Appl. Phys. B 81, 43–47 (2005)
DOI: 10.1007/s00340-005-1831-4

Applied Physics B
Lasers and Optics

R. LISIECKI[1, ✉]
W. RYBA-ROMANOWSKI[1]
T. LUKASIEWICZ[2]

Blue up-conversion with excitation into Tm ions at 808 nm in YVO_4 crystals co-doped with thulium and ytterbium

[1] Institute of Low Temperature and Structure Research, Polish Academy of Sciences, ul. Okólna 2, 50-950 Wrocław, Poland
[2] Institute of Electronic Materials Technology, Wolczynska 133, 01-919 Warsaw, Poland

Received: 4 January 2005 / Revised version: 14 March 2005

ABSTRACT The up-conversion of infrared radiation at 808 nm, emitted by a diode laser, into blue emission centered at 480 nm in 1 at.% Tm, 5 at.% Yb: YVO_4; 1 at.% Tm, 8 at.% Yb: YVO_4 and 2 at.% Tm, 5 at.% Yb: YVO_4 has been studied. The highest intensity of blue emission is found for the 1 at.% Tm, 8 at.%Yb: YVO_4 system. The power dependence of up-converted emission upon continuous-wave excitation as well as the time evolution of its intensity upon short-pulse excitation were found to be consistent with a two-step excitation mechanism in which the forward Tm^{3+}–Yb^{3+} energy transfer is followed by the back Yb^{3+}–Tm^{3+} energy transfer. The effect of dopant concentrations on the up-conversion process is interpreted taking into account dynamics of the excited states involved.

PACS 42.55.Xi; 42.62.Fi

1 Introduction

Conversion of infrared radiation around 1000 nm into blue emission in various matrices co-doped with Tm^{3+} and Yb^{3+} has been reported in numerous works (see e.g. [1]). It has been ascertained that the up-conversion process involved consists of three consecutive energy transfers from ytterbium ions to thulium ions. The efficiency of this up-conversion in matrices characterized by low phonon cut-off frequency is found to be sufficiently high to ensure the population inversion and sustain laser oscillation. An alternative up-conversion process in the Tm–Yb system in which the blue emission follows the excitation around 800 nm is less documented. This phenomenon was first discovered in $LiYF_4$, BaY_2F_8 and KYF_4 crystals co-doped with Tm^{3+} and Yb^{3+} [2]. In contrast to the former excitation method, the radiation around 800 nm brings about direct excitation of the $^3H_4$ multiplet of Tm^{3+}. Nevertheless, the presence of ytterbium ions appears to be crucial since the up-converted emission was not observed in crystals singly doped with thulium. It was then concluded that the up-conversion process consists of an energy transfer from thulium to ytterbium, followed by a back transfer from ytterbium to thulium. Subsequent reports of up-conversion phenomena in Yb, Tm co-doped ZBLAN glass, oxyfluoride glass and glassy $Tm_{0.03}Yb_{0.18}La_{0.79}P_5O_{14}$ [3, 4] as well as recent investigation of Tm, Yb co-doped silica based glass ceramics [5] fully supported the initially proposed mechanism. The most important and unexpected result obtained was the demonstration that the efficiency of this up-conversion process in matrices with high-energy lattice vibrations as exemplified by pentaphosphate glass is comparable to that recorded with heavy-metal fluoride glass [3]. This finding opens new possibilities in the search for potential laser materials operating in the visible with infrared pumping.

In this work we examine the process of conversion of infrared radiation at 808 nm, emitted by a diode laser, into blue emission in YVO_4 crystals co-doped with thulium and ytterbium. Up-conversion of infrared radiation at $\lambda = 975$ nm into blue emission was found to be quite effective in this system [6]. Spectroscopic properties of YVO_4 singly doped with thulium were reported in Refs. [7, 8] and data gathered therein will be used to interpret our results.

