Role of oxygen hole centres in the photodarkening of ytterbium-doped phosphosilicate fibre

A.A. Rybaltovsky, A.A. Umnikov, K.K. Bobkov, D.S. Lipatov, A.N. Romanov, M.E. Likhachev, V.B. Sulimov, A.N. Gur'yanov, M.M. Bubnov, E.M. Dianov

Abstract. **We have studied the photodarkening in active fibres with an ytterbium-doped phosphosilicate glass core under IR irradiation with a pump source (920 nm) and UV irradiation (193 nm). Analysis of absorption and luminescence spectra suggests that such irradiations produce phosphorus–oxygen–hole centres (P-OHCs) in the core glass network and lead to the reduction of the ytterbium ions to a divalent state (Yb^{2+}). The photoinduced optical loss in the fibres in the visible range (400–700 nm) is mainly due to absorption by the P-OHCs. A quantum-mechanical model is proposed for P-OHC and Yb^{2+} formation.**

1. Introduction

Photodarkening is one of the key factors limiting the performance of high-power ytterbium-doped amplifiers and determining their service life. Photodarkening is a gradual increase in optical loss in Yb-doped fibres under the effect of IR pumping (920–980 nm). Its nature is not yet fully understood, but the effect in phosphosilicate (P_2O_5/SiO_2) glass fibres has been shown to be markedly weaker than that in germanosilicate (GeO_2/SiO_2) and aluminosilicate (Al_2O_3/SiO_2) glass fibres [1–4]. Moreover, the IR- and UV-induced absorption spectra of $Yb_2O_3/Al_2O_3/SiO_2$ core fibres were demonstrated to be essentially identical in shape [2].

As shown earlier [5, 6], exposure of phosphosilicate glasses to ionising or UV radiation produces phosphorus–oxygen–hole centres (P-OHCs) absorbing in the visible range. The purpose of this work was to study in detail the photoinduced colour centres responsible for the IR-induced absorption in ytterbium-doped phosphosilicate fibres.

A.A. Rybaltovsky, K.K. Bobkov, M.E. Likhachev, M.M. Bubnov, E.M. Dianov Fiber Optics Research Center, Russian Academy of Sciences, ul. Vavilova 38, 119333 Moscow, Russia;
e-mail: wittkoss@gmail.com, likhachev@fo.gpi.ru, dianov@fo.gpi.ru;
A.A. Umnikov, D.S. Lipatov, A.N. Gur'yanov G.G. Devyatykh Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, ul. Tropinina 49, 603950 Nizhnii Novgorod, Russia;
e-mail: umnikov@ihps.nnov.ru, lidenis@yandex.ru, tvs@ihps.nnov.ru;
A.N. Romanov, V.B. Sulimov Research Computing Center, M.V. Lomonosov Moscow State University, Vorob'evy gory, 119992 Moscow, Russia

2. Experimental

Fibre preforms for this investigation were produced by the MCVD process. Silica glass was vapour-phase-doped using high-purity $SiCl_4$ and $POCl_3$ and the metal-organic complex $Yb(thd)_3$. The preforms were then drawn into single-mode fibres 125 μm in outer diameter.

The chemical composition of the preforms was determined with an accuracy of 0.1 wt% on a JEOL JSM-5910LV equipped with an X-ray microanalysis system. The refractive index profiles across the preforms were obtained with a York Technology P102 preform analyser. The core–cladding index difference was determined in our experiments with an accuracy of 0.0005. The chemical compositions and index contrasts of the preforms are given in Table 1.

Table 1. Main characteristics of the samples.

Sample	mol% P_2O_5	wt%Yb	Core–cladding index difference
P-1	3	0	0.003
P-2	7	0	0.0065
Yb/P-1	4.5	0.5	0.004
Yb/P-2	7	1.8	0.008

Initial and photoinduced absorption spectra in the UV and visible spectral regions (190–800 nm) and luminescence spectra were taken using 0.2- and 1-mm-thick transverse sections of the preforms. In addition, we measured visible and near-IR (450–1100 nm) absorption spectra of fibres about 4 cm long.

Prior to UV irradiation, some of the preforms were exposed to a hydrogen atmosphere for six days at 110°C and 115 atm. In this way, sections of the preforms were loaded with molecular hydrogen in order to examine its effect on the photoinduced formation of colour centres in the glass network.

