Enhanced Nonlinear Optical Response of Composite Materials

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We present experimental results which demonstrate that the effective third-order susceptibility of a composite optical material can exceed those of the materials from which it is constructed. In particular, we have formed a composite of alternating, sub-wavelength-thick layers of titanium dioxide and the conjugated polymer poly(*p*-phenylene-benzobisthiazole), and find that its nonlinear susceptibility exceeds that of its more nonlinear constituent by 35%. The enhancement of the nonlinear susceptibility, which under more ideal but still realistic conditions can be as large as a factor of 10, can be understood as a consequence of local field corrections.

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There is a great need for nonlinear optical materials with large nonlinear coefficients and fast response. Many applications of nonlinear optics that have been demonstrated under controlled laboratory conditions could become practical for technological uses if such materials were available. Nonlinear optical switching devices for use in photonics and real-time coherent optical signal processors are examples of applications of nonlinear optics that would benefit from the development of fast, low-loss materials with large values of the third-order nonlinear susceptibility $\chi^{(3)}$ [1].

The most common approach to the development of new nonlinear optical materials involves the search for materials in which the constituent molecules possess an inherently large nonlinear response [2]. In contrast, in this Letter we describe a technique that can be used to increase the $\chi^{(3)}$ value of a nonlinear optical material by forming a composite of that material and another material having a different value of the linear refractive index. The two constituent materials can be optically lossless, and the response time of the composite is essentially the same as that of the nonlinear constituent. The two materials are intermixed on a distance scale of the order of 50 nm, which is much larger than an atomic dimension but much smaller than the wavelength of light used in our experiment. Consequently, the structural properties of each constituent material are essentially the same as those of a bulk sample of that material, but the propagation of light through the composite can be described by effective values of the linear and nonlinear optical susceptibilities that are obtained by performing suitable volume averages. The reason why this technique leads to an enhancement of $\chi^{(3)}$ is that the electric field amplitude of an incident laser beam becomes nonuniformly distributed between the two constituents of the composite, and under suitable conditions the electric field strength within the more nonlinear constituent will exceed the spatially averaged field strength. Under these conditions, the effective third-order susceptibility $\chi^{(3)}_{\text{eff}}$ of the composite can exceed that of either of its constituents.

We have previously performed detailed theoretical studies of composite materials of the sort mentioned above both for the case in which small inclusion particles are embedded in a host material [3] and for the case of alternating layers of two dissimilar materials [4]. In each case we found that an enhancement of the third-order susceptibility occurs if the more nonlinear component has the smaller linear refractive index and that the enhancement increases rapidly with the difference in refractive indices of the materials. The enhancement can be as large as a factor of 10 if the refractive indices of the two materials differ by a factor of 2. The idea of enhancing optical nonlinearities by means of the dielectric properties of inhomogeneous materials has been discussed previously in a somewhat different context by Chemla and Miller [5].

The experimental study described in this Letter involves a composite material of the sort shown in Fig. 1, which consists of alternating layers of materials of linear refractive indices $n_a = \sqrt{\varepsilon_a}$ and $n_b = \sqrt{\varepsilon_b}$ and nonlinear susceptibilities $\chi^{(3)}_a$ and $\chi^{(3)}_b$, respectively. We denote the volume fraction of each material as f_a and f_b. It is shown in Ref. [4] that for light polarized perpendicular to the planes of the layers the effective linear refractive index $n_{\text{eff}} = \sqrt{\varepsilon_{\text{eff}}}$ of the material is given by $1/\varepsilon_{\text{eff}} = f_a/\varepsilon_a + f_b/\varepsilon_b$, and that in the limit in which the nonlinear response of one of the components (say component b) is vanishingly small the effective nonlinear susceptibility is given by

$$\chi^{(3)}_{\text{eff}} = \left| \frac{\varepsilon_{\text{eff}}}{\varepsilon_a} \right|^2 \left(\frac{\varepsilon_{\text{eff}}}{\varepsilon_a} \right)^2 f_a \chi^{(3)}_a. \qquad (1)$$

