

doi:10.3788/gzxb20144303.0316001

Bi 和 Bi/Er 共掺钙铝锗酸盐玻璃的 超宽带红外发光

何禧佳^{1,2}, 周大成¹, 李臣¹, 陈明厚¹, 魏生贤², 邱建备¹

(1 昆明理工大学 材料科学与工程学院, 昆明 650093)

(2 曲靖师范学院 物理与电子工程学院, 云南 曲靖 655000)

摘 要: 研究了铋掺杂以及铋铒共掺铝钙锗酸盐玻璃的超宽带红外发光性质. 采用传统的熔融-退火方法获得所需玻璃. 铋离子掺杂钙铝锗酸盐红外发光峰可以分为 1 265 nm 和 1 420 nm 处的两个峰, 1 420 nm 处的峰强度较弱. X 射线光电子能谱测试结果表明, 玻璃中的铋离子以混合价态形式存在, 三价的铋离子可能被还原为低价态铋离子. 实验结果表明, 铋离子红外发光源于低价态铋离子, 可能源于一价 Bi^+ ; 铒离子掺杂影响铋离子发光, 随着铒离子浓度的增加, 铋离子红外发光减弱, 说明存在铋离子向铒离子的能量传递.

关键词: 近红外发光; 光学碱度; 能量传递; 光放大器; 吸收光谱; 锗酸盐玻璃

中图分类号: O433

文献标识码: A

文章编号: 1004-4213(2014)03-0316001-5

Bi-doped and Bi/Er Co-doped Calcium Aluminum Germanate Glasses with Ultra-broadband Infrared Luminescence

HE Xi-jia^{1,2}, ZHOU Da-cheng¹, LI Chen¹, TRAN Minh Hau¹,
WEI Sheng-xian², QIU Jian-bei¹

(1 College of Materials Science and Engineering, Kunming University of Science and
Technology, Kunming 650093, China)

(2 College of Physical and Electronic Engineering, Qujing Normal University, Qujing, Yunnan 655000, China)

Abstract: Luminescence from Bi and Bi/Er doped aluminum calcium germanate glasses were investigated. The glasses were prepared by conventional melting-quenching technique. The near infrared luminescence of Bi-doped calcium aluminum germanate glasses can be divided into two Gaussian peaks which are located at 1 265 and 1 420 nm separately. The X-ray photoelectron spectroscopy spectrum indicates the valence state of Bi ions in the calcium aluminum germanate glasses is the mixed. Bi^{3+} ions could be reduced to low valence states bismuth ions. The experiments support the assumption that the near-infrared luminescence is connected with a low valence state of Bi, may be Bi^+ . Er^{3+} was introduced to adjust the 1420 nm band of Bi-related fluorescence. With the increment of Er^{3+} concentration, near-infrared fluorescence relative intensity of Bi ions is decreasing, which implies the energy transfer from Bi ions to Er^{3+} .

Key words: Near infrared luminescence; Optical basicity; Energy transfer; Amplifier; Absorption spectra; Germanate glass

OCIS Codes: 160.2750;160.4670;300.6280

Foundation item: The National Natural Science Foundation of China (Nos. 51272097, 61265004)

First author: HE Xi-jia(1983-), female, lecturer, Ph. D candidate, mainly focuses on optical function material. Email: hexijia0521@163.com

Responsible author (Corresponding author): QIU Jian-bei(1970-), male, professor, Ph. D. degree, mainly focuses on optical function material. Email: qiu@kmust.edu.cn

Received: Jun. 14, 2013; **Accepted:** Sep. 23, 2013

<http://www.photon.ac.cn>

0 Introduction

The low loss wavelength region of dry optical fibers has been expanded from 1 200 to 1 700 nm^[1]. But the bandwidth of the traditional rare earth doped luminescent materials cannot surpass 100 nm due to the f-f transition confined in the inner shell^[2]. It is essential to explore new luminescent materials with much broader bandwidth covering this region for developing new amplifiers or lasers. Bismuth-doped glasses have been shown to be promising active material in this broadband Near - Infrared (NIR) region^[3].

Silica fiber is usually drawn at above 2 000 °C, whereas the boiling point of bismuth oxide is 1 890 °C, causing the lower concentration could leave in it^[4]. The melting temperature of GeO₂ glasses is lower than that of silicate glasses. Moreover, germanate glasses have better infrared transmittance character, more stable chemical durability, higher mechanical stability and lower phonon energy. Germanate glasses are attractive for their unique physical properties and have been extensively studied. However, there are few researches about calcium aluminum germanate glasses. Study found that Al₂O₃ and CaO could lead some good properties for germanate glasses^[4]. Ren *et al.* reported that the NIR emissions covering the whole low loss wavelength region of dry optical fibers from 75GeO₂-20CaO-5Al₂O₃-1Bi₂O₃ glass^[5]. This super broadband luminescence is not flatly and asymmetrically. Co-doping with some optically active species is a method to adjust emission schemes.