The preforms were irradiated by focusing a laser beam onto the core area, and the fibres, by launching a beam into their core. The irradiation conditions are summarised in Table 2. Since the pump diode laser L2 had an output fibre pigtail, its beam was coupled into the fibre core through a fusion splice. In our experiments, the ytterbium excited state population in the fibres was about 65%.

The absorption spectra of the preforms were measured on a McPherson VUVAS 1000 vacuum spectrophotometer at wavelengths shorter than 190 nm (vacuum UV) and on a PerkinElmer Lambda 900 spectrophotometer in the range

Table 2. Preform and fibre irradiation conditions.

Source	Wavelength/nm	Photon energy/eV	Intensity/W cm^{-2}	Fluence/J cm^{-2}
CL-5000 ArF laser (L1)	193	6.4	10^7	3×10^2
Oclaro BMU25A-915-01-R diode laser (L2)	915	1.35	1.5×10^5	1.6×10^9

190–850 nm. The absorption spectra of the fibres and the luminescence spectra were obtained with an Ocean Optics Maya 2000 Pro minispectrometer. During irradiation, the luminescence of the preform or fibre was detected at 90° to the beam direction using a multimode undoped silica glass (KU-1) core fibre coupled to a spectrometer.

All irradiations, as well as the luminescence and photoinduced absorption measurements, were performed at room temperature.

3. Results and discussion

As shown earlier [7], centres resulting from Yb doping of glass and absorbing in the UV spectral region are precursors of UV- and IR-induced colour centres in the glass network. Figure 1 compares the UV spectra of two preforms with phosphosilicate glass cores: ytterbium-free (solid line) and containing ytterbium as a codopant (dashed line). The absorption by the ytterbium-free preform in the range 5–7 eV is seen to be represented primarily by a band around 6.9 eV, corresponding to a singlet–singlet transition of phosphorus-related oxygen-deficient centres (PODCs) [8]. The presence of ytterbium ions in the glass network gives rise to an additional absorption in the range 5.5–6.5 eV, different from the absorption due to the PODC.
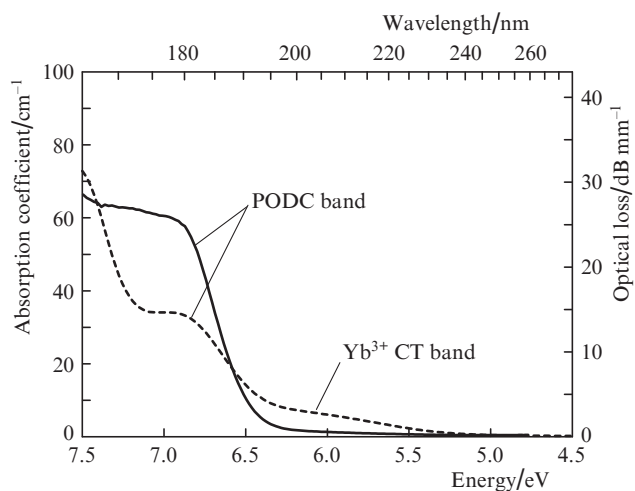

Figure 1. UV transmission spectra of the P-2 (solid line) and Yb/P-1 (dashed line) samples before irradiation.

According to Van Pieterson et al. [9] and Dorenbos et al. [10], who studied the optical properties of ScPO$_4$:Yb^{3+} and LiYP$_4$O$_{12}$:Yb^{3+} phosphate crystals, respectively, the absorption near 6 eV is due to a transition of the Yb^{3+} ion to a charge-transfer (CT) state. We believe that the same applies to the ytterbium-doped phosphosilicate glass. According to a theoretical model proposed by Krasikov et al. [11], excitation to a charge-transfer state in ytterbium-containing crystals may lead to reduction of Yb^{3+} to a divalent state (Yb^{2+}) as a

result of electron transfer from a nearest neighbour oxygen to the ytterbium ion. Thus, excitation of the trivalent ion Yb^{3+} to a charge-transfer state may produce two new absorbing centres: a divalent ytterbium ion (Yb^{2+}) and an oxygen hole centre (OHC). The structure and optical properties of oxygen hole centres have been described in sufficient detail in reports concerned with the effect of UV or gamma radiation on undoped silica glass [12–14]. In phosphorus-doped silica glass, the structure and properties of photoinduced oxygen hole centres are determined predominantly by the presence of phosphorus atoms near a nonbridging oxygen atom (P-OHC) [5, 6, 15, 16].

