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Yb: Borate Glass with High Emission Cross Section

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The emission cross section for the $^2F_{5/2}$–$^2F_{7/2}$ transition of Yb^{3+} has been determined from absorption and emission measurements of some borate glasses at room temperature. By systematic variations in the spectroscopic properties with composition, a glass composition with emission cross sections of more than 1.70 pm^2 and fluorescence lifetimes longer than 1.0 ms is obtained; this composition has advantages over some excellent laser glasses reported in published papers. © 1999 Academic Press

***Key Words*: Yb^{3+}; borate glass; emission cross section.**

1. INTRODUCTION

Crystals and glasses doped with trivalent ytterbium ions exhibit highly efficient emission using InGaAs laser diodes as pump sources. Since there are only two manifolds in the Yb^{3+} energy level scheme, the $^2F_{7/2}$ ground state and $^2F_{5/2}$ excitation state, it is commonly believed that concentration quenching and multiphonon relaxation should not affect the excitation wavelength. The Yb^{3+} ion is of interest in lasers for next-generation nuclear fusion and a sensitizer of energy transfer for infrared to visible upconversion and infrared laser.

Laser glasses are usually evaluated by emission cross section and fluorescence lifetime. These properties are calculated using intensity parameters Ωt ($t = 2, 4, 6$) based on the Judd–Ofelt theory (1, 2). The Judd–Ofelt (JO) parameters contain odd crystal field terms, radial integrals, and perturbation energy denominators and are related to local structure and chemical bonding surrounding rare-earth ions in glasses. The optical and spectroscopic properties of rare-earth ion-doped glasses have been discussed in the terms of the variation of Ωt parameters with composition (3–5). Since there is only the $^2F_{7/2}$–$^2F_{5/2}$ transition for Yb^{3+}, it is impossible to calculate directly three Ωt parameters for Yb^{3+}, for this reason the compositional dependence of optical and spectroscopic properties of Yb^{3+}-doped glasses are not well established. Up to now, there are only a few papers involving in the effect of composition on the emission cross section of Yb^{3+} in simple systems such as borate, phosphate, and silicate glasses (6–9). The results show that the integrated absorption cross section is mainly determined by site asymmetry of the Yb^{3+} ion and covalency of the Yb–O bond or polarizability of O^{2-} ion, meanwhile, addition of La_2O_3 to borate or addition of Nb_2O_5 to phosphate glass can enhance the asymmetry and polarizability, thus the emission cross section increases. In these glasses, the largest emission cross section is less than 1.35 pm^2.

In this paper, spectroscopic properties of Yb^{3+}-doped borate glasses containing ZnO, La_2O_3, and Nb_2O_5 are measured and calculated and compared to tailor emission cross sections and fluorescence lifetimes.

2. EXPERIMENT

2.1. Sample Preparation

B_2O_3 is introduced in the form of reagents H_3BO_3, other materials are 99.99% purity oxides or carbonates. The glass melts were poured onto a stainless-steel plate. Each glass was annealed for 2 h near the transition temperature.

2.2. Measurement of Refractive Index and Spectroscopic Properties

Glass samples with two polished faces were used for refractive index, absorption, emission, and fluorescence lifetime measurements. The absorption spectra were measured by a Hitachi 330 spectrophotometer in the 800–1100 nm range at room temperature. The emission spectra were obtained by exciting the samples with LD970 nm as a pumping laser (excited at 970 nm). The light from the source was chopped at 80 Hz and focused to the front surface of sample. A position 1 mm from the edge was excited to minimize the reabsorption of emission. The emission from the sample was focused to a monochromator and detected by Ge detector in the 800–1100 nm range. The fluorescence lifetimes were measured by exciting the samples with the same LD970 nm as above and were detected by a photomultiplier tube and Ge detector. The fluorescence decay curves were recorded and averaged with a computer-controlled transient digitizer.

