Nonlinear optical effects and carbon nanotubes

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(December 3, 2001)

Abstract

Materials with large second or third order optical nonlinearities are of great interest for data processing in photonic computing. Since the invention of laser in 1960 by Maiman and the first discovery of nonlinear optical (NLO) effect of quartz crystals, there has been a great deal of research directed at finding new materials with higher order NLO properties. Only noncentrosymmetric or polar materials could possess second order NLO susceptibility $\chi^{(2)}$. For most third order NLO materials, their $\chi^{(3)}$'s are generally too low for practical applications. Since the discovery of carbon nanotubes, which possess optimal properties (like highest thermal conductivity, Young modulus 100 times higher than steel, zero bandgap metal, ballistic conductance, simple structure, nanometer-size and ultra-light weight) by a NEC scientist Sumio Iijima in 1991, a heat of studying and engineering the properties of carbon nanotubes has been raised worldwide. Experimentalists recently discovered that carbon nanotube is also a NLO material with amazingly high third order NLO susceptibilities. And, up to now, there is no publication about the experimental proof of the second order NLO properties of carbon nanotubes. In this paper, we will review the basic physics of NLO properties of materials, and state the reasons of high $\chi^{(3)}$ and practically zero $\chi^{(2)}$ of carbon nanotubes.

Before the invention of laser, the intensity of light is approximately 1 V/cm and nearly all materials exhibit linear relationship between the polarization of the materials and the incoming optical electric field **E**. When the high intensity (10^6-10^9 V/cm) coherence light was first provided by the first laser, which was invented by Maiman in 1960 [1], the nonlinear relationship between the averaged electric field inside material **D** and the incoming optical **E** field, as shown in Fig. 1, implying nonlinear polarization was discovered. When a red laser light enters a quartz crystal, as shown in Fig. 2, the outcoming light is blue, and this indicates that the frequency of outcoming light is doubled. This is a nonlinear optical (NLO) effect called Second Harmonic Generation (SHG). Since then, there has been a great deal of research directed at finding new materials with higher order nonlinear optical properties.

NLO effects are defined on the tensor of optical susceptibility χ, which is the transformation matrix of the incoming **E** vector to the resulting polarization **P** vector inside the material. For linear materials or incoming light with intensity $\sim$ 1 V/cm, the relation $\mathbf{P} = \chi\mathbf{E}$ is essentially linear. However, when the light intensity reaches $\sim 10^6$-10^9 V/cm, the relationship between **P** and **E** is no longer linear. For second order NLO behavior, **P** will be related with **E** as follows:

$$P = \epsilon_0(\chi^{(1)} E_0 \cos\omega t + \chi^{(2)} E_0^2 \cos^2 \omega t) \tag{1}$$

For third order NLO behavior, **P** will be related with **E** as follows:

$$P = \epsilon_0(\chi^{(1)} E_0 \cos\omega t + \chi^{(2)} E_0^2 \cos^2 \omega t + \chi^{(3)} E_0^3 \cos^3 \omega t) \tag{2}$$

The tensors $\chi^{(2)}$ and $\chi^{(3)}$ in equations (1) and (2) are second and third order NLO susceptibilities respectively.

In order to see the properties of the outcoming light, we expand equations (1) and (2) by simple trigonometry, yield the following equations (3) and (4) respectively.

$$P = \frac{1}{2}\epsilon_0\chi^{(2)} E_0^2 + \epsilon_0\chi^{(1)} E_0 \cos\omega t + \frac{1}{2}\epsilon_0 E_0^2 \cos 2\omega t \tag{3}$$

$$P = \frac{1}{2}\epsilon_0\chi^{(2)} E_0^2 + (\epsilon_0\chi^{(1)} E_0 + \frac{3}{4}\epsilon_0\chi^{(3)} E_0^3) \cos\omega t + \frac{1}{2}\epsilon_0 E_0^2 \cos 2\omega t + \frac{1}{2}\epsilon_0\chi^{(3)} E_0^3 \cos 3\omega t \tag{4}$$

$$\chi_{ijk}(2)(0;-\omega,\omega) = \chi_{ijk}(2)(\omega;0,-\omega) \tag{5}$$

According to the experimentally found relation (5) as above [3], the effects of the first and second terms in equation (3) are cancelled, leaving the last term describing the outcoming light with doubled incoming frequency. Hence this second order NLO effect causes frequency doubling. For equation (4), the effects of the first two terms are also cancelled, leaving the last two terms. If the last term is predominant, the outcoming light will possess frequency three times that of the incoming light. In order to understand the relation between centrosymmetry and NLO properties, Prasad and William have given an argument as follows [4]. Consider a third order NLO material that can exhibit polarization liked the following equations (6) or (7).

$$P_x = \alpha E + \gamma E^3 \tag{6}$$

$$P_x = \alpha E + \beta E^2 + \gamma E^3 \tag{7}$$

For materials exhibit polarization as equation (6), the relation between potential V(E) and the **E** field will be symmetrical like equation (8).

