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LETTER TO THE EDITOR

Up-conversion luminescence in the $Ca_3Ga_2Ge_3O_{12}$:Nd^{3+} laser garnet crystal

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Abstract. The infrared to visible luminescence of the Nd^{3+} ion in the $Ca_3Ga_2Ge_3O_{12}$:Nd garnet crystal at different Nd concentrations has been investigated in the excitation spectral range corresponding to diode pumping (720–840 nm) under continuous wave and pulsed pumping. Three visible bands centred at 541, 601 and 677 nm were observed, these emissions mainly departing from the excited state $^4G_{7/2}$. By using a simple rate equation model to fit the experimental data, it was possible to infer that this excited state is populated via up-conversion energy transfer between Nd^{3+} ions in the garnet crystal.

1. Introduction

Neodymium is the most common activator in laser crystals, owing to its intense luminescence, and it is, therefore, of considerable interest in quantum electronics and its applications. Thus, the study of the optical properties of Nd^{3+}-doped garnet crystals has played an important role in the physics of solid-state laser materials [1, 2]. Up to now, it has been possible to obtain laser action in many garnet crystals activated with neodymium [3, 4]. Diode pumped solid state lasers have achieved great importance since high power lasers have become commercially available. Up to now, YAG:Nd is still the most common laser crystal for diode pumping. However, it has some disadvantages: (a) The Nd^{3+} concentration in the crystal without quenching is limited to 1.1 at.%; this low concentration induces a long absorption length for pump light, and hence a larger internal loss factor, which is proportional to the crystal length, and (b) the YAG:Nd growth is relatively expensive because of its very high melting point (1960 °C).

The $Ca_3Ga_2Ge_3O_{12}$ garnet activated with Nd^{3+} ions (CGGG:Nd) emerges as an interesting laser crystal because of its lower melting point, about 1400 °C. The crystal growth can be easily obtained by means of a common silicon carbide oven. A peculiar characteristic of this crystal is its disordered structure due to the formation of rare earth ions and excess charge compensator associations. This phenomenon leads to the formation of several multisites for the activator ion in accordance with the possible charge compensation centres. Six non-equivalent Nd sites were previously found in this crystal [2]. As a consequence of both disordered structure and multisites, CGGG:Nd shows considerably broader absorption bands than YAG:Nd. Thus, accurate temperature stabilization of the diode pump source is not necessary as it is for

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YAG:Nd. Recently, the spectroscopic properties for laser application of CGGG:Nd have been systematically investigated by Ramos *et al* [5]. Actually, it has been possible to obtain laser action in the region of 1 μm in CGGG:Nd crystals by Ti:sapphire end pumping (simulating the diode pumping) [4].

It is known that excited state absorption of pump radiation (ESAPR) can lead to considerable losses in the laser gain. Information on the relevance of ESAPR can be partially obtained by studying the infrared (IR) to visible up-converted luminescence, which is typically observed in Nd-doped compounds. In fact, this visible up-converted luminescence is usually used to focus the pump beam in end-pumped lasers.

In this work, we report a systematic study of the concentration dependence of the up-converted luminescence of the Nd^{3+} ion in the CGGG:Nd crystal in the spectral region of interest for diode pumping (720–840 nm). Several experiments were carried out under continuous wave (cw) and pulsed excitation in order to investigate the states involved in the up-conversion luminescence. We also investigated the responsible mechanisms for the population of the emitting states.

It is well documented that the processes leading to the up-converted luminescence from rare-earth ions embedded in a host material can be due to energy transfer up-conversion (ETU) [6] or ESAPR [7]. Their relative contributions depend on several parameters, such as the excitation wavelength, the excitation density and the rare-earth concentration [8]. It is known that at low concentrations ESAPR is the dominant up-conversion process, but with increasing concentration ETU processes start to compete and finally dominate over excited-state absorptions [9]. ETU is an energy transfer process in which two nearby excited ions are necessary to interact with each other, and because of their interaction, one ion goes to a lower state, releasing some amount of energy. The second ion uses this energy and goes to a higher excited state. ESAPR is a sequential two-photon excitation process. One ion, originally in the ground state, is resonant with a pump photon and goes to an upper excited state. Later the ion decays to an excited metastable state through a fast nonradiative process from where it is excited to an even higher state by absorbing a second pump photon. The ETU and ESAPR processes can coexist, both contributing to the population of the highest excited states. That both processes can be present can be testified by the recent development of up-conversion lasers [10, 11]. In this work we are interested in knowing the dominant process that populates the excited states.

