

Violet-green excitation for NIR luminescence of Yb³⁺ ions in Bi₂O₃-B₂O₃-SiO₂-Ga₂O₃ glasses

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Abstract: 60Bi₂O₃-20B₂O₃-10SiO₂-10Ga₂O₃ glasses doped with 1-9 mol% Yb₂O₃ were prepared and investigated mainly on their violet-green excitation for the typical NIR emission of Yb³⁺, generally excited in the NIR. Two violet excitation bands at 365 nm and 405 nm are related to Yb²⁺ and Bi³⁺. 465 nm excitation band and 480 nm absorption band in the blue-green are assigned to Bi⁰ metal nanoparticles/grains. Yb-content-dependence of the excitation and absorption means that Bi⁰ is the reduced product of Bi³⁺, but greatly competed by the redox reaction of Yb²⁺ ↔ Yb³⁺. It is proved that the violet-green excitations result in the NIR emission of Yb³⁺. On the energy transfer, the virtual level of Yb³⁺-Yb³⁺ as well as Bi⁰ dimers probably plays an important role. An effective and controllable way is suggested to achieve nano-optical applications by Bi⁰ metal nanoparticles/grains and Yb³⁺.

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1. Introduction

While Bi_2O_3 acts as a main component, such a heavy metal oxide glass can now be prepared with a stable structure [1]. These glasses possess high refractive index and exhibit nonlinear optical behavior due to the large polarizability and low field strength of Bi^{3+} ions, and they are suitable to make optical devices such as ultrafast all-optical switch, optical isolator, and optical Kerr shutter [2]. Another important application is the production of various light sources. Some rare earth ions in bismuthate glasses show good spectroscopic properties, for example, Nd^{3+} ions in $\text{Bi}_2\text{O}_3\text{-PbO-Ga}_2\text{O}_3$ glasses [3]. For incoherent and coherent light sources, there has been substantial progress in Pb-free bismuthate glasses. For Yb, Nd co-doped $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ based glasses [4], their effective output is an urgent need as the light source for optical coherence tomography. For highly Yb-doped Bi_2O_3 based fiber [5], the laser output has been realized with a slope efficiency of 36%. Development of these optical devices relies on the further improvement of bismuthate glasses. Especially, the optical and spectroscopic stability of Yb-doped bismuthate glass will be challenged by the stability of Bi ions from the host, as well as the stability of Yb ions from the doping.

Bi can exist in the form of Bi_2O_3 matrix, while the luminescence center is a rare earth ion [5]. On the other hand, Bi can also exist as the main group luminescence center in the form of different valence states [6]. A good work is to implement co-doping of Bi and Yb, which is suitable to be pumped by 980 nm LD [7]. In Yb-doped laser glass, crystal and ceramic, there is always a problem on the valence state of Yb. Most of Yb^{3+} ions are stable, while a certain amount of Yb^{3+} ions will be converted into Yb^{2+} ions [8, 9].

On the basis of analyzing Bi and Yb centers in Yb_2O_3 -doped $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2\text{-Ga}_2\text{O}_3$ glasses, the characteristics on the violet-green excitation of Yb^{3+} are investigated in this paper. In section 3, excitation, absorption, the emission spectra and decay curves are presented. In section 4, the ascription of 465 nm excitation and 480 nm absorption bands, the assignment of 405 and 365 nm excitation bands, the competition between redox reactions of $\text{Bi}^0 \leftrightarrow \text{Bi}^{3+}$ and $\text{Yb}^{2+} \leftrightarrow \text{Yb}^{3+}$, and the energy transfer from Bi^0 metal nanoparticles/grains to Yb^{3+} are discussed.

2. Experimental

Glass samples of formula $60\text{Bi}_2\text{O}_3\text{-}20\text{B}_2\text{O}_3\text{-}10\text{SiO}_2\text{-}10\text{Ga}_2\text{O}_3\text{-}x\text{Yb}_2\text{O}_3$ (so called BBSG) where $x = 1\text{-}9$ mol% were prepared. The raw materials were high-purity (3N) Bi_2O_3 , H_3BO_3 , SiO_2 , Ga_2O_3 and Yb_2O_3 (5N) powders. Well-mixed 50g batches of powders were firstly placed in alumina crucible. To prevent evaporation of bismuth oxide, the compound was presintered at 650 °C, and then melted in Si-C electric furnace at 1000~1100 °C for 30 minutes. After dehydrating, the melt was quickly poured on preheated stainless-steel mold and annealed near the transition temperature. Two hours later, the glass was cooled to 100 °C at a rate of 10 °C /hr, and then switched off the muffle furnace. Such prepared brown and transparent samples were polished to $10 \times 10 \times 1\text{mm}^3$ before spectroscopy test. For a certain doping content of Yb_2O_3 , the same sample was used in the tests of absorption, excitation and emission spectra.

