

Nonlinear optical response of layered composite materials

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We present a theoretical formalism that describes the nonlinear phase shift acquired by a laser beam in passing through an anisotropic material oriented at an arbitrary angle with respect to the beam. We use this theory to analyze the results of z -scan measurements made on layered composite materials. Samples are constructed from alternating, subwavelength-thick layers of titanium dioxide and the conjugated polymer poly (p -phenylenebenzobisthiazole). Effective-medium theory predicts an enhancement of 35% in the third-order susceptibility when the electric field is polarized normal to the layers. Good agreement between theory and experiment is observed.

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I. INTRODUCTION

The practical development of nonlinear optical devices is often hindered by the lack of materials with the proper combination of desirable properties such as large nonlinear response, short response times, and high damage thresholds. For this reason, much effort has recently been directed toward the development of materials possessing these desirable properties. The most common approach for doing so is to search for materials, or to synthesize new materials, that possess these desirable attributes as inherent properties. An alternative approach is to fabricate composites from one or more constituents in such a manner that the composite material possesses attributes superior to those of its constituent materials. The second approach underlies the work reported in this paper.

There is a substantial history of work aimed at understanding the optical properties of composite materials. Maxwell Garnett [1], for example, presented in 1905 a model that successfully explained many of the linear optical properties of glasses containing metallic particles. More recently, Jain and Lind [2] measured large third-order nonlinear optical susceptibilities in glasses doped with CdSe crystallites; Ricard, Roussignol, and Flytzanis [3] measured large third-order nonlinearities in metal colloids, especially at frequencies near the surface plasmon resonance. Subsequently, extensive research has investigated the third-order nonlinear optical susceptibilities of composite materials containing either metallic [4–8] or semiconductor [9–13] particles. Related theoretical work has dealt both with the situation of randomly interdispersed composite materials [14–16] and with more exotic geometric structures such as those with fractal structures [17,18].

A different sort of insight into the development of composite nonlinear optical materials was presented by two of the present authors, who noted that under proper conditions the nonlinear susceptibility of a composite material can exceed those of the constituent materials from which the composite is formed [19,20]. This result was demonstrated by explicit calculations both for the geometry of inclusion particles embedded in a host material [19] and the geometry of

alternating layers of two materials [20]. We recently verified the prediction of enhanced nonlinear optical response for the case of a layered composite material and published a brief account of this work [21]. The composite material was comprised of alternating layers of titanium dioxide and the conjugated polymer poly (p -phenylenebenzobisthiazole). The experimental technique used to determine the nonlinear optical susceptibility entailed measuring the nonlinear contribution to the phase shift acquired by a laser beam in passing through the material as a function of the angle of incidence of the laser. The primary intent of the current paper is to present a detailed account of the mathematical procedure used in analyzing the results of this experiment. However, for reasons of completeness, we also present a brief summary of our experimental procedure and our experimental results.

II. THEORETICAL FORMALISM

The starting point for the theoretical formalism is the macroscopic Maxwell equations

$$c \nabla \times \mathbf{E} + \dot{\mathbf{B}} = \mathbf{0}, \quad (1a)$$

$$c \nabla \times \mathbf{B} - \dot{\mathbf{D}} = 4 \pi \dot{\mathbf{P}}^{\text{NL}}, \quad (1b)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (1c)$$

$$\nabla \cdot \mathbf{D} = -4 \pi \nabla \cdot \mathbf{P}^{\text{NL}}. \quad (1d)$$

Here \mathbf{P}^{NL} is the nonlinear polarization and \mathbf{D} is the displacement field containing the linear polarization \mathbf{P}^{L} , i.e., $\mathbf{D} = \mathbf{E} + 4 \pi \mathbf{P}^{\text{L}}$. We neglect any magnetic effects and have taken $\mathbf{H} = \mathbf{B}$. From these equations we derive, in the usual way, the wave equation for the electric field

$$\nabla^2 \mathbf{E} - \frac{1}{c^2} \ddot{\mathbf{D}} - \nabla (\nabla \cdot \mathbf{E}) = \frac{4 \pi}{c^2} \ddot{\mathbf{P}}^{\text{NL}}. \quad (2)$$

Assuming solutions of the form

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}) e^{-i \omega t} + \text{c.c.}, \quad (3)$$

the wave equation takes the form

$$\nabla^2 \mathbf{E} + k_0^2 \mathbf{D} - \nabla(\nabla \cdot \mathbf{E}) = -4\pi k_0^2 \mathbf{P}^{\text{NL}}, \quad (4)$$

where $k_0 = \omega/c$; we henceforth use \mathbf{E} to denote $\mathbf{E}(\mathbf{r})$ rather than $\mathbf{E}(\mathbf{r}, t)$ [see Eq. (3)] and likewise for the other fields. Our approach to this problem consists of four steps. First we solve the linear problem ($\mathbf{P}^{\text{NL}}=0$) to determine the wave vectors and eigenpolarizations in the linear medium. Next we develop a Green's function relating the electric field to a driving polarization and thus determine the waves generated by the nonlinear polarization. From these solutions we derive and solve simple first-order differential equations for the nonlinear phase shift induced on propagation through the material. Finally, we determine the full tensor form of $\chi^{(3)}$ for a layered composite and use this in our expression for the nonlinear phase shift.