$$V_x(E) = -[(1/2)\alpha E^2 + (1/4)\gamma E^4] \tag{8}$$

The symmetrical potential of materials under the influence of an incoming optical **E** field implies that the material is centrosymmetrical that the electron polarizations in the positive and negative x direction are the same. The relation can be plotted as Fig. 3. The materials possessing centrosymmetry must have structures lower than cubic symmetry. For materials exhibit polarization as in equation (7), the potential **V(E)** is asymmetrical as the form of equation (9) below:

$$V_x(E) = -[(1/2)\alpha E^2 + (1/3)\gamma E^3 + (1/4)\gamma E^4] \tag{9}$$

Then for second order NLO materials possessing the second term of equation (7) must have an asymmetrical potential that is a symbol of noncentrosymmetry. The polarization versus **E** curve is shown in Fig. 4. Thus the basic requirement for second order NLO behavior is noncentrosymmetry. Materials possessing noncentrosymmetry are anisotropic crystals having structures from cubic to triclinic.

As the anisotropic materials generally possess second order NLO properties while the materials of third order NLO behavior are having too low $\chi^{(3)}$ for any practical applications, the search for materials having large $\chi^{(3)}$ is of first priority in NLO research. Since the discovery of carbon nanotubes (CNT) by a NEC scientist Sumio Iijima in 1991 [5], optimal properties like highest thermal conductivity [6], Young's modulus higher than steel [7], ballistic conductance [8], nanometer-size [9] and ultra-light weight [10] of CNT have been revealed by experiments. Amazingly, experimentalists recently discovered that CNT is also a NLO material with very high $\chi^{(3)}$ [11]. Carbon nanotubes are rolled-up graphene sheets with hemisphere caps. All carbon atoms in a molecule of CNT are sp^2 hybridized that each carbon atom has a π electron and 3 sharing σ orbital electrons. The π electrons are very delocalized that they can delocalized over the whole tube, while the σ electrons are very localized. The structure of carbon nanotube is composed of hexagonal benzene rings except the hemisphere caps, which have pentagons too. A benzene molecule has centrosymmetry and possesses zero $\chi^{(2)}$. When benzene is bonded with an electron donor or acceptor group, it is essentially a noncentrosymmetric molecule, and it has non-zero $\chi^{(2)}$. For symmetrical benzene has a π delocalized system, the π electron distribution is thus highly deformable, and the $\chi^{(3)}$ becomes significant. CNT has significant amount of benzene rings and forms a very efficient π delocalization system and behave the same as benzene. This is consistent with the experiments that the CNT was found to have large $\chi^{(3)\prime}$s($\sim 10^{-11}$ esu) compared to the $\chi^{(3)}$ of C_{60} ($\sim 3 \times 10^{-34}$ esu), as shown in Table 1, but no experiments showed that CNT has non-zero $\chi^{(2)}$'s [11].

Also, the $\chi^{(3)}$ is more significant when the **E** field is along the tube axis [10]. And this indicates that the π delocalization has a significant contribution to the third order NLO properties of CNT.

Table 1. $\chi^{(3)}_{1111}$ measured by laser Nd:YAG for the carbon nanotube solution. [11]

Wavelength (nm)	$\chi^{(3)}_{1111}$(solution) ($\times 10^{-11}$ esu)	$\chi^{(3)}_{1111}$(solvent) ($\times 10^{-11}$ esu)	$\chi^{(3)}_{1111}$(CNT) ($\times 10^{-11}$ esu)
1064	2.429	1.250	1.179
332	0.586	0.277	0.309

To characterize the NLO properties of CNT, we need to dissolve CNT in a polar solvent. Sometimes a non-zero $\chi^{(2)}$ could be yielded because (1) the caps of CNT are very chemically active and will bond with donor or acceptor groups to make the whole tube becomes polarized (2) molecular reorientation can be possible in a non-ultrasonically dispersed sample (3) doped CNT is essentially noncentrosymmetrical as the doped sites are effective electron traps.

Due to the existence of centrosymmetry and π-electrons that can be delocalized throughout the whole molecule, carbon nanotube is experimentally proved to be a third order NLO material with high enough $\chi^{(3)}$ for photonic applications like third harmonic generation (THG). However, there is not much experimental research on NLO properties of carbon nanotubes and it is still required to search for higher order NLO properties of carbon nanotubes. Also the unique tube-filling property of carbon nanotubes provides an insight to change the photonic properties by filling the carbon nanotubes with dielectrics and metals. As defected carbon nanotubes have obviously deformed π-delocalization and the photonic properties are still unknown, more efforts are required to study in this area.

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FIGURES

FIG. 1. Nonlinear relationship between **D** and **E** at high optical **E** field.

FIG. 2. Laser beam enters quartz crystal as red light and emerges as blue light (a second order NLO effect: second harmonic generation).[2]

FIG. 3. A symmetric P-E curve of centrosymmetrical materials. The figure in lower right corner indicates centrosymmetry.[4]

FIG. 4. An asymmetric P-E curve of noncentrosymmetrical materials. The figure in lower right corner indicates noncentrosymmetry.[4]

FIG. 5. TEM picture of carbon nanotubes.[8]

FIG. 6. Pictorial structure of single walled carbon nanotube