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RATE EQUATION DESCRIPTION OF MULTI-PHOTON CREATION OF COLOR CENTERS AND SIMULTANEOUS ONE-PHOTON ANNIHILATION *

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Pumping the lowest 4f→5d absorption band of the Ce^{3+} ions in Ce^{3+}:CaF_2 with a 308 nm XeCl laser results in the photoionization of Ce^{3+} due to an excited-state absorption which terminates in the conduction band. The photo-electron can be trapped at a Ce^{3+} ion with O_h symmetry thus forming a divalent cerium ion color center. However, these divalent cerium ions are photobleached by both the 308 nm excitation light and the Ce^{3+} fluorescence. The rate equation which describes the number of divalent cerium ions must include both the two-step creation process, which is quadratic in the laser intensity, as well as a linearly dependent bleaching mechanism. The solutions to the rate equation are in agreement with the observed growth and saturation characteristics of the number of divalent ions.

1. Introduction

The photoionization of the Ce^{3+} ions in Ce^{3+}:CaF_2 by the 308 nm light from a XeCl excimer laser results from an excited-state transition from the 5d state to the CaF_2 conduction band [1,2]. Although the dominant site symmetry of the Ce^{3+} ions is C_{4v}, there are a few Ce^{3+} ions with cubic O_h symmetry [3]. The Ce^{3+} ions at these O_h sites act as efficient electron acceptor sites due to the nonlocal character of their charge compensation mechanism [4]. The electrons from the photoionization of the Ce^{3+} ions can trap at the O_h sites, resulting in Ce^{2+} ions having cubic symmetry. It is these Ce^{2+} ions which give the crystal its reddish brown coloration following exposure to the 308 nm laser. The Ce^{2+} ions are known to be photochromic [5,6] and they can be bleached by the 308 nm excitation light as well as the 310–370 nm emission of the excited Ce^{3+} ions.

2. Rate equations

We have been able to describe the number of divalent cerium ions (n_d) created by the XeCl laser light with a rate equation of the form

$$dn_d/dt = n_c n_t a I^2 - n_d b I. \tag{1}$$

The creation term is quadratic in the laser intensity I, since two photons are required to photoionize the Ce^{3+} ions. The parameter a is the product of the 4f→5d cross section, the cross section for the 5d→conduction band transition and a probability for electron capture at the O_h site. Since it is a two-center process, the creation term must also involve the number of Ce^{3+} ions at tetragonal sites which can be photoionized (n_t) and the number at cubic sites which can act as electron acceptor sites (n_c). The annihilation term is linear in the laser intensity since the Ce^{2+} centers can be photo-bleached by a single photon. This term is also dependent on the number of divalent cerium centers and a bleaching cross section b. The ion densities are constrained by the relation $n_c + n_d = n_{c0}$, where n_{c0} is the initial density of Ce^{3+} ions at cubic sites. We have also assumed that $n_t \gg n_{c0}$ and that n_t remains approximately constant.

The solution to eq. (1) can easily be found for a train of laser pulses, where the time dependence of each pulse is a rectangular function of intensity I and duration Δt [7]. The elapsed time is represented by $t = N\Delta t$, where N is the accumulated number of pulses. With these approximations and assuming $n_d(0) = (0)$, the solution to eq. (1) is

$$n_d(N) = n_d(\infty)[1 - \exp(-n_t a I^2 - bI) N\Delta t], \tag{2}$$

where $n_d(\infty)$ is the steady state number of divalent ions,

$$n_d(\infty) = \frac{n_{c0} n_t a I}{n_t a I + b} = \frac{n_{c0} I}{I + b/n_t a}. \tag{3}$$

The steady state limit is linear in the intensity for $I \ll b/n_t a$, and then saturates at n_{c0} for high intensity values.

For small values of the argument of the exponential function of eq. (2), the number of divalent centers can be approximated by

$$n_d(N) \approx n_{c0} n_t a I^2 N\Delta t. \tag{4}$$

This quadratic behavior corresponds to the limit where both N and I are sufficiently small, thus $n_d \approx 0$ and the bleaching process can be ignored.