In this article, bismuth singly doped and Bi/Er co-doped Calcium Aluminum Germanate (CAG) glasses were investigated. GeO₂ was selected as glass network former, CaO was flux agent, and Al₂O₃ was both glass network former and network modifier. The optical basicity of CAG glass matrix is introduced to explain the origin of NIR luminescence of bismuth ions. And the energy transfer from bismuth ions to Er³⁺ is discussed.

1 Experiment

Three groups of glasses were prepared. The compositions of glasses are as follow:

Group one:

70GeO₂ · 18CaO · 12Al₂O₃ · *x*Bi₂O₃ (*x*=0, 0.5, 1.0 and 1.5 mol %).

Group two:

70GeO₂ · 18CaO · 12Al₂O₃ · 1Bi₂O₃ · *y*Er₂O₃ (*y*=0.05, 0.10 and 0.20 mol %).

Group three:

70GeO₂ · (18 - *z*)CaO · *z*Al₂O₃ · 1Bi₂O₃ ·

0.1Er₂O₃ (*z*=14,16 and 18 mol %).

Analytic reagents GeO₂, CaCO₃, Al₂O₃, Bi₂O₃ and Er₂O₃ were selected as raw materials. The 8g batches corresponding to the CAG glasses were respectively weighted and thoroughly homogenized in an agate mortar, and then melted at 1 550 °C for 30 min in alumina crucibles in air. Then the melts were cast onto a stainless steel plate and annealed at 560 °C for 3 hours. Each obtained glass sample was cut and polished into pieces with size of 10 × 10 × 2 mm³ for measurement.

The absorption spectra were performed using a Hitachi U-4100 spectrophotometer. The infrared luminescence spectra were obtained with a Zolix SBP300 spectrofluorometer with an InGaAs detector excited by 808 nm LD. The X-ray Photoelectron Spectra (XPS) were recorded on Aphi5000 VersaProbe spectrometer, the binding energy (BE) was referenced to the adventitious C1s line at 284.8 eV. All measurements were performed at room temperature.

2 Results

The color of the group one glasses turned gradually from colorless to deep reddish brown with increase of bismuth ions. The NIR emission of group one glasses firstly increase and then decline, the strongest fluorescence intensity was obtained in about 1.0 mol% bi-doped glass under the same measurement conditions at room temperature. Fig. 1 showed the emission spectrum of the 70GeO₂ · 18CaO · 12Al₂O₃ · 1Bi₂O₃ glass sample in the range of 1000 ~ 1800 nm excited by the 808 nm LD at room temperature. As can be seen in the figure, the peak was at about 1 300 nm and the Full Width at Half Maximum (FWHM) was more than 300 nm. According to the asymmetric feature of the spectrum, it could be decomposed into two Gaussian peaks which are at 1 265 and 1 420 nm separately, with a FWHM of 178 and 302 nm, respectively. The relative intensity of 1 265 nm was stronger than one of 1 420 nm.

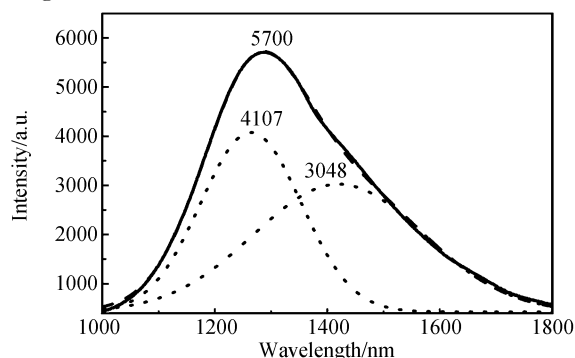


Fig. 1 Luminescence spectrum of 70GeO₂ · 18CaO · 12Al₂O₃ · 1Bi₂O₃ glass

The chemical state of Bi ions in the glass was obtained by Aphi5000 VersaProbe spectrometer. Fig. 2 shows the Bi 4f XPS spectrum of $70\text{GeO}_2 \cdot 18\text{CaO} \cdot 12\text{Al}_2\text{O}_3 \cdot 1\text{Bi}_2\text{O}_3$. The peaks of Bi $4f_{5/2}$ and Bi $4f_{7/2}$ were centered at 158.7 and 164.0 eV, which were consistent with that of Bi^{3+} reported [6]. However, the two peaks had asymmetric shape with small shoulders on the low binding energy side. The shoulders situated at about 157.4, 158.2, 162.6 and 163.3 eV, respectively. The shoulders of 157.4 and 162.6 eV could be assigned to the metal $\text{Bi}^{[6]}$. Generally, the higher binding energy of atom mean a higher valent state. The shoulders of 158.2 and 163.3 eV might origin from a medial state between Bi^0 and Bi^{3+} .

