Nonlinear optical scattering and absorption in bismuth nanorod suspensions

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The authors present the results of optical limiting measurements of ~ 10 nm wide bismuth nanorods suspended in chloroform. Their Z-scan measurements reveal that optical limiting under 532 nm excitation stems from a strong nonlinear scattering (NLS) subsequent to nonlinear absorption (NLA) by suspension. On the other hand, the optical limiting is entirely due to NLA when excited with 1064 nm excitation in the nanosecond regime. The occurrence of NLS at one wavelength and absence at another is unusual, especially when compared to the behavior of carbon nanotubes under similar conditions, in which NLS is dominant at both wavelengths. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2776020]

Nonlinear optical (NLO) measurements in low-dimensional materials continue to draw considerable attention since the nonlinear behavior of the complex refractive indices lead to unique optical phenomena.[1–3] For example, optical switching, saturable absorption, and optical limiting properties of one-dimensional nanomaterials have shown considerable promise. Of interest to this letter are the NLO properties of Bi nanostructures which are known to exhibit interesting linear optical properties relative to those present in the bulk form. A semimetal to semiconductor transition occurs in the low-dimensional forms due to quantum confinement effects and has been experimentally confirmed in Bi nanoparticles[4] and nanowires.[5–7] When such a transition occurs, it is expected that several material properties undergo a radical change. For example, the thermoelectric figure of merit is poor in bulk Bi due to nearly equal and opposite contributions from electrons and holes but is high, ~ 2, in small diameter Bi nanowires.[8,9] Herein, we report a similar change in the optical limiting properties of Bi in going from bulk to the one-dimensional form.

We used visible and IR laser pulses from a Nd doped yttrium aluminum garnet laser (Quanta system, 7 ns, 10 Hz at both 532 and 1064 nm) to measure the optical limiting performance of Bi nanorod suspensions by the Z-scan technique at room temperature (~ 300 K).[10] To separate the contributions of nonlinear absorption (NLA) and nonlinear scattering (NLS), we use a Z-scan setup following Jourdier *et al.*[11] (Fig. 1). Scattering involves the spatial redistribution of beam intensity over a cross-sectional area larger than that of the incident beam leading to two components in the beam transmitted through the sample—the *unscattered* part ("dark-filled" central region) and the *scattered* part ("faded" region).

The beam is split 50:50 (BS2) to reach two detectors D2 and D3 to measure the transmittance T of the sample with detector D1 as a reference. A 2 in. wide lens (L4) collects light both from the scattered and unscattered parts making D2 insensitive to transmittance changes due to spatial redistribution. This ensures that our collection efficiency is $>90\%$. Thus, D2 records changes in transmittance solely due to absorptive effects and the nonlinear extinction coefficient measured by the Z-scan curve is only due to contributions from NLA. On the other hand, D3 detects only the unscattered part since aperture (A) can be adjusted to prevent the scattered part from reaching D3. Therefore, D3 records a reduced transmittance due to NLS and NLA unlike the case of D2. Venkatram *et al.*[12] recently used a similar configuration for quantitative studies on CdS nanocrystals.

Crystalline Bi nanorods were prepared using a pulsed laser vaporization (PLV) technique as described in Ref. 9. The inset panels in Fig. 2 show the transmission electron microscope (TEM) images for isolated Bi nanorods [inset
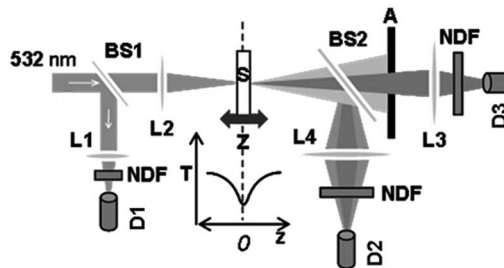

