Photoexcited Carrier Lifetime and Refractive Nonlinearity in Direct and Indirect Band Gap Crystals on the Z-Scan Technique

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Abstract— The Photoexcited carrier lifetime (τ) and peak to valley transmission difference (ΔT_{p-v}) in direct and indirect band gap crystals has been investigated by the use of single beam open and closed aperture z-scan technique using frequency doubled Nd:YAG laser. The peak to valley transmission difference (ΔT_{p-v}) is found to be of the order of 10^{-2} in case of direct band gap crystals and of the order of 10^{-3} in case of indirect band gap crystals. The carrier life time (τ) is found to be in nanoseconds range in case of direct band gap crystals and picoseconds range in case of indirect band gap crystals. Lower value of (τ) and (ΔT_{p-v}) in case of indirect band gap crystals can be attributed to the reduction in the value of carrier density (N) and small value of nonlinear phase shift ($\Delta\varphi$), respectively.

KEYWORDS: Direct and indirect band gap crystals, Nonlinear refraction, Nonlinear phase shift, Peak to valley transmission difference, Photo excited carrier life time.

I. INTRODUCTION

Over the last few years the z-scan technique [1, 2] has been extensively used as an important tool to explore the optical nonlinearities of materials like two photon absorption (2 PA) and nonlinear refractive index and free carrier nonlinearities due to the photo excitation of free carrier [3].The determination of optical nonlinearities and their response time in semiconductor is of the great relevance to the practical application possibility of optical limiting devices and all switching elements. It is known that the third/ fourth order nonlinearities are important in the picoseconds/ femtoseconds time while the free carrier nonlinearities become significant for laser pulses of nanosecond duration and longer.

The open and closed aperture z-scan method provides a sensitive and experimentally straight forward method for determination of nonlinear absorption and refraction. A thin sample of the material is scanned across the focus of the Gaussian beam and the transmittance as a function of the sample position is recorded through a pair of energy detectors.

The z-scan method has been employed to measure the optical nonlinearities in large number of direct band gap semiconductors. This kind of measurements is simple but gives no distinction between the contribution from bound electrons and from photo excited free carriers unless a relaxation time is assumed for the excited carriers and also no attempts was made to study photo excited free carrier parameters in case of indirect band gap crystals because the lattice vibration and carriers concentration makes the calculations

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more difficult [4]-[7]. The photo excited free carrier plays an important role in calculating the carrier life time in indirect band gap crystals due to phonon assisted transitions.

In addition to this, refractive nonlinearity, the amplitude of the transmitted intensity changes as a function of the sample position because the nonlinear medium acts as a positive lens (for $n_2>0$) and a negative lens (for $n_2<0$). Thus a prefocal transmittance maximum (peak) followed by a postfocal transmittance minimum (valley) is the z-scan signature of negative refractive non-linearity. This kind of nonlinearity plays an important role in calculating the peak to valley transmission difference (ΔT_{p-v}) in closed aperture z-scan for direct and indirect band gap crystals. So a comprehensive study of optical nonlinearity associated with photo excited carrier life time and refractive nonlinearity in direct and indirect band gap crystals with a nanosecond laser is needed. We report in the present course of investigation the open and closed aperture z-scan technique to calculate the free carrier life time and peak to valley transmission difference in various CdS, ZnS, ZnO, GaN direct band gap crystals and CdI_2, PbI_2 indirect band gap crystals. For these studies, we have used frequency doubled Nd:YAG laser (λ=532nm, hυ=2.34eV).

II. Z-SCAN DETAILS

A. *Open aperture z-scan*

An open-aperture z-scan measures the change in intensity of a beam, focused by lens L as in Figure (1), in the far field at photo detector (PD), which captures the entire beam.

B. *Closed aperture z-scan*

A closed-aperture z-scan measures the change in intensity of a beam, focused by lens L, as the sample passes through the focal plane. Photo detector (PD) collects the light that passes through an axially centered aperture A in the far field. The focused beam has greatest intensity at the centre and will create a change in index of refraction forming a lens in a nonlinear sample as shown in figure (2).