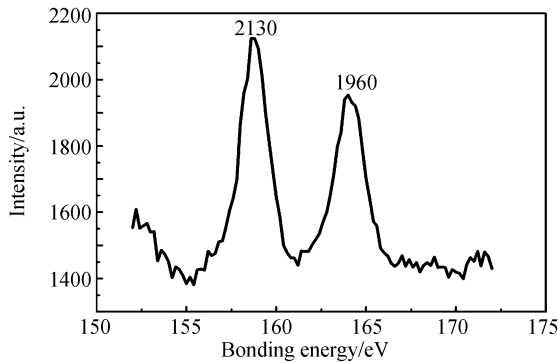


Fig. 2 Bi4f XPS for $70\text{GeO}_2 \cdot 18\text{CaO} \cdot 12\text{Al}_2\text{O}_3 \cdot 1\text{Bi}_2\text{O}_3$ glass

In order to improve the tail intensity of NIR luminescence of bismuth doped glasses, Er_2O_3 was introduced into samples. Fig. 3 shows the Er, Bi singly doped, Er-Bi co-doped and nothing doped glass samples' optical absorption spectra. The strong absorption bands below 300 nm could be ascribed to the intrinsic absorption of the CAG matrix. There were two absorption peaks at about 500 and 710 nm at the range of 200 to 1000 nm wavelength band of Bi singly doped glass. The phenomenon was similar with the silica-based glasses of work in reference [7]. Er^{3+} related absorption peaks located at 365, 378, 488, 521 and 652 nm. They could be assigned to the transitions from ground state $^4I_{15/2}$ to corresponding excited states.

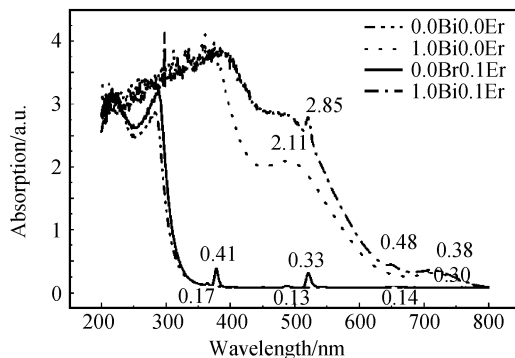


Fig. 3 Absorption spectra of Bi, Er singly-doped and Bi/Er co-doped CAG glasses

Fig. 4 showed the normalized fluorescence spectra

of $70\text{GeO}_2 \cdot 18\text{CaO} \cdot 12\text{Al}_2\text{O}_3 \cdot 1\text{Bi}_2\text{O}_3 \cdot y\text{Er}_2\text{O}_3$ ($y = 0, 0.05, 0.10, 0.20$ mol %) samples. With the increment of Er_2O_3 concentration, the relative intensities of Bi ions spectra decrease.

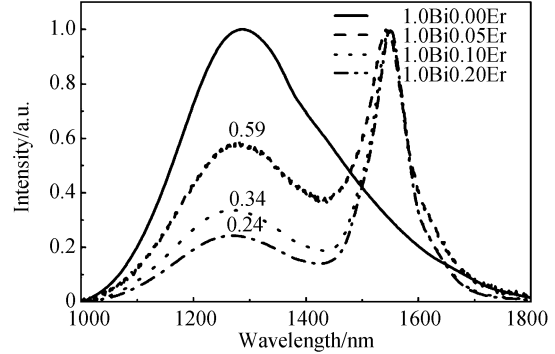


Fig. 4 Normalized luminescence spectra of $70\text{GeO}_2 \cdot 18\text{CaO} \cdot 12\text{Al}_2\text{O}_3 \cdot 1\text{Bi}_2\text{O}_3 \cdot y\text{Er}_2\text{O}_3$ ($y = 0, 0.05, 0.10, 0.20$) glasses

The NIR emission of bismuth ion was sensitive to crystal field. The relative fluorescence intensity of bismuth ions varied with glass compositions. As shown in Fig. 5, we could find that the NIR emission intensities of Bi/Er co-doped CAG glasses might be improved with the decrement of $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio.

