Lasing improvement of Yb: phosphate glass with GeO_2 modification

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A B S T R A C T

A series of GeO_2 modified Yb: phosphate glasses were studied, covering thermal, optical, and fluorescence properties relevant to lasing performance. The host phosphate glass modified by introducing a second glass former, GeO_2, was shown to have improved thermal stability, i.e., higher glass transition temperature (T_g) and lower coefficient of thermal expansion (CTE). Enlargement of Yb^{3+} $^2F_{7/2}$: Stark splitting, broadening of effective fluorescence linewidth ($\Delta\lambda_{eff}$) and longer fluorescent lifetime (τ_f) were also achieved at the same time, whereas emission cross section (σ_{emi}) of the modified glasses were kept nearly constant. Selective laser experiments were performed; while the baseline host phosphate glass failed in lasing, a GeO_2-modified phosphate glass was able to deliver 370 mW laser output at 1063 nm. Significant improvement of the lasing performance was further demonstrated using a newly designed GeO_2-modified Yb: phosphate glass based on our study, which demonstrated 724 mW laser output at 1063 nm. The overall results from our study showed that germanium-phosphate glass system can be developed as a promising material for high energy, large scale Yb^{3+} laser.

1. Introduction

Ytterbium (Yb^{3+}) possesses many advantages over neodymium (Nd^{3+}), such as low quantum defect, high doping ability and high energy storage ability. Among all of the lasing materials used in laser systems to date, only Yb^{3+}-doped fluorophosphate (FP) glass has achieved laser output reaching more than 10 TW [1,2]. Gain media of large-scale laser systems for high energy and ultra-short pulse applications should offer following key characteristics: large manufacturing scaling capability, high Yb^{3+} solubility, high energy storage, large emission cross section, proper Stark splitting, as well as good thermomechanical properties [3,4]. Up to this date, however, suitable Yb^{3+} materials have not been identified to meet all of the above requirements. Single crystals still cannot be utilized in high energy Yb^{3+} lasers due to their size limitations in fabrication. Except for laser ceramics [5–7], some selective glass systems may provide attractive options as lasing materials because of their large scale manufacturing capability, high optical quality, low loss, and high Yb^{3+} solubility, whereas other conventional glass systems still fail to meet the requirements of high energy Yb^{3+} laser system. For example, glasses with good thermomechanical and Stark splitting properties, such as silicate and germanate systems [8], show low Yb^{3+} solubility and short emission lifetime. Those with higher Yb^{3+} solubility, high emission cross section, and longer emission lifetime, such as phosphate glass, however, possess very low Stark splitting levels [9], which in turn induce serious thermal

blocking effect or a series of thermal problems. As a result, it is difficult to use Yb^{3+} doped phosphate glass to generate higher laser output at room temperature. Since the demonstration of 440 mW output with QX/Yb glass [10], to the best of our knowledge, there is no new Yb: phosphate glasses reported for room-temperature, linear cavity, single-slab lasers. But a 2.8 W cw output power was achieved in QX/Yb glass by double diodes pumping with a special water-cool device [11]. FP glass was shown to meet many of the aforementioned requirements, combined with a broad and flat gain profile, low nonlinear refractive index, and negative thermal refractive index change. But the drawback of FP glass comes from its relatively lower thermomechanical properties, comparing with silicate, germanate or phosphate glasses; in turn, it limits further use of FP glass as a gain medium for high energy, repetitive frequency laser systems. Yb^{3+}-doped aluminosilicate glasses offer broadband emission and good thermomechanical properties [12–14]. However, significantly higher melting temperature is required to produce high quality glass, plus a challenging issue of its complicated OH^- quenching processes. A long way to mass production of the Yb^{3+}:aluminosilicate glass is anticipated.

