

# Nonlinear-optical response of porous-glass-based composite materials

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We formed composite materials with geometries approximating that of the Bruggeman model by filling the pores of a porous glass with optically nonlinear fluids spanning a range of linear refractive indices. The effective linear refractive indices of the composites were measured with a Mach-Zehnder interferometer. The effective nonlinear refractive indices were determined by the Z-scan method. In both cases good agreement between the experimental data and theoretical predictions was found. © 1997 Optical Society of America [S0740-3224(97)00808-4]

There is great interest in studying the linear- and nonlinear-optical properties of composite materials. Recent interest has been motivated by the hope that composite materials can display desirable nonlinear-optical behavior for photonic devices. However, even the determination of the linear-optical properties of composites is a problem of long standing. One of the earliest theoretical analyses was performed by Maxwell Garnett<sup>1</sup> in 1904 in an attempt to explain the colors exhibited by metal-doped glasses. He modeled the metal particles as spheres whose diameters were much smaller than an optical wavelength, replaced the spheres in the analysis with their equivalent electric dipoles, and used the Clausius-Mossotti relationship to determine the effective dielectric constant. This theory is one of the two predominant effective-medium theories in use today. The other widely used theory is that of Bruggeman,<sup>2</sup> which describes composites consisting of two interdispersed materials (see Fig. 1). The Maxwell Garnett model treats the two constituent materials asymmetrically (inclusion particles in a host material), whereas the Bruggeman model treats the constituents symmetrically. There are conditions for which the predictions of the two models differ greatly. The Maxwell Garnett theory correctly predicts features (such as the surface plasmon resonance frequency for metallic particles) when one constituent occupies a small volume fraction of the whole but becomes inaccurate when the two constituents occupy comparable volume fractions. On the other hand, the Bruggeman theory may be accurate when the two materials occupy comparable volume fractions of the composite. One of the important predictions of the Bruggeman model is the percolation threshold; as the volume fraction of one mate-

rial is increased, the grains of the material link and form chains percolating through the composite. Because of assumptions regarding the composite geometry used in the derivation,<sup>3</sup> the model predicts that this threshold will occur at a volume fraction of 33%. The Maxwell Garnett model does not predict a percolation threshold.

The effective nonlinear-optical properties of composites have received considerable interest only in recent years. Jain and Lind<sup>4</sup> first measured the nonlinear refractive index of semiconductor-doped glasses in 1983. Flytzanis and coworkers performed the first measurement of the nonlinear response of metal colloids.<sup>5</sup> Subsequently they performed experiments on and formulated theories describing glasses doped with metal colloids or semiconductor nanocrystallites to determine their effective nonlinear refractive indices.<sup>5-7</sup> Numerous other authors<sup>8-16</sup> have contributed to our understanding of such composites.

Whereas a large volume of research has been directed toward Maxwell Garnett-style composites, only a small volume has been directed toward Bruggeman-style composites. Several theories<sup>17,18</sup> derive general expressions for the effective optical constants of composites into which one can place the geometric parameters of a Bruggeman composite to determine an explicit prediction. Zeng *et al.*<sup>17</sup> derived a simple theory based on the assumptions that the electric field within each constituent is uniform and that the nonlinearity makes only a small contribution to the refractive index. In this case one can simply perform a Taylor expansion of the expression for the effective dielectric constant to determine the effective nonlinear susceptibility. The expression derived in this manner is

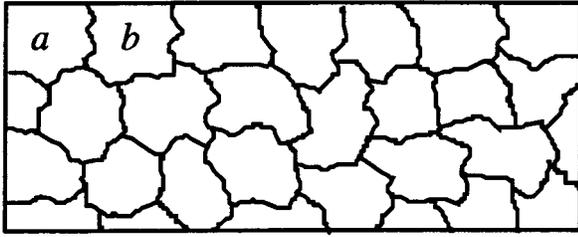


Fig. 1. Bruggeman composite geometry.

$$\chi_{\text{eff}}^{(3)} = \frac{1}{f_a} \left| \frac{\partial \epsilon_{\text{eff}}}{\partial \epsilon_a} \right| \left( \frac{\partial \epsilon_{\text{eff}}}{\partial \epsilon_a} \right) \chi_a^{(3)} + \frac{1}{f_b} \left| \frac{\partial \epsilon_{\text{eff}}}{\partial \epsilon_b} \right| \left( \frac{\partial \epsilon_{\text{eff}}}{\partial \epsilon_b} \right) \chi_b^{(3)}, \quad (1)$$

where for a Bruggeman-type composite the effective linear dielectric constant is given by