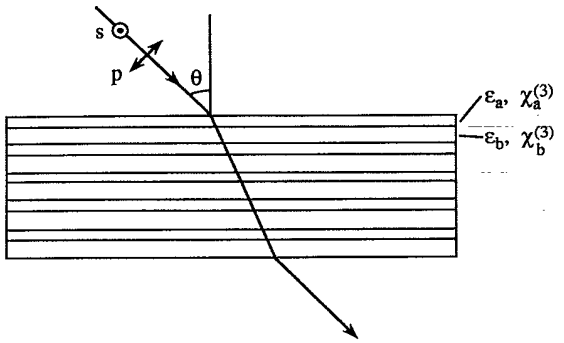

FIG. 1. Composite optical material having a layered geometry. Each layer is much thinner than an optical wavelength.

The prefactor involving the fourth power of $\varepsilon_{\text{eff}}/\varepsilon_a$ can be interpreted as a local field enhancement of the nonlinear susceptibility. For light polarized parallel to the planes of the layers, ε_{eff} and $\chi^{(3)}_{\text{eff}}$ are given by simple volume averages, that is, by $\varepsilon_{\text{eff}} = f_a\varepsilon_a + f_b\varepsilon_b$ and $\chi^{(3)}_{\text{eff}} = f_a\chi^{(3)}_a$. The enhancement predicted by Eq. (1) can be appreciable. Figure 2 shows a plot of the enhancement in $\chi^{(3)}$, that is, a plot of $\chi^{(3)}_{\text{eff}}/\chi^{(3)}_a$, as a function of the volume fill fraction f_a of component a. Special cases that are shown include the curve labeled $\varepsilon_b/\varepsilon_a = 4$, which corresponds to materials that differ by a factor of 2 in linear refractive index, and the curve labeled $\varepsilon_b/\varepsilon_a = 1.77$, which corresponds to the materials used in our experimental investigation. Note that the maximum enhancement in this case is 35%.

The measurements described below were performed on a composite comprised of alternating layers of titanium dioxide and the nonlinear optical polymer poly(p-phenylene-benzobisthiazole) (PBZT). Samples were formed by spin casting alternating layers of the component materials onto glass substrates. The titanium dioxide constitutes the high-index component having essentially linear response. It was spin cast from a sol-gel precursor [6] and cured for 24 h at 200 °C to yield a material with a refractive index of 2.2 ± 0.1. Its nonlinear susceptibility [7] $\chi^{(3)} \approx 10^{-13}$ esu is several orders of magnitude smaller than that of PBZT. The PBZT was also spin cast from an isotropic solution in nitromethane-$AlCl_3$, washed in methanol, and dried for 24 h under vacuum at 70 °C [8]. It has a linear refractive index of 1.8 ± 0.05 and nonlinear susceptibilities of $|\chi^{(3)}| = 5 \times 10^{-11}$ esu as measured by third-harmonic generation, and $\chi^{(3)} = (-2.7 \pm 0.3) \times 10^{-10}$ esu as measured by the z-scan method [9]. Refractive index values were determined from the spacings of the interference fringes present in the transmission spectra of thin films of each pure material that were fabricated by a procedure identical to that used in forming the composite. Layer thicknesses of 40 nm for the PBZT and 50 nm for the titanium dioxide were used. The thickness ratio is close to the ideal value as predicted by Eq. (1). The sample contains five layers of each material.

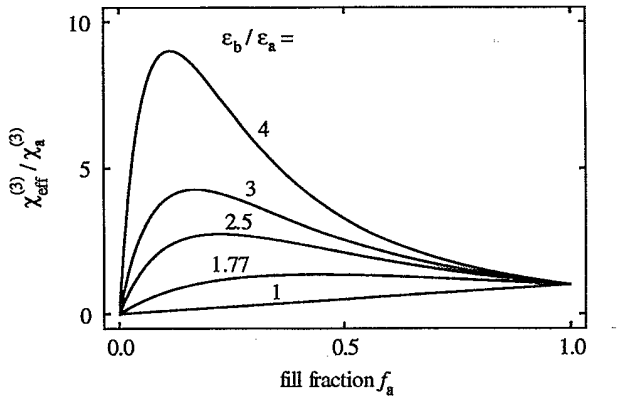

FIG. 2. Predicted enhancement of the third-order nonlinear susceptibility plotted as a function of the volume fill fraction of component a for several values of the ratio of optical frequency dielectric constants of the two components.

