Detailed characterization of pump-induced refractive index changes observed in Nd:YVO$_4$, Nd:GdVO$_4$ and Nd:KGW

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Abstract: The refractive index changes which can be induced in the Nd:YVO$_4$, Nd:GdVO$_4$ and Nd:KGW high gain laser crystals, when their Nd$^{3+}$ laser active ions are pumped from their ground- to excited- energy levels, have been carefully measured and characterized. By using two complementary optical techniques based on pump-probe interferometry and transient diffraction grating, the electronic and thermal contributions to the observed refractive index variations have been accurately determined and successfully exploited to derive various parameters such as polarizability changes, thermo-optic coefficients and thermal diffusivities.

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OCIS codes: (160.3380) Laser materials; (190.4720) Optical nonlinearities of condensed matter; (140.5680) Rare earth and transition metal solid-state lasers.

References and links

Observation of athermal refractive index variations in highly pumped laser materials is a topic which motivates the interest of several research groups for different reasons [1–6]. It primarily raises very fundamental questions. It seems indeed that a great part of these refractive index changes can be assigned to a purely dispersive (non-resonant) effect [7] coming from variations of polarisabilities of the laser active ions when they are brought from their ground- to their excited electronic energy levels. In highly pumped laser materials, it was shown, for example, that the effect of these refractive index variations could be comparable.
and eventually larger than the usual thermal lensing effects, depending on the nature of the laser active ion, of the host material and on the configuration of the laser medium (bulk crystal, microchip or fiber).

A first detailed study was recently performed in the case of the well-known high power laser material Nd:YAG. This experimental and theoretical investigation [3] has shown rather unambiguously for the first time (which was anticipated in the past via four-wave mixing experiments [8]) that the major part of the observed effects was likely due to the existence of absorption bands associated with 4f→5d interconfigurational transitions of the Nd\(^{3+}\) ions. It was noticed [2,8], however, that other types of absorption bands such as “ligand to metal” charge transfer (LMCT) transitions could also contribute. Such a contribution seems to be predominant for example in Yb:YAG, another very important rare-earth doped material for high power laser applications in which large refractive index variations have been recently observed [9, 10]. Such types of refractive index variations also seems to be responsible for the nanosecond self-Q-switching behaviour recently observed in such a transition-metal-ion doped laser material as Cr:LiSAF [11], a material which gave rise over the past few years to the most compact and low threshold diode-pumped femtosecond laser system.

As a matter of fact, for materials doped with rare-earth ions such as Nd\(^{3+}\) and Yb\(^{3+}\) as well as for materials doped with transition-metal ions such as Cr\(^{3+}\), a number of questions need to be addressed. Deeper experimental and theoretical investigations are necessary to better understand and estimate the relative contributions to the observed refractive index changes. One needs first to clearly discriminate between the thermal and the electronic contributions which may be very different from one system to the other. Indeed, the host materials may have very different thermo-mechanical properties and the optical excitation and emission processes involved with the various laser active ions may be generating more or less phonons, thus heat, in the considered laser hosts.

One also needs to clearly discriminate between the resonant and non-resonant contributions and, depending on the host and active ion laser system, between the contributions of the interconfigurational and the ligand-to-metal charge transfer transitions. This type of information should most useful when investigating and engineering some host materials with specific compositions and/or codopants.

The nonlinear properties based on athermal refractive index changes in ion-doped materials also play an important role in the study of slow and fast light. Slow and fast light effects were observed recently, for example, in Cr\(^{3+}\) doped crystals such as ruby and alexandrite [12]. Because these results were obtained based on coherent population oscillations (CPO) and because CPO do not require constraining conditions such as atomic dipole coherence, which simplifies experimental set-ups, they motivated first the investigation of several other systems such as Er doped fiber amplifiers [13,14] and semiconductors [15]. Because they arose some controversy, these results also motivated more recently a significant work [2] aimed at the discrimination of the resonant and non-resonant contributions to the resulting nonlinear refraction spectroscopy of both Nd\(^{3+}\) and Cr\(^{3+}\) doped crystals. This work proved that both contributions need to be considered together, without neglecting one for the other, since they can interfere, and that further investigations still need to be performed not only to better characterize and to find the way to enhance these effects but also to exploit them in specific laser systems.

Last but not the least, athermal refractive index variations resulting from non-resonant effects in highly pumped laser materials definitely offer a new alternative for coherent laser beam combining and new laser applications such as adaptive interferometric remote sensors. These effects are based on energy transfer via two-wave mixing in the laser medium itself. Energy transfer has been studied in absorbing media with low efficiency [16,17]. However, in gain media, two-wave mixing based on saturable gain gratings lead to the depletion of the weak signal beam. The understanding and the optimization of athermal refractive index gratings in gain media open very interesting new possibilities to perform efficient energy
transfer between several interacting coherent beams. It could be possible for instance to amplify one beam by several other beams via energy transfer and thus to perform coherent combining.

The present paper concentrates on the case of the well-known Nd\(^{3+}\) doped high gain laser crystals YVO\(_4\), GdVO\(_4\) and KGW, and a comparison is made with what is found in the case of Nd:YAG. Our first goal is to show in the case of such 4-levels laser systems how electronic and thermal contributions, and thermal contributions coming from multiphonon relaxations in the upper and lower lying energy levels of the Nd\(^{3+}\) laser transition can be really discriminated experimentally, and thus how reliable refractive index and corresponding polarizability changes can be derived. Our second purpose is to discuss on the origin of the polarizability changes involved in these specific crystals, the vanadate and tungstate molecular ions exhibiting strong optical transitions in the near UV spectral range, and to derive values at other wavelengths than the probe wavelength used in the considered experiments.

2. Experimental methods

The pump-induced refractive index changes observed in the studied crystals were investigated by using two complementary pump-probe techniques: an interferometric technique based on a so-called Jamin-Lebedev interferometer and a transient grating technique. This was necessary to fully discriminate between the above mentioned contributions.