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

To achieve some intuition regarding the predictions of Eq. (1), we plotted the effective third-order susceptibility versus fill fraction of constituent *a*, assuming that only constituent *a* displays a nonlinear response (see Fig. 2). The ratio of the linear dielectric constants of the constituents is used as a parameter. From Fig. 2 it is seen that the effective nonlinearity is below the weighted average value [ $f_a \chi_a^{(3)}$ ] if the ratio  $\epsilon_b/\epsilon_a$  is less than unity and is above this value if the ratio is greater than unity. This is due to the local field effects; the electric field is nonuniformly distributed between the two constituents. When the dielectric constant of constituent *a* is smaller than that of constituent *b*, the electric field in *a* is larger than the average, so the effective nonlinear response is also larger than the weighted average (and vice versa). Note that this local field effect can lead to an enhancement of the overall nonlinearity, i.e., there are conditions for which the effective nonlinearity of the composite is larger than that of the pure nonlinear material.

Previous studies describing the nonlinear optical properties of Bruggeman geometry composites are entirely theoretical. To our knowledge, no experimental determination of the effective nonlinear susceptibility of such composites has been performed. In this paper we describe our efforts along this line. We have formed composites of porous glass saturated with various nonlinear fluids.

The glass matrix used for the composite was Corning Vycor glass,<sup>19–21</sup> which is a mostly silica glass (with approximately 4% impurities) whose linear refractive index is 1.46.<sup>20,21</sup> It is an open-cell, porous glass with void space of approximately 28% of the volume<sup>19,20</sup> and an average pore diameter of 4 nm. The pores interconnect throughout the samples. Therefore it is reasonable to expect that composites made with porous Vycor should be described by a Bruggeman model, which predicts a percolation threshold. (However, it is important to remember that the Bruggeman model predicts a percolation threshold of 33%, whereas this actual material exhibits percolation at a lower volume fraction.)

The first step in preparing the samples was to clean the Vycor glass by placing it in a 30% hydrogen peroxide solution and heating it to approximately 100 °C. After

cooling, the Vycor was rinsed in deionized water and then baked under an oxygen atmosphere. The temperature of the oven was slowly increased from room temperature to 100 °C (at a rate of 1 °/min) to allow the water to escape the glass without causing damage. After the samples were baked at this temperature for 1 h the temperature was increased rapidly to 300 °C and the glass was baked for several hours. The samples were then cooled and immersed in the nonlinear fluids immediately to avoid contamination. The glass absorbed the liquids quickly; the samples appeared completely saturated within minutes of immersion.

The fluids were selected for their range of linear refractive indices. At a wavelength of 532 nm the refractive index of methanol is approximately 1.32; that of carbon tetrachloride, 1.46; that of carbon disulfide, 1.63; and that of diiodomethane, 1.72. For the measurement of the effective linear refractive index several additional fluids, air, water, and a Cargille index fluid with a linear refractive index of 1.78, were used to increase this range.

Most methods used to determine refractive indices (refractometry, ellipsometry, prism angular deviation, etc.) rely on reflection and refraction at surfaces. However, effective-medium theories are based on volume averages; the surface may not be a valid representation of the whole. Additionally, the nature of the composites precludes the possibility of a high-quality, optically flat surface. Thus it was unlikely that any of the aforementioned methods would yield a reliable estimate of the refractive index. A method that depends on propagation of light through the bulk material was required.

The solution was to use a Mach–Zehnder interferometer (see Fig. 3). A helium–neon laser was used as the source. Each sample was mounted upon a high-resolution rotation stage with rotational accuracy of 1 arc-min and was immersed in a large cell containing the same fluid that filled the pores of the Vycor glass. This procedure avoided the potential difficulty of fluid evaporation from the surface of the composite. First the sample was rotated until the laser beam was normally incident. This result was accomplished by observation of the fringes:

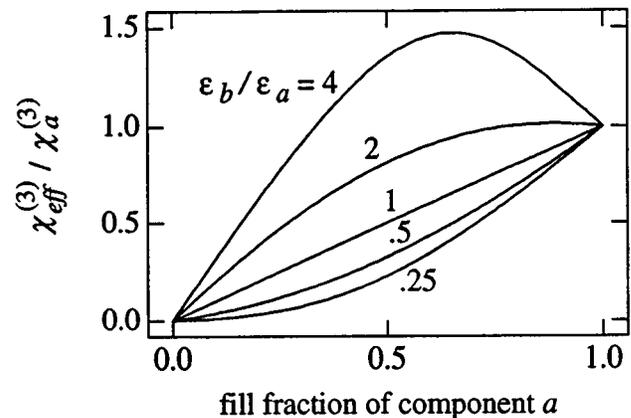


Fig. 2. Theoretical predictions of the Bruggeman model for the effective third-order susceptibility plotted versus volume fill fraction of constituent *a*. It is assumed that only constituent *a* displays a third-order nonlinearity. The ratio of the linear dielectric constants is used as a parameter.

