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Diffusion of color centers generated by two-photon absorption at 532 nm in cubic zirconia

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We have recently reported the formation of color centers in stabilized cubic zirconia (ZrO_2 , 18% Y_2O_3) by two-photon absorption at 532 nm. Here we present the results of measurements of the transmission of the colored samples as a function of time at room temperature. The results are found to be in good agreement with theory that assumes the color centers diffuse out of the irradiated region. The initial distribution of centers is assumed to have a Gaussian profile. For this model, the diffusion equation was solved exactly and the diffusion constant obtained ($\sim 3.4 \times 10^{-8}$ cm²/s).

We have reported¹⁻³ that the transmission of stabilized cubic zirconia (ZrO_2 , 18% Y_2O_3) is decreased (about 15%) by exposing the samples to high-irradiance nanosecond and picosecond, 532-nm pulses. The mechanism was found to be due to formation of color centers by two-photon absorption.^{2,3} The induced color centers can be removed by repeated irradiation with relatively low irradiance at the same wavelength (532 nm) as shown in Fig. 1. These processes (coloring and discoloring) have potential application in making erasable optical memory devices.

In the present experiment, the transmission of colored samples (i.e., the density of color centers) was measured as a function of time at room temperature and was found to decrease due to diffusion to the surrounding medium. The measurement of the diffusion constant is presented.

The laser used in this study was a Nd:YAG oscillator-amplifier system, which has been described elsewhere.³ The laser was actively *Q* switched, operating at 1064 nm. Single pulses of measured Gaussian spatial profile were produced by the oscillator and amplified by a single pass through the amplifier. A KD*P crystal was used to produce pulses at 532 nm. Residual 1064-nm radiation was eliminated by reflecting off three dichroic mirrors. The temporal pulse width was approximately 15 ns (FWHM) at 532 nm. The temporal width of each pulse was monitored by a *p-i-n* photodiode detector and fast storage oscilloscope.

The laser beam was focused into the sample using a single element "best-form" lens designed for minimum spherical aberrations. The lens was a $f = 999$ mm, which provided a nominal focal spot size of 155 μ m (HW $1/e^2$ M in irradiance). For this measurement the actual focused spot sizes were obtained by scanning the spatial profile in both the horizontal and vertical dimensions with a 5- μ m-diam pinhole placed in the plane of the sample. By using a rotating half-wave plate/polarizer combination to vary the irradiance on the sample, the beam profile for high and low irradiance was held constant. The incident energy was continuously monitored by a sensitive photodiode where the output was digitized and calibrated with respect to pyroelectric energy meters.

We measured the transmission of the colored samples as a function of time in the following sequence. First, the stabi-

lized cubic zirconia (ZrO_2 , 18% Y_2O_3) sample was colored by exposing it to high-irradiance laser pulses at 532 nm. Second, after different time delays, the transmission of the sample was monitored by low-irradiance laser pulses at the same wavelength (532 nm) as shown in Fig. 2. As clearly indicated in the graph, when the sample was irradiated with high irradiance (~ 300 MW/cm²), the transmission started to decrease, which indicated that color centers were generated in this material. After some number of shots, the transmission remained constant with further irradiation showing the saturation effects of the formation of these induced centers.