FIG. 1. Schematic of the experimental setup used in this study. A combination of lenses (L1–L4), beam splitters (BS1 and BS2), neutral density filters (NDFs), aperture A, and detectors (D1–D3) are used to measure contributions to optical limiting from the scattered and unscattered components for sample S.
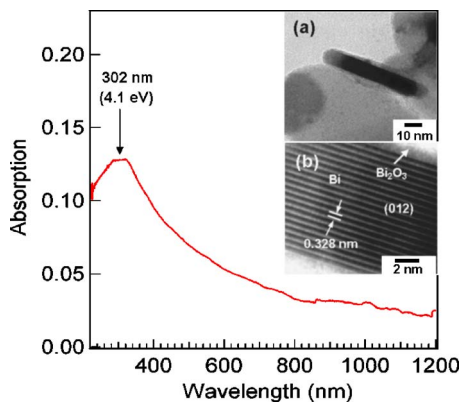
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FIG. 2. (Color online) UV-visible aborption of Bi nanorod suspension in the range of 200–1200 nm. The broad peak at 302 nm is due to surface plasmons. TEM images of isolated Bi nanorods encased inside a thin oxide layer (inset a) and the crystalline planes (012) of trigonal Bi (inset b).

(a)] with a lattice spacing of 0.328 nm [inset (b)] corresponding to the trigonal structure encased inside a thin Bi_2O_3 layer (<2 nm in thickness). The dominant width and length of the nanorods were found to be ~10 and ~200 nm, respectively.[9] The UV-visible absorption spectrum (Fig. 2) of the Bi nanorods suspended in chloroform was recorded on a Perkin-Elmer Lambda 950 spectrometer. About 0.5 mg of Bi nanorod sample was dispersed in 25 ml of chloroform to obtain a stable suspension without the addition of any surfactant. A broad surface plasmon (SP) peak at 302 nm (4.1 eV) is observed and is redshifted relative to the 281 nm plasmon absorption peak (4.4 eV) reported for 6.5 nm Bi nanoparticles.[4] Interestingly, the bulk form does not possess this spectral feature and we will return to the significance of this SP peak after discussing the NLO data for the Bi nanorod suspensions.

The intensity variation along the beam propagation direction (z) in a medium having a third order nonlinearity is described as $dI/dz = -\alpha_0 I - \alpha_2 I^2$, where α_0 is the linear absorption coefficient and α_2 is the total nonlinear extinction coefficient. The coefficient α_2 is a sum of contributions from both NLA (α_{2A}) and NLS (α_{2S}): $\alpha_2 = \alpha_{2A} + \alpha_{2S}$. The position dependent transmittance (the "Z-scan curve") is given by[3,10] $T(z) = [1/\pi^{1/2}] \int_{-\infty}^{+\infty} \ln[1+q(z)\exp(-\zeta^2)]d\zeta$, where z is the sample position with respect to the focus and $q(z) = \alpha_2 I_0 L/[1+(z/z_0)^2]$, with I_0 being the peak intensity at the focal point. L is the effective length of the sample given by $[1-\exp(\alpha_0 l)/\alpha_0]$, where l is the sample length, and $z_0 = \pi\omega_0^2/\lambda$ is the Rayleigh range, where ω_0 is the beam waist radius at focus and λ is the wavelength of light. The value

for α_2 is obtained by fitting the $T(z)$ equation to the experimental data. In the context of our experiment, the Z-scan curve of D3 gives α_2 and the D2 curve is fit with α_{2A}. Thus, α_{2S} can be extracted.

The Z-scan curves for the Bi nanorod suspension (optical transmittance of 60%) in a 1 mm cuvette (made of fused silica) under a 55 μJ, 532 nm (7 ns) excitation, are shown in Fig. 3. The suspension remained stable for ~6 h which permitted us to collect reliable data from Z-scans that lasted ~10 min each. Figure 3(a) shows the Z-scan curves recorded by detectors D2 (NLA alone) and D3 (NLA and NLS). The depth of the valley in the Z-scan curve is a direct measure of the extent of optical limiting, and is different in the D2 and D3 curves with dips of ~0.65 and ~0.25, respectively. Since, D2 records the contribution due to NLA alone and the D3 curve has contributions of NLS added to this, it is clear that NLS induced by NLA makes a significant contribution to the total extinction. In fact, the contribution of NLS to optical limiting is greater than that due to NLA. Interestingly, in the case of 1064 nm excitation (55 μJ, 7 ns) the D2 and D3 curves overlap [Fig. 3(b)] and the minimum transmittance in both the cases is ~0.75. Thus, NLS is absent at 1064 nm, and only NLA makes a contribution to the total extinction observed at this wavelength. At 532 nm, however, both NLA and NLS are responsible for the observed optical limiting unlike the 1064 nm case. This is very unlike the behavior of carbon black and single and multiwalled carbon nanotubes in suspensions, where NLS dominates at both 532 and 1064 nm excitations.[13,14] Lastly, it should be mentioned that we also performed measurements on bulk metallic Bi (●) and Bi_2O_3 (○) powders suspended in chloroform [inset of Fig. 3(b)]. These additional experiments were needed to unambiguously rule out contribution from residual Bi and Bi_2O_3 to the features described in Fig. 3.