2 Experimental

YVO_4 crystals containing nominally 1 at.% of Tm^{3+} + 5 at.% of Yb^{3+}; 1 at.% of Tm^{3+} + 8 at.% of Yb^{3+} and 2 at.% of Tm^{3+} + 5 at.% of Yb^{3+} were grown by the Czochralski method. Samples have been oriented by the X-ray technique and cut and polished to parallelepipeds of a few millimeters edge. Polarized absorption spectra were measured at room temperature and at 4.2 K with a Varian model 5E UV-VIS-NIR spectrophotometer. The resolution was 0.2 nm in the UV-VIS region and 1 nm in the near infrared. Infrared light with a wavelength of about 800 nm emitted by an AlGaAs diode laser with highest available power of 1 W has been used to excite up-converted emission, dispersed by a 1-m double-grating monochromator with a spectral bandwidth set to 2 cm^{-1} and detected by a photomultiplier with S-20 response. The resulting signal was analyzed by a Stanford model SRS 250 boxcar integrator and stored in a personal

---

✉ Fax: +48-71-344-10-29, E-mail: lisiecki@int.pan.wroc.pl

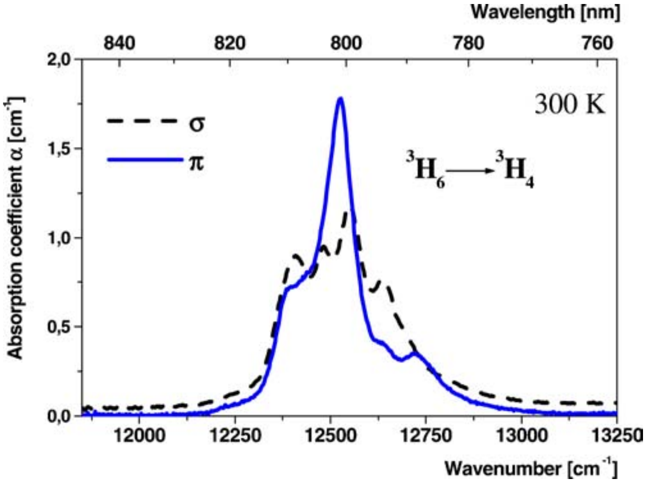

FIGURE 1 Absorption bands associated with $^3H_6$–$^3H_4$ transitions of Tm^{3+} in YVO_4 for polarizations π (*solid line*) and σ (*dashed line*) recorded at room temperature

computer. Luminescence transients were recorded with a Tektronix model TDS 3052 digital oscilloscope following selective excitation with short pulses provided by a Continuum Surelite 1 optical parametric oscillator (OPO) pumped by a third harmonic of a Nd:YAG laser. For low-temperature measurements samples were mounted in an Oxford model CF 1204 continuous-flow helium cryostat equipped with a temperature controller.

3 Results and discussion

Room-temperature absorption spectra associated with the $^3H_6$–$^3H_4$ transition, recorded with light polarized perpendicular to the optical axis (σ spectrum) and parallel to the optical axis (π spectrum) of the crystal are shown in Fig. 1. The spectra consist of poorly resolved bands resulting from the superposition of lines associated with transitions between individual crystal field levels of the two multiplets involved, additionally broadened by electron–phonon interaction. Strong homogeneous broadening of absorption bands is advantageous for optical excitation particularly when laser diode sources are used. Typically, a laser diode emission has a large bandwidth amounting to several nanometers and exhibits a significant spectral shift of about 0.3 nm/°C induced by the variation of the laser diode temperature. Unless absorption bands are conveniently broad, stringent control of temperature is necessary to maintain the absorption efficiency at a desired level. It can be seen in Fig. 1 that the excitation wavelength $\lambda = 808$ nm matches perfectly the absorption band and that the anisotropy of the crystal would weakly influence the absorption efficiency. Excitation in the $^3H_4$ level of Tm^{3+} did not produce up-converted emission in YVO_4 crystals singly doped with thulium, whereas intense blue luminescence appeared in all samples containing thulium and ytterbium. It has been ascertained that the spectrum of this up-converted emission at 300 K consists of a single broad band centered at about 476 nm. Based on results of a previous spectroscopic study of YVO_4:Tm [7], the band is assigned to the $^1G_4$–$^3H_6$ transition of Tm^{3+}. This assignment is further supported by the up-conversion emission spectrum recorded at 70 K, which is dominated by three lines associated with transitions on the crystal field levels located at 385, 210 and 52 cm^{-1} above the ground level (see Fig. 2). It should be noted here that, in contrast to other materials co-doped with ytterbium and thulium, we were not able to discern any up-converted emission originating in the $^1D_2$ level of Tm^{3+}. This is likely due to the interaction of thulium ions with vanadate $VO_4{}^{3-}$ groups. The dependence of up-converted luminescence intensities upon the intensity of excitation at 808 nm with a diode laser is shown in Fig. 3. Slopes of the lines of 2.01, 1.84 and 1.62 for 1 at.% Tm, 5 at.% Yb: YVO_4; 1 at.% Tm, 8 at.% Yb: YVO_4 and 2 at.% Tm, 5 at.% Yb: YVO_4 respectively indicate that the up-converted luminescence originating in the $^1G_4$ level of Tm^{3+} when excited by 808 nm with a diode laser is consistent with a two-photon excitation mechanism. The corresponding up-conversion excitation scheme is depicted in Fig. 4. The first-step energy transfer from excited Tm^{3+} ions in the $^3H_4$ level to nearby Yb^{3+} ions results in population of the $^2F_{5/2}$ level. The excited