2. Experimental

The CGGG crystals doped with Nd^{3+} ions used in this work were grown from the melt by the Czochralski technique using platinum crucibles. The Nd concentration in the melt was changed from 0.5 to 16 at.%, so that five different samples were obtained with 0.5, 1, 2, 8 and 16 at.%. The actual Nd concentration in the crystals was not known, so we will always refer to the atomic concentration in the melt. All these samples were carefully cut and polished in the same conditions.

Absorption spectra were obtained using a Perkin-Elmer 330 spectrophotometer. Fluorescence (emission, excitation and decay time) measurements were obtained by means of a cw-argon pumped Ti-sapphire tunable laser (Spectra Physics 3900). The pulsed excitation required for lifetime data was achieved using a chopper PAR EG&G capable of generating 400 Hz laser pulses. The luminescence was dispersed by a 500M SPEX monochromator and detected with a cooled photomultiplier or a cooled Ge detector (depending upon the spectral range). The signals were recorded using a SR400 two-channel gated photon counter. The decay time measurements were performed using a Tektronix 2400 digital storage oscilloscope.

3. Results and discussion

Figure 1 shows the energy level diagram of Nd^{3+} ion in the CGGG:Nd crystal, which was obtained from our previous studies [2, 5]. The width of the lines in each state indicates the extent of the crystalline field splitting. The diagram also shows the two possible mechanisms, ETU (left part) and ESAPR (right part), leading to a visible luminescence after infrared excitation. It can be seen that both mechanisms populate the excited state $^4G_{7/2}$. Later we will show that the up-conversion luminescence originates mainly from this excited state.

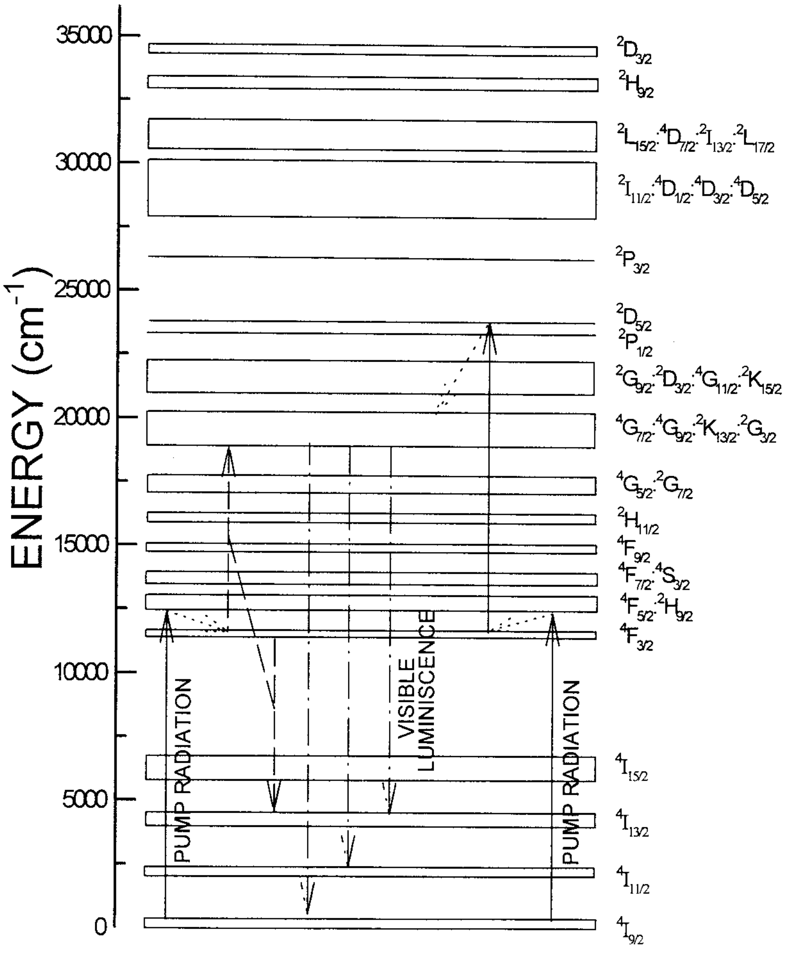

Figure 1. Energy level diagram of CGGG:Nd showing the ETU and ESAPR processes leading to infrared to visible up-converted luminescence.