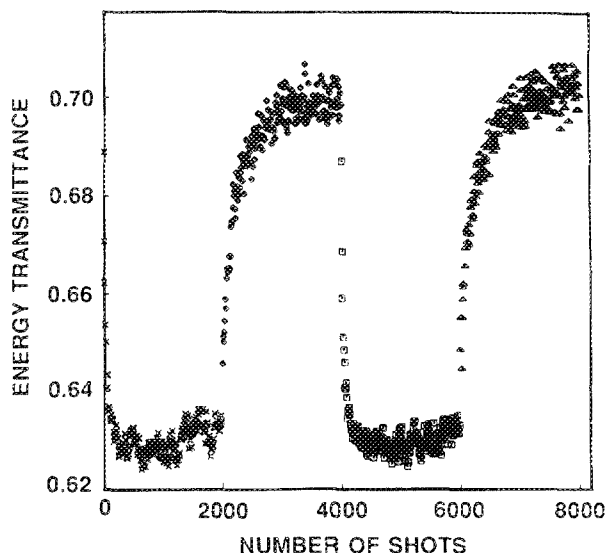


FIG. 1. Formation and bleaching of color centers in the stabilized cubic zirconia (ZrO_2 , 18% Y_2O_3) sample. The change of transmission is shown as a function of number of laser shots at various input irradiance levels in the ZrO_2 sample with 15-ns, 532-nm pulses. Note that in the first set of data (shown by \times 's) the transmission decreases with successive high-irradiance pulses of 300 MW/cm² until the effect (formation of color centers) saturates. The second set of data (shown by diamonds) was taken immediately after the first one by irradiating the sample at the same position with low-irradiance pulses of 20 MW/cm². As indicated in the figure, the transmission increased, and after some number of shots the transmission remained constant and equal to its value prior to the high-irradiance laser radiation. The other two sets of data show that the processes of generating and bleaching of the color centers are repeatable.

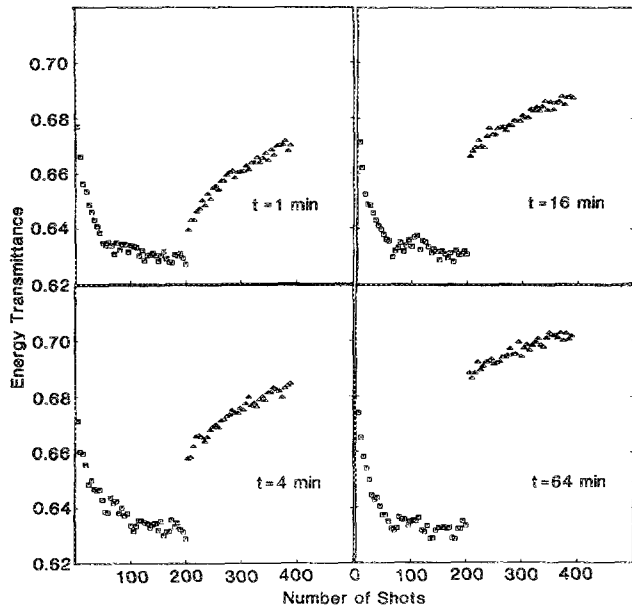


FIG. 2. The transmission of the irradiated region in stabilized cubic zirconia (ZrO_2 , 18% Y_2O_3) for 15-ns, 532-nm laser pulses. The jump shown after 200 laser firings appears after shutting off the laser for times of $t = 1, 4, 16,$ and 64 min.

This allowed us to probe the transmission of the colored region of the sample for different time lapses before low-irradiance exposure (~ 20 MW/cm²). As clearly indicated in Fig. 2, the transmission of the colored specimen increases with time (i.e., the density of color centers decreases) at room temperature. In the paragraphs to follow, it will be shown that this is due to diffusion of the color centers to the surrounding medium.

The general diffusion equation for the density $N(r,t)$ of the color centers is given by

$$\frac{\partial}{\partial t} N(r,t) = D \nabla^2 N(r,t), \quad (1)$$

where D is the diffusion coefficient and has units of cm²/s. Since the color centers are induced by irradiating the stabilized cubic zirconia (ZrO_2 , 18% Y_2O_3) samples with well-collimated laser pulses, the initial distribution of these centers was modeled as cylinders of Gaussian profile extending in the radial direction. For cylindrical symmetry, the diffusion equation [Eq. (1)] is simplified to

$$\frac{\partial}{\partial t} N(r,t) = D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} N(r,t) \right), \quad (2)$$

subject to the initial condition ($t = 0$) of

$$N(r,0) = N_0 \exp\left(-\frac{r^2}{(\Delta w)^2}\right), \quad (3)$$

where Δw is the $1/e$ radius of the spatial irradiance profile of the laser pulses. The contribution of diffusion of the color centers in the z direction is neglected, since in the case of a thick sample (~ 1 cm) the net flux is very small. Also, as discussed in the previous paragraph, the transmission change saturates after a number of high-irradiance pulses giving rise to constant color center density in the z direction.

