Enhancement of the nonlinear optical properties of fluorescin doped boric-acid glass through cooling

Wayne R. Tompkin, Michelle S. Malcuit, and Robert W. Boyd

We examine, both theoretically and experimentally, the temperature dependence of the nonlinear optical response of fluorescein doped boric-acid glass. The third-order nonlinear susceptibility is increased by an order of magnitude over its room temperature value to greater than 10 esu by cooling the sample to a temperature below 200 K. *Keywords:* nonlinear optical materials, organic materials, four wave mixing, saturable absorption.

I. Introduction

Organic dyes doped into solid hosts form a class of nonlinear optical materials that can be used for many applications involving low intensity light sources. Saturable absorption in organic molecules doped into solid matrices can be exploited to achieve very large optical nonlinearities.[1–13] In fact, studies[3,5,13] have shown that at room temperature fluorescein doped boric-acid glass has a saturation intensity as low as 15 mW cm^{-2} and a third-order nonlinear optical susceptibility $\chi^{(3)}$ larger than 1 esu. In this paper, we report the results of an investigation of the temperature dependence of the nonlinear optical response of fluorescein doped boric-acid glass. In particular, we have found that the nonlinear optical response can be enhanced dramatically by cooling the samples; for example, the third-order nonlinear optical susceptibility can be larger than 10 esu for samples that are cooled to sufficiently low temperatures. We have studied the temperature dependence of the third-order nonlinear susceptibility by measuring, as functions of temperature, the saturation intensity and the phase conjugate reflectivity.

II. Model of Temperature Dependence

The reason why the nonlinear optical response of fluorescein doped boric-acid glass is temperature dependent can be understood from a consideration of the energy level diagram illustrated in Fig. 1. Following

optical excitation from the singlet ground state, population can make an intersystem crossing from the exited singlet state into the lowest lying triplet state. In fluorescein doped boric-acid glass, the lowest-lying triplet state has an extremely long lifetime due to the absence of quenching mechanisms that are usually present for organic dyes in liquid solution. The principal relaxation route out of the lowest-lying triplet state at room temperature is thermally activated delayed fluorescence. By lowering the temperature of the sample, the rate of delayed fluorescence is decreased, leading to an increase in the lifetime of the triplet state. A saturable absorber can be characterized by a saturation intensity I_s which can be related to other optical properties by the formula $I_s = \hbar\omega/\sigma_o\tau$, where ω is the laser frequency, σ_o is the absorption cross section of the singlet ground state at the laser frequency, and τ is the effective lifetime for the return of population to the singlet ground state. Hence, as the lifetime of the triplet state increases with cooling, the saturation intensity decreases. Under the assumption that the absorption lineshape is Lorentzian, the nonlinear susceptibility can be expressed in terms of the unsaturated absorption coefficient at the laser frequency α_o, the unsaturated refractive index n_o, and the saturation intensity I_s as

$$\chi^{(3)} = \frac{n_o^2 c^2 \alpha_o}{24\pi^2 \omega I_s}(\delta - i) \tag{1}$$

where $\delta = (\omega - \omega_o)T_2$ is the normalized detuning of the laser frequency ω from the resonance frequency ω_o and T_2 is the dipole dephasing time. Thus, as the saturation intensity decreases with cooling, the nonlinear susceptibility increases.

