Beneficial effect of Lu^{3+} and Yb^{3+} ions in UV laser materials

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Abstract

Several Lu^{3+}- and Y^{3+}-based oxide and fluoride single crystals with isomorphic structures and doped with Ce^{3+} (or Pr^{3+}) or codoped with Yb^{3+} ions have been grown and studied to show the beneficial effects of the Lu^{3+} and Yb^{3+} ions on their broad-band UV luminescence properties. Time-resolved color center absorption measurements clearly show the reduction of the usually observed UV laser pump-induced optical losses and thus confirm the previous gain and laser results obtained in these materials. Some preliminary interpretations of the involved mechanisms are advanced.
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1. Introduction

Most of the Ce^{3+} or Pr^{3+} doped materials known for their broad-band 5d–4f UV emissions and which have been investigated in the past for their potentials as tunable solid-state laser media suffer from photochromic (solarization) effects, when they are pumped in the near UV spectral domain, which usually limit their laser performance or even hinder any laser action [1,2]. However, several recent works involving materials with Lu^{3+} instead of Y^{3+} or codoped with Yb^{3+} ions showed reduced solarization effects and improved laser performance [3–7].

The present paper thus gives the state of the art in this field of research and some preliminary interpretations of the beneficial effects of these Lu^{3+} and Yb^{3+} ions. Crystal characteristics are gathered in Section 2. Transient absorption measurement conditions are described in Section 3. Section 4 gives a comparison of the results obtained in the Lu^{3+}- and Y^{3+}-based materials. Finally, Section 5 presents the results obtained in Ce^{3+} doped crystals codoped with Yb^{3+} ions.

2. Crystal growth and sample characteristics

In order to verify the beneficial effect of Lu^{3+}, two families of single crystals—namely $LiY(Lu)F_4$ and $Y(Lu)PO_4$—were synthesised. These materials were selected for their perfect isomorphisms and because they have already demonstrated interesting and encouraging properties for a laser emission

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in the UV-based on the $5d \rightarrow 4f$ optical transition. Crystals were doped with Ce^{3+} ions and others codoped with Ce^{3+} and Yb^{3+} to study the effect of Yb^{3+} on color-center formation. KY_3F_{10} crystals were also grown because Ce^{3+} ions (as well as Pr^{3+} ions) presents exceptionally broad luminescence bands. However until now, the solarization effects have always prevented this material from lasing in the UV domain. Therefore, it would be particularly useful from a practical point of view to find the way which could also prevent color-center formation in KY_3F_{10} crystals.

Fluorides were obtained by using the Czochralski technique whereas oxides were obtained by using the flux method. In both cases, the starting chemical compounds were commercially available ultra-pure powders, to avoid at best any impurity centers. In addition, in order to avoid any trace of hydroxyl ions OH^- (which are known to be very detrimental for crystal quality) the choice was made, in the case of the rare-earth fluorides REF_3, to start with fluorides obtained after home-made fluorination of the corresponding oxides RE_2O_3. The fluorination agent used for the synthesis of fluorides was ammonium hydrogen fluoride $NH_4(HF_2)$ and the complete reaction starting from the oxide needs two steps.

The first step is made in open air at a temperature of 150 °C for 6 h in a platinum or a graphite crucible:

$$(Y/RE)_2O_3 + 6NH_4(HF_2)$$
$$\rightarrow 2(Y/RE)F_3 + 6NH_4F + 3H_2O$$
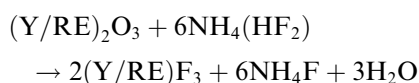
immediately followed by a second step in controlled atmosphere (mixture of argon + tetrafluoromethane CF_4) in a resistive oven, at a temperature of 600 °C for 1 h (in order to eliminate excess of NH_4F):

$$(Y/RE)_2O_3 + 6NH_4F$$
$$\rightarrow 2(Y/RE)F_3 + 6NH_3 + 3H_2O$$
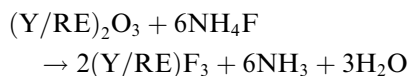
It is worth noting, at this point, that the isomorphs $LiYF_4$ and $LiLuF_4$ grow slightly differently, since the former grows incongruently (melting temperature $T_f = 842$ °C [8]), which is taken into account by starting with 52% LiF + 48% YF_3 compositions, whereas the latter grows congru-

ently (melting temperature $T_f = 825$ °C [9]). This means that crystal growth of $LiLuF_4$ should be facilitated because it would not need LiF excess, as in the case of $LiYF_4$, which could always create small inclusions in the crystal. This suggests already a possible difference between the two isomorphs which could play a significant role in the UV spectral domain. As a matter of fact, though excellent quality crystals can be obtained in both cases, $LiLuF_4$ crystals generally present a slightly better optical quality than their isomorphs.

