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Effect of optical basicity and energy transfer on near-infrared luminescence in Bi/Yb^{3+} co-doped germanate glasses

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Abstract: Bi/Yb^{3+} co-doped germanate glasses were prepared by conventional melting-quenching technique. Near infrared (NIR) luminescence properties in Bi/Yb^{3+} co-doped germanate glasses were investigated by the absorption spectrum, NIR luminescence spectra, and fluorescence lifetime measurement. NIR luminescence of both Yb^{3+} and Bi ions was observed simultaneously, either under 980 or 808 nm excitation LD. The results show that ET process existed between Bi-related NIR emission centre and Yb^{3+} ions. With the increasing in Yb^{3+} ions concentration, both ET efficiency from Yb^{3+} ions to Bi ion and optical basicity of glass matrix are increased. The competitive effects of enhancing by the ET process and weakening by optical basicity on NIR luminescence properties of Bi ions were investigated.

Key words: Bi/Yb^{3+} co-doped, energy transfer, near infrared luminescence, optical basicity, germanate glass
PACS: 42.70.-a

光学碱度与能量传递对 Bi/Yb^{3+} 共掺杂锗酸盐玻璃近红外发光性质的影响

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摘要:采用传统高温熔融法制备了 Bi/Yb^{3+} 共掺杂锗酸盐玻璃,通过吸收光谱、近红外光谱和荧光衰减寿命测试,研究了玻璃样品的近红外发光性质.研究结果表明,玻璃样品在 980 nm 或 808 nm 激光激发下,均能同时观察到 Yb^{3+} 离子和 Bi 离子的近红外发光,Yb^{3+} 离子与 Bi 离子之间存在相互能量传递.随着 Yb^{3+} 离子浓度的增加,玻璃基质的光学碱度和 Yb^{3+} 离子到 Bi 离子的能量传递效率均增加,讨论了能量传递效率的提高对 Bi 离子发光的增强作用与光学碱度增加对 Bi 离子发光的削弱作用的竞争影响机制,获得了 Bi/Yb^{3+} 离子共掺杂锗酸盐玻璃的近红外发光的机理.

关 键 词:Bi/Yb^{3+} 共掺杂;能量传递;近红外发光;光学碱度;锗酸盐玻璃

中图分类号:O482.3 **文献标识码**:A

Introduction

Bismuth-doped glass has been applied as a novel promising active material for broadband near-infrared (NIR) tunable amplification and lasing[1]. The quantum yield of the NIR luminescence is very low due to the stimulated emission cross section of Bi-doped glasses and

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very small at 1 100 ~ 1 300 nm wavelengths. Thus, it is necessary to use commercially LDs as pumping sources in practical applications. Considering this new material perspective, there are many concernable problems need to be solved, which can be summarized as these two aspects: identifying the NIR emission centre and improving the luminescent properties further.

Generally, the luminescent center responsible for the NIR emission of Bi ion is not clearly identified up to now[2-6] because that Bi ions' outer shell electrons are greatly influenced by the environment and testing technology limitation[7]. Base on the joint efforts of researchers and the application prospect of Bi doped material, bismuth doped NIR of ultra-wideband luminescence materials have made speedy progress even though the mechanism of the observed NIR emission is still in controversy. NIR bismuth broadband emission has been discovered in various types of oxide glasses—silicate, phosphate, borate and germinate glasses[8-11]. Recently, Sheng et al[12,13] reported that the area stimulated emission of radiation in the pumping band were broaden by Yb^{3+} ions energy transfer (ET) in Yb/Bi co-doped borophosphate, and strong broadband NIR luminescence ranging from 1 000 to 1 650 nm was observed when the sample was excited by 980 nm laser. Doping Lu^{3+} can further improve the NIR emission of Bi ions in Yb/Bi ions co-doped phosphate glasses. The improvement effects of Al_2O_3 composition on the NIR emission in Bi-doped and Yb/Bi-codoped silicate glasses were also reported by Jiang[14] *et al*. However, according to Zhou[8] works, the higher optical basicity in the glass matrix make against the NIR luminescence of Bi ion. The introduction of Al_2O_3 or Lu_2O_3 increases the optical basicity in glass substrate, which decreases the enhancing effect on the NIR luminescence properties of Bi ions. Thus the competitive relationship between optical basicity of glass substrate and energy transfer efficiency of Yb to Bi ions is important and nonnegligible.