A. Linear solution

With \mathbf{P}^{NL} set equal to zero, the wave equation becomes

$$\nabla^2 \mathbf{E} + k_0^2 \mathbf{D} - \nabla(\nabla \cdot \mathbf{E}) = 0, \quad (5)$$

where $\mathbf{D} = \boldsymbol{\varepsilon} \cdot \mathbf{E}$ and

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_x & 0 & 0 \\ 0 & \varepsilon_x & 0 \\ 0 & 0 & \varepsilon_z \end{pmatrix}.$$

Note that the z direction is defined to be parallel to the optic axis, so that $\varepsilon_y = \varepsilon_x$. The wave vector \mathbf{k} may be decomposed into components parallel and perpendicular to the optic axis. For a plane-wave solution, we thus have

$$\mathbf{E}(\mathbf{r}) = \mathbf{E} e^{i\mathbf{k}_\perp \cdot \mathbf{r}} e^{\pm ik_z z}, \quad (6)$$

where $\mathbf{k}_\perp = (k_x, k_y, 0) = k_\perp \hat{\mathbf{k}}_\perp$. A new unit vector $\hat{\mathbf{s}} \equiv \hat{\mathbf{k}}_\perp \times \hat{\mathbf{z}}$ is defined to construct an orthonormal coordinate system, where we consider $\hat{\mathbf{k}}_\perp$ fixed and real. Substituting Eq. (6) into Eq. (5), we obtain the eigenvalue equation

$$[k_0^2 \boldsymbol{\varepsilon} - (k_\perp^2 + k_z^2) \mathbf{I}] \cdot \mathbf{E} + (\mathbf{k}_\perp \pm k_z \hat{\mathbf{z}})(\mathbf{k}_\perp \pm k_z \hat{\mathbf{z}}) \cdot \mathbf{E} = 0. \quad (7)$$

Here \mathbf{I} is the identity matrix.

One solution, corresponding to the usual s -polarized wave, results from an electric field of the form $\mathbf{E} = E \hat{\mathbf{s}}$ ($\mathbf{D} = D \hat{\mathbf{s}}$). For this field the second term on the left-hand side of Eq. (7) vanishes. Thus the z component of the wave vector is given by $\pm k_z^s$, where $k_z^s = \sqrt{k_0^2 \varepsilon_x - k_\perp^2}$; the complete wave vectors are given by $\mathbf{k}_\pm^s = \mathbf{k}_\perp \pm k_z^s \hat{\mathbf{z}}$. The sign in the wave vector \mathbf{k}_\pm^s determines whether the wave is traveling (or possibly evanescent) in the positive or negative z direction; in all square roots we taken $\text{Im} \sqrt{z} \geq 0$, with $\text{Re} \sqrt{z} \geq 0$ if $\text{Im} \sqrt{z} = 0$. Regardless of their traveling or evanescent character, we refer generally to waves characterized by wave vectors of the type \mathbf{k}_+^s as "upward traveling" and waves characterized by wave vectors of the type \mathbf{k}_-^s as "downward traveling." Note that our development here and below carries through whether ε_x and ε_z are purely real or complex. For the s -polarized waves presently being considered we define a

refractive index $n^s \equiv \sqrt{\mathbf{k}_\pm^s \cdot \mathbf{k}_\pm^s} / k_0$. We find $n^s = \sqrt{\varepsilon_x}$, independent of the direction of propagation.

To determine the other solution, we take $\mathbf{E} = E_\perp \hat{\mathbf{k}}_\perp + E_z \hat{\mathbf{z}}$, corresponding to a p -polarized wave. Substitution into the eigenvalue equation (7) yields wave vectors given by $\mathbf{k}_\pm^p = \mathbf{k}_\perp \pm k_z^p \hat{\mathbf{z}}$, with $k_z^p = \sqrt{k_0^2 \varepsilon_x - (\varepsilon_x / \varepsilon_z) k_\perp^2}$. For these waves the unit vectors identifying the direction of the displacement field are easily found to be $\hat{\mathbf{d}}_\pm^p = (k_\perp \hat{\mathbf{z}} \mp k_z^p \hat{\mathbf{k}}_\perp) / k_0 n^p$, where

$$n^p \equiv \sqrt{\mathbf{k}_\pm^p \cdot \mathbf{k}_\pm^p} / k_0 = \left[\varepsilon_x + \left(1 - \frac{\varepsilon_x}{\varepsilon_z} \right) \frac{k_\perp^2}{k_0^2} \right]^{1/2}$$

is the effective index of refraction experienced by the wave. The direction of the electric field for these waves is not parallel to the displacement field, since ε_x and ε_z are in general different. Instead it is given by $\boldsymbol{\varepsilon}^{-1} \cdot \hat{\mathbf{d}}_\pm^p$. To simplify the form of subsequent equations, it is convenient to work with nonnormalized vectors identifying the electric field direction. We define

$$\mathbf{q}_\pm = (n^p)^2 \boldsymbol{\varepsilon}^{-1} \cdot \hat{\mathbf{d}}_\pm^p \quad (8)$$

for the electric-field direction vectors for the upward and downward traveling waves. Note that this expression is equivalent to

$$\mathbf{q}_\pm = (n^p)^2 \left[\frac{k_\perp}{\varepsilon_z k^p} \hat{\mathbf{z}} \mp \frac{k_z^p}{\varepsilon_x k^p} \hat{\mathbf{k}}_\perp \right]. \quad (9)$$

