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Influence of SiO_2 on the Stark splitting and spectroscopic properties of Yb^{3+} in phosphate glass

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ABSTRACT

This study focuses on the Stark splitting, spectroscopic properties and lasing performance parameters of Yb^{3+} in conventional phosphate glass modified by SiO_2. Introducing silica into phosphate glass is an effective method to increase the maximum Stark splitting energy of $^2F_{7/2}$ (E_d). The E_d in phosphate glass with 25 mol% silica was enhanced by 203 cm^{-1}. Interestingly, phosphate glass with 5 mol% silica offers small coefficients of thermal expansion, most obvious Stark splitting improvement, higher stimulated emission cross-section, longer lifetime and the largest SFL, which may ascribed to the formation of $Si^{(6)}$. From the point of the comprehensive performance of the material, it suggests that the introduction of small amount of SiO_2 is better for Yb^{3+} doped phosphate glass.

1. Introduction

Large-sized laser materials have been thoroughly investigated in recent years with the aim of developing petawatt-class laser by diode-pumped amplification [1,2]. Yb^{3+}-doped materials have attracted a lot of attention due to their simple energy levels [3,4], long excited state lifetimes (1–2 ms), high cross-sections [5] as well as broad and smooth emission bands [6]. Yb^{3+}-doped laser materials have been used in the POLARIS [7] and PeNELOPE [8] facilities as the crucial components of ultra-high peak power laser applications.

Glass are promising candidates as Yb^{3+}-doped host materials because of the ease with which large sizes, high quality materials can be produced at low cost. Compared with other types of glass, phosphate glass possess higher Yb^{3+} solubility, higher emission cross sections, lower thermal expansion coefficients, lower dispersions, and perfect glass forming ability [3,9–12]. Hence, Yb^{3+}-doped phosphate glass are used as a gain medium for high power Yb^{3+}-lasers.

However, the two-energy-level configuration of Yb^{3+} leads to two drawbacks: high threshold and serious thermal load, because both the terminal laser manifold and the ground manifold belong to the same energy level $^2F_{7/2}$ [10,13,14]. For the population evacuation of the terminal laser level, a ground-state splitting, which is as large as possible, is desirable. Unfortunately, the overall splitting of the $^2F_{7/2}$ manifold in conventional phosphate glass is relatively low [13,15,16]. Considering of the good spectroscopic properties of Yb^{3+}-phosphate glass, it is then necessary to develop new kinds of Yb^{3+}-phosphate glass to achieve larger Stark splitting and higher output power [10].

Silicate glass exhibit larger Stark splitting than phosphate glass and tend to operate close to the quasi-four-level scheme [13]. In addition, silicate glass perform much better mechanical, thermal and chemical stability than phosphate glass, which is very important for solid-state Yb^{3+} laser system. Therefore, a certain amount of silica was introduced into phosphate glass to evaluate the physical and Stark splitting properties of the conventional Yb^{3+}: phosphate glass in this paper.

2. Experimental

A series of $(70\text{-}x)P_2O_5-15(B_2O_3+Al_2O_3+Nb_2O_5)-15(BaO+K_2O)\text{-}xSiO_2-1.25Yb_2O_3$ glasses (named as PSx, x = 0, 5, 10, 15, 20 and 25) were synthesized by the traditional melt-quenching method with high-purity reagents as the raw materials. The mixture batches were melted at 1250–1350 °C for 1 h in quartz crucibles. The glass melts were bubbled with O_2 for OH^- removal, and then transferred to Pt crucibles. After stirring and refining process, the melt was cast into preheated steel molds and annealed at the corresponding transition temperature in muffle furnace. All of the samples were cooled down to room temperature, then cut and polished for tests.

Densities were measured by the Archimedes method. Refractive index were obtained by the prism-minimum-deviation method. Transition temperature (Tg) were achieved using a

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NetzschSTA449/C differential scanning calorimeter (DSC) at a heating rate of 10°C/min. The coefficients of thermal expansion (CTE) were measured using a thermal dilatometer, Netzsch DIL402EP with a precision of 8 nm. The absorption spectra were recorded on a Perkin-Elmer 900UV/VIS/NIR spectrophotometer. A FLSP920 spectrofluorometer (Edinburg Co., UK) was used to measure the infrared luminescence spectra, with 896 nm pumping, as well as to measure the fluorescence lifetimes, with 980 nm diode pumping. The Raman scattering spectra for the glass were recorded with a Fourier transform Raman spectrophotometer (Nicolet Module) Nd: Yttrium Aluminume Garnet operating at 785 nm in the wavenumber range of 100–1400 cm^{-1}. All tests were carried out at room temperature.

3. Results and discussion

Table 1 shows some physical properties of all the specimens, including density, refractive index (n_d), T_g and CTE. The most interesting and abnormal variation is in PS5. 5 mol% SiO_2 resulted in an increase in density and n_d, which is contradictory with the fact that SiO_2 glass performs lower density than phosphate glass. Furthermore, density and n_d returned to be normal from sample PS10.

