J Mater Sci (2006) 41:6174–6177
DOI 10.1007/s10853-006-0159-8

LETTER

Radiative trapping effect of Yb^{3+} ions in lead-germanate glasses

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Received: 11 June 2004 / Accepted: 21 October 2005 / Published online: 11 July 2006

Yb^{3+} is a good candidate as a pump source because there are only two manifolds in the Yb^{3+} energy level scheme, the $^2F_{7/2}$ ground state and the $^2F_{5/2}$ excited state, and thus concentration quenching and excited-state absorption should not affect the lasing or the excitation wavelength [1]. Extensive investigations have been of Yb^{3+}-doped glasses, fibers, and crystals [2–5]. The relatively long fluorescence lifetime, as well as the broad absorption and emission bands, is more prominent for Yb-doped glasses than for crystals, making the glasses attractive for diode-pumped generation of ultra-short pulses, high-power ultra-short pulse amplification and tunable laser sources [6]. In addition, the ability to achieve high concentrations of Yb^{3+} ions and low loss also triggered the rapid development of various Yb^{3+}-doped glasses such as phosphate, borate, and silicate glasses. However, up to now, there are few systematic investigations of the optical properties of Yb^{3+}-doped germanate glasses. In this work, the spectroscopic properties of germanate glasses with different concentrations of Yb^{3+} ions and different thicknesses were investigated.

Glasses with compositions (mol%) $10Na_2O–60GeO_2–30PbO–xYb_2O_3$ (x = 0.2, 0.6, 1.0, 1.4, and 2.0) were prepared using regent-grade powders Na_2CO_3, Pb_3O_4, and high purity GeO_2 (>99.999%). Yb^{3+} was introduced as Yb_2O_3 with 99.9% purity. Batches of 20 g were well mixed in appropriate proportions and melted at 1050 °C in a covered alumina crucible in a SiC-resistance electric furnace. The liquids were held for 15 min and the homogenous bubble-free melts were cast on a stainless plate preheated at about 150 °C. The samples were well annealed in a muffle furnace to reduce thermal stress.

The annealed samples were cut using a low-speed diamond saw and polished with 5 μm diamond paste. Plates of dimensions 20 mm × 10 mm × 2 mm with two polished faces were used for optical measurements.

The refractive index of the studied glass was measured using the Brewster angle method. The density of the sample was measured using the Archimedes' liquid-immersion method on an analytical balance with a precision of 0.0001 g.

Absorption spectra of the glass sample were recorded with a Perkin-Elmer-Lambda 900UV/VIS/NIR spectrophotometer in the range 850–1100 nm. Fluorescence measurements were performed with a 940 nm diode laser excitation and detected by a TRIAX550 spectrophotometer controlled by a computer. The infrared fluorescence lifetime was determined by modulating the pump laser diode drive current with a square-pulse duration of 40 ms at a repetition of 10 Hz.

All the measurements were performed at room temperature.

The important spectroscopic parameters required include the effective emission and absorption cross sections of the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition and the upper laser level lifetimes of Yb^{3+}. The emission cross section can be determined by either the method of reciprocity or the Fuchtbauer–Ladenburg formula. On the basis of the reciprocity method described by McCumber [7], the emission cross section, σ_{emi} can be calculated from the measured absorption cross section, σ_{abs}, i.e.

$$\sigma_{\mathrm{emi}} = \sigma_{\mathrm{abs}}(\lambda)\frac{Z_l}{Z_u}\exp\left(\frac{E_{Zl} - hc\lambda^{-1}}{kT}\right) \qquad (1)$$

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$$\sigma_{\mathrm{abs}}(\lambda) = \frac{2.303\log(I_0/I)}{Nl} \tag{2}$$

where $\log(I_0/I)$ is absorbance, l is the thickness, and N is the concentration of Yb^{3+} ions, Z_l and Z_u are the partition functions for lower and upper levels, E_{Zl} represents the zero line energy which is defined to be the energy separation between the lowest components of the upper and lower states and k, T, h, and c represent Boltzman's constant, temperature (K), Planck constant, and velocity of light, respectively.