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2.3. Sample Evaluation

2.3.1. Spectroscopic properties. The integrated absorption cross section ($\int k d\lambda$ or $\sum_{\text{abs}}$), the spontaneous emission probability (A_R), the emission cross section (σ_{em}) and effective fluorescence linewidth ($\Delta\lambda_{\text{eff}}$) of Yb^{3+} were calculated by (10, 11)

$$A_R = \frac{8\pi c n^2 (2J' + 1)}{\lambda_p^4 (2J + 1)} \int k d\lambda \qquad [1]$$

$$\sigma_{\text{em}} = \frac{\lambda^4 A_R}{8\pi c n^2 \Delta\lambda_{\text{eff}}} \qquad [2]$$

$$\Delta\lambda_{\text{eff}} = \frac{\int I(\lambda) d\lambda}{I_{\max}}, \qquad [3]$$

where J', J are the total momentums for the upper and lower levels, $k(\lambda)$ is the absorption coefficient, and λ_p is the absorption peak wavelength.

From Eqs. [1] and [2], glass with a large integrated absorption area should be pursued in order to get a high emission cross section. Based on this idea, we investigated experimentally the relationship between the integrated absorption cross section and the glass composition and searched for glass composition with a high emission cross section and long fluorescence lifetime.

2.3.2. Laser performance parameters. For the two-level laser with broad emission and absorption spectra, σ_{em} is given by the reciprocity equation (6)

$$\sigma_{\text{em}}(\lambda) = \sigma_{\text{abs}}(\lambda) \frac{Z_l}{Z_u} \exp\left[\frac{(E_{zl} - hc\lambda^{-1})}{kT}\right], \qquad [4]$$

where Z_l, Z_u, k, and E_{zl} represent the partition functions for lower and upper levels, Boltzman's constant, and zero-line energy which is defined to be the energy separation between the lowest components of the upper and lower states, respectively. In the high temperature limit, the ratio of Z_l/Z_u simply becomes the degeneracy weighting of the two state.

Yb^{3+} ions are basically two-level laser, emission and absorption coexist at a given wavelength. Therefore, the figure of merits of Yb^{3+} laser material is given by $I_{\min}$, which is a measure of the ease of pumping the laser material, and σ_{em}, which is a measure for extracting the stored energy. $I_{\min}$ is given by (6)

$$I_{\min} = \beta_{\min} \cdot I_{\text{sat}} \qquad [5]$$

$$\beta = \frac{\sigma_{\text{abs}}(\lambda_0)}{\sigma_{\text{em}}(\lambda_0) + \sigma_{\text{abs}}(\lambda_0)} = \left\{1 + \frac{Z_l}{Z_u} \exp\left[\frac{E_{zl} - hc\lambda_0^{-1}}{kT}\right]\right\}^{-1} \qquad [6]$$

$$I_{\text{sat}} = \frac{hc}{[\lambda_p \sigma_{\text{abs}}(\lambda_p)\tau_f]} \qquad [7]$$

$$I_{\min} = \frac{hc}{[\lambda_p \sigma_{\text{abs}}(\lambda_p)\tau_f]} \left\{1 + \frac{Z_l}{Z_u} \exp\left[\frac{(E_{zl} - hc\lambda_0^{-1})}{kt}\right]\right\}^{-1}, \qquad [8]$$

where $\beta_{\min}$ is defined as the minimum fraction of Yb^{3+} ions that must be excited to balance the gain exactly with the ground-state absorption at laser wavelength. I_{sat} is the pumping saturation intensity. The ease with which the ground-state depletion may be accomplished depends on the absorption cross section σ_{abs} and fluorescence lifetime τ_m.