We determined the nonlinear optical properties of the composite sample by measuring the nonlinear phase shift acquired by a laser beam in propagating through the material as a function of the angle of incidence θ for both p-polarized (**E** in the plane of Fig. 1) and s-polarized (**E** perpendicular to the plane of Fig. 1) light. Only for the case of p polarization does the electric field within the sample possess a component perpendicular to the plane of the layers, and it is this component that leads to an enhancement of $\chi^{(3)}$. The nonlinear phase shift was measured using the z-scan technique. Measurements were performed at a wavelength of 1.9 μm to avoid two-photon absorption in the polymer. This wavelength was obtained by shifting the output of a Nd:YAG laser by stimulated Raman scattering in hydrogen. The results of these measurements are shown in Fig. 3. For p polarization, the nonlinear phase shift first increases as a function of θ because of the enhancement of $\chi^{(3)}$ as described above and eventually decreases because the beam intensity within the sample decreases due to geometrical effects and to Fresnel reflection losses. For s polarization, the nonlinear phase shift decreases monotonically with the angle of incidence. Note that the data points are very well described by the theoretical curves, which are shown as solid lines. These curves were obtained by solving the wave equation for propagation through the effective medium, taking account of the Fresnel reflection loss at the entrance to the sample and the tensor nature of the effective nonlinear susceptibility. This procedure leads to the prediction

$$\phi^{\text{NL}} = \frac{-2\pi\omega^2 L\varepsilon_{\|}}{c^2 w_p \eta_p^2}\,\mathbf{q}\cdot\overleftrightarrow{\chi}^{(3)}\!:\mathbf{qqq}\,t^2E_0^2, \qquad (2)$$

where $w_p = (\omega/c)[\varepsilon_{\|} - (\varepsilon_{\|}/\varepsilon_{\perp})\sin^2\theta]^{1/2}$, $\eta_p^2 = \varepsilon_{\|} + (1 - \varepsilon_{\|}/\varepsilon_{\perp})\sin^2\theta$, $\mathbf{q} = \hat{\mathbf{x}}q_x + \hat{\mathbf{z}}q_z$, $q_x = \eta_p w_p c/\omega\varepsilon_{\|}$, $q_z = \eta_p \sin\theta/\varepsilon_{\perp}$, t is the transmission coefficient given by Fresnel's formulas, θ is the angle of incidence, L is

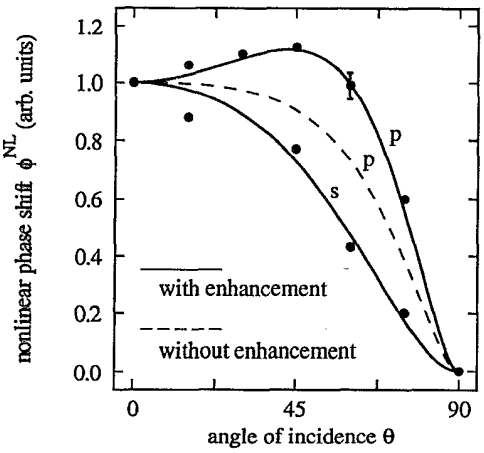

FIG. 3. Measured nonlinear optical response of the PBZT/titanium dioxide composite for both s- and p-polarized light. The solid curves show the theoretical predictions and the dashed curve shows the expected behavior if there was no local field enhancement of $\chi^{(3)}$.