We now have the homogeneous solutions for the electric field of both the upward and downward traveling waves. To determine the magnetic fields, we use the Maxwell equation

$$\mathbf{B} = \frac{1}{ik_0} \nabla \times \mathbf{E}. \quad (10)$$

The solutions for the upward traveling waves are

$$\mathbf{E}_+(\mathbf{r}) = E_+^s \hat{\mathbf{s}} e^{i\mathbf{k}_+^s \cdot \mathbf{r}} + E_+^p \mathbf{q}_+ e^{i\mathbf{k}_+^p \cdot \mathbf{r}}, \quad (11a)$$

$$\mathbf{B}_+(\mathbf{r}) = -n^s E_+^s \hat{\mathbf{p}}_+ e^{i\mathbf{k}_+^s \cdot \mathbf{r}} + n^p E_+^p \hat{\mathbf{s}} e^{i\mathbf{k}_+^p \cdot \mathbf{r}} \quad (11b)$$

and for the downward traveling waves are

$$\mathbf{E}_-(\mathbf{r}) = E_-^s \hat{\mathbf{s}} e^{i\mathbf{k}_-^s \cdot \mathbf{r}} + E_-^p \mathbf{q}_- e^{i\mathbf{k}_-^p \cdot \mathbf{r}}, \quad (12a)$$

$$\mathbf{B}_-(\mathbf{r}) = -n^s E_-^s \hat{\mathbf{p}}_- e^{i\mathbf{k}_-^s \cdot \mathbf{r}} + n^p E_-^p \hat{\mathbf{s}} e^{i\mathbf{k}_-^p \cdot \mathbf{r}}. \quad (12b)$$

With these solutions it is a simple matter to derive the transmission coefficients for a wave propagating from air into the material. For the case of s polarization the refractive index is independent of the angle of incidence, so the result is the standard Fresnel coefficient

$$t^s = \frac{2 \cos \theta_i}{\cos \theta_i + n^s \cos \theta_t} = \frac{2k_{0z}}{k_{0z} + k_z^s} \quad \text{where } k_{0z} = k_0 \cos \theta_i. \quad (13)$$

For p polarization we assume incident and reflected fields of the form

$$\mathbf{E}_i = E_0 \hat{\mathbf{p}}_{0-} e^{-ik_0 z}, \quad \mathbf{B}_i = E_0 \hat{\mathbf{s}} e^{-ik_0 z}, \quad (14)$$

$$\mathbf{E}_r = r E_0 \hat{\mathbf{p}}_{0+} e^{ik_0 z}, \quad \mathbf{B}_r = r E_0 \hat{\mathbf{s}} e^{ik_0 z}, \quad (15)$$

where $\hat{\mathbf{p}}_{0\pm} = (k_{\perp} \hat{\mathbf{z}} \mp k_0 \hat{\mathbf{k}}_{\perp})/k_0$. The transmitted field is taken from Eqs. (12a) and (12b):

$$\mathbf{E}_t = t^p E_0 \mathbf{q}_{-} e^{-ik_z^p z}, \quad \mathbf{B}_t = n^p t^p E_0 \mathbf{s} e^{-ik_z^p z}. \quad (16)$$

The Maxwell ‘‘jump’’ conditions across the interface lead to the Fresnel transmission coefficient

$$t^p = \frac{2k_0 \varepsilon_x / n^p}{\varepsilon_x k_0 z + k_z^p}. \quad (17)$$

B. Green’s function

Our derivation of the Green’s function for this system follows that described earlier [22]. First we restore \mathbf{P}^{NL} to the Maxwell equations and use Eq. (3) to find

$$\nabla \times \mathbf{E} - ik_0 \mathbf{B} = \mathbf{0}, \quad (18a)$$

$$\nabla \times \mathbf{B} + ik_0 \mathbf{D} = -4\pi ik_0 \mathbf{P}^{\text{NL}}, \quad (18b)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (18c)$$

$$\nabla \cdot \mathbf{D} = -4\pi \nabla \cdot \mathbf{P}^{\text{NL}}. \quad (18d)$$

Our approach is to consider the nonlinear polarization as a specified driving term in these equations, with the tensor ε treated initially as uniform. Since a Green’s function is simply the system impulse response, we choose the impulse to have the form

$$\mathbf{P}^{\text{NL}}(\mathbf{r}) = e^{i\mathbf{k}_{\perp} \cdot \mathbf{r}} [P_k \hat{\mathbf{k}}_{\perp} + P_z \hat{\mathbf{z}} + P_s \hat{\mathbf{s}}] \delta(z). \quad (19)$$

