# Chromium-Doped Saturable Absorbers Investigated by the Z-scan Technique

L. C. Oliveira* and S. C. Zilio
*Instituto de Física de São Carlos, Universidade de São Paulo*
*Caixa Postal 369, 13560-970 São Carlos, SP, Brasil*

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The well known nonlinear optical materials: ruby, alexandrite and $GdAlO_3:Cr^{3+}$ are used to investigate the use of the Z-scan technique in the case where tlie phase of the electric field departs from a Gaussian due to saturation. The transmittance through the aperture in the far field was found to saturate with the liglit intensity. The method is shown to be accurate for measurements of the dispersive part of the nonlinear index in these materials, but the determination of the absorptive contribution was not possible with this technique.

The recently introduced Z-scan technique[1,2] is a sensitive method to determine botli the real ($n_2'$) and imaginary ($n_2''$) parts of the nonlinear refractive index of optical materials. Up to now, this technique has been applied to the study of fast (subnanosecond) response Kerr-like media in the pulsed radiation regime. Examples of materials investigated with this method are wide gap dielectrics and semiconductors[2,3], semiconductor doped glasses[4] and polymer thin films[5]. On the other hand, Cr-doped crystals such as ruby, alexandrite and gadolinium aluminate have their nonlinear indices well characterized mainly by means of degenerate four-wave mixing[6–8] (DFWM) and nearly-degenerate two-wave mixing[9–12] (NDTWM) techniques. Owing to this knowledge, these materials can be used as guides in the investigation of the Z-scan signal behavior in the case of slow (millisecond) response saturable absorbers in the c.w. radiation regime. As the light intensity increases, the population of the $^2E$ metastable state saturates and so does the nonlinear index. As a consequence, the phase of the electric field passing through the sample departs from the usual Gaussian spatial profile and flattens at the top (close to r = 0) due to saturation[13]. This is a situation not studied witli the Z-scan technique yet and its knowledge is important in researches with dye-doped glasses and polymers, amorphous and porous silicon, etc. Since the phase is not Gaussian, the Gaussian decomposition (GD) method introduced by Weaire et al[14] cannot be employed and the theory developed by Sheik-Bahae et al[2] does not apply to our experimental situation. This work addresses this problem and shows experimental results whose main feature is the saturation of the Z-scan signal witli the intensity. Concerning to the real part of the nonlinear index, we have shown that this simple method can provide information as accurate as more complex techniques such as NDTWM and DFWM. However, the determination of $n_2''$ in these materials was not possible with the Z-scan technique.

Tlie experimental set up used is schematically shown in Fig. 1. The light source is either an $Ar^+$ laser (operating at 514.5 nm or 488 nm) or a c.w. ring dye laser (operating at 570, 580,590 or 600 nm). In order to avoid any beam pointing instability and keep the same optical alignment, an electro-optical modulator (EOM) is used to change the light intensity. The use of this device is important because the sample polishing is not perfect and the laser beam has to impinge always at the same point such that any linear effect can be subtracted. A spatial filter (SF) assures a good transverse mode quality. After passing through the spatial filter the beam is split in two parts which follow equal paths.

*Permanent address: Universidade Federal da Paraíba, Campus I, 58059-900 João Pessoa, PB, Brasil

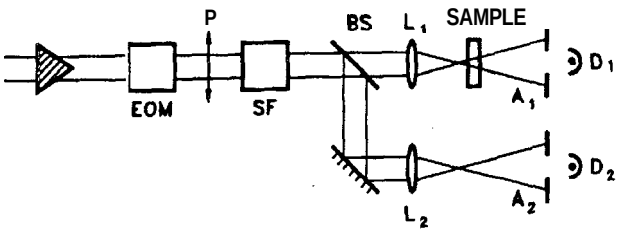


Figure 1: Experimental apparatus used for Z-scan measurements. P: linear polarizer, SF: spatial filter, BS: beam splitter, $L_1$ and $L_2$: lenses, $A_1$ and $A_2$: apertures, $D_1$ and $D_2$: detectors.

