

Nonlinear-optical properties of lead-tin fluorophosphate glass containing acridine dyes

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A new nonlinear-optical material based on lead-tin fluorophosphate glass doped with the organic dyes Acridine Orange and Acridine Yellow has been developed. These materials are saturable absorbers characterized by saturation intensities of ~ 100 mW cm $^{-2}$, response times of ~ 1 msec, and third-order nonlinear susceptibilities of ~ 0.1 esu. The low melting temperature of the lead-tin fluorophosphate glass permits doping with many organic dyes without causing their decomposition.

INTRODUCTION

Recent work has shown that organic materials often possess highly desirable nonlinear-optical properties. This work has involved the studies of organic materials in the form of single crystals,^{1,2} polymers,^{3,4} liquid crystals,⁵ thin films,^{6,7} liquid solutions,⁸⁻¹¹ and doped solids.¹²⁻¹⁴ In the present paper we report the results of an experimental study of the nonlinear-optical properties of lead-tin fluorophosphate glass containing acridine dyes. We selected this system for investigation because of the high optical quality, low melting temperature, and durability of the host and because the spectral characteristic of the dye molecules allowed for resonant excitation by argon-ion lasers. Recent studies¹⁴ of the nonlinear-optical properties of fluorescein in boric acid glass showed that this material possesses a large third-order nonlinear susceptibility $\chi^{(3)}$ of ~ 1 esu but that the usefulness of the material was limited by the low durability and poor homogeneity of the boric acid host. In the present study we find that the doped lead-tin fluorophosphate glass has a very large third-order nonlinear susceptibility and retains the desirable properties of the host.

The origin of the large nonlinear susceptibility $\chi^{(3)}$ at room temperature for lead-tin fluorophosphate glass doped with Acridine Yellow and Acridine Orange is illustrated in Fig. 1. Following optical excitation from the ground singlet state to the first excited singlet state, an intersystem crossing transfers population to the lowest-lying triplet state. Delayed fluorescence from the excited singlet state eventually occurs after an intersystem crossing that returns the population to the excited singlet state from vibrationally excited states of the lowest-lying triplet manifold. Many of the mechanisms that can quench the triplet state do not exist when the dye is held rigidly in a solid matrix, and hence the lowest-lying triplet state has a very long lifetime. Because of the longevity of the triplet state, significant population can be trapped in that state even by weak optical fields. The saturation intensity I_s is therefore quite small (~ 100 mW cm $^{-2}$), and, since the nonlinear susceptibility $\chi^{(3)}$ varies inversely with I_s ,

the nonlinear $\chi^{(3)}$ susceptibility is extremely large, ~ 0.1 esu as compared with $\sim 10^{-12}$ esu for the liquid CS $_2$.

PROPERTIES OF LEAD-TIN FLUOROPHOSPHATE GLASS

In most inorganic glasses a general reciprocal relation exists between melting temperature and durability: systems that are less refractory (e.g., borates, halides) are more susceptible to attack by atmospheric water than are more refractory glasses (e.g., silicates, borosilicates). Recently, a family of glasses within the lead-tin fluorophosphate system was discovered that exhibits a significant departure from this general relationship.¹⁵ The viscosity characteristics of these durable glasses make melting and forming possible at a temperature compatible with many organic dyes.

The multicomponent nature of this system makes a simple description of the glass-forming composition space difficult. However, the tin content is the dominant factor controlling most physical and optical properties. The range of tin content in which clear transparent glasses are formed is from 35 to 75 cation mol. %, resulting in widely varied properties. At the low-tin boundary of this composition space, typical values of the density ρ , the glass transition temperature T_g , the thermal expansion coefficient α_t , and the index of refraction n_D are 3.5 g cm $^{-3}$, 220°C, 14×10^{-6} °C $^{-1}$, and 1.65, respectively. At the high-tin boundary, ρ , T_g , α_t , and n_D are typically 4.4 g cm $^{-3}$, 50°C, 35×10^{-6} °C $^{-1}$, and 1.90, respectively. A more restricted region of composition space with a lead content from 3 to 6 cation % and a tin content from 40 to 60 cation % yields exceptional durability. In a water immersion test at 50°C for 24 h, dissolution rates in these compositions can be less than 1 mg cm $^{-2}$ day $^{-1}$. For comparison, soda-lime float (window) glass typically dissolves at a rate of 0.02 mg cm $^{-2}$ day $^{-1}$. The Knoop hardness of these glasses is in the range 90-120, as compared with a typical value of 330 for soda-lime glass and 20 for the polymer, polymethyl methacrylate.