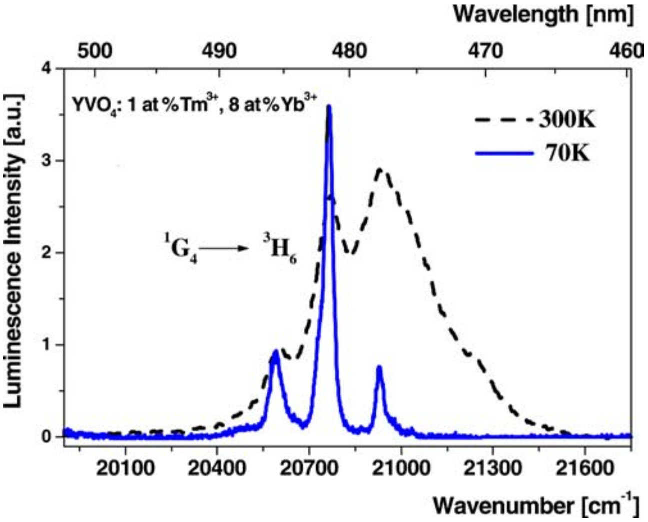

FIGURE 2 Spectra of up-converted luminescence originating in the $^1G_4$ level of Tm^{3+} excited at 808 nm recorded at 300 K (*dashed*) and 70 K (*solid*) with a sample containing 1 at.% Tm^{3+} and 8 at.% Yb^{3+}

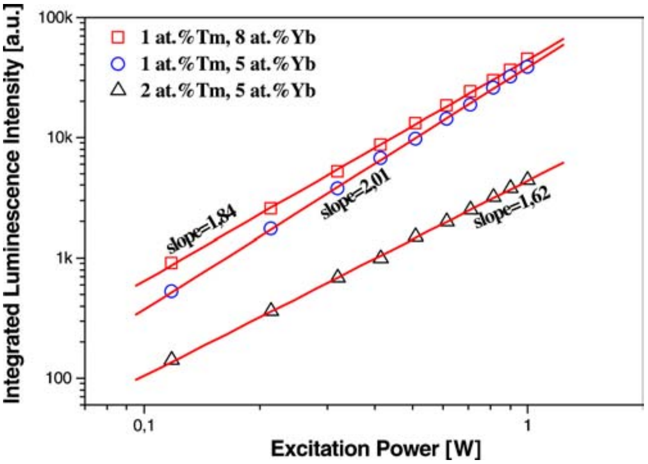

FIGURE 3 Integrated emission intensity versus incident excitation power for YVO_4:Yb, Tm systems. The excitation wavelength was 808 nm

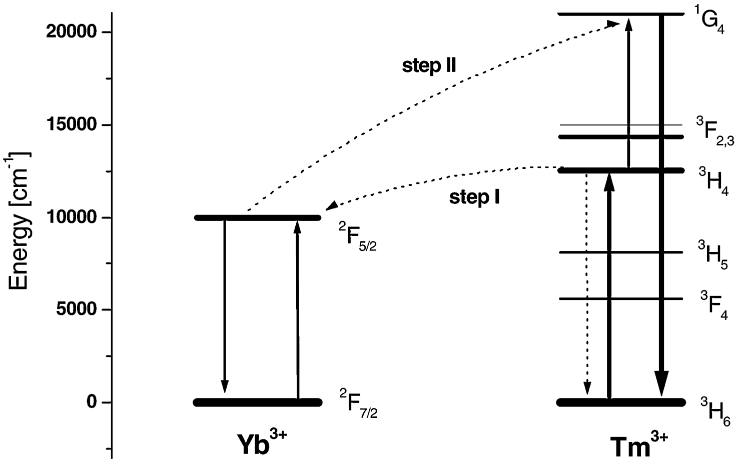

FIGURE 4 Scheme of energy levels for YVO$_4$ containing Yb^{3+} and Tm^{3+}. *Solid arrows* indicate transitions with absorption or emission of photons. *Dotted arrows* indicate nonradiative transitions