With identical lenses ($L_1$, $L_2$), apertures (Ai, $A_2$) and detectors ($D_1$, $D_2$), any mode fluctuation is cancelled when the ratio $D_1/D_2$ is measured. For the determination of $n_2''$ both apertures are removed. The refractive contribution to the Z-scan transmittance is obtained as usual, by dividing a closed aperture ($S < 1$) normalized Z-scan by aiother one without the aperture ($S = 1$). The measurements were carried out for samples of ruby, alexandrite and $GdAlO_3:Cr^{3+}$, for intensities ranging from 0.05 to 2.0 kW/cm$^2$. Although c.w. lasers are used in the present work, the thermal effect does not contribute to the value of $n_2$ due to the good heat conductivity of these samples, as already verified in Ref. 15. Table 1 presents some properties of the crystals used in this work.

Fig. 2 shows typical results for the $GdAlO_3:Cr^{3+}$ sample at 51.4.5 nm. Ruby and alexandrite present similar curves for the refractive part of $n_2$, but their absorptive contributions to the Z-scan transmittance were not observed. Let us first discuss the results due to the real part of the nonlinear index. The separation between the peak and the valley of Fig. 2a is about $\Delta Z_{pv} = 6.5$ mm, which is compatibie with the beam waist used ($\omega_0 = 25\ \mu$m) and a cubic nonlinearity. The dashed line represents the Z-scan transmittance that one would expect from the data of Table 1 and the theory based on the GD method (Eq. (6) of Ref. 1). The discrepancy between this curve and the experimental points is a cleitr indication that the theoretical analysis developed for a Kerr medium is not suitable in describing these satutable absorbers. Even if we take a value for $n_2'$ different from the one presented in Table 1, in a way to have transmittances of the same order, we may observe that the experimental data does not follow the theoretical curve (full line) exactly. However, although the GD method is not adequate to describe the present situation, since we do not have an alternative theory developed at the moment, we will tentatively apply it to our results in order to find out what kind of information we can get. The on-axis phase shift $\Delta\Phi_0$ was determined by measuring the difference between the normalized peak and valley transmittances of signals similar to those of Fig. 2a, as discussed in Ref. 2. This is a good approximation for $\Delta\Phi_0 \leq \pi$. An interesting result is the saturation of $\Delta\Phi_0$ with the intensity, according to $(1 + I/I_s)^{-1}$, where $I_s$ is the saturation intensity at a given wavelength. Fig. 3 shows such a dependence, in a linearized scale, for the three samples studied here at 514.5 nm. For other wavelengths the same type of behavior is obtained but the lines have different slopes (different $n_2'(\lambda)$) and saturation intensities, as expected.