Reviewing all of the existing Yb^{3+}-doped laser glass media [15], including lasing properties of the Yb^{3+}-doped phosphate and FP glass [16], phosphate glass system is still considered as the most preferred medium for high energy Yb^{3+} laser if $^2F_{7/2}$: Stark splitting can be enlarged, which motivates our research, focusing on improving the Yb^{3+} Stark splitting properties of the phosphate based glass and maintaining
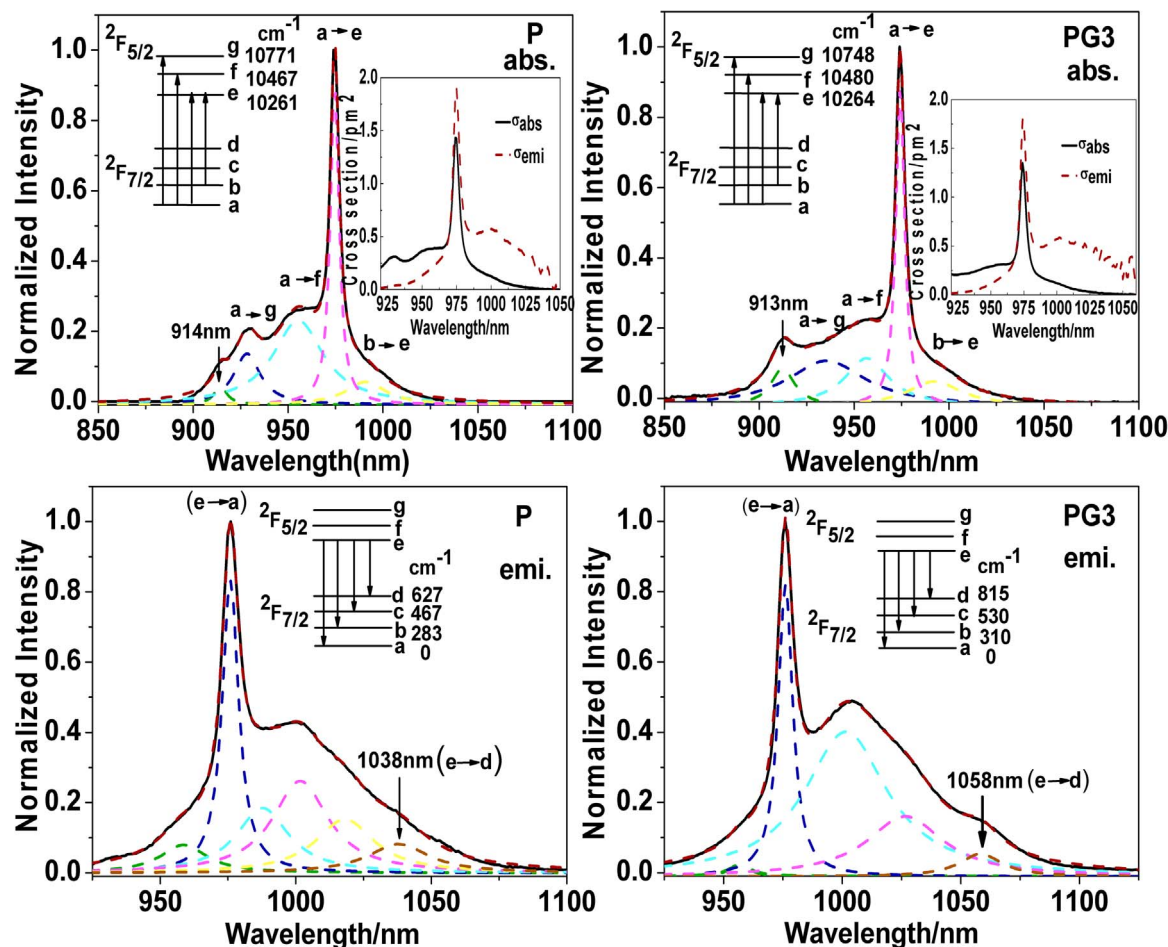
Fig. 1. Deconvoluted absorption and emission spectra of Yb^{3+} in P and PG3 glass (insets are the corresponding cross section spectra of P and PG3).

spectroscopic advantages of the original host matrix as close as possible. Our hypothesis was that a new glass former with a larger Yb^{3+} Stark splitting could be introduced into conventional phosphate glass to enhance the degree of Yb^{3+} asymmetry and its lasing performance. Based on previous research findings [15], we selected GeO$_2$ as a second glass former to validate our hypothesis.

2. Experimental

Glass compositions selected in this study were (60P$_2$O$_5$-7.5Al$_2$O$_3$-15K$_2$O-17.5BaO)-1Yb$_2$O$_3$-(0, 2, 10, 20 GeO$_2$) in mol%, and labeled as P and PG1, 2, 3, respectively, in sequence. Each batch, 300 g in size, was melted in a pure fused silica crucible with dehydration procedure by O$_2$ bubbling, and the melt was then transferred to a platinum crucible for fining and homogenization. The final melts were cast into preheated steel molds for subsequent annealing. Annealed samples were cut and polished to a dimension of 20 mm × 10 mm × 1 mm for spectroscopic property measurements.

Glass transition temperature (T$_g$) was measured using a Netzsch STA449/C differential scanning calorimeter (DSC). Coefficient of thermal expansion (CTE) was determined by using NETZSCH DIL 402 PC thermal dilatometer. Absorption spectra over the range of 850–1050 nm were collected on Lambda 900 UV/VIS/NIR spectrophotometer (PerkinElmer Inc., USA). Fluorescence spectra and lifetime were measured by using FLSP920 spectrofluorimeter (Edinburg Co., UK) with 896 nm flash light pumping. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Stark splitting manifolds

To investigate the effect of GeO$_2$ on Stark splitting and fluorescence properties, optical absorption and fluorescence spectra of the P and PG glasses were deconvoluted using Lorentzian functions according to the literature [16], from which the Stark levels were determined. As an example, Fig. 1 depicts optical absorption (top) and fluorescence (bottom) spectra along with individual bands derived from the curve deconvolution procedure for the P and PG3 glass. And also the insets showed the corresponding absorption and emission cross section spectra. The related Stark level assignments are also included, from which corresponding values of Stark splitting were calculated. For the optical absorption spectra, individual band positions were determined by using a second-order derivative. The most important band is located at 974 nm, which defines the lowest Yb^{3+} (^{2}F$_{5/2}$) Stark splitting manifold that sets the reference determining Yb^{3+} (^{2}F$_{7/2}$) manifolds. The absorption bands at 913 nm or 914 nm have been reported in the literature [17,18] and have shown no effect on the energy of the highest ^{2}F$_{7/2}$ manifold whether they come from vibronic or electronic contribution of the glass [19]. For the fluorescence spectra, although the second-order derivative can not indicate individual peak positions for every bands, the location of the maximum emission peak, which determines the energy of the d-manifold, should not change because it is a definite emission at the edge of the spectrum. Results provided a proof that the PG3 glass with mixed glass formers (P$_2$O$_5$, GeO$_2$) exhibited a wider emission band, making the e→d transition shift from 1038 nm for the P glass to 1058 nm for the PG3 glass.