3. Experimental results

To measure the absorption which is proportional to the number of Ce^{2+} ions, a coaxial pump-probe geometry was

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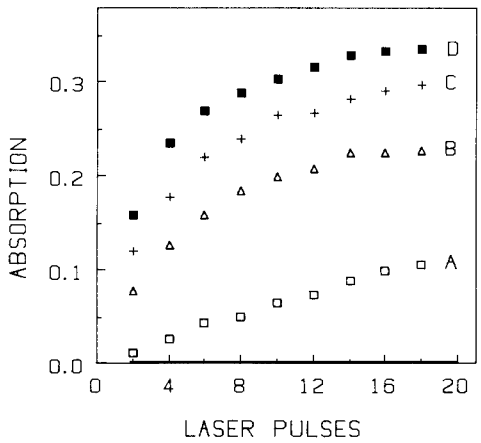

Fig. 1. The absorption ($\ln I_0/I$) of a 520 nm probe beam due to the growth of the divalent cerium centers with accumulated exposure to the pulsed 308 nm laser. The laser intensities in MW/cm^2 are: A, 10; B, 23; C, 33 and D, 44.

used. The probe wavelength of 520 nm is strongly absorbed by the Ce^{2+} ions, but not by the Ce^{3+} ions. The samples used were grown by Optovac and had a 0.1% Ce^{3+} concentration.

The absorption at 520 nm as a function of the number of XeCl laser pulses is shown in fig. 1. The growth curves are well described by a single exponential in eq. (2), indicating a single type of center is created. The steady state absorption values are clearly dependent on the laser intensity and this relationship is illustrated in fig. 2. The curve displayed in fig. 2 is a least-squares fit to eq. (3). The asymptotic high intensity limit, which corresponds to n_{c0} is $\alpha_{520}L=0.8$ and the other fit parameter is $b/n_1a=58$. The linear behavior at low intensity represents the competition between the quadratic creation and the linear annhilation processes. The saturation behavior at high intensity reflects the finite number of electron acceptor sites.

The initial slope of the growth curves from fig. 1 is displayed in fig. 3. At low values of the intensity, the absorption has a quadratic dependence of the laser intensity, in agreement with eq. (4). At higher values of the intensity, the relationship is sub-quadratic, indicating a breakdown of the approximations that led to eq. (4). For these high intensity values, there is significant photo-bleaching of the divalent population even during the first laser pulse. It should also be pointed out that at high intensity, it is possible to saturate the excited 5d state of the Ce^{3+} ions, which will also result in a sub-quadratic behavior.

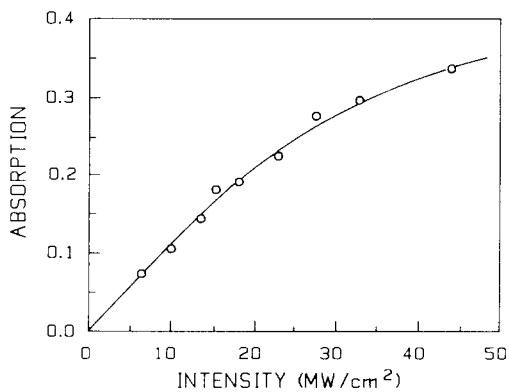

Fig. 2. Steady state absorption ($\ln I_0/I$) at 520 nm as a function of the intensity of the 308 nm laser. The curve represents the least-squares fit to eq. (3).

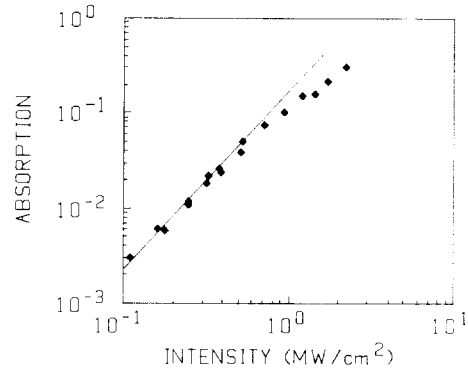

Fig. 3. Initial value of the change per laser pulse in the absorption of the 520 nm probe beam. The values for the lower intensity points depend quadratically on the laser intensity, as indicated by the straight line of slope 2.

4. Conclusions

Multiphoton transitions in impurity doped solids can lead to a photoionization process. This will result in the formation of color centers in systems where there are alternate electron acceptor sites. If the color center can be photo-bleached by the same wavelengths that are responsible for its formation, then the formation kinetics can be described by a rate equation which incorporates both the multiphoton creation term and a photo-annihilation term. For the case of Ce^{3+}:CaF_2, the steady state and saturation characteristics and the initial growth of the color centers can be fully described by the solutions to such a rate equation. The modeling of such processes is an important part of understanding the solarization of optical materials [8], and in the development of materials for color center laser [9] and frequency-domain optical storage technologies [10].

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