Incidently, $\Delta E = E_{zl} - hc\lambda^{-1}$ does not change very much in glass, nor does $\beta_{\min}$. Since Eq. [4] expresses the relationship between σ_{em} and σ_{abs}, I_{sat} becomes lower when σ_{em} is higher and τ_{em} is longer. As a result, $I_{\min}$ is mainly determined by σ_{em} and τ_m, the figure of merits of Yb^{3+} laser material is given by the $I_{\min}$ and σ_{em}, and it turns out to be given by emission cross section σ_{em} and flourescence lifetime τ_m, higher σ_{em} and longer lifetime τ_m give better Yb^{3+} laser material.

3. RESULTS

3.1. Effect of Nb_2O_5 on the Spectroscopic Properties of Yb^{3+} in Glasses

The change of refractive index (n_d) and spectroscopic properties with Nb_2O_5 content in a series of $(45 - x)$ B_2O_3–xNb_2O_5–$10La_2O_3$–$38BaO$–$5ZnO$–$2Yb_2O_3$ glasses are shown in Table 1.

As shown in Table 1, there is a systematic red shift of the wavelength of the emission peak wavelength. The peak absorption cross section (σ_p), integrated absorption cross section (Σ_{abs}), spontaneous emission probability (A_R), and fluorescence effective linewidth ($\Delta\lambda_{\text{eff}}$) increase with Nb_2O_5 content, but fluorescence lifetime (τ_m) change slightly.

TABLE 1
Variation of Refractive Index and Spectroscopic Properties of Yb^{3+}-Doped Borate Glasses at Room Temperature with Nb_2O_5 Content

X	n_d	λ_{zl} (nm)	σ_p (pm^2)	Σ_{abs} (10^4 pm^3)	A_R (s^{-1})	$\Delta\lambda_{\text{eff}}$ (nm)	λ_{em} (nm)	σ_{em} (pm^2)	τ_m (ms)
1	1.8461	974.4	1.32	5.02	1906	51	1016	1.31	0.60
5	1.8675	974.2	1.34	5.05	1962	51	1020	1.32	0.50
10	1.9550	974.4	1.40	5.54	2360	52	1024	1.40	0.60
15	2.0155	974.4	1.50	5.98	2708	54	1026	1.48	0.68
20	2.0881	974.5	1.55	6.20	3066	55	1030	1.50	0.62

Note. Glass composition (mol%): $(45 - x)B_2O_3$–xNb_2O_5–$10La_2O_3$–$38BaO$–$5ZnO$–$2Yb_2O_3$.

TABLE 2
Variation of Refractive Index and Spectroscopic Properties of Yb^{3+}-Doped Borate Glasses at Room Temperature with B_2O_3 Content

X	n_d	λ_p (nm)	σ_p (pm^2)	Σ_{abs} (10^4 pm^3)	A_R (s^{-1})	$\Delta\lambda_{eff}$ (nm)	λ_{em} (nm)	σ_{em} (pm^2)	τ_m (ms)
30	1.7185	974.2	1.41	4.20	1383	50	1016	1.12	0.90
35	1.7248	974.2	1.47	5.43	1476	50	1016	1.45	1.00
40	1.7310	974.2	1.49	6.43	1814	50	1016	1.71	1.10
45	1.7373	974.2	1.37	4.84	1629	51	1016	1.27	0.92
50	1.7435	974.2	1.31	4.30	1458	51	1016	1.12	0.90

Note. Glass composition (mol%): $(90-x)B_2O_3$–$10La_2O_3$–$xZnO$ (Yb_2O_3 3 wt%).

3.2. *Effect of B_2O_3 Content on the Spectroscopic Properties of Yb^{3+} in Borate Glasses*

The effects of B_2O_3 content in a series of $(90-x)$ B_2O_3–$10La_2O_3$–xZnO(Yb_2O_3 3 wt%) on spectroscopic properties are summarized in Table 2. The largest A_R and σ_{em} occur at $x = 40$, showing boro-abnormal phenomenon in borate glasses.