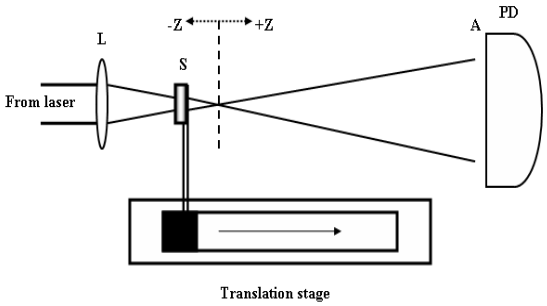


Fig. 1 Open aperture z-scan

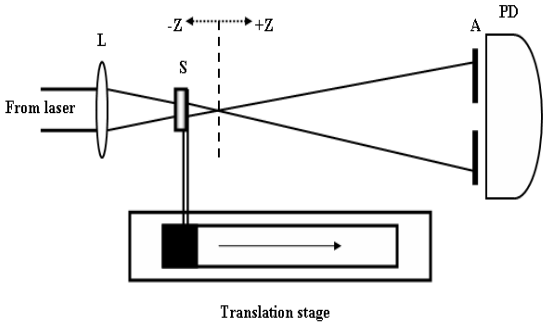


Fig. 2 Closed aperture z-scan

The relative on-axis transmittance of the sample measured (at the small aperture of the far-field detector) is given by [8]:

$$T\left(z,\Delta\phi_0\right)=1+\frac{4\Delta\phi_0\left(z/z_0\right)}{\left[\left[\left(z^2/z_0^2\right)+9\right]\left[\left(z^2/z_0^2\right)+1\right]\right]} \quad (1)$$

where, T is the transmittance through the aperture, which is a function of the sample position z, and Z_0 is the diffraction length.

The nonlinear phase shift ($\Delta\varphi$) is calculated by the following formula

$$\Delta\varphi = kn_2 I_0 l_{eff} \quad (2)$$

where, n_2 is the nonlinear refractive index, $k=2\pi/\lambda$, λ is the wavelength of the beam. I_0 is the intensity at the focal spot. l_{eff} the effective length of the sample, can be determined from the following formula.

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$$l_{eff} = \left(1 - e^{-\alpha l}\right) / \alpha \quad (3)$$

where, l is the sample length, α is the linear absorption coefficient.

The intensity at the focal spot is given by,

$$I_0 = 2P_{peak} / \pi w_0^2 \quad (4)$$

where, w_o is the beam radius at the focal point, P_{peak} is the peak power given by

$$P_{peak} = E / \Delta t \quad (5)$$

where, E is the energy of the pulse, Δt is the pulse duration.

III. Results and Analysis

1) Using the slowly varying envelope approximation, we can separate the wave equation into an equation for the phase and an equation for the irradiance [9]:

$$\frac{d\Delta\varphi}{dz'} = k\,\Delta n \quad (6)$$

$$\frac{dI}{dz'} = -\left(\alpha_0 + \beta I + \sigma_{ab} N\right) I \quad (7)$$

where Δn is the change in the index of refraction, k is the magnitude of the wave vector in the free space, α_0 is the residual linear absorption and z' is the propagation distance within the sample which is to be distinguished from z, the sample position with respect to the focal plane. σ_{ab} is the carrier absorption cross-section and N is carrier density.

We verified that free-carrier absorption was negligible in our experiments by measuring the same 2 PA coefficient at several irradiance levels. On the other hand, we find that the refraction arising from these carriers cannot be neglected [10]. Thus Δn in Equation (6) is written as

$$\Delta n = \gamma I + \sigma_r N \quad (8)$$

where γ is the nonlinear index that is due to bound electrons and is related to the usual nonlinear index n_2 through $n_2(esu) = (cn_0/40\pi)\gamma\left(m^2/W\right)$ with c the speed of light in meters per second and σ_r the change in the index of refraction per unit photo excited charge-carrier density N. If 2 PA is the only mechanism for generating carriers, the carrier generation rate is given by:

$$dN/dt = \alpha_0 I / \hbar w + \beta I^2 / 2\hbar w \quad (9)$$

It should be noted that Eq. (9) includes both one-photon and two-photon-excited carrier generation. This is due to the fact that linear generation α_o=19.4 cm^{-1} contributing to free carrier generation should be considered in our measurements at the excitation wavelength of 532 nm. The diffusion process is neglected in this equation since the diffusion time of the carriers in bulk semiconductors is longer than the pulse width of our laser [11, 12]. Using equations (7) and (9), one can obtain the numerical solution to the energy transmittance for open aperture z-scan as a function of the sample position. It is almost impossible to solve the above nonlinear differential equation to obtain the analytical solution of I and N. Therefore we employed the iteration method to obtain the energy transmittance *T(z)*. The details of the calculations may be found in Ref. 4.In the expression of *T(z)* for open aperture z-scan experiments, the unknown parameter is σ_{ab}. By fitting the theoretical transmittance *T(z)* to the experimental data, we can obtain σ_{ab} in the case of direct and indirect band gap crystals. The values of σ_{ab} were determined to be $(0.85\pm0.15)\times10^{-18}$ cm^2 and $(0.56\pm0.12)\times10^{-22}$ cm^2 in the case of direct and indirect band gap crystals respectively. These values are in good agreement as reported earlier [13]. In order to determine the carrier life time equation (9) describing the carrier generation rate should be modified as:

$$dN/dt = \alpha_0 I / \hbar w + \beta I^2 / 2\hbar w - N/\tau \quad (10)$$

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where τ is recombination time of free carriers.

To determine the carrier lifetime τ, we simulate the open aperture z-scan by using equations (7) and (10). All the parameters in equations (7) and (10) were determined from the nanosecond z-scan measurements, except that τ is treated as free parameter. The best fit to the value of τ is obtained by putting the different value of τ in equation (10) and fitting the curves with experimentally obtained open aperture curves for various direct band gap crystals (CdS, ZnS, ZnO, GaN) and indirect band gap crystals (CdI_2 and PbI_2) hence the best fit to the open aperture nanosecond z-scan measurements gives τ=(1.3±0.6) ns in the case of direct band gap crystals while τ=(1.1±0.04) ps in the case of indirect band gap crystals as displayed in figure (3) and (4). We can fit the open aperture nanosecond z-scan at various input irradiance ranging from 20 to 80 MW/cm^2. As reported earlier [6], it is known that the relaxation time of the photo excited carriers in semiconductors is typically of the order of nanosecond.

Earlier Lami and Hirlimann [14] reported the carriers interband recombination time of 0.1 ns in the CdS direct band crystal with femtosecond laser pulses at 627nm with intensity 10 GW/cm^2.We note that there is some difference in the carrier life time between our measured value and Lami's results. This may be attributed to:

a) We have used frequency doubled Nd:YAG laser with excitation wavelength of 532nm and it is near the absorption edge, where as the wavelength of 627nm in the Lami's *et al*. experiment is far away from the band gap.

b) In our carrier life time measurements we have used low irradiance ranging from 20 to 80 MW/cm^2, while the intensity in the Lami's measurements is of the order of 10 GW/cm^2. We have observed that the value of carrier lifetime in the case of indirect band gap crystals is the picosecond regime. This may be interpreted in the reduction of carrier density N. In general the carrier density N is given by the relation [15]:

$$N = \alpha \xi_{ad} / h\nu \tag{11}$$

where α is the absorption coefficient, ξ_{ad} is the energy area density and $h\nu$ is the energy of the photon. As reported earlier [16,17] in the case of indirect band gap crystals, the value of absorption coefficient/ cross section is small as compared to direct band gap crystal due to the phonon assisted transitions. As the value of α is reduced in case of indirect band gap crystals, the carrier density (N) is also reduced, and hence for the best fit we have measured τ in the picoseconds regime.

2. The nonlinear index $n_2(w)$ is determined using a Kramers-Kronig relation given by M. Sheikh Bahae [1]:

$$n_2(w) = \frac{K'\sqrt{E_p}}{n_0^2 E_g^{\,4}} G_2\left(\frac{\hbar w}{E_g}\right) \tag{12}$$

where, $G_2\left(\hbar w / E_{gap}\right) = \dfrac{\left(2\hbar w / E_{gap} - 1\right)^{3/2}}{\left(2\hbar w / E_{gap}\right)^5}$,