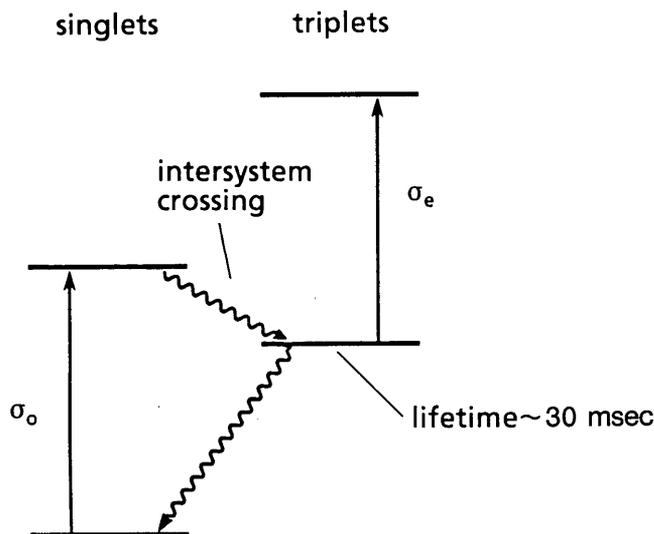


Fig. 1. Energy-level diagram showing the relevant optical interactions in lead-tin fluorophosphate glass containing acridine dyes. Because of its long luminescent lifetime, the lowest-lying triplet state acts as a trap level. σ_0 and σ_e denote the absorption cross sections of the ground and excited states, respectively.

Glasses within the lead-tin fluorophosphate system seem to be ideal solid-state hosts for organic dyes. They are transparent in the near infrared and visible, with the onset of electronic band-edge absorption beginning at 350 nm. They are easily melted at or below 500°C and can be cooled to 300°C, at which temperature the viscosity of the melt is low enough for complete dissolution and mixing of many organic dopants without thermal decomposition. Dopant concentrations as high as $4.8 \times 10^{18} \text{ cm}^{-3}$ have been observed, making the solubility limit of the glass comparable with those of many organic solvents. The glasses are durable and hard enough for polishing by conventional methods.

SAMPLE PREPARATION

The base glass composition used in the present study is given in Table 1. The batch materials were weighed, mixed, and melted at 400°C in air by using vitreous carbon crucibles. After the initial meltdown reactions were complete, the glass was cooled to 300°C, 2.0 mg of the organic component was added to the melt, and the solution was thoroughly mixed. When homogenization was achieved, the crucible was removed from the furnace and allowed to cool. This procedure yielded glass disks that were annealed at 90°C and then ground and polished to the appropriate sample thickness. The density of the base glass is 4.273 g cm^{-3} with an index of refraction $n_D = 1.765$.

The absorption spectra of glasses doped with Acridine Yellow and Acridine Orange are shown in Fig. 2. The spectra are typical of these dyes in liquid solvents. The Acridine Yellow sample has a peak location at 464 nm and a band FWHM of 51 nm; the same dye at room temperature in ethanol has a peak at 460 nm and a FWHM of 46 nm. The peak location of the Acridine Orange sample is 512 nm with a FWHM of 51 nm, as compared with a peak location of 491 nm and a FWHM of 47 nm with ethanol as the solvent. Since some volatilization of the batch constituents occurs during melting, an accurate value of the dopant concentra-

tion is difficult to obtain without chemical analysis. However, if the peak absorption cross section of the dyes is approximately the same in glass as in ethanol, estimated concentrations of 7.7×10^{17} and $8.0 \times 10^{17} \text{ molecules cm}^{-3}$ for the Acridine Yellow and Acridine Orange samples, respectively, are obtained.

