path length of a saturated CuSO$_4$ solution (transmission from 380 nm to 600 nm) used as a filter resulted in complete bleaching in 30 to 60 minutes. Corning filter #2030 (2-64) transmitting from 680 nm to 4500 nm produced little bleaching after 90 minutes. After 60 minutes about 50% bleaching was obtained with filter #3385 (3-71) which transmits from 500 nm to 4500 nm. Finally, complete bleaching occurred after approximately 60 minutes, using filter #3060 (3-75) which transmits from 380 nm to 4500 nm. The most effective optical bleaching is carried out when the samples are irradiated in the wavelength region from 380 nm to 600 nm.

3. Optical measurements

The absorption spectra were recorded with both a Cary 14 and a Perkin-Elmer Lambda-19 spectrophotometers and are presented in Fig. 1. This figure shows the absorption spectrum of Nd$^{3+}$:CAZGAR in the colored and in the bleached states indicated by the dashed and solid curves respectively. The sharp lines in this spectrum are due to Nd$^{3+}$ absorption bands at 360, 520, 580, 680, 740, 800, and 880 nm. The

![Fig. 1. The irradiated (dashed) and bleached (solid) absorption spectrum of Nd$^{3+}$:CAZGAR at room temperature. The sample thickness was 0.39 cm and spectral band width was set at 0.5 nm.](http://www.docudesk.com)
Nd$^{3+}$:CAZGAR absorptions are approximately 2.5 times broader than those of Nd$^{3+}$:YAG. The extremely broad band in the dashes curve from 350 to 700 nm is due to the absorption of the color centers formed by the ultraviolet portion of the flashlamp pulse. This spectrum in conjunction with the optical bleaching experiments described earlier indicate that the most effective bleaching is carried out by irradiating the sample in the absorption band produced by the color centers.

An excitation spectrum was recorded on a modified Perkin-Elmer 301 spectrophotometer using a Jarrel-Ash 1/4 meter monochromator to separate the incident radiation. Fig. 2 shows this spectrum where the bleached and colored states are represented by the solid and dashed lines respectively. These data show that when the color centers are present in the crystal all of the absorption bands of Nd$^{3+}$ are diminished in the visible region where they overlap the absorption band of the color centers.

The fluorescence spectra were recorded with the Perkin-Elmer 301 incorporating a 10 cm pathlength CuSO$_4$ solution filter to shield the near infrared radiation of the excitation source. Figs. 3 and 4 show the relative fluorescence spectra of the colored and uncolored (bleached) samples with a spectral resolution of 0.5 nm. The peak emission wavelengths are 941.0 nm and 1058.7 nm for the $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4I_{11/2}$ transitions, respectively. In these figures the dashed line is the emission of the crystal in the colored state and the solid line the emission in the un-
colored state. It is evident that these centers are not enhancing the Nd$^{3+}$ fluorescence output. The relative fluorescence output from the $^4F_{3/2} \rightarrow ^4I_{9/2}$ (Fig. 3) and from the $^4F_{3/2} \rightarrow ^4I_{11/2}$ (Fig. 4) are reduced by approximately 10% when the crystals are in the colored state. If the samples were stimulated with radiation above 750 nm the relative fluorescence intensities of the colored and uncoupled states were the same. The room temperature fluorescence decay of the $^4F_{3/2}$ metastable state in our sample was a single exponential, and the lifetime was measured to be $285 \pm 10 \mu s$ [14].

4. Judd-Ofelt calculations

Nine absorption bands identified in the room temperature absorption spectrum between 300 and 900 nm were chosen to determine the Judd-Ofelt (J-O) parameters. A brief outline of the J-O analysis is given below. A more detailed theory and applications can be found in the literature [15–19]. Measured line strengths, $S_{\text{mean}}(J \rightarrow J')$, of the chosen bands are determined by using Eq. (1):

$$S_{\text{mean}}(J \rightarrow J') = \frac{3ch(2J+1)}{8\pi^3\alpha\Delta\varepsilon^2\rho} \frac{n^4}{(n^2+2)^2} \Gamma,$$

where $J$ and $J'$ are total angular momentum quantum numbers of the initial and final states, respectively, $n$ is the refractive index, $\rho$ is the Nd$^{3+}$-concentration, $\Delta\varepsilon$ is the mean wavelength of the specific absorption band, $\Gamma = \int \alpha(\lambda) d\lambda$ is the integrated absorption coefficient as a function of $\lambda$, and $c$ and $h$ have their usual meaning. The measured line strengths were then used to calculate the J-O parameters $\Omega_2$, $\Omega_4$, and $\Omega_6$ by solving a set of equations for the corresponding transitions between $J$ and $J'$ manifolds, in the form:

$$S_{\text{calc}}(J \rightarrow J') = \sum_{r=2,4,6} \Omega_r |\langle S, L | J | U(0) || (S', L') J' \rangle|^2,$$

where the matrix elements $|\langle U(0) || (S', L') J' \rangle|$ are double-reduced unit-tensor operators of rank $l$ calculated in the intermediate-coupling approximation and do not depend on the crystal host. However, the parameters $\Omega_2$, $\Omega_4$, and $\Omega_6$ exhibit influence of the host on the transition probabilities since they contain the crystal-field parameters, interconfigurational radial integrals, and the interaction between the central ion and the immediate environment. Values of the reduced matrix elements for the chosen Nd$^{3+}$ bands portrayed in Fig. 1, are taken from Carnall et al. [20]. When two or more absorption manifolds overlapped, the matrix element was taken to be the sum of the corresponding squared matrix elements. For these calculations of absorption line strengths and other spectroscopic parameters, the index of refraction was taken to be 1.83 (independent of wavelength) and $\rho$ was adjusted such that the total radiative lifetime was equal to the fluorescence lifetime and was set at $5.3 \times 10^{-9}$ cm$^3$. The concentration derived from the J-O analysis yields a Nd$^{3+}$ distribution coefficient of 12%. This value is reasonable, since the Nd$^{3+}$ distribution coefficient for another Y containing garnet, Nd:YAG, is 18%. A least-squares fitting of $S_{\text{calc}}$ to $S_{\text{mean}}$ tabulated in Table 1, provides the following values for the three J-O parameters for Nd$^{3+}$ : CAZGAR:

$$\Omega_2 = 0.98 \times 10^{-20} \text{ cm}^2,$$

$$\Omega_4 = 3.20 \times 10^{-20} \text{ cm}^2,$$

$$\Omega_6 = 3.63 \times 10^{-20} \text{ cm}^2.$$

The accuracy of the fit is determined by the rms deviation: $\Delta S_{\text{rms}} = \left[ \text{sum of squares of deviations} / (\text{no. of transitions} - \text{no. of parameters}) \right]^{1/2}$. Using the values in Table 1, we have found an rms deviation of $0.432 \times 10^{-20}$ cm$^2$. The rms line strength is $1.768 \times 10^{-20}$ cm$^2$. The quotient of these values gives rise to an rms error of 24%. The large discrepancy between $S_{\text{mean}}$ and $S_{\text{calc}}$ arises primarily from the $^4F_{3/2}$ absorption band and is attributed to two factors: (i) the weakness of this particular transition and (ii) the occurrence of a VIS to near IR detector change at the wavelength that falls within this band. However, this error is within the 5–25% range found by applying the J-O theory to other systems [21].

The parameters thus obtained follow the trend: $\Omega_4 > \Omega_2 > \Omega_6$, which agrees with that of other Nd$^{3+}$- based laser hosts. These parameters can now be applied to Eq. (2) to calculate the line strengths corresponding to transitions from the metastable $^4F_{3/2}$ state to the lower $^4I_{15/2}$, $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$ manifolds. Using these line strengths, the radiative transition rates, $A(J \rightarrow J')$, can be calculated by
Table 1
Integrated absorption coefficients and line strengths (measured and calculated) for Nd$^{3+}$ : CAZOGAR

<table>
<thead>
<tr>
<th>Excited manifold</th>
<th>$\lambda$ (nm)</th>
<th>$\Gamma$ (nm/cm)</th>
<th>$S_{\text{meas}}$ (10$^{-20}$ cm$^2$)</th>
<th>$S_{\text{calc}}$ (10$^{-20}$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4D_{3/2} + ^4D_{5/2} + ^2P_{3/2} + ^2D_{3/2}$</td>
<td>358</td>
<td>4.31</td>
<td>1.34</td>
<td>0.97</td>
</tr>
<tr>
<td>$^4G_{11/2}$</td>
<td>459</td>
<td>0.91</td>
<td>0.22</td>
<td>0.05</td>
</tr>
<tr>
<td>$^2K_{3/2} + ^2G_{5/2} + ^2(D, P)_{1/2}$</td>
<td>479</td>
<td>0.87</td>
<td>0.20</td>
<td>0.29</td>
</tr>
<tr>
<td>$^2K_{3/2} + ^4G_{5/2} + ^4G_{9/2}$</td>
<td>523</td>
<td>8.15</td>
<td>1.73</td>
<td>1.22</td>
</tr>
<tr>
<td>$^4G_{3/2} + ^2G_{7/2}$</td>
<td>584</td>
<td>16.1</td>
<td>3.06</td>
<td>3.10</td>
</tr>
<tr>
<td>$^4F_{5/2}$</td>
<td>682</td>
<td>2.04</td>
<td>0.33</td>
<td>0.18</td>
</tr>
<tr>
<td>$^4F_{7/2} + ^4S_{5/2}$</td>
<td>745</td>
<td>16.4</td>
<td>2.44</td>
<td>2.54</td>
</tr>
<tr>
<td>$^4F_{7/2} + ^2H_{9/2}$</td>
<td>805</td>
<td>20.3</td>
<td>2.80</td>
<td>2.75</td>
</tr>
<tr>
<td>$^4F_{5/2}$</td>
<td>880</td>
<td>0.96</td>
<td>0.12</td>
<td>0.93</td>
</tr>
</tbody>
</table>