The choice of a sheet impulse in the $z=0$ plane reflects the geometry of the problem of interest; the resulting Green’s function will depend only on z and on the transverse component of the wave vector \mathbf{k}_{\perp} . We find that we can construct a solution of Eqs. (18) and (19) as an electromagnetic field consisting of an upward traveling wave in the $+z$ half space, a downward traveling wave in the $-z$ half space, and an electric impulse in the plane $z=0$. That is, we assume a solution of the form

$$\mathbf{E}(\mathbf{r}) = \theta(z) \mathbf{E}_+(\mathbf{r}) + \theta(-z) \mathbf{E}_-(\mathbf{r}) + \hat{\mathbf{z}} E \delta(z) e^{i\mathbf{k}_{\perp} \cdot \mathbf{r}}, \quad (20a)$$

$$\mathbf{B}(\mathbf{r}) = \theta(z) \mathbf{B}_+(\mathbf{r}) + \theta(-z) \mathbf{B}_-(\mathbf{r}), \quad (20b)$$

where $\theta(z)$ is the usual step function, i.e., $\theta(z)=0$ and 1 as $z<0$ and $z>0$, respectively. We justify the assumed form (20) by showing that we can indeed find $\mathbf{E}_+(\mathbf{r})$, $\mathbf{E}_-(\mathbf{r})$, and E such that Eqs. (18) and (19) are satisfied. The solution for s polarization (i.e., with only $P_s \neq 0$) is essentially the same as in an isotropic medium and follows that derived earlier [22]. We restrict ourselves here to the p polarization, for which the polarization impulse is of the form

$$\mathbf{P}^{\text{NL}}(\mathbf{r}) = e^{i\mathbf{k}_{\perp} \cdot \mathbf{r}} [P_k \hat{\mathbf{k}}_{\perp} + P_z \hat{\mathbf{z}}] \delta(z) = e^{i\mathbf{k}_{\perp} \cdot \mathbf{r}} \mathbf{P} \delta(z). \quad (21)$$

Recall from the linear calculation that the electric field for an upward traveling wave is given by

$$\mathbf{E}_+(\mathbf{r}) = E_+^p \mathbf{q}_+ e^{i\mathbf{k}_+^p \cdot \mathbf{r}} \quad (22)$$

and for a downward traveling wave is given by

$$\mathbf{E}_-(\mathbf{r}) = E_-^p \mathbf{q}_- e^{i\mathbf{k}_-^p \cdot \mathbf{r}}. \quad (23)$$

We substitute these expressions in the Maxwell equations and, using the identity $\nabla \theta(z) = \hat{\mathbf{z}} \delta(z)$, set equal the singular parts of the equations. Simple algebra yields

$$\begin{aligned} E_+^p &= 2\pi i k_{\perp} \left(\frac{k^p}{k_z^p} \frac{\varepsilon_x}{\varepsilon_z (n^p)^2} \right) P_z - \frac{2\pi i k_0}{n^p} P_k \\ &= \frac{2\pi i k_0^2 \varepsilon_x}{k_z^p (n^p)^2} \mathbf{q}_+ \cdot \mathbf{P}, \end{aligned} \quad (24)$$

$$E_-^p = \frac{2\pi i k_0^2 \varepsilon_x}{k_z^p (n^p)^2} \mathbf{q}_- \cdot \mathbf{P}. \quad (25)$$

Therefore the electric field resulting from a polarization impulse located at $z=0$ is given by

$$\mathbf{E}(\mathbf{r}) = e^{i\mathbf{k}_{\perp} \cdot \mathbf{r}} \mathbf{E}(z), \quad (26)$$

where

$$\begin{aligned} \mathbf{E}(z) &= \frac{2\pi i k_0^2 \varepsilon_x}{k_z^p (n^p)^2} \theta(z) \mathbf{q}_+ \mathbf{q}_+ \cdot \mathbf{P} + \frac{2\pi i k_0^2 \varepsilon_x}{k_z^p (n^p)^2} \theta(-z) \mathbf{q}_- \mathbf{q}_- \cdot \mathbf{P} \\ &\quad - \frac{4\pi}{\varepsilon_z} \delta(z) \hat{\mathbf{z}} \hat{\mathbf{z}} \cdot \mathbf{P}. \end{aligned}$$

From the relationship $\mathbf{E}(z) = \int \mathbf{G}(\mathbf{k}_{\perp}, z-z') \cdot \mathbf{P}^{\text{NL}}(z') dz'$, which defines the Green’s function, we find that $\mathbf{G}(\mathbf{k}_{\perp}, z)$ is given by

$$\begin{aligned} \mathbf{G}(\mathbf{k}_{\perp}, z) &= \frac{2\pi i k_0^2 \varepsilon_x}{k_z^p (n^p)^2} \theta(z) \mathbf{q}_+ \mathbf{q}_+ + \frac{2\pi i k_0^2 \varepsilon_x}{k_z^p (n^p)^2} \theta(-z) \mathbf{q}_- \mathbf{q}_- \\ &\quad - \frac{4\pi}{\varepsilon_z} \delta(z) \hat{\mathbf{z}} \hat{\mathbf{z}}. \end{aligned} \quad (27)$$