According to Griscom et al. [5], the P-OHC has visible absorption bands peaking at 2.2, 2.5 and 3.1 eV. The bands at 2.2 and 2.5 eV strongly overlap, so in the spectrum of a UV-irradiated phosphosilicate glass they usually appear as one absorption band peaking at ~2.3 eV [15, 16]. Moreover, according to Hosono et al. [16] no P-OHC generation and no corresponding absorption occur in H$_2$-loaded phosphorus-doped glasses. Hosono et al. [16] believe that hydrogen present in the glass network interacts with oxygen hole centres to form hydroxyl (OH) groups and PHO$_2$ centres. It is seen in Fig. 2 that the photoinduced absorption spectra of the P-1 and Yb/P-1 samples [spectra (1), (2)] have a local peak at 2.3 eV, which is, however, missing in the spectrum of the Yb/P-1 sample irradiated after H$_2$ loading [spectrum (3)].

It is of interest to compare the photoinduced absorption spectra of the Yb/P-2 samples after UV exposure and high-power IR pumping [Fig. 2, spectra (4), (5)]. Despite the weak intensity and the associated uncertainty in the photoinduced
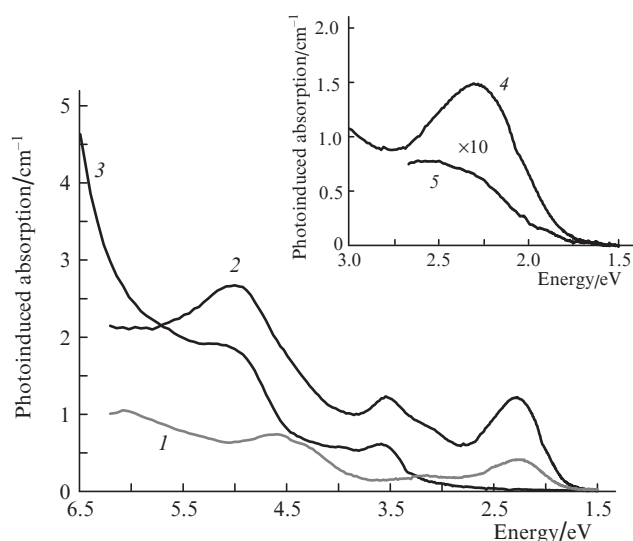

Figure 2. Photoinduced absorption spectra of samples obtained under different irradiation conditions. The P-1 (1), Yb/P-1 (2), H$_2$-loaded Yb/P-1 (3), and Yb/P-2 (4) preforms were exposed to the L1 laser beam ($\lambda = 193$ nm), and the Yb/P-1 fibre (5) was exposed to the L2 laser beam ($\lambda = 915$ nm).

absorption peak position (~2.5 eV), it is worth noting that the long-wavelength tails of spectra (*4*) and (*5*) are markedly similar in shape. As shown earlier [7, 17], high-energy gamma or UV (>5 eV) irradiation of an ytterbium-doped aluminosilicate glass network produces the same colour centres as prolonged pumping. In this study, we assume that (like UV radiation) IR pumping produces P-OHCs in phosphosilicate fibres.

It should be noted however that the efficiency of P-OHC formation under IR laser pumping is about eight orders of magnitude lower than that under UV laser irradiation (see the fluences in Table 2). The L2 laser photon energy is ~1.3 eV, whereas it is known that an ArF laser output with a photon energy of 6.4 eV is needed to produce P-OHCs in a phosphosilicate glass network [16]. Thus, pump laser radiation may only produce P-OHCs through cooperative interaction between several closely spaced Yb^{3+} ions (at least five in the case of phosphosilicate glass) in an excited state. The total energy of such a cluster of excited Yb^{3+} ions is sufficient for initiating photochemical processes in the doped silica glass network. To simplify calculation, a number of experimental and theoretical studies treated the interaction between the excited ions in such a cluster as interaction between pairs of Yb^{3+} ions (Yb^{3+}–Yb^{3+} ion pairs) [18, 19]. According to a model proposed earlier [7], interaction between two ion pairs accounts for photoinduced oxygen hole centre generation in an ytterbium-doped aluminosilicate glass network (Al-OHC). In this study, we will also rely on this model, assuming photoinduced P-OHC formation to be due to concurrent interaction between several (at least three) ion pairs.