To solve this problem, we introduce the Fourier transform pair for N :

$$N(\mathbf{k},t) = \frac{1}{(2\pi)^n} \int_{-\infty}^{+\infty} N(\mathbf{r},t) \exp(i\mathbf{k}\cdot\mathbf{r}) d^n r, \quad (4)$$

and

$$N(\mathbf{r},t) = \int_{-\infty}^{+\infty} N(\mathbf{k},t) \exp(-i\mathbf{k}\cdot\mathbf{r}) d^n k, \quad (5)$$

where n determines the dimension of the problem. We substitute (5) into (1) and perform the ∇^2 operation. Then Eq. (2) reduces to

$$\frac{\partial}{\partial t} N(\mathbf{k},t) + D k^2 N(\mathbf{k},t) = 0, \quad (6)$$

where $k^2 = \mathbf{k}\cdot\mathbf{k}$. The general solution of this ordinary differential equation is

$$N(\mathbf{k},t) = C(\mathbf{k}) \exp(-Dk^2 t), \quad (7)$$

where $C(\mathbf{k})$ is the Fourier transform of the initial distribution of color centers $N(\mathbf{r},0)$:

$$C(\mathbf{k}) = \frac{1}{(2\pi)^n} \int_{-\infty}^{+\infty} N(\mathbf{r},0) \exp(i\mathbf{k}\cdot\mathbf{r}) d^n r. \quad (8)$$

Performing the inverse Fourier transform of $N(\mathbf{k},t)$, we obtain

$$N(\mathbf{r},t) = \int_{-\infty}^{+\infty} \left(\frac{1}{(2\pi)^n} \int_{-\infty}^{+\infty} N(\mathbf{r}',0) \exp(i\mathbf{k}\cdot\mathbf{r}') d^n r' \right) \times \exp(-Dk^2 t) \exp(-i\mathbf{k}\cdot\mathbf{r}) d^n k. \quad (9)$$

Rearranging the order of integration,

$$N(\mathbf{r},t) = \frac{1}{(2\pi)^n} \int_{-\infty}^{+\infty} N(\mathbf{r}',0) \left(\int_{-\infty}^{+\infty} (-Dk^2 t) \times \exp[-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')] d^n k \right) d^n r'. \quad (10)$$

The Fourier transform of $\exp(-Dk^2 t)$ is given in Ref. 4 as

$$\frac{1}{(2\pi)^n} \int_{-\infty}^{+\infty} \exp(-Dk^2 t) \exp[-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')] d^n k = \frac{1}{(2\pi)^n} \left(\frac{\pi}{Dt} \right)^{n/2} \exp\left(-\frac{(\mathbf{r}-\mathbf{r}')^2}{4Dt}\right).$$

Hence

$$N(\mathbf{r},t) = \left(\frac{1}{4\pi Dt} \right)^{n/2} \int_{-\infty}^{+\infty} \exp\left(-\frac{(\mathbf{r}-\mathbf{r}')^2}{4Dt}\right) N(\mathbf{r}',0) d^n r'. \quad (11)$$

Since we have cylindrical symmetry and the diffusion occurs in the radial direction, $n = 2$ and Eq. (11) can be reduced using Eq. (3) to

$$N(r,t) = \frac{1}{4\pi Dt} \int_0^{2\pi} d\theta \int_0^\infty r' dr' \exp\left(-\frac{(r-r')^2}{4Dt}\right) \times N_0 \exp\left(-\frac{r'^2}{(\Delta w)^2}\right). \quad (12)$$

Performing the integration over θ and r , we obtain

$$N(r,t) = \frac{N_0}{1 + [4D/(\Delta w)^2]} \exp\left(\frac{-r^2}{(\Delta w)^2 + 4Dt}\right). \quad (13)$$

Note that the solution has a Gaussian profile which broadens in time.

The total number of carriers in an element of sample length dz is given by $\eta(t)dz$ where

$$\eta(t) = \int_0^{2\pi} d\theta \int_0^\infty r dr N(r,t).$$

If we weight this function with the Gaussian irradiance distribution, we obtain the effective number of color centers per unit length encountered by the beam in the irradiated region $M(t)$:

$$M(t) = \int_0^{2\pi} d\theta \int_0^\infty r dr N(r,t) \exp\left(\frac{-r^2}{(\Delta w)^2}\right). \quad (14)$$

Substituting for $N(r,t)$ from Eq. (13) and performing the integration, the expression for $M(t)$ can be found as

$$M(t) = \frac{\pi}{2} N_0 \frac{(\Delta w)^4}{(\Delta w)^2 + 2Dt}. \quad (15)$$

The number of carriers at $t = 0$ is

$$M(0) = \frac{\pi}{2} N_0 \pi (\Delta w)^2. \quad (16)$$

Rewriting Eq. (15) in terms of the initial carrier density ($t = 0$), we have

$$\frac{M(0)}{M(t)} = 1 + \frac{2D}{(\Delta w)^2} t, \quad (17)$$

which indicates that the ratio of the initial number of color centers per unit length $M(0)$ to $M(t)$ is a linear function of t with slope $2D/(\Delta w)^2$.