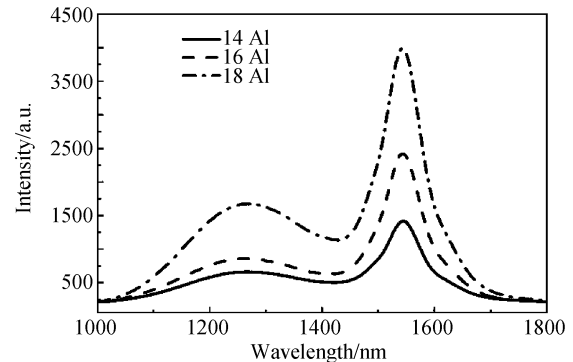


Fig. 5 Luminescence spectra of $70\text{GeO}_2 \cdot (18-z)\text{CaO} \cdot z\text{Al}_2\text{O}_3 \cdot 1\text{Bi}_2\text{O}_3 \cdot 0.1\text{Er}_2\text{O}_3$ ($z = 14, 16, 18$) glasses

3 Discussion

As can be seen in Fig. 1, the NIR emission of Bi could overlap the whole optical communication region. It was an attractive material for optical communication. Fujimoto *et al* concluded that the NIR emission would come from Bi^{5+} according to their experimental analysis [3,6]. In contrast, many experts considered lower valent bismuth ions, such as $\text{Bi}^{+[8-14]}$, Bi cluster [15], Bi_2 , Bi_2^- , $\text{Bi}_2^{2-[16-17]}$, etc, as the origin of NIR emission. However, the mechanism of Bi-related NIR luminescence has been still unclear.

The XPS spectrum indicated the valence state of Bi ions in the CAG glasses was the mixed. Bi^{3+} ions could be reduced to low valence states of Bi and Bi^{5+} ions would be less likely to be induced in these glasses. Bi^{5+}

ions might not be the NIR emission center.

According to optical basicity theory, the higher optical basicity favors the higher valence state of the multivalence metal ions. The optical basicity of glass matrix could be calculated as follow [18]:

$$\Lambda = x_1\Lambda_1 + x_2\Lambda_2 + x_3\Lambda_3 + \dots + x_n\Lambda_n \quad (1)$$

where, Λ_n was the optical basicity quantity of the n th composition of glass, and x_n was the molar fraction of the n th composition. The values Λ_n were from Ref. [19]. The calculated results of the optical basicity of group three glasses showed that the intensities of Bi-related emission decrease with the increase of the optical basicity (Fig. 5). We could infer that the Bi-related NIR fluorescence might originate from lower valence bismuth ions rather than Bi^{5+} .

In process of experiment, we found that the color of CAG glasses become more and more deep with the concentration of bismuth ions increasing, and small particles were sometimes observed at the bottom of crucibles. Romanov *et al* reported that adding Bi metal could produce black coloration of glass [20]. These small particles might be Bi metallic colloids [21,22]. When the CAG glasses become darker, viz. Bi metallic colloids increase, the Bi-related NIR luminescence didn't always increase, therefore the luminescent center may not be the Bi metallic colloids.

Bi^{3+} and Bi^{2+} were usually excluded as the NIR emission centers [6, 23-24]. But the NIR luminescence ranging from 1300 to 1700 nm wavelength region was observed from BiF, BiCl, BiBr, and BiI [20]. Base on above analysis, the NIR emission might arise from Bi^+ ions. But there has been no direct evidence identifying this conjecture.

Khonthon *et al.* suggested that $\text{Bi}_2^0/\text{Bi}_2^+$ may be responsible for NIR luminescence in Bi-doped glasses [20]. Sokolov *et al.* performed quantum chemical calculations on the electronic states of Bi_2^0 and Bi_2^+ and the results showed they are possible NIR emission centers [15], and so on. Further investigations are necessary to make the mechanisms of the Bi-related NIR luminescence clear.

