Spectroscopic properties of Yb^{3+}-doped TeO_2–BaO–BaF_2–Nb_2O_5-based oxyfluoride tellurite glasses*

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A series of oxyfluoride glasses with the compositions of 75 mol% TeO_2, 10 mol% Nb_2O_5, (15 mol%$-x$) BaO, x BaF_2 ($x = 0$ mol%, 5 mol%, 10 mol%, 15 mol%) doped with Yb_2O_3 were prepared by the melt-quenching method. Their emission cross-sections, fluorescence lifetimes, and gain properties were investigated by using the absorption spectra and the fluorescence decay curves. The results show that by substituting BaF_2 for BaO, the emission cross-section decreases from 1.37 pm^2 to 1.21 pm^2, and the fluorescence lifetime increases from 0.71 ms to 0.96 ms. These properties indicate that this oxyfluoride tellurite glass may have potential uses as the Yb_2O_3-doped gain medium in a solid laser.

Keywords: Yb, oxyfluoride tellurite glass, spectroscopic properties, gain coefficient

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1. Introduction

Yb^{3+}-doped materials have been used in diode-pumped, tunable, and ultra-fast high-power laser sources because of their broad absorption and emission band widths and low thermal loading. Additionally, they are desirable for ultra-short pulse amplification or Q switching due to the long fluorescence lifetime (1–2 ms).[1] Yb^{3+} ions have only two manifolds in the energy level scheme, namely, the $^2F_{7/2}$ ground state and the $^2F_{5/2}$ excited state, therefore, it is commonly believed that concentration quenching should not affect the radiative emission.[2]

Tellurite glasses, owing to their wide infrared transparency (0.35–5 μm), high refractive index, low phonon energy (~ 800 cm^{-1}), high rare-earth solubility, good thermal stability, and excellent corrosion resistance, are uniquely suitable for non-linear laser applications.[3,4]

Yb^{3+}-doped tellurite glasses have been reported in TeO_2–WO_3–Nb_2O_5,[4] TeO_2–ZnO–Nb_2O_5,[5,6] TeO_2–ZnO–$ZnCl_2$,[7] and so on. Compared with other tellurite glasses, the TeO_2–BaO–BaF_2–Nb_2O_5-based glasses possess the good performance of lower phonon energy, because the phonon energies of TeO_2, BaF_2, and Nb_2O_5 are about 750 cm^{-1}, 346 cm^{-1}, and 860 cm^{-1}, respectively.[8–10] Meanwhile, Nb_2O_5 and BaO possess larger polarizabilities and ionic radii.[11] In addition, the introduction of BaF_2 into the tellurite glass can remove the OH^- groups in the glass. Thus, the TeO_2–BaO–BaF_2–Nb_2O_5 glass doped with Yb_2O_3 is expected to have a longer fluorescence lifetime and a larger emission cross-section. However, to our knowledge, the glass system of TeO_2–BaO–BaF_2–Nb_2O_5 doped with Yb^{3+} has rarely been reported.

In this work, Yb^{3+} doped TeO_2–BaO–BaF_2–Nb_2O_5 glasses with different compositions are prepared. The emission cross-sections, fluorescence lifetime, and gain properties are analyzed. Meanwhile the relations between the spectroscopic properties and the compositions of the glasses are discussed.

2. Experiment

Tellurite glasses with the compositions of 75 mol% TeO_2, 10 mol% Nb_2O_5, (15 mol%$-x$) BaO, and x BaF_2 ($x =$ 0 mol%, 5 mol%, 10 mol%, and 15 mol%, named as TNBF0, TNBF1, TNBF2, and TNBF3, respectively) were prepared by melt-quenching techniques. Each sample was doped with 1.0 wt.% Yb_2O_3. Reagents with high purity ($> 99.99\%$ pure) were used as the starting materials. The mixed reagents were melted in alumina crucibles at 860–900 °C for 35 min, the melts were poured onto a preheated brass mold and annealed at near the glass transition temperature for 4 h, finally, the annealed glasses were slowly cooled to room temperature in 48 h to remove the thermal press. The samples were cut and pol-

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ished into the sizes of 10 mm × 10 mm × 2 mm for the spectroscopic measurements.

Absorption spectra were measured by a UV/VIS/NIR spectrophotometer (JASCO V-570, Japan) over the range of 850–1100 nm, and the fluorescence lifetime was measured by using a 980 nm laser diode and a 300 MHz Tektronix oscilloscope. The density was measured using the Archimedes method, with distilled water as the immersion liquid.

