Influence of Stark splitting levels on the lasing performance of Yb^{3+} in phosphate and fluorophosphate glasses

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Abstract: Lasing properties have been investigated for Yb^{3+} doped glasses with similar emission cross sections (σ_{emi}) and lifetime while possessing different Stark levels. Narrow Stark splitting of Yb^{3+}-phosphate glass is responsible for severe heat generation, narrow emission band and much smaller σ_{emi} at lasing wavelength, making Yb^{3+}-phosphate glass unsuccessful to achieve laser output, whereas 1.166W cw laser was obtained in Yb^{3+}-fluorophosphate (FP) glass with broader Stark splitting. Analysis on laser system levels reveals that under room temperature, Yb^{3+} laser is quasi-3.13-level in phosphate glass and quasi-3.36-level in FP glass. These demonstrations suggest that unless the Stark splitting is enlarged, conventional Yb^{3+}-phosphate glass is not a good gain medium for bulk Yb^{3+}-laser.

OCIS codes: (140.3615) Lasers, ytterbium; (140.3580) Lasers, solid-state; (300.6170) Spectra .

References and links

1. J. Hein and M. C. Kaluza, “POLARIS: an all diode-pumped ultrahigh peak power laser for high repetition rates,” Lect. Notes Phys. **694**, 47–66 (2006).
2. L. Zhang, L. Hu, and Z. Jiang, “Yb^{3+} doped fluorophosphate glasses a good candidate for high energy, ultrashort pulse, tunable fiber lasers,” Prog. Phys. **23**, 473–483 (2003).
3. D. Ehrt and T. Toepfer, “Preparation, structure and properties of Yb^{3+} FP laser glass,” Proc. SPIE **4102**, 95–105 (2000).
4. M. Loeser, F. Röser, A. Reichelt, M. Siebold, S. Grimm, D. Litzkendorf, A. Schwuchow, J. Kirchhof, and U. Schramm, “Broadband, diode pumped Yb^{3+}:SiO_2 multicomponent glass laser,” Opt. Lett. **37**(19), 4029–4031 (2012).
5. K. Lu and N. K. Dutta, “Spectroscopic properties of Yb^{3+}-doped silica glass,” J. Appl. Phys. **91**(2), 576–581 (2002).
6. M. Hornung, R. Bödefeld, M. Siebold, A. Kessler, M. Schnepp, R. Wachs, A. Sävert, S. Podleska, S. Keppler, J. Hein, and M. C. Kaluza, “Temporal pulse control of a multi-10 TW diode-pumped Yb^{3+}: glass laser,” Appl. Phys. B **101**(1-2), 93–102 (2010).
7. B. H. Yang, X. Q. Liu, X. Wang, J. J. Zhang, L. L. Hu, and L. Y. Zhang, “Compositional dependence of room-temperature Stark splitting of Yb^{3+} in several popular glass systems,” Opt. Lett. **39**(7), 1772–1774 (2014).
8. G. Boulon, “Why so deep research on Yb^{3+}-doped optical inorganic materials?” J. Alloy. Comp. **451**(1-2), 1–11 (2008).
9. R. Koch, W. A. Clarkson, D. C. Hanna, S. Jiang, M. J. Myers, D. Rhonehouse, S. J. Hamlin, U. Griebner, and H. Schönnagel, “Efficient room temperature cw Yb^{3+}:glass laser pumped by a 946nm Nd:YAG laser,” Opt. Commun. **134**(1-6), 175–178 (1997).
10. C. Hönninger, R. Paschotta, M. Graf, F. Morier-Genoud, G. Zhang, M. Moser, S. Biswal, J. Nees, A. Braun, G. A. Mourou, I. Johannsen, A. Giesen, W. Seeber, and U. Keller, “Ultrafast yetterbium-doped bulk lasers and laser amplifiers,” Appl. Phys. B **69**(1), 3–17 (1999).
11. S. Dai, A. Sugiyama, L. Hu, Z. Liu, G. Huang, and Z. Jiang, “The spectrum and laser properties of ytterbium doped phosphate glass at low temperature,” J. Non-Cryst. Solids **311**(2), 138–144 (2002).
12. J. F. Philipps, T. Töpfer, H. Ebendorff-Heidepriem, D. Ehrt, and R. Sauerbrey, “Spectroscopic and lasing properties of Er^{3+}:Yb^{3+}-doped fluoride phosphate glasses,” Appl. Phys. B **72**(4), 399–405 (2001).
13. A.-F. Obaton, C. Parent, G. Le Flem, P. Thony, A. Brenier, and G. Boulon, “Yb^{3+}-Er^{3+}-codoped LaLiP4O12 glass: a new eye-safe laser at 1535nm,” J. Alloy. Comp. **300–301**, 123–130 (2000).