Zeng, et al. [17] used high-temperature Raman and Nuclear Magnetic Resonance (NMR) to reveal the mechanism of transformation between the $Si^{(4)}$ and $Si^{(6)}$ silicon oxide structures in phosphate glass. They found that density and n_d increased first and then decreased because when a small amount of silicon was introduced into phosphate glass, all silicon atoms exist as $Si^{(6)}$ and with the increasing of silicon in the phosphate glass, $Si^{(4)}$ started to appear and always increased in the entire process of SiO_2 increasing. The same structure change may also appear in the PS series glasses. In PS5, it is possible that when a small amount of P_2O_5 is replaced by SiO_2, the formation of $Si^{(6)}$ results in a more compact structure, which leads to the incremental in density and n_d. When the content of SiO_2 is increased further, the excess silicon exists in the form of $Si^{(4)}$. As a result, the density and n_d decrease with further increase of SiO_2. It is difficult to analysis the PS series glasses by NMR because of complicated compositions, then Raman spectra were used to identify the structure variations after the introduction of SiO_2. Deconvolution Raman spectra of PS0, PS5 and PS25 are given in Fig. 1. A significant band intensity and position changes were noticed near 850 cm^{-1} when P_2O_5 was replaced by SiO_2. As Ref [18] shows, the 850 cm^{-1} band corresponds to Nb–O in [NbO_4] tetrahedral structure. Compared with the Raman spectra in PS0, the band positions shifted from 851 cm^{-1} to 866 cm^{-1} and the intensity of the bands increased, which may be caused by the introduction of SiO_2 since the content of Nb_2O_5 remained constant. However, it is difficult to identify if $Si^{(6)}$ vibration was packaged in this band because there is no studies about $Si^{(6)}$ in Raman spectra. When the concentration of SiO_2 increased to 25 mol%, an obvious enhanced intensity was observed for this band, meanwhile, band positions shift to 882 cm^{-1}. The band at 882 cm^{-1} is attributed to the stretching vibrations of

Table 1
Physical properties of PSx (x=0, 5, 10, 15, 20 and 25) glasses.

Glass	Density(g/cm^3)	n_d	α(× 10^{-6}/K)	T_g(°C)
PS0	2.8539	1.5432	9.03	541
PS5	2.8552	1.5435	8.54	569
PS10	2.8505	1.5429	8.17	576
PS15	2.8443	1.5414	8.06	585
PS20	2.8403	1.5401	7.75	587
PS25	2.8356	1.5386	7.43	589

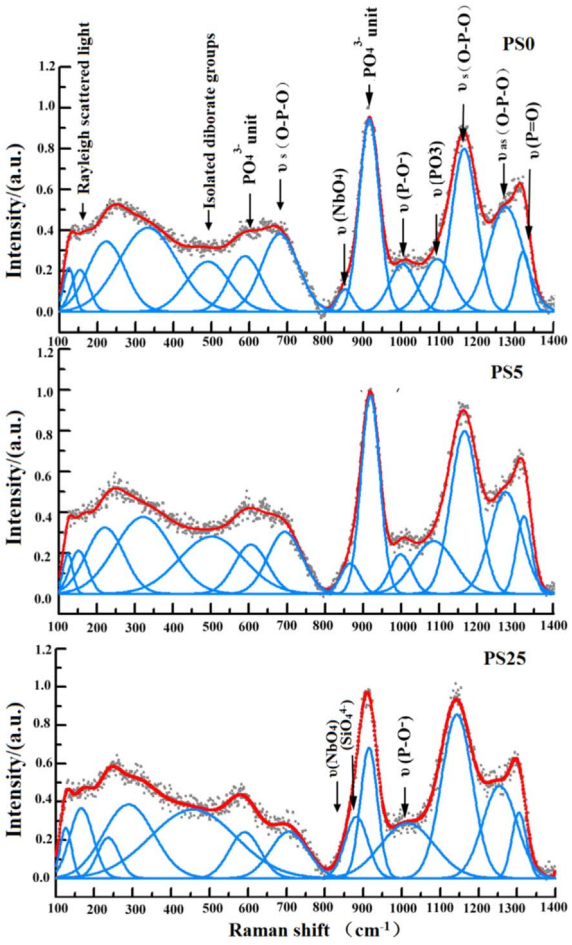

Fig. 1. Deconvolution of the Raman spectra for PS0, PS5 and PS25.

monomer SiO_4^{4-} unit [19]. Undoubtedly, there is an overlap between [NbO_4] and SiO_4^{4-}. Large amount of $Si^{(4)}$ existed PS25 reduced the decrease in density and n_d. Moreover, CTE decreases with the increase of SiO_2, even as low as 7.43×10^{-6} K^{-1} in PS25, which is beneficial for the high-power Yb^{3+} laser systems because gain medium with high thermo-mechanical-shock resistance is needed.

Fig. 2 shows the Stark splitting configurations of PS0 and PS25 that derived from the Lorentz fitting of the absorption and emission spectra respectively. The original spectra are marked with red, while the black curves represent the cumulative Lorentz fits. In general, there are three absorption and four emission peaks in the Yb^{3+} spectra [3]. However, five absorption and six emission peaks were observed in the spectra of PS0, while five absorption and five emission peaks were observed in the spectra of PS25. It is obvious that vibronic peaks exist in the spectra [20]. As Ref. [3] shows, the 974 nm peak corresponds to the transition between the lowest manifolds of $^2F_{7/2}$ and $^2F_{5/2}$. Therefore, whether the other peaks in the absorption spectra are vibronic or electronic has no effect on the energy determination of the highest manifold of $^2F_{7/2}$. For the fluorescence spectra, undoubtedly, the peak around 1000 nm is taken as the second emission peak in Yb^{3+}-phosphate glass [9,10,21]. Here we also believe that the 1002 nm peak in PS0 and the 1004 nm peak in PS25 is electronic and the peak around 985 nm is vibronic [20]. It is important to understand the nature of the longest emission peak, which determines the maximum Stark splitting energy of $^2F_{7/2}$. Zhang, et al. and Yang, et al. [10,13] have demonstrated that the 1053 nm peak is vibronic in phosphate glass, then the 1035 nm peak was used to determine the Stark