3.3. *Effect of Modifier Ions on the Spectroscopic Properties of Yb^{3+} in $50B_2O_3$–$10La_2O_3$–20ZnO–20RO*

The effects of modifier ions on spectroscopic properties in a series of $50B_2O_3$–$10La_2O_3$–20ZnO–20RO(R_2O) are listed in Table 3.

Obviously, as R_2O (or RO) change from K_2O to Na_2O (or BaO to ZnO), the emission cross section changes from 0.9 to 1.34 (or 1.19 to 1.71 pm^2).

3.4. *Concentration Effect of Yb^{3+} Ion in $50B_2O_3$–$10La_2O_3$–40ZnO Borate Glass*

Relative fluorescence intensity (I) and fluorescence lifetime (τ_m) of $50B_2O_3$–$10La_2O_3$–40ZnO glass with different concentrations of Yb^{3+} ion are shown in Table 4. It is clear that the quenching effect of Yb^{3+} ion in this glass exists when the concentration varies from 0 to 14×10^{20} ion/cm^3, the largest fluorescence intensity occurs about 7.5×10^{20} ion/cm^3 and the lifetimes shorten gradually. The quenching mechanism of Yb^{3+} ion in this glass will be discussed in another paper.

TABLE 3
Variation of Spectroscopic Properties of Yb^{3+} with Modifier Ions at Room Temperature

RO	n_d	λ_p (nm)	σ_p (pm^2)	Σ_{abs} (10^4 pm^3)	A_R (s^{-1})	$\Delta\lambda_{eff}$ (nm)	λ_{em} (nm)	σ_{em} (pm^2)	τ_m (ms)
BaO	1.762	974.6	1.34	4.47	1571	50	1016.0	1.19	0.76
SrO	1.744	974.6	1.23	3.81	1291	50	1016.0	1.02	1.05
CaO	1.734	974.4	1.50	4.58	1534	50	1016.0	1.22	1.10
MgO	1.713	974.6	1.50	4.40	1438	51	1016.0	1.15	1.05
ZnO	1.731	974.2	1.49	6.43	1814	50	1016.0	1.71	1.10
K_2O	1.703	974.6	1.19	3.49	1127	50	1016.5	0.90	1.10
Na_2O	1.706	974.4	1.46	5.01	1624	50	1016.5	1.34	1.00

Note. Glass composition $50B_2O_3$–$10La_2O_3$–20ZnO–20RO (Yb_2O_3 3 wt%).

TABLE 4
Concentration Effect of Yb^{3+} Ion in $50B_2O_3$–$10La_2O_3$–40ZnO

Concentration (10^{20} ion/cm^3)	λ_{em} (nm)	σ_{em} (pm^2)	I (arb. units)	τ_m (ms)
1.5	1016.0	1.73	60	1.15
4.5	1016.0	1.71	70	1.10
7.5	1016.5	1.70	100	0.76
10.5	1018.0	1.63	80	0.39
13.5	1020.0	1.60	60	0.25

According to the above results, we believe $50B_2O_3$–$10La_2O_3$–40ZnO is a better composition with higher emission cross section (more than 1.70 pm^2) and longer fluorescene lifetime ($0.76 \sim 1.10$ ms). Figure 1 shows the absorption and emission spectra of this composition.

4. DISCUSSION

4.1. *Relationship between Emission Cross Section and Integrated Absorption Cross Section*

Figure 2 shows the relationship between emission cross section (σ_{em}) and integrated absorption cross section (Σ_{abs}).