The absorption spectrum was tested at room temperature with Perkin-Elmer Lambda 900 UV/VIS/NIR spectrophotometer. The spectrum was scanned from visible to NIR under the same test condition. The excitation and emission spectra, fluorescence lifetime were carried out using an Edinburgh FLSP 920 Time-resolved Fluorescence Spectrometer. NIR emission was tested by a Hamamatsu R5509 detector with liquid nitrogen refrigeration, and excited by steady-state or microsecond Xenon lamp. The resolution for spectrum measurement was 0.25 nm. During the test process, important test parameters such as the power of the lamp, the slits of monochromators, the sample position, the high voltage to the detector, remained the same.

3. Results

3.1 Excitation spectra in the violet-green

Typical for Yb-doped materials, there is a NIR absorption band for $x\text{Yb}_2\text{O}_3$ -doped BBSG ($x = 1$ -9 mol%) glasses in the wavelength range of 850-1050 nm, corresponding to $^2\text{F}_{7/2}$ to $^2\text{F}_{5/2}$ transition of Yb^{3+} . Excitation by this NIR absorption band will result in a NIR emission band from 900 to 1100 nm, corresponding to the transition from $^2\text{F}_{5/2}$ to $^2\text{F}_{7/2}$ multiplets of Yb^{3+} .

Figure 1 presents the excitation spectra in the violet-green region for BBSG glasses with doping 1-9 mol% Yb_2O_3 . Owing to serious radiation trapping at 975 and 1003 nm emission peak of Yb^{3+} , the monitoring wavelength was at 1020 nm, which also corresponds to $^2\text{F}_{5/2}$ to $^2\text{F}_{7/2}$ transition of Yb^{3+} . It is found out clearly that the violet-green excitation really can result in a NIR emission.

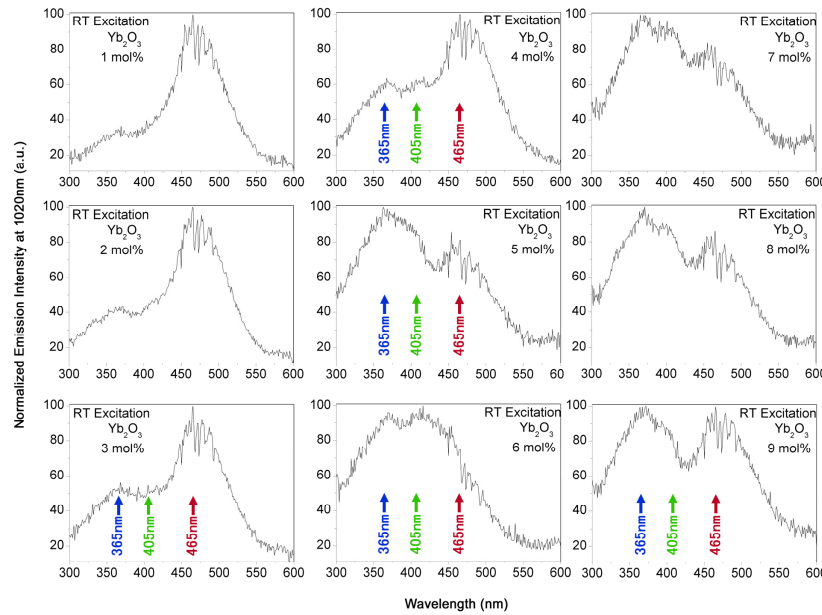


Fig. 1. Content dependence of excitation spectra for $x\text{Yb}_2\text{O}_3$ -doped BBSG glasses by monitoring 1020 nm emission of Yb^{3+} , $x = 1, 2, 3, 4, 5, 6, 7, 8, 9$ mol%, respectively.

As shown in Fig. 1, the violet-green excitation actually contains three separate bands, two strong bands around 365 and 465 nm, and one weak band around 405 nm. It is worth noting that the changes of the relative intensity ratio for these three bands show a certain correlation with Yb_2O_3 doping content of BBSG glasses. Figure 2 shows the plot of the emission intensity at 1020 nm versus Yb_2O_3 doping content of BBSG glasses, excited at 365, 405 and 465 nm, respectively.

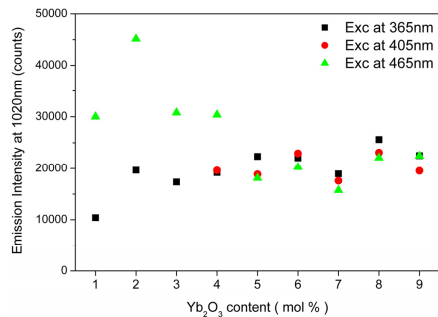


Fig. 2. NIR emission intensity at 1020 nm versus Yb₂O₃ doping content of BBSG glasses, excited at 365, 405 and 465 nm, respectively.