Analysis of the spectra in Fig. 2 shows that, in the visible range (1.5–3 eV), the photoinduced absorption spectrum of the undoped phosphosilicate glass (P-1) is markedly similar in shape to that of the ytterbium-doped glass (Yb/P-1). These spectra, however, differ significantly in the UV. In particular, the spectrum of Yb/P-1 contains prominent bands centred at 3.5 and 5 eV, which are missing in the spectrum of P-1. In contrast to the absorption bands of the P-OHC, these bands are present as well in the spectrum of the Yb/P-1 sample irradiated after hydrogen loading. We assume that these bands are due to the photoinduced formation of colour centres structurally related to ytterbium ions in the glass network. Absorption spectra of ytterbium-containing MgF_2 crystals are known to contain similar bands (at 3.3, 3.7 and 5.1 eV), which are thought to arise from Yb^{2+} $4f^{14} \rightarrow 4f^{13}5d$ transitions [20, 21]. Thus, earlier results [20, 21] lead us to conclude that the bands observed at 3.5 and 5 eV in the spectrum of the Yb/P-1 sample are due to the Yb^{2+} ions reduced from the initial state Yb^{3+} as a result of irradiation. The mechanism of such conversion ($Yb^{3+} \rightarrow Yb^{2+}$) in ytterbium-containing crystals and glasses is commonly interpreted in terms of Yb^{3+} excitation to a charge-transfer state [11, 22]. Note that this process is usually accompanied by characteristic luminescence with a peak emission wavelength in the visible range (400 to 600 nm, depending on the composition of the material) [9, 23, 24]. To examine in situ the $Yb^{3+} \rightarrow Yb^{2+}$ conversion process in our samples, we analysed luminescence spectra excited by the L1 UV laser beam (Fig. 3).

It is seen in Fig. 3a that all of the samples have a luminescence peak near 3.05 eV. In addition, the spectra of the phosphorus-rich samples (P-2 and Yb/P-2) have a well-defined contribution of a luminescence band centred at 2.65 eV (Fig. 3b). The luminescence band centred at ~3 eV was assigned by Origlio et al. [25] to a triplet–singlet ($T_1 \rightarrow S_0$)
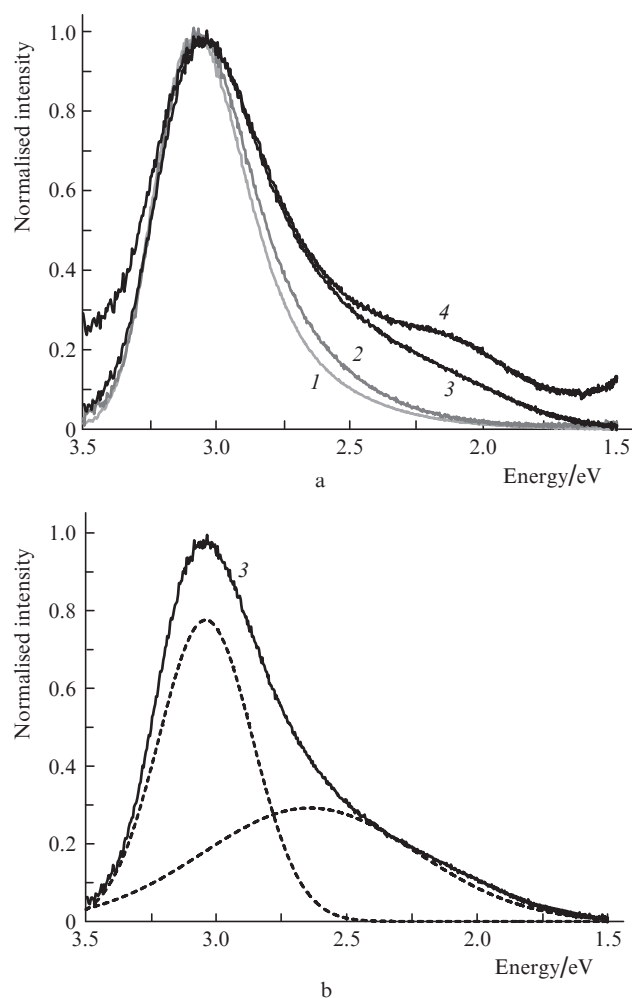