KY_3F_{10} also grows congruently (melting temperature $T_f = 1030$ °C [10]) and good crystals can be obtained rather easily. However, the crystal growth of KY_3F_{10} has been less studied in the past and the optical quality of our samples, though being good enough for spectroscopy, was not ideal, as the crystals were slightly milky.

Phosphate crystals were grown by employing $Pb_2P_2O_7$ as a solvent in the 800–1300 °C temperature range [11]. The molar percentage of the starting composition was $50NH_4H_2PO_4$, 48PbO, 2Y(or Lu)$_2O_3$. Dopants were added in the form of oxides Yb_2O_3 or/and CeO_2. The Pt crucible containing the charge was heated at a rate of about 15–20 °C h^{-1} to 1300 °C in a horizontal furnace under air atmosphere. After a soaking time of 18 h, the temperature was lowered to 900 °C at a rate of about 2 °C h^{-1}. The crucible was then drawn out from the furnace and quickly inverted to separate the crystals grown at the bottom of the crucible from the flux.

With the Czochralski method, fluoride crystals of the order of 2 cm^3 and of excellent quality could be grown. These crystals were cut and polished in the form of parallelepipeds of $5 \times 5 \times 5$ mm^3. In the case of the uniaxial systems $YLiF_4$ and $LiLuF_4$ (space group C_{4h}^6, Y^{3+} or Lu^{3+} local site symmetry S_4 [12]) the faces were oriented perpendicular to the main crystallographic c-axis in order to record π and σ polarized spectra. This was not necessary in the case of the cubic system KY_3F_{10} (space group O_h^5, Y^{3+} local site symmetry C_{4v} [13]).

In the case of phosphate single crystals, the shape of samples obtained after crystal growth were needles of about $0.7 \times 0.7 \times 5$ mm^3 and were used as such (sometimes polished to eliminate the last traces of flux) since they are tetragonal zircon

type systems (space group D_{4h}^{19}, Y^{3+} or Lu^{3+} local site symmetry D_{2d} [14]) and there were naturally oriented along the principal crystallographic c-axis.

3. Transient absorption measurements conditions

UV excitation pump-induced solarization effects usually consist in the formation of transient or quasi-permanent color centers leading to the appearance of broad absorption bands with very different temporal characteristics. Experimentally, we thus have to distinguish between two types of transient absorption losses: those having very short lifetimes, of the order of a few tens of nanoseconds, thus comparable with the lifetimes of the Ce^{3+} (or Pr^{3+}) emitting ions, and those having long lifetimes, of the order of a few microseconds or longer.

In both cases, transient absorption losses were examined by using standard pump–probe techniques.

To record the absorption bands corresponding to the short-lived color centers with lifetimes of a few tens of nanoseconds, i.e. in the order of magnitude of the lifetime of the 5d emitting levels—, we used exclusively pulsed pump and probe lights. The pump beam was either a frequency-quintupled Nd:YAG laser at 213 nm (DIVA II, Thomson-CSF Laser), a frequency-quadrupled Nd:YAG laser at 266 nm (DIVA II, Thomson-CSF Laser) pumping a Ce:LiSAF laser tuned at $\lambda = 290$ nm [4,7], or a frequency-quadrupled Nd:YAG laser at 266 nm (Spectron model 404G) spectrally shifted using stimulated Raman scattering in a high pressure ($P = 30$ bars) CH_4 Raman cell (2914 cm^{-1} vibration) and providing radiations at 288 nm (Stokes 1) and 315 nm (Stokes 2). On the other hand, because we had no laser which could be easily tuned in a sufficiently wide spectral domain, the probe beam was that of a pulsed Xe lamp (Hamamatsu Model L2436) delivering 400 ns light pulses associated with a monochromator (Jobin-Yvon model TRIAX 550 equipped with a grating of 1200 grooves/mm and blazed at 300 nm). The brightness of this lamp, however, was not high enough to overcome the strong UV luminescence of the studied materials. Therefore, photo-induced

absorption bands could be recorded only outside the considered emission domains. This problem was partially solved by extrapolating by straight lines the absorption data obtained on each side of these emission domains. Since it was necessary to compare the results under the same experimental conditions, the pump fluence was always maintained close to 0.23 J/cm^2.