Under 365 nm excitation, 1020 nm emission intensity is relatively low at 1 mol%, and then enhanced from the point of 2 mol%, as shown in Fig. 2. Subsequently it tends to be a constant, but remains an enhanced trend. Correspondingly, 365 nm excitation band becomes stronger with increasing Yb₂O₃ content and always appears in the excitation spectra of Fig. 1.

Under 405 nm excitation, 1020 nm emission may be too weak to be observed from 1 to 3 mol%. But from 4 to 9 mol%, the intensity has a tendency to increase, as shown in Fig. 2. Correspondingly, 405 nm excitation band only appear when Yb₂O₃ content is more than 3 mol% and the most obvious band occurs at 6 mol%, as shown in the excitation spectra of Fig. 1.

Under 465 nm excitation, if neglecting the point of 1 mol%, 1020 nm emission intensity is firstly reduced and then increased again, as shown in Fig. 2. Figure 1 shows that 465 nm excitation band becomes more obvious only when doping a lower or higher Yb₂O₃ content in BBSG glasses. It should be pointed out that the band almost disappears at 6 mol%.

Two characteristics can be found out: (1) For the relative intensity ratio between 365 and 465 nm excitation bands, there exists a turning point between 4 and 5 mol%, where the relative intensity ratio starts to inverse, as shown in Fig. 1. (2) For 465 nm excitation band, there exists a zero point around 6 mol%, as shown in Fig. 1. Especially, 465 nm excitation band exhibits a non-monotonic dependence with increasing Yb₂O₃ content of BBSG glasses, as shown in Fig. 1 and 2.

3.2 Absorption spectra in the blue-green

Figure 3 shows the visible absorption spectra of BBSG glasses doped with 1-9 mol% Yb₂O₃. The absorption edge in the short wavelength range shows a blue shift with the increase of Yb₂O₃ content. It should be noted that our BBSG glasses were prepared by a way that a few percentage of Yb₂O₃ was externally doped into the raw powders of 100 mol% BBSG glasses. With increasing Yb₂O₃ content, the proportion of Bi₂O₃ would decrease a little. In bismuth borate glasses [10], with the increase of Bi₂O₃ the absorption edge shows a red shift, which is attributed to the increase of the concentration of non-bridging oxygens.

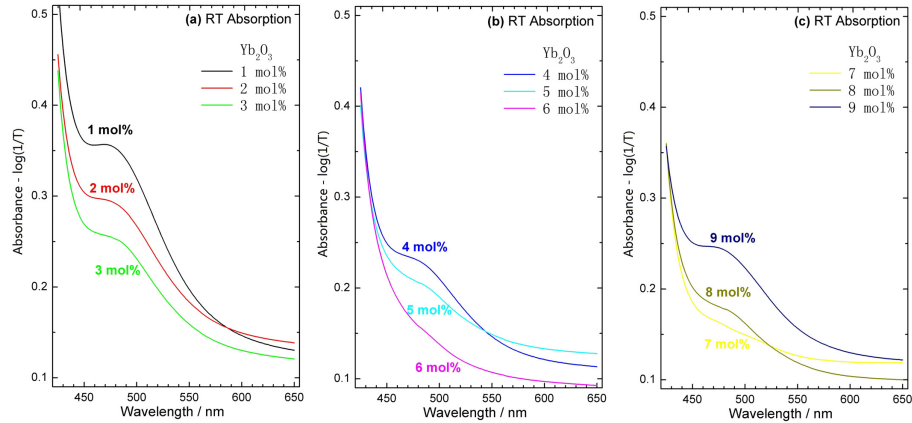


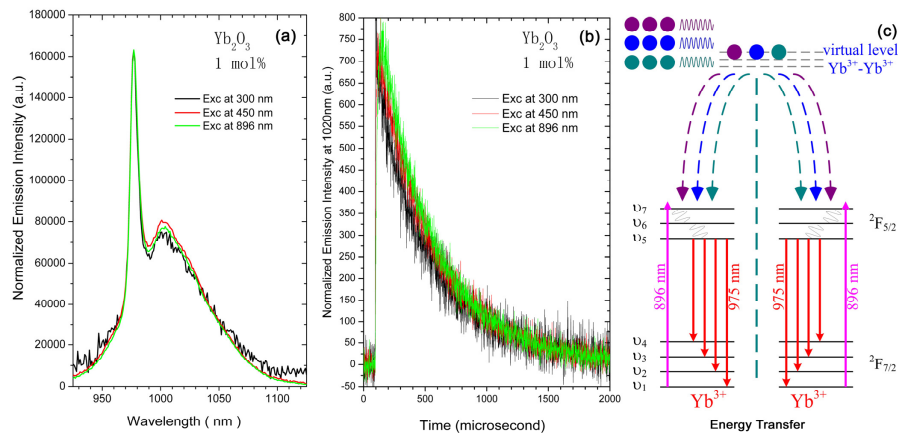
Fig. 3. Visible absorption spectra of BBSG glasses with Yb_2O_3 of (a) 1, 2, 3 mol%, (b) 4, 5, 6 mol% and (c) 7, 8, 9 mol%.