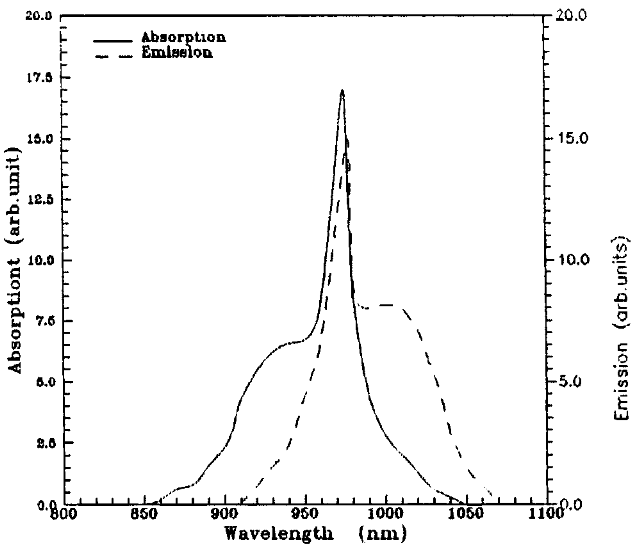

FIG. 1. Absorption and emission spectra of $50B_2O_3$–$10La_2O_3$–38ZnO–$2Yb_2O_3$.

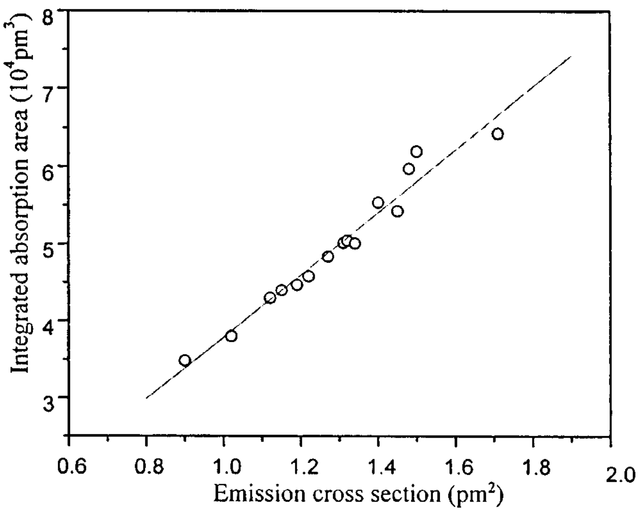

FIG. 2. Relationship between emission cross section (σ_{em}) and integrated absorption cross section (Σ_{abs}).

There is almost a linear relationship between σ_{em} and Σ_{abs}. This means that the emission cross section is nearly determined by the integrated absorption cross section as we expected.

4.2. *Effect of Nb_2O_5 on Integrated Absorption Cross Section of Yb^{3+}*

The integrated absorption cross section (Σ_{abs}) increases as the Nb_2O_5 content changes from 1 to 20 mol%. This is explained in Fig. 3; Nb^{5+} ions exist in the form of a $[NbO_6]$ octahedron, enhancing both site asymmetry and polarizability of Yb^{3+} ions, which leads to an increasing of Σ_{abs} and a red-shift of emission peak wavelength.

4.3. *Effect of B_2O_3 Content on Integrated Absorption Cross Section of Yb^{3+}*

The Σ_{abs} depends on the coordination of the Yb^{3+} ion. In $(90-x)B_2O_3$–$10La_2O_3$–xZnO glasses, as $x < 40$, B_2O_3/Σ (ZnO, La_2O_3) is more than 1:1, all O^{2-} in La_2O_3 may be provided for B_2O_3 to form partial BO_4 tetrahedron and ZnO, which cannot obtain enough nonbridge O^{2-} to form four coordination, exists in the form of octahedron or 6 coordination (Fig. 4a). As $x = 40$, $BO_3 + BO_4$ group content decrease, ZnO can obtain a fraction of nonbridge O^{2-} from

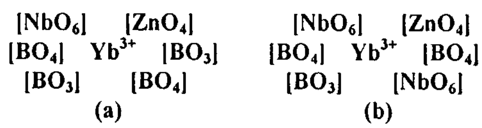

FIG. 3. Coordination of Yb^{3+} ion in glasses with different Nb_2O_5 content.