The Fuchtbauer–Ladenburg (F–L) formula is [8]

$$\sigma_{\mathrm{emi}} = \frac{\lambda^4 A_{\mathrm{rad}}}{8\pi c n^2 \Delta\lambda_{\mathrm{eff}}} \tag{3}$$

$$\Delta\lambda_{\mathrm{eff}} = \frac{\int I(\lambda)d\lambda}{I_{\mathrm{P}}} \tag{4}$$

$$A_{\mathrm{rad}} = \frac{1}{\tau_{\mathrm{rad}}} = \frac{8\pi c n^2(2J'+1)\int \alpha(\lambda)d\lambda}{\lambda_{\mathrm{P}}^4 N(2J+1)} \tag{5}$$

where A_{rad} is the spontaneous emission probability, n is the refractive index, $I(\lambda)$ is the intensity at the wavelength λ, I_{P} is the intensity at the peak wavelength λ_{P} and τ_{rad} is the radiative lifetime.

Figure 1 shows the absorption spectra of Yb^{3+}-doped lead germanate glasses. Three peaks at 906, 952, 975 nm are observed in the absorption spectra, which originate from the stark splitting of J manifolds of Yb^{3+} ions. However, due to the low symmetry at Yb^{3+} sites in glasses, only the transition between the lowest Stark levels of the $^2F_{7/2}$ and $^2F_{5/2}$ manifold at about 974~978 nm (1–1 transition) is clearly resolved in the glasses [2]. Inhomogeneous broadening and vibrational transitions combine to reduce the resolvability of the other transitions.

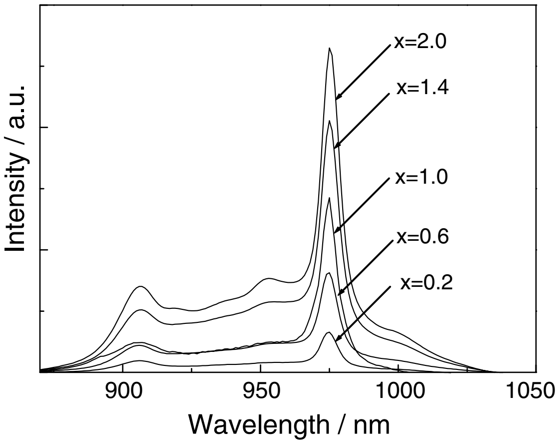

Fig. 1 Absorption spectra of $10Na_2O$–$60GeO_2$–$30PbO$–xYb_2O_3 glasses with a thickness of 2 mm

Table 1 shows the Yb^{3+} concentration, peak absorption and emission cross sections (σ_{pa} and σ_{pe}) calculated by the reciprocity method and F–L approach. As evident in Table 1, σ_{pa} is almost unchanged with increasing Yb^{3+} concentration and correspondingly the σ_{pe} calculated from the reciprocity method is constant within the error of determination. However, the σ_{pe} calculated by the F–L approach decreases with the Yb^{3+} content. Moreover, the σ_{pe} is affected by the thickness of the samples, that is, it slightly decreases with increase in thickness. In addition, it is noted that the values of the σ_{pe} calculated by F–L approach are smaller than those calculated from the reciprocity method. This is because the σ_{pe} calculated by the McCumber method is only dependent on the absorption coefficient of Yb^{3+}, whereas that calculated by the F–L approach is affected by the radiative decay rate and the effective linewidth. With the increase of sample thickness, the radiative decay rate is nearly unchanged, while the effective linewidth increases as shown in Table 2. Therefore, for Yb^{3+}-doped germanate glass we suggest that the peak emission cross section is calculated using the McCumber approach to avoid the effect of sample thickness.

