**Spectroscopic discrimination of resonant and nonresonant contributions to the nonlinear refractive index in ion doped solids**

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**Abstract**

A simple extension of the two-color Z-scan technique is reported in order to discriminate the resonant and nonresonant contribution to the nonlinear refractive index change, $\Delta n$, of the R lines of ruby and alexandrite crystals. $\Delta n$ can be explained by the resonant interaction and by a nonresonant contribution that is due to the difference in polarizability between $Cr^{3+}$ excited and ground states. For ruby, the resonant contribution to the technique is approximately 10 % of the nonresonant contribution. However, for alexandrite both contributions are comparable.

There has been great interest in studies of the nonlinear properties of ion-doped materials as a result of the existence of spatial hole burning, which can induce both refractive-index and gain gratings, in the implications of these properties in laser behavior (including bistability and instability), and in their applications such as in phase conjugation of high-power laser systems [1-5].

Although a great number of materials have been studied, most of the quantitative measurements of the nonlinear refractive line shape $n_2$ have been performed in systems doped with $Cr^{3+}$ and $Nd^{3+}$ [2, 4]. It is well known that in these cases the ion's excited state has a polarizability, $\alpha_{ex}$, that is higher than that from the ground state, $\alpha_g$. This polarizability difference, $\Delta\alpha = \alpha_{ex} - \alpha_g$, is accounted by the large oscillator strength charge transfer bands (in the UV) that are far from resonance of the laser transition in these systems [3]. Therefore, in the context of this work, $\Delta\alpha$ is considered a nonresonant contribution to $\Delta n$. Usually, $\Delta\alpha$ is studied by populating the ion metastable state through the excitation of a higher-energy absorption band that nonradiatively decays to the metastable state. Recently, $\Delta\alpha$ was studied by populating the ruby ($Al_2O_3:Cr^{3+}$) and alexandrite ($BeAl_2O_4:Cr^{3+}$) laser R lines resonantly [6]. In this case, the contributions of this resonant interaction to the susceptibility was also considered and a simple extension of the time-resolved Z-scan method was introduced in order to verify it experimentally. The $n_2$ line shape to both crystals was measured and the results show a interference of nonresonant ($\Delta\alpha$) and the resonant (two-level system) contributions.

In this work, a simple adaptation of the two-color nonlinear technique (based in the Z-scan method) was used to distinguish the resonant and the nonresonant contributions to $\Delta n$. In these experiments, the alexandrite and ruby laser R lines ($^2E$) were populated by an intermediate excitation of the $^4T_2$ absorption band, and the refractive index changed was probed by a tunable dye laser, in resonance with the R lines (from ground to metastable state).

In ion doped solids, the resonant and nonresonant contributions to the nonlinear susceptibility can be taken into account by [7]:

$$\chi = \chi_m + N_g\alpha_g + N_{ex}\alpha_{ex} - \frac{a_o}{2\pi k_p}\left(\frac{i+\delta}{1+\delta^2+s_p}\right) \tag{1}$$

where $\chi_m$ represents the host matrix susceptibility and $N_g$ ($N_{ex}$) the ground (excited) state population. The last term in Eq. (1) represents the pure two-level system susceptibility, where $\delta = 2\pi(\nu-\nu_o)T_2$ is the detuning parameter, $T_2$ is the dephase characteristic time, $k_p = 2\pi(\nu_o/c)$, $a_o = n_o\sigma_g(N_g - N_{ex})/2\ f_L^2$ is the line center small-signal-field attenuation coefficient, $f_L = (n_o^2 + 2)/3$ is the Lorenz local field correction factor, $n_o$ is the refractive index and $\sigma_g$ is the ground state absorption cross section. The probe beam saturation parameter is given by $s_p = I_p/I_{sp}$, where $I_p$ and $I_{sp} = h\nu_o/2\sigma_g\tau_o$ are the probe beam incident and saturation intensities, respectively, and $\tau_o$ is the excited state lifetime. Since the other energy levels are far from resonance, they are not populated. Therefore, the total ion concentration is approximately given by $N_o = N_{ex} + N_g$, where $N_{ex}$ and $N_g$ can be calculated using rate equations of the three-levels model which, after substituting in Eq. (1), results in:

$$\chi = \chi_m + N_o\alpha_g + \frac{n_o}{4\pi k_p f_L^2}N_o\sigma_g\left[2A\frac{s_{ex}}{(1+s_{ex})} - \frac{(1-s_{ex})}{(1+s_{ex})}\frac{\delta+i}{(1+\delta^2+s_p)}\right] \tag{2}$$

with

$$A = \frac{4\pi^2}{\lambda_p}\frac{f_L^2}{n_o}\frac{\Delta\alpha}{\sigma_g} \tag{3}$$

where $s_{ex} = I_{ex} / I_{sex}$ is the excitation beam saturation parameter, with $I_{ex}$ and $I_{sex}$ being the excitation beam incident and saturation intensities, respectively. Factor $A$ introduces the effect of $\Delta\alpha$ in the resonant interaction. For $A = 0$, we again obtain the standard two-level system susceptibility. In the general case, $A$ is proportional to the susceptibility difference between excited and ground states, ($\chi_{ex}$-$\chi_g$), with its real part proportional to $\Delta\alpha$ and its imaginary part proportional to $\Delta\sigma = \sigma_{ex} - \sigma_g$ ($\sigma_{ex}$ is the excited state absorption cross section). For $Cr^{3+}$ and $Nd^{3+}$ doped solids, it is well known that the imaginary part of ($\chi_{ex}$-$\chi_g$) is typically less than the real part [7, 8], hence was neglected in Eq. (3). In this case, the imaginary part of the susceptibility is equal to the two-level system one.

Since the laser-induced refractive index change is defined as $\Delta n = 2\pi ( f_L^2/n_o)\Delta\chi$, by Eq. (2), $\Delta n$ can be written as

$$\Delta n = \frac{N_o\sigma_g}{2k_p}\frac{1}{(1+s_{ex})}\left[2As_{ex} - (1-s_{ex})\frac{\delta + i}{(1+\delta^2+s_p)}\right]. \tag{4}$$

In this expression, the first and second terms in bracket correspond to the nonresonant and resonant contributions to $\Delta n$, respectively. Note that if the probe wavelength is far from resonance, the second term is negligible, resulting the nonresonant contribution due $\Delta\alpha$ (first term). In the opposite case, with the probe wavelength near resonance, the second term (with dispersive real part) is added to the nonresonant contribution. In order to verify this behavior experimentally we studied the ruby and alexandrite crystals with the two-color Z-scan experiment in an adapted form. For this, an $Ar^+$ laser at 514 nm was used by populating the metaestable level ($^2E$) via an excitation of the intermediate band ($^2T_4$) of the $Cr^{3+}$, and a standing-wave Oxazina 720 cw dye laser (in a opposite propagation direction) was used to probe the refractive index change.

To align the experimental setup, the Z-scan characteristic curve was measured to the alexandrite crystal for both beams, independently, so that the peak and valley positions were found. Consequently, the spot size of the beams were also determined. The exact position of the peak or valley is very important because they correspond approximately to the best sensible position for the experiment. The alexandrite crystal was firstly excited in resonance with the $R_1$ line (680.4 nm) and in sequence, it was excited with the $Ar^+$ laser at 514 nm. After that, the sample was fixed, in relation to the probe beam, at $Z_p = 1.34Z_{cp}$, where $Z_{cp}$ is the confocal parameter of the probe laser beam (~ 1.12 cm). In the sample position, the excitation beam spot size is $2.3\times10^{-3}$ cm, which is 3.6 times smaller than the probe beam spot size. The basic idea is to modulate the excitation laser beam with a chopper and scan the probe laser frequency across the range of interest. The transmitted probe beam was detected in closed- ($S_1$) and open- ($S_2$) aperture detectors of the Z-scan setup. Because $Cr^{3+}$-doped crystals have slow nonlinearities, we can eliminate the effect of linear absorption from the spectrum by using the time-resolved normalization procedure $I(\nu,t)/I(\nu,t = 0)$. Figure 1 shows the time normalized spectra detected in both detectors ($S_1$ = 100 % and $S_2$ = 50 %) for the alexandrite crystal (similar curves were also obtained to the ruby). $S_1$ and $S_2$ exhibit peaks near resonance that are due to absorption saturation. The closed-aperture signal ($S_2$) far from resonance is large (~ 1.05 – 1.00) and it is attributed to the non-resonant contribution.