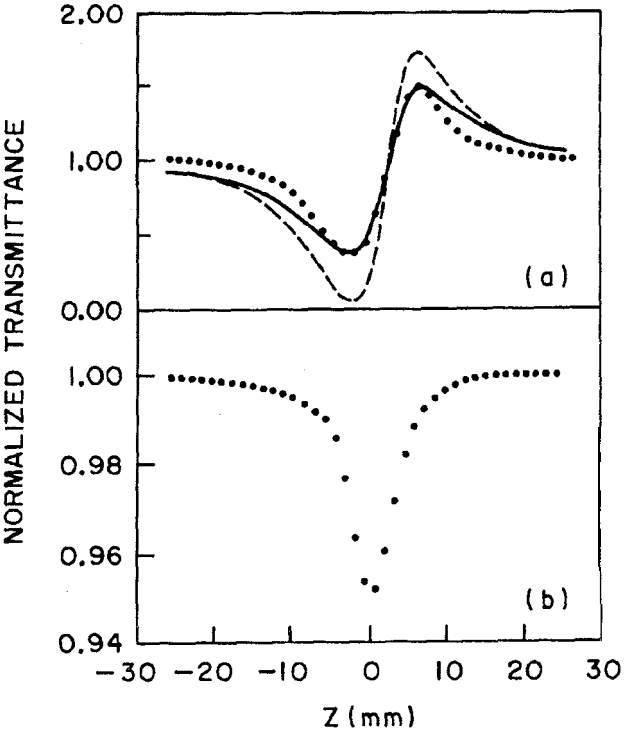


Figure 2: Contributions of the refractive (a) and absorptive (b) parts of the nonlinear index to the Z-scan transmittance of $GdAlO_3:Cr^{3+}$ at 514.5 nm and $I = 1.6$ kW/cm$^2$. In (a), the dashed curve represents the theoretical curve for a Kerr medium and the data of Table 1 while in the full line curve the value of $n_2'$ was taken as 11 x $10^{-5}$ cm$^2$/kW.

In order to roughly explain the saturation effect, we may write a pair of equations describing the phase shift $\Delta\Phi$ and the intensity $I$ of the light beam inside, the saturable absorber as[13,16]:

Table 1. Crystals characteristics: $Cr^{3+}$ concentration ($N_0$), length (L), saturation intensity (I,), linear absorption coefficient (a) and nonlinear index ($n_2'$ and $n_2''$) at 514.5 nm.

| Sample | $N_0$ x $10^{19}$ ($cm^{-3}$) | L (cm) | $I_s$ ($kW/cm^2$) | $a$ ($cm^{-1}$) | $n_2$ x $10^{-5}$ ($cm^2/kW$) | $n_2''$ x $10^{-5}$ ($cm^2/kW$) |
|---|---|---|---|---|---|---|
| Ruby | 1.1 | 0.32 | 1.6 | 0.8 | 1.25[a] | 0.05[b] |
| Alexandrite[c] | 8.0 | 0.25 | 0.8 | 1.2 | 4.0 | 0.12 |
| $GdAlO_3$[d] | 15.0 | 0.14 | 1.2 | 4.2 | 18.0 | 1.4 |

[a] Reference 15, [b] Reference 12, [c] Measured by us with NDTWM, [d] Reference 16.

$$\frac{d\Delta\Phi}{dz} = kn_2' I/(1 + I/I_s) , \qquad (1)$$

$$\frac{dI}{dz} = -[\alpha + 2kn_2'' I/(1 + I/I_s)]I , \qquad (2)$$

where $a$ is the linear absorption. For a Kerr medium ($I \ll I_s$), these equations can be solved analitically and their solutions are used to find an expression for the Z-scan signal[2]. On the other hand, the analitical solution is difficult to be obtained for arbitrary intensities, but in the case of small $n_2''$ and optically thin samples ($\alpha L \ll 1$), we may find an approximate solution by neglecting the second term in the right-hand side of Eq. (2) and the dependence of **I** on $z$ in the denominator of Eq. (1). With these simplifications, the theoretical analysis given in Ref. 2 is approximately valid below saturation if the saturation term is included in the on-axis phase shift $\Delta\Phi_0$. A more accurate calculation for the Z-scan signal is being carried out numerically by means of the zeroth-order Hankel transformation of the electric field and will be presented elsewhere.

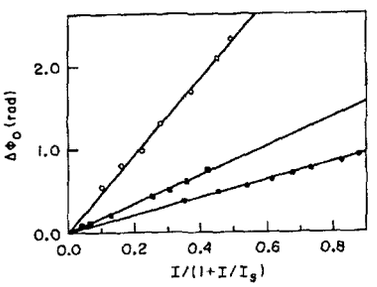


Figure 3: Phase shift as a function of the intensity for ruby (solid circles, $I_s = 1.6$ $kW/cm^2$) alexandrite (squares, $I_s = 0.8$ $kW/cm^2$) and GdAlO3:$Cr^{3+}$ (open circles, $I_s = 1.2$ $kW/cm^2$) at 514.5 nm.