$A(J\rightarrow J')$

$$A(J\rightarrow J') = \frac{64\pi^4e^2}{3h(2J+1)\lambda^3} \frac{n(n^2+2)^2}{9} S_{\text{calc}}(J\rightarrow J') .$$  \hspace{1cm} (3)

The radiative lifetime, $\tau_{\text{rad}}$, for an excited state $(J)$ is calculated by

$$\tau_{\text{rad}} = \frac{1}{\sum A(J\rightarrow J')},$$  \hspace{1cm} (4)

where the sum runs over all terminal states, $J'$. The luminescence branching ratios, $\beta(J\rightarrow J')$, can be determined from the radiative decay rates by

$$\beta(J\rightarrow J') = A(J\rightarrow J') / \sum A(J\rightarrow J')$$

$$= A(J\rightarrow J') \tau_{\text{rad}},$$  \hspace{1cm} (5)

where the sum is also over all final states $J'$. The luminescence branching ratio is a critical parameter to the laser designer, because it characterizes the possibility of attaining stimulated emission from any specific transition. In Table 2, the radiative rates, branching ratios, and line strengths for all four transitions from the $^4F_{3/2}$ to $^4L_P$ manifolds are tabulated.

The peak emission cross section for the Nd$^{3+}$ transition from the lower Stark level of the $^4F_{3/2}$ manifold ($R_1$) to the upper Stark level of the $^2I_{9/2}$ manifold ($X_3$) corresponding to the peak wavelength of 941 nm is found to be $\sigma_p(R_1\rightarrow X_3) = 3.3 \times 10^{-20}$ cm$^2$ [14].

5. EPR spectra

A Varian E-12 X-band spectrometer was used to detect the color centers at room temperature. Before inserting the sample in the microwave cavity the sample was colored with a single 10 J flashlamp pulse. This was sufficient to create a strong EPR signal which was characterized by an isotropic $g$ equal to 2.0065, a value close to standard $g$ values for color centers [22]. 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. The EPR spectra are shown in Fig. 5 for the dc magnetic field aligned along the three crystallographic directions [100], [110] and [111], respectively. The strongest EPR signal was obtained when the dc magnetic field was applied along the [111] direction.

Information regarding the site location of these centers can be obtained by comparing our results with the results of experiments performed by Geschwind [23] on Fe$^{3+}$ in yttrium gallium garnet. The garnet structure is cubic and has 24 tetrahedral sites, 16 octahedral sites and 24 dodecahedral sites, with oxygen ions located at the vertices and cations at the centers of these sites. The octahedral site is somewhat distorted and has a $C_{3v}$ symmetry characterized by threefold axes of rotation coinciding with the [111] crystallographic directions. The tetrahedral site is also distorted but has a symmetry $S_4$, with the four-fold
Table 2
Predicted radiative decay rates, branching ratios, and line strengths for Nd³⁺:CAZGAR

<table>
<thead>
<tr>
<th>Transition from</th>
<th>λ (nm)</th>
<th>$A(J\rightarrow J')$ (s⁻¹)</th>
<th>$\beta(J\rightarrow J')$</th>
<th>$S_{calc}$ (10⁻²⁰ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4I_{13/2}$</td>
<td>1835 *</td>
<td>17</td>
<td>0.005</td>
<td>0.10</td>
</tr>
<tr>
<td>$^4I_{13/2}$</td>
<td>1330 *</td>
<td>322</td>
<td>0.093</td>
<td>0.77</td>
</tr>
<tr>
<td>$^4I_{11/2}$</td>
<td>1056.5</td>
<td>1725</td>
<td>0.500</td>
<td>1.93</td>
</tr>
<tr>
<td>$^4I_{9/2}$</td>
<td>889.2</td>
<td>1408</td>
<td>0.406</td>
<td>0.94</td>
</tr>
</tbody>
</table>