We model fluorescein doped boric-acid glass as the four-level system shown in Fig. 1. A molecule in the ground state, level 0, absorbs light at a rate $R_o = \sigma_o I/\hbar\omega$; this process transfers the population to the excited
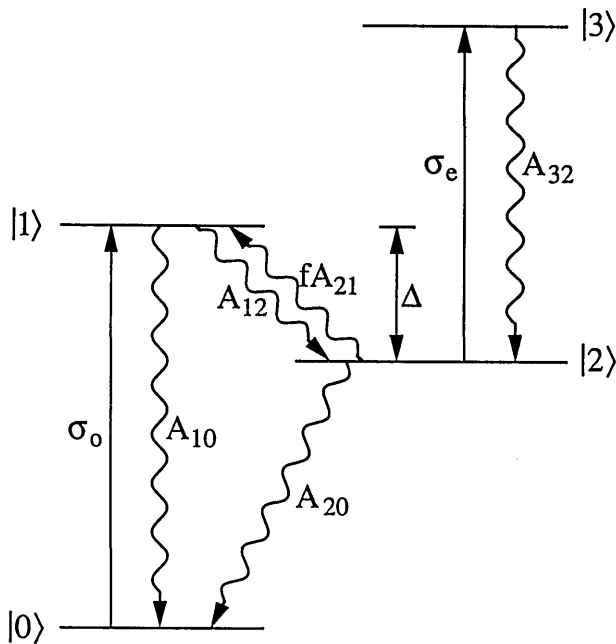
Fig. 1. Energy-level diagram showing the relevant optical interactions in fluorescein doped-boric-acid glass. Levels 0 and 1 represent singlet states, and levels 2 and 3 represent triplet states. Due to its long luminescent lifetime, the lowest lying triplet state, level 2, acts as a trap level. At room temperature, the principal relaxation route out of level 2 is delayed fluorescence; that is, thermally excited transfer from level 2 to level 1 is followed by fluorescence decay back to the ground state.

singlet state, level 1. The population of the excited singlet state can return to the ground state via fluorescence with transition rate A_{10} or can make an intersystem crossing to the lowest-lying triplet state, level 2. The transition probability per unit time for an intersystem crossing is A_{12}. The population in the lowest-lying triplet state can return to the singlet manifold either through the phosphorescence at a rate A_{20} or through thermally activated delayed fluorescence. We describe delayed fluorescence theoretically by assuming that the population in the lowest-lying triplet state is distributed among its vibrational sublevels in accordance with a Boltzmann distribution. We designate the energy separation of the lowest-lying triplet state and the first excited singlet state as Δ, and we assume that the population in the vibrational manifold having vibrational energy greater than Δ returns to the excited singlet state with a rate A_{21}. The rate of thermally activated delayed fluorescence is then given by[14] fA_{21} with $f = \exp(-\Delta/k_BT)$, where T is the temperature and k_B is the Boltzmann constant. It has been shown[15-17] that, for most fluorescence dyes, the rate A_{21} is of the same order of magnitude as A_{12}. The rate at which population is raised from level 2 to level 3 is equal to $R_e = \sigma_e I/\hbar\omega$, where σ_e is the cross section for triplet–triplet absorption. We assume that population raised to the higher lying triplet state quickly returns to the lowest-lying triplet state at a rate we call A_{32}. Thus, we assume that the transition between levels 2 and 3 cannot be saturated.

The rate equations for the fractional populations P_i of the energy levels i of Fig. 1 can be written in the following form:

$$\dot{P}_0 = R_o(P_1 - P_0) + A_{10}P_1 + A_{20}P_2,$$

$$\dot{P}_1 = -R_o(P_1 - P_0) - A_{10}P_1 - A_{12}P_1 + fA_{21}P_2,$$

$$\dot{P}_2 = A_{12}P_1 - A_{20}P_2 - fA_{21}P_2 + R_e(P_3 - P_2) + A_{32}P_3,$$

$$\dot{P}_3 = -R_e(P_3 - P_2) - A_{32}P_3 \qquad (2)$$

From the steady state solution to the above set of equations, we obtain the steady state populations P_i^{ss} given by

$$P_0^{ss} = \frac{(A_{10} + R_0)(fA_{21} + A_{20})/A_{12} + A_{20}}{(2R_0 + A_{10})(fA_{21} + A_{20})/A_{12} + (A_{20} + R_0) + R_0R_e/(R_e + A_{32})},$$

$$P_1^{ss} = [(fA_{21} + A_{20})/A_{12}]P_2^{ss},$$

$$P_2^{ss} = \frac{R_o}{[2R_o + A_{10}](fA_{21} + A_{20})/A_{12} + (A_{20} + R_o) + R_oR_e/(R_e + A_{32})},$$

$$P_3^{ss} = \frac{R_e}{R_e + A_{32}} P_2^{ss}. \qquad (3)$$

These solutions reduce to those of Hercher,[18] when delayed fluorescence is ignored (i.e., for $f = 0$).