Corresponding to 465 nm excitation band shown in Fig. 1, there is a blue-green absorption band located around 480 nm, as shown in Fig. 3. Firstly, the absorption intensity gradually declines when Yb_2O_3 content increases from 1 to 5 mol%. And especially, the absorption band almost fully disappears at 6 mol%. And then with Yb_2O_3 content further increased from 7 to 9 mol%, the absorption band reappears and becomes stronger again. The same non-monotonic dependence occurs for 480 nm absorption band, as 465 nm excitation band behaves in Fig. 1 and Fig. 2. Both of these two bands should result from the same center. The center is not related to Yb ions, otherwise it is difficult to explain their non-monotonic dependence with Yb_2O_3 content.

In our Yb_2O_3 -doped BBSG glasses, there really contains Fe of 15-25 ppm as detected by ICP-AES. However, its concentration in the samples does not show any regularity. Generally, the absorption of $\text{Fe}^{2+}/\text{Fe}^{3+}$ should be around 300 nm or deeper UV [11]. On the other hand, there seems no possibility to generate color centers with an absorption in the blue-green region. Since dry oxygen gas was bubbled to decrease the hydroxyl groups for a long time in the process of glass preparation, there should be no large amount of oxygen vacancies produced in the preparation. Figure 3 shows that the long-wavelength side of 480 nm absorption band ends at 600 nm. If adopting wavenumber or energy as the abscissa of the excitation spectra in Fig. 1, it could be observed that the corresponding 465 nm excitation band is narrower than other two excitation bands. The center responsible for 465 nm excitation and 480 nm absorption does not show a definite characteristic of a color center.

3.3 NIR 1 μm emission and decay of Yb^{3+} excited in the violet-green and NIR

To ascertain the origin of 465 nm excitation band in Fig. 1 and 480 nm absorption band in Fig. 3, it is necessary to make clear if NIR emission is the same when excited by either 465 nm blue-green excitation band or NIR absorption band of Yb^{3+} . For the sample doped with 1 mol% Yb_2O_3 , the NIR emission and lifetime decay curves excited at 300, 450 and 896 nm are shown in Fig. 4(a) and 4(b), respectively. Yb^{3+} can be excited directly at 896 nm, as shown in the energy level scheme of Fig. 4(c). Whether excitation is at violet-green (300, 450 nm) or NIR (896 nm) region, the emission spectra and emission decay curves are the same, respectively. The above fact definitely indicates that Yb^{3+} can be excited at 300 or 450 nm. Therefore, under both 300 nm and 450 nm excitation, the final emission center must be Yb^{3+} , and there must be a path to transfer the energy absorbed in the violet-green region to Yb^{3+} in BBSG glass.



3.4 NIR 1.3 μm emission of a Bi-related center excited by a 3 W 808 nm LD

Besides one NIR emission (900-1100 nm) of Yb^{3+} as shown in Fig. 4(a), there would be other NIR emission (1150-1550 nm) related to Bi in our Yb_2O_3 -doped BBSG glasses. While excited in the visible-NIR (high power Xe-lamp), BBSG glasses only show that NIR emission band of Yb^{3+} , and no emission band can be observed in the range of 1150-1550 nm. In Yb/Bi co-doped silicate glasses [12], two NIR emission bands of Yb and Bi-related center could be observed simultaneously. Moreover, 1230 nm emission band of Bi_2O_3 - B_2O_3 - SiO_2 - PbO glass could be observed with a 785 nm laser of 100 mW [13]. However, only when using a 808 nm LD up to 3000 mW to excite BBSG samples with about 5 mm thickness, an emission band peaking around 1325-1340 nm can be observed, as shown in Fig. 5. The wavelength range of this emission band is similar to the reported, and it should result from that Bi-related center [12–23]. With increasing Yb_2O_3 content, the emission intensity does not show a clear regularity. It should be pointed out that the long-wavelength side of 1 μm emission band of Yb^{3+} is also shown in the left of Fig. 5. As can be seen in Fig. 4(a), the emission intensity at 1100 nm is very weak compared to the peak emission of Yb^{3+} . But it exhibits relatively higher intensity than 1325-1340 nm emission in Fig. 5. It clearly shows that the concentration of Bi-related center is very low in our BBSG glasses. The product of emission cross section and lifetime of this Bi-related center can reach up to $10^{-24} \text{ cm}^2\cdot\text{s}$, even higher than that of Ti^{3+} : sapphire [17]. Therefore, Bi-related center would not be the center which is responsible for 465 nm excitation and 480 nm absorption bands.