The two techniques were already used and recently compared in the case of Yb:YAG [9]. As it is a quasi 3-levels laser system, however, only multiphonon relaxation of the excitation in the high lying energy levels of the Yb\(^{3+}\) ions really contributes to the thermally induced change of refractive index and the extraction of the electronic contribution is more direct and can be realized by using any technique.

The situation is somewhat different in such a 4-levels laser system as Nd\(^{3+}\) (see in Fig. 1). Indeed, the non-radiative relaxations of the excitations within the \(^4\!I_{15/2},\ ^4\!I_{13/2},\ ^4\!I_{11/2}\) and \(^4\!I_{9/2}\) terminal levels of the Nd\(^{3+}\) emission transitions will constitute a delayed thus a slower thermal load than the one coming from the non-radiative relaxation within the \(^4\!F_{5/2}\) and \(^4\!F_{3/2}\) upper excited levels. In this case, as it is shown in the following, the interferometric and transient grating techniques give very useful complementary data.

The Nd\(^{3+}\) doped laser crystals were pumped at about 808 nm with the aid of a pulsed Ti: Sapphire laser delivering pulses up to 5 mJ at a repetition rate of 10 Hz. The refractive index variations were probed with a He-Ne laser at 632.8 nm. The average excited-state population densities

\[
\Delta N(t=0) = \int_0^l \Delta N(r=0,z,t=0)dz/l
\]

(where \(l\) is the thickness of the crystal and \(z\) the coordinate normal to the sample surface) were evaluated by assuming that the pump beam was gaussian and knowing the absorbed pump energy in the crystal. The polarisability change of Nd\(^{3+}\) ions labelled \(\Delta \alpha_p\) was deduced from the purely electronic contribution to the measured refractive index change by using the expression

![Fig. 1. Origin of thermal loads in 4-level laser systems](image)
\[
\Delta n_r(t = 0) = 2\pi f_s^2 \Delta \alpha_r \frac{\Delta N(t = 0)}{n_0}
\]  
(1)

where \( f_s = (n_0^2 + 2)/3 \) is the usual Lorentz correction factor and \( n_0 \) the linear refractive index of the material at 632.8 nm.

As mentioned above, the first technique is based on a Jamin-Lebedev polarization interferometer. With such an experimental set-up, whose description can be found in [5,9], it is possible to detect optical path variations of the order of \( \lambda/5000 \). The pump-induced refractive index changes lead to phase-shift variations which can be evaluated from the observed relative intensity modulation of the interference signal \( \Delta I(t)/2I_0^{+} \) through the expression (in case of small modulations):

\[
\frac{\Delta I(t)/2I_0^{+}}{\Delta \phi(t)} \approx \frac{\Delta n(t)}{\Delta \phi(0)} = 2\pi n_0 \frac{\Delta \Delta n(t)}{\Delta \phi(0)} (2l) / \lambda_0
\]  
(2)

where \( \lambda_0 \) is the wavelength of the probe beam.

The measured refractive index variations were transient signals \( \Delta n(t) \) resulting from the overlap of the pump and probe beam distributions inside the crystal and the \( \Delta n \) (\( r = 0, t = 0 \)) value was obtained, because beams were gaussian beams with beam waist radii \( \omega_{pump} \) and \( \omega_{probe} \), by dividing \( \Delta n(t = 0) \) by the factor \( \frac{\omega_{pump}^2}{\omega_{pump}^2 + \omega_{probe}^2} \).

Maximum refractive index variations usually ranged between about \( 5 \times 10^{-6} \) and \( 5 \times 10^{-5} \) and transient signals were registered up to 100 ms after the excitation pump pulse. Within this temporal window, the measured phase-shift signals usually consist of two decaying components, a short-lived one, which is generally assigned to a purely electronic refractive index change, and a long-lived one which is assigned to the contribution from the thermally induced refractive index variation [5].

These transients can be satisfactorily described by such an expression as:

\[
\Delta \phi(t) = \Delta \phi_{lo} \times \exp(-t/\tau_e) + \Delta \phi_{20}/(1 + t/\tau_{th}) + \Delta \phi_0
\]  
(3)

where \( \Delta \phi_{lo} \) and \( \Delta \phi_{20} \) stand for the phase-shift changes associated with the short- and long-lived components with time constants \( \tau_e \) and \( \tau_{th} \), respectively, and \( \Delta \phi_0 \) accounts for the residual thermal phase shift difference which subsists between the two probe channels more than 100 ms after the pump pulse. Fitting of the experimental data with Exp. (3) led to a characteristic time-constant \( \tau_e \) equal to the lifetime of the active ion metastable level when the pump waist radius \( \omega_{pump} \) was equal or larger than 450 µm but to a larger value when this waist size was smaller. In the same way, the ratio defined by \( \Delta \phi_0/(\Delta \phi_{lo} + \Delta \phi_{20} + \Delta \phi_0) \), thus the ratio of the amplitude of the short-time portion over the total amplitude, remained constant when the pump waist radius \( \omega_{pump} \) was larger than 450µm, but increased when the pump size was smaller. Thus, in our experimental set-up the pump beam inside the crystal had a beam-waist radius of 450 µm and the one for the two testing cross-polarized beams was 150 µm, giving a factor \( \frac{\omega_{pump}^2}{\omega_{pump}^2 + \omega_{probe}^2} \) equal to 0.9.

The ratio \( \Delta \phi_0/(\Delta \phi_{lo} + \Delta \phi_{20} + \Delta \phi_0) \) will be used in the following to distinguish between the up and down contributions to the thermally induced refractive index change from the purely electronic one. Indeed, it will be shown that the short part of the interferometric
transient signal in a 4-level system is not only due to a purely electronic refractive index change but that it also contains some thermal refractive index change contribution.