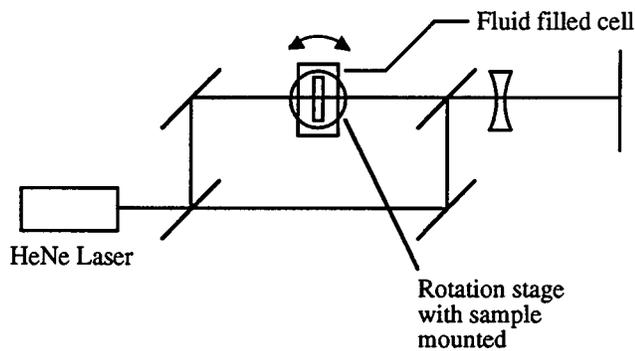


Fig. 3. Experimental setup used to measure the linear refractive index of the composites.

As the sample rotated, the fringes shifted in one direction until normal incidence was achieved, after which the fringes shifted in the opposite direction. From this position the sample was rotated so the fringes shifted an integral number of periods, typically 5, 10, 25, or 50 periods, corresponding to phase shifts of  $\pm 10\pi$ ,  $\pm 20\pi$ ,  $\pm 50\pi$ , and  $\pm 100\pi$ , respectively. (The sign of the phase shift depended on the refractive index of the fluid: Fluids with smaller indices than that of silica glass yielded positive phase shifts; fluids with larger indices than that of silica glass yielded negative phase shifts.) The angle corresponding to each phase shift was recorded. Based on this angle and on knowledge of the linear refractive index of the fluid, the linear refractive index of the composite was determined. (Note: The porosity of several of the glass samples was measured and found to be nearly 28% in all cases, so this number was used in all the analyses.)

The results of the measurements are given in Table 1 and displayed in Fig. 4, which plots the effective index versus the index of the fluid. The solid line depicts the Bruggeman prediction assuming a volume fill fraction of the fluid of 28% and a refractive index of the glass of 1.46. Very good agreement between theory and experiment was found, implying that the Bruggeman theory models the linear-optical properties of these composites well.

The nonlinear susceptibilities of the composites were measured with a standard Z-scan<sup>22</sup> setup. The samples were pressed between two microscope cover slips to prevent fluid evaporation from the surface. (A fluid-filled cell was not used for these measurements because any layer of pure fluid between the sample and the cell window would make the data analysis difficult.) For those samples filled with a fluid that evaporated readily, a dropper was used to wet the sample edges during the scan so that no fluid could escape from the region intersecting the laser beam. The laser used for the measurements was a Q-switched, mode-locked Nd:YAG laser, which produced 30-ps pulses at a 10-Hz repetition rate. The pulses were doubled to a wavelength of 532 nm. Before the beam reached the sample, a beam splitter directed part of the energy onto a pulse energy meter. In this way a computer could select only those pulses within a narrow energy range, thus minimizing the effects of shot-to-shot fluctuations. The signal was detected in the far field (through an aperture) by another pulse energy meter head. The computer collected a user-defined number of shots (typically 10 to 50) at each sample  $z$  position and

controlled a translation stage to move the sample. Two scans were necessary for each data point: one of the composite and one of a cell of the pure fluid. These two scans were performed one immediately following the other at the same reference energy to ensure that the laser characteristics were the same in each case.

Data analysis was performed in two ways. In the first method the data were normalized to unity at sample positions far from the beam focus and the difference between the maximum signal energy and the minimum signal energy was determined. This was a direct measurement of the desired Z-scan parameter  $\Delta T_{pv}$ . The ratio of the values of  $\Delta T_{pv}$  for the two scans yielded a value proportional to the ratio of the two nonlinear susceptibilities. (To determine the actual ratio of the nonlinear susceptibilities, it was necessary to multiply by the ratio of the linear refractive indices of the samples.) In the second method, the data were fitted to a curve describing the results of a Z scan of a thin sample with a weak nonlinearity (see, e.g., Ref. 22). The formula used was the following:

$$T = T_n + \frac{4x\Delta\phi}{(1+x^2)(9+x^2)}, \quad (3)$$

where

**Table 1. Comparison of Experimentally Determined Effective Refractive Indices with Those Predicted by the Bruggeman Theory**