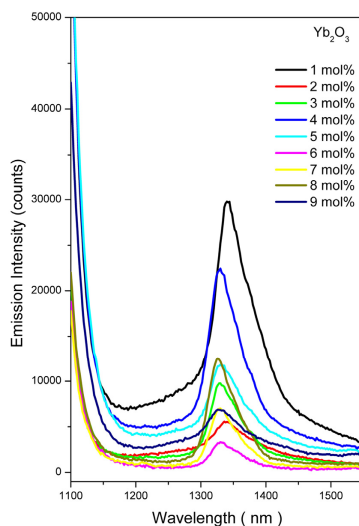


Fig. 5. Emission spectra of a Bi-related center in $x\text{Yb}_2\text{O}_3$ -doped BBSG glasses excited by a 3W 808 nm LD, $x = 1, 2, 3, 4, 5, 6, 7, 8, 9$ mol%, respectively.

About Bi-related center, there are many deep investigations [12–23] in the recent years. Those materials emitting Bi-related NIR emission show 500 nm absorption band, near 480 nm absorption band as shown in Fig. 3. But that 500 nm absorption band is always accompanied by a weak absorption band at 700 nm [12–23]. Some Bi-doped glasses also show other accompanied absorption bands at 800 nm, 1000 nm and 1400 nm [13–16, 21–23]. However, besides the absorption edge of BBSG host and NIR absorption of Yb^{3+} , there is only one 480 nm absorption band shown in Fig. 3, no other detectable absorption band.

Although the origin of Bi-related NIR center is not yet fully conclusive, it is most likely caused by Bi^{5+} [22], Bi^+ [16, 17, 23–26], BiO radicals [18], Bi atoms [13], Bi clusters [15], Bi atom dimers [17, 19, 20, 26–28], Bi^+ /subvalent diamagnetic bismuth cluster ions [29]. According to [13, 15, 17], they conclude that the origin of the Bi-related NIR center is not Bi^0 metal nanoparticles/grains. Thus, if we assign Bi^0 metal nanoparticles/grains to the center responsible for 465 nm excitation and 480 nm absorption bands, it is in agreement with above analysis for Fig. 5, that the center responsible for 465 nm excitation and 480 nm absorption bands is not that Bi-related NIR center producing the emission band shown in Fig. 5.

4. Discussion

4.1 Ascription of the origin of 480 nm absorption and 465 nm excitation bands

As stated in section 3.4, 480 nm absorption band shown in Fig. 3 is not related to Bi-related NIR center producing 1.3 μm emission as shown in Fig. 5.

For Bi-doped B_2O_3 -BaO- Al_2O_3 glass [25], the 700 nm absorption band which is the weaker one among the absorption bands, disappears when BaO is above 25 mol%. For B_2O_3 - Al_2O_3 -ZnO- K_2O - Bi_2O_3 glass [26], the weaker absorption band at 717 nm disappears with increasing B_2O_3 . However, 465 nm [25] or 455/460 nm [26] absorption band still remains. The intensity of 455/460 nm [26] or 465 nm [13] absorption band has a certain relationship with the melting temperature. For some bismuth borate glasses and bismuth potassium phosphate glasses, there is also a single absorption band at 475 nm or 443 nm [29]. For Bi_2O_3 - SiO_2 - GeO_2 glass [30], an absorption band near 500 nm can be observed without other accompanied bands until 1100 nm, and its intensity is related to the melting time. Although there is still no unanimous opinion about the nature of 500 nm absorption (Bi^+ , Bi^{2+} , Bi^{5+} , dimers, etc) [30], the above reported experimental results implies that 480 nm absorption band

shown in Fig. 3, as well as those reported absorption bands located at similar wavelength range, they are a common characteristic for some bismuthate or Bi-doped glasses, and they should be related to Bi. Due to energy level splitting in the ligand field, as well as possible different valence states, it seems difficult to identify an impurity ion as the center only producing a single 480 nm absorption band.

In our BBSG glasses, we did not observe any effective emission in the visible region when excited at 365, 405 and 465 nm. In Bi-doped sodium borosilicate glasses [24], there are 420 nm blue emission of Bi^{3+} excited by 312 nm, as well as 618 nm red emission of Bi^{2+} excited by 468 nm. And especially, if Bi-related NIR center producing 1.3 μm emission as shown in Fig. 5 indeed originates from Bi^+ as reported in [16, 17, 23–26], or Bi atoms as reported in [13], it can be suggested that: (1) the concentration of Bi^{3+} and Bi^{2+} is too low to be observed, since there is no effective visible emission for our Yb_2O_3 -doped BBSG glasses; (2) there is only a small amount of Bi^+ and/or Bi atoms in our Yb_2O_3 -doped BBSG glasses. As stated in section 3.4, the intensity of 1.3 μm emission band is far lower than that of 1.0 μm emission band of Yb^{3+} , as shown in Fig. 5. The concentrations of Bi^0 , Bi^+ , Bi^{2+} and Bi^{3+} would depend on a self-reduction process during glass preparation. The fact that there are less Bi^{3+} and Bi^{2+} indicates that the reduction reaction should be very strong. On the other hand, a lower content of Bi^+ and Bi^0 implies that most of the products of this reduction are most probably Bi^0 metal nanoparticles/grains clustered and accumulated from Bi^0 atoms.