It is worth noting here that the thermal time-constant $\tau_{th}^{\text{int}}$ which appears in the interferometer technique is given by the thermal diffusion of a two-dimensional Gaussian distribution of heat, thus, assuming that the gradient of heat along the pump beam propagation direction can be neglected, by the expression:

$$
\tau_{th}^{\text{int}} = \omega_{\text{pump}}^2 / 8 \chi
$$

where $\chi$ stands for the thermal diffusivity.

The second technique used here is based on laser induced grating [18,19]. It is less sensitive than the former ($\lambda/1000$) but it presents the same signal to noise ratio (SNR = 20) for optical path variations of about $\lambda/100$. Thus, this method is as much reliable as the former for such high optical path variations. A diffraction beam splitter was used on the pump beam to generate a population grating in the sample with a period of $\Lambda = 32 \mu$m and the radius of the resulting pump-induced grating was 850 $\mu$m. On the other hand, the beam waist of the probe beam was adjusted on the front facet of the sample with a radius of 250 $\mu$m. In this way, both the $+1$ and $-1$ orders diffracted by the pump-induced phase grating were detected on a photodetector and the 0 order was detected on a second one for evaluation of the diffraction efficiency.

By using crystals with thicknesses of about 1 mm, it was possible to have the condition:

$$
Q \nu \leq 1
$$

where $Q = \frac{2\pi\lambda_0 l}{n_1 \Lambda^2}$ is the wave vector mismatch and $\nu$ the grating strength parameter $\nu = \frac{\pi\Delta n l}{2\lambda_0}$. Thus, even though the incomplete popular condition $Q < 1$ was not satisfied, the diffraction regime was a Raman-Nath regime [20] for which the diffraction efficiency can be approximated (within about 1%) by the following expressions [18,19,21]:

$$
D(t) = \frac{P_1}{P_0} = \left( \frac{\pi}{\lambda_0} \right)^2 \left[ \frac{\pi \Delta n(0) l}{\lambda_0} \right]^{2.5} \left[ \eta_e \exp(-t / \tau_e) + \eta_a \exp(-t / \tau_a^{\text{th}}) \right]^2
$$

where

$$
\left( \frac{\pi \Delta n(0) l}{\lambda_0} \right)^{2.5} = \left( \frac{\pi l}{\lambda_0} \right)^2 \left( \frac{\int \left[ E(x, y) \Delta n(t = 0, x, y) \right]^2 dx dy}{\int \left[ E(x, y) \right]^2 dx dy} \right)
$$

thus

$$
\left( \frac{\pi \Delta n(0) l}{\lambda_0} \right)^{2.5} = \left( \frac{\pi \Delta n(0) l}{2\lambda_0} \right)^2 \left( \frac{\omega_{\text{pump}}^2}{\omega_{\text{pump}}^2 + (\sqrt{2} \omega_{\text{probe}})^2} \right)
$$

in the case of gaussian beams.

The expression $\frac{\omega_{\text{pump}}^2}{\omega_{\text{pump}}^2 + (\sqrt{2} \omega_{\text{probe}})^2}$ was equal to 0.85 in our experimental set-up. $P_1$ and $P_0$ are the power diffracted in the $+1$ or $-1$ orders and the total diffracted power, respectively.
$\eta_e$ and $\eta_{th}$ are the relative amplitudes of the electronic and thermal contributions with the time-
constants $\tau_e$ and $\tau_{th}$, respectively.

According to Exp. (6), in the transient grating technique, the square root of the diffraction
efficiency signal also consists of two decaying components. In this case, however, the thermal
contribution to the diffraction efficiency, thus to the refractive index variation, is governed by
the thermal diffusion along the grating vector, i.e. over the short distance $\Lambda$, with the
characteristic time constant:

$$\tau_{th}^{\text{eff}} = \Lambda^2 / 4 \pi^2 \chi$$

(8)

This thermal contribution thus will be generally contained in the short time portion of the
signals, whereas the electronic contribution will essentially appear at the longest times after
the exciting laser pulse. To correctly discriminate between these two contributions, however,
the period of the grating must be adjusted as a function of the considered emission lifetime.
The emission lifetime of the studied materials being relatively short ($\tau_e \approx 60 - 90 \mu s$)
compared to the ones investigated in the past [5, 9, 21], it is the reason why we chose a small
grating period of 32 $\mu$m.

3. Results of interferometric and transient grating experiments

As an illustration, we show in Fig. 2 the phase shift variations and the square root of the
diffraction efficiencies measured with the interferometric and the transient grating techniques,
for two probe beam polarizations in the case of $1\%$ Nd$^{3+}$ doped YVO$_4$.

![Fig. 2. Kinetics of the phase shift changes (a, b) and of the square root of the diffraction
efficiencies (c, d) measured with the interferometric and transient grating techniques,
respectively, for $E_{/\parallel}$ (a, c) and $E_{/\perp}$ (b, d) probe beam polarisations in a $1\%$ Nd$^{3+}$
doped YVO$_4$ crystal]