For fluorescein doped boric-acid glass using low power, continuous wave excitation, the rates of pumping are much smaller than the rates of decay for the excited singlet state A_{10} and the excited triplet state A_{32}, that is, $R_0 \ll A_{10}$ and $R_e \ll A_{32}$. Under these conditions, excited states 1 and 3 contain almost no population, and the expression for the steady-state population of the lowest-lying triplet state (level 2) reduces to $P_2^{ss} = (R_o\tau)[1 + R_o\tau]^{-1}$, where

$$\tau = \left[\frac{A_{10}}{A_{12}}(fA_{21} + A_{20}) + A_{20}\right]^{-1} \qquad (4)$$

defines an effective lifetime, which gives the recovery time of the saturable absorber.[18] We note further that $R_o\tau$ can be identified as the saturation parameter I/I_s.

We have measured the values of the parameters f, R_o, R_e, A_{10}, A_{12}, A_{21}, and A_{20} for fluorescein doped boric-acid glass. The sample was excited by 30-ps pulses from a frequency-doubled Nd:YAG laser and the prompt fluorescence from the excited singlet state was measured with a photodiode placed behind a bandpass filter. The singlet decay time A_{10}^{-1} was found to be approximately 5 ns. Figure 2 compares the luminescent spectra for a sample that is cooled to 100 K with that of a sample at room temperature. The samples were illuminated by an argon-ion laser operating at 457 nm. From the emission spectra shown in Fig. 2, the separation of the fluorescent and the phosphorescent peaks is measured to be 77 nm, which corresponds to an energy separation Δ between the excited singlet state and the lowest-lying triplt state of approximately 0.4 eV. We substitute this value of the energy separation Δ into the expression for the factor f and find that $f = \exp(-\Delta/k_BT)$ is approximately equal to $\exp(-4500/T)$, where T is the temperature in degrees kelvin.
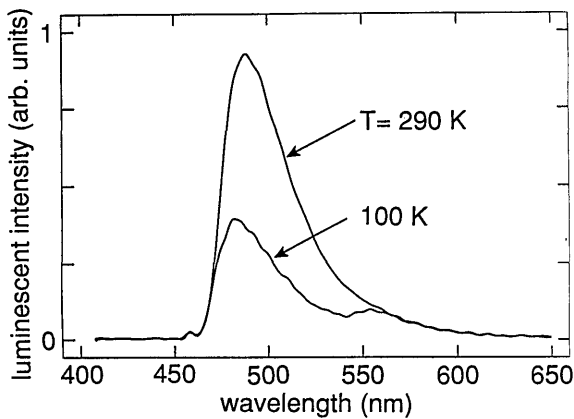
Fig. 2. Luminescence spectra of fluorescein doped boric-acid glass at 100 and 290 K. The contributions due to phosphorescence and to fluorescence are separated at 100 K. The sample was excited by an argon ion laser operating at 457.9 nm.

To determine the phosphorescent decay time A_{20}^{-1}, the light beam illuminating a sample cooled to 100 K was cut off abruptly and the decay of a 20-nm wide portion of the phosphorescent emission centered at 560 nm was measured using a photodetector. The phosphorescence was observed to decay exponentially with a decay time A_{20}^{-1} of 2.5 s.

The rate A_{12} was found from the emission spectrum at low temperatures. At 100 K, the ratio of the integrated area of the fluorescent peak to the integrated area of the phosphorescent peak was ~4.75. This ratio should be equal to the ratio of P_1^{ss} to $P_2^{ss}A_{20}$, which, by Eq. (3), implies the following:

$$\frac{A_{10}}{A_{20}A_{12}}(fA_{21} + A_{20}) = 4.75. \tag{5}$$

We can solve Eq. (5) for A_{12} and find $A_{12} = 4.2 \times 10^7 \text{ s}^{-1}$.

