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Nonlinear Coloration Effects in Transition-Metal-Doped $SrTiO_3$ Crystals*

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Nonlinear coloration effects were discovered in doped crystals of $SrTiO_3$ and were attributed to two-photon excited electron-hole pairs that subsequently become trapped by color centers. An induced absorption coefficient of 2.6 cm^{-1} was measured at 6328 Å in samples doped with Ni and Mo when exposed to ruby laser pulses with peak intensities of 160 MW/cm^2 and about 15-nsec duration. Calculated and previously reported experimental values of the two-photon absorption coefficient for $SrTiO_3$ are in good agreement with these results. A model which assumes a coloration rate proportional to the square of the intensity and a simultaneous first-order bleaching process was found to give a good fit to the experimental data on coloration versus intensity.

INTRODUCTION

CHARGE-TRANSFER processes induced by conventional light sources and leading to coloration changes in transition-metal-doped $SrTiO_3$ crystals have been described recently by Faughnan and Kiss.[1] This paper reports on nonlinear coloration effects that were observed in these crystals and which were attributed to two-photon excitation of electron-hole pairs.[2] This interpretation was in agreement with the observation of transient free-carrier absorption and photoconductivity in undoped crystals of $SrTiO_3$ induced by Q-switched ruby laser pulses.[3]

Strontium titanate crystals are of the cubic perovskite structure with an oxygen $2p$ valence band and a titanium $3d$ conduction band.[4] The pure crystals are transparent insulators with an optical band gap of $\sim$3.2 ev. The absorption properties of the undoped crystals were studied by Noland[5] and Levin *et al.*[6] More recent studies of the optical properties were carried out by several researchers.[7] The band structure of the material was calculated by Kahn and Leyendecker,[4] who predicted that the lowest conduction band should have minima along the $\langle 100 \rangle$ axes at the edges of the Brillouin zone. The crystals can be rendered semiconducting by oxidation or doping[8] and the free-carrier absorption of such samples was studied by Baers.[9] The effects of doping and heat treatments on the coloration of the materials was first studied by Gandy[10] and optically induced reversible color changes were noted in powders of the material by McMaverin and Ogle.[11]

The samples that were used for the nonlinear experiments that are described here were doped with iron and molybdenum or nickel and molybdenum. They are characterized by a ground (clear) state in which they appear nearly transparent in the visible, and a colored (dark) state which shows a broad absorption region in the visible, with broad peaks at different wavelengths depending on the dopant. The coloration changes are caused by the transfer of electrons from one type of impurity ion to another (or to a different localized center). The details of the optical absorption spectrum in the two states and various aspects of the switching behavior are described elsewhere.[1,2]

The absorption curves for two typical samples, one doped with Fe and Mo, the other with Ni and Mo, are

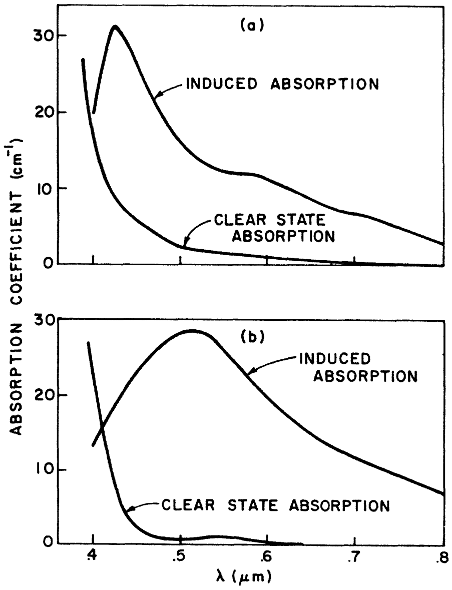

FIG. 1. Clear-state absorption versus wavelength and induced absorption for sample doped with (a) 0.03% Fe and 0.03% Mo and for sample doped with (b) 0.02% Ni and 0.15% Mo. Tr °300 K.