CHARACTERIZATION OF NONLINEAR-OPTICAL PROPERTIES

The fluorescent decay of Acridine Yellow and Acridine Orange in lead-tin fluorophosphate glass was studied in order to characterize the time response of these materials. A continuous-wave (cw) argon-ion laser beam illuminated each sample and was abruptly cut off by a beam chopper having a cutoff time of $\sim 15 \mu\text{sec}$. A photomultiplier tube monitored the subsequent time evolution of the fluorescence; the output signal was digitized and sampled by a microcomputer. The temporal evolutions of the fluorescence signals are plotted on a semilogarithmic scale in Fig. 3. For both samples the decay is seen to be nonexponential, with decay times varying between approximately 20 and 40 msec for the sample doped with Acridine Yellow and between approximately 15 and 30 msec for the sample doped with Acridine Orange. Our finding of nonexponential decay is in contrast to the exponential decay observed by Bryukhanov *et al.*¹⁶ for acridine dyes in polyvinyl alcohol matrices. We posit that the decay is nonexponential for the case of the lead-tin fluorophosphate glass because of site-to-site variations in the local

Table 1. Low-Melting-Temperature Base-Glass Composition

| Batch Component | Mol. % | Batch Weight (g) |
|-------------------------------------|--------|-------------------|
| SnF ₂ | 52.2 | 27.3 |
| SnO | 10.5 | 4.7 |
| PbF ₂ | 5.1 | 4.1 |
| 1/2(P ₂ O ₅) | 32.1 | 12.3 ^a |

^a As NH₄H₂PO₄.

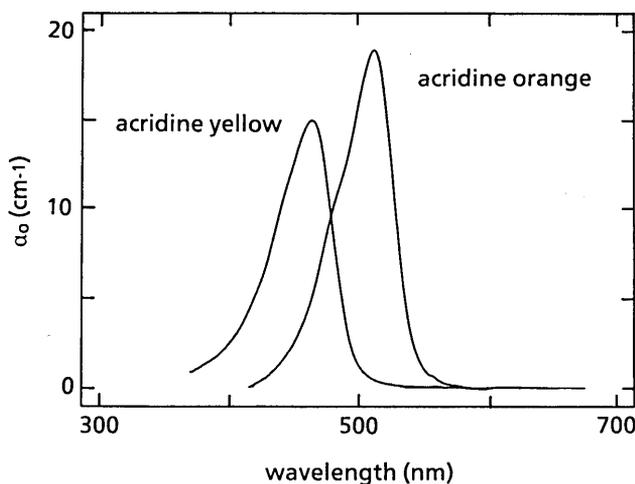


Fig. 2. Absorption spectra of lead-tin fluorophosphate glass containing Acridine Yellow at a concentration of $7.7 \times 10^{17} \text{ molecules cm}^{-3}$ or Acridine Orange at a concentration of $8.0 \times 10^{17} \text{ molecules cm}^{-3}$.

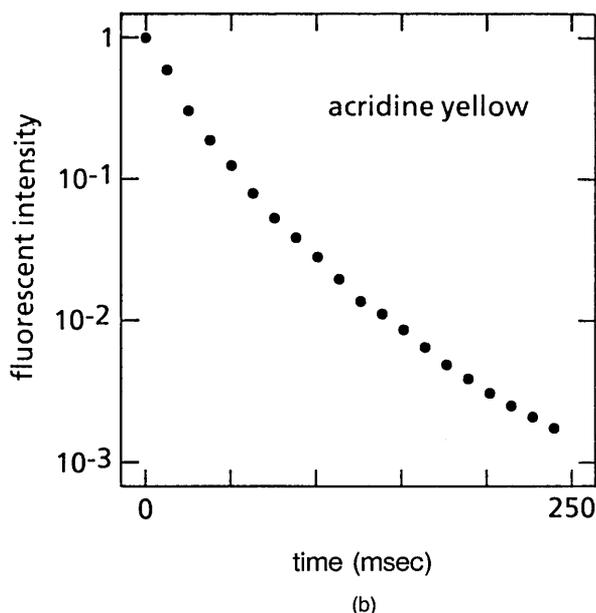
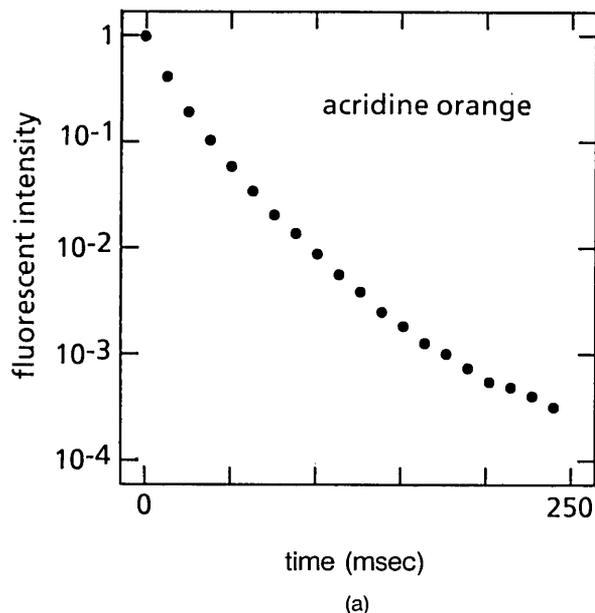