the thickness of the sample, $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ are the effective linear dielectric constants for light polarized parallel and perpendicular to the planes of the layers, and E_0 is the electric field amplitude of the incident light. In order to obtain an explicit prediction for the tensor nature of the effective nonlinear susceptibility, we model the polymer as a lossless isotropic material possessing Kleinman symmetry. The nonvanishing components of $\chi^{(3)}_{\text{eff}}$ are then given by $\chi_{zzzz} = f_a(\varepsilon_{\perp}/\varepsilon_a)^4\chi^a_{1111}$, $\chi_{xxzz} = \chi_{xzxz} = \chi_{xzzx} = \chi_{zzxx} = \chi_{zxzx} = \chi_{zxxz} = \frac{1}{3}f_a(\varepsilon_{\perp}/\varepsilon_a)^2\chi^a_{1111}$, and $\chi_{xxxx} = f_a\chi^a_{1111}$, where χ^a_{1111} denotes the diagonal component of the nonlinear susceptibility for the polymer. Under these assumptions, the shapes of the theoretical curves shown in Fig. 3 depend only on the ratio of the linear refractive indices of the constituent materials. To obtain the good agreement shown in the figure, we have adjusted the ratio n(titania)/n(PBZT) slightly from the measured value of 1.22 ± 0.10 to the value 1.33. The uncertainties in the refractive index reflect primarily the range of refractive indices that result from imperfect control of the processing condition of our spin-cast films. Also shown in Fig. 3 as the dashed curve is the behavior that would be expected for p-polarized light if there were no enhancement of the nonlinear optical susceptibility, that is, if the local field enhancement factors involving powers of $\varepsilon_{\perp}/\varepsilon_a$ were replaced by unity in the expressions quoted in the previous sentence. Clearly the data are not in agreement with this curve, and this fact indicates that enhanced nonlinear response does, in fact, occur in composite nonlinear optical materials. Note that only one curve is shown for the case of s polarization, because for s polarization the predictions are identical whether or not local field effects are taken into account, because the general theory of Ref. [5] predicts that there is no enhancement for the case of s polarization.

The model used to obtain the theoretical predictions of Fig. 3 assumes that the material in each nonlinear layer is optically isotropic. The good agreement between theory and experiment evident in Fig. 3 suggests that this assumption is valid. As an independent check of this assumption, we prepared a sample consisting of a single 40-nm-thick layer of PBZT, heat treated this sample in a manner identical to that used to produce our layered composite sample, and repeated the measurements of Fig. 3. We find that for this sample the nonlinear phase shift for p polarization decreases monotonically with the angle of incidence and is well described by the dashed curve of Fig. 3, which was obtained under the assumption of an isotropic nonlinear material. This observation rules out the possibility that the enhancement measured for our layered composite sample was the consequence of some anisotropy of the individual nonlinear layers. We suspect that the heat treatment required to cure the titania layers removes through annealing any anisotropies produced by the spin-casting process.

Much of the previous work on composite nonlinear optical materials has concentrated on the situation in which small particles are embedded in a host material [10–17]. Especially interesting is the case in which the inclusion particles are metallic in nature. In this case, large enhancements in the nonlinear optical response have been predicted [10–12] and observed [13–15] if the laser frequency is selected to excite the surface plasmon resonance of the particles. These studies differ from that of the present Letter in that they did not establish (nor were they motivated at establishing) that the nonlinear susceptibility of a composite can exceed those of its constituent materials. Layered organic-inorganic composite materials have been explored previously in a different context by Takada *et al.* [18].

In summary, we have shown experimentally that it is possible to construct a composite nonlinear optical material in such a manner that the effective third-order susceptibility of the material exceeds those of its constituent materials. For the sample used in this study, an enhancement of 35% was achieved, that is, $\chi^{(3)}_{\text{eff}}$ is equal to 1.35 times that of pure PBZT. However, our theoretical model, which is well supported by our experimental results, predicts that an enhancement of a factor of 10 is possible for materials whose refractive indices differ by a factor of 2, which is approximately the range of refractive indices that occurs in nature. This maximum enhancement can be realized only for light polarized perpendicular to the plane of the layers. Guided-wave nonlinear optical devices with the light propagating along the plane of the layers would naturally lend themselves to this sort of geometry. Finally, we stress that the idea of enhancing optical nonlinearities through the formation of composite geometries is very general in nature. The technique described in this Letter can be used to enhance the nonlinear response of almost any pure nonlinear optical material by forming

a composite of that material. Moreover, the theory presented in Ref. [4] shows that layered composite materials can also display an enhanced second-order nonlinear optical susceptibility, and the theory of Ref. [3] shows that enhancement can occur in geometries other than the layered geometry studied in this work.