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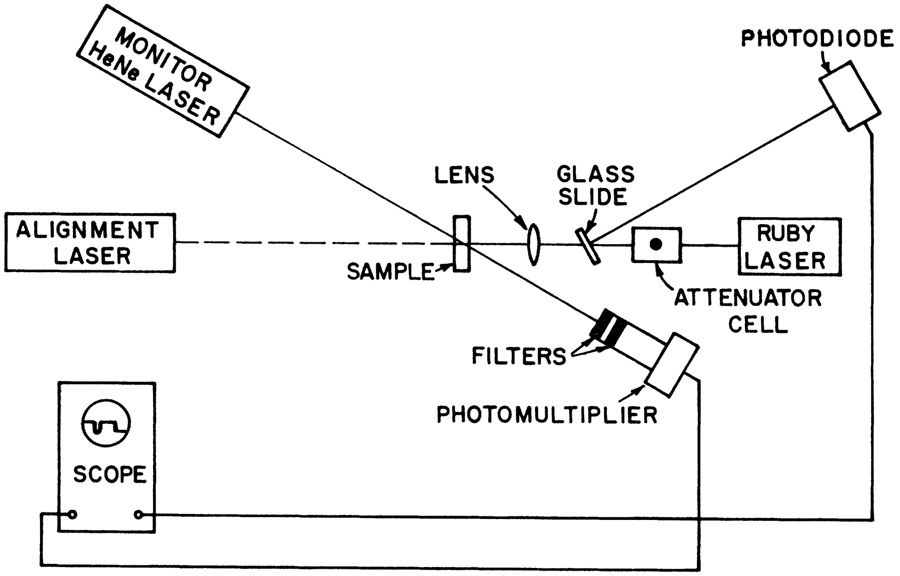

FIG. 2. Schematic of experimental setup.

given in Figs. 1(a) and 1(b), respectively. The induced part of the absorption coefficient is the difference between the clear-state and the dark-state absorption coefficients. The level of coloration induced by conventional sources varies with the wavelength of the light. To switch from the clear to the dark state one must expose these samples to radiation between ~3800 and 4700 Å; radiation of wavelengths longer than ~5000 Å, at normal intensity levels, will return the sample to the clear state. The fact that many of the samples are essentially transparent at 6943 Å when in the clear state made this material an attractive candidate for nonlinear coloration studies with Q-switched ruby laser pulses. It was discovered that significant darkening could be induced in all the samples at the intensity levels attainable from focused Q-switched pulses, while the same lasers when not Q-switched would effectively bleach the samples to the clear state. These results suggested that nonlinear absorption may be responsible for the observed coloration, with the terms proportional to the square of the intensity dominating over the linear bleaching processes at the higher intensities. Possible alternate models, such as time-dependent effects due to intermediate trapping, did not seem to play an important role in the behavior of these samples. The results that are presented here further suggested that the nonlinear process in question is two-photon excitation of electron-hole pairs followed by trapping of these carriers by the color centers.

EXPERIMENTAL PROCEDURE

The samples used in this work were cut from boules of doped $SrTiO_3$ crystals purchased from the National Lead Co. The boules were grown by the flame fusion technique with the dopant being added to the furnace feed material in the percentage weights given as nominal concentrations. The samples varied in thickness between 1 and 3 mm and the faces were polished in several steps; the final polishing used 0.3 (Linde A) powder in distilled water as the agent.

The experimental setup used for these tests is shown in Fig. 2. The ruby laser consisted of a $\frac{1}{4}\times 3$ in.-ruby rod; it was passively Q-switched by a saturable dye of $10^{-5}\%$ vanadil pthalocyanine solution in DMF. The laser produced pulses of up to 300 mJ with half-widths between 10 and 20 nsec. The induced absorption was monitored by a He-Ne laser whose beam was made to traverse the sample at the center of the area covered by the ruby laser output. The ruby laser pulse was attenuated by passing it through an optical cell containing a variable concentration solution of $CuSO_4$ in distilled water; it was then measured by reflecting a portion of the pulse to a photodiode shown in back of the ruby laser. The output of the photodiode was displayed on a Tektronix 581 oscilloscope; it was calibrated to read peak intensity at the center of the ruby laser pulse by measuring the energy through a 1-mm-diam aperture aligned with the monitor source (at the position of the sample). The energy was measured using a Westinghouse Model RN-1 radiometer and the calibration was carried out with the attenuator cell and focusing lens in place. The transmitted power of the He-Ne probe beam was monitored by a photomultiplier whose output was delayed by means of about 100 ft of 50-Ω coaxial cable (RG-8/U) and displayed on the oscilloscope. The outputs from the photomultiplier and from the photodiode were added algebraically and displayed on the same trace of the oscilloscope, the time delay serving to separate the two signals. All the tests were done at room temperature.

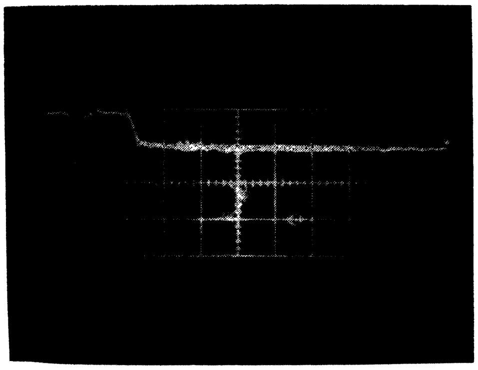

FIG. 3. Oscilloscope trace showing ruby laser pulse followed by drop in intensity of He-Ne laser probe beam. Time scale: 0.1 μsec/div.