We have also verified the assumption made above that the pumping rate R_o is much smaller than the decay rate A_{10} and that R_e is much smaller than A_{32}. We substitute the previously reported values[13] $\tau = 0.1$ s and $I_s = 15$ mW cm^{-2}, along with the largest values for the intensity I reached in this experiment (1 W cm^{-2}), into the expression $R_o = I/I_s\tau$; we find the maximum value of R_o is approximately equal to 700 s^{-1}, which is much smaller than the fluorescent decay rate $A_{10} = 2.0 \times 10^8 \text{ s}^{-1}$. It has been shown[19] that the absorption cross section of the lowest-lying triplet state σ_e is smaller than the singlet ground state absorption cross section σ_o; therefore, since R_e is smaller than 700 s^{-1}, R_e is much smaller than the triplet decay rate A_{32} which is believed[8,15] to be of the order of 10^{12} s^{-1}.

Theoretical predictions for the dependence of the saturation intensity on the temperature can be found from Eq. (4) using the relation that $I_s = \hbar\omega/\sigma_o\tau$. Since the saturation intensity is inversely proportional to the effective lifetime τ and since we have found that σ_o is independent of temperature, the ratio of the saturation intensity at room temperature to the value of the

saturation intensity at temperature T is equal to the ratio:

$$\frac{I_s(290 \text{ K})}{I_s(T)} = \frac{\tau(T)}{\tau(290 \text{ K})} = \frac{(A_{10}/A_{12})(f(290 \text{ K})A_{21} + A_{20}) + A_{20}}{(A_{10}/A_{12})(f(T)A_{21} + A_{20}) + A_{20}}, \tag{6a}$$

where $\tau(T)$ and $\tau(290 \text{ K})$ are effective lifetimes as defined by Eq. (4) at temperature T and at room temperature, respectively. We have measured the ratio $\tau(T)/\tau(290 \text{ K})$ at several temperatures and we have substituted these measured values into the above expression, along with the values of the constants. We find that A_{21} is approximately 3×10^7 s^{-1}. We can then introduce the measured values into Eq. (6a) and find that numerically

$$\frac{I_s(290 \text{ K})}{I_s(T)} = \frac{\tau(T)}{\tau(290 \text{ K})} = [0.08 + (5 \times 10^6) \exp(-4500 \text{ K}/T)]^{-1}. \tag{6b}$$

III. Saturated Absorption

The temperature dependence of the nonlinear susceptibility was studied experimentally through measurements of the saturated absorption of a sample of fluorescein doped boric-acid glass. The incident pump light can be absorbed by molecules either in the ground state or in the lowest lying triplet state. The singlet ground state absorption cross section σ_o has a value[19] of approximately 3×10^{-16} cm^2 at a wavelength of 457.9 nm; the absorption cross section of the lowest-lying triplet state σ_e has a value of approximately 1.5×10^{-16} cm^2. The total absorption coefficient α_{TOT}^{ss} in steady state for a sample containing N molecules per unit volume is the sum of the absorption coefficient for the singlet—singlet transition $\alpha_o^{ss} = N\sigma_o P_o^{ss}$ and the absorption coefficient for the triplet—triplet transition $\alpha_e^{ss} = N\sigma_e P_2^{ss}$.