In this paper, we prepared germanate glass, including single Bi doped, Yb^{3+} doped and Bi/Yb^{3+} doped, and investigated their spectral properties. The influence of the introduction of Yb_2O_3 on the optical basicity, ET and NIR luminescence of those glass, and its excitation mechanism were also discussed and analyzed.

1 Experimental

The compositions of the prepared glass were (100-x-0.1) GeO_2-$x$$Li_2O-0.1Bi_2O_3$ (x = 10, 12, 15, 18 mol%), simplified as GLB1, GLB2, GLB3, GLB4; 85GeO_2-(15-y) Li_2O-$y$$Yb_2O_3$ (y = 1, 1.5, 2, 3 mol%), simplified as GLY1, GLY2, GLY3, GLY4; 85GeO_2-(15-0.1-x) Li_2O-0.1% Bi_2O_3-x% Yb_2O_3 (x = 1, 1.5, 2, 3 mol%), simplified as GLBY1, GLBY2, GLBY3, GLBY4; respectively. High purity GeO_2, Li_2O, Bi_2O_3, and Yb_2O_3 were used as starting materials. The weighed starting materials (about 10 g) were firstly ground and mixed thoroughly using a mortar. Then, the mixture was compacted into a platinum crucible. The mixture was melted at 1 450℃ for 20 min in air. When the melting was completed, the liquid was poured on a preheated stainless steel plates. The obtained glasses were annealed at the glass-transition temperatures. Finally, the glass samples were shaped into 10 mm × 10 mm × 3 mm and their surfaces were polished.

The optical absorption spectra were obtained in the wavelength range of 300 to 2 000 nm in HITACHI U-4100 spectrophotometer. The fluorescence spectra in the wavelength range of 900 to 2 000 nm were measured with a ZOLIX SBP300 spectrophotometer under 980 nm (2.0 W) and 808 nm LD excitation (2.0 W). The fluorescence decay curves in near-infrared regions were recorded by using a FLS920 fluorescence spectrophotometer made by Edinburgh Instruments Ltd, U. K. All the spectral measurements were performed at ambient temperature.

2 Results and discussion

2.1 Absorption spectra

The absorption spectra of Yb^{3+} doped (GLY) and Bi/Yb^{3+} co-doped (GLBY) germanate glasses are shown in Fig. 1. There are three absorption peaks around 490 nm, 710 nm and 960 nm in the GLBY glasses system. Comparing with the absorption spectra of single Yb^{3+} doped glasses, there are two absorption peaks around 490 nm and 710 nm, corresponding to Bi-related centers, especially for the low-valence Bi as that observed in most Bi doped glasses[3-4,9-13].

The strong absorption peak around 960 nm belongs to Yb ions $^2F_{7/2}$-$^2F_{5/2}$ energy level transition. The inset figure is the absorption spectra of GLBY glasses with the increase of Yb_2O_3. It shows that the Yb^{3+} ion absorption intensity increases with the increase of Yb_2O_3 concentrations, meanwhile Bi ions absorption intensity decreases. The absorption band around 490 nm shows a slight red-shift. The phenomena suggests that it may be caused by the doped Yb_2O_3. With the increasing of Yb_2O_3 concentration, some network structure of glasses matrix breaks down and non-bridging oxygen is created, leading to the reduction in the phonon vibration energies[15].

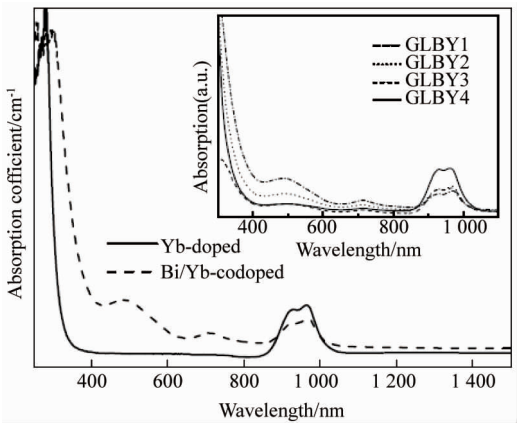

Fig. 1 Absorption spectrum of GLY and GLBY germanate glasses

图1 GLY 和 GLBY 锗酸盐玻璃样品的吸收光谱，内插图是随 Yb^{3+} 离子浓度变化的吸收谱

2.2 NIR luminescence and ET process in single Yb doped and Bi/Yb^{3+} codoped germanate glass

Figure 2 (a) shows the NIR emission in the 900 ~ 1 150 nm wavelength range in Yb doped glasses, under 980nm excitation. The emission band around 1 030 nm is characteristic luminescence of Yb^{3+}: $^2F_{5/2}$-$^2F_{7/2}$ energy levels transition. With the increasing of Yb^{3+} concentration, the luminescence intensity increases firstly and then decreases, the emission intensity of Yb^{3+} ion in GLY3 glass is the highest one and the concentration quenching happens in GLY4 glasses. In contast, there is no emission band observed in GLB glass under 980 nm excitation.