Thus, there should be much more Bi^0 metal nanoparticles/grains in our Yb_2O_3 -doped BBSG glasses. It could be suggested that these Bi^0 metal nanoparticles/grains should be responsible for 480 nm absorption band in Fig. 3. In [31, 32], they ascribe 460 nm absorption of B_2O_3 -ZnO- Bi_2O_3 - SiO_2 - K_2O glass to metallic Bi^0 nanoparticles with 2–15 nm size, and these metal colloids with a certain size far smaller than the wavelength of incident light will result in surface plasmon resonance absorption. Although [33] does not show the spectroscopic result of 460 nm absorption perhaps due to dark sample color, a reduction reaction mechanism from $2\text{Bi}_2\text{O}_3$ to $4\text{Bi}^0 + 3\text{O}_2$ was proposed and confirmed on the basis of investigation on optical properties under various kinds of preparation conditions. In our opinion, it is reasonable to ascribe 460 nm absorption band to the surface plasmon resonance absorption on Bi^0 metal nanoparticles/grains [31, 32].

Although an excitation in 460 nm absorption band [32] presents a red emission at 630 nm, it is still suggested for Yb_2O_3 -doped BBSG glass that its 480 nm absorption, which cannot present any red emission, can be ascribed to the surface plasmon resonance absorption as stated in [31, 32]. The reason is that there is Bi^{2+} in B_2O_3 -ZnO- Bi_2O_3 - SiO_2 - K_2O glass [32], but there may be no Bi^{2+} in our BBSG glasses as stated in the above. Moreover, the refractive index of BBSG glass is generally greater than 2, and the index of B_2O_3 -ZnO- Bi_2O_3 - SiO_2 - K_2O is 1.76 [31]. Thus, it is 480 nm for the surface plasmon resonance absorption in our BBSG glass, rather than 460 nm [31].

As stated in section 3.2, both of 480 nm absorption and 465 nm excitation bands should result from the same center. Thus, Bi^0 metal nanoparticles/grains should be also responsible for 465 nm excitation band as shown in Fig. 1.

4.2 Assignment of the 405 nm excitation band

405 nm excitation band shown in Fig. 1 most probably corresponds to Bi^{3+} [10, 11] in our BBSG glass. For Bi_2O_3 - B_2O_3 glass containing 20–66 mol% of Bi_2O_3 [10], there is no absorption band around 480 nm. When Bi_2O_3 is more than 33 mol%, an absorption band appears in the wavelength range of 360–400 nm. With further increasing Bi_2O_3 , the absorption band is located at 400 nm [10]. This peak position corresponds to 405 nm excitation band of BBSG glass containing 60 mol% of Bi_2O_3 .

Usually, spectroscopic properties of Bi^{3+} ions in glasses and crystals are interpreted by the $^3\text{P}_1$, $^3\text{P}_0$, $^1\text{S}_0$ three-level scheme associated to absorption bands in UV and emission bands in the near UV and visible. The main reason for the observation of strongly forbidden transitions like

${}^3A_{1u}({}^3P_0) \rightarrow A_{1g}({}^1S_0)$ is the mixing of ${}^3T_{1u}({}^3P_1)$ and ${}^3A_{1u}({}^3P_0)$ electronic states by the T_{1g} vibrations [34].

According to the Yb_2O_3 -content dependence of 405 nm excitation in section 3.1, there is almost no Bi^{3+} when Yb_2O_3 is less than 4 mol%. With increasing Yb_2O_3 content, there exist a small amount of Bi^{3+} ions in BBSG glasses.

As stated in section 3.2, Yb_2O_3 -content dependence of 480 nm absorption band is really non-monotonic, as shown in Fig. 3. But a comparison between Fig. 3(a) and Fig. 3(b)/3(c) shows that the content of Bi^0 metal nanoparticles/grains is generally higher in the lower Yb_2O_3 doping range, as shown in Fig. 3(a); the content is generally lower in the higher Yb_2O_3 doping range, as shown in Fig. 3(b)/3(c). Thus: when the content of Bi^0 metal nanoparticles/grains is higher, there is almost no Bi^{3+} ; when the content of Bi^0 metal nanoparticles/grains becomes lower, there appears some Bi^{3+} .