Yb^{3+} ions may relax to the ground state radiatively, emitting light around 980 nm and/or by transferring the energy back to Tm^{3+} ions. Thus, the blue-emitting level can be populated efficiently through two sequential energy-transfer processes described by the following relations:

$$[^3H_4(Tm^{3+}) \rightarrow {}^3H_6(Tm^{3+});\ {}^2F_{7/2}(Yb^{3+}) \rightarrow^2 F_{5/2}(Yb^{3+})], \tag{1}$$

$$[^2F_{5/2}(Yb^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+});\ {}^3H_4(Tm^{3+}) \rightarrow {}^1G_4(Tm^{3+})]. \tag{2}$$

It follows from the examination of the energy-level structures of Tm^{3+} and Yb^{3+} in YVO$_4$ that the energy transfers according to expressions (1) and (2) above are far from resonance and have to be assisted by emission of phonons. In particular, the lowest crystal field component of the $^3H_4$ multiplet of Tm^{3+} has been located at 12 523 cm^{-1}, based on low-temperature absorption spectra. The energy of the highest crystal field component of the $^2F_{5/2}$ multiplet of Yb^{3+} cannot be determined precisely because strong electron–phonon interaction prevents the assignment of the electronic origin in the absorption band even at liquid-helium temperature [6]. It is likely to be about 10 500 cm^{-1} and certainly not higher than 10 600 cm^{-1}. Taking into account that the overall splitting of the ground multiplet of thulium in YVO$_4$ is 385 cm^{-1}, the energy mismatch in the first step of energy transfer is not smaller than 1638 cm^{-1}. In a similar way, the energy mismatch of about 1200 cm^{-1} in the second step of energy transfer has been estimated. The phonon spectrum of YVO$_4$ stretches to about 900 cm^{-1} [9]. Thus, at least two phonons are needed to conserve the energy in both steps of energy transfer.

The overall up-conversion efficiency depends on inherent quantum efficiencies of excited levels of interacting ions and on the efficiency of energy-transfer processes. It can be seen in Fig. 3 that the up-converted luminescence intensity is influenced by concentrations of ytterbium and thulium ions. The intensity recorded with a sample containing 2 at.% of Tm^{3+} and 5 at.% of Yb^{3+} is the weakest because the increased thulium content favors the self-quenching of the $^3H_4$ and $^1G_4$ emissions. Strong self-quenching of luminescence originating in the $^3H_4$ level of Tm^{3+} ions in YVO$_4$ is evidenced by reported results of lifetime measurement. The $^3H_4$ lifetime of 176 μs was measured for 0.5 at.% Tm: YVO$_4$ [6], 100 μs was reported for 1 at.% Tm: YVO$_4$ [10] and only 7 μs was found for 6 at.% Tm: YVO$_4$ [6]. The importance of this self-quenching process in our co-doped samples becomes apparent when we compare the $^3H_4$ lifetimes amounting to 94 μs for 1 at.% Tm, 5 at.% Yb: YVO$_4$ and to 55 μs for 2 at.% Tm, 5 at.% Yb: YVO$_4$. The $^1G_4$ lifetimes of 67 μs and 51 μs measured respectively for these two samples indicate that the self-quenching of the $^1G_4$ emission is less effective, but not negligible. It follows from these considerations that the Tm^{3+} concentration should be kept small, likely below 1 at.%, in order to obtain a high intensity of the up-converted emission. On the other hand, increase of ytterbium concentration is expected to enhance the rate and, hence, the efficiency of energy transfer between thulium and ytterbium. The energy-transfer rate from Tm^{3+} to Yb^{3+} ions, $W_{\mathrm{Tm-Yb}}$, can be calculated from the Tm^{3+} decay times obtained in samples with and without Yb^{3+} ions:

$$W_{\mathrm{Tm-Yb}} = \frac{1}{\tau_{\mathrm{Tm,Yb}}} - \frac{1}{\tau_{\mathrm{Tm}}}, \tag{3}$$