These observations can be explained using the following phenomenology. A small band overlap (~38 meV) makes bulk Bi a semimetal with a small electron effective mass in the range of $0.001m_0 - 0.26m_0$, depending on the crystalline direction.[15] When irradiated by the 532 nm laser pulses, the sample absorbs energy via interband and intraband transitions, free carrier absorption, and two-photon excitation. The presence of the SP peak (see Fig. 2) makes the absorption a "near-resonant" process. The absorbed energy is transferred to the surrounding medium through nonradiative deexcitation, resulting in localized heating. Optically induced thermal effects and heating using the SP resonance in nanoparticles are well-established and have been exploited in various applications.[16] Local change in temperature causes local re-
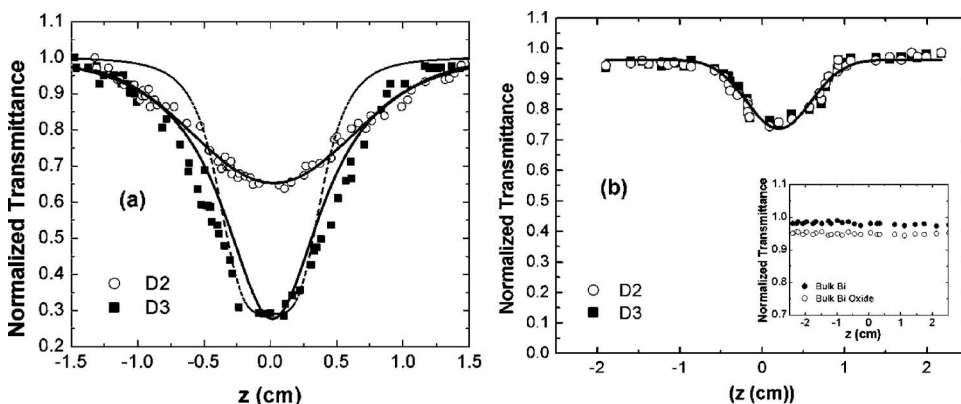

FIG. 3. (a) Z-scan curves for a Bi nanorods suspension in chloroform having linear transmittance of 60% at 532 nm excitation recorded by D2 and D3 for an input energy of 55 μJ. Solid lines show the corresponding I^2 dependent fits while the broken line shows an I^3 dependent fit for the D3 case. (b) Same as in (a) using the 1064 nm excitation for an input energy of 55 μJ. The overlapping curves confirm that nonlinear scattering is absent when excited with 1064 nm in contrast to the 532 nm case. Inset shows the "flat" Z-scan curves of the bulk Bi (●) and Bi_2O_3 (○) suspensions.

fractive index gradients (Δn) depending on the fluence (F_0), thermo-optic coefficient (dn/dT), absorption coefficient (α), density (ρ), and specific heat (C_v) of the medium since $\Delta n = (dn/dT)(F_0\alpha/2\rho C_v)$.[10,12] The refractive index gradients centered at the nanorod sites act as scattering centers. The leading part of the pulse creates these scattering centers and the remaining part of the pulse gets scattered. Hence, the nonlinear intensity dependent scattering. This mechanism has been used to explain the optical limiting behavior of carbon nanotubes as well.[14]

At 1064 nm although NLA is significant, it is much weaker than that at 532 nm where the 302 nm SP peak makes the interaction near resonant. NLA at 1064 nm is not large enough to create sufficiently strong thermal refractive index gradients (since Δn is proportional to α), at the nanorod sites which can act as scattering centers. The propensity of scattering at 1064 nm is further diminished by a factor of 16 when compared to 532 nm, considering the simple case of Rayleigh scattering (scattering cross section is proportional to λ^{-4}). Nonetheless, the nonlinear intensity dependent absorption at 1064 nm is sufficient for an appreciable optical limiting performance.