Figure 3. (a) Luminescence spectra of the (*1*) P-1, (*2*) Yb/P-1, (*3*) P-2 and (*4*) Yb/P-2 samples under excitation by the L1 laser beam (λ = 193 nm). (b) Decomposition of the spectrum of the P-2 sample into Gaussian components (dashed lines).

transition of the photoinduced phosphorus-containing centre $[(O–)_2P(–O)_2]^+$. The 2.65-eV luminescence band is attributable to the relaxation of the PODC from an excited state. A similar relaxation process, and the corresponding luminescence band at 2.7 eV, were reported earlier for silicon-related oxygen-deficient centres (SiODCs) [26].

The spectrum of the Yb/P-2 sample contains, in addition to the bands at 3.05 and 2.7 eV, a luminescence band peaking near 2.1 eV. A similar luminescence band, peaking at 630 nm, was observed by Yoo et al. [27] in $Ba_5(PO_4)_3Cl : Yb^{2+}$ phosphate crystals under illumination at a wavelength of 400 nm. Comparison of the luminescence spectrum of the Yb/P-2 sample with the spectrum presented in Ref. [27] leads us to assume that the weak luminescence band peaking at 2.1 eV is due to Yb^{2+} reduced ions and corresponds to Yb^{2+} relaxation from the $4f^{13}5d$ excited state to the $4f^{14}$ ground state [24, 27].

Thus, both IR pumping and UV irradiation cause photochemical reactions in the ytterbium-doped phosphosilicate glass network, which lead to the formation of pairs of hole (P-OHC) and electron (Yb^{2+}) centres, like in crystals [11, 24]. The precursors of the Yb^{2+} centres are Yb^{3+} ions reduced to a divalent state as a result of electron capture. We assume as well that the P-OHCs form in the immediate vicinity of ytterbium ions.

To verify and improve the hypothesis inferred from analysis of the experimental data, we performed quantum-chemical simulation. A model for calculation was chosen under the assumption that an ytterbium ion in phosphosilicate glass was surrounded by SiO_4 and PO_4 tetrahedra so that its nearest neighbour environment was formed by oxygens (octahedral coordination) [28–30]. Under this assumption, the ground state of the ytterbium centre is Yb^{3+} (this state will be denoted as Yb^{3+}–O, where O stands for a bridging oxygen between the ytterbium ion and a phosphorus or silicon atom).

Optical excitation of the Yb^{3+}–O centre by a UV laser (or by the energy resulting from interaction between several ion pairs) transfers an electron from one of the nearest neighbour bridging oxygens to the ytterbium ion, which converts from Yb^{3+} to Yb^{2+}, and the entire centre, composed of the ytterbium ion and its nearest neighbour oxygens, undergoes the Yb^{3+}–O $\rightarrow$ Yb^{2+}–O^+ transformation, which produces a hole at one or several oxygens in the nearest neighbour environment of the ytterbium ion. In other words, this transformation in the glass network produces an Yb^{2+} ion and a nearby oxygen hole centre (P-OHC in phosphosilicate glass). Such vertical charge transfer excitation must be followed by the relaxation of the atoms around the ytterbium ion, stabilising the Yb^{2+}–O^+ centre through either Yb–O bond breaking and nonbridging oxygen formation or hole self-trapping. According to our ideas, it is hole centres in the glass network that are responsible for the photoinduced absorption in the visible range. Therefore, illumination in the visible range should cause an inverse transformation of the Yb^{2+}–O^+ centre, i.e. a photoinduced electron transfer from the ytterbium ion to nearest neighbour oxygens, restoration of the Yb^{3+}–O centre and the associated bleach of the photoinduced absorption [31]. Figure 4 presents the simplest energy diagram for the transitions above.
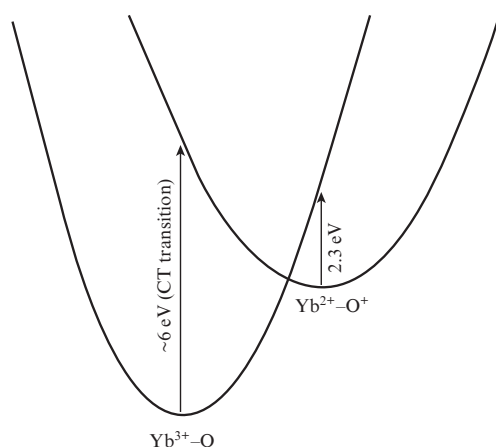