As predicted by Exp.(3) and Exp. (6), two decreasing components clearly appear in each
case and the time constants which appear in the short-time and long-time portions of the
interferometric and transient grating signals, respectively, are clearly the same and equal (to
within about 10%) to the expected emission lifetime of Nd$^{3+}$ in YVO$_4$ (see in the Tables 1 and
2).
Table 1. Data and parameters used in the fitting of the interferometric transient signals with Exp. (3) in the text.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Active ion doping</th>
<th>$\Delta N_{\text{c}} \times 10^{18}$ cm$^{-1}$</th>
<th>$\Delta \phi_{10}$ (rad)</th>
<th>$\Delta \phi_{20}$ (rad)</th>
<th>$\Delta \phi_{1}$ (rad)</th>
<th>$\Delta \phi_{10} + \Delta \phi_{20} + \Delta \tau_{\text{e}}$ (µs)</th>
<th>Measured emission lifetime (µs)</th>
<th>$\tau_{\text{int}}$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdVO$_4$</td>
<td>1%</td>
<td>19</td>
<td>0.155</td>
<td>0.151</td>
<td>-0.010</td>
<td>52%</td>
<td>84</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>$\bar{E} \parallel c$</td>
<td>19</td>
<td>0.082</td>
<td>0.137</td>
<td>-0.009</td>
<td>39%</td>
<td>92</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>$\bar{E} \parallel a$</td>
<td>24</td>
<td>0.028</td>
<td>0.081</td>
<td>-0.004</td>
<td>27%</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>$\bar{E} \parallel c$</td>
<td>21</td>
<td>0.007</td>
<td>0.064</td>
<td>-0.004</td>
<td>10%</td>
<td>130</td>
<td>60</td>
</tr>
<tr>
<td>YVO$_4$</td>
<td>1%</td>
<td>15</td>
<td>0.094</td>
<td>0.154</td>
<td>-0.009</td>
<td>39%</td>
<td>93</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>$\bar{E} \parallel c$</td>
<td>15</td>
<td>0.139</td>
<td>0.102</td>
<td>-0.007</td>
<td>59%</td>
<td>82</td>
<td>92</td>
</tr>
<tr>
<td>KGW</td>
<td>0.86%</td>
<td>4.5</td>
<td>0.069</td>
<td>-0.133</td>
<td>0.132</td>
<td>102%</td>
<td>97</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>$\bar{E} \parallel n$</td>
<td>4.5</td>
<td>0.057</td>
<td>0.003</td>
<td>0.000</td>
<td>96%</td>
<td>95</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>$\bar{E} \parallel n$</td>
<td>9.2</td>
<td>0.164</td>
<td>0.026</td>
<td>0.001</td>
<td>86%</td>
<td>61</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>$\bar{E} \parallel n$</td>
<td>9.2</td>
<td>0.121</td>
<td>0.051</td>
<td>-0.007</td>
<td>73%</td>
<td>63</td>
<td>60</td>
</tr>
</tbody>
</table>

The other time-constants which appear in the tail and at the beginning of the interferometric and transient grating signals are about 100 times larger and 5-10 times smaller, respectively, that this emission lifetime. All the parameters used to fit the data with Exp.(3) and Exp. (6), including the $\Delta N_{\text{c}}$ estimated values and the amplitude parameters, have been reported in the Tables 1 and 2.
Table 2. Data and parameters used in the fitting of the transient grating signals with Exp. (6) in the text.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Active ion concentration</th>
<th>$\frac{\Delta N}{10^6}$</th>
<th>$\Delta n_{max}(0) \times 10^{-6}$</th>
<th>$\eta_e$</th>
<th>$\tau_e$ (µs)</th>
<th>$\tau_{th}$ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdVO₄ 1%</td>
<td>$\overline{E} / \bar{l}$</td>
<td>11</td>
<td>8.8</td>
<td>68%</td>
<td>89</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>$\overline{E} / \bar{a}$</td>
<td>10</td>
<td>6.7</td>
<td>77%</td>
<td>88</td>
<td>11.2</td>
</tr>
<tr>
<td>GdVO₄ 3%</td>
<td>$\overline{E} / \bar{l}$</td>
<td>21</td>
<td>19</td>
<td>74%</td>
<td>65</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>$\overline{E} / \bar{a}$</td>
<td>19</td>
<td>12</td>
<td>84%</td>
<td>65</td>
<td>15.0</td>
</tr>
<tr>
<td>YVO₄ 1%</td>
<td>$\overline{E} / \bar{l}$</td>
<td>12</td>
<td>9.5</td>
<td>72%</td>
<td>88</td>
<td>11.3</td>
</tr>
<tr>
<td></td>
<td>$\overline{E} / \bar{a}$</td>
<td>10</td>
<td>7.7</td>
<td>77%</td>
<td>88</td>
<td>11.2</td>
</tr>
<tr>
<td>KGW 0.86%</td>
<td>$\overline{E} / n_{eg}$</td>
<td>5.0</td>
<td>1.9</td>
<td>93%</td>
<td>90</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>$\overline{E} / n_{em}$</td>
<td>6.2</td>
<td>2.5</td>
<td>84%</td>
<td>85</td>
<td>13.0</td>
</tr>
<tr>
<td>KGW 1.77%</td>
<td>$\overline{E} / n_{eg}$</td>
<td>4.0</td>
<td>1.2</td>
<td>81%</td>
<td>60</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>$\overline{E} / n_{em}$</td>
<td>4.4</td>
<td>2.2</td>
<td>91%</td>
<td>59</td>
<td>13.0</td>
</tr>
</tbody>
</table>

As shown by the graphs reported in the left hand side of the Fig. 3, the total refractive index change normalized by the number of excited ions per cm$^3$ remains about the same whatever the technique is used because only the electronic refractive index change and the thermal refractive index change coming from the non-radiative relaxation within the $^4F_{5/2}$ and $^4F_{3/2}$ upper excited levels appear. However the ratio between the component with the decay time equal to the emission lifetime and the amplitude at time $t = 0$ is different. Indeed, the thermal diffusion time is very different from one technique to the other leading to a contribution from the non-radiative relaxation between the $^4I_{15/2}$, $^4I_{13/2}$, $^4I_{11/2}$ and the $^4I_{9/2}$ energy levels of Nd$^{3+}$ in the interferometric signal but not at all in the transient grating one.