We obtained a value for the total extinction coefficient α_2 of 5.3 cm/GW for input pulses of 55 μJ at 532 nm by fitting the $T(z)$ equation in the D3 curve of Fig. 3(a). This value does not change significantly for other input optical energies of 10, 20, and 40 μJ. In Fig. 3(a) the dashed line shows a fitting for an I^3 dependence of the total extinction. Clearly the I^2 curve fits data better than the I^3 curve. Thus, higher-order contributions to the nonlinear processes are negligible. However, our value for the total extinction coefficient α_2 differs in sign and magnitude from the value of -3.97 cm/W reported by Liu *et al.*[8] for Bi films (~7 nm). Liu *et al.* postulated localized melting as the mechanism responsible for an observed giant nonlinear response under quasicontinuous wave (25 ms pulses) 532 nm excitation. The differences in the magnitude and the sign of the nonlinear coefficient are primarily due to the widely different excitation regimes and nature of the media of interest, viz., short 7 ns pulses and two-component medium (this work) and quasi-cw 25 ms pulses and a single component medium (Liu *et al.*). The quasi-cw and the single-component medium in the latter case aid accumulative effects that result in large nonlinearities in the film.

To complete this study, we also recorded the nonlinear transmittance at various incident energies for both 532 and 1064 nm excitations. Figures 4(a) and 4(b) show the *Z*-scan curves recorded by detector D3 and the guide to the eye for each curve. Fitting the $T(z)$ equation to the *Z*-scan curve of Fig. 4(b), the total extinction coefficient α_2 at 1064 nm for an input optical energy of 50 μJ was determined to be 2.4 cm/GW. Collectively, they show that the extent of optical limiting increases with an increase in the input energy of the incident optical pulse. Notwithstanding the difference in mechanism of optical limiting at 532 and 1064 nm, Bi nanorods suspensions display excellent optical limiting properties and are potential candidates for applications as broadband optical limiters.
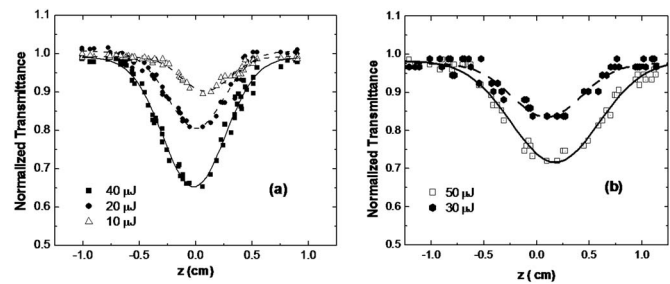

FIG. 4. *Z*-scan curves for a Bi nanorods suspension in chloroform having linear transmittance of 60% at 532 nm excitation recorded by D3, with contributions from both nonlinear absorption and scattering, for (a) 532 nm excitation at optical input energies of 10, 20, and 40 μJ and (b) 1064 nm excitation at optical input energies of 30 and 50 μJ.

In conclusion, we have synthesized ~10 nm dia. Bi nanorods using a PLV method and investigated its optical limiting properties by suspending them in chloroform. We find that the nanorod suspension displays excellent optical limiting properties at both 532 and 1064 nm excitations in the nanosecond laser pulse regime. At 532 nm excitation, both NLA and NLS contribute to the limiting process, while NLA alone is responsible for the observed optical extinction at 1064 nm excitation. This behavior is unusual vis-a-vis carbon nanotube suspensions. The presence of the characteristic SP peak at 302 nm is responsible for the observations described in this study.

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