In the case of the long-lived color centers, the pump was again one of the above mentioned pulsed laser emitting at a fixed wavelength but the probe beam was provided by a continuous wave (CW) Xe lamp (OSRAM, 75 W, high pressure lamp) associated again with a monochromator.

The transient signals from the pulsed Xe lamp were detected using a fast photomultiplier tube (Hamamatsu, model R3896) and was temporally analysed using a digital oscilloscope (Tektronix TDS350). The transient absorption spectra were obtained from the difference observed on the transient signals corresponding to the probe light transmitted by the crystal when the pump laser was on and off.

The long-lived ones were recorded basically with the same experimental set-up except that the probe beam was provided by the CW Xe lamp and that the signal was integrated at a longer time delay after the pump pulse.

4. Comparison between Lu^{3+}- and Y^{3+}-based isomorphic materials

For sake of clarity, let us first report in Figs. 1 and 2 the polarized absorption and emission spectra respectively in $Ce:LiLuF_4$ and $Ce:LuPO_4$. Those corresponding to $Ce:LiYF_4$ and $Ce:YPO_4$ are not reproduced here because they are only slightly different, in terms of spectral bandshapes and cross-sections, from the spectra of their respective isomorphs. Pumping was realized at 288 or 290 nm for the fluorides and at 315 nm for the oxides, thus within their lowest absorption band.

Short-lived and long-lived polarized transient absorption spectra were recorded first in Ce^{3+} doped $LiYF_4$ and $LiLuF_4$ then in Ce^{3+} doped YPO_4 and $LuPO_4$ single crystals. Figs. 3–5 give some of the transient absorption spectra obtained
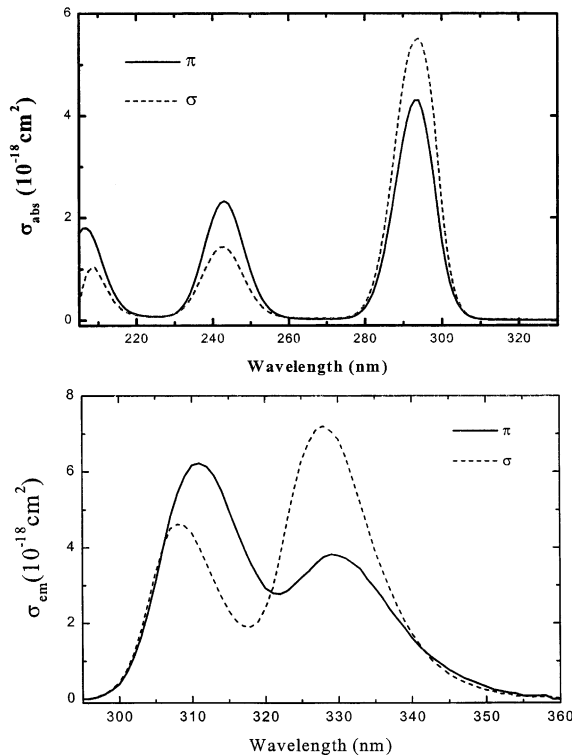
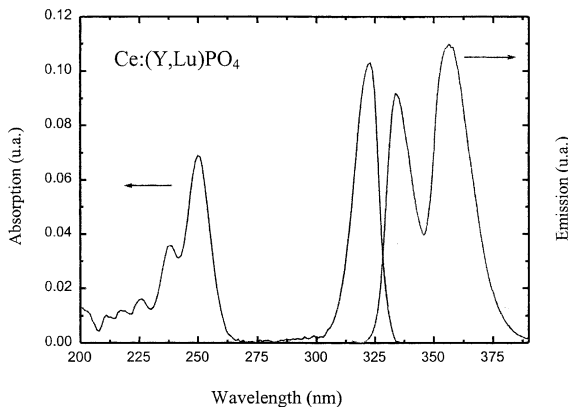Fig. 1. Polarized absorption (above) and emission (below) spectra of Ce:LiLuF$_4$.