Fig. 3. Comparison of the total refractive index changes $\Delta n_{max}(0)$ normalized by the number of excited ions per cm$^3$ obtained with each technique (left) and comparison of the ratios $\eta_e$, $\frac{\Delta \phi_{10}}{\Delta \phi_{10} + \Delta \phi_{00} + \Delta \phi_{1}}$ and $\frac{\Delta \phi_{10}}{\Delta \phi_{10} + \Delta \phi_{00} + \Delta \phi_{1}}$ between the components with the decay time equal to the emission lifetime and the amplitudes measured at time $t = 0$ with the transient grating and the interferometric techniques, respectively (right). Vertical lines stand for error bars.
With the aid of the two techniques it is thus possible to distinguish between the up and down contributions to the thermally induced refractive index change from the purely electronic one by writing:

\[
\eta_e = \frac{\Delta n_e}{\Delta n_t + \Delta n^e} \quad \text{and} \quad \Delta \phi^{th} = \frac{\Delta \phi^{th}_{up + \Delta \phi^{th}_{20}}}{\Delta n_t + \Delta n^e} = \frac{\Delta n_e^{up} - \Delta n_e^{down}}{\Delta n_t + \Delta n^e}
\]

(9)

where \(\Delta n_e\) is the average induced electronic refractive index change and \(\Delta n_e^{up}\) and \(\Delta n_e^{down}\) are the average induced thermal refractive index changes coming from the up and down excited levels. We have reported each of these contributions in the left hand side of the Fig. 4. The total thermal refractive index change is approximately equal to the electronic refractive index change in the vanadates whereas it is nearly negligible in the case of the tungstates.

This behaviour can be related to the respective \(\partial n / \partial T\) values of the considered materials. Indeed, the local temperature variation is given by:

\[
\Delta T(r, z) = \frac{E_{abs}(r, z)}{\rho C_p d^3 r}
\]

(10)

where \(E_{abs}(r, z)\) is the absorbed energy at the coordinates \((r, z)\), \(\rho\) is the density, \(C_p\) the specific heat of the bulk material and \(d^3 r\) the elementary volume.

Thus the average thermal refractive index variation at \(r = 0\) is given by:

\[
\frac{\Delta n_{up} + \Delta n^{down}_{th}}{\Delta n_t} = \frac{\partial n}{\partial T} = \eta_h \frac{h \nu}{\rho C_p} \frac{\Delta N}{\partial T}
\]

(11)

with \(\eta_h\) the fraction of the absorbed energy transformed into heat and \(h \nu\) the energy of the pump photons. The resulting \(\partial n / \partial T\) values are reported in the Table 3 assuming that \(\eta_h\) is equal to 40%, which is the value found by Fan [22] for 1\%Nd:YAG.
Table 3. Thermal parameters for GdVO₄, YVO₄ and KGW calculated with Exp. (4), Exp. (8) and Exp. (12) in the text (references to literature data appear within parentheses)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample</th>
<th>κ (W.m⁻¹K⁻¹)</th>
<th>ρ (Kg.m⁻³)</th>
<th>Cᵥ (J.Kg⁻¹K⁻¹)</th>
<th>ĉn / ĈT (10⁻⁴K⁻¹)</th>
<th>ĉn / ĈT (10⁻⁴K⁻¹)</th>
<th>χ_{dif} (mm²/s)</th>
<th>χ_{int} (mm²/s)</th>
<th>χ_{theo} (mm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KGW: 0.86%Nd</td>
<td>KGW: 0.86%Nd</td>
<td>3 [26]</td>
<td>7270</td>
<td>500</td>
<td>−0.47</td>
<td>4.3 [26], 0.4 [27]</td>
<td>3.2</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>KGW: 1.77%Nd</td>
<td>KGW: 1.77%Nd</td>
<td>3 [26]</td>
<td>7270</td>
<td>500</td>
<td>0.48</td>
<td>−18.2 (E/n_s)</td>
<td>6.5 (E/n_m) [28]</td>
<td>2.0</td>
<td>1.8</td>
</tr>
</tbody>
</table>

These estimated values are in rather good agreement with the values found in the literature [25, 27]. They substantially differ, however, in the case of KGW, with the values reported by Filipov and Biswal [28, 29] (the ones are given for the different polarisations but disagree both in sign and value between each other).

Thermal diffusivities can be estimated by using Exp. (4) and Exp. (8) and knowing $\tau_{th}$, $\alpha_{pump}$ and $\Lambda$. These estimated values are also gathered in the Table 3 and compared with the theoretical ones which can be calculated from the expression:

$$\chi_{theo} = \frac{\kappa}{\rho C_v}$$

(12)

where $\kappa$ stands for the thermal conductivity. The estimated values differ from the theoretical ones by about 35% for vanadates, which is satisfactory, but by more than 80% for tungstates, probably because of the small thermal contribution to the signals.

The extracted electronic refractive index changes then can be converted into polarisability changes by using Exp. (1). The results have been reported on the right hand side of the Fig. 4. The resulting $\Delta \alpha_p$ values range between $2.8 \times 10^{-26}$ cm³ and $5 \times 10^{-26}$ cm³ for the vanadates and between $2.5 \times 10^{-26}$ cm³ and $3.3 \times 10^{-26}$ cm³ for the tungstates. For the same doping level, the $\Delta \alpha_p$ value for YVO₄ appears slightly larger than that found for GdVO₄. The latter, however, substantially increases with the dopant concentration. In the case of Nd:KGW, polarisations and doping levels do not really appear as critical parameters.
Fig. 4. Up and down thermal and purely electronic contributions to the refractive index changes normalized by the number of excited ions per cm$^3$ (left) and extracted polarizability changes at 633 nm (right) calculated with Exp. (1) in the text. Error bars are indicated by vertical lines.

Discussion of the results:

Concerning the derived $\partial n / \partial T$ values, it is worth noting that the measurements can be impacted by stress distribution effects. Knowing, however, that the strain change dynamics is usually very short, of the order of a few ps, if this stress distribution effects contribute to the optical path variations in our experiments it should have the same dynamics as $\partial n / \partial T$. Moreover, except for the case of Nd:KGW, the deduced $\partial n / \partial T$ values do not differ so much from the thermo-optic coefficients already reported in the literature. It is clear, however, that more careful and complete measurements should be probably made in the case of a very anisotropic and thermal stress sensitive material as Nd:KGW to get unambiguous $\partial n / \partial T$ values, but this is out of the scope of this communication.

