PHYSICAL REVIEW B **79**, 033108 (2009)

Nonlinear refraction and absorption through phase transition in a Nd:SBN laser crystal

A. Ródenas,[1] C. Jacinto,[2,*] L. R. Freitas,[3] D. Jaque,[1] and T. Catunda[3]
[1]*Departamento de Física de Materiales, C-IV, Universidad Autónoma de Madrid, 28049 Cantoblanco, Madrid, Spain*
[2]*Instituto de Física, Universidade Federal de Alagoas, CEP 57072-970, Maceió, AL, Brazil*
[3]*Instituto de Física de Sao Carlos, Universidade de São Paulo, CEP 13560-960, São Carlos, SP, Brazil*

(Received 24 October 2008; revised manuscript received 16 December 2008; published 27 January 2009)

Time-resolved *Z*-scan measurements were performed in a Nd^{3+}-doped $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$ laser crystal through ferroelectric phase transition. Both the differences in electronic polarizability $(\Delta\alpha_p)$ and cross section $(\Delta\sigma)$ of the neodymium ions have been found to be strongly modified in the surroundings of the transition temperature. This observed unusual behavior is concluded to be caused by the remarkable influence that the structural changes associated to the ferro-to-paraelectric phase transition has on the $4f\rightarrow 5d$ transition probabilities. The maximum polarizability change value $\Delta\alpha_p=1.2\times 10^{-25}$ cm^3 obtained at room temperature is the largest ever measured for a Nd^{3+}-doped transparent material.

DOI: 10.1103/PhysRevB.79.033108 PACS number(s): 64.70.−p, 42.65.An, 42.70.Mp

The study of the nonlinear variations in the refractive index in laser materials is a hot topic because standing waves in laser cavities can entail complex dynamical processes, such as self-focusing, temporal and spatial self-phase modulations, and light-induced gratings, that could significantly deteriorate the laser performance.[1–5] In addition to the nonlinear Kerr and the pump-induced thermal lens (TL) effects, it is well known that the refractive index of rare earth or transition-metal ion-doped transparent materials can be also modified by pump-induced changes in the population of the electronic states.[1–3,6–8] This pump-induced refractive index variation is attributed to the differences in polarizability $(\Delta\alpha)$ and absorption cross section $(\Delta\sigma)$ between the excited and ground states of the laser active ions. A systematic study of the dependence of the $\Delta\alpha$ parameter on the character of the host matrix has concluded that $\Delta\alpha$ can vary up to 1 order of magnitude depending on the host matrix and that it is bigger for oxides than for fluorides.[1,2,6,9] In the case of Nd^{3+} ions, the dominant contribution to $\Delta\alpha$ was attributed to a nonresonant contribution from the strong $4f$-$5d$ interconfigurational absorption transitions.[9] A similar explanation was also given for the case of Yb^{3+}-doped crystals and glasses.[2,3,10] However, a recent work on Yb^{3+}:YAG and Yb^{3+}:KGW crystals suggested that the observed refractive index changes can be more likely related to polarizability changes caused by strong ligand-to-metal charge-transfer absorption bands.[11] Due to the high sensitivity of theses states/bands to the lattice environment, a large variation of $\Delta\alpha$ might be expected in the presence of a structural phase transition.

Strontium barium niobate crystal ($\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$, hereafter, SBN) emerges as a promising candidate for the corroboration of this possibility. It is a relaxor ferroelectric crystal with a displacitive phase transition at a relatively low Curie temperature (50 °C–150 °C depending on the composition). SBN crystals have been widely studied in the past because of its high nonlinear, pyroelectric, acousto-optic, and electro-optical coefficients as well as because of its ferroelectric properties. It also shows the advantage of easy doping with rare-earth and transition-metal ions, presenting interesting optical features as a multifunctional laser system as well as a rich variety of luminescent phenomena related to the ferro-to-paraelectric (f-p) phase transition.[12,13] Indeed, thermally induced bistable spontaneous emission related with the phase-transition structural hysteresis was observed in Cr^{3+} (Ref. 14) and Yb^{3+} (Ref. 15)-doped SBN crystals, showing that these ions can be used as optical probes due to their high sensitivity to small changes in the local crystalline field. However, in the case of Nd^{3+} ions, the spectroscopic properties have been found to be insensitive to the f-p phase transition.[16] In this work, time-resolved *Z*-scan measurements were performed in order to investigate the dependence of the cw electronic population-induced nonlinear refractive index (n_2) of Nd^{3+}:SBN laser crystals with the structural phase transition.