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[1] See, for example, P. W. Smith, Philos. Trans. R. Soc. London A **313**, 349–355 (1984); *Nonlinear Photonics,* edited by H. M. Gibbs, G. Khitrova, and N. Peyghambarian (Springer-Verlag, New York, 1990); G. I. Stegeman, in *Contemporary Nonlinear Optics,* edited by G. P. Agrawal and R. W. Boyd (Academic Press, Boston, 1992).

[2] See, for example, D. C. Dodenberger, J. R. Heflin, and A. F. Garito, Nature (London) **359**, 309 (1992); C. Halvorson, T. W. Hagler, D. Moses, Y. Cao, and A. J. Heeger, Chem. Phys. Lett. **200**, 364 (1992); S. K. Ghoshal, P. Chopra, B. P. Singh, J. Swiatiewicz, and P. N. Prasad, J. Chem. Phys. **90**, 5078 (1989).

[3] J. E. Sipe and R. W. Boyd, Phys. Rev. A **46**, 1614 (1992).

[4] R. W. Boyd and J. E. Sipe, J. Opt. Soc. Am. B **11**, 297 (1994).

[5] D. S. Chemla and D. A. B. Miller, Opt. Lett. **11**, 522 (1986).

[6] S. M. Melpolder, A. W. West, C. L. Barnes, and T. N. Blanton, J. Mater. Sci. **26**, 3585 (1991).

[7] W. E. Tourellas, L. A. Weller-Brophy, R. Zanoni, G. I. Stegeman, Z. Osborne, and B. J. J. Zelinski, Appl. Phys. Lett. **58**, 1128 (1991).

[8] H. Vanherzeele, J. S. Meth, S. A. Jenekhe, and M. F. Roberts, J. Opt. Soc. Am. B **9**, 524 (1992); H. Vanherzeele, J. S. Meth, S. A. Jenekhe, and M. F. Roberts, Appl. Phys. Lett. **58**, 663 (1991); S. A. Jenekhe, J. A. Osaheni, J. S. Meth, and H. Vanherzeele, Chem. Mater. **4**, 683 (1992); J. A. Osaheni and S. A. Jenekhe, Chem. Mater. **4**, 1282 (1992).

[9] M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Van Stryland, IEEE J. Quantum Electron. **26**, 760 (1990).

[10] G. S. Agarwal and S. Dutta Gupta, Phys. Rev. A **38**, 5678 (1988).

[11] A. E. Neeves and M. H. Birnboim, J. Opt. Soc. Am. B **6**, 787 (1989).

[12] J. W. Haus, R. Inguva, and C. M. Bowden, Phys. Rev. A **40**, 5729 (1989).

[13] D. Ricard, P. Roussignol, and C. Flytzanis, Opt. Lett. **10**, 511 (1985).

[14] J. W. Haus, N. Kalyaniwalla, R. Inguva, M. Bloemer, and C. M. Bowden, J. Opt. Soc. Am. B **6**, 797 (1989).

[15] L. Yang, K. Becker, F. M. Smith, R. H. Magruder, R. F. Haglund, L. Yang, R. Dorsinville, R. R. Alfano, and R. A. Zuhr, J. Opt. Soc. Am. B **11**, 1 (1994).

[16] K. C. Rustagi and C. Flytzanis, Opt. Lett. **9**, 344 (1984).

[17] P. Roussignol, D. Ricard, J. Lukasik, and C. Flytzanis, J. Opt. Soc. Am. B **4**, 5 (1987).

[18] J. Takada, H. Awaji, M. Koshioka, A. Nakajima, and W. A. Nevin, Appl. Phys. Lett. **61**, 2184 (1992).