Concerning uncertainties made in the two types of experiments, error bars have been indicated both in the Fig. 3 and the Fig. 4. Concerning the total $\Delta n_{\text{max}} / \Delta N$ ratios reported on the left side of Fig. 3, we see that uncertainties are much bigger with the transient grating (TG) technique (~25%) than with the interferometric (INT) one (~10%). For both techniques, the signal-to-noise-ratios of the measured optical path variations remain very good (~50), but the calibration in the INT technique can be simply made by rotating the birefringent plate and by inducing a phase shift of $\pi/2$, whereas calibration is more delicate for the TG technique. Thus the measured refractive index change (RIC) is typically known with a precision of about 3% for the INT technique and 15% for the TG technique. Additionally, the average probed ion density was known to within 7% for the INT and 10% for the TG technique giving the above indicated overall uncertainties on $\Delta n_{\text{max}} / \Delta N$.

The polarisability change for an optically active ion in a specific material should not be dependent, in principle, on the ion concentration. But, increasing the ion concentration can lead to concentration quenching and upconversion type energy transfers. When upconversion occurs, higher energy levels associated with higher polarisabilities can be populated and additional non-radiative multiphonon relaxations also occur. It is thus possible to observe stronger electronic and thermal refraction index changes. This may be at the origin of the increasing electronic and thermal contributions to the refractive index changes observed with the 1% and 3% Nd doped GdVO$_4$ crystals, respectively, and for which we have indeed found non-exponential fluorescence decays and decreasing fluorescence decay times. We have to be very careful, however, with such an interpretation. Indeed, the same decreasing fluorescence decay times have been found for the 0.86% and 1.77%Nd doped KGW crystals without any significant variations in the resulting electronic and thermal refractive index variations. A more detailed and specific study of the dopant concentration effects on the electronic and thermal refractive index changes in these Nd doped materials thus should be made to really clarify this point.
4. Origin of the polarisability changes and data extrapolation at various wavelengths

As already discussed in the past, both theoretically [19] and via four wave mixing experiments [8], different interconfigurational and charge transfer ultraviolet optical transitions can be invoked to account for the polarisability changes of the Nd$^{3+}$ ions when they are brought from their ground to their excited energy levels. As was shown recently, interconfigurational 4f-5d transitions seem to play a major role in such an ionic systems as Nd:YAG. However, some uncertainty was found for this system between the reported $\Delta \alpha_p$ experimental values [5, 8] and the one derived theoretically [3], i.e. around 4 to 4.5$x10^{-26}$ cm$^3$ against 2 to 2.5$x10^{-26}$ cm$^3$, respectively. A new experiment made in the same conditions as the ones reported above for vanadates and tungstates was thus performed here in the case of Nd:YAG. Carefully discriminating between the up and down thermal contributions and the purely electronic one, we finally ended with a $\Delta \alpha_p$ value of $(3\pm0.2)x10^{-26}$ cm$^3$, thus an intermediate value which reconciles the previous experimental and theoretical values, the ones being probably overestimated and the other ones underestimated because of inherent uncertainties. This means that it is not really necessary to involve a supplementary contribution (other than a 4f-5d transition) to account for the electronic polarisability variation and the resulting refractive index change observed in the case of Nd:YAG. However, as asserted by the authors of Ref [8], who reported a polarisability change of about 9.6$x10^{-26}$ cm$^3$ (at the wavelength of 514 nm) in the case of Nd:YVO$_4$ (about twice the value which is reported here at 633 nm), the polarisability of the Nd$^{3+}$ ion in the vanadate and tungstate crystals considered in the present paper could be also affected by the neighboring VO$_3^-$ and WO$_3^-$ molecular ions. As already recently discussed in the case of Yb:KGW [10], polarisability changes in these systems could be influenced indeed by charge transfer (CT) transitions occurring in fact between mixed orbitals Nd$^{3+}$(4f),O$^{2-}$(2p) and V$^{5+}$(5d) or W$^{6+}$(5d). Since such conclusions can be only supported by molecular orbital calculations, which lies outside the scope of the present paper, only extrapolations from the literature data will be attempted hereafter.

Let us check first, from the data obtained for other rare-earth ions in the same vanadate and tungstate materials, whether or not it is possible to position their respective 4f-5d transitions and, knowing these positions, assess $\Delta \alpha_p$ values could result.

No information is available in the literature concerning the position of the 4f-5d band of any trivalent rare-earth ion in YVO$_4$. This is due to the rather small band-gap $E_g \approx$3.6 eV $\approx$ 29050 cm$^{-1}$ of this material. It can be supposed [30], however, that the strength of the crystal-field splitting which determines the position of the lowest 4f-5d band in this material is roughly similar to that found in the case of the isostructural YPO$_4$ system, a system for which, because of a larger band-gap $E_g \approx$8.3 eV, both the Ce$^{3+}$ and the Pr$^{3+}$ 4f-5d bands have been observed [31,32]. This hypothesis is justified by the fact that the average Y-O distances in YVO$_4$ and YPO$_4$ are very similar with values of 2.365 and 2.377 Å, respectively. This is further confirmed by an evaluation of the average oscillator strengths of the 4f-4f optical transitions of Nd$^{3+}$ in these two materials [33], since they are strongly related to the admixture of 4f and 5d orbitals, thus to the positions of the 5d bands. This evaluation indeed showed that the oscillator strengths found in the case of Nd:YPO$_4$ were about 86% of that found in the case of Nd:YVO$_4$. Thus, starting, for instance, from the position $E_{d5}$(Ce$^{3+}$,YPO$_4$) $\approx$31050 cm$^{-1}$ of the 4f-5d band observed in Ce:YPO$_4$, and using the empirical relation proposed by Dorenbos [34], i.e.