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14. A. Speghini, R. Francini, A. Martinez, M. Tavernese, and M. Bettinelli, "Spectroscopic properties of Er^{3+}, Yb^{3+} and Er^{3+}/Yb^{3+} doped metaphosphate glasses," Spectrochim. Acta A Mol. Biomol. Spectrosc. **57**(10), 2001–2008 (2001).
15. A.-F. Obaton, C. Parent, G. Le Flem, P. Thony, A. Brenier, and G. Boulon, "Excited state absorption in Yb^{3+}-Er^{3+}-codoped phosphate glasses(ZnO-An_2O_3-La_2O_3-P_2O_5) around the ${}^4I_{13/2}\rightarrow{}^4I_{15/2}$ emission spectral range," Spectrochimica Acta Part A **55**(2), 263–271 (1999).
16. Y. Guyot, H. Canibano, C. Goutaudier, A. Novoselov, A. Yoshikawa, T. Fukuda, and G. Boulon, "Yb^{3+}-doped $Gd_3Ga_5O_{12}$ garnet single crystals grown by the micro-pulling down technique for laser application. part I: spectroscopic properties and assignment of energy levels," Opt. Mater. **27**(11), 1658–1663 (2005).
17. A. S. Pinheiro, A. M. Freitas, G. H. Silva, M. J. V. Bell, V. Anjos, A. P. Carmo, and N. O. Dantas, "Laser performance parameters of Yb^{3+} doped UV-transparent phosphate glasses," Chem. Phys. Lett. **592**, 164–169 (2014).
18. J. O. White, "Parameters for quantitative comparison of two-,three-, and four-level laser media, operating wavelengths, and temperatures," IEEE J. Quantum Electron. **45**(10), 1213–1220 (2009).

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1. Introduction

In order to generate pulses with peak powers over 1 PW and intensities beyond 10^{21} W/cm^2, large size laser materials are used in facilities with pulse energy of a few 10's J or a couple of 100's J [1]. It is known that Yb^{3+} is valued by the characteristics of simple energy levels, high quantum efficiency, high energy storage and high doping ability. Therefore, Yb^{3+}-laser is regarded as the most promising candidate for high energy, ultra-short-pulse laser that is needed in inertial confinement fusion experiments [2, 3]. During the past decades, solid-state Yb^{3+}-lasers have been witnessed great advancement [1,4–6]. But the two-energy-level configuration of Yb^{3+} results in two disadvantages for Yb^{3+}-laser: high threshold and serious thermal load of the gain media for the reason that both the lower and ground laser manifolds belong to ${}^2F_{7/2}$ level [7,8]. In that case, Yb^{3+} doped laser materials are expected having broad Stark splitting to promote efficient steady-state lasing [8].