EXPERIMENTAL RESULTS

Figure 3 shows a typical oscilloscope trace with the ruby laser pulse followed by a step change in transmitted intensity of the He-Ne probe beam. The step corresponds to a drop in transmission of about 25% in a 1-mm-thick sample of $SrTiO_3$ doped with Ni and Mo. The delay seen separating the pulse and the response corresponds to that inserted by the delay line. The pulse widths and rise time shown in this figure are limited by the oscilloscope preamplifier. Careful measurements of delay and rise time carried out with a faster preamplifier showed that the increase in optical density coincides with the ruby laser pulse and there are no measurable delays or significant rise-time limitations that one would associate with intermediate trapping.

The dependence of the induced absorption on the intensity of the ruby laser pulse was investigated by changing the concentration of the $CuSO_4$ solution used to attenuate the laser output. This was accomplished by adding a few drops of saturated solution to the cell which initially contained only distilled water. In this manner the critical alignment of the components was not disturbed, and the ruby laser was operated at the same pumping energy for each pulse. The results of these measurements for a 0.13-cm-thick $SrTiO_3$ crystal doped with 0.03% Fe and 0.03% Mo are shown in Fig. 4(a). They exhibit an initial parabolic dependence of the induced absorption on peak intensity of the pulse, followed by a more linear region at the higher levels of induced absorption. Figure 4(b) shows the induced absorption for a 0.1-cm sample doped with 0.02% Ni, 0.15% Mo which, at the lower range of intensities, behaves in a similar manner to the Fe-Mo doped sample, the larger value of absorption being attributable mainly to the higher absorption cross section of the color centers at the probe wavelength (6328 Å). At the higher levels of induced absorption, however, the coloration versus intensity becomes less than linear.

The level of induced absorption could not be correlated to the clear-state absorption coefficient of the crystals at the ruby laser wavelength (6943 Å).

DISCUSSION AND CONCLUSIONS

It was pointed out earlier that the fact that the same wavelength could either bleach or color the sample, depending on the intensity level, could be due to intermediate states or traps. Many of the samples exhibit sufficient absorption at 6943 Å to cause the observed coloration; that this does not occur at low levels of intensity could be due to the strong reverse bleaching process at this wavelength. If the intermediate traps had little absorption at this wavelength, and thermal lifetimes longer than the duration of the Q-switched pulses, they could account for this peculiar behavior. The absence of observable delays or slow rise times for the induced absorption (measured with resolution down to ~2 nsec), would argue against this possibility. Thus, it is reasonable to assume that the coloring and bleaching processes occur simultaneously during the pulse, and that the resultant coloration is an equilibrium level between these two opposing processes. Measurements carried out on samples that had been partially colored by a cw source showed that, when the initial level of coloration was near that induced by a given intensity pulse, the ruby laser pulse would have negligible effect on the optical density of the sample. This lends further support for disregarding intermediate trapping, since such an effect should lead to nearly complete initial bleaching followed by a net increase in optical density at the termination of the pulse.

Assuming that the above model is correct and that the fraction of the centers being switched is small, the switching process should be governed by an equation of the form

$$dn/dt = C_2 I^2 - C_1 n I\,, \tag{1}$$

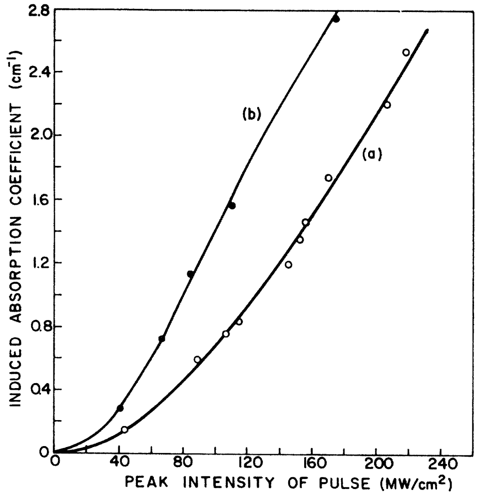

FIG. 4. Induced absorption versus peak intensity of ruby laser pulse for (a) $SrTiO_3$: Fe, Mo and (b) $SrTiO_3$: Ni, Mo.

where n is the number of color centers switched, C_1 and C_2 are constants, and I is the intensity of the light.