Figure 2 shows the RT emission spectrum recorded for different Nd concentrations when the sample is pumped at 800 nm using a cw-Ti-sapphire laser as pump source. In this measurement, an infrared filter was used to avoid both the pump radiation and the infrared luminescence departing from the metastable state $^4F_{3/2}$. Three structured bands centred at 541, 601 and 677 nm can be seen for each concentration. From this spectrum and from the energy level diagram of figure 1, it can be concluded that the observed bands mainly originate

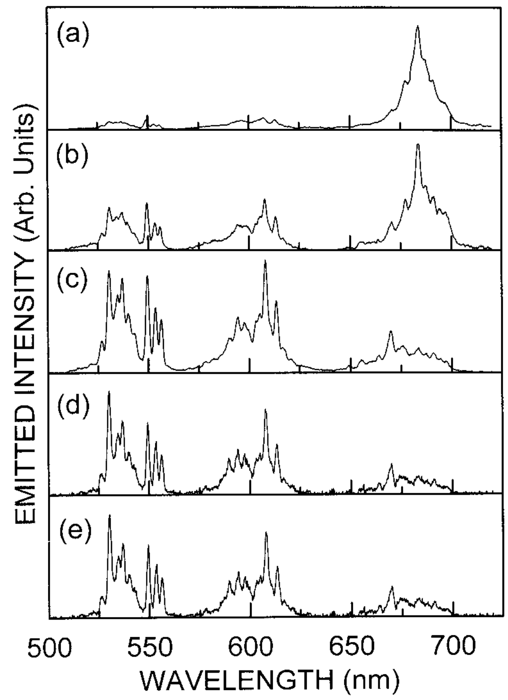

Figure 2. Up-conversion emission spectra obtained under excitation at 800 nm in CGGG doped with (a) 16, (b) 8, (c) 2, (d) 1 and (e) 0.5 at.% of Nd^{3+}.

from the $^4G_{7/2}$ excited state, and thus they can be assigned as follows:

541 nm band : $^4G_{7/2} \rightarrow {}^4I_{9/2}$ transitions(green)

601 nm band : $^4G_{7/2} \rightarrow {}^4I_{11/2}$ transitions (yellow)

677 nm band : $^4G_{7/2} \rightarrow {}^4I_{13/2}$ transitions (red).

The fluorescence transitions involving such states have been indicated in the energy level diagram of figure 1. Since the 677 nm band is considerably wider than the other two bands, it is reasonable to suggest that it may also involve the transitions $^4G_{5/2} \rightarrow {}^4I_{11/2}$ and $^4F_{9/2} \rightarrow {}^4I_{9/2}$. The emission intensity of the $^4G_{7/2} \rightarrow {}^4I_{9/2}$ and $^4G_{7/2} \rightarrow {}^4I_{11/2}$ transitions decreases with the increase in Nd concentration (0.5–16 at.%). These emissions are almost extinguished at 16 at.%. On the other hand, the intensity of the $^4G_{7/2} \rightarrow {}^4I_{13/2}$ transitions gradually increases with Nd concentration, and it is the most intense band at 16 at.%. At present, we have no explanation for the evolution of the shape in the up-conversion emission spectra with the Nd content. Additional experiments are now in progress in order to elucidate on this aspect.

The $^4G_{7/2}$ excited state can be populated, at least in principle, by ETU or ESAPR mechanisms, so that the emission spectra do not give information about which process produces the visible luminescence. To obtain such information, we investigated systematically the excitation spectrum of the visible luminescence in the region 720–840 nm.