This ratio can be determined by monitoring the transmission of the sample as a function of time, given the transmission $T(t)$ of the sample:

$$T(t) = T' \exp[-\alpha M(t)L], \quad (18)$$

where α is the linear absorption coefficient, T' shows the linear transmission of the unirradiated sample, and L is the thickness of the sample. Thus $M(t)$ can be found from

$$\alpha M(t) = -\frac{1}{L} \ln\left(\frac{T(t)}{T'}\right), \quad (19)$$

where $M(t)$ denotes the number of color centers encountered by the beam at time t (i.e., for a given pulse at time t).

In the process of coloring the sample as is presented in Fig. 2, the saturation effect on the formation of the color centers was observed and the transmission remained constant at $T(0)$. Thus the initial number density of centers can be found from

$$\alpha M(0) = -\frac{1}{L} \ln\left(\frac{T(0)}{T'}\right). \quad (20)$$

Using Eqs. (23) and (24), $M(0)/M(t)$ can be written as

$$\frac{M(0)}{M(t)} = \frac{\ln\left(\frac{T(0)}{T'}\right)}{\ln\left(\frac{T(t)}{T'}\right)} = 1 + \frac{2D}{(\Delta w)^2} t. \quad (21)$$

The experimental results of $M(0)/M(t)$ as a function of t are presented in Fig. 3. The solid line presents the theoretical fit [Eq. (25)] with the extracted diffusion constant ($D = 3.4 \times 10^{-8}$ cm²/s).

In order for a color center to diffuse at room tempera-

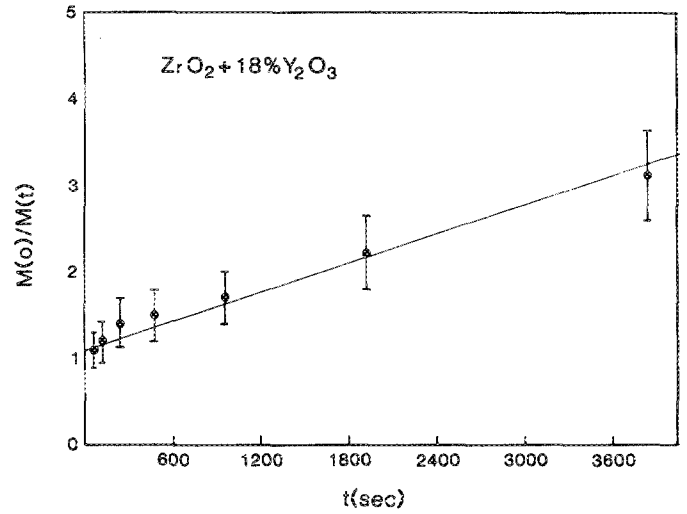


FIG. 3. The ratio of induced color center density at time $t = 0$ to the density at time t as a function of t .

ture, it must have sufficient thermal energy to overcome the potential energy barrier presented by its neighbors. This activation energy E is related to the diffusion coefficient D which is generally described by⁵

$$D = D_0 \exp\left(-\frac{E}{kT}\right), \quad (22)$$

where D_0 is a temperature independent factor. Using the values of $D_0 = 1.3$ cm²/s (Ref. 6) and $T = 300$ K, one can obtain the activation energy of approximately 0.5 eV given the diffusion coefficient obtained by our model. This activation energy is the right order of magnitude for migration of anion vacancies as obtained in Ref. 7 for cubic zirconia.

To conclude, we have shown that the density of color centers generated by two-photon absorption at 532 nm in stabilized cubic zirconia (ZrO_2 , 18% Y_2O_3) decreases due to slow diffusion to the surrounding medium with a diffusion coefficient of $D = 3.4 \times 10^{-8}$ cm²/s at room temperature. This can be seen by the fit of experimental results with the diffusion model in Fig. 3.

ACKNOWLEDGMENTS

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