Fig. 2. Unpolarized absorption and emission spectra of Ce:LuPO$_4$.

at short- and long-time delays after the excitation pump pulse. A number of remarks can be made

concerning these spectra. They extend first in a broad spectral domain from the near UV to the red. In the case of fluorides, they are associated, on the one hand, with short-lived color centers with lifetimes ranging roughly between 50 and 350 ns, depending on the origin of the samples and, on the other hand, with long-lived ones with lifetimes longer than 10 s. Long-lived color centers were present in LiLuF$_4$ but their absorption (not represented) was always lower than 10%, then strongly reduced compared to the case of LiYF$_4$ (see in Fig. 4). Curiously, only long-lived color center absorption bands with lifetimes of the order of 10 ms and 4 s (see in Fig. 5) could be detected in the case of phosphates. Both in the fluorides and the oxides, however, the spectra appear to be strongly anisotropic. Moreover, let us point out the fact that the shape of the absorption spectra appears to be reproducible whatever the quality of the sample studied is, especially in the case of short-lived color centers. That is to say, they could be considered as a spectroscopic characteristic for a given combination of dopant and crystalline host material. Additionally, they are much more intense, at least in the emission domain of each material (300–340 nm in the case of fluorides and 325–375 nm for oxides) in σ than in π polarization (see in Figs. 3–5) and, depending on polarization, in particular for short-lived absorption centers (see in Fig. 3), absorptions occur in rather different spectral regions. Therefore, after coloration, the photo-induced extra-absorptions appear to be strongly anisotropic and dichroic.

It can be finally noticed that absorption losses are substantially stronger in the case of the Ce^{3+} doped Y-based compounds than in the case of the Lu ones, under similar pumping conditions. In the case of Ce:LiYF$_4$ and Ce:LiLuF$_4$, the property seems to be general since the same result was found with crystals coming from different origins. This is reflected in the gain characteristics and the laser performance of each system [15]. In particular, whereas the laser wavelength of Ce:LiLuF$_4$ could be continuously tuned between 304 and 335 nm [16], thus over most of the associated emission domain, Ce:LiYF$_4$ could be operated only around 310 and 325 nm and provided that the pump was π polarized.
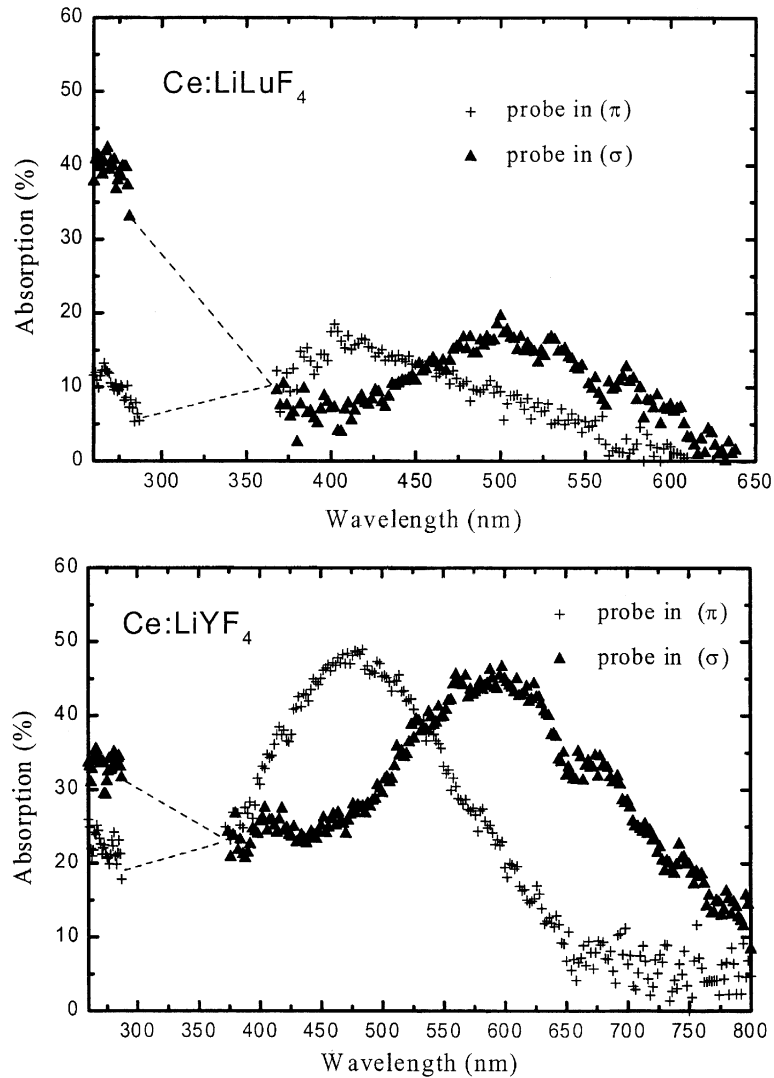
Fig. 3. Short-lived transient absorption spectra recorded in the case of Ce:LiYF$_4$ and Ce:LiLuF$_4$.