We must now generalize this result to an impulse at an arbitrary z position. Since the tensor ε is assumed to be uniform, placing the polarization impulse at an arbitrary z' rather than at $z'=0$ simply shifts the Green’s function argument from z to $z-z'$. To summarize, for

$$\mathbf{P}^{\text{NL}}(\mathbf{r}) = \mathbf{P}^{\text{NL}}(\mathbf{k}_{\perp}, z) e^{i\mathbf{k}_{\perp} \cdot \mathbf{r}} \quad (28a)$$

we have

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}(\mathbf{k}_{\perp}, z) e^{i\mathbf{k}_{\perp} \cdot \mathbf{r}}, \quad (28b)$$

$$\mathbf{E}(\mathbf{k}_{\perp}, z) = \int \mathbf{G}(\mathbf{k}_{\perp}, z-z') \cdot \mathbf{P}^{\text{NL}}(\mathbf{k}_{\perp}, z') dz', \quad (28c)$$

where the Green’s function (including now the s -polarization part) is given by

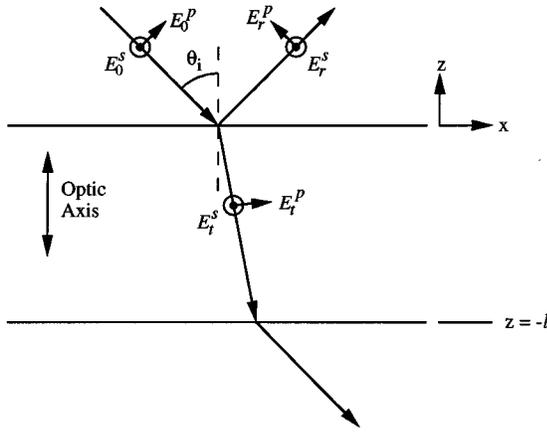


FIG. 1. Plane wave incident on uniaxial medium.

$$\begin{aligned} \mathbf{G}(\mathbf{k}_\perp, z-z') &= 2\pi i k_0^2 \theta(z-z') \left[\frac{\hat{\mathbf{S}}\hat{\mathbf{S}}}{k_z^s} e^{ik_z^s(z-z')} \right. \\ &+ \left. \frac{\varepsilon_x}{k_z^p(n^p)^2} \mathbf{q}_+ \mathbf{q}_+ e^{ik_z^p(z-z')} \right] + 2\pi i k_0^2 \theta(z'-z) \\ &\times \left[\frac{\hat{\mathbf{S}}\hat{\mathbf{S}}}{k_z^s} e^{ik_z^s(z'-z)} + \frac{\varepsilon_x}{k_z^p(n^p)^2} \mathbf{q}_- \mathbf{q}_- e^{ik_z^p(z'-z)} \right] \\ &- \frac{4\pi}{\varepsilon_z} \hat{\mathbf{z}}\hat{\mathbf{z}} \delta(z-z'). \end{aligned} \quad (29)$$

C. Nonlinear phase shift

The complete solution (homogeneous plus particular) for the electric field in this system is

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}(z) e^{i\mathbf{k}_\perp \cdot \mathbf{r}} e^{-i\omega t}, \quad (30a)$$

$$\begin{aligned} \mathbf{E}(z) &= E_{0+}^s \hat{\mathbf{s}} e^{ik_z^s z} + E_{0-}^s \hat{\mathbf{s}} e^{-ik_z^s z} + E_{0+}^p \mathbf{q}_+ e^{ik_z^p z} + E_{0-}^p \mathbf{q}_- e^{-ik_z^p z} \\ &+ \frac{2\pi i k_0^2}{k_z^s} \hat{\mathbf{S}}\hat{\mathbf{S}} \cdot \int_{-\infty}^z e^{ik_z^s(z-z')} \mathbf{P}^{\text{NL}}(z') dz' + \frac{2\pi i k_0^2}{k_z^s} \hat{\mathbf{S}}\hat{\mathbf{S}} \cdot \int_z^{\infty} e^{-ik_z^s(z-z')} \mathbf{P}^{\text{NL}}(z') dz' \\ &+ \frac{2\pi i k_0^2 \varepsilon_x}{k_z^p(n^p)^2} \mathbf{q}_+ \mathbf{q}_+ \cdot \int_{-\infty}^z e^{ik_z^p(z-z')} \mathbf{P}^{\text{NL}}(z') dz' + \frac{2\pi i k_0^2 \varepsilon_x}{k_z^p(n^p)^2} \mathbf{q}_- \mathbf{q}_- \cdot \int_z^{\infty} e^{-ik_z^p(z-z')} \mathbf{P}^{\text{NL}}(z') dz' - \frac{4\pi}{\varepsilon_z} \hat{\mathbf{z}}\hat{\mathbf{z}} \cdot \mathbf{P}^{\text{NL}}(z). \end{aligned} \quad (30b)$$

This may be divided into four parts corresponding to the s and p polarization of the upward and downward traveling waves. Based on the geometry of the problem at hand (Fig. 1), we will be concerned only with waves traveling in the downward direction. For these waves it is readily seen that

$$E_-^s(z) = E_{0-}^s + \frac{2\pi i k_0^2}{k_z^s} \hat{\mathbf{s}} \cdot \int_z^{\infty} e^{ik_z^s z'} \mathbf{P}^{\text{NL}}(z') dz', \quad (31)$$

$$E_-^p(z) = E_{0-}^p + \frac{2\pi i k_0^2 \varepsilon_x}{k_z^p(n^p)^2} \mathbf{q}_- \cdot \int_z^{\infty} e^{ik_z^p z'} \mathbf{P}^{\text{NL}}(z') dz'. \quad (32)$$