Figure 3 shows the excitation spectra of the 601 nm band (using the Ti-sapphire tunability) at different Nd concentrations (0.5, 1, 2, and 8 at.%). The absorption spectra (absorbence *vs* wavelength) are displayed in the inset for the sake of comparison. In contrast to other Nd doped materials, such as YAG:Nd [12], no differences are observed between both spectra. This is a

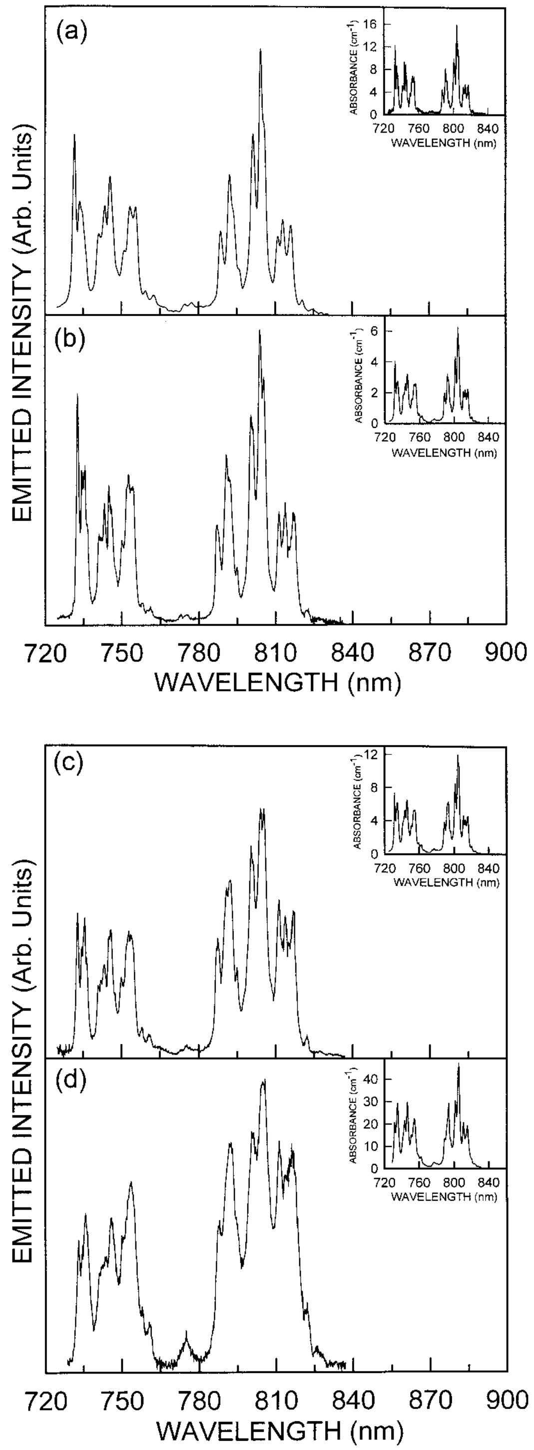

Figure 3. Up-conversion excitation spectra taken at 601 nm for different Nd concentrations: (a) 0.5, (b) 1, (c) 2 and (d) 8 at.% . The insets show the absorption spectra (absorbence *vs* wavelength).

clear indication that no resonant absorption of the pump radiation takes place at any particular wavelength. Therefore, we can conclude that in the CGGG:Nd crystal resonant absorption of pump radiation was not produced from the metastable state $^4F_{3/2}$. An ETU process seems, then, to be required to take into account the observed visible luminescence.

Let us now analyse the data obtained in cw experiments to be sure that ETU is the dominant process. For this, a three-level system model is considered, in which the following rate equations are fulfilled:

$$\frac{dN_0}{dt} = -N_0\sigma I + N_1\frac{1}{\tau_{10}} + N_2\frac{1}{\tau_{20}} \tag{1}$$

$$\frac{dN_1}{dt} = -kN_1^2 + N\sigma I - \sigma_p I N_1 - \frac{N_1}{\tau_{10}} + \frac{N_2}{\tau_{21}} \tag{2}$$

$$\frac{dN_2}{dt} = kN_1^2 + \sigma_p I N_1 - \frac{N_2}{\tau_{20}} - \frac{N_2}{\tau_{21}} \tag{3}$$

where N_0 is the number of Nd^{3+} ions in the ground state 0 ($^4I_{9/2}$); N_1 and N_2 are the number of Nd^{3+} ions in the excited states 1 ($^4F_{3/2}$) and 2 ($^4G_{7/2}$), respectively; σ is the pump absorption cross section; I is the pumping intensity (measured as a flux of incident photons per unit area per unit time); k and σ_p (cross section) are coefficients related to the ETU and ESAPR processes, respectively; $1/\tau_{10}$ and $1/\tau_{20}$ are the transition rates from the 1 and 2 states, respectively, to the ground state 0 ($^4I_{9/2}$); and $1/\tau_{21}$ is the transition rate from state 2 to state 1.