$$\alpha_{TOT}^{ss} = N(\sigma_o P_o^{ss} + \sigma_e P_2^{ss}) \tag{7a}$$

$$= (N\sigma_e) + \frac{N}{1 + I/I_s}(\sigma_o - \sigma_e), \tag{7b}$$

where in obtaining the second form we used the results $P_2^{ss} = (I/I_s)[1 + I/I_s]^{-1}$ and $P_o^{ss} = 1 - P_2^{ss}$. The first term on the right-hand side of Eq. (7b) gives the unsaturable part of the absorption coefficient, which we call α_u^{ss}, and the second term gives the saturable part of the absorption coefficient, which we call α_s^{ss}. We see that a consequence of our assumption that the triplet state absorption cannot be saturated is that the transmission of the sample approaches the value $\exp(-\alpha_u^{ss}\ell)$ for very large laser intensities, where ℓ is the length of the nonlinear optical material. Since the saturation intensity I_s is temperature dependent, the absorption coefficient α_{TOT}^{ss} is temperature dependent. In the above, we have ignored the polarization dependence of the absorption[13] to simplify the analysis.

We have studied the temperature dependence of the saturation intensity by measuring the transmission of a sample as a function of intensity for a variety of temperatures; typical data are shown in Fig. 3. The experiment was performed using the 457.9-nm output of an argon-ion laser. To vary the intensity of the laser
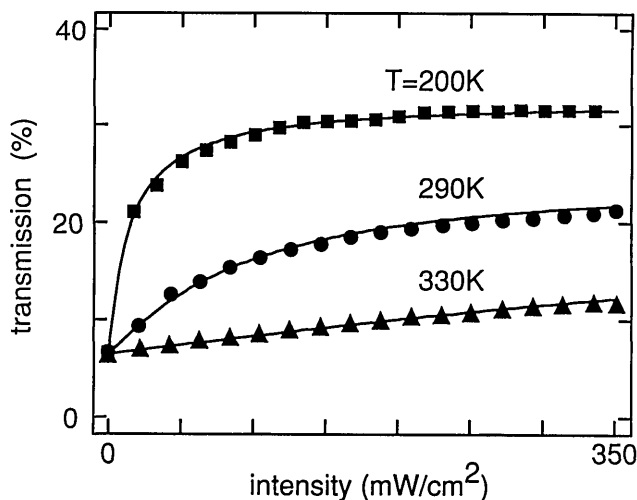
Fig. 3. Transmission of fluorescein doped boric-acid glass as a function of laser intensity at wavelength 457.9 nm for three temperatures. The data points are the measured values and the solid lines are theoretical predictions using the following parameters: $\alpha_0\ell = 2.67, \alpha_e\ell = 1.14, I_s(200\text{ K}) = 2\text{ mW/cm}^2, I_s(290\text{ K}) = 23\text{ mW/cm}^2$, and $I_s(330\text{ K}) = 160\text{ mW/cm}^2$.

beam, the laser beam was passed through a Pockels cell followed by a linear polarizer. The solid lines shown in Fig. 3 represent the transmittance predicted theoretically, including the effects of propagation, excited state absorption and site to site variations in the electric field. The predicted transmittance is found by numerically integrating the differential equation for the intensity I:

$$\frac{dI}{dz} = -\alpha_{\text{TOT}}^{ss}I,\qquad (8)$$

where α_{TOT}^{ss} was determined by averaging predictions of Eq. (7) over a spread of energy separations Δ with the distribution being described by a Gaussian whose standard deviation is 40% of the mean. It has been shown previously that site to site variations in the local fields that the molecules experience[20,21] cause a variation in the energy of the lowest-lying triplet state and, hence, to a spread in the decay times.[19,22,23] It is easy to understand the origin of this effect from Fig. 1; the rate of thermally activated delayed fluorescence depends very sensitively on the energy separation between the lowest-lying triplet and the excited singlet states, and any site to site variations in the local fields that the molecules experience will change the energy separation.