Fig. 3. Temporal evolution of the luminescent decay from (a) Acridine Orange and (b) Acridine Yellow. In each case, the decay is nonexponential.

environment, as is the case for fluorescein-doped boric acid glass.^{14,17,18}

We have studied the saturation behavior of Acridine Orange and Acridine Yellow in lead-tin fluorophosphate glass by using a linearly polarized beam from a cw argon-ion laser. The intensity of the laser beam incident upon the sample was varied by using a Pockels cell followed by a linear polarizer. The transmission was measured as a function of the incident laser intensity. Typical results are shown in Figs. 4(a) and 4(b). The solid curves are theoretical fits to the data. The theory used to obtain these curves models the saturation behavior of randomly oriented anisotropic molecular absorbers that are held rigidly in a solid matrix. The saturation behavior of such a material is different from that of a conventional saturable absorber, in which the molecules are free to rotate.¹⁴ The absorption coefficient α is found by performing an angular average of the absorption cross section σ_f for a molecule of fixed orientation that can absorb only that component of the optical field that is parallel to the molecular axis. The absorption coefficient for linearly polarized light is found to be¹⁴

$$\alpha = \frac{N\sigma_0}{S} \left(1 - \frac{1}{\sqrt{3S}} \tan^{-1} \sqrt{3S} \right), \quad (1)$$

where N is the number of molecules per unit volume, σ_0 is the unsaturated absorption cross section averaged over all solid angles, $S = I/I_s$ is the saturation parameter, I is the intensity of the linearly polarized beam, and I_s is the saturation intensity. The theoretical curves in Fig. 4 are calculated by numerically integrating the differential equation for the intensity I :

$$\frac{dI}{dz} = -(\alpha + \alpha_e)I, \quad (2)$$

where $\alpha_e = N_e\sigma_e$ is the excited-state absorption coefficient. Here σ_e is the excited-state absorption cross-section, and N_e is the excited-state population given by $N_e = N[1 - (\alpha/\alpha_0)]$, where $\alpha_0 = N\sigma_0$. For the Acridine Orange sample with

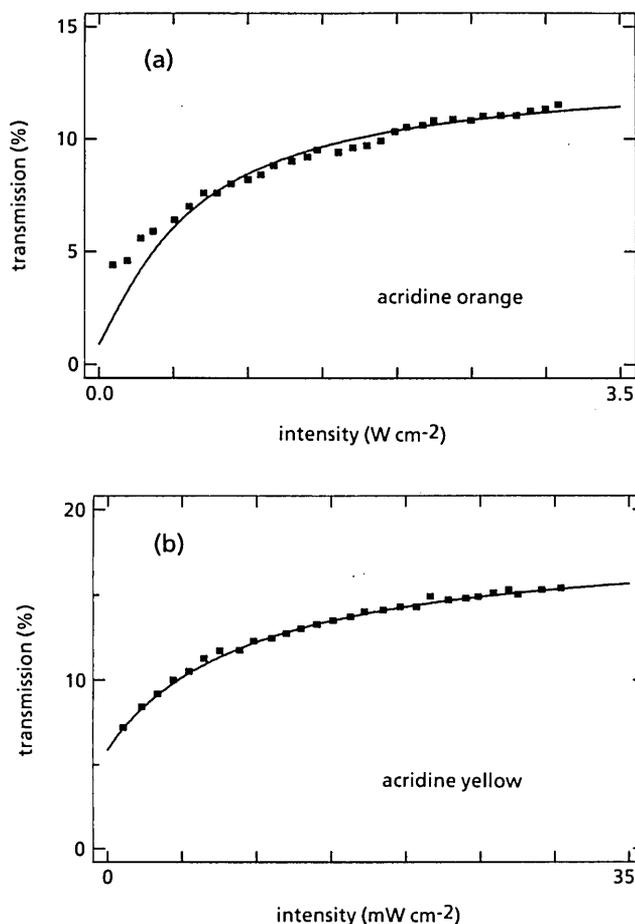


Fig. 4. (a) Transmission of lead-tin fluorophosphate glass containing Acridine Orange as a function of laser intensity for a laser wavelength of 514 nm. The solid curve represents a fit to the data based on the theory described in the text, assuming a saturation intensity of 75 mW cm⁻². (b) Transmission of lead-tin fluorophosphate containing Acridine Yellow at a wavelength of 476 nm. The theoretical curve assumes a saturation intensity of 30 mW cm⁻².