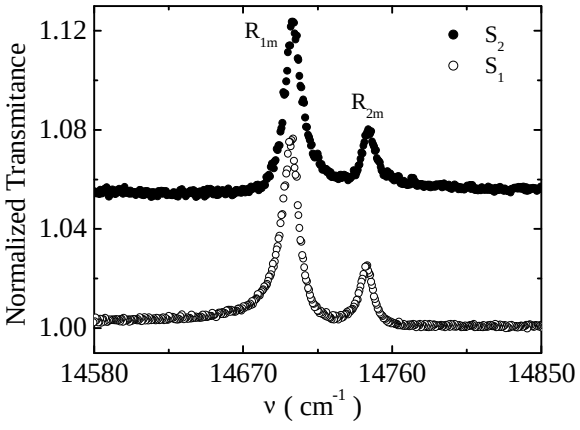


**Figure 1:** *Normalized Transmittance of the open- and closed-aperture ($S_1$ and $S_2$ respectively) for the alexandrite. The saturation parameters used for excitation and probe lasers were $s_{ex}$ = 2.2 and $s_p$ = 0.05, respectively.*

The $S_2$ signal is normalized by $S_1$ one in order to eliminate the saturation absorption signal of $S_2$ signal, as usually done in Z-scan method [9, 10]. The resultant signal is proportional to the pump induced refractive index change $\Delta n$. Figure 2 shows $\Delta n(\nu)$ spectra for ruby (a) and alexandrite (b) versus the probe beam frequency. The inset figures show the linear and nonlinear absorption spectra just for comparison. We note that they are very similar. The linear absorption spectra was fitted by two Lorentzian giving the exact position of the line center and the full width of the half maximum (FWHM) for the lines. These parameters were used as fix parameters in two dispersive curves (similar to Eq. (4)) to fit the $\Delta n$ curves. The solid line in figure represents the fit curve, which coincide very well with the experimental data. By the fit, $A$ = 26 and 40 for the $R_1$ and $R_2$ lines, respectively, to the ruby crystal was determined. The found values to alexandrite were $A$ = 1.5 and 4.4 for the $R_{1m}$ and $R_{2m}$ lines, respectively. These values are in good agreement with those measured recently by the single wavelength Z-scan technique ($A$ = 16 and 20 were measured for $R_1$ and $R_2$ lines of the ruby and 1.9 and 5 for the $R_{1m}$ and $R_{2m}$ lines of the alexandrite) [6]. It should be noted that $\Delta n(\nu)$ is normalized to the nonresonant signal $\Delta n_o \propto N_{ex}\Delta\alpha$. For instance, in ruby, close to $R_1$ line $\Delta n(\nu)$ varies between (0.16 – 0.145)$\Delta n_o$ due to the resonant interaction, i.e., a maximum variation of ~ 10 % over the nonresonant contribution (~ 0.153$\Delta n_o$). This indicate that the $R_1$ line resonant contribution represents approximately 10 % of the total signal. In the case of alexandrite crystal, $\Delta n(\nu)$ varies (0.06 - 0.035)$\Delta n_o$ for the $R_{1m}$ line. So, to alexandrite the resonant contribution corresponds to 50 % of the total nonlinear refractive index change (~ 0.053$\Delta n_o$). The small resonant contribution for the $R_2$ line for both crystals is expected because its ground state absorption cross section is smaller than the $R_1$ line value (see Eq. (3)).

