

## Nonlinear optical properties of nanocomposite materials

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**Abstract.** This paper reviews some of the authors' recent research aimed at obtaining an understanding of the physical processes that determine the linear and nonlinear optical properties of nanocomposite materials. One result of this research is the prediction and experimental verification that under proper conditions two materials can be combined in such a manner that the nonlinear susceptibility of the composite exceeds those of the constituent materials. This paper also presents a survey of the various geometrical structures of composite materials.

### 1. Introduction

A common approach to the development of nonlinear optical materials entails searching for materials that possess, at the molecular level, desirable nonlinear optical properties. An alternative approach, which will be explored in this paper, entails combining known materials into a composite material. Under proper conditions, this composite material might combine the more desirable properties of the starting materials, or ideally, might possess properties superior to those of the starting materials.

Some of the commonly encountered structures of composite materials are shown in figure 1. The Maxwell Garnett [1] geometry consists of small inclusion particles embedded in a host material. The Bruggeman [2] geometry consists of two intermixed components. These two model geometries are the structures most often encountered in theoretical discussions of composite materials. Two additional structures are that of porous silicon and that of layered materials. Recent research [3] has shown that an electrochemical etching procedure can be used to turn silicon into a porous structure. The resulting structure then contains 'worm holes' which can be modelled as cylindrical columns in which the silicon has been eaten away from the host material. When still more material has been eaten away, the resulting structure can be modelled as cylindrical columns of silicon surrounded by voids. In either case, the voids can be filled with a second material to form a composite structure. These composite materials can be thought of as a two-dimensional version of the Maxwell Garnett structure. Research on porous silicon is still quite new and will not be discussed further in this paper. The final structure illustrated in figure 1 is the layered geometry, consisting of alternating layers of two materials with different linear and nonlinear optical properties.

In all of the structures shown in figure 1, we assume that the two materials are intermixed on a distance scale much smaller than an optical wavelength. Under these conditions, the propagation of light can be described by effective values of the optical constants that are obtained by performing a suitable volume average of the local optical response of the material. In fact, performing such an average can be rather subtle for situations involving the nonlinear optical response, because it is the nonlinear polarization that must be averaged, and the nonlinear polarization depends on the spatially inhomogeneous electric field amplitude

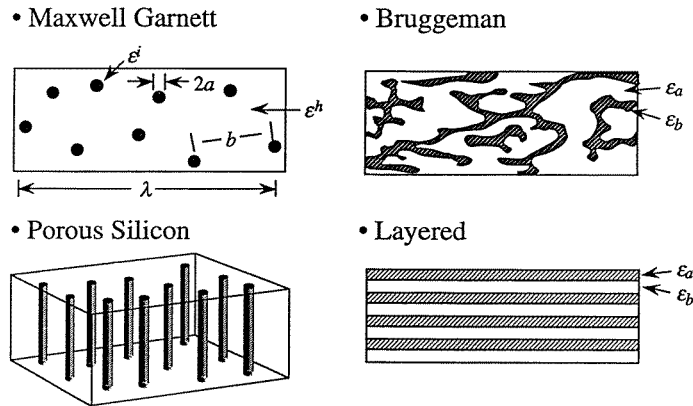


Figure 1. Some examples of composite nonlinear optical materials.

in the composite material. The results of some of these calculations are described below. We will, however, make the assumption that the spatial extent of each region is sufficiently large that we can describe its response using macroscopic concepts such as susceptibilities rather than using microscopic concepts such as polarizabilities. Roughly speaking, this assumption requires that many molecules be contained in even the smallest region of each component.