Figure 4. A model for the transformation of an ytterbium centre responsible for the photoinduced absorption in the visible and near-IR spectral regions. The transition energies correspond to the experimentally determined peak absorption wavelengths.

Structural models for evaluating the spectral properties and mutual transformations of the Yb^{3+}–O and Yb^{2+}–O^+ centres were based on the crystal structure of ytterbium metaphosphate [32], represented in the Inorganic Crystal Structure Database (ICSD) [33]. From this crystal structure, we derived an $Yb(PO_2)_6^{3+}$ system, where the ytterbium atom was coordinated to six oxygens, and the phosphorus atoms in the second neighbour environment were coordinated to the other oxygens. Since structures cut from a crystal have unsaturated valences, the dangling bonds of the oxygens were saturated with fluorine (as an element most similar to phosphorus), having a valence of unity (Fig. 5). Thus, the $Yb(PO_2F_2)_6^{3-}$ cluster consisted of 31 atoms.

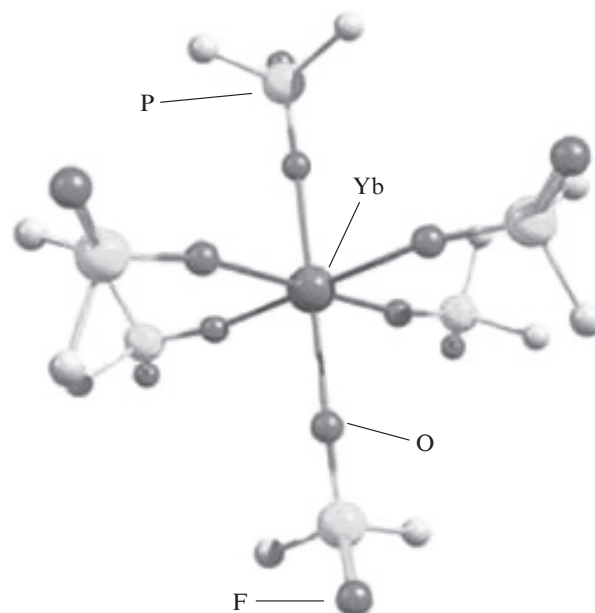**Figure 5.** Structure of the $Yb(PO_2F_2)_6^{3-}$ cluster (RHF method).

We computed the ground and first excited states of the cluster. For this purpose, we used the quantum chemistry packages MOLPRO [34] and Firefly QC [35], the latter partially based on the GAMESS (US) source code. The basis set was taken from the basis set library in MOLPRO. In the first step, computations were aimed at optimising the cluster geometry at varied numbers of degrees of freedom of the atoms. The geometry was optimised by a DFT method with the BHHLYP hybrid functional, using the 6-31G** basis set and ECP59MWB pseudopotential [36]. The computation procedure was as follows: First, Yb^{2+} molecular orbitals were obtained by restricted Hartree–Fock (RHF) calculations. The molecular orbitals obtained were used as input data in complete active space self-consistent field (CASSCF) calculations with 25 (7 f-type and 18 p-type) orbitals. The ground and excited states were computed using the Stuttgart RSC 1997 ECP basis set and pseudopotential (28 core electrons, explicitly described f-shells) [37]. Analysis of the molecular orbitals showed that the seven upper double-filled molecular orbitals consisted predominantly of ytterbium f-functions. The lower energy filled molecular orbitals consisted mainly of oxygen p-functions. The molecular orbitals obtained were used as the first approximation in CASSCF calculations.