We see from Fig. 3 that the saturation intensity decreases as the temperature is lowered, as expected. We determine the saturation intensity from the best fit of theory to the data and we find the saturation intensity at room temperature to be 23 mW cm^{-2}. The value of the third-order nonlinear susceptibility $\chi^{(3)}$ corresponding to this saturation intensity is approximately $(3 - 3i)$ esu as calculated using Eq. (1), assuming that $n_0 = 1.5, \alpha_0\ell = 2.76, \ell = 75 \pm 20 \mu$m, $\lambda = 457.9$ nm and $\delta = 1$. The detuning from line center δ and the small-signal, single-pass absorption $\alpha_0\ell$ at the laser

wavelength were found from the measurement of the wavelength dependence of the small-signal absorption. The saturation intensity at 200 K was lower than the room temperature value by a factor of 11 and at 327 K it was larger than the room temperature value by a factor of 6.9. These experimental results agree fairly well with the predicted values for these ratios which are 12 and 5.5, respectively, as calculated from Eq. (6b).

IV. Optical Phase Conjugation

The nonlinar susceptibility of fluorescein doped boric-acid glass was also determined by measuring the phase conjugate reflectivity using the standard geometry of degenerate four wave mixing (DFWM) with counterpropagating pump beams. Our experimental results were compared to theoretical predictions of the phase conjugate reflectvity which were obtained by including the effects of excited state absorption in the theory of Abrams and Lind.[24] We assume that the absorption coefficient is given by Eq. (7) and we perform a derivation similar to that described by Abrams and Lind. We find that the phase conjugate reflectivity is given by[13]

$$R = \frac{|\kappa \sin(\omega\ell)|^2}{|\omega \cos(\omega\ell) + (\alpha_u^{ss} + \gamma) \sin(\omega\ell)|^2},\qquad (9)$$

where

$$\omega = \sqrt{|\kappa|^2 - (\alpha_u^{ss} + \gamma)^2},\qquad (10a)$$

$$\gamma = N(\sigma_o - \sigma_e)\frac{1 + 2I/I_s}{(1 + \delta^2)(1 + 4I/I_s)^{3/2}},\qquad (10b)$$

$$\kappa^* = iN(\sigma_o - \sigma_e)\frac{(1 - i\delta)}{(1 + \delta^2)}\frac{2I/I_s}{(1 + 4I/I_s)^{3/2}},\qquad (10c)$$

and where ℓ is the length of the nonlinear medium. Since the saturation intensity decreases as the temperature is lowered, the phase conjugate reflectivity peaks at smaller intensities for lower temperatures. Thus, to achieve high phase conjugate reflectivities with weak pump beams, it is advantageous to cool the material sample.

Experiments on DFWM were performed to measure the phase conjugate reflectivity as a function of intensity. An argon-ion laser operating at a wavelength of 457.9 nm was used to produce counterpropagating pump beams of equal intensity. The probe beam had an intensity equal to 5% of that of one of the pump beams and made an angle of less than 10° with the forward-going pump. The sample of fluorescein doped boric-acid glass used in this experiment had a small-signal, single-pass absorption $\alpha_0\ell = 2.76$ at 457.9 nm and a thickness of 75 $\pm$ 20 μm.

We measured the phase conjugate reflectivity as a function of intensity for various temperatures and then determined the saturation intensity of the sample at each temperature from the best fit of theory to the measured curves of reflectivity vs intensity. The theoretical fit of the data was found using Eq. (9) along with the assumption that there is a Gaussian spread of
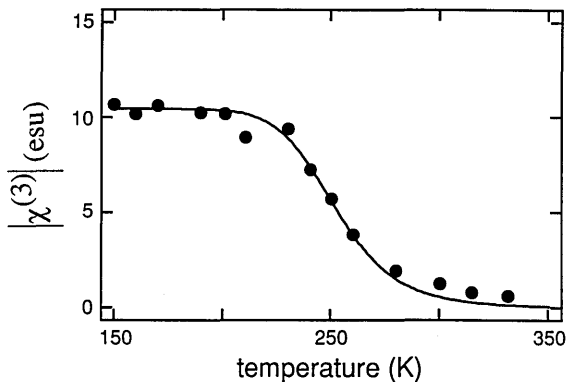
Fig. 4. Modulus of the complex third-order nonlinear susceptibility $|\chi^{(3)}|$ plotted as a function of temperature. The data points are the measured values as determined by phase conjugation experiments at 457.9 nm, and the solid line is a theoretical prediction using Eq. (6b) with $|\chi^{(3)}(290\,\text{K})| = 1.4$ esu. In these experiments, the laser intensity was kept below the saturation intensity.