Table 1 Peak absorption and emission cross sections at 975 nm in the $10Na_2O$–$60GeO_2$–$30PbO$–xYb_2O_3 glasses

x	N ($\times10^{-20}$ ions/cm^3)	σ_{pa} ($\times10^{-20}$ cm^2)	σ_{pe} ($\times10^{-20}$cm^2)		
			Reciprocity	F–L	
0.2	0.98	0.76 ± 0.05	0.91 ± 0.05	0.66 ± 0.03[a]	0.59 ± 0.03[b]
0.6	2.92	0.64 ± 0.04	0.86 ± 0.04	0.48 ± 0.02[a]	0.43 ± 0.02[b]
1.0	4.82	0.65 ± 0.04	0.88 ± 0.04	0.44 ± 0.02[a]	0.39 ± 0.02[b]
1.4	6.81	0.71 ± 0.05	0.96 ± 0.06	0.36 ± 0.02[a]	0.33 ± 0.02[b]
2.0	9.37	0.65 ± 0.04	0.89 ± 0.05	0.26 ± 0.01[a]	0.24 ± 0.01[b]

[a] 1-mm thick samples

[b] 2-mm thick samples

Table 2 Spontaneous emission probability (A_{rad}), calculated lifetime (τ_{rad}), measured lifetime (τ_{f}) and effective linewidth ($\Delta\lambda_{\mathrm{eff}}$) for $10Na_2O$–$60GeO_2$–$30PbO$–xYb_2O_3 glasses

x	Thickness (mm)	A_{rad} (s^{-1})	$\Delta\lambda_{\mathrm{eff}}$ (nm) (±0.2)	τ_{rad} (ms)	τ_{f} (ms) (±0.02)
0.2	1.0	844	49.3	1.18	1.00
	2.0	843	58.4	1.18	1.04
0.6	1.0	801	59.1	1.25	0.94
	2.0	801	65.6	1.25	0.92
1.0	1.0	785	62.7	1.27	0.88
	2.0	785	71.3	1.27	0.90
1.4	1.0	703	68.7	1.42	0.78
	2.0	701	76.3	1.43	0.82
2.0	1.0	517	70.6	1.93	0.68
	2.0	515	77.0	1.94	0.66

Figures 2 and 3 show the fluorescence spectra of the Yb^{3+}-doped glasses of 1- and 2-mm thickness, respectively. It is clear that the fluorescence spectra consist of two peaks, a main peak located at 976 nm and a sub-peak at 1006 nm. With the increase of Yb^{3+} content, the fluorescence intensity increases. Moreover, the shape of the fluorescence band also changes. The intensity of the main peak increases slowly whereas the sub-peak intensity increases rapidly. The intensity ratios between the sub-peak and the main peak are shown in Fig. 4. It is evident that for the same thickness samples the ratios increase rapidly and then decrease slightly with increasing Yb^{3+} content. By comparing the fluorescence spectra in Figs. 2 and 3, it is surprising to note that with increasing thickness of sample, for the samples with the same Yb^{3+} concentration, the shape of fluorescence band broadens and the intensity ratio between the sub-peak and main peak increases. These results demonstrate the existence of radiative trapping in lead germanate glasses. The radiative trapping is due to the large overlap between the absorption and emission spectra of Yb^{3+} ions in germanate glass. Yb^{3+} ion can reabsorb the spontaneous emission from itself and deform the fluorescence spectrum. The fluorescence emission in the wavelength range $<\lambda_P$ (975 nm) is strongly reabsorbed because the absorption cross section at this wavelength range is larger than at wavelength $>\lambda_P$. This results in the decrease of emission intensity of the main peak in the fluorescence spectrum with increase in thickness of sample. But the extent of decrease of the main peak intensity is highly dependent on the Yb^{3+} concentration because the radiative trapping is proportional to the Yb^{3+} concentration [8]. At lower concentrations of Yb^{3+} ions the difference in the intensity ratio of the sub-peak to the main peak between the 1- and 2-mm thick samples is small, as shown in Fig. 4. With increases in Yb^{3+} concentration the difference becomes larger. It is found that higher Yb^{3+} contents, stronger the reabsorption, even in the 1-mm thick samples.