According to the reported redox equilibrium between Bi^{3+} and Bi^0 [33], the concentrations of Bi^{3+} and Bi^0 must be changed reversely when the total amount of Bi is a constant.

4.3 Assignment of the 365 nm excitation band

Divalent Yb^{2+} ion [8, 9] should be the origin of 365 nm excitation band. It can be seen from Fig. 2 that the intensity of 365 nm excitation band generally tends to enhance with increasing Yb_2O_3 content in BBSG glasses. The assignment of Yb^{2+} is reasonable, since the concentration of Yb^{2+} in BBSG glasses should increase when doping more Yb_2O_3 . But the intensity of 365 nm excitation band has not a great increase from 6 to 7 mol%, as shown in Fig. 2. The reason will be discussed in section 4.4.

4.4 Two competing redox reactions

When oxidizing agent such as KNO_3 [31] or $K_2S_2O_8$ [32] was added into the bismuthate glass, the 460 nm absorption band becomes weaker and weaker. However, for Yb_2O_3 -doped BBSG glass, both 465 nm excitation and 480 nm absorption bands exhibit the same non-monotonic relation with Yb_2O_3 content. Their intensities are firstly decreased and then increased again, and especially a zero-intensity point occurs at 6 mol%, whether in the excitation or absorption spectra as shown in Fig. 1 and Fig. 3. It means that the content of Bi^0 metal nanoparticles/grains is firstly decreased greatly and then increased a little, with increasing Yb_2O_3 in BBSG glasses.

In our opinion, there should be two oxidation-reduction reaction processes in preparing Yb_2O_3 -doped BBSG glasses. One is between $Yb^{2+} \leftrightarrow Yb^{3+}$, other one is between $Bi^0 \leftrightarrow Bi^{3+}$. Especially, they will compete with each other, since these two reactions take place in the same glass host simultaneously. When increasing Yb_2O_3 content in BBSG glasses, there will be more and more Yb^{3+} ions. But Bi^{3+} ions come from BBSG glasses with an unchanged composition ratio. The initial concentration of Bi^{3+} , which could be utilized for reduction, should be a constant.

When Yb_2O_3 content level is below 4 mol%, a large percentage of Yb^{3+} is reduced and the concentration of Yb^{2+} is increased greatly. However, the reduction of Yb^{3+} restrains the reduction of Bi^{3+} . Thus, the contents of Bi^0 and Bi^0 metal nanoparticles/grains are decreased.

Especially when doping 6 mol% Yb_2O_3 , there seems no more reducing ability to reduce Bi^{3+} that could be reduced when there is not too many Yb^{2+} , because electrons have been attracted by more Yb^{3+} . Just at 6 mol%, 405 nm (Bi^{3+}) excitation band becomes dominating but 465 nm (Bi^0 metal nanoparticles/grains) excitation band almost fully disappears.

When doping more Yb_2O_3 , the concentration of Yb^{2+} is so high that it begins to further restrain the reduction of Yb^{3+} , due to balancing the redox reaction of $Yb^{2+} \leftrightarrow Yb^{3+}$. Thus, the concentration of Yb^{2+} tends to be a constant, and the remained reducing ability should be utilized to reduce Bi^{3+} . It is the reason that the content of Bi^0 (Bi^0 metal nanoparticles/ grains)

increases again in the Yb_2O_3 doping range of 7-9 mol%. The result is that the same non-monotonic dependence occurs for 480 nm absorption and 465 nm excitation bands.

4.5 Energy transfer to Yb^{3+}

896 nm excitation results in direct absorption transition of Yb^{3+} . There is no difference among the emission decay curves of Fig. 4(b), exciting at 300/450 nm and 896 nm, respectively. But the emission spectra and lifetime excited at 300 nm and 450 nm, as shown in Fig. 4(a) and 4(b), indicate definitely that the energy absorbed by Yb^{2+} and Bi^0 metal nanoparticles/grains is really transferred to Yb^{3+} in BBSG glasses.

About the energy transfer between Yb^{2+} and Yb^{3+} , there is some deep research on optical inorganic materials doped by Yb^{3+} [35, 36], including the charge transfer of Yb^{2+} and Yb^{3+} . Either by the f-d absorption or the charge transfer absorption of Yb^{2+} , Yb^{2+} can dissipate the absorbed energy to Yb^{3+} by a cooperative energy transfer. It is recently reported that three photon and phonon-assisted two photon cutting processes could be also the paths transferring from Yb^{2+} to Yb^{3+} [36].

After Bi^0 metal nanoparticles/grains absorb energy by their surface plasmon resonance absorption, they have to transfer the energy absorbed in the blue-green region to Yb^{3+} . Regarding the energy transfer path for silver nanocomposite glasses [37], it is suggested that the energy from the surface plasmon resonance absorption of Ag nanoparticles can be transferred to ionic Ag pairs/dimers by plasmon resonance energy transfer. As stated in section 4.4, Bi^0 metal nanoparticles/grains is the product accumulated from Bi^0 . During the clustering process, there may be some Bi^0 dimers formed in BBSG.