Similar results were found in the case of the Ce^{3+} doped phosphates YPO$_4$ and LuPO$_4$. As a consequence, as shown in Fig. 6, for an absorbed pump fluence of about 0.18 J/cm^2 at 315 nm, a laser gain of about 15% was measured around 355 nm in the case of Ce:LuPO$_4$ (25% for a pump fluence of 0.27 J/cm^2) whereas only 4% were obtained under similar pumping conditions in the case of Ce:YPO$_4$ at the same wavelength. It is worth noting here that it was the first time that

gain could be demonstrated in a Ce^{3+} doped oxide [5].

5. Influence of Yb^{3+} codoping

An illustration of the beneficial influence of Yb^{3+} codoping on the color-center formation is shown in Fig. 7 where the long-lived transient absorption spectra are shown, recorded in the case
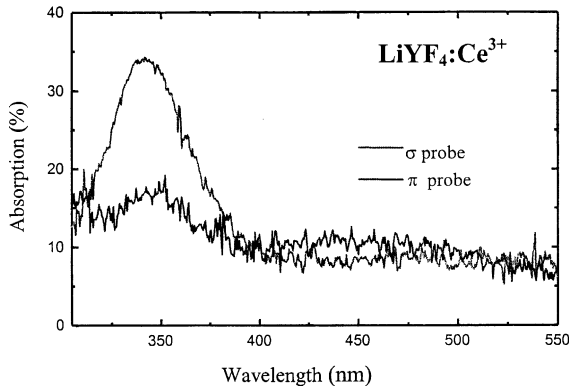
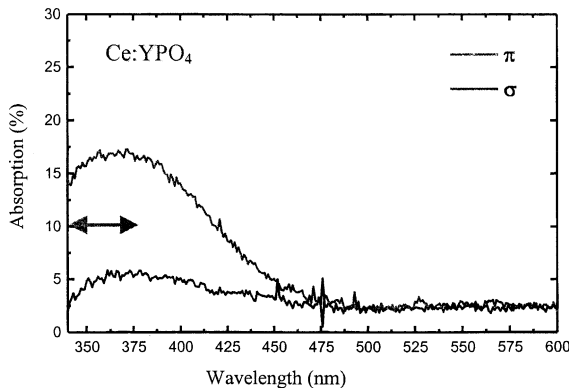Fig. 4. Long-lived transient absorption spectra recorded in the case of Ce:LiYF$_4$.

Fig. 5. Long-lived transient absorption spectra recorded in the case of Ce:LuPO$_4$ (the arrow indicates the emission range).
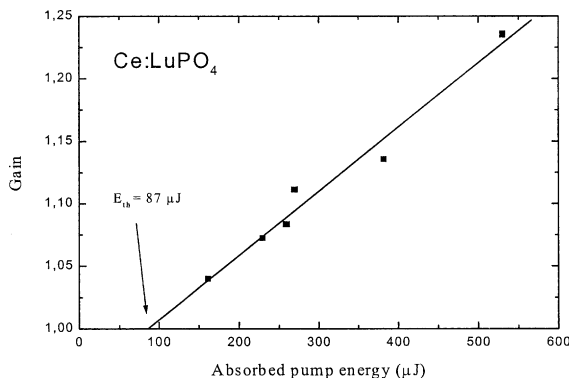