According to our calculations, the lower seven quasi-degenerate states of the $Yb(PO_2F_2)_6^{3-}$ cluster correspond to a hole localised on one of the seven 4f sublevels (Table 3). The next three states are attributable to a hole in the 2p orbitals of one of the oxygens (Yb^{2+}–O^+ states). The energy of excited hole states was estimated at ~7 eV, which roughly corre-

Table 3. Excited state energies of the cluster (MCSCF calculations).

State	Energy relative to the ground state/eV	State	Energy relative to the ground state/eV
1	0	6	0.0999
2	0.025	7	0.109
3	0.055	8	7.327
4	0.077	9	7.622
5	0.081	10	7.749

sponds to the Yb^{3+} charge transfer band whose long-wavelength edge is seen in Fig. 1. It is important to note in this context that, even though located predominantly in three p-orbitals, the hole is, to some extent, spread over the p-orbitals of all six oxygens.

4. Conclusions

We have studied the absorption spectra of ytterbium-doped phosphosilicate glass core preforms and fibres before irradiation and their photoinduced absorption spectra after IR laser pumping and UV irradiation. The UV absorption spectra of the unirradiated ytterbium-doped samples were found to contain a broad (~1.5 eV) band centred near 6 eV and corresponding to a transition to a charge-transfer state. Just like UV irradiation, IR irradiation with a pump source at a photon energy of 1.3 eV produced visible absorption bands, which were tentatively attributed to phosphorus–oxygen–hole centres.

UV irradiation of the ytterbium-doped preforms produced a luminescence band centred at 2.1 eV, which had been observed previously in spectra of Yb^{2+}-doped phosphate crystals. By analogy with the spectra of the crystals, we assume that the luminescence in the glass is also due to Yb^{2+} ions produced by the irradiation. The Yb^{2+} ions are presumably generated through the excitation of Yb^{3+} transitions to a charge-transfer state as a result of absorption at 6.4 eV under UV irradiation or absorption of the total energy of a cluster consisting of several (at least five) closely spaced ytterbium ions under irradiation with an IR pump source. Some of the Yb^{3+} ions thus excited capture an electron of one of the nearest neighbour oxygens and convert to a divalent state, which leads to the formation of defect pairs in the glass network: divalent ytterbium ion + phosphorus–oxygen–hole centre.

The present calculations lend support to the proposed model of colour centre generation: they demonstrate an electron transition from an orbital of the nearest neighbour oxygens to an ytterbium ion, with the transition energy roughly corresponding to the charge transfer band observed in the absorption spectrum of the samples.