When a Nd^{3+}-doped transparent solid is optically pumped, for instance, by a green photon in resonance with a higher-lying state, the system rapidly decays (∼picoseconds) to the $^4F_{3/2}$ metastable level. Under cw excitation, the $^4F_{3/2}$-excited state is usually assumed as the unique Nd^{3+}-excited level. Therefore, one can assume $N_t\approx N_g+N_{\text{ex}}$, where N_i represents the total Nd^{3+} concentration, the ground, and metastable state Nd^{3+} populations, for $i=t$, g, and ex, respectively. The population dynamics of such a system can be obtained by standard rate equations. In the low pump intensity regime $I\ll I_s$ (where $I_s=h\nu/\sigma\tau$ is the saturation intensity, $h\nu$ is the pump photon energy, σ is the ground-state absorption cross section, and τ is the excited-state lifetime) these calculation, supposing that the pump laser is turned on at $t=0$, results in $N_{\text{ex}}(t)\approx N_t[1\text{-exp}(\text{-}t/\tau)]I/I_s$.[17] Since for $I\ll I_s$ the transient complex refractive index change is proportional to $N_{\text{ex}}(t)$, it can therefore be written as

$$\Delta n(t)=n_2I(1-e^{-t/\tau}), \tag{1}$$

where the nonlinear refractive index is given by ($n_2=n_2'$-in_2'') (Refs. 2, 8, and 17)

$$n_2=\frac{N_t}{I_s}\left(\frac{2\pi}{n_0}f_L^2\Delta\alpha-i\frac{\lambda}{4\pi}\Delta\sigma\right), \tag{2}$$

being $\Delta\sigma=(\sigma_{\text{ex}}-\sigma_g)$ as the absorption cross-section difference between the excited and ground states, n_{o} as the unperturbed linear refractive index, and $f_L=(n_{\text{o}}^2+2)/3$ as the local-

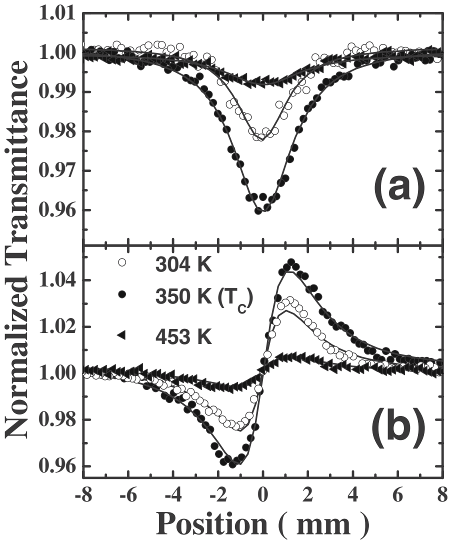

FIG. 1. Normalized transmittance at $T=304$, 350, and 453 K: (a) open and (b) closed apertures signals samples for an incident laser power of 90 mW and chopper frequency of 770 Hz.

field factor. Thus, Nd^{3+}-doped transparent materials can behave similarly to a nonlinear Kerr medium since the excited-state population is proportional to the pump intensity (in a first-order approximation). Therefore, the refractive index change can be similarly written as $\Delta n = n_2 I$ [Eq. (1)].