K' is a material independent coefficient. E_p and E_g are given in eV. $G_2\left(\hbar w / E_g\right)$ again depends only on the ratio of the photon energy to the energy gap of the material. With the help of equation (12), we have estimated the value of the nonlinear index n_2 (w) in case of direct band gap crystals CdS, ZnS, ZnO, GaN, as -5.01×10^{-18} (m^2/W), -1.43×10^{-18} (m^2/W), -3.35×10^{-18} (m^2/W), and -1.39×10^{-18} (m^2/W) respectively. These results are in good agreement with measurements made at 610nm wavelengths for direct band gap crystals [5]. In order to find theoretically the value of $n_2^t(w)$ $n_2(w)$ for indirect band gap crystals, one finds with the help of equation [1]:

$$n_2^t(CdI_2) \cong \left(\frac{n_0 X}{n_o CdI_2}\right)^2 \left(\frac{E_{gap} X}{E_{gap} CdI_2}\right)^3 \left(\frac{G_2(\hbar w \pm \hbar\Omega) / E_{gap} CdI_2}{G_2(\hbar w) / E_{gap} X}\right) n_2 X \tag{13}$$

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where, X is any direct band gap crystal, Ω is frequency of phonons and $\hbar\Omega$ is energy of phonons. We have estimated the value of $n_2^t(w)$ in (m^2/W) for indirect band gap crystals CdI_2 and PbI_2 by comparing with all direct band gap crystals CdS, ZnS, ZnO and GaN. Table1 lists all the value of $n_2(w)$. It has been found that the value of $n_2(w)$ in case of indirect band gap is 10^{-1} times smaller in comparison to direct band gap crystals.

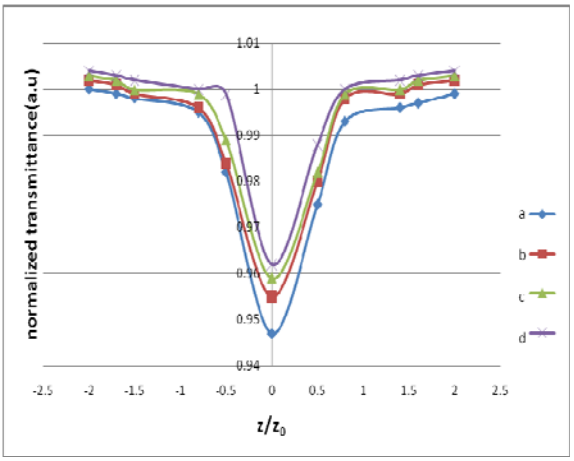


Fig. 3 Normalized open aperture Z-scan data of (a) CdS (b) ZnS (c) ZnO (d) GaN (direct band gap crystals) measured with 7ns pulses at λ=532 nm. The solid curves are the theoretical fit with τ=(1.3±0.6) ns.

The nonlinear phase shift ($\Delta\varphi$) is related to $n_2(w)$ through the formula, $\Delta\varphi = kn_2(w)I_0 l_{eff}$, further, in the absence of nonlinear absorption, the difference in transmittance between the peak and the valley (ΔT_{p-v}) in a z-scan, is related to the on axis phase change at focus ($\Delta\varphi$), through the following equation [3]

$$\Delta T_{p-v} = 0.406(1-S)^{0.27}\Delta\varphi \qquad (14)$$

where, S is the transmission aperture, we calculate the value of ΔT_{p-v} for direct and indirect band gap crystals at 40% aperture (S=0.4). The estimated value of ΔT_{p-v} in case of direct band gap CdS, ZnS, ZnO and GaN crystals is of the order of 10^{-2} and for indirect band gap crystals CdI_2 and PbI_2 is of the order of 10^{-3} respectively. Table1 lists the exact value of ΔT_{p-v} for various direct and indirect band gap crystals calculated theoretically. Also, the value of transmission difference (ΔT_{p-v}) is calculated experimentally by closed aperture z-scan measurements for direct and indirect band gap crystals with 7ns pulse at λ=532nm. The peak to valley profiles determined experimentally by closed aperture z-scan shown in figure 5, 6, 7 and 8. Using equation (1), where $x=z/z_o$

$$T(z,\Delta\phi) = 1+\frac{4x\Delta\varphi}{[x^2+9]\,[x^2+1]} \qquad (15)$$

We have calculated theoretically the value of transmittance and plotted graphs for various direct and indirect band gap crystals. The solid curves shown in these figures are the theoretical fit to the experimental data, By calculating the ΔT_{p-v} from Figs. (5, 6, 7, and 8), it has been found that the theoretical values are in good agreement with the experimental values.