The NIR luminescence of bismuth in CAG glasses was not symmetrical. Er^{3+} was introduced to improve its tail intensity. As shown in Fig. 4, the relative intensities of Bi-related luminescence decrease with the increasement of Er^{3+} concentration. This may be ascribed to energy transfer from Bi ions to Er^{3+} . The possible mechanism of the energy transfer could be drawn as Fig. 6. Since the origin of Bi-related NIR fluorescence was still ambiguous, we draw the Bi energy level on the basis of absorption spectra and emission spectrum. The ground state was defined as GS. The excited states were ES_1 , ES_2 , ES_3 , ES_4 and

ES_5 , corresponding to the peaks at 1420, 1265, 808, 710 and about 500 nm, respectively. Non-radiative transitions were showed by dotted lines. Radiative transitions were marked by solid lines. According to the Fig. 6, pumping at 808 nm the electrons would be excited to the third excited state in Bi and $^4\text{I}_{9/2}$ in Er^{3+} . If interaction between two states was neglected, the electrons would jump to ES_1 , ES_2 and $^4\text{I}_{13/2}$ states with a non-radiative process, respectively. And then release photons back to ground states. Noteworthy, $^4\text{I}_{9/2}$ and $^4\text{I}_{13/2}$ of Er^{3+} were partially overlapping ES_3 and ES_1 of Bi, the energy transfer between ES_3 and $^4\text{I}_{9/2}$ as well as ES_1 and $^4\text{I}_{13/2}$ would be induced by cross relaxations. The efficient energy transfer occurred from Bi ions to Er^{3+} ions. The Bi ions were sensitizers for the luminescence of Er^{3+} .

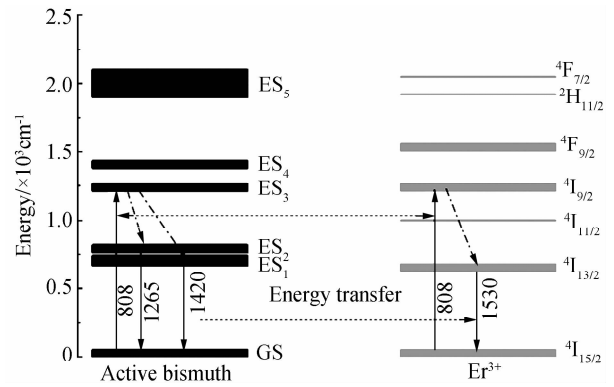


Fig. 6 Possible energy transfer mechanism from active Bi to Er^{3+}

4 Conclusions

In summary, the spectra of bismuth singly doped and Bi/Er co-doped CAG glasses were investigated. Enhanced Bi-related supper broadband NIR luminescence has been observed in CAG glasses when the optical basicity of glass matrix decreases. The NIR emission of Bi ions may arise from low valence bismuth ions, possible from Bi^+ . Er^{3+} co-doping leads to a decrease of Bi-related emission intensity but adjust schemes of the NIR luminescence. The NIR luminescence of Er_2O_3 could be sensitized by bismuth active centers.

References

- [1] THOMAS G, SHRAIMAN B, GLODIS P, *et al.* Towards the clarity limit in optical fiber[J]. *Nature*, 2000, **404**(6775): 262-264.
- [2] ZHOU Da-cheng, SONG Zhi-guo, CHI Guang-wei, *et al.* NIR broadband luminescence and energy transfer in Er^{3+} - Tm^{3+} -co-doped telluride glasses[J]. *Journal of Alloys and Compounds*, 2009, **281**(1-2): 881-884.
- [3] FUJIMOTO Y, NAKATSUKA M. Infrared luminescence from bismuth-doped silica glass [J]. *Japanese Journal of Applied Physics*, 2001, **40**(Part 2, No. 3B): L279-L281.
- [4] DVOYRIN V, MASHINSKY V, BUFETOV L, *et al.* Bismuth-doped-glass optical fibers - a new active medium for

- lasers and amplifiers[J]. *Optics Letters*, 2006, **31**(20): 2966-2968.
- [5] REN Jin-jun, QIU Jian-rong, WU Bo-tao, et al. Ultrabroad infrared luminescences from Bi-doped alkaline earth metal germanate glasses[J]. *Journal of Materials Research*, 2007, **22** (6): 1574-1578
- [6] FUJIMOTO Y. Local structure of the infrared bismuth luminescent center in bismuth-doped silica glass[J]. *Journal of the American Ceramic Society*, 2010, **93**(2): 581-589.
- [7] DAI Neng-li, XU Bing, JIANG Zou-wen, et al. Effect of Yb³⁺ concentration on the broadband emission intensity and peak wavelength shift in Yb/Bi ions co-doped silica-based glasses[J]. *Optics Express*, 2010, **18** (18): 18642-18648.
- [8] MENG Xian-geng, QIU Jian-rong, PENG Ming-ying, et al. Near infrared broadband emission of bismuth-doped aluminophosphate glass[