where τ_{Tm} and $\tau_{\mathrm{Tm,Yb}}$ are the emission decay times of the Tm^{3+}–$^3H_4$ state without and with the presence of Yb^{3+} ions in the YVO$_4$ crystals, respectively. With the lifetime values mentioned above, the energy-transfer rate from Tm^{3+} to Yb^{3+} for 1 at.% Tm, 5 at.% Yb: YVO$_4$ is $\sim 640\ \mathrm{s}^{-1}$. The $^3H_4$ lifetime of 79 μs for 1 at.% Tm, 8 at.% Yb: YVO$_4$ implies the energy-transfer rate of $\sim 2700\ \mathrm{s}^{-1}$, a value roughly four times higher than that reported for 1 at.% Tm, 10 at.% Yb: LiYF$_4$ [2]. In a similar way, the rates of back transfer from ytterbium to thulium can be estimated. To do this, we assume that the intrinsic lifetime of the $^2F_{5/2}$ level of Yb^{3+} in YVO$_4$ is close to the calculated radiative lifetime of 285 μs [11]. With measured lifetimes of 177 μs for 1 at.% Tm, 5 at.% Yb: YVO$_4$ and 134 μs for 1 at.% Tm, 8 at.% Yb: YVO$_4$, we obtain the energy-transfer rates $\sim 2142\ \mathrm{s}^{-1}$ and $\sim 3954\ \mathrm{s}^{-1}$, respectively. However, it should be remembered that two different processes may be involved in the energy transfer from ytterbium to thulium. One of them, consistent with relation (2), feeds the $^1G_4$ level directly. The second process involves transfer of the Yb^{3+} excitation to the $^3H_5$ level followed by multiphonon relaxation to the $^3F_4$ level of Tm^{3+}. In the latter case the $^1G_4$

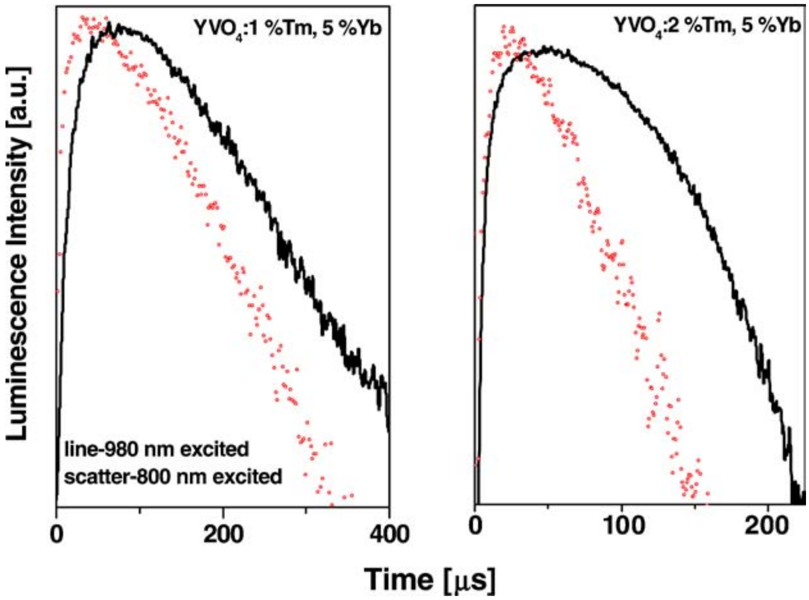

FIGURE 5 Time evolution of up-converted emission in the YVO$_4$ crystal containing 1 at.% of Tm^{3+}, 5 at.% of Yb^{3+} and 2 at.% of Tm^{3+}, 5 at.% of Yb^{3+}, excited with a 4-ns pulse. Excitation wavelengths 800 nm (*dotted*) and 975 nm (*solid*)

level may be populated through a three-step process that is encountered upon excitation into the Yb^{3+} absorption band at about 980 nm. The dependence of the up-converted luminescence intensity on excitation power shown in Fig. 3 indicates that the two-step process occurs. This conclusion is further confirmed by the dynamics of the up-converted luminescence. In Fig. 5 the time dependences of blue emission in Yb, Tm:YVO$_4$ excited at 808 nm and 975 nm with short pulses provided by an OPO are compared. The intensity of the blue emission rises more quickly upon excitation at 808 nm, in agreement with the expectation that the two-step process is faster than the three-step process. The decay of the blue emission is markedly slower upon short-pulse excitation at 975 nm, since in the corresponding three-step excitation process the long-lived $^3F_4$ level is involved. The detrimental effect of increased Tm^{3+} concentration on the up-conversion efficiency is evidenced by the time dependences recorded. For the two excitation wavelengths the blue emission in 2 at.% Tm, 5 at.% Yb: YVO$_4$ decays completely in a time shorter by roughly a factor of two as compared to that in 1 at.% Tm, 5 at.% Yb: YVO$_4$.