$$E_{d5}(\text{Nd}^{3+},\text{YPO}_4) \approx E_{d5}(\text{Ce}^{3+},\text{YPO}_4) + \frac{E_{d5}(\text{Nd}^{3+})-E_{d5}(\text{Ce}^{3+})}{(22700 \pm 650) \text{ cm}^{-1}}$$

(13)

with $E_{d5}(\text{Nd}^{3+})-E_{d5}(\text{Ce}^{3+}) = (22700 \pm 650) \text{ cm}^{-1}$, the position of the lowest 4f-5d band of Nd$^{3+}$ in YPO$_4$, thus approximately in YVO$_4$, should be around 54000 cm$^{-1}$ (6.7 eV).
This is to be compared with the case of Nd:YAG. In this material, indeed, the position of the first 4f-5d band is found around 44400 cm\(^{-1}\) [3], thus nearly 10000 cm\(^{-1}\) lower than in the case of Nd:YVO\(_4\).

Using then the usual approximative expression [8, 35]:

\[
\Delta \alpha_p(\nu) = 7.1 \times 10^{11} \left[ \frac{f_g}{(\nu_{ex} - \Delta \nu) - \nu} - \frac{f_{ex}}{\nu_{ex} - \nu} \right]
\]

(14)

where \(\nu_{ex}\) is the energy (in cm\(^{-1}\)) of the excited level (here the 5d level) making the dominant contribution to the polarisability change, \(\Delta \nu\) is the energy of the populated metastable state (\(^4\)F\(_{3/2}\) in the case of Nd\(^{3+}\)) and \(f_g\) and \(f_{ex}\) the oscillator strengths associated with the ground and excited-state absorption transitions (to the 5d level), it is possible to evaluate at a certain wavelength \(\lambda = 632.8\) nm, thus at a certain energy \(\frac{1}{\nu} = 1/\lambda \approx 15800\) cm\(^{-1}\), and by assuming \(f_g \approx f_{ex} = f\) the ratio between the \(\Delta \alpha_p\) values for Nd:YVO\(_4\) and Nd:YAG as:

\[
\frac{\Delta \alpha_p^{\text{YVO}_4}}{\Delta \alpha_p^{\text{YAG}}} \approx 0.43 \times \frac{f^{\text{YVO}_4}}{f^{\text{YAG}}}
\]

This means, in case of similar 4f-5d oscillator strengths, a \(\Delta \alpha_p\) value for Nd:YVO\(_4\) about half that found in the case of Nd:YAG, which is the reverse of what is obtained experimentally. This discrepancy, however, is not so large and could be easily accounted for by assuming stronger 4f-5d transitions in the case of Nd:YVO\(_4\) compared to Nd:YAG, as it is the case for the oscillator strengths of their respective 4f-4f optical transitions.

Let us examine the case of Nd:KGW by starting now from the ESA measurements performed and reported in the case of Pr:KGW [36]. These unpolarized time-resolved ESA measurements indeed revealed a strong and broad absorption band extending from about 300 to 650 nm and peaking around 400 nm (25000 cm\(^{-1}\)) with a lifetime of about 40 \(\mu\)s indicating that the band was originating from the \(^1\)D\(_2\) energy level of Pr\(^{3+}\) in this material. This level being located around 16500 cm\(^{-1}\), it gives an absorption level located around 41500 cm\(^{-1}\). Assuming that this level is the lowest 5d level of Pr\(^{3+}\) in KGW, thus writing \(E_{5d}(\text{Pr}^{3+}, \text{KGW}) \approx 41500\) cm\(^{-1}\), and using the empirical relation given by Dorenbos [34] between the average positions of the Nd\(^{3+}\) and Pr\(^{3+}\) 5d bands, i.e.

\[
E_{5d}(\text{Nd}^{3+}, \text{KGW}) = E_{5d}(\text{Pr}^{3+}, \text{KGW}) + E_{5d}(\text{Nd}^{3+}) - E_{5d}(\text{Pr}^{3+})
\]

with \(E_{5d}(\text{Nd}^{3+}) - E_{5d}(\text{Pr}^{3+}) = (10500 \pm 1400)\) cm\(^{-1}\), the position of the lowest 4f-5d band of Nd\(^{3+}\) in KGW should peak around 52000 cm\(^{-1}\). As in the case of Nd:YVO\(_4\), the \(\Delta \alpha_p\) experimental value which is found in the case of Nd:KGW (about equal to that found in the case of Nd:YAG) thus could be easily accounted for by assuming a 4f-5d oscillator strength about twice that found in the case of Nd:YAG.

Let us examine now whether the observed polarisability changes could be accounted for by an additional contribution from some charge transfer (CT) transitions. According to the recent literature [37], especially in the case of materials made of molecular groups such as vanadates and tungstates, two kinds of charge transfer mechanisms could be invoked: LMCT (for ligand-to-metal charge transfer) and IVCT (for inter-valence charge transfer) transitions. The former corresponds to the transfer of an electron from a ligand, here an O\(^{2-}\) anion, to the nearest-neighbour trivalent rare-earth dopant, and the second, to the transfer of an electron from this rare-earth ion to the nearest transition metal cation, a V\(^{5+}\) ion in the case of vanadates and a W\(^{6+}\) ion for the tungstates. In each case, the occurrence and the position of