The above equation system is greatly simplified by considering that under cw conditions a steady state is achieved, and then all the time derivatives become zero. Thus, equations (1) and (3) are reduced to:

$$0 = -N_0\sigma I + N_1\frac{1}{\tau_{10}} + N_2\frac{1}{\tau_{20}} \tag{4}$$

and

$$0 = kN_1^2 + \sigma_p I N_1 - \frac{N_2}{\tau_2} \tag{5}$$

where $1/\tau_2 = 1/\tau_{20} + 1/\tau_{21}$.

Let us now to consider either ETU or ESAPR as the dominant process.

(1) ETU as the dominant process.

We can make the following valid approximation: $\sigma_p I N_1 \ll kN_1^2$, so that equation (5) is reduced to:

$$kN_1^2 - \frac{N_2}{\tau_2} = 0. \tag{6}$$

The ratio between the intensity of the visible luminescence, I_2, and the square of the intensity of the IR luminescence, I_1, can be estimated by considering that such intensities are proportional to N_2 and N_1, respectively. Thus, from equation (6) we have that:

$$\frac{I_2}{I_1^2} \propto \frac{N_2}{N_1^2} = k\tau_2. \tag{7}$$

Therefore, if ETU is the dominant process, the quotient I_2/I_1^2 should be a constant independent of the excitation wavelength.

(2) ESAPR as the dominant process.

We can make two assumptions: $\sigma_p I N_1 \gg k N_1^2$ and $N_1 \gg N_2$. The second assumption and $N_0 \approx N_{tot}$ allow us to solve equation (4) and get:

$$I = \frac{1}{N_{tot}\sigma\tau_{10}} N_1. \tag{8}$$

Equation (5) plus the $\sigma_p I N_1 \gg k N_1^2$ assumption gives:

$$\frac{N_2}{\tau_2} = \sigma_p I N_1. \tag{9}$$

Now, substituting equation (8) into equation (9):

$$\frac{N_2}{N_1^2} = \frac{\sigma_p \tau_2}{\sigma N_{tot}\tau_{10}} \tag{10}$$

and therefore:

$$\sigma \frac{I_2}{I_1^2} \propto \sigma \frac{N_2}{N_1^2} \propto \sigma_p. \tag{11}$$

Equation (11) indicates that if ESAPR is the dominant process, $\sigma I_2/I_1^2$ must reproduce the spectral dependence of the excited state coefficient, σ_p, of pump radiation, which is different from the absorption coefficient α.

In the Nd concentration range 0.5–8 at.% it was found that the ESAPR coefficient $\sigma_p(\propto\ I_2/I_1^2)$ displays a similar shape, within the experimental error, to the absorption coefficient $\alpha = \sigma N_{tot}$ and that the ratio I_2/I_1^2 is practically independent of the wavelength. These two results, which can be visualized for the CGGG:Nd (2 at.%) crystal in figure 4, indicate clearly that ETU is the dominant process taking place in the visible luminescence.

Finally, the time evolution of the visible luminescence after pulsed excitation for different Nd concentrations (1, 2, 8 and 16 at.%) has been analysed. This requires the solution of equations (1)–(3) for a non-steady state with $I(t = 0) = 0$ as the initial condition. Such coupled equations can be solved assuming that $N_1/\tau_{10} \gg kN_1^2$, and consequently $N_1 \gg N_2$, under infrared pumping. Therefore, equations (2) and (3) can be written as:

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = -\frac{N_1}{\tau_{10}} \tag{12}$$

and

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = -\frac{N_2}{\tau_2} + kN_1^2. \tag{13}$$