The important spectroscopic parameters for Yb^{3+}-doped laser glasses include absorption cross-section σ_{abs}, emission cross-section σ_{emi}, fluorescence decay lifetime τ_f, integrated absorption cross-sections Σ_{abs}, and gain coefficient $\sigma_{emi} \times \tau_f$. The absorption cross-section is calculated from the absorption spectrum and the emission cross section is calculated from the absorption spectrum based on the reciprocity method.[12] The equations[11–14] used are

$$\sigma_{abs}(\lambda) = \frac{2.303 \log(I_0/I)}{Nl}, \tag{1}$$

$$\sigma_{emi} = \sigma_{abs}(\lambda) \frac{Z_l}{Z_u} \exp\left(\frac{E_{Z1} - hc\lambda^{-1}}{kT}\right), \tag{2}$$

$$E_{Z1} = hc\lambda_p^{-1}, \quad \Sigma_{abs} = \int \sigma_{abs}(\lambda)\, d\lambda, \tag{3}$$

where $\sigma_{abs}(\lambda)$ is the absorption cross-section at wavelength λ, $\log(I_0/I)$ represents the absorption intensity, N represents the doping concentration of Yb^{3+} ions, l represents the thickness of the sample, and h, c, k, T, and λ_p are the Planck constant, the light velocity, Boltzmann's constant, the absolute temperature, and the peak wavelength of the absorption band, respectively. The Z_l and Z_u stand for the partition functions of the lower and the upper levels, respectively.

The fluorescence lifetime τ_0, that is the time in which the fluorescence intensity decays to 1/e of the initial intensity, can be found using the equation[14]

$$I = I_0 \exp(-t/\tau_0), \tag{4}$$

where I_0 and I represent the initial fluorescence intensity and the fluorescence intensity τ at time t, respectively.

The free OH^- group concentration in the glass can be found through the Fourier transform infrared (FTIR) spectra via the following equations:[6]

$$N_{OH} = \frac{N_A}{\varepsilon}\alpha, \tag{5}$$

$$\alpha = \frac{\ln(T_0/T)}{l}, \tag{6}$$

where α is the OH^- absorption coefficient, T_0 and T are the maximum transmittance and the transmittance at the absorption peak, respectively, l represents the sample thickness, N_A is the Avogadro number, and ε stands for the molar absorptivity of the free OH^- groups in the glass, here a value of 4.91×10^4 cm^2/mol is used.

3. Results and discussion

3.1. Effect of F^- ion addition on the density

The densities of the Yb^{3+}-doped TeO_2–BaO–BaF_2–Nb_2O_5 tellurite samples are shown in Table 1. As observed, with the increase of BaF_2, the density of the sample decreases gradually from 5.286 g/cm^3 to 4.982 g/cm^3. It is due to the replacement of the Ba=O double bond by two Ba–F single bonds; O^{2-} can act as the bridge oxygen to connected Te^{4+}, but F^- cannot act as the bridge oxygen, so the structure of the glass becomes loose, the glass density decreases.

Table 1. Densities, spectroscopic properties, and gain parameters of Yb^{3+}-doped TeO_2–BaO–Nb_2O_5-based tellurite samples.

Sample No.	d/g·cm^{-3}	λ_p/nm	σ_{abs}/pm^2	$\Sigma_{abs}/10^4$ pm^3	λ_{em}/nm	σ_{emi}/pm^2	τ_f/ms	$\sigma_{emi}\tau_f$/pm^2·ms
TNBF0	5.286	976	1.94	7.28	1003	1.37	0.71	0.97
TNBF1	5.162	976	1.87	6.97	1003	1.30	0.81	1.05
TNBF2	5.077	976	1.84	6.87	1003	1.27	0.85	1.08
TNBF3	4.982	976	1.77	6.57	1002	1.21	0.96	1.16

3.2. Effect of F^- ion addition on the cross-section

The absorption and the emission cross-sections of the samples are shown in Figs. 1 and 2 and Table 1. As observed, with the increase of the BaF_2 concentration, the emission cross-section decreases from 1.37 pm^2 to 1.21 pm^2, the integrated absorption cross-section decreases from 7.28×10^4 pm^3 to 6.57×10^4 pm^3. This can be explained as follows. The polarization force of O^{2-} is bigger than that of F^-, with the replacement of the Ba=O double bond by two Ba–F single bonds, the splitting of the Stark energy levels of Yb^{3+} becomes small, so the emission cross-section and the integrated absorption cross-section decrease.

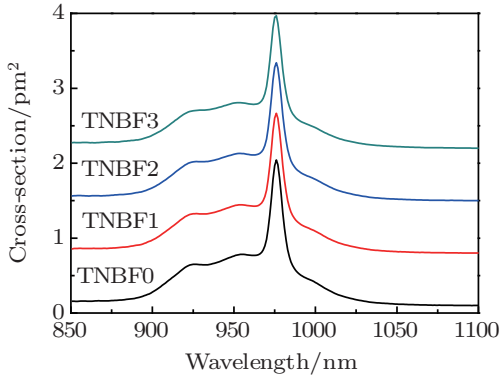


Fig. 1. (color online) Absorption cross-sections of the TNBF glasses.