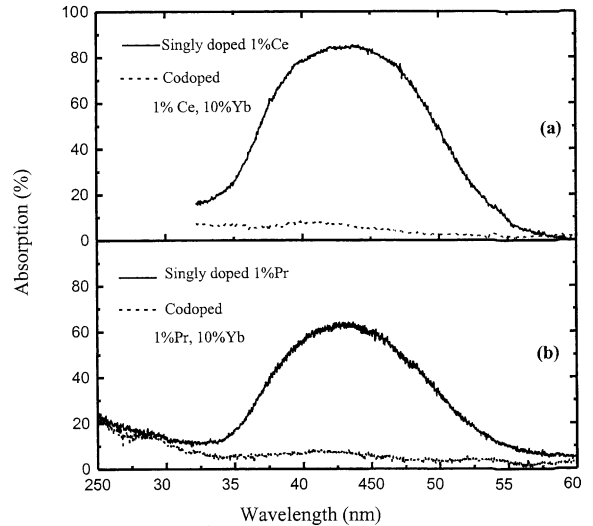Fig. 6. Gain versus absorbed pump energy curve for Ce:LuPO$_4$ (pump at 315 nm, probe at 355 nm).

Fig. 7. Long-lived transient absorption spectra recorded in the case of Ce^{3+} and Ce^{3+}, Yb^{3+} doped KY$_3$F$_{10}$ and of Pr^{3+} and Pr^{3+}, Yb^{3+} doped KY$_3$F$_{10}$ single crystals.

of Ce^{3+} and Ce^{3+}, Yb^{3+} doped KY$_3$F$_{10}$ as well as in the case of Pr^{3+} and Pr^{3+}, Yb^{3+} doped KY$_3$F$_{10}$ single crystals. The effect is clear: absorption losses due to long-lived color centers have nearly disappeared. In the case of Ce^{3+}:KY$_3$F$_{10}$, for example, which only suffers from these long-lived absorbing color centers, it means that a real hope exists to find some gain in Ce^{3+}, Yb^{3+}:KY$_3$F$_{10}$, provided that the dopant concentrations are chosen judiciously. This was confirmed, in fact, very recently, since gain could be demonstrated in this system at about 362 nm [6].

The beneficial effect of Yb^{3+} codoping was further confirmed in the case of Ce:LiLuF$_4$ via gain and laser measurements. Codoping of crystals with only 1% Yb^{3+} improved laser gain, significantly, especially when the pump was σ polarized (which is known to be the worse pump condition in terms of color-center formation); preliminary results indicated an improvement by about 35% [7]. Codoping with about 1% Yb^{3+} increased the laser efficiency of this system, already known to be the highest one among all the Ce^{3+} doped laser systems [4,17], from about 55% to 62% [6], which is now the new record.

6. Discussion/conclusion

At the moment, there are no definitive explanations of the favourable effects of Lu^{3+} or Yb^{3+} ions on the laser performance of the considered UV emitting laser materials. There are only tentative interpretations.

Concerning the effect of Lu^{3+}, several reasons can be invoked. One may invoke first crystal growth and the resulting crystal quality. Indeed, as mentioned at the beginning, $LiLuF_4$ grows congruently whereas $LiYF_4$ does not. It means that crystal growth of $LiLuF_4$ is generally easier than that of $LiYF_4$ and that $LiLuF_4$ crystals generally present a better optical quality in terms of lattice defects and of lattice strains. This may explain, in particular, the higher laser damage threshold which is generally observed with the Lu-based than with the Y-based laser crystals. This may explain the better luminescence and/or laser properties of $LiLuF_4$ when doped with rare-earth ions such as Nd^{3+} [18], Tm^{3+} and Ho^{3+} [19]. This effect may be somewhat counterbalanced, however, after rare-earth ion codoping. Indeed, because of their ionic radii, these trivalent ions more easily substitute for Y^{3+} than for Lu^{3+} ions, for which the ionic radii, assuming a coordination value of 8, are of the order of 1.16 and 1.12 Å, respectively. This is especially true with ions as large as Ce^{3+} and Pr^{3+} for which the ionic radii are of the order of 1.28 and 1.27 Å, respectively [20]. It also means that less rare-earth codopants can be incorporated in the Lu- than in the Y-based laser crystals. However, this is not really an issue when strong electric-dipole allowed transitions such as the 4f–5d transitions of rare-earth ions are involved. This may be annoying in the case of 4f–4f transitions, especially for those which are characterized by weak cross sections. On the other hand, a smaller substitution site such as that of Lu^{3+} also means a larger crystal field at the rare-earth dopant, thus stronger Stark splittings which may induce more favorable thermal populations of the involved energy levels. This was invoked to interpret the better laser results obtained with codoped Tm,Ho:LLF compared to Tm,Ho:YLF [21,22] but this is doubtful. Another explanation can be found in the positions of the energy levels of the rare-earth ions within the bandgap of the host crystals. Indeed, preliminary calculations [23] indicate that the energy gap of $LiLuF_4$, for example, is broader than that found in the case of $LiYF_4$, with values of about 11.5 and 10 eV, respectively. Assuming, according to recent XPS measurements [24–26] made on various kinds of materials for the scintillator applications such as $LuAlO_3$ and $YAlO_3$ or Lu_2SiO_5 and Y_2SiO_5, that the 4f ground-state energy level of a given rare-earth dopant lies at about the same energy above the top of the valence band [27] in corresponding isomorphs, the ground-state and excited-state photoionisation processes and the subsequent solarisation effects should occur at higher energies in the case of rare-earth doped Lu-based crystals that in the case of their Y-based isomorphs. In other words, excitation pump-induced solarisation effects should be less effective in the case of the rare-earth doped Lu-based crystals, which indeed seems to be observed.