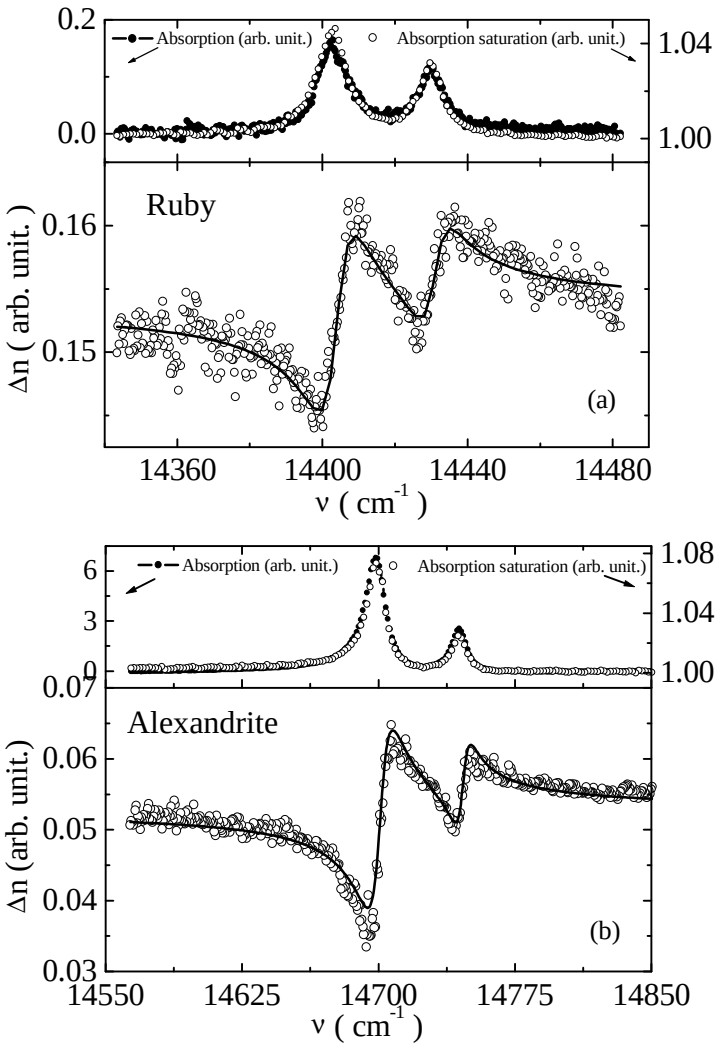


**Figure 2:** *Pump induced refractive index change, $\Delta n(\nu)$, versus probe beam frequency, $\nu$, for ruby (a) and alexandrite (b) crystals. The $\Delta n(\nu)$ curve were fitted by two dispersive equations like Eq. (4). The inset show the linear and nonlinear absorptions spectra. The saturation parameters used for excitation and probe lasers were $s_{ex}$ = 83 and $s_p$ = 0.06, respectively, for ruby, and $s_{ex}$ = 2.2 and $s_p$ = 0.05 for alexandrite.*

In summary, the $Cr^{3+}$ metastable state ($^2E$) of ruby and alexandrite crystals was excited through the intermediate $^2T_4$ band, and the nonlinear refractive index change spectroscopy was measured scanning a dye laser across the R lines. This experiments demonstrated a new application of the two-color Z-scan technique, which is convenient for use in studying resonant interactions. The dispersive behavior for the nonlinear refractive index change resembles the refractive index lineshape $n(\nu)$, measured by interferometry in Ref. [11] in ruby. Our main observations are in agreement with the proposed theoretical model, which takes into account both the resonant and the nonresonant contributions to $\Delta n$.

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