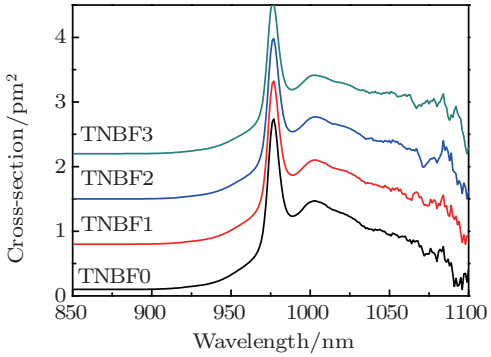


Fig. 2. (color online) Emission cross-sections of the TNBF glasses.

3.3. Effect of F^- ion addition on the fluorescence lifetime

Figure 3 shows the fluorescence decay curves of these tellurite glasses. All the decay curves can be well non-linear fitted with a single-exponential function, by which the fluorescence lifetime can be found, as given in Table 1. As shown, when the content of BaF_2 increases from 0 to 15%, the fluorescence lifetime of the glass increases from 0.71 ms to 0.96 ms.

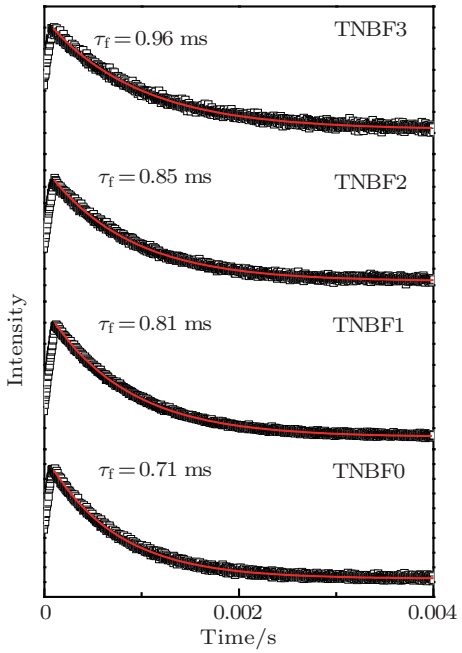


Fig. 3. (color online) Fluorescence decay curves of the TNBF glasses (solid red line represents the fitting curve, while black square frame indicates the experimental data).

The measured fluorescence lifetime τ_f can be expressed as[15]

$$1/\tau_f = W_{rad} + W_{nrad}, \tag{7}$$

where $W_{rad} = 1/\tau_{rad}$ and W_{nrad} are the radiative and the non-radiative decay rates, respectively, and τ_{rad} is the radiative lifetime. The W_{nrad} is a sum of contributions from all non-radiative processes

$$W_{nrad} = W_{MP} + W_{Yb} + W_{OH} + \sum W_{TM} + \sum W_{RE}, \tag{8}$$

where W_{MP} refers to the multi-phonon relaxation and is an intrinsic loss which depends on the temperature and the glass matrix; W_{Yb} is the contribution of Yb^{3+} ion concentration quenching and refers to the energy exchange between the Yb^{3+} ions due to the possible clustering effect; and W_{OH}, W_{TM}, and W_{RE} are related to the interactions between the Yb^{3+} ions and impurities such as OH^- groups, transition-metal ions, and other rare-earth ions. In this work, because the starting materials are high purity, the effect of the transition-metal ions and other rare-earth ions can be ignored. So W_{nrad} is mainly determined by W_{Yb}, W_{OH}, and W_{MP}. As the doped concentration is the same, the different fluorescence lifetime is mainly due to different W_{OH}, W_{MP}, and W_{rad}.

Figure 4 gives the infrared absorption coefficients of the glass samples, which are calculated by using Eq. (6) with the infrared transmission spectra of serial TNBF glasses. The free OH^- group concentration can be estimated by using Eq. (5) with the peak OH^- absorption coefficient at about 3200 cm^{-1}. The calculated free OH^- group concentration is showed in Table 2. With increasing BaF_2 content, the OH^- group concentration decreases from 5.24×10^{19} ions/cm^3 to 2.88×10^{19} ions/cm^3. This can be explained as follows. Due to the introduction of BaF_2 into the glass, the hydroxyl ions can be easily replaced by fluorine during melting through the reaction $OH^- + F^- \rightarrow HF + O^{2-}$. Therefore, with increasing BaF_2, the OH^- group concentration decreases, and W_{OH} decreases.