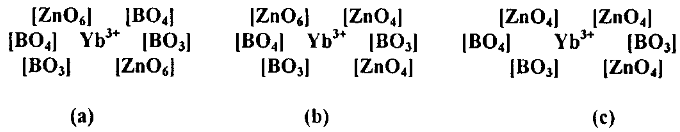

FIG. 4. Coordination of the Yb^{3+} ion in glasses with different B_2O_3 content.

La_2O_3 to form $[ZnO_4]$, forming the coordination shown in Fig. 4b. When $x > 40$, the $[ZnO_4]/[ZnO_6]$ ratio increases, forming the coordination shown in Fig. 4c. Obviously, the coordination in Fig. 4b has the highest asymmetry, therefore Yb^{3+} in this site has the largest Σ_{abs}.

4.4. *Borate Laser Glass with a Good Combination of Properties*

We calculate the minimum pumping intensity (I_{min}) of some laser glasses (QX, ADY, LY, PN, FP) reported in published papers (6, 12, 13) and borate glass (YBG) studied in present work. The spectroscopic properties and minimum pump intensities of these glasses are shown in Table 5.

Table 5 and Fig. 5 show the figure of merits of some excellent Yb^{3+}-doped laser material including the borate glass (YBG). It is shown that the figure of merits of present YBG has an advantage over some excellent laser glasses and is comparable to Yb:YAG, Yb:YAP laser crystals; therefore, we believe YBG glass is a promising laser glass for high-peak power and high-average power laser.

5. CONCLUSION

5.1.

By systematic studies on the dependence of spectroscopic properties of Yb^{3+} on glass composition, the better composition with Yb^{3+} emission cross section more than 1.70 pm^2 and fluorescence lifetime 1.0 ms can be obtained.

5.2.

The concentration quenching effect of Yb^{3+} in borate glass exists, as Yb^{3+} ion concentration varies in the range of

TABLE 5
The Spectroscopic Properties and Minimum Pump Intensities of Some Laser Glasses

Glasses	σ_{em} (pm^2)	τ_m (ms)	λ_{em} (nm)	τ_m/σ_{em} (pm^2/ms)	I_{min} (kW/cm^2)
QX	0.70	2.0	1018	1.40	1.80
ADY	1.03	1.58	1020	1.63	1.12
LY	0.80	1.68	1028	1.35	1.95
PN	1.35	1.36	1035	1.83	0.59
FP	0.50	1.20	1020	0.60	0.80
YBG	1.71	1.10	1016	1.88	1.34

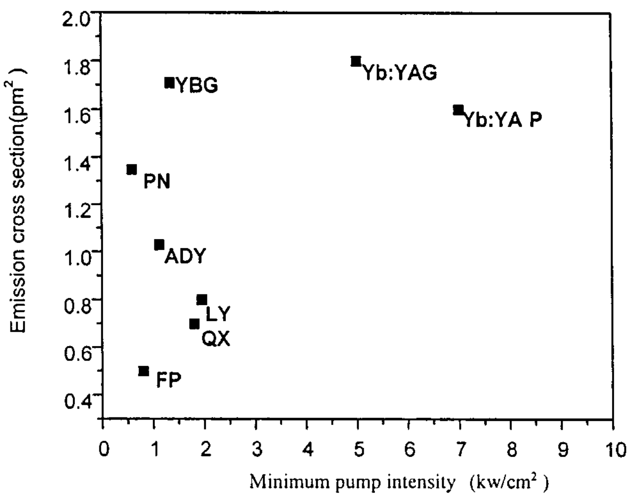

FIG. 5. Relationship between emission cross section (σ_{em}) and minimum pump intensity (I_{min}).

$0\text{–}14 \times 10^{20}$ ion/cm^3, the largest fluorescence intensity occurs at about 7.5×10^{20} ion/cm^3, and fluorescence lifetime is shortened.

5.3.

The figure of merits of present Yb:Borate glass has an advantage over some excellent laser glasses and is comparable to Yb:YAG, Yb:YAP laser materials. Therefore, we believe YBG is a promising laser glass for high-peak power and high-average power laser.

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