The *Z*-scan technique is a simple, popular, and accurate method for the determination of the real and imaginary parts of n_2.[18] It is based on the monitoring of a laser beam transmission through a nonlinear media while it is self-affected by the profile of the laser-induced refractive index change, increasing or reducing the on-axis intensity in the far field. For systems with slow response times (microseconds to milliseconds), such as Nd^{3+}-doped materials,[2,10] the time-resolved *Z*-scan method has proved to improve the sensitivity by eliminating parasitic linear effects.[2,19–21] The results obtained with this method are in agreement with those obtained from other techniques, particularly, in the case of Cr^{3+}-doped crystals, which were most extensively studied by several kinds of interferometric and wave-mixing techniques.[22]

In this work, this method was applied to a $Nd^{3+}:SBN_{61}$ ($Sr_{0.61}Ba_{0.39}Nb_2O_6$ with 0.5 at. % Nd^{3+} concentration) crystal, having a ${}^4F_{3/2}$ fluorescence lifetime of $\tau=230$ μs. In order to investigate the effect of the phase transition on n_2, the crystal was put in a temperature-controlled oven and photorefractive effects were minimized by placing the sample with its optical axis parallel to the beam propagation direction.[16,23] The *Z*-scan experiment was performed with an Ar^+ laser at 514.5 nm focused by a 12 cm focal lens, resulting in a beam waist at the sample position of $w_o=14$ μm. After passing the sample, the beam was split in order to detect both open ($S_1=100\%$) and closed ($S_2=50\%$) apertures signals, as usually done in *Z*-scan measurements.[18]

Figure 1 shows representative obtained results for the open and closed apertures for a chopper frequency of 770 Hz (the measurements were made at $t_f=650$ μs) and corresponding to ferroelectric phase (304 K), Curie ($T_c=350$ K), and paraelectric phase (453 K) temperatures. Figure 1(a) depicts the open aperture (S_1) curve, which accounts for a decrease in the transmittance due to excited-state absorption. Following the standard *Z*-scan procedure,[2,18] the closed aperture signal (S_2) was normalized dividing it by the S_1 signal. The S_2/S_1 normalized signal is shown in Fig. 1(b). In order to avoid saturation effects, the maximum intensity was always kept below 15 kW/cm^2, which corresponds to ~5% of the I_s value (3.4×10^5 W/cm^2 at 514.5 nm).

Most of the rare-earth ion-doped solids present simultaneously both TL and population len (PL) contributions due to the ubiquitous presence of both radiative and nonradiative decays.[2,20,21] Thermal processes, such as the thermal variation in refractive index, thermal expansion, and thermally induced stress, are also very important effects to be taken into account in solid-state laser engineering.[24] The TL phase shift is given by $\Delta\phi_{th}=\varphi P_{abs}(ds/dT)/\lambda K$, where φP_{abs} is the fraction of absorbed power (P_{abs}) converted into heat (the thermal power), ds/dT is the temperature coefficient of optical path length, and K is the thermal conductivity. The heat efficiency factor is given by $\varphi = 1-\eta\lambda_{exc}/\langle\lambda_{em}\rangle$, where η is the fluorescence quantum efficiency of the ${}^4F_{3/2}$ Nd^{3+} emitting level, λ_{exc} and $\langle\lambda_{em}\rangle$ are excitation and average emission wavelengths, respectively. The PL phase shift is given by $\Delta\phi_{pop}=(2\pi/\lambda)n_2 I_o L_{eff}$, where I_o is the on-axis intensity, $L_{eff}=[1\text{-}\exp(\text{-}\alpha_a L)]$, L is the sample thickness, and α_a is the optical-absorption coefficient ($\alpha_a=\sigma_g N_t$). In order to analyze the contributions of PL and TL effects to the nonlinear refractive index, it is interesting to investigate the relative magnitude of their phase shifts, which is given by[2]

$$\frac{\Delta\varphi_{pop}}{\Delta\varphi_{th}} = \frac{4n_2'}{w_o^2\alpha_a} \times \frac{K}{\varphi(ds/dT)}. \tag{3}$$

The first term in Eq. (3) is proportional to $\Delta\phi_{pop}$ and the second term is inversely proportional to $\Delta\phi_{th}$. Alternatively, a focal length (f) or dioptric power ($D=1/f$) can be associated with both PL and TL effects, $D_{pop}=2\lambda\Delta\phi_{pop}/(\pi w_o^2)$ and $D_{th}=\lambda\Delta\phi_{pop}/(\pi w_o^2)$, respectively. The ratio between D_{pop} and D_{th} is proportional to the magnitude of their phase shifts: $(D_{pop}/D_{th})=2\Delta\phi_{pop}/\Delta\phi_{th}$.