We convert these integral equations into differential equations

$$\frac{dE_-^s}{dz} = -\frac{2\pi i k_0^2}{k_z^s} e^{ik_z^s z} \hat{\mathbf{s}} \cdot \mathbf{P}^{\text{NL}}(z), \quad (33)$$

$$\frac{dE_-^p}{dz} = -\frac{2\pi i k_0^2 \varepsilon_x}{k_z^p(n^p)^2} e^{ik_z^p z} \mathbf{q}_- \cdot \mathbf{P}^{\text{NL}}(z). \quad (34)$$

The nonlinear driving polarization is given by

$$\mathbf{P}^{\text{NL}}(\mathbf{r}) = \chi^{(3)}(\omega = \omega + \omega - \omega) : \mathbf{E}(\mathbf{r}) \mathbf{E}(\mathbf{r}) \mathbf{E}^*(\mathbf{r}). \quad (35)$$

Consider first the case of an s -polarized wave. We assume a solution for the electric field that has a constant amplitude, but experiences a phase shift due to the nonlinear polarization:

$$E_-^s(z) = t^s E_0 e^{-i\phi^{\text{NL}}(z)}, \quad (36)$$

where E_0 is the electric-field amplitude of a wave incident on the composite through air and t^s is the transmission coefficient for s -polarized light. Substituting this expression into Eqs. (33) and (35), we obtain

$$t^s E_0 \left(-i \frac{d\phi^{\text{NL}}}{dz} \right) e^{-i\phi^{\text{NL}}(z)} = -\frac{2\pi i k_0^2}{k_z^s} e^{ik_z^s z} \hat{\mathbf{s}} \cdot \mathbf{P}^{\text{NL}}(z) \quad (37)$$

and

$$\mathbf{P}^{\text{NL}}(z) = \chi^{(3)}(\omega = \omega + \omega - \omega) : \hat{\mathbf{S}}\hat{\mathbf{S}}\hat{\mathbf{S}} (t^s E_0)^3 e^{-ik_z^s z} e^{-i\phi^{\text{NL}}(z)}. \quad (38)$$

Combining these expressions, we find

$$\frac{d\phi^{\text{NL}}}{dz} = \frac{2\pi k_0^2}{k_z^s} \hat{\mathbf{s}} \cdot \chi^{(3)}(\omega = \omega + \omega - \omega) : \hat{\mathbf{S}}\hat{\mathbf{S}}\hat{\mathbf{S}} (t^s E_0)^2. \quad (39)$$

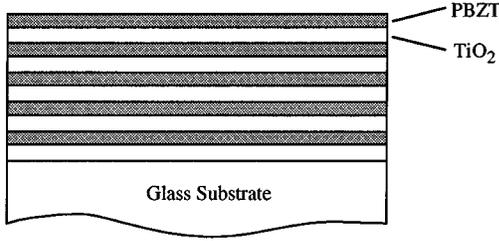


FIG. 2. PBZT–titanium dioxide composite.

If the sample thickness is l , then the total nonlinear phase shift imparted on the wave is

$$\phi^{\text{NL}}(-l) = -\frac{2\pi k_0^2 l}{k_z^s} \hat{\mathbf{s}} \cdot \chi^{(3)}(\omega = \omega + \omega - \omega) : \hat{\mathbf{s}} \hat{\mathbf{s}} \hat{\mathbf{s}} (t^s E_0)^2. \quad (40)$$

For p polarization the steps are the same. Assuming that the electric field is given by

$$E_-^p(z) = t^p E_0 e^{-i\phi^{\text{NL}}(z)}, \quad (41)$$

we find the following differential equation for the nonlinear phase shift:

$$\frac{d\phi^{\text{NL}}}{dz} = \frac{2\pi k_0^2 \varepsilon_x}{k_z^p (n^p)^2} \mathbf{q}_- \cdot \chi^{(3)}(\omega = \omega + \omega - \omega) : \mathbf{q}_- \mathbf{q}_- \mathbf{q}_- (t^p E_0)^2. \quad (42)$$

The solution of this equation is

$$\phi^{\text{NL}}(-l) = -\frac{2\pi k_0^2 \varepsilon_x l}{k_z^p (n^p)^2} \mathbf{q}_- \cdot \chi^{(3)}(\omega = \omega + \omega - \omega) : \mathbf{q}_- \mathbf{q}_- \mathbf{q}_- (t^p E_0)^2. \quad (43)$$

Equations (40) and (43) are the main results of this section. They give us explicit expressions for the nonlinear phase shift a plane wave experiences on passing through a uniaxial material.