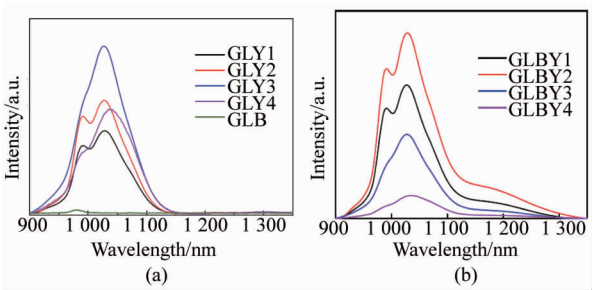

Fig. 2 Infrared luminescence spectra of (a) single Bi doped and Yb^{3+} doped, and (b) Bi/Yb^{3+} co-doped GLBYglasses, excited by 980 nm LD

图 2 在 980 nm 激光激发下 (a) Bi、Yb^{3+} 离子单掺杂锗酸盐玻璃的近红外发光谱,(b) Bi/Yb^{3+} 离子共掺杂锗酸盐玻璃近红外发光谱

Figure 2 (b) shows the NIR emission at 900 ~ 1 350 nm wavelength range in GLBY glasses, under 980 nm excitation. There are main two emission bands around 1 030 nm and 1 180 nm. The emission peaks around 1 030 nm is characteristic luminescence of Yb^{3+}: $^2F_{5/2}$-$^2F_{7/2}$ energy levels transition. Comparing with GLY glasses, the emission wavelength around 1 180 nm is ascribed as Bi NIR related emission center. The appeared emission peaks at 1 180 nm suggests that the ET process from Yb^{3+} ion to Bi-related NIR emitting centers existed in GLBY glasses, under 980 nm excitation. According to our previous work, the emission peaks at 1 180 nm is assigned to Bi^0 ions[16].

With the increasing in Yb^{3+} concentration, NIR luminescence intensity of Yb^{3+} ions firstly increase then decrease, and the emission intensity of Yb^{3+} ion in GLBY2 glass is the highest one. Comparing with GLY glasses, the luminescence intensity of Yb^{3+} ions decrease early. This phenomenon can be ascribed to ET progress from Yb^{3+} ions to Bi ions. As a result, NIR fluorescence decay curves of GLY glasses and GLBY glasses at the same Yb^{3+} ion concentration were investigated under 980 nm excitation.

Figure 3 shows the fluorescence decay curves at $^2F_{5/2}$ energy levels of GLY and GLBY glasses, under 980 nm excitation. The Yb^{3+} ion single doped sample shows a non-exponential fluorescence decay curve[15] as depicted in Fig. 3. Its value was confirmed from the numeric fitting to be τ_{Yb}. Figure 3 also demonstrates that the intensity of the fluorescence decays at the $^2F_{5/2}$ energy levels of Yb^{3+} ion for the samples in the order of GLBY1, GLBY2, GLBY3, and GLBY4. It can be seen that the fluorescent decays become quicker when the Bi is introduced as an acceptor of energy transfer. Meanwhile, it was found that all curves can be well fitted by a second-order exponential decay mode as the following equation[19]:

$$I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

where I presents the luminescence intensity, A_1 and A_2 are fitting parameters, t is the time, τ_1 and τ_2 are rapid and slow lifetimes for exponential components, respectively. Based on these parameters, the average decay times of Yb^{3+} ion ($\tau_{Yb\text{-}Bi}$) can be calculated by the following equation[17]:

$$\tau_{Yb-Bi} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (2)$$

the ET efficiency can be calculated by the following equation,

$$\eta_{ET} = 1 - \frac{\tau_{Yb-Bi}}{\tau_{Yb}} \quad (3)$$

the values of τ_{Yb}, $\tau_{Yb\text{-}Bi}$ and η_{ET} are calculated from the above formula. With the Yb^{3+} ion concentration increasing, the fluorescence decay times of Yb^{3+} ions in GLY glasses is 230.30 μs, 269.21 μs, 300.45 μs, 255.87 μs, respectively. The one of Yb^{3+} ions in GLBY glasses is 180.15 μs, 204.27 μs, 170.43 μs, 161.47 μs, respectively. According to Eq. 3, the calculated values of η_{ET} are 21.77 %, 24.12 %, 43.27 %, 36.89 %, respectively. With the addition of Yb^{3+} ions, ET efficiency increases at first and then decrease. With the increasing of the Yb^{3+} ion concentration, the population of the ET progress increases and the ET efficiency increases also. As a result, the luminescence intensity of Yb^{3+} ions decreases early in Bi/Yb^{3+} codoped GLBY glasses comparing with GLY glasses. When the concentration quenching happens in GLY4 glasses, the ET efficiency decreases.

NIR emission intensity of Bi ion is still decreased even though the ET efficiency increases for GLBY3 as shown in Fig. 2 (b). As well known, luminescence properties of Bi ions is strongly influenced by the structure of glass matrix due to the electron configuration of Bi is $6s^26p^3$. The effect of glass matrix on Bi ion NIR luminescence is nonegligible when the glass matrix is doped with Yb^{3+} ions, because Yb^{3+} ion has not only a high coordination number but also a high degree of affinity for a variety of hybrid atoms.

For glass matrix, optical basicity is a reflection of glass microstructure and macro properties, which also directly affect the physical and chemical properties of the glass. Optical basicity is fundamentally related to the chemical bonding in a solid and is related to the optical properties of a material through the polarizability of electron clouds around atoms (ions) by electromagnetic waves. According to a previous report[18], when the optical basicity increases from 0.547 9 to 0.591 8 in borate glasses, the concentration of [BO_4] tetrahedrons decreases from 25 to 10 mol% and the boron coordination has

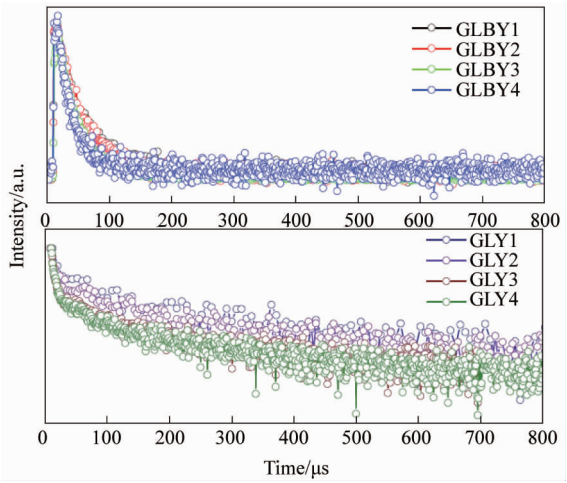

Fig. 3 The fluorescence decay curves near 1 030 nm of single Yb^{3+} doped and Yb/Bi codoped germanate glasses excited by 980 nm LD

图3 980 nm激光激发下,Yb^{3+}离子单掺杂和Bi/Yb^{3+}离子共掺杂锗酸盐玻璃中Yb^{3+}离子荧光衰减曲线

changed from [BO_4] tetrahedrons to [BO_3] in Bi doped borosilicate glasses. Thus, the effects of glass matrix on NIR luminescence properties of Bi^0 ions could be considered similarly to the impacts of optical basicity of glass matrix.

2.3 Optical basicity and NIR luminescence in single Bi doped and Bi/Yb^{3+} codoped germanate glass

The optical basicity (Λ) of glasses is calculated from the empirical formula proposed by Duffy[19]:

$$\Lambda = X_A\Lambda_A + X_B\Lambda_B + \cdots Xn\Lambda n \quad , \quad (4)$$

where X_A, X_B, $\cdots$ are the equivalent fractions of A, B $\cdots$ and Λ_A, $\Lambda_B\cdots$ are corresponding moderating parameters. The calculated optical basicity of GLBY1, GLBY2, GLBY3, and GLBY4 are 0.689, 0.698, 0.708, and 0.728, respectively. With the increase in Yb_2O_3 concentration, optical basicity increases.