It should be noticed that both PL and TL are proportional to the laser power, so that the ratio $\Delta\phi_{pop}/\Delta\phi_{th}$ is independent of the pump power (in a first-order approximation). However, the PL effect is proportional to the laser intensity, which is inversely proportional to the square of the beam waist (w_o). Using $\eta=\tau/\tau_{rad}$, with $\tau=230$ μs and $\tau_{rad}=254$ μs, we estimated $\eta=0.90$ and $\varphi=0.56$ for $\lambda_{exc}=514.5$ nm and $\langle\lambda_{em}\rangle=1.06$ μm. The values of K and ds/dT for SBN were recently determined in a mode-mismatched TL experiment.[16] Using these values, we estimated that under our experimental conditions and at room temperature, $\Delta\phi_{pop}\approx 32\Delta\phi_{th}$. This $\Delta\phi_{pop}/\Delta\phi_{th}$ value is very high compared with other materials that present high TL effect, such as fluoride glasses, for instance.[2] TL effect in SBN is small because the $K^{-1}ds/dT$ factor is comparable to the YAG value and ~6 times smaller than that of typical fluoride or aluminosilicate glasses.[2,24] Although the magnitude of the TL effect nearly doubles from room to the phase-transition temperatures,[16] its effect on the *Z*-scan curves observed in this work can be considered negligible.[20]

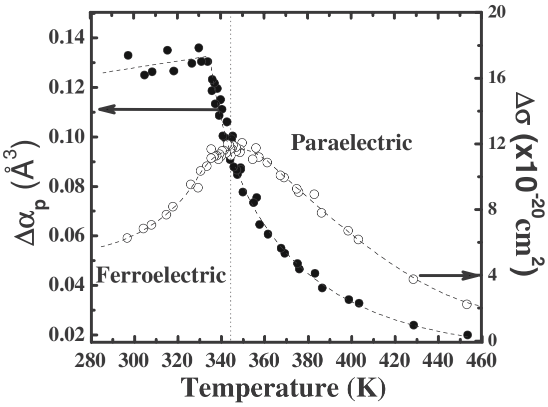

FIG. 2. (Left) Difference in polarizability and (right) absorption cross-sections of the Nd^{3+}:SBN ions in the metastable excited state versus the ground state, as a function of temperature throughout the ferroelectric to paraelectric phase transition.

The transient behavior of $\Delta n(t)$ was also investigated to confirm the absence of thermal effects. The measurements were performed by placing the sample at the valley position of the division curve [see Fig. 1(b)] and recording the signals in both detectors (S_1 and S_2), as performed in Ref. 17. The obtained result was an exponential curve with a time decay $\tau \approx 230$ μs, $\Delta n(t) \propto (1\text{-}e^{-t/\tau})$, in agreement with the Nd^{3+} lifetime.