D. Tensor $\chi^{(3)}$ for a layered composite

To make use of Eqs. (40) and (43), one final step must be performed: the full tensor form of the effective third-order susceptibility of a layered composite must be determined. From Ref. [20] we know that the diagonal components of the nonlinear susceptibility are

$$\chi_{xxxx}^{(3)} = \chi_{yyyy}^{(3)} = f_a \chi_{1111}^a + f_b \chi_{1111}^b, \quad (44a)$$

$$\chi_{zzzz}^{(3)} = f_a \left| \frac{\varepsilon_{\text{eff},z}}{\varepsilon_a} \right|^2 \left(\frac{\varepsilon_{\text{eff},z}}{\varepsilon_a} \right)^2 \chi_{1111}^a + f_b \left| \frac{\varepsilon_{\text{eff},z}}{\varepsilon_b} \right|^2 \left(\frac{\varepsilon_{\text{eff},z}}{\varepsilon_b} \right)^2 \chi_{1111}^b. \quad (44b)$$

These results assume isotropic constituent materials a and b . For our problem, we may make additional simplifying assumptions. First, the constituents are considered to be non-absorbing, so that ε_a and ε_b are real. Second, only one of the constituents is assumed to be nonlinear, i.e., $\chi_{ijkl}^b = 0$. Finally,

we assume that the nonlinearity of material a is electronic in nature. These assumptions imply that

$$\chi_{1111}^a = \chi_{2222}^a = \chi_{3333}^a, \quad (45a)$$

$$\chi_{1221}^a = \chi_{1212}^a = \chi_{1122}^a = \dots = \frac{1}{3} \chi_{1111}^a. \quad (45b)$$

Therefore Eqs. (44) may be rewritten in the following manner:

$$\chi_{xxxx}^{(3)} = \chi_{yyyy}^{(3)} = f_a \chi_{1111}^a, \quad (46a)$$

$$\chi_{zzzz}^{(3)} = f_a \left(\frac{\varepsilon_{\text{eff},z}}{\varepsilon_a} \right)^4 \chi_{1111}^a. \quad (46b)$$

The off-diagonal components can be deduced trivially from the analysis given in Ref. [20]. The number of local field correction factors appearing in any component of $\chi^{(3)}$ equals the number of times the z component of the electric field appears in the term for the polarization. Thus we have

$$\chi_{xzxx}^{(3)} = \chi_{xzxz}^{(3)} = \dots = \frac{1}{3} f_a \left(\frac{\varepsilon_{\text{eff},z}}{\varepsilon_a} \right)^2 \chi_{1111}^a. \quad (47)$$

With these results we may determine the values of the tensor terms in Eqs. (40) and (43). They are

$$\hat{\mathbf{s}} \cdot \chi^{(3)}(\omega = \omega + \omega - \omega) : \hat{\mathbf{s}} \hat{\mathbf{s}} \hat{\mathbf{s}} = f_a \chi_{1111}^a, \quad (48a)$$

$$\begin{aligned} \mathbf{q}_- \cdot \chi^{(3)}(\omega = \omega + \omega - \omega) : \mathbf{q}_- \mathbf{q}_- \mathbf{q}_- &= f_a \left(\frac{\varepsilon_{\text{eff},z}}{\varepsilon_a} \right)^4 (q_z)^4 \chi_{1111}^a \\ &+ f_a (q_x)^4 \chi_{1111}^a + 2f_a \left(\frac{\varepsilon_{\text{eff},z}}{\varepsilon_a} \right)^2 (q_z q_x)^2 \chi_{1111}^a. \end{aligned} \quad (48b)$$

This completes the theoretical formalism.

Let us discuss the implications of these results. Consider first the case of an s -polarized wave. The angular dependence of ϕ^{NL} arises solely from the transmission coefficient t^s and the z component of the wave vector, k_z^s , i.e., $\phi^{\text{NL}} \propto (t^s)^2 / k_z^s$. This expression decreases monotonically with increasing angle of incidence θ_i , so the nonlinear phase shift also decreases monotonically with θ_i .

For the case of a p -polarized wave we have additional angularly dependent terms due to the tensor nature of $\chi^{(3)}$. These terms may lead to qualitatively different behavior: if the local field correction factor is greater than unity, the magnitude of the effective nonlinearity increases with increasing angle, while the transmitted electric field energy density decreases with increasing angle. Since the decrease of the transmitted energy density with increasing angle is very small near normal incidence, the nonlinear phase shift will typically increase at first. For larger angles the transmission coefficient will dominate the other angular effects and ϕ^{NL} will decrease. Thus the curve will exhibit a peak whose position is critically dependent on the relative magnitudes of the two effects, i.e., on the tensor nature of $\chi^{(3)}$ and the linear optical properties of the material. Behavior of this sort is shown in the next section, which summarizes our experimental results.

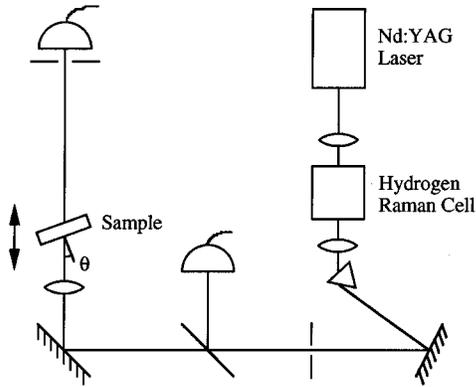


FIG. 3. Experimental setup.