References

1. Shubin A., Yashkov M., Melkumov M., Smirnov S., Bufetov I., Dianov E. *Proc. CLEO/Europe-IQEC* (Baltimor, 2007) paper CJ3-1-THU.
2. Engholm M., Norin L. *Opt. Express*, **16** (2), 1260 (2008).
3. Unger S., Schwuchow A., Jetschke S., Reichel V., Scheffel A., Kirchhof J. *Proc. SPIE Int. Soc. Opt. Eng.*, **6890**, 689016 (2008).
4. Mattsson K.E. *Opt. Express*, **19** (21), 19797 (2011).
5. Griscom D.L., Friebele E.J., Long K.J., Fleming J.W. *J. Appl. Phys.*, **54** (7), 3743 (1983).
6. Fanciulli M., Bonera E., Nokhrin S., Pacchioni G. *Phys. Rev. B*, **74**, 134102 (2006).
7. Rybaltovsky A.A., Aleshkina S.S., Likhachev M.E., Bubnov M.M., Umnikov A.A., Yashkov M.V., Gur'yanov A.N., Dianov E.M. *Kvantovaya Elektron.*, **41** (12), 1073 (2011) [*Quantum Electron.*, **41** (12), 1073 (2011)].
8. Rybaltovsky A.A., Sokolov V.O., Plotnichenko V.G., Lanin A.V., Semjonov S.L., Gur'yanov A.N., Khopin V.F., Dianov E.M. *Kvantovaya Elektron.*, **37** (4), 388 (2007) [*Quantum Electron.*, **37** (4), 388 (2007)].
9. Van Pieterson L., Heeroma M., De Heer E., Meijerink A. *J. Lumin.*, **91**, 177 (2000).
10. Dorenbos P., Shalapska T., Stryganyuk G., Gektin A., Voloshinovskii A. *J. Lumin.*, **131**, 633 (2011).
11. Krasikov D.N., Scherbinin A.V., Vasil'ev A.N., Kamenskikh I.A., Mikhailin V.V. *J. Lumin.*, **128**, 1748 (2008).
12. Munekuni S., Yamanaka T., Shimogaichi Y., Tohmon R., Ohki Y., Nagasawa K., Hama Y. *J. Appl. Phys.*, **68** (3), 1212 (1990).
13. Pacchioni G., Ierano G. *Phys. Rev. B*, **57** (2), 818 (1998).
14. Hosono H., Kajihara K., Suzuki T., Ikuta Y., Skuja L., Hirano M. *Solid State Commun.*, **122**, 117 (2002).
15. Ehrt D., Ebeling P., Natura U. *J. Non-Cryst. Solids*, **263&264**, 240 (2000).
16. Hosono H., Kajihara K., Hirano M., Oto M. *J. Appl. Phys.*, **91** (7), 4121 (2002).
17. Arai T., Ichii K., Tanigawa S., Fujimaki M. *OFC Conf. OSA Techn. Dig.* (San Diego, 2009) paper OWT2; http://www.opticsinfobase.org/abstract.cfm?uri=OFC-2009-OWT2.
18. Ishii T. *J. Chem. Phys.*, **122**, 024705 (2005).
19. Kir'yanov A.V., Barmenkov Y.O., Martinez I.L., Kurkov A.S., Dianov E.M. *Opt. Express*, **14** (9), 3981 (2006).
20. Lizzo S., Meijerink A., Dirksen G.J., Blasse G. *J. Lumin.*, **63**, 223 (1995).
21. Kuck S., Henke M., Rademaker K. *Laser Phys.*, **11** (1), 116 (2001).
22. Engholm M., Norin L. *Proc. SPIE Int. Soc. Opt. Eng.*, **6873**, 68731E (2008).
23. Engholm M., Norin L., Aberg D. *Opt. Lett.*, **32** (22), 3352 (2007).
24. Strek W., Marciniak L., Bednarkiewicz A., Lukowiak A., Wiglusz R., Hreniak D. *Opt. Express*, **19** (15), 14083 (2011).
25. Origlio G., Messina F., Cannas M., Boscaino R., Girard S., Boukenter A., Ouerdane Y. *Phys. Rev. B*, **80**, 205208 (2009).
26. Skuja L. *J. Non-Cryst. Solids*, **167**, 229 (1994).
27. Yoo H.S., Vaidyanathan S., Kim S.W., Jeon D.Y. *Opt. Mater.*, **31**, 1555 (2009).
28. Yamamoto T., Tanaka T., Matsuyama T., Funabiki T., Yoshida S. *Solid State Commun.*, **111**, 137 (1999).
29. Sen S., Rakhmatullin R., Gubaidullin R., Pöppl A. *Phys. Rev. B*, **74**, 100201 (2006).
30. Deschamps T., Ollier N., Vezin H., Gonnet C. *J. Chem. Phys.*, **136**, 014503 (2012).
31. Guzman-Chavez A.D., Kir'yanov A.V., Barmenkov Yu.O., Il'ichev N.N. *Laser Phys. Lett.*, **4** (10), 734 (2007).

32. Hong H.Y.-P. *Acta Crystallogr., Sect. B: Struct. Sci.*, **30**, 1857 (1974).

33. Bergerhoff G., Brown I.D., in *Crystallographic Databases*. Allen F.H. et al. (Eds) (Chester: International Union of Crystallography, 1987); http://www.fiz-karlsruhe.de/icsd.html.

34. Werner H.-J., Knowles P. J., Knizia G., Manby F.R., Schütz M., et al. MOLPRO, version 2010.1, a package of ab initio programs; http://www.molpro.net.

35. Granovsky A.A. Firefly version 7.1.G; http://classic.chem.msu.su/gran/firefly/index.html.

36. Dolg M., Stoll H., Savin A., Preuss H. *Theor. Chim. Acta*, **75**, 173 (1989).

37. Dolg M., Stoll H., Preuss H., Pitzer R.M. *J. Phys. Chem.*, **97**, 5852 (1993).