The optical properties of composite materials can in many ways be understood in terms of local field effects. In standard discussions of the optical properties of homogenous materials, one introduces the concept of the local field [4]

$$E_{loc} = E + \frac{4\pi}{3} P \quad (1)$$

as the effective field that acts to polarize an individual molecule. By performing a spatial average of the response of the total system, one can derive the Lorentz–Lorenz law

$$\varepsilon = 1 + 4\pi L N \alpha \quad (2)$$

where  $L$  is a local field correction factor

$$L = \frac{1}{1 - \frac{4}{3}\pi N \alpha} = \frac{\varepsilon + 2}{3}. \quad (3)$$

This model can be extended to the nonlinear optical response. One finds, for example, [4, 5] that

$$\chi^{(3)}(\omega_4, \omega_3, \omega_2, \omega_1) = L(\omega_4)L(\omega_3)L(\omega_2)L(\omega_1)N\gamma \quad (4)$$

where  $\gamma$  is the second hyperpolarizability. Note that the local field correction factor appears to fourth order in this expression. In the theory of composite materials, one finds that the effective nonlinear susceptibility has a form analogous to that of (4) where the local field factor now provide a measure of how the average electric field in a given component of the composite is related to the spatially averaged electric field. Since this correction factor appears to high order (fourth order for  $\chi^{(3)}$ ) one expects that the enhancement of the nonlinear response can become large. Such behaviour will be illustrated in the specific examples shown below. We next turn to a more detailed discussion of some of the geometries illustrated in figure 1.

## 2. Layered geometry composites

We have performed theoretical [6] and experimental [7] studies of the nonlinear optical response of composite optical materials possessing a layered structure. Materials of this sort are inherently anisotropic. For light polarized parallel to the layers of the structure, we find that both the linear and nonlinear optical susceptibilities are given by simple volume averages of the properties of the constituent materials, that is,

$$\epsilon_{\text{eff}} = f_a \epsilon_a + f_b \epsilon_b \quad \text{and} \quad \chi^{\text{NL}} = f_a \chi_a^{\text{NL}} + f_b \chi_b^{\text{NL}}. \quad (5)$$

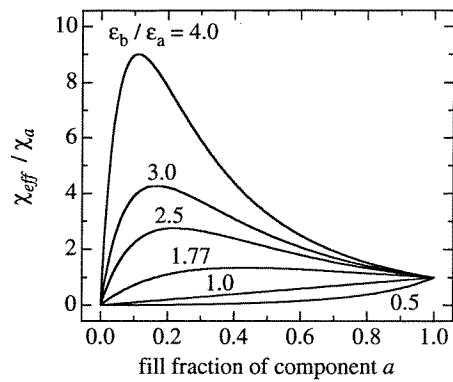
Here  $f_a$  and  $f_b$  denote the volume fill fractions of components a and b. However, for light polarized perpendicular to the plane of the layers the linear dielectric constant is given by

$$\frac{1}{\epsilon_{\text{eff}}} = \frac{f_a}{\epsilon_a} + \frac{f_b}{\epsilon_b} \quad (6)$$

and the third-order susceptibility is given by

$$\chi_{\text{eff}}^{(3)}(\omega = \omega + \omega - \omega) = \left| \frac{\epsilon_{\text{eff}}}{\epsilon_a} \right|^2 \left( \frac{\epsilon_{\text{eff}}}{\epsilon_a} \right)^2 f_a \chi_a^{(3)} + \left| \frac{\epsilon_{\text{eff}}}{\epsilon_b} \right|^2 \left( \frac{\epsilon_{\text{eff}}}{\epsilon_b} \right)^2 f_b \chi_b^{(3)}. \quad (7)$$

Note that the factor  $\epsilon_{\text{eff}}/\epsilon_a$  can be interpreted as a local field correction factor for component a. Equation (7) predicts that under proper conditions a layered composite material can display enhanced response. Such results are illustrated in figure 2, under the assumption that only component a of the composite displays a nonlinear response. We see that the enhancement in the nonlinear susceptibility can be as large as a factor of nine if the two constituents differ by a factor of two in their linear refractive indices. A smaller enhancement is predicted if the refractive indices of the two materials differ by a smaller factor. For example, the curve labelled 1.77 corresponds to the conditions of our initial experimental study of these effects, and it predicts an enhancement of 35%.