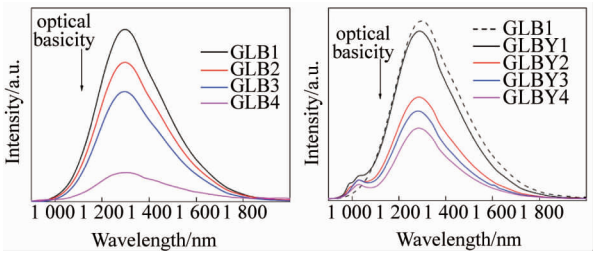

Fig. 4 NIR luminescence of GLB and GLBY glass, under 808 nm excitation

图4 在808 nm激光激发下,GLB和GLBY玻璃样品的近红外发光谱

Figure 4 shows the change of NIR luminescence in GLB and GLBY glasses with the increase of optical basicity under 808 nm excitation. As shown in Fig. 4 (a), the peak band around 1 300 nm is ascribed to Bi-related NIR emitting centre, and assigned to Bi^+ ions from our previous work[16]. According to optical basicity theory, the higher optical basicity favors the higher valence state of the multivalence metal ions. Increasing the optical basicity, the number of Bi^+ ions decreases, as well as the NIR luminescence intensity of Bi^+ ions.

From Fig. 4 (b), there are two main emission bands around 1 030 nm and 1 300 nm. The peak band around 1 300 nm is ascribed to Bi^+ ion NIR emitting centre. The peak band around 1 030 nm emission is the characteristic luminescence of Yb^{3+}: $^2F_{5/2}$-$^2F_{7/2}$ energy levels transition. The result implies that energy transfer progress from Bi^+ ions to Yb^{3+} ions may occur under 808nm excitation. Accompanying the increase in optical basicity, all of the NIR luminescence intensities decrease.

According to our previous work[16], under 690 nm excitation, the NIR emissions of Bi ion appeare at two bands around 1 180 (ascribed in Bi^0 ion) and 1 300 nm (ascribed in Bi^+ ion) in GLBY glass, and their emission intensities decrease with the Yb^{3+} ion concentration increased. The increase of Yb^{3+} ion concentration indicates that the optical basicity increases, which proves that the emission band of Bi^0 ion should be decreased with the increase optical basicity. These results highly agree with Zhou's view[8].

In general, the energy transfer progress from Yb^{3+} ion to Bi^0 ion will increase the emission intensity of Bi^0 ion, however, optical basicity of glass matrix will decrease the emission intensity of Bi^0 ion with the increase in Yb_2O_3 concentration. Thus, we further discussed the dependence of $I_{1\,160\,nm}/I_{1\,030\,nm}$ and the energy transfer efficiency (η_{ET}) on the optical basicity in GLBY glasses, under 980 nm LD excitation.

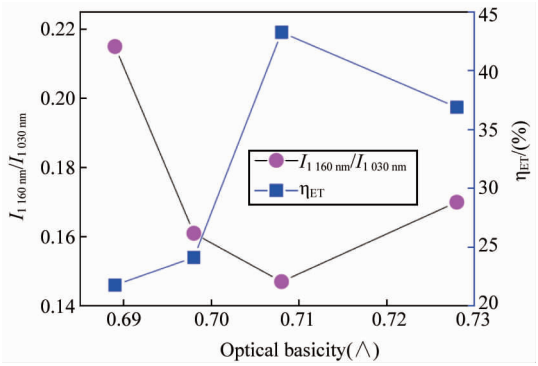

Fig. 5 The dependence of $I_{1\,160\,nm}/I_{1\,030\,nm}$ and the energy transfer efficiency (η_{ET}) on the optical basicity in GLBY glasses, under 980 nm LD excitation

图5 在980 nm激光激发下,GLBY玻璃样品中,$I_{1\,160\,nm}/I_{1\,030\,nm}$和$\eta_{ET}$随光学碱度变化谱

The dependence of $I_{1\,160\,nm}/I_{1\,030\,nm}$ and ET efficiency (η_{ET}) on the optical basicity in GLBY glasses is shown in Fig. 5. The ET efficiency increases firstly and then decreases with the increase of optical basicity, the change of $I_{1\,160\,nm}/I_{1\,030\,nm}$ is opposite to the variation of ET efficiency.