If one assumes that the sample is thin enough that the intensity of the pulse is not affected by the induced coloration, this equation would predict that a square pulse of light of duration t_0 would result in a concentration of switched center $n(t_0)$ given by

$$n(t_0) = (C_2/C_1)I(1-e^{-C_1 I t_0}). \qquad (2)$$

For very small and large values of the exponent, this expression could be approximated by

$$\begin{aligned} n(t_0) &\approx C_2 t_0 I^2 \quad \text{for} \quad C_1 I t_0 \ll 1, \\ &\approx (C_2/C_1) I \quad \text{for} \quad C_1 I t_0 \gg 1. \end{aligned}$$

Thus, for a constant pulse width, the above model would predict a concentration of switched centers that increases first as the square of the intensity but tends towards a linear dependence as this concentration increases and bleaching becomes significant. Furthermore, if one takes into account the decrease in the intensity of the light with increasing coloration, the rate would become less than linear at sufficiently high levels of induced absorption. This could be responsible for the less than linear behavior of the curve for the nickel-doped sample at higher intensities. The smooth curve shown for the Fe doped sample [Fig. 4(a)] was obtained using Eq. (2) with a value of C_2 chosen to match the initial curvature and C_1 was used as an adjustable parameter. The value of C_1 giving the best fit was within 30% of the number calculated using an independent measurement of the bleaching efficiency at 6943 Å.

The question as to what type of second-order absorption process is responsible for the results is difficult to answer purely on the basis of the data on the photochromic samples. Essentially all of these samples showed residual absorption at 6943 Å which could result in two-step excitation processes of sufficient magnitude to cause the effects. On the other hand, if this absorption was due to an impurity state close to the center of the ~3.2-eV band gap (which could act as an energy conserving intermediate state for two-photon absorption) one would expect considerable variations in the magnitude of the results from sample to sample. As was pointed out before, this was not seen experimentally to be the case. One could still argue that this process can occur via an "intrinsic" defect, whose concentration was independent of the doping (while the variation of the absorption was due to impurity states that did not contribute to this process). This is conceivable, although it is hard to visualize how such a defect could appear in about the same concentration nearly independently of the doping. Some evidence against this model is furnished by the experiments with pure samples,[2] where free carriers were generated by the nonlinear absorption. These samples showed absorption coefficients of less than 0.01 cm^{-1} at 6943 Å, which should have been too small to justify the magnitude of the results.

On the basis of these arguments, it was concluded that the most likely explanation of the nonlinear results is intrinsic two-photon excitation of electron-hole pairs which subsequently become trapped by the color centers.

The absorption coefficient for two-photon excitation of electron-hole pairs at the ruby laser wavelength had been estimated from experimental data to be[3]

$$\alpha_2 \approx 2.5 \times 10^{-10} I \quad \text{cm}^{-1},$$

where I is the ruby laser intensity in W/cm^2.

Theoretical estimates using approximate formulas for band-to-band two-photon absorption given by Mahan[12] give values of α_2 which are in reasonable agreement with the above ($\alpha_2 \sim 2 \times 10^{-10} I$). Simple calculations, based on experimental estimates of the absorption cross section of the color centers,[1] show that the minimum value of α_2 required to account for the observed coloration (assuming ideal quantum conversion efficiency) need only be about $1 \times 10^{-10} I$. Based on these estimates, it appears that the quantum conversion efficiency from electron-hole pairs to switched centers is of the order of unity (the above numbers would indicate about $\frac{1}{2}$ for this sample). This high quantum conversion efficiency implies that the color centers act as effective traps for the carriers, competing quite successfully with other recombination processes.

In concluding, one might point out that the nonlinear properties exhibited by these samples allow coloring and bleaching at the same wavelength, a feature that has many practical possibilities. At the same time, the nonlinear excitation process offers a good tool for the study of many bulk properties of the doped or intrinsic material at high carrier concentration levels. These concentrations could not be reached with conventional techniques of optical pumping.

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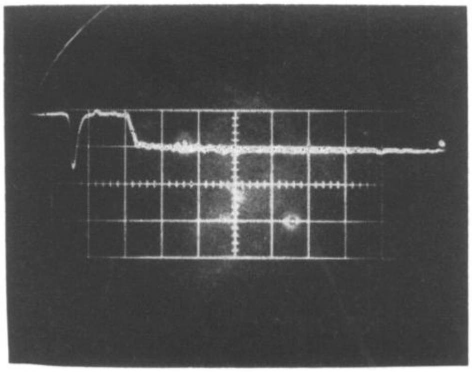

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