#119029 - $15.00 USD  Received 26 Oct 2009; revised 14 Dec 2009; accepted 15 Dec 2009; published 13 Jan 2010  (C) 2010 OSA 18 January 2010 / Vol. 18, No. 2 / OPTICS EXPRESS 1566
the associated absorption bands depend on several parameters. Without entering into the
details, which can be found in [37] and the refs therein (in particular by Boutinaud, Dorenbos
and collaborators), it is worth to realize first that the occurrence of both types of charge
transfer transitions primarily depends on the positions of the 4f ground levels of the rare-earth
ion in its divalent and trivalent valence states within the band-gap of the host material. A
LMCT transition indeed usually occurs between the top or near the top of the valence band,
which is predominantly made of the 2p orbitals of the O\(^{2-}\) ligands, and the ground level of the
considered rare-earth dopant in its divalent state. Such a transition thus is observed only when
this ground level is lying within the band-gap. On the other hand, an IVCT transition usually
occurs from the 4f ground level of the trivalent rare-earth ion to the bottom of the conduction
band which is itself made predominantly, in the case of vanadates and tungstates, of the
orbitals of the V\(^{5+}\) and W\(^{6+}\) transition metal cations. Such a transition is thus possible, in
principle, whenever the 4f ground level of the trivalent rare-earth dopant is lying above the
top of the valence band.

Additionally, it is now well-known that the relative positions of the 4f ground levels of the
rare-earth ions, whatever their valence states are, remain approximately constant in all the
materials, in the insulators as well as in the semiconductors. The 4f ground level of Pr\(^{3+}\) for
example always lies about 10000 cm\(^{-1}\) above the Nd\(^{3+}\) ground state, and the latter about 8100
cm\(^{-1}\) above that for Yb\(^{3+}\).

With this in mind, we can examine first the case of the vanadates. IVCT absorption bands
were indeed recently reported for Pr\(^{3+}\) in YVO\(_4\), GdVO\(_4\) and LaVO\(_4\) around 26100, 27760 and
28800 cm\(^{-1}\), respectively [38]. According to the analysis of the results found in particular in
the case of LaVO\(_4\) [39], these transitions occur in the case of Pr\(^{3+}\) because the 4f ground level of
this rare-earth ion would be located just above the top of the valence band. This means in
turn that the 4f ground level of Nd\(^{3+}\) would be located itself well below the top of the valence
band, thus preventing any IVCT transitions with this ion in this family of compounds. There
should not be any LMCT transition either. According to [39], the 4f ground level of the Nd\(^{3+}\)
ion would be located indeed well above the bottom of the conduction band.

Let us examine the case of the tungstates by considering now the excited-state absorption
(ESA) band already discussed above in the case of Pr\(^{3+}\) doped KGW [36] and the one recently
reported with Yb\(^{3+}\) [10]. According to the Yb\(^{3+}\) data and knowing that the band-gap of KGW
is about 4eV (32250 cm\(^{-1}\)), the 4f ground-level of Yb\(^{3+}\) in this host material is probably lying
more than 7500 cm\(^{-1}\) below the top of the valence band. Remembering then that the 4f
ground-level of Nd\(^{3+}\) lies about 8100 cm\(^{-1}\) above that for Yb\(^{3+}\), the former should be located
in the vicinity or above the top of the valence band. In this hypothesis, since the 4f ground-
level of Pr\(^{3+}\) is about 10000 cm\(^{-1}\) higher than that for Nd\(^{3+}\), the Pr\(^{3+}\) absorption band located
around 41500 cm\(^{-1}\) is definitely attributed to a 4f-5d band. As a matter of fact, if a LMCT or
an IVCT transition occurred in the Nd\(^{3+}\) doped compound, it would have about the same
energy as the band-gap and the resulting effect on the polarisability change, assuming an
oscillator strength of the same order of magnitude as in the other systems, would be probably
more important than it is observed.

Finally, going back to our previous assignments in terms of 4f-5d interconfigurational
transitions, it is possible to use the estimated positions of these bands and Exp. (14) to
extrapolate the polarisability changes obtained at 632 nm to any other wavelengths, in
particular around 1.06 \(\mu\)m which is the main laser wavelength. Taking a common value of
about 53000 cm\(^{-1}\) for the position of the lowest 4f-5d transition in all the studied materials, it
was found that the \(\Delta\alpha_{\rho}\) values at 632 nm and 1.06 \(\mu\)m could be deduced from each other by
writing \(\Delta\alpha_{\rho}(1.06\mu m) \approx 0.85\Delta\alpha_{\rho}(632nm)\).
5. Conclusion

Excited-state absorption as well as refractive index change (RIC) measurements using complementary pump-probe interferometric and transient grating techniques have been performed in the case of the most famous Nd$^{3+}$ doped vanadates and tungstates laser crystals YVO$_4$, GdVO$_4$ and KGd(WO$_4$)$_2$. A clear distinction has been made in each case between the electronic and thermal contributions to the measured RICs and between the thermal contributions originating from the multiphonon relaxations of the excitations between the involved upper and lower energy levels of the Nd$^{3+}$ ions. Assuming the same fraction of absorbed energy transformed into heat as in Nd:YAG, values for the thermo-optic coefficients and the thermal diffusivities have been extracted and found in rather good agreement with those reported in the literature. Some discrepancies, however, still remain which will probably need to be addressed more specifically in the future. Finally, as in the case of Nd:YAG, interconfigurational 4f-5d transitions seem to play a major role in the pump-induced electronic polarisability and refractive index changes observed in the Nd doped vanadates and tungstates studied here.

Acknowledgements:

Thanks are expressed to Dr. O. Ereymekin from IAP (Nizhny-Novgorod) for his help in the first interferometric measurements, to Drs A. Brignon and J.P. Huignard from Thales (Palaiseau) for their interest in this research, to Pr. Ph. Boutinaud from UCP (Clermont-Ferrand) and Pr. M. Bettinelli from Verona University for sending us some spectroscopic data. Thanks are also expressed to DGA (French Army Delegation) for providing the PhD scholarship of one of us (R.S) and to CNRS (France), NASB (Belarus) and RAS (Russia) for giving us the opportunity to develop such a study within the framework of specific exchange and PICS research programs.