In all of the Yb^{3+} doped laser materials, glass is a kind of powerful competitor that possesses the advantages as large size, high quality, bulk supply and low cost. To minimize the heat generation in Yb^{3+} doped glasses, high Yb^{3+} dopant density is preferred to reduce the thickness of the glass disk. Furthermore, glasses with negative thermal refractive index and low non-linear refractive index (n_2) can partially compensate self-focusing effect in the amplifiers [1]. Phosphate and fluorophosphate (FP) are two glass systems that meet the requirements above mentioned. In comparison, phosphate glass is provided with the properties of high Yb^{3+} solubility, high lifetime, high emission cross section, lower thermal expansion coefficient, better thermal conductivity and perfect glass forming ability [9–11], while the merits of FP glass are broader Stark splitting levels [7] and lower n_2. Consequently, Yb^{3+}-phosphate glass has been taken as a good gain medium for high power Yb^{3+}-laser.

Since Yb^{3+}-laser operates under quasi-three or quasi-four -level, more work is needed to determine the dependence of lasers on Stark splitting degree in Yb^{3+} doped glasses. Essentially, it is an interesting topic to study the lasing performance of Yb^{3+} in the gain media with similar spectroscopic properties while different Stark splitting. Herein we presented such a study by determining relatively accurate Stark splitting levels of Yb^{3+} from low temperature absorption and emission spectra in phosphate and FP glasses with similar spectroscopic properties, followed by comparative laser experiments in a simple linear cavity under room temperature. Finally, the actual laser system levels of Yb^{3+} in phosphate and FP glasses were estimated.

2. Experiment

Molar compositions of Yb^{3+} doped phosphate and FP glasses are $72.5P_2O_5$-$5.2B_2O_3$-$10.4BaO$-$3.1Al_2O_3$-$3.1Nb_2O_5$-$4.1K_2O$-$1.6Yb_2O_3$ and $6Al(PO_3)_3$-$8Sr(H_2PO_4)_2$-$53RF_2$-$20AlF_3$-$3YbF_3$ (R = Mg, Ca, Sr, Ba), respectively. Glasses were prepared with 1.0 kg reagent grade raw materials. For phosphate glass, raw materials were firstly melted in a SiO_2 crucible, and meanwhile glass liquid was bubbled with $CCl_4 + O_2$ for OH^- removal. Then the melt was transferred to a Pt crucible. FP glass was prepared in a Pt crucible in open atmosphere. After stirring and refining process, the glasses were cast into heated steel molds for further annealing, then were cut and polished for the spectroscopic tests and laser experiments. Glass transition temperature Tg were characterized with a NetzschSTA449/C differential scanning calorimeter (DSC). Absorption spectra were recorded at 4k by a Cary-Varian 5000 Scan spectrometer equipped with an Oxford CF 1204 helium flow cryostat. With 896nm pump, the emission spectra and lifetimes were measured by a FLSP920 spectrofluorimeter cooled with liquid helium (Edingburg Co., UK) under 9k. Reciprocity method was used to calculate the emission cross sections of Yb^{3+} [12]. The experimental set-up will be described in detail later.

3. Results and Discussion

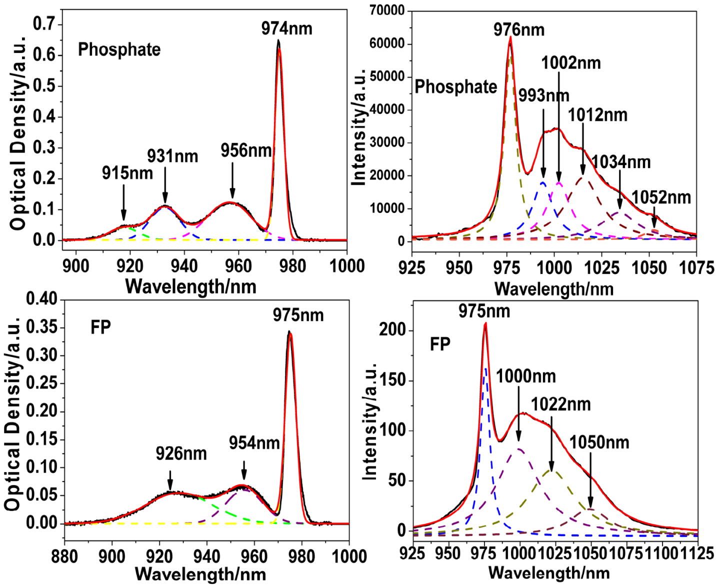

Fig. 1. Low temperature absorption & emission spectra and the corresponding Gaussian fitting in Yb^{3+} doped phosphate and FP glasses.