saturation intensities having a width that is 40% of the mean. We used Eq. (1) to calculate the third-order susceptibility $\chi^{(3)}$ using our measured value of the saturation intensity I_s and the values $n_o = 1.5$, $\alpha_o = 370$ cm^{-1}, $\lambda = 457.9$ nm, and $\delta = 1.0$. A plot of the modulus of the nonlinear susceptibility $|\chi^{(3)}|$ as a function of temperature is shown in Fig. 4; the circles in the figure show the measured values of $\chi^{(3)}$. Since the nonlinear susceptibility is directly proportional to the response time, the value of the nonlinear susceptibility $\chi^{(3)}(T)$ at temperature T is related to its value at room temperature $\chi^{(3)}(290\,\text{K})$ by the factor $\tau(T)/\tau(290\,\text{K})$. The solid curve in Fig. 4 shows the predictions of Eq. (6b) with $|\chi^{(3)}(290\,\text{K})| = 1.4$ esu. We see that by cooling the sample we have realized an enhancement of the nonlinear susceptibility over its room temperature value by about an order of magnitude and that the modulus of the third-order nonlinear optical susceptibility $|\chi^{(3)}|$ was ~11 esu when the sample was cooled below 200 K. The order of magnitude increase in $|\chi^{(3)}|$ agrees fairly well with the value 11 measured by the technique described in the previous section and the theoretical prediction of 12.

V. Conclusions

We have examined the temperature dependence of the nonlinear optical response due to saturated absorption for fluorescein doped boric-acid glass. It was found that one could effectively freeze out the process of delayed fluorescence, which is the principal decay mechanism for fluorescein doped boric-acid glass at room temperature, to lengthen the response time of the material and thereby lower the saturation intensity. Theory predicts that, by cooling the sample, the nonlinear susceptibility $\chi^{(3)}$ can be increased by more than an order of magnitude over its room temperature value. The results agree well with theory, and the nonlinear susceptibility was greater than 10 esu when the sample of fluorescein doped boric-acid glass was cooled to sufficiently low temperatures.