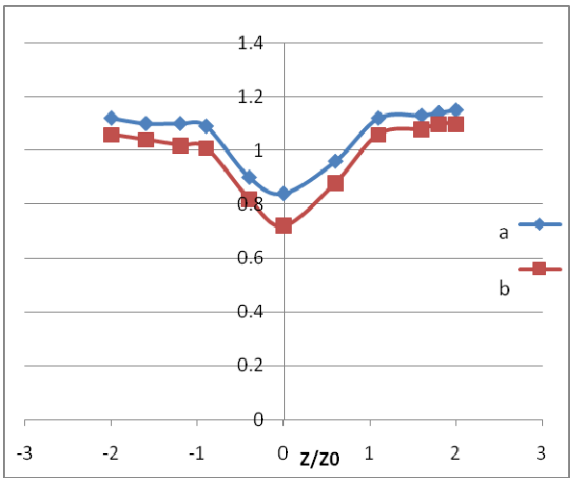


Fig. 4 Normalized open aperture Z-scan data of a) CdI_2 and b) PbI_2 (indirect band gap crystals) measured with 7ns laser pulses at λ=532nm. The solid curves are the theoretical fit with τ=(1.1±0.04) ps.

Also, it has been observed that the ΔT_{p-v} is less for indirect band gap crystals than for direct band gap crystals by a factor of 10^{-1}. The reduction in ΔT_{p-v} for indirect band gap crystals is due to the small value of nonlinear phase shift ($\Delta\varphi$), which further depend on

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$n_2(w)$. This can be explained by using the fact that the refractive nonlinearities are attributed to the free carriers such as electrons in the conduction band and holes in the valence band due to the photo induced interband transitions. These carriers in turn block further interband transitions, giving rise to saturation in the absorption above the band gap. This results in a reduction in the refractive index for photon having energies below the band gap. The reduction in the nonlinear index in the case of indirect band gap crystals is due to the lattice vibrations in the excited state.

Table 1 Values of Nonlinear index [$n_2(w)$ (m^2 /W)], Nonlinear phase shift (-Δφ) and comparison of theoretical and experimental calculated Peak to valley transmission difference (ΔT_{p-v}) for direct and indirect band gap crystals.

Crystals	Energy Gap (eV)	$n_2(w)$ (m^2 /W) (-10^{-18}) (-10^{-19})	-Δφ	(ΔT_{p-v}) (Theo.)	(ΔT_{p-v}) (Exp.)
CdS	2.42	5.09	0.1266	0.0447	0.0312
CdI_2	3.20	6.53	0.0162	0.0057	0.0039
PbI_2	3.02	7.65	0.01899	0.0067	0.0046
ZnS	3.54	1.43	0.0355	0.0126	0.0088
CdI_2	3.20	4.40	0.0109	0.0038	0.0026
PbI_2	3.02	5.24	0.0130	0.0046	0.0032
ZnO	3.20	3.35	0.0832	0.0294	0.0205
CdI_2	3.20	3.95	0.0098	0.0035	0.0024
PbI_2	3.02	4.69	0.0116	0.0041	0.0028
GaN	3.39	1.39	0.0346	0.0122	0.0085
CdI_2	3.20	5.32	0.0132	0.0047	0.0030
PbI_2	3.02	6.40	0.0159	0.0056	0.0040

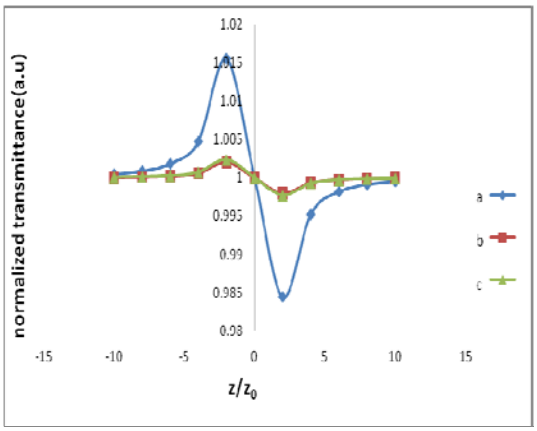


Fig. 5 Normalized closed aperture Z-scan (S=0.4) of a) CdS direct band gap crystal and b) CdI_2, c) PbI_2 indirect band gap crystals showing ΔT_{p-v} at λ=532nm. The solid curves are the theoretical fit with experimental data.