Stark splitting levels were derived from Gaussian or Lorentz fitting based on the low temperature absorption and emission spectra, shown in Fig. 1. Black lines are the original spectra, while the reds offer the fitting lines composed of the corresponding multi-fitting peaks. Regularly, there are three absorption and four emission peaks in Yb^{3+} spectra, similar with the situation of Yb^{3+}-FP glass in Fig. 1. However, four absorption and six emission peaks were observed in the studied Yb^{3+}-phosphate glass. Definitely, vibronic peaks exist in the spectra. The assignment of pure electronic lines is rather difficult due to a strong electron-phonon coupling. Moreover, the additional vibronic peaks have to be distinguished with the electronic ones which are used for the confirmation of Stark splitting. Since the lowest Stark splitting manifold of $^4F_{5/2}$ is determined by the 974nm peak, thus, whether the 915nm band is vibronic [11,13] or electronic does not influence the energy of the highest manifold of $^4F_{7/2}$. In addition, 915nm absorption peak has been reported in other Yb^{3+}-phosphate glasses [13–15]. Whereas, the maximum emission peak of the fluorescence spectrum is indispensable in the determination of the maximum Stark splitting manifold of $^4F_{7/2}$ level. Hence, the attribute of 1052nm peak is needed to be defined. Same situation has been reported in [11] by omitting the1050nm peak and taking the 1030nm band as the maximum emission peak.

In order to discriminate the 1052nm peak in Yb^{3+}-phosphate glass, Raman spectrum of the non-doped phosphate glass was provided to compare with the absorption (subtracted by 0-phonon energy) and emission (minus 0-phonon energy) spectra which were adjusted to the same energy scale [16], shown in Fig. 2. Except for the independent 976nm and 1034nm emissions, 915nm, 1002nm and 1052nm peaks totally, while others partly, overlap with Raman vibration bands. Combined with the 1050nm peak that was observed in the

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fluorescence spectrum of non-doped phosphate glass [17], we believe that the 1050nm peak is vibronic. Therefore, the 1034nm peak is used for the Stark splitting determinations. Although the properties of 993nm and 1002nm emission maintain ambiguous, fortunately, the energy of the highest manifold of $^2F_{7/2}$ is determined by the 1034nm band. In general, the peak around 1000nm is taken as the second emission peak in Yb^{3+}-phosphate glass, such as in [11, 16, 17], thence the 1002nm peak is thought to be electronic.

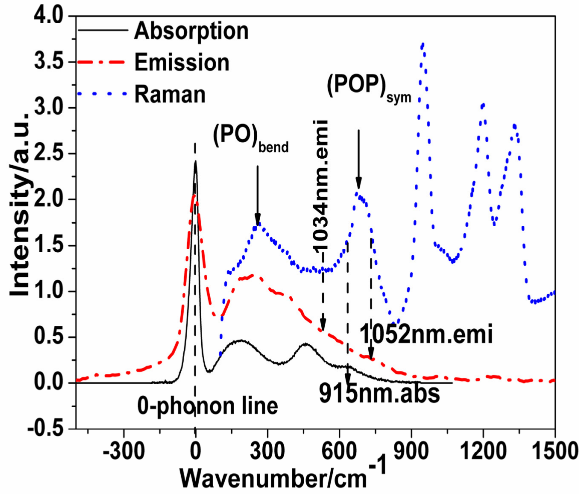

Fig. 2. Comparisons of the absorption spectrum (subtracted by 0-phonon energy) with the emission spectrum (minus 0-phonon energy) and Raman spectrum.