**Figure 2.** Predicted enhancement of the nonlinear optical susceptibility for a layered geometry composite.

Our experimental system [7] consists of alternating layers of the conjugated polymer PBZT and of titanium dioxide. Layers were spin coated with a thickness of approximately 50 nm and were cured at elevated temperatures after each deposition. After curing, the PBZT has a refractive index of 1.65 and the titanium dioxide has a refractive index of 2.2. The third-order susceptibility of PBZT is several orders of magnitude larger than that of titanium dioxide and is responsible for essentially the entire measured nonlinear response of the composite material. Since the more nonlinear constituent of the composite has the smaller linear refractive index, this composite structure is predicted to possess an enhanced nonlinear response.

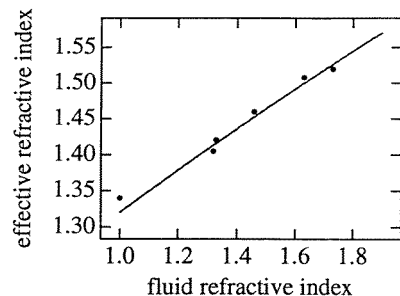
These samples were studied experimentally by measuring the nonlinear refractive index experienced by an intense light beam. The details of our measurement procedure are described in [7]. Basically, our procedure involves measuring, as a function of the angle of incidence, the nonlinear phase experienced by the incident light beam. The phase shift was measured using the induced focusing technique [8]. For s-polarized light, the measured phase shift was found to decrease uniformly with the angle of incidence. This behaviour occurs because the light intensity inside the material decreases with increasing angle of incidence because of Fresnel reflection losses. An enhancement of the nonlinear response is predicted only for p-polarized light, because in this case the electric field of the incident light wave has a component perpendicular to the planes of the layers of the composite. For p-polarized light, we find that the measured nonlinear phase shift first increases with increasing angles of incidence and begins to decrease only for larger values of the incidence angle. This behaviour was found to be in good quantitative agreement with the predictions of theory. Plans are now under way to find other materials for which an enhancement greater than 35% can be achieved.

### 3. Bruggeman geometry composites

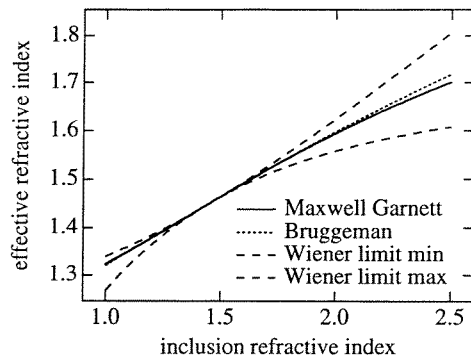
This geometry consists of two intermixed components possessing in general different linear and nonlinear optical properties. The linear optical properties are described by the equation

$$0 = f_a \frac{\epsilon_a - \epsilon_{\text{eff}}}{\epsilon_a + 2\epsilon_{\text{eff}}} + f_b \frac{\epsilon_b - \epsilon_{\text{eff}}}{\epsilon_b + 2\epsilon_{\text{eff}}} \quad (8)$$

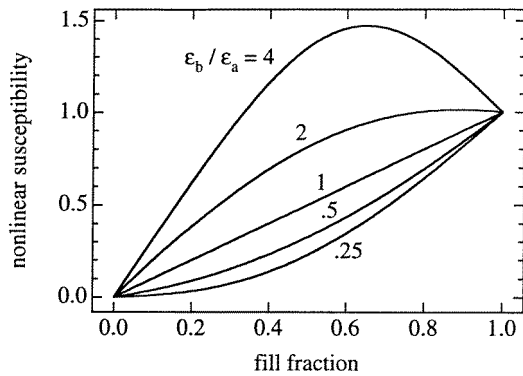
which was derived initially by Bruggeman [2]. Alternative deviations have been devised by Landauer [9] and by Aspnes [10]. We have recently tested the prediction of (8) by measuring the refractive index of material samples composed of porous glass (Corning Vycor) containing one of several different nonlinear optical liquids: diiodomethane, carbon disulphide, carbon tetrachloride and methanol. The porous Vycor glass has an average pore size of 4 nm and a 28% porosity. Results of this measurement are shown in figure 3, along with the theoretical prediction of (2). Although the agreement seen in figure 3 is extremely good, we have found that the predictions of the Maxwell Garnett model are nearly indistinguishable from those of the Bruggeman model for the present conditions at the resolution of figure 3. A comparison of various theoretical models for the effective linear refractive index is shown in figure 4. Note that the horizontal scale extends to larger values here than in figure 3. The parameters used in evaluating the various theoretical expressions are the same as in figure 3, that is,  $f_{\text{pores}} = 0.28$ ;  $n_{\text{glass}} = 1.51$ . In addition to the Bruggeman and Maxwell Garnett models, we also show the Wiener limits [11]. It has been shown theoretically that in any linear theory the effective refractive index