Fluid	$n$ (fluid)	$n$ (Effective)	
		Experiment	Theory
Air	1.00	1.34	1.327
Methanol	1.32	1.40	1.420
Water	1.33	1.42	1.423
Carbon tetrachloride	1.46	1.46	1.460
Carbon disulfide	1.63	1.50	1.507
Diiodomethane	1.72	1.51	1.531
Index fluid	1.78	1.54	1.547

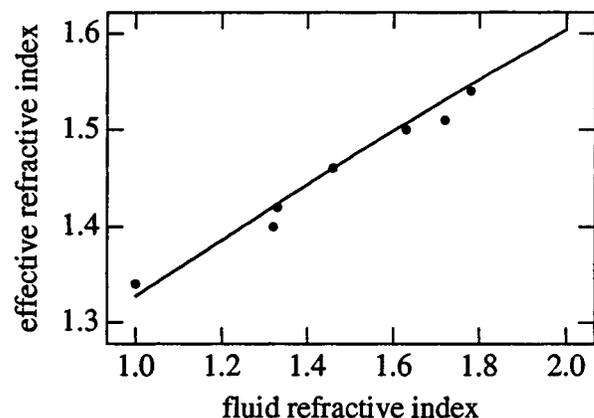


Fig. 4. Effective refractive index of porous Vycor glass filled with fluids of various refractive indices versus the fluid refractive index. Solid line, theoretical prediction of the Bruggeman model.

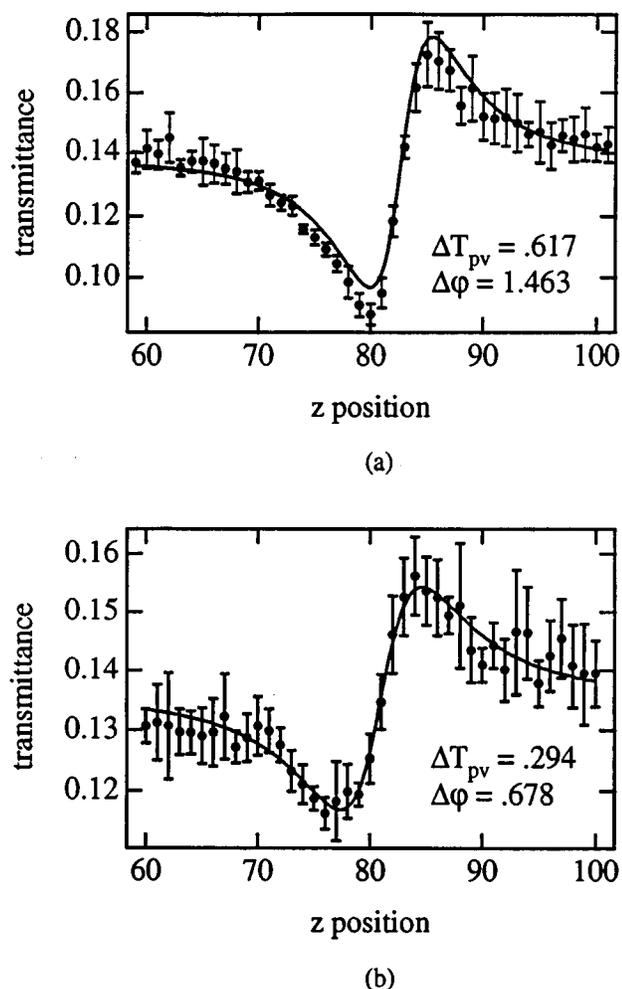


Fig. 5. Typical Z-scan data. Error bars, one standard deviation to each side of the mean. Solid curves, best fits of Z-scan thin sample formula. (a) 4-mm-thick sample of pure carbon tetrachloride. (b) 4-mm-thick Vycor glass-carbon tetrachloride composite.

$$x \equiv \frac{z - z_f}{z_0}. \quad (4)$$

Inasmuch as the data were not normalized and the beam focus was not at the zero position of the translation stage, four parameters were used in the fit: the phase shift  $\Delta\phi$ , the confocal parameter  $z_0$ , the position of the focus  $z_f$ , and a normalization parameter  $T_n$ . The desired result is the phase shift divided by the normalization parameter.