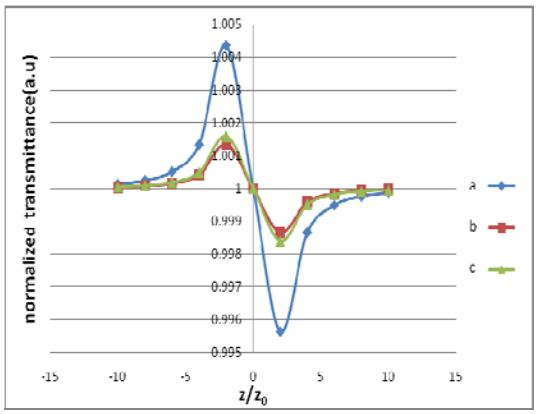


Fig. 6 Normalized closed aperture Z-scan (S=0.4) of a) ZnS direct band gap crystal and b) CdI_2, c) PbI_2 indirect band gap crystals showing ΔT_{p-v} at λ=532nm. The solid curves are the theoretical fit with experimental data.

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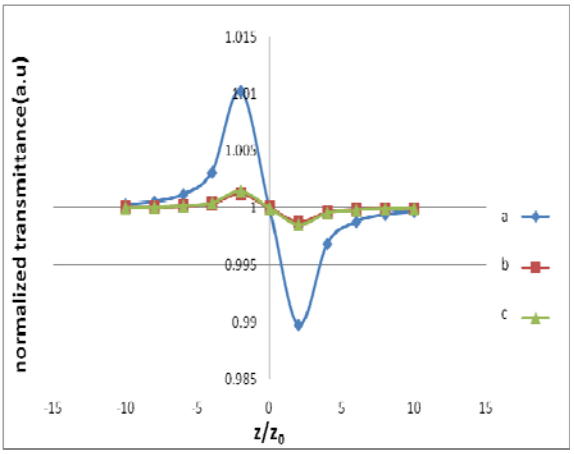


Fig. 7 Normalized closed aperture Z-scan (S=0.4) of a) ZnO direct band gap crystal and b) CdI_2, c) PbI_2 indirect band gap crystals showing ΔT_{p-v} at λ=532nm. The solid curves are the theoretical fit with experimental data.

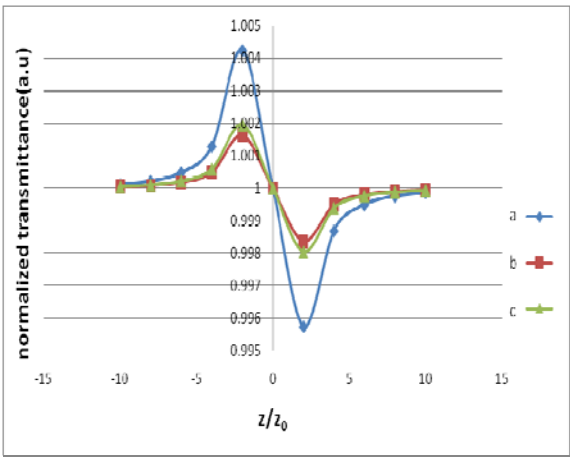


Fig. 8 Normalized closed aperture Z-scan (S=0.4) of a) GaN direct band gap crystal and b) CdI_2, c) PbI_2 indirect band gap crystals showing ΔT_{p-v} at λ=532nm. The solid curves are the theoretical fit with experimental data.

IV. Conclusion

Nonlinear absorption and refraction were observed in the case of direct and indirect band gap crystals at low power density in z-scan experiments with nanosecond laser pulses. The nonlinearities have been attributed to the free charge carriers generated by two-photon absorption. The values of the carrier lifetime, τ, peak to valley transmission difference (ΔT_{p-v}) have been calculated in both direct and indirect band gap crystals. These values were found to be smaller in the case of indirect band gap crystals as compared to direct band gap crystals. The smaller value of τ, ΔT_{p-v} in the case of indirect band gap crystals have been attributed to the reduction in the value of carrier density (N) and small value of non linear phase shift ($\Delta\varphi$) respectively.

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