**Figure 3.** Measured linear refractive index of a composite material composed of a nonlinear liquid embedded in porous Vycor glass, plotted as a function of the liquid refractive index.



**Figure 4.** Comparison of the predictions of various theoretical models using the parameters relevant to Vycor glass.



**Figure 5.** Predicted enhancement of the nonlinear susceptibility, i.e.  $\chi_{\text{eff}}^{(3)}/\chi_a^{(3)}$  for a Bruggeman geometry composite plotted as a function of the fill fraction of component a.

must lie between the two limiting values which are shown. We conclude that while the present data are unable to distinguish between the Bruggeman and Maxwell Garnett models, they do validate the effective medium approach for describing the linear optical properties of composite materials and are able to rule out some of the possible models which are consistent with the Wiener limits.

Strictly speaking, the nonlinear optical properties of a Bruggeman composite structure need to be described by a statistical theory, because by assumption the two constituents are randomly interspersed. As a simplifying assumption, one can assume that the field is spatially uniform within each component. One is thereby led to the prediction [12]

$$\chi_{\text{eff}}^{(3)} = \sum_i \frac{1}{f_i} \left| \frac{\partial \epsilon_{\text{eff}}}{\partial \epsilon_i} \right| \left( \frac{\partial \epsilon_{\text{eff}}}{\partial \epsilon_i} \right) \chi_i^{(3)}. \tag{9}$$

Theoretical predictions based on this equation are shown in figure 5. Note that the theory predicts that an enhancement of the nonlinear optical response is possible, that is, the effective nonlinear optical response can exceed that of the constituents from which the composite is constructed. We are currently in the process of testing the predictions of (9) for the nonlinear optical properties.

#### 4. Maxwell Garnett geometry composites

In the Maxwell Garnett geometry, small spherical inclusion particles are imbedded in a host material. The linear optical properties of such a material have been the subject of active study ever since the time of the pioneering work on these materials by Maxwell Garnett [1].

In the linear case, the effective dielectric constant of the composite material is given by

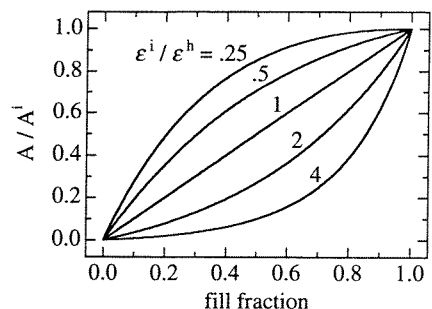
$$\varepsilon_{\text{eff}} = \varepsilon_h \left( \frac{1 + 2\beta f}{1 - \beta f} \right) \quad \text{where} \quad \beta \equiv \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h} \quad (10)$$