III. EXPERIMENT

We have constructed layered composite samples consisting of alternating layers of titanium dioxide and the conjugated polymer poly (*p*-phenylenebenzobisthiazole) (PBZT). (See Fig. 2.) Samples were formed by spin casting alternating layers of the materials onto glass substrates. The TiO_2 layers were spin cast from a sol-gel precursor [23] and cured for 24 h at 200 °C, which yielded a linear refractive index of 2.2 ± 0.1 . To determine the linear refractive indices of the TiO_2 , as well as that of the PBZT, thick ($\sim 1 \mu\text{m}$) single layers were prepared and measured using a spectrophotometer. The sample transmission data exhibited a fringe pattern, which was used to determine the refractive index at wavelengths corresponding to the transmission peaks. These indices were fit to a Sellmeier equation, which was then used to determine the linear refractive index at the experimental wavelength of $1.9 \mu\text{m}$. The PBZT was spin cast from an isotropic solution in nitromethane- AlCl_3 , washed in methanol, and dried for 24 h under vacuum at 70 °C [24]. Its linear refractive index was 1.8 ± 0.05 . The quoted uncertainty is due to the uncertainty in the thickness of the measured samples and to the differences in the heat treatment of the different samples. The third-order susceptibility of TiO_2 is approximately 10^{-13} esu [25], which is several orders of magnitude smaller than that of PBZT. ($\chi = -2.7 \times 10^{-10}$ esu.) Therefore, for the purpose of our theoretical analysis it is reasonable to assume that the material consists of one nonlinear component and one linear component. The individual layer thicknesses in the composite were 50 nm for the TiO_2 and 40 nm for the PBZT. These thicknesses correspond to a fill fraction of 44.4% for the PBZT, which is near the ideal fill fraction given the linear parameters. The maximum enhancement of $\chi^{(3)}$ expected for this composite is approximately 35%.

The experimental setup, shown in Fig. 3, is a typical *z*-scan setup [26]. The 30-ps output pulses from a *Q*-switched, mode-locked Nd:YAG laser (where YAG denotes yttrium aluminum garnet) were Raman shifted by a high-pressure hydrogen cell, producing pulses with a wavelength of $1.9 \mu\text{m}$ and pulse energy of approximately 200 μJ . These pulses were focused by a 30-cm focal length lens and detected in the far field through a 2-mm-diam aperture. Part of the energy was split off before the lens and was used

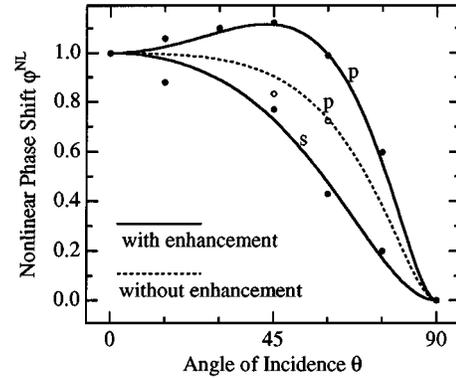


FIG. 4. Measured nonlinear response of the PBZT-titanium dioxide composite for both *s*- and *p*-polarized light (solid dots) and of pure PBZT for *p*-polarized light (open dots). The solid curves show the theoretical predictions and the dashed curve shows the expected behavior if there is no local field enhancement of $\chi^{(3)}$.

as a reference. A computer selected pulses within a reference energy window and averaged between 50 and 100 shots for each *z* position of the sample.

The result of a *z* scan is a dispersive shaped curve of transmittance versus sample position. It is shown in Ref. [26] that for a thin sample and a small aperture, the change in the normalized transmittance from the peak of the curve to the valley (ΔT_{pv}) is directly proportional to the nonlinear phase shift imparted on the beam, i.e.,

$$\Delta T_{pv} = 0.406 |\Delta \Phi_0| \quad \text{where} \quad \Delta \Phi_0 = k_0 n_2 I L_{\text{eff}}.$$

As stated previously, the sample was oriented at various angles with respect to the beam axis. The results of the measurements are shown in Fig. 4. The vertical axis represents the normalized value of ΔT_{pv} . The solid dots are the actual data points and the solid lines show the best-fit theoretical predictions. For these lines the ratio $n_a/n_b = 1.33$ was used. This value is slightly higher than the expected ratio of 1.22, but is still reasonable given the uncertainties in the refractive indices of spin cast materials. The dashed line shows the prediction in the artificial case in which local field effects are assumed not to enhance the nonlinearity for the *p* polarization. This line decreases monotonically and thus cannot fit the data. The good agreement between the data and the theoretical lines indicates that local field effects do play an important role and enhance the nonlinear susceptibility.

Another possible explanation for the observed angular dependence of the nonlinear phase shift would be an anisotropy of the polymer layers; the nonlinear susceptibility could be larger in the normal direction due to molecular orientation. (However, for a rigid rod polymer such as PBZT, spin casting is more likely to produce an anisotropy with the larger nonlinearity in the plane of the material.) To demonstrate that this is not the case for our composites, thin single-layer samples of the polymer were cast and then measured in our *z*-scan setup. The results are represented by the open dots in Fig. 4. Notice that these points follow the dashed curve, which is the theoretical prediction for *p*-polarized light inci-

dent on an isotropic material without local field effects. These results demonstrate that our polymer layers are isotropic.

IV. CONCLUSION

In summary, we have derived an expression predicting the results for a z -scan measurement of a uniaxial material (with optic axis normal to the surface) oriented at arbitrary angle with respect to the beam axis. We have then applied this result to the effective-medium representation of layered composite materials. We have constructed layered composites out of titanium dioxide and the conjugated polymer PBZT and have measured their nonlinear optical response in a z -scan setup. Good agreement between experimental data and the

theory has been found, indicating the accuracy of the effective medium predictions.

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