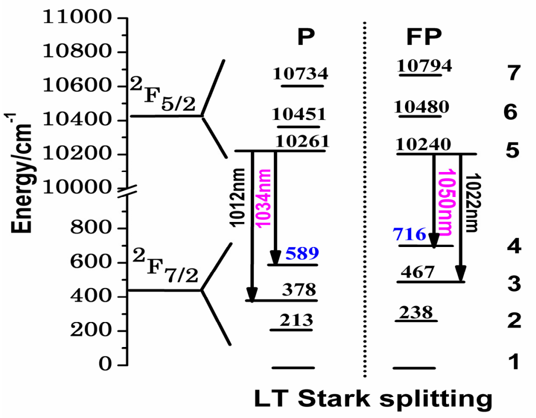

Fig. 3. Low temperature Stark splitting levels of Yb^{3+} doped phosphate and FP glasses. Both maximum manifolds of $^2F_{7/2}$ level and the corresponding lasing wavelength were highlighted.

According to the results analyzed above, detailed Stark splitting manifolds in both Yb^{3+} doped glasses are depicted in Fig. 3. The maximum Stark splitting energy of $^2F_{7/2}$ level in phosphate and FP glass is 589cm^{-1} and 716cm^{-1}, respectively. Stark splitting of Yb^{3+} in FP glass is broader than that in phosphate glass. Naturally, narrow Stark splitting represents narrow emission bandwidth, consistent with the cognition that Yb^{3+} usually performs narrower gain bandwidth in phosphate glass [10]. Manifold 3 is commonly considered as the lower laser level, but manifold 2 and 3 often degenerate because of the small energy gap between them. Narrow Stark splitting makes the dramatically increased populations on the lower laser level difficult to transfer to the ground state effectively and quickly, and thereby

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induces the laser lasing at a longer wavelength. Regularly, manifold 4 becomes the actual lower laser level, and the red-shift lasing wavelength corresponds to a smaller σ_{emi}.

Table 1 illustrates some properties of the studied glasses. Both glasses, especially Yb^{3+}-phosphate glass, possess high σ_{emi} and high fluorescence lifetime (τ_f). However, σ_{emi} of Yb^{3+}-phosphate glass at the possible lasing wavelength (for example, at 1030nm, 1032nm and 1034nm) decreases fast, which is only 1/5 to 1/25 of that in Yb^{3+}-FP glass. Obviously, narrow fluorescence effective linewidth ($\triangle\lambda_{eff}$) well explains the low σ_{emi} @ lasing wavelength in Yb^{3+}-phosphate glass, as well as in all the Yb^{3+} doped conventional phosphate glasses.

Table 1. Properties of the studied glasses

Glass	**Yb^{3+}-phosphate**	**Yb^{3+}-FP**
σ_{abs}@pump/pm^2	1.08	1.48
σ_{emi}@second eak/pm^{2*}	0.94	0.76
τ_f/ms	2.0	1.8
$\sigma_{emi} \times \tau_f$/pm^2.ms	1.88	1.368
σ_{emi}@lasing peak/pm^2	0.09@1.030μm 0.03@1.032μm 0.02@1.034μm	0.49@1.055μm
$\triangle\lambda_{eff}$/nm	40	50
Refective index n_d	1.52	1.51
$n_2/10^{-13}$esu	1.1	0.81
α / × 10^{-6}/k	12.0	14.5
Tg/°C	501	492

* second peak is the emission peak around 1000nm

Subsequently, lasers were end-pumped by a fiber coupled 976nm LD in a simple resonant cavity under room temperature, depicted in Fig. 4. The incident laser was focused into the glass by a lens with focal length of 60mm. The plane incoupling mirror M1 was highly reflective (R>99%) above 1045 ± 30nm and highly transmissive (T>95%) at 976nm. Planoconcave mirror M2 is the outcoupling mirror with transmission 3% above 1045 ± 30nm. The water for sample mount hydrocooling was set as 14°C. Yb:glasses were cut and polished to $3 \times 3 \times 2mm^3$ with anti-reflective coating at 976nm (R>0.2%).