and where  $f$  denotes the fill fraction of inclusion material and  $\varepsilon_i$  and  $\varepsilon_h$  denote the linear dielectric constants of the inclusion and host materials, respectively. More recent work [13–15] has been devoted to the nonlinear optical properties of these materials. This work has shown that these materials can possess large optical nonlinearities, both for the case in which the inclusion particles are metallic in nature and for the case in which both constituents are dielectrics but with very different dielectric constants. Our own work has stressed this latter situation in an attempt to avoid the loss inherent to metallic materials. For this all-dielectric case, theory [14] predicts that enhancement of the nonlinear response occurs when high-index (but linear) inclusion particles are embedded in a nonlinear host, because in this case the electric field tends to be concentrated in the nonlinear constituent of the composite. Host materials that are presently under investigation include fluorescein-doped boric acid glass, rhodamine 6G and Cu-phthalocyanine; inclusion materials include titanium dioxide and semiconductor nanocrystallites. To date, our experimental studies of these materials have been thwarted by the clumping of inclusion particles that tends to occur at large packing densities, leading to unacceptably large scattering losses.

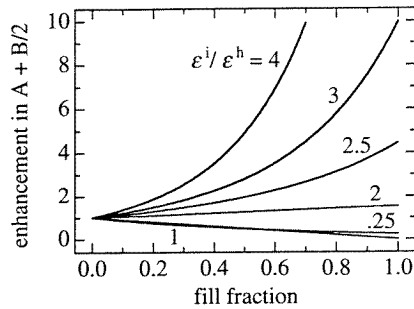
The predictions of the Maxwell Garnett model are shown explicitly in figures 6 and 7. Figure 6 refers to the case in which nonlinear inclusion particles are imbedded in a nonlinear host, both of which are assumed to be lossless, i.e. to be dielectrics. The theory of [15] then predicts that the effective value of  $A = 6\chi_{1122}^{(3)}(\omega; \omega, \omega, -\omega)$  is related to that of the inclusion particles  $A_i$  by

$$A = \left| \frac{\varepsilon + 2\varepsilon_h}{\varepsilon_i + 2\varepsilon_h} \right|^2 \left( \frac{\varepsilon + 2\varepsilon_h}{\varepsilon_i + 2\varepsilon_h} \right)^2 f A_i. \quad (11)$$

We see from figure 5 that in all cases  $A$  increases uniformly with  $f$  but in no case is there an enhancement of the nonlinear response, that is, in no case does  $A/A_i$  exceed unity. Note that the Maxwell Garnett model is strictly valid only in the limit of small fill fractions, that is, for  $f \ll 1$ . The reason for this restriction is that for a dense collection of inclusion particles, the polarization induced in a given particle depends both on the average electric field in the material and on the dipole fields of its neighbouring particles. This latter contribution is not properly accounted for in Maxwell Garnett's treatment of the linear response or in our treatment of the nonlinear response. Although the limit of validity is strictly  $f \ll 1$ , in fact the Maxwell Garnett model is usually assumed to be valid for fill factors up to 0.5, above which these correlations between the polarizations of neighbouring particles become dominant.



**Figure 6.** Predictions of the Maxwell Garnett model for the case of nonlinear inclusion particles imbedded in a linear host material. The model is unreliable for fill fractions greater than approximately 50%.



**Figure 7.** Predictions of the Maxwell Garnett model for the case of linear inclusion particles imbedded in a nonlinear host material. The model is unreliable for fill fractions greater than approximately 50%.

Figure 7 shows the opposite limiting case, that is, the case of linear inclusion particles imbedded in a nonlinear host material. The prediction in this case is given by a complicated expression quoted in [15]. The expression is much more complicated in this case because the host experiences the spatially nonuniform dipole field of each inclusion particle. The predictions shown in figure 7 illustrate that in this case an enhancement of the nonlinear response is possible, for sufficiently large fill fractions and for the case where the inclusion particles possess a larger dielectric constant than the host.

## 5. Summary

We have described several different architectures for the fabrication of composite nonlinear optical materials and have reviewed current theoretical models for describing the linear and nonlinear optical properties for each such architecture. Under certain conditions such materials can give rise to an enhanced nonlinear optical response. We have also described some recent experimental investigations of these materials. We conclude that composite optical materials possess interesting and potentially useful nonlinear optical properties.

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