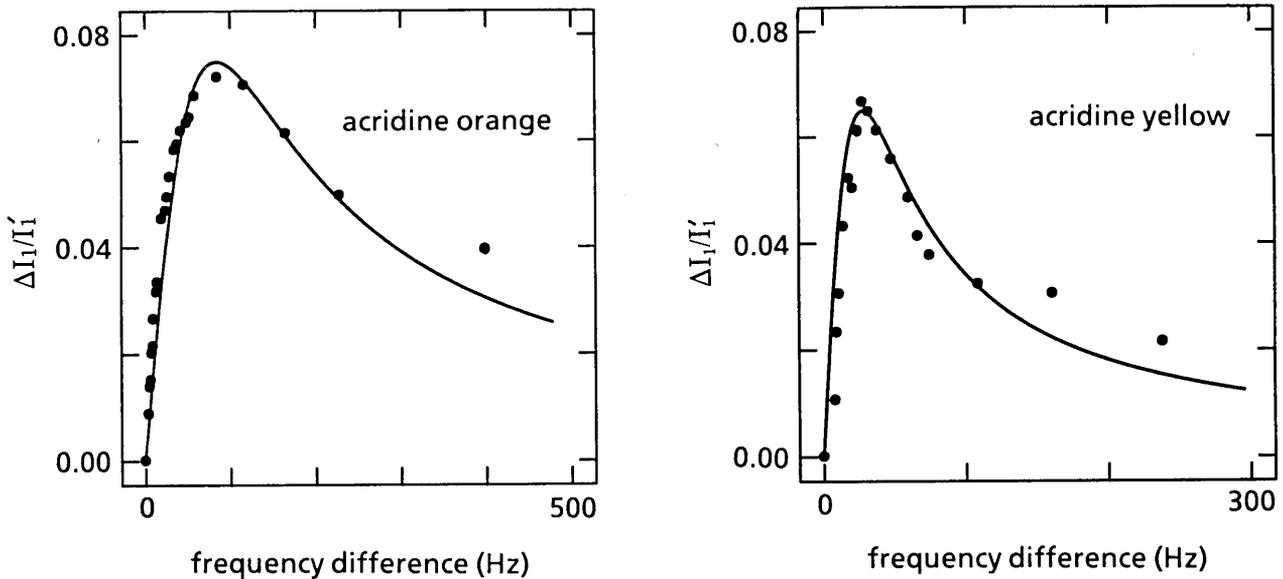


Fig. 5. Fractional change in intensity owing to two-beam coupling, plotted as a function of the frequency difference between the pump and probe beams. The solid curves are theoretical predictions based on Eq. (5). For Acridine Orange, the experiment was performed at 514 nm, and the solid curve assumes the values $\tau = 1.9$ msec and $|\chi^{(3)}| = 0.39$ esu. For Acridine Yellow, the experiment was performed at 476 nm, and the solid curve assumes the values $\tau = 5.6$ msec and $|\chi^{(3)}| = 0.08$ esu.

thickness $l = 1$ mm at the wavelength $\lambda = 514.5$ nm, good agreement between theory and experiment is obtained by using $\alpha_0 l = 4.6$, $\alpha_e l = 2.0$, and $I_s = 75$ mW cm $^{-2}$. For the Acridine Yellow sample of thickness $l = 2$ mm at the wavelength $\lambda = 476.5$ nm, the data are fitted by the values $\alpha_0 l = 2.8$, $\alpha_e l = 1.67$, and $I_s = 30$ mW cm $^{-2}$. The values of $\alpha_0 l$ were chosen in both cases to agree with the absorption measured by a spectrophotometer at the given wavelength.