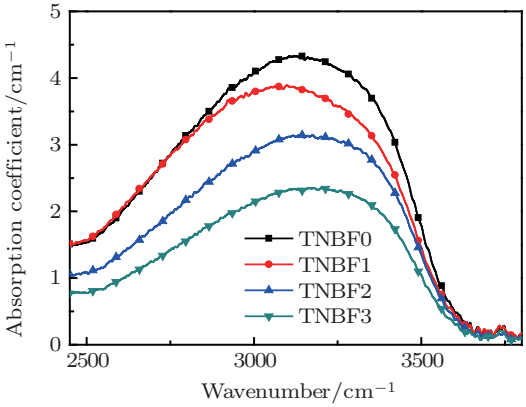


Fig. 4. (color online) IR absorption coefficients of serial TNBF glasses.

Table 2. Fluorescence lifetime, free OH^- group absorption coefficients, free OH^- group concentrations of the samples.

Sample No.	TNBF0	TNBF1	TNBF2	TNBF3
α_{OH}/cm^{-1}	4.27	3.72	3.12	2.35
$N_{OH}/10^{19}$ cm^{-3}	5.24	4.57	3.83	2.88

On the other hand, the phonon energy of BaF_2 is lower than that of BaO, so by substituting BaF_2 for BaO, the phonon energy of the glass gradually reduces, thus W_{MP} decreases.

The W_{rad} can be calculated by the equation[16]

$$W_{rad} = \frac{32\pi cn^2}{3\lambda_p^4}\Sigma_{abs}, \quad (9)$$

where Σ_{abs} is the integral absorption cross-section, λ_p is the peak wavelength of the absorption band, and n is the refractive index at the peak wavelength. As π and c are constants, W_{rad} is decided by n, λ_p, and Σ_{abs}. For this glass system, with BaF_2 substituted BaO, the refractive index decreases, at the same time, Σ_{abs} also decreases from 7.28×10^4 pm^3 to 6.57×10^4 pm^3 and λ_p keeps the same value at 976 nm. So W_{rad} also decreases with increasing concentration of BaF_2.

As discussed above, W_{OH}, W_{MP}, and W_{rad} all decrease as BaF_2 substitutes TeO_2, thus, $1/\tau_f$ decreases and τ_f increases.

3.4. Comparison with some other tellurite glasses

Table 3 lists the spectroscopic properties of some tellurite laser glasses reported. It can be seen that for the previous studied tellurite glasses, the longest fluorescence lifetime is 0.94 ms,[18] the largest emission cross-section is 1.42 pm^2,[5] and the largest gain efficient is 1.21 ms·pm^2.[14] While, the TNBF0 glass sample has a larger emission cross-section of 1.37 pm^2, and the TNBF3 glass sample has a longer fluorescence lifetime of 0.96 ms, meanwhile this glass has a high gain efficient of 1.16 ms·pm^2. It indicates that the TNBF glass has relatively good laser gain properties compared with the other Yb_2O_3-doped tellurite glasses. So this glass may be a candidate for a new Yb^{3+}-doped tellurite glass based laser gain medium.

Table 3. Spectroscopic properties of some tellurite glasses doped with Yb_2O_3.

Glass	σ_{emi}/pm^2	τ_f/ms	$\sigma_{emi}\tau_f$/ms·pm^2	Ref.
TeO_2–WO_3–Bi_2O_3	0.99	0.4	0.396	[4]
TeO_2–Nb_2O_5–ZnO–PbF_2–ZrF_4	1.42	0.85	1.207	[5]
TeO_2–K_2O–ZnO–Al_2O_3–MgF_2	1.39	0.87	1.21	[14]
TeO_2–Nb_2O_5–K_2O–Li_2O	1.1	0.6	0.66	[17]
TeO_2–ZnO–PbO–La_2O_3–Na_2O–K_2O	1.25	0.94	1.18	[18]
TeO_2–GeO_2–La_2O_3–Na_2O–K_2O	1.23	0.92	1.13	[19]
TeO_2–ZnO–B_2O_3–BaF_2	1.416	0.72	1.02	[3]
75TeO_2–10Nb_2O_5–15BaO (TNBF0)	1.37	0.71	0.97	this work
75TeO_2–10Nb_2O_5–15BaF_2 (TNBF3)	1.21	0.96	1.16	this work

4. Conclusion

The spectroscopic and the gain properties of the TeO_2–BaO–BaF–Nb_2O_5 glasses doped with Yb_2O_3 have been studied. The variation of the BaF_2 content influences the spectroscopic and the gain properties of the glasses significantly. As BaF_2 substitutes BaO, the emission cross-section decreases from 1.37 pm^2 to 1.21 pm^2, the fluorescence lifetime increases from 0.71 ms to 0.96 ms. These indicate that this glass may be potentially used as a Yb^{3+}-doped gain medium for the solid laser.

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