According to the reports of Sheng[13] and Jiang[14], the ligand structure influences strongly the ET efficiency from Yb^{3+} ions to Bi infrared emission centers. In our previous work, increasing the optical basicity, partial $[GeO_6]$ octahedrons change to $[GeO_4]$ tetrahedrons in binary lithium germanate glass matrix[20]. The structure of glass matrix becomes loose. The $[GeO_4]$ six-member ring clearance radius in glass matrix decreases after adding Yb^{3+} ions with a high coordination number. As a result, the ET efficiency increases. On the other hand, partial $[GeO_6]$ octahedrons change to $[GeO_4]$ tetrahedrons in glass matrix, which makes the ET efficiency decrease. Thus, the ET efficiency from Yb^{3+} ions to Bi^0 ions increases with the increase of Yb^{3+} ions concentration. Especially, when the η_{ET} is up to 42.27 %, the effect of ET efficiency on Bi ion's NIR luminescent properties makes up the limits caused by the glass network structure or optical basicity, leading to an improvement in the bismuth ions NIR emission.

Therefore, the $I_{1\,160\ nm}/I_{1\,030\ nm}$ decreases firstly and then increases in Bi/Yb^{3+} codoped glasses, which are caused by both effects of optical basicity and ET efficiency. At low concentration of Yb^{3+} ions, the enhanced effect of ET on the NIR luminescence of Bi^0 ion only makes the NIR luminescence intensity decrease slowly. The NIR luminescence intensity continues to decrease, but the ration of $I_{1\,160\ nm}/I_{1\,030\ nm}$ changes into increasing when ET efficiency is over 42.27%.

2.4 Energy transfer in Bi/Yb^{3+} codoped germanate glass

In this study, according to the comprehensive survey of the NIR emission performances of Bi/Yb^{3+} co-doped germanate glasses, the ET processes can be understood by the simplified energy schematic (shown in Fig. 6). When excited at the absorption bands at 980 nm around $^2F_{5/2}$ level of Yb^{3+} center, the electron on ES_1 energy level of Bi^0 can be excited through the energy transfer process, and the emission of 1 030 nm from Yb^{3+} as well as the emission of 1 1 180180 nm from Bi^0 can be observed simultaneously. The similar situation also happens when excited at 808 nm of Bi^+ ion, NIR emissions from Bi^+ (1 300 nm) as well as Yb^{3+} (1 030 nm) occur. Therefore, these ET processes, from Bi^0 to Yb^{3+} and from Bi^+ to Yb^{3+}, are proved by experimental data. Due to the splitting of 6p-excitation level of low valence Bi ions in solid-state compounds, the energy level depends strongly on the strength of crystal field or glass coordination field, and the ET process between Yb^{3+} and Bi-NIR-emitting centers might be changed in various glass hosts.

3 Conclusions

The effects of optical basicity and ET on the NIR luminescence properties in Bi/Yb^{3+} co-doped germanate glass were investigated. The 1 030 nm emission of Yb^{3+} ions and 1 180 nm emission of Bi^0 ions were observed under excitation at 980 nm. The 1 030 nm emission of Yb^{3+} ions and 1 300 nm emission of Bi^+ ions were observed under excitation at 808 nm. The results indicate

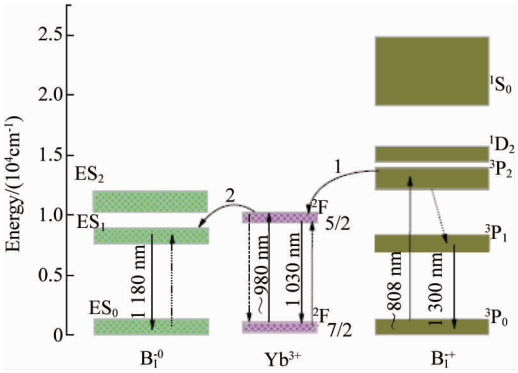

Fig. 6　Schematic energy level diagrams of Bi^+, Bi^0 and Yb^{3+} in Bi/Yb^{3+} co-doped germanate glasses

图 6　Bi/Yb^{3+} 共掺杂锗酸盐玻璃中,Bi 和 Yb^{3+} 离子的发光机理

that ET exists between Bi-related NIR emission centre and Yb^{3+} ions. With the increase of Yb^{3+} ions concentration, ET efficiency from both Yb^{3+} ions to Bi^0 NIR emission centre and optical basicity of the glass matrix is increased. The ET progress increases the NIR emission of Bi^0 ions, but the optical basicity is unfavorable for Bi^0 ions NIR emission. The enhancement effects of ET progress on the NIR luminescence of Bi^0 ion make the NIR luminescence intensity decrease slowly with increasing optical basicity. These experimental results are useful for obtaining high NIR luminescence and can act as a guidance principle to obtain broadband fiber amplifiers in wavelength division multiple systems.

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