The ratio of the normalized phase shifts of the two scans again yielded a value proportional to the ratio of the susceptibilities. This second method should, of course, yield the same value as the first method. Typically the values were indeed very close to each other. The benefit of using two methods occurs when the data set is of poor quality. Poor quality data do not produce agreement between the two methods, and also the second method yields a large chi-square value describing the fit of the theoretical curve.

A typical pair of Z scans is shown in Fig. 5. In this case the composite consists of porous Vycor glass filled with carbon tetrachloride. The filled circles represent the average signal, and the error bars represent plus and minus one standard deviation from the mean. The solid curves are the best-fit theoretical curves for the data. A comparison of the results of the two data analysis methods shows good agreement. The ratio of the change in transmission parameters ( $\Delta T_{pv}$ ) yields a value of 0.48; the ratio of the phase shifts ( $\Delta\phi$ ) yields a value of 0.46. In addition, the chi-square values for the fits are small, indicating good fits.

This particular scan is an important one for the following reason: The linear refractive index of carbon tetrachloride is to high accuracy the same as that of the glass, so the local field effects are trivial for this composite. Thus the total nonlinear susceptibility is simply the weighted average of the nonlinear susceptibilities of the constituents, i.e.,

$$\chi_{\text{eff}}^{(3)} = f_a \chi_a^{(3)} + f_b \chi_b^{(3)}. \quad (5)$$

Therefore it is possible to use this measurement to determine the nonlinearity of the glass relative to that of carbon tetrachloride. We determined the relation to the other fluids by measuring the nonlinearities of the fluids relative to that of carbon tetrachloride. This procedure was necessary because the nonlinear susceptibility of the glass was not negligible compared with those of several of the nonlinear fluids.

The results of the measurements are given in Table 2. (The asterisk next to the theoretical entry for carbon tetrachloride is a reminder that this value agrees with the experimental result by assumption according to our data analysis procedure.) We see by comparison with the experimental results that the predictions of the Bruggeman model give reasonable estimates of the effective nonlinearity. In all cases the experimental results follow the trend indicated by the theory, and the differences between the theoretical and the experimental values are

**Table 2. Comparison of Experimentally Determined Nonlinear Susceptibilities with Those Predicted by Bruggeman and Maxwell Garnett Theories**

Fluid	Fluid Index	Experiment		Nonlinear Bruggeman Theory, $\chi_{\text{eff}}^{(3)}/\chi_{\text{fluid}}^{(3)}$ <sup>a</sup>	Naive Theory, $\Sigma f_i \chi_i^{(3)}$
		$\chi_{\text{glass}}^{(3)}/\chi_{\text{fluid}}^{(3)}$	$\chi_{\text{eff}}^{(3)}/\chi_{\text{fluid}}^{(3)}$		
Methanol	1.33	0.62	0.80	0.750	0.726
Carbon tetrachloride	1.46	0.32	0.51	0.51*	0.510
Carbon disulfide	1.63	0.00	0.25	0.231	0.280
Diiodomethane	1.72	0.03	0.20	0.222	0.302

<sup>a</sup> Asterisk, theory and experiment for carbon tetrachloride in Vycor glass agree by assumption according to our data analysis procedure.

small. Thus this theory does model the optical properties of these composites well. For comparison purposes, we have included the predictions of a naïve model in Table 2. In this simple model the effective nonlinear susceptibility is taken to be the weighted average of the nonlinear susceptibilities of the constituents. It can be seen from the table that this model yields predictions worse than those of the Bruggeman model in all cases except that of carbon tetrachloride in Vycor, for which by construction the predictions are identical. To quantify this comparison, we note that the normalized mean-square difference between theory and experiment, that is,  $Q = \sum_i [r_i(\text{expt})/r_i(\text{theory}) - 1]^2$ , where  $r_i = \chi_{\text{eff}}^{(3)}/\chi_{\text{fluid}}^{(3)}$  for fluid  $i$ , is given by  $Q = 0.021$  for the nonlinear Bruggeman model and  $Q = 0.136$  for the naïve model. Therefore the Bruggeman model is the superior model for these materials.

In summary, we have measured the effective linear and nonlinear refractive indices of porous-glass-based composites and compared the results with the predictions of the Bruggeman model. Good agreement between theory and experiment was found, indicating the utility of this effective medium theory. These results are significant because the model predicts that it is possible to construct composites that display enhanced nonlinear-optical response. For the Bruggeman model the maximum enhancement that can be reasonably expected is approximately 50%, but models for other composite geometries<sup>14,23</sup> predict larger enhancements. The good agreement between theory and experiment found in the present study suggests that these large enhancements may be achievable and that these composite materials may be useful for improving the performance of photonic devices.

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