The size of the nonlinearity of these materials can be estimated by using the results of the saturation experiment. The third-order nonlinear susceptibility $\chi^{(3)}$ is related to the saturation intensity I_s by

$$\chi^{(3)} = \frac{n_0^2 c^2 \alpha_0}{24 \pi^2 \omega I_s} (\delta + i), \quad (3)$$

where α_0 is the unsaturated absorption coefficient, n_0 is the unsaturated refractive index, and $\delta = (\omega - \omega_0) T_2$ is the detuning of the laser frequency ω from the resonance frequency ω_0 , normalized to the dipole dephasing time T_2 , which we obtain from the absorption spectrum under the assumption that the transition is homogeneously broadened. For the sample of Acridine Orange used for Fig. 4, the saturation experiment gives the parameters $\alpha_0 = 46$ cm $^{-1}$, $\lambda = 514.5$ nm, $n_0 = 1.77$, $I_s = 75$ mW cm $^{-2}$, and $\delta = 0.1$, which predict a nonlinear susceptibility given by $\chi^{(3)} = 0.02 + 0.20i$ esu and imply a line-center saturation intensity of $I_s^0 = I_s / (1 + \delta^2) = 74$ mW cm $^{-2}$. For the sample of Acridine Yellow used for Fig. 4, the saturation experiment gives $\alpha_0 = 14$ cm $^{-1}$, $\lambda = 476.5$ nm, $n_0 = 1.77$, $I_s = 30$ mW cm $^{-2}$, and $\delta = 0.4$; the predicted value of the nonlinear susceptibility is $\chi^{(3)} = 0.06 + 0.14i$ esu, and the line-center saturation intensity is $I_s^0 = 26$ mW cm $^{-2}$.

In order to measure the third-order nonlinear susceptibility $\chi^{(3)}$ and the response time τ directly, we have studied two-beam coupling in these materials. Two-beam coupling is the transfer of energy from one laser beam to another. In order for two-beam coupling to occur, it is necessary for the nonlinear response grating to be shifted relative to the inten-

sity pattern that formed it. If the two interfering beams have slightly different frequencies, the interference pattern will move with respect to the stationary material, and because of the nonzero response time of the material the grating will be shifted in phase with respect to the interference pattern. In our experiment a frequency shift is imposed on one beam by reflecting it off a mirror that is translated at a constant velocity by a piezoelectric transducer.

Two-beam coupling in a saturable absorber can be described analytically by including the effects of absorption in a derivation analogous to that of Silberberg and Bar-Joseph.¹⁹ The refractive index is written as a complex quantity,

$$n = n_0 + n_2 I = n' + in'' + (n_2' + in_2'') I, \quad (4)$$

which includes the effects of saturable absorption and dispersion. The intensity $I_1 = (n_0 c / 2\pi) |E_1|^2$ of one of the beams can be shown¹⁴ to vary spatially as

$$\begin{aligned} \frac{dI_1}{dz} = & -\alpha I_1 + \frac{4\pi}{n_0 c} k n_2'' (I_1 + I_2) I_1 + \frac{4\pi}{n_0 c} k n_2'' \frac{I_1 I_2}{1 + \Delta^2} \\ & + \frac{4\pi}{n_0 c} k n_2' \frac{\Delta}{1 + \Delta^2} I_2 I_1, \end{aligned} \quad (5)$$

where I_2 is the intensity of the second beam, k is the propagation constant, and $\Delta = (\omega_1 - \omega_2)\tau$; ω_1 and ω_2 are the frequencies of the two interacting beams and τ is the response time of the medium. The last term on the right-hand side of Eq. (5), which is due to dispersion, is responsible for two-beam coupling; the first three terms on the right-hand side of Eq. (5) describe linear absorption and predict increased transmission at high intensities, owing to saturation effects.

In Fig. 5 the change in intensity of one of the beams caused by two-beam coupling is plotted as a function of the frequency difference between the two beams. The solid lines in the figures are theoretical fits of the data to the dependence on the frequency shift predicted by the last term of Eq. (5).

Table 2. Nonlinear-Optical Constants of Lead-Tin Fluorophosphate Glass Containing Acridine Orange or Acridine Yellow

| Constant | Value for the Following | |
|---|--------------------------------------|--------------------------------------|
| | Acridine Orange | Acridine Yellow |
| Molecular concentration | $8.0 \times 10^{17} \text{ cm}^{-3}$ | $7.7 \times 10^{17} \text{ cm}^{-3}$ |
| Luminescent decay time | 15–30 msec (nonexponential) | 20–40 msec (nonexponential) |
| Measurement wavelength | 514 nm | 476 nm |
| Saturable absorption coefficient, α_0 | 46 cm^{-1} | 14 cm^{-1} |
| Nonsaturable absorption coefficient, α_e | 20 cm^{-1} | 8 cm^{-1} |
| Saturation intensity | 75 mW cm^{-2} | 30 mW cm^{-2} |
| Response time | 1.9 msec | 5.6 msec |
| $\chi^{(3)}$ (measured by two-beam coupling) | $0.04 + 0.39i \text{ esu}$ | $0.03 + 0.07i \text{ esu}$ |
| $\chi^{(3)}$ (from saturation data) | $0.02 + 0.20i \text{ esu}$ | $0.06 + 0.14i \text{ esu}$ |