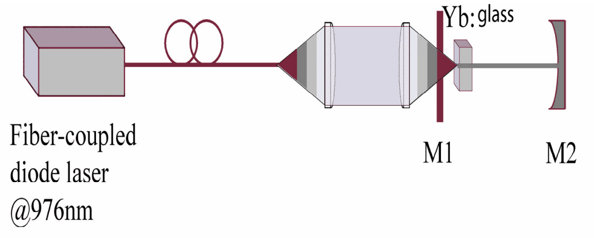

Fig. 4. Experimental scheme of the cw Yb^{3+}-glass laser.

Examined by the STR-1 stripe detector and a home-built bubble examination instrument, Yb^{3+}-phosphate glass was proved possessing much better optical homogeneity than Yb^{3+}-FP glass. For Yb^{3+}-phosphate glass, we tried 1002 nm, 1012nm, 1034nm and 1052nm output respectively, and no laser was achieved. While in Yb^{3+}-FP glass, 1.166W cw output centered at 1056nm was obtained from 8.86w pump power. Glass damage occurred when pump power was enhanced further. Figure 5 shows the output power as a function of the pump power in Yb^{3+}-FP glass. Besides, we note that, although not being measured with an infrared thermometer, Yb^{3+}-phosphate glass apparently had higher temperature than Yb^{3+}-FP glass when being touched right after the laser experiment.

For Yb^{3+}-FP glass, better output characteristics can be achieved if the optical quality of the glass is improved. In literatures about single-slab Yb^{3+}-phosphate glass lasers, 2mw laser at

1001nm was demonstrated under 8K [11], and 440mW unpolarized as well as 335mW polarized lasers were obtained at 1032nm in QX/Yb glass with the sample mount kept constant at 15°C [9]. QX/Yb glass is a commercial Yb^{3+}-phosphate glass with perfect optical homogeneity and the highest energy storage ability, but no further single-slab bulk lasers about it were reported. A pivotal factor may interpret the unsatisfactory lasing performance of Yb^{3+}-phosphate glass: narrow Stark splitting results in serious thermal blocking, narrow emission bandwidth together with quite small σ_{emi} at the lasing wavelength.

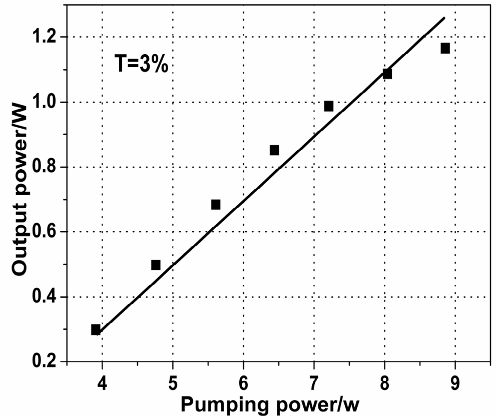

Fig. 5. Output power verses pumping power in Yb^{3+}-FP glass.

Based on the occupation probability of absorbing and emitting as well as pump and laser levels, a method was proposed for describing the statistical thermodynamic component of the exchange of photons between a pump and a laser beam [18]. For example, under 976nm pumping, Yb^{3+} lasers are usually thought to operate as quasi-three-level. However, Yb^{3+} laser strongly depends on the Stark splitting of $^4F_{7/2}$ level in the gain media, then how to discriminate the differences on laser operation? This method provided a clue that the system level of Yb^{3+} laser can be taken as a parameter that varies continuously with temperature and the Stark splitting levels, with which the characteristics of Yb^{3+} laser in different gain media will be distinguished.