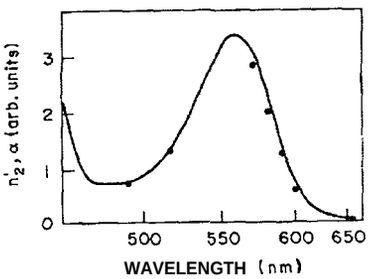


Figure 4: Dependence of the real part of the nonlinear index on the wavelength for the sample of $GdAlO_3$:$Cr^{3+}$ (solid circles). The curve represents the linear absorption coefficient $\alpha$.

Another important aspect of the results presented in Fig. **3** is that the values of $n_2'$ obtained from those plots are about twice the values found with other techniques and given in Table 1. At the present time we do not know the origin of this factor, but is quite possible that it is related to the unadequacy of our theoretical approach. Further work is necessary to clear this point out. Anyways, we experimentally found that the GD method can be used if we take the on-axis phase shift in these Cr-doped saturable absorbers as:

$$\Delta\Phi_o = \frac{4\pi}{\lambda} n_2' L_{eff} I/(1 + I/I_s) , \qquad (3)$$

where $L_{eff} = (1 - e^{-\alpha L})/\alpha$. With this expression and the experimental points of Fig. 3, the values of $n_2'$ are found to be: 1.5 x $10^{-5}$ $cm^2/kW$ (ruby), 3.3 x $10^{-5}$ $cm^2/kW$ (alexandrite) and 18 x $10^{-5}$ $cm^2/kW$ ($GdAlO_3$:$Cr^{3+}$), which are in good agreement witk the values presented in Table 1. The dependence of $n_2'$ on the wavelength for the sample of $GdAlO_3$:$Cr^{3+}$ is represented by the solid circles of Fig. 4. It is clear that $n_2'(\lambda)$ follows the absorption curve of this material and this behavior is consistent with the fact that the charge-transfer (CT) band located around 46000 $cm^{-1}$ produces the main contribution to the nonlinear index of $GdAlO_3$:$Cr^{3+}$, as already pointed out in Ref. 16.

Referring to the imaginary part of the nonlinear index, the open aperture transmittance ($S = 1$) have shown an observable effect just in the case of the gadolinium aluminate sample and even though, for intensities close to saturation. The shape shown in Fig. 2b is in agreement with previous results showing that the excited state absorption is Iiigher than the ground state absorption at that intensity. The reason for this behavior is the occurrence of a photon-assisted off-resonance energy transfer (PAORET) between excited $Cr^{3+}$ at neighboring positions[16,17], which produces a dependence of the nonlinear absorption on the intensity according to:

$$n_2''(I) = n_2''(O)\left[1 - \frac{\beta I/I_s}{1 + I/I_s}\right] \qquad (4)$$

At low intensities, the term in the denominator of (4) is negligible and the open aperture transmittance would present an increase of the transmitted intensity when $z \rightarrow 0$ (absorption saturation). On the other hand, in the case of liigher intensities, the second term in the denominator predominates and the transmittance has the opposite behavior, presenting a decrease of intensity, as show ı in Fig. 2b. No such effect was observed for ruby and alexandrite and therefore we conclude that the Z-scsn technique is less adequate for the measurement of $n_2''$ in these materials than the NDTWM technique[16,17]. The reason of this relies on the fact that the nonlinear index has its origin in a CT band located in the ultra-violet region. As the frequency approaches the visible region, the imaginary part of $n_2$ decreases faster than the real part such that around 500 nm it is just a few percent of it.

In conclusion, we have found that the real part of the nonlinear index can be accurately determined with the Z-scan method together with the usual theory based on a Gaussian decomposition provided that the on-axis phase shift $\Delta\Phi_0$ given in Eq. (3) is used. The imaginary part of the nonlinear index in our samples is too small to be measured with this technique, but it doesn't rule out the possibility of its use for other saturable absorbers such as dye molecules. The results obtained can not be explained in the frame of the conventional saturable absorption theory for a two-level system but an excited level has to be involved. We are performing calculations along these lines and our preliminary results are encouraging.

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