Good agreement between theory and experiment is obtained through the use of $\tau = 1.9 \text{ msec}$ for Acridine Orange and $\tau = 5.6 \text{ msec}$ for Acridine Yellow. The results of this experiment can also be used to estimate the size of the nonlinearity of these materials. The first three terms in Eq. (5) can be approximated by aI_1 , where a is an effective absorption coefficient that describes the effects of saturated absorption. We then find, in the approximation in which the pump intensity I_2 is assumed constant, that the maximum intensity transfer to the probe beam, which occurs when $\Delta = 1$, is given by

$$\Delta I_1 = \frac{2\pi}{n_0 c} k l n_2' I_2 I_1', \quad (6)$$

where $I_1' = I_1(z=0)\exp(-al)$ and where n_2 is related to the nonlinear susceptibility through $n_2 = 3\pi\chi^{(3)}/n_0$. For the sample of lead-tin fluorophosphate glass doped with Acridine Orange (Fig. 5), Eq. (6) implies a nonlinear refractive index $n_2 = 0.21 + 2.08i \text{ esu}$, where $\lambda = 514.5 \text{ nm}$, $\delta = 0.1$, $\alpha_0 = 20.7 \text{ cm}^{-1}$, $l = 0.2 \text{ cm}$, $n_0 = 1.77$, $(\Delta I_1/I_1')_{\text{max}} = 0.075$, and $I_2 \sim (50 \text{ mW cm}^{-2})\exp(-2) = 7 \text{ mW cm}^{-2}$. It then follows that $\chi^{(3)} = 0.04 + 0.39i \text{ esu}$ and $I_s = 17 \text{ mW cm}^{-2}$. Similarly, for lead-tin fluorophosphate glass doped with Acridine Yellow (Fig. 5), where $\lambda = 476.5 \text{ nm}$, $\delta = 0.4$, $\alpha_0 = 20 \text{ cm}^{-1}$, $l = 0.2 \text{ cm}$, $n_0 = 1.77$, $(\Delta I_1/I_1')_{\text{max}} = 0.065$, and $I_2 \sim (60 \text{ mW cm}^{-2})\exp(-2) = 8.1 \text{ mW cm}^{-2}$, one finds that $n_2 = 0.16 + 0.37i \text{ esu}$, $\chi^{(3)} = 0.03 + 0.07i \text{ esu}$, and $I_s \sim 87 \text{ mW cm}^{-2}$. We have been unable to rule out entirely the possibility of a thermal origin for this effect. However, we believe that it is unlikely that thermal effects play more than a minor role in this system because a nonlinearity as large as that observed is inconsistent with a thermal origin and because for the similar system of fluorescein in boric acid glass it is known that the nonlinearity is not thermal.¹⁴ We showed that the nonlinearity in that case was not thermal by replacing the fluorescein with a dye that had similar absorption characteristics but had a short luminescent lifetime and observing that the nonlinearity with this dye was orders of magnitude smaller than that with fluorescein.

DISCUSSION

The results of this study are summarized in Table 2. We note that the response time relevant to a nonlinear-optical interaction is approximately 1 order of magnitude shorter than the characteristic luminescent decay time. Such behavior has been noted previously¹⁴ for the case of materials with a nonexponential luminescent decay. The nonlinear susceptibility measured directly by the two-beam coupling experiment is in good factor-of-2 agreement with that inferred from the saturation measurements. By way of comparison, the nonlinear susceptibility of fluorescein in boric acid glass¹⁴ is of the order of 1 esu, and the response time is 0.1 sec. Although the magnitude of the nonlinearity of the materials described in the present paper is considerably smaller, their response time is very much shorter. In addition, the materials based on lead-tin fluorophosphate glass have better optical quality and are much more environmentally robust. For these reasons, this class of materials is potentially useful for applications in nonlinear optics in which very large nonlinearities and millisecond response times are required.

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