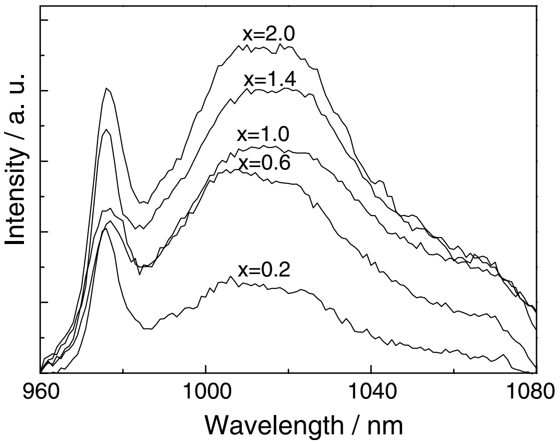

Fig. 2 Fluorescence spectra of $10Na_2O–60GeO_2–30PbO–xYb_2O_3$ samples with a thickness of 2 mm

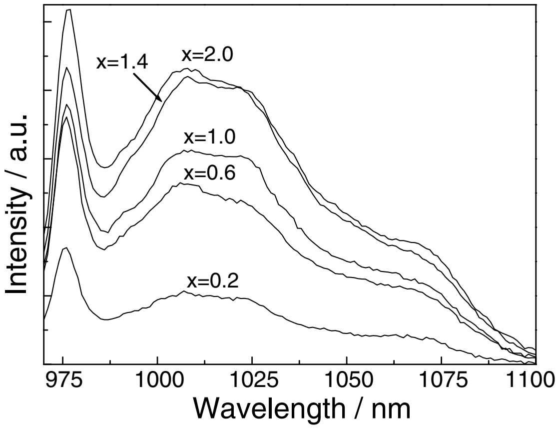

Fig. 3 Fluorescence spectra of $10Na_2O–60GeO_2–30PbO–xYb_2O_3$ samples with a thickness of 1 mm

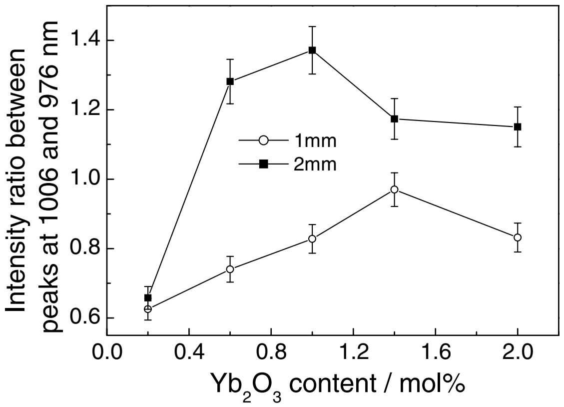

Fig. 4 Intensity ratio between peaks at 1006 and 976 nm

Table 2 shows the radiative decay rate (A_{rad}), effective linewidth ($\Delta\lambda_{eff}$), radiative lifetime (τ_{rad}) and fluorescence lifetime (τ_f). As evident form Eq. (5), the spontaneous emission probability is dominated only by the absorption coefficient of the germanate glasses because the peak wavelength and refractive index are nearly unchanged with Yb^{3+} content. Therefore, the radiative decay rate is unrelated to the thickness. With the increase of Yb^{3+} content the decrease of spontaneous emission probability is due to the increase of non-radiative transition rate [9, 10]. The effective linewidth increases with both the Yb^{3+} content and the thickness of samples due to the radiative trapping.

In conclusion, in the Yb^{3+}-doped germanate glasses, the radiative trapping, which is due to the large overlap between the absorption and emission band, leads to a broadening in fluorescence band, an increase in effective linewidth, and a decrease in the peak emission cross section calculated by F–L approach with increasing thickness of samples.

Acknowledgements The authors would like to give thanks to Dr. S. Dai for his helpful discussions. This work is supported by the

National Natural Foundation of China (Project No. 60307004 and 50472053), DSTG (Guangzhou 2004Z2-0131), Program for New Century Excellent Talents in University (Grant No. NCET-04-0821) and the open foundation of the Key Laboratory of Silicate Materials Science and Engineering (Wuhan University of Technology) of Ministry of Education (Grant No. SYSJJ2004-04).

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