To solve the above equation system it can be considered that $N_2(t = 0) = 0$. The solutions for N_1 and N_2 are then

$$N_1 = Ae^{-t/\tau_{10}} \tag{14}$$

and

$$N_2 = B(e^{-2t/\tau_{10}} - e^{-t/\tau_2}) \tag{15}$$

where A and B are positive constants. Equation (15) shows that the time evolution of the intensity of the up-converted visible luminescence, I_2, consists, in principle, of a rise time with lifetime of level 2, τ_2, and an exponential decay time with a lifetime equal to $\tau_{10}/2$. The 600 nm emission time decay was recorded after infrared pumping at 800 nm for different Nd concentrations (1, 2, 8 and 16 at.%). For all these concentrations the shape of the fluorescence decay is nonexponential, with a rise time τ_2 shorter than about 5 μs, while for longer times the

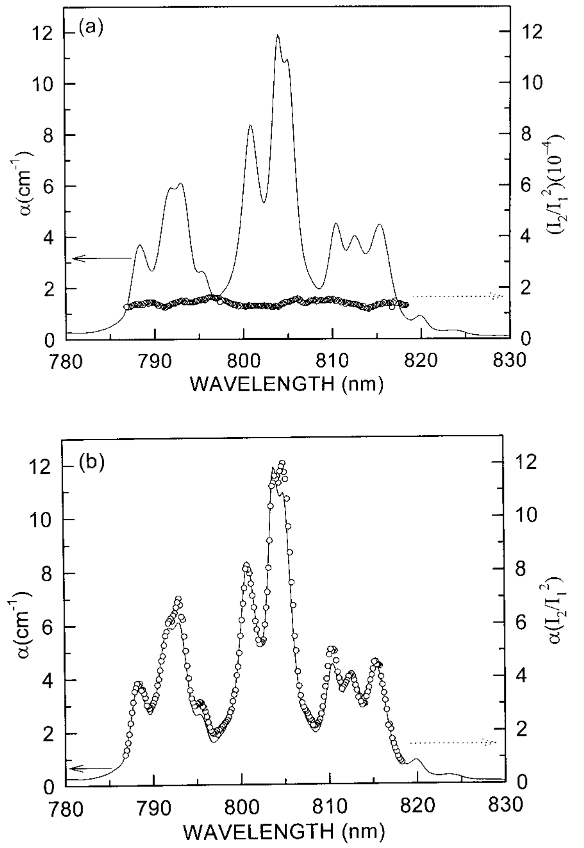

Figure 4. Wavelength dependence of the absorption coefficient α and (a) the I_2/I_1^2 ratio and (b) the $\alpha I_2/I_1^2$ product for the CGGG:Nd (2 at.%) crystal. I_2 and I_1 were obtained from excitation spectra with $\lambda_{em} = 600$ and 1060 nm, respectively.

Table 1. Lifetimes measured for the up-converted visible (τ_{10}^{vis}) and radiative (τ_{10}) luminescence in CGGG:Nd crystals doped with different Nd concentrations.

% at Nd	τ_{10}^{vis} (μs)	τ_{10} (μs)
1	102	221
2	88	181
8	22	36
16	12	22

decay becomes exponential with a lifetime near that ($\tau_{10}/2$) predicted by equation (15). The observation of this rise occurring after the completion of a short IR excitation pulse provides clear evidence that the ESAPR process is not important. The lifetimes associated with the up-converted visible luminescence (τ_{10}^{vis}) and with the radiative emission (τ_{10}) are listed in table 1.

It is important to remark that the simple rate equation model here proposed does not include the nonexponentiality of the $^4F_{3/2}$ state decay at the short times usually observed in energy transfer processes. However, the experimentally recorded fluorescence decay pattern from this level did not present such nonexponential initial decay, even at the highest pumping intensities. In fact, the up-converted visible luminescence was observed to be so weak that the infrared fluorescence from the $^4F_{3/2}$ metastable state was not affected.

4. Conclusions

From a spectroscopy analysis of the infrared to visible fluorescence of Nd^{3+} in the CGGG:Nd crystal under continuous wave and pulsed excitation it is inferred that energy transfer up-conversion is the process responsible for the visible luminescence in the Nd concentration range 0.5–8 at.%. A simple rate equation model with three levels: the ground state $^4I_{9/2}$ and two excited states $^4G_{7/2}$ and $^4F_{3/2}$, can explain the emission *vs* excitation intensity dependence as well the long decay time of the visible luminescence.

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