From the *Z*-scan curves of Fig. 1, we obtained at room temperature $n_2=(4.9-i0.62)\times 10^{-10}$ cm^2/W. Substituting this n_2 value in Eq. (2), $\Delta\alpha=1.3\times 10^{-25}$ cm^3 and $\Delta\sigma=6.1\times 10^{-20}$ cm^2 were calculated. The $\Delta\alpha=1.3\times 10^{-25}$ cm^3 obtained at room temperature is the largest measured for Nd^{3+}-doped materials.[1,2,9] It is only comparable to $\Delta\alpha=9.6\times 10^{-26}$ cm^3 obtained for YVO_4 and approximately the double of the YAG value[7] and that of other oxide crystals.[9] The most remarkable result is the $\Delta\alpha(T)$ behavior (shown in Fig. 2), which is observed to decrease from 1.3×10^{-25} cm^3 in the ferroelectric phase, down to 2.0×10^{-26} cm^3 in the paraelectric phase. This 1 order of magnitude variation is comparable to that one observed for $\Delta\alpha$ with the composition by Powell *et al.*[9] in a systematic study performed on 21 different Nd^{3+}-doped materials (crystals and glasses). They attributed this strong variation of $\Delta\alpha$ to the sensitivity of the $\langle 4f|r|5d\rangle$ radial integral to host matrix. Consequently, we can conclude that although the f-p phase transition has a negligible effect in the 4*f* states of Nd^{3+} ions in the SBN system;[13,25] it indeed can cause an extremely large variation in the $\langle 4f|r|5d\rangle$ radial integral because the weaker screening of the 5*d* states.

The $\Delta\sigma$ temperature dependence shown in Fig. 2 follows the typical behavior of a phase transition in relaxor ferroelectrics. Provided the fact that the ground-state absorption cross section is not affected by the f-p phase transition, we can conclude that the excited-state absorption nearly doubles its value from room temperature up to the peak at ~344 K, which is the transition temperature in agreement with the value obtained for TL (Refs. 16 and 23) and dielectric constant measurements.[26,27] The peak value $\Delta\sigma=12\times 10^{-20}$ cm^2 is also surprisingly large, 1 order of magnitude larger than the ground-state cross section ($\sigma_g \approx 0.5\times 10^{-20}$ cm^2 at 514.5 nm), so $\Delta\sigma \approx \sigma_{ex}$. This indicates a strong excited-state absorption (ESA) to a state at $\sim 3.1\times 10^4$ cm^{-1}, which lies above the absorption edge of the SBN host matrix. At this point we state that this strong ESA occurs probably due to an intrinsic defect state of SBN.

It is interesting to remark that the fluorescence lifetime, the emission cross section, and band shape of Nd^{3+}:SBN crystals are temperature independent in the range of 300–470 K.[16,25] This behavior can be attributed to the weak sensitivity of the Nd^{3+} $4f \rightarrow 4f$ transitions to the crystalline field, as opposed to the Yb^{3+} case.[15] Therefore, the results of this work indicate that the $\Delta\alpha$ parameter provides access to excited states which are weakly screened and therefore are more sensitive to changes in the crystalline field compared to linear spectroscopic properties.

In summary, time-resolved *Z*-scan measurements were performed in Nd^{3+}:SBN as a function of temperature, through the ferroelectric-to-paraelectric phase transition. Very strong temperature dependences were observed for the real and imaginary parts of the nonlinear susceptibility, which is proportional to n_2. It was found that the dominant contribution to the *Z*-scan signal is associated with the electronic population lens (the $\Delta\alpha$ effect), with negligible contribution of the thermal lens effect. In addition, the nonlinear absorption and refraction are strongly affected by the phase transition. Considering that the linear spectroscopic properties of 4*f* states of Nd^{3+} ions in the SBN system are not affected by the phase transition, we correlate these changes to the influence of the phase-transition-induced structural changes in the properties of the weakly screened 5*d* Nd^{3+} states. The results included in this work evidence the suitability of the *Z*-scan technique for the characterization and detection of electronic and structural changes in rare-earth-doped optical systems.

A.R. would like to thank S. Carinelli for fruitful discussion and technical support. This work has been financially supported by the Spanish Comunidad Autónoma de Madrid (CAM) and Universidad Autónoma de Madrid (UAM) under research Projects No. MAT2004-03347, No. MAT2007-64686, and No. CCG07-UAM/MAT-1861 and by the Brazilian agencies CNPq, FAPESP, CAPES, FAPEAL, and FINEP.

*Corresponding author; cjacinto@if.ufal.br

[1] R. C. Powell, *Physics of Solid-State Laser Materials* (Springer, New York, 1998).

[2] C. Jacinto, D. N. Messias, A. A. Andrade, S. M. Lima, M. L. Baesso, and T. Catunda, J. Non-Cryst. Solids **352**, 3582 (2006).