Concerning the effect of Yb^{3+} codopants, some preliminary interpretation is already available. It is illustrated in Fig. 8 in which we have reported some tentative excitation and recombination schemes to show the influence of Yb^{3+} ions in a Ce^{3+} doped compound. According to this scheme, excitation of Ce^{3+} ions may lead to photoionisation via
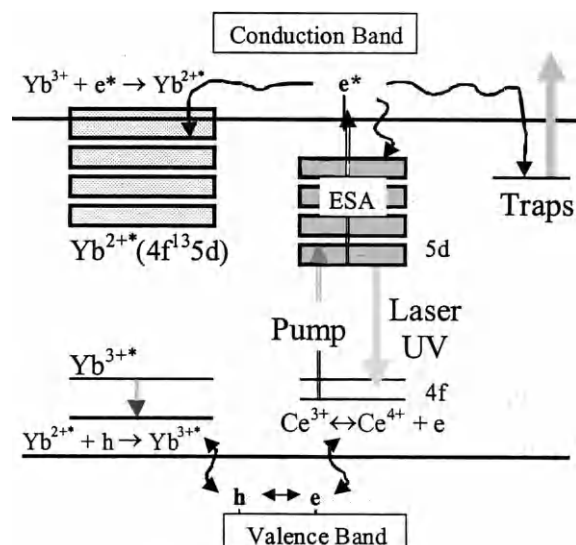

Fig. 8. Pump and recombination processes in Ce^{3+} doped crystals codoped with Yb^{3+} ions.

excited-state absorption into the conduction band of the crystal and produce some free electrons which can be trapped at lattice defects or impurity centers leading to the formation of color center absorption bands. In this case, some Ce^{3+} ions relax down to their ground state by emitting UV photons but some of these UV photons can be absorbed by color centers, a phenomenon at the origin of the well-known solarisation effect. In case of Yb codoping, however, some of the excitation pump-induced free electrons may be trapped, instead, at Yb^{3+} ions leading to excited Yb^{2+} ions. Then, the Ce^{4+} ions resulting from the photoionisation of the excitation pumped Ce^{3+} ions can transform back into Ce^{3+} after capture of valence band electrons and the production of valence band holes which can recombine with Yb^{2+} ions to give back Yb^{3+} ions. Some preliminary results seem to confirm this mechanism [28]. As a matter of fact, optical losses due to color center absorption of UV laser photons are reduced in Yb, Ce doped systems.

Acknowledgements

References

[1] D.J. Ehrlich, P.F. Moulton, R.M. Osgood Jr., Opt. Lett. 4 (1979) 184.

[2] K.-S. Lim, D.S. Hamilton, J. Lumin. 40/41 (1988) 319; J. Opt. Soc. Am. B 6 (1989) 1401.

[3] M.A. Dubinskii, V.V. Semashko, A.K. Naumov, R.Yu. Abdulsabirov, S.L. Korableva, Laser Phys. 4 (1994) 480.