References

1. T. A. Shankoff, "Recording Holograms in Luminescent Materials," Appl. Opt. 8, 2282–2284 (1969).
2. Y. Silberberg and I. Bar-Joseph, "Low Power Phase Conjugation in Thin Films of Saturable Absorbers," Opt. Commun. 39, 265–268 (1981); "Transient Effects in Degenerate Four-Wave Mixing in Saturable Absorbers," IEEE J. Quantum Electron. QE-17, 1967–1970 (1981).
3. T. Todorov, L. Nikolova, N. Tomova, and V. Dragostina, "Photochromism and Dynamic Holographic Recording in a Rigid Solution of Fluorescein," Opt. Quantum Electron. 13, 209–215 (1981).
4. I. Bar-Joseph and Y. Silberberg, "Real-time Holography Through Triplet State Absorption in Organic Dyes," Opt. Commun. 41, 455–458 (1982).
5. M. A. Kramer, W. R. Tompkin, and R. W. Boyd, "Nonlinear Optical Properties of Fluorescein in Boric-Acid Glass," J. Lumin. 31/32, 789–791 (1984).
6. H. Fugiwara and K. Nakagawa, "Phase Conjugation in Fluorescein Film by Degenerate Four Wave Mixing," Opt. Commun. 55, 386–390 (1985); "Transient Phase Conjugation by Degenerate Four-Wave Mixing in Saturable Dyes," J. Opt. Soc. Am. B 4, 121–128 (1987).
7. W. R. Tompkin, R. W. Boyd, D. W. Hall, and P. A. Tick, "Nonlinear-Optical Properties of Lead-Tin Fluorophosphate Glass Containing Acridine Dyes," J. Opt. Soc. Am. B 4, 1030–1034 (1987).
8. M. Montecchi, M. Settembre and M. Romagnoli, "Optically Induced Birefringence and Dichroism in Rigidly Held Dye Molecules," J. Opt. Soc. Am. B 5, 2357–2362 (1988).
9. S. Speiser, V. H. Houlding and J. T. Yardley, "Nonlinear Optical Properties of Organic Dye Dimer-Monomer Systems," Appl. Phys. B 45, 237–243 (1988).
10. S. A. Boothroyd, J. Chrostowski and M. S. O'Sullivan, "Two-Wave Mixing by Phase and Absorption Gratings in Saturable Absorbers," J. Opt. Soc. Am. B 6, 766–771 (1989).
11. S. A. Boothroyd, J. Chrostowski and M. S. O'Sullivan, "Determination of the Phase of the Complex Nonlinear Refractive Index by Transient Two-Wave Mixing in Saturable Absorbers," Opt. Lett. 14, 945–948 (1989).
12. G. R. Kumar, B. P. Singh, and K. K. Sharma, "Optical Phase Conjugation in Rhodamine-6G Doped Boric Acid Glass," Opt. Commun. 73, 81–84 (1989).
13. M. A. Kramer, W. R. Tompkin, and R. W. Boyd, "Nonlinear-Optical Interactions in Fluorescein-Doped Boric Acid Glass," Phys. Rev. A 34, 2026–2031 (1986).
14. A. Jablonski, "Über den mechanismus der Photolumineszenz von Farbstoffphosphoren," Z. Physik 94, 38–46 (1935).
15. C. A. Parker, Photoluminescence of Solutions (Elsevier, Amsterdam, 1968), p. 69.
16. G. A. Ketsle, L. V. Levshin, and Yu. A Soinikov, "Effect of a Heavy Atom on the Thermostimulated Delayed Fluorescence and Phosphorescence of Xanthene Dyes," Opt. Spektrosk. 52, 657–662 (1982) [Opt. Spectrosc. (USSR) 52, 392–395 (1982)].
17. V. V. Bryukhanov, L. V. Levshin, Zh. K. Smagulov, and Z. M. Muldakhmetov, "Effect of External Heavy Atoms on Thermally Stimulated Delayed Fluorescence of Acridine Dyes in Polyvinyl Alcohol Matrices," Opt. Spekrosk. 59, 896–899 (1985) [Opt. Spectrosc. (USSR) 59, 540–542 (1985)].

18. M. Hercher, "An Analysis of Saturable Absorbers," Appl. Opt. 6, 947–954 (1967).

19. G. N. Lewis, D. Lipkin, and T. T. Magel, "Reversible Photochemical Processes in Rigid Media. A Study of the Phosphorescent State," J. Am. Chem. Soc. 63, 3005–3018 (1941).

20. M. Frackowiak and J. Heldt, "Investigation of an Organophosphor in the Preexcited State," Acta Phys. Pol. 18, 93–106 (1959).

21. T. Tomashek, "Zur Kenntnis der Borsäurephosphore," Ann. Phys. (Leipzig) 67, 622–646 (1922).

22. D. W. Greggs and H. G. Drickamer, "Effect of Pressure on the Optical Properties of Organic Phosphors," J. Chem. Phys. 35, 1780–1788 (1960).

23. V. A. Pilipovitch and B. T. Sveshnikov, "O Zakhone Zatukhaniya Dlitil'nogo Srecheniya Organolyuminoforov," Opt. Spektrosk. 5, 290–296 (1958).

24. R. L. Abrams and R. C. Lind, "Degenerate Four-Wave Mixing in Absorbing Media," Opt. Lett. 2, 94–99 (1978); "Degenerate Four-Wave Mixing in Absorbing Media: Errata," Opt. lett. 3, 205 (1978).