[3] A. A. Fotiadi, O. L. Antipov, and P. Mégret, Opt. Express **16**, 12658 (2008).

[4] P. Sillard, A. Brignon, and J. P. Huignard, J. Opt. Soc. Am. B **14**, 2049 (1997).

[5] S. Stepanov and E. Hernandez, Opt. Lett. **30**, 1926 (2005).

[6] R. C. Powell and S. A. Payne, Opt. Lett. **15**, 1233 (1990).

[7] J. Margerie, R. Moncorge, and P. Nagtegaele, Phys. Rev. B **74**, 235108 (2006).

[8] S. M. Lima and T. Catunda, Phys. Rev. Lett. **99**, 243902 (2007).

[9] R. C. Powell, S. A. Payne, L. L. Chase, and G. D. Wilke, Phys. Rev. B **41**, 8593 (1990).

[10] D. N. Messias, T. Catunda, J. D. Myers, and M. J. Myers, Opt. Lett. **32**, 665 (2007).

[11] R. Moncorge, O. N. Eremeykin, J. L. Doualan, and O. L. Antipov, Opt. Commun. **281**, 2526 (2008).

[12] E. M. Rodríguez, D. Jaque, J. García Solé, and R. Pankrath, Appl. Phys. Lett. **92**, 181107 (2008).

[13] M. O. Ramirez, D. Jaque, L. E. Bausa, J. García Solé, and A. A. Kaminskii, Phys. Rev. Lett. **95**, 267401 (2005).

[14] M. O. Ramirez, D. Jaque, M. Montes, J. García Solé, L. E. Bausa, and L. Ivleva, Appl. Phys. Lett. **84**, 2787 (2004).

[15] M. O. Ramirez, L. E. Bausa, A. Speghini, M. Bettinelli, L. Ivleva, and J. García Solé, Phys. Rev. B **73**, 035119 (2006).

[16] C. Jacinto, T. Catunda, D. Jaque, J. García Solé, and A. A. Kaminskii, J. Appl. Phys. **101**, 023113 (2007).

[17] V. Pilla, P. R. Impinnisi, and T. Catunda, Appl. Phys. Lett. **70**, 817 (1997).

[18] M. Sheik-bahae, A. A. Said, and E. W. V. Stryland, Opt. Lett. **14**, 955 (1989).

[19] L. C. Oliveira and S. C. Zilio, Appl. Phys. Lett. **65**, 2121 (1994).

[20] L. R. Freitas, C. Jacinto, A. Rodenas, D. Jaque, and T. Catunda, J. Lumin. **128**, 1013 (2008).

[21] A. A. Andrade, E. Tenorio, T. Catunda, M. L. Baesso, A. Cassanho, and H. P. Jenssen, J. Opt. Soc. Am. B **16**, 395 (1999).

[22] L. C. Oliveira, T. Catunda, and S. C. Zilio, Jpn. J. Appl. Phys., Part 1 **35**, 2649 (1996).

[23] C. Jacinto, D. Jaque, E. M. Rodriguez, and J. García Solé, Appl. Phys. Lett. **88**, 161116 (2006).

[24] C. Jacinto, A. A. Andrade, T. Catunda, S. M. Lima, and M. L. Baesso, Appl. Phys. Lett. **86**, 034104 (2005).

[25] U. Caldino, P. Molina, M. O. Ramirez, D. Jaque, L. E. Bausa, C. Zaldo, L. Ivleva, M. Bettinelli, and J. García Solé, Ferroelectrics **363**, 150 (2008).

[26] J. Dec, W. Kleemann, S. Miga, C. Filipic, A. Levstik, R. Pirc, T. Granzow, and R. Pankrath, Phys. Rev. B **68**, 092105 (2003).

[27] A. S. Bhalla, R. Guo, L. E. Cross, G. Burns, F. H. Dacol, and R. R. Neurgaonkar, Phys. Rev. B **36**, 2030 (1987).