[4] P. Rambaldi, R. Moncorgé, J.P. Wolf, C. Pédrini, J.Y. Gesland, Opt. Commun. 146 (1998) 163.

[5] M. Laroche, S. Girard, R. Moncorgé, K. Lebbou, T. Fukuda, M. Bettinelli, CLEO Europ Tech. Digest 2001, Munich, Germany, June 2001, p. 55.

[6] V.V. Semashko, M.A. Dubinskii, R.Yu. Abdulsabirov, S.L. Korableva, A.K. Naumov, A.S. Nizamutdinov, M.S. Zhuchkov, in: SPIE Proceed. XI Int. Feofilov Symp., 24–28 September 2001, Kazan, Russia, vol. 4766, in press.

[7] M. Laroche, Doctoral thesis, Universitéde Caen, September 2001, France.

[8] P. Rogin, J. Hulliger, J. Cryst. Growth 179 (1997) 551.

[9] R.E. Thoma, G.D. Brunton, R.A. Penneman, T.K. Keenan, Inorg. Chem. 9 (1970) 1096.

[10] B. Chai, J. Lefaucheur, A. Pham, G. Lutts, J. Nicholls, SPIE 1863 (1993) 135.

[11] M. Laroche, S. Girard, J. Margerie, R. Moncorgé, M. Bettinelli, E. Cavalli, J. Phys.: Cond. Matter 13 (2001) 765.

[12] A.A. Kaminskii, Crystalline Lasers, CRC Press, Boca Raton, 1996.

[13] R.Yu. Abdulsabirov, M.A. Dubinskii, B.N. Kazakov, N.I. Silkin, Sh.I. Yagudin, Sov. Phys. Crystallogr. 34 (1987) 559.

[14] W.O. Milligan, D.F. Mullica, G.W. Beall, L.A. Boatner, Inorg. Chem. Acta 60 (1982) 39.

[15] M. Laroche, S. Girard, R. Moncorgé, CLEO Tech. Digest 2002, Long Beach, USA, April 2002, paper CMS4, p. 90.

[16] A.J.S. McGonigle, R. Moncorgé, D.W. Coutts, Appl. Opt. 40 (2001) 4326.

[17] A.J.S. McGonigle, S. Girard, D.W. Coutts, C.E. Webb, R. Moncorgé, Electron. Lett. 35 (1999) 1640.

[18] E.P. Maldonado, N.U. Wetter, I.M. Ranieri, E.A. Barbosa, L.C. Couurol, N.D. Viera Jr., OSA Tops Adv. Solid State Lasers 26 (1999) 642.

[19] M.G. Jani, N.P. Barnes, K.E. Murray, D.W. Hart, G.J. Quarles, V.K. Castillo, IEEE J. Quantum Electron. QE 33 (1997) 112.

[20] R.D. Shannon, Acta Cryst. A 32 (1976) 751.

[21] E.D. Filer, C.A. Morrison, N.P. Barnes, B.M. Walsh, OSA Proc. Adv. Solid State Lasers 20 (1994) 127.

[22] N.P. Barnes, in: G.J. Quarles, L. Esterowitz, L.K. Cheng (Eds.), Solid State Lasers and Nonlinear crystals, Proc. SPIE, vol. 2379, 1995, p. 2.

[23] A. Hairie, M. Laroche, private communication.

[24] C. Pédrini, D. Bouttet, C. Dujardin, A. Belsky, A. Vasil'ev, in: Proc. Int. Conf. on Inorganic Scintillators and their Applications SCINT95, Delft University Press, The Netherlands, 1996, p. 103.

[25] C. Dujardin, C. Pedrini, J.C. Gâcon, A.G. Petrosyan, A.N. Belsky, A.N. Vasil'ev, J. Phys. Cond. Matter 9 (1997) 5229.

[26] O. Guillot-Noel, B. Bellamy, B. Viana, D. Gourier, Phys. Rev. B 60 (1999) 1668.

[27] R. Moncorgé, in: P. Misra, M.A. Dubinskii (Eds.), Ultraviolet Spectroscopy and UV Lasers, Marcel-Dekker Inc., New York, 2002, p. 337 (Chapter 9).

[28] H. Taupin, A. Braud, R. Moncorgé, S. Girard, to be submitted.