At this point, some comments regarding slopes of power dependences indicated in Fig. 3 should be made. It can be seen in the figure that the slopes are inferior to the expected value of 2 except for the 1 at.% Tm, 8 at.% Yb: YVO$_4$ sample. The problem of the power dependence of the up-conversion luminescence in lanthanide and transition-metal-ion systems has been treated extensively [12]. The authors showed that the dependence of the up-converted luminescence intensity following an n-photon excitation scheme on the excitation power P is close to P^{n} for infinitely small up-conversion rates only. In real systems this dependence may be substantially less than P^{n} as a result of the competition between linear decay and up-conversion for the depletion of the intermediate excited states. In the case of YVO$_4$ crystals considered here, additional effects associated with the interaction of luminescent ions with unintentional defect centers may be involved. The presence of optically active defects has been evidenced by the appearance of up-converted broad-band blue emission in nominally undoped YVO$_4$ [13]. The nature of these defects and their coupling to luminescent ions still await an explanation.

As noticed above, both the forward energy transfer from thulium to ytterbium and the back energy transfer from ytterbium to thulium are not resonant and have to be assisted by phonons. Estimated values of the energy mismatch are significantly higher than the cut-off phonon energy in all known fluoride matrices and in the majority of oxide matrices. Rates of energy transfer between thulium and ytterbium in matrices with an extended phonon spectrum may be larger because a smaller number of phonons will provide the conservation of energy. That is why the up-converted emission in the Yb, Tm: YVO$_4$ system may be easily excited in spite of the relatively short lifetimes of the excited states involved.

4 Conclusions

The blue emission peaking at around 480 nm excited at 808 nm with a diode laser was observed in YVO$_4$ crystals co-doped with Yb^{3+} and Tm^{3+} ions. The dependences of up-converted emission intensities on the power of the infrared excitation as well as the time evolution of the up-converted emission imply a two-step excitation mechanism. The up-conversion efficiency is found to be influenced by both the thulium and ytterbium concentrations. Increase of Yb^{3+} content in the crystal is found to be advantageous, whereas the Tm^{3+} concentration should be small in order to reduce the self-quenching of the luminescence. It has been supposed that an extended vibrational spectrum of the matrix enhances rates of nonresonant energy-transfer processes, thereby compensating short intrinsic lifetimes of interacting luminescent ions.

REFERENCES

1 X. Zou, H. Toratani, J. Non-Cryst. Solids **181**, 87 (1995)
2 X.X. Zhang, P. Hong, M. Bass, B.H.T. Chai, Phys. Rev. B **51**, 9298 (1995)

3 X.B. Chen, W.M. Du, N. Sawanobori, G.Y. Zhang, Z.F. Song, Opt. Commun. **181**, 171 (2000)

4 I.R. Martin, J. Mendez-Ramos, V.D. Rodriguez, J.J. Romero, J. Garcia-Sole, Opt. Mater. **22**, 327 (2003)

5 F. Lahoz, I.R. Martin, J. Mendez-Ramos, J. Chem. Phys. **120**, 6180 (2004)

6 W. Ryba-Romanowski, P. Solarz, G. Dominiak-Dzik, R. Lisiecki, T. Lukaszewicz, Laser Phys. **14**, 250 (2004)

7 K.D. Knoll, Phys. Status Solidi **45**, 553 (1971)

8 C. Xueyuan, L. Zundu, J. Phys.: Condens. Matter **9**, 7981 (1997)

9 E.D. Reed, H.W. Moos, Phys. Rev. B **8**, 980 (1973)

10 F.S. Ermeneux, C. Goutaudier, R. Moncorge, M.T. Cohen-Adad, M. Bettinelli, E. Cavalli, Opt. Mater. **8**, 83 (1997)

11 R. Lisiecki, W. Ryba-Romanowski, T. Lukaszewicz, H. Mond, K. Petermann, Laser Phys. **15**, 306 (2005)

12 M. Pollnau, D.R. Gamelin, S.R. Lüthi, H.U. Güdel, M.P. Hehlen, Phys. Rev. B **61**, 3337 (2000)

13 W. Ryba-Romanowski, S. Gołb, P. Solarz, G. Dominiak-Dzik, T. Lukasiewicz, Appl. Phys. Lett. **80**, 1183 (2002)