* Values were not measured, but were taken from Ref. [25].

axes of rotation coinciding with the [100] crystallographic directions. The Fe³⁺ ions are located in the octahedral and tetrahedral sites and the rare-earth or other large size ions go into the dodecahedral sites. In addition, Fe³⁺ has a preference for the octahedral sites, which shows up in the EPR spectra as follows. When the magnetic field is oriented along one of the three-fold rotation axes [111], only the octahedral sites contribute to the spectrum. When the field is along one of the [100] axes, both the octahedral and tetrahedral sites contribute to the spectrum, the tetrahedral contribution being smaller than the octahedral contribution. The presence of a strong signal, when the magnetic field is oriented along a [111] direction, seems therefore to suggest the predominance of the magnetic ion in the octahedral sites. In our case, one can therefore conclude that the color centers are located in the octahedral sites which are normally occupied by zinc ions. A rotation of the sample in a plane perpendicular to the [111] direction gives an exact $C_{3v}$ symmetry, thereby supporting this conclusion.

6. Discussion

In some materials, the presence of color centers does not degrade the laser performance of the material, and in others it can prevent laser oscillation. Color centers have been used to enhance the fluorescence output of Er³⁺ ions in CaF₂ as reported by Forrester and Sampson [8]. They found Er³⁺ laser lines in this material which are aided by energy transfer from the color centers. More recently, it is also reported that the color center enhanced the Er³⁺ oscillator strength by an order of magnitude in RbMgF₃ [24]. Another instance, where color centers have been found to be advantageous, is reported by Snitzer and Woodcock [11]. They were able to obtain self $Q$-switched pulses in a glass co-doped with UO₂²⁺ and Nd³⁺ by saturated absorption of color centers formed in the glass by ultraviolet radiation shorter than 200 nm.

Color centers in laser materials can be harmful either by interfering with the emission lines or the pump absorption bands. Absorption by color centers of the laser wavelength degrades laser performance and when the absorption bands of the color centers overlap the absorption bands to the active ion again, the laser performance is usually degraded. Stickley et
al. [7] have shown that pump light absorption by the color centers produced by the ultraviolet content of the pump light accounts for the degradation observed in the laser output of ruby. The nature of the centers in the study of ruby was not known but was attributed to the impurities present in the ruby samples other than Cr$^{3+}$ impurities. Bulk absorption at the laser wavelength, 694 nm, can lead to the catastrophic damage in ruby. In the crystal studied here, the possibility of catastrophic damage due to bulk absorption at the laser wavelength is unlikely. That is, the active ion Nd$^{3+}$ would lase at approximately 941 and 1059 nm which are not in the region of the observed absorption band produced by the color centers. At GaAlAs diode laser wavelengths near 805 nm, the pump absorption bands are unaffected also.

Figs. 3 and 4 illustrate that the undesired bulk and surface absorption of the pump light limits the fluorescence output of this material. Damage to the surface (approximately 1 mm deep) of Nd$^{3+}$:CAZGAR rods following flashlamp irradiation leads to the strong, undesired absorption at or near the surface and causes the pumping losses due to an overlap of the absorption bands in the visible and UV to such an extent that it prevents lasing in these garnets. The coloration by incoherent pumping can be avoided by using UV absorbing flashlamp cooling jackets. These filters reduce the rate of color center formation permitting the remaining portion of the flashlamp pulse to effectively pump the Nd$^{3+}$ absorption bands in the visible and near infrared.

In summary, the J-O analysis has been employed to the measured absorption data to calculate the radiative decay rates for various transitions from the Nd$^{3+}$ $F_{3/2}$ metastable level to $I_J$ manifolds. The 285 µs fluorescence lifetime of Nd$^{3+}$:CAZGAR is capable of storing higher energy in this material than in Nd$^{3+}$:YAG. The spectroscopic quality factor, $X = \Omega_4/\Omega_6$, of this sample is approximately 0.88, which yields a greater branching ratio for the $I_{9/2}$ transitions, at the expense of the $I_{11/2}$ manifold. This quality factor is larger than that of Nd$^{3+}$:YAG [25]. Finally, owing to its broad absorption at about 805 nm, and its greater energy storage capability, Nd$^{3+}$:CAZGAR can be an excellent candidate for a laser material that can be pumped by high power GaAlAs laser diode and shall emit at 941 nm.

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References