The absorbed energy by 465 nm excitation is a little higher than the virtual energy level of Yb^{3+} - Yb^{3+} . The virtual level lies around 500 nm, as shown in Fig. 4(c). It is most probably a very important link for the energy transfer relating to Yb^{3+} either for up-conversion or down-conversion [9, 35, 36].

Thus, the following energy transfer paths may occur for our Yb_2O_3 -doped BBSG. Probably Bi^0 dimer is the first link between Bi^0 metal nanoparticles/grains and the virtual energy level for Yb^{3+} . When the energy absorbed in the blue-green is transferred from Bi^0 metal nanoparticles/grains to the virtual level, there should be almost no quantum loss. And especially, the energy on the virtual level of Yb^{3+} - Yb^{3+} will excite two Yb^{3+} ions simultaneously. Finally, these two excited Yb^{3+} ions will produce 1 μm NIR emission from $^2\text{F}_{5/2}$ to $^2\text{F}_{7/2}$. Such an energy transfer mechanism could be of high transfer efficiency, which should be as high as the quantum cutting or down-conversion [36]. And thus it will play an important role in fluorescence enhancement, quantum cutting, etc, like observed for Ag or Au metal particles in luminophors.

5. Conclusions

There are three excitation bands located at 365 nm, 405 nm and 465 nm for $60\text{Bi}_2\text{O}_3$ - $20\text{B}_2\text{O}_3$ - 10SiO_2 - $10\text{Ga}_2\text{O}_3$ - $x\text{Yb}_2\text{O}_3$ ($x = 1$ -9 mol%) glasses. Yb_2O_3 -content-dependent excitation and absorption spectra in the blue-green exhibit the same non-monotonic relation between the intensities and Yb-content, revealing that both 465 nm excitation and 480 nm absorption bands originate from the same center. The intensity of 1 μm emission of Yb^{3+} excited in 465 nm and 480 nm bands is much stronger than that of 1.3 μm emission of a Bi-related center. The fact indicates that 465 nm and 480 nm bands are not related to the Bi-related center, which is not Bi^0 metal nanoparticles/grains and would be Bi^+ or Bi^0 atom as reported [13, 15–17, 23–26]. When excited at 365 nm, 405 nm and 465 nm, no visible emission can be observed, which means there are only a little Bi^{3+} and Bi^{2+} in the glasses and there exists a stronger reduction reaction between Bi^0 and Bi^{3+} . However, there exists other reduction reaction between Yb^{2+} and Yb^{3+} , indicated by 365 nm excitation band that is assigned to Yb^{2+} . Thus, there are two competing redox reactions in our Yb_2O_3 -doped BBSG glasses, causing the non-monotonic

Yb₂O₃-content dependence of 465 nm excitation and 480 nm absorption bands. Accordingly, both bands are ascribed to Bi⁰ metal nanoparticles/grains, which is the origin of 460 nm absorption band as reported in [31–33]. The red shift of 480 nm absorption band is mainly due to BBSG glass, a heavy metal oxide glass with a refractive index greater than 2.

The emission spectra and its decay curves excited in the violet-green and NIR range confirm the violet-green excitations can result in the NIR emission of Yb³⁺, and there must be energy transfer paths. If the ascription of 480 nm absorption and 465 nm excitation bands is true, it is of great importance to confirm the energy transfer between Bi⁰ metal nanoparticles/grains in BBSG glasses and Yb³⁺, i.e., Bi⁰ metal nanoparticles/grains can transfer the energy absorbed in the blue-green region to Yb³⁺ and finally result in the NIR emission. On the energy transfer paths, it could be suggested that: (1) By plasmon resonance energy transfer, Bi⁰ metal nanoparticles/grains transfer the energy to Bi⁰ dimers, like Ag pairs/dimers as reported in [37]; (2) Lying around 500 nm, the virtual energy level of Yb³⁺-Yb³⁺ might be the link between Bi⁰ dimers and Yb³⁺, which could excite two Yb³⁺ ions simultaneously, like two photon cutting process as reported in [36]. Of special interest is the material constitution of Yb₂O₃-doped BBSG glasses. It consists of two main parts: (1) Yb, which is an excellent laser ion for LD pumping; (2) Bi, which could be clustered to form nanoparticles. And especially, Bi⁰ metal nanoparticles/grains formed in Yb₂O₃-doped BBSG glass can be under controlled, not only by preparation parameters as well as an optional glass composition, and also by two competing redox reactions of Bi⁰↔Bi³⁺ and Yb²⁺↔Yb³⁺. It could achieve laser output in a subwavelength microresonator by the excitation of localized surface plasmons in metal nanoparticles with a designed structure [38, 39].