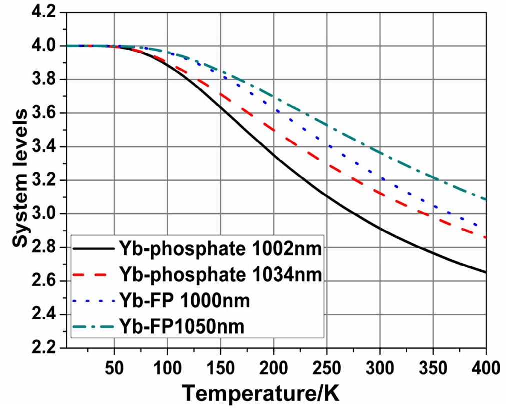

Fig. 6. Temperature dependence of the lasing system levels in the studied Yb^{3+} doped glasses.

Laser system levels (quasi-three or quasi-four) of the studied Yb^{3+}-phosphate and Yb^{3+}-FP glasses were estimated, described in Fig. 6. It shows that laser system levels of Yb^{3+}-phosphate glass are quite lower than that of Yb^{3+}-FP glass. For instance, under 300K, system level of Yb^{3+}-phosphate glass around 1034nm is quasi-3.13-level, while that of Yb^{3+}-FP glass around 1050nm is quasi-3.36-level, which represents that Yb^{3+}-phosphate glass performs

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more severe thermal blocking than Yb^{3+}-FP glass under laser operation. The fractional laser system doesn't mean that Yb^{3+} laser operates as 3.13 or 3.36 levels. It represents that Yb^{3+} laser is closer to quasi-four-level in FP glass than in phosphate glass, or the population accumulated on the lower laser level exhibits an easier transition to the ground state in FP glass than in phosphate glass. Additionally, Yb^{3+}-phosphate laser around 1002nm is not recommended due to its quasi-2.9-level system. It also reveals that the behavior of system levels makes Yb^{3+}-laser tend to output at longer wavelength with small σ_{emi} other than at the expected wavelength with large σ_{emi}. In other words, for Yb^{3+}-laser, efforts on enhancing system level and Stark splitting of Yb^{3+} in the gain media are more valuable than σ_{emi} and τ_f improvement.

4. Conclusion

In comparison, we studied the low temperature spectra, Stark splitting levels, bulk laser and laser system levels in Yb^{3+} doped phosphate and FP glasses, elaborating the importance of Stark splitting of the materials to the operation of Yb^{3+}-laser. In Yb^{3+}-phosphate glass, four absorption and six emission peaks exist, and Raman, absorption and emission spectra were compared to exclude the 1052nm vibronic peak from the bands that are needed in the determination of Yb^{3+} Stark splitting. Narrow Stark splitting of Yb^{3+}-phosphate glass ($^4F_{7/2}$:589cm^{-1}) is responsible for a series of problems: severe thermal blocking during laser operation, narrow emission band and much lower emission cross section at lasing wavelength, which induces the studied Yb^{3+}-phosphate glass with good optical homogeneity unsuccessful to achieve laser output. Meanwhile, Yb^{3+}-FP glass with higher Stark splitting ($^4F_{7/2}$:716cm^{-1}) obtained 1.166W output power. Results indicate that discrepancies in Stark splitting make Yb^{3+} doped phosphate and FP glasses exhibit quite different laser performance, although they have similar emission cross section and fluorescence lifetime. Analysis on the laser system levels reveals that under 300K, Yb^{3+}-laser operates as quasi-3.13-level in phosphate glass and quasi-3.36-level in FP glass. Moreover, Yb^{3+}-laser tends to operate at longer wavelength because the system level of Yb^{3+} increases with it, and efforts on enhancing system level and Stark splitting of Yb^{3+} in the gain media are more valuable than σ_{emi} and τ_f improvements. Results suggest that unless the Stark splitting of Yb^{3+} is enlarged, conventional Yb^{3+}-phosphate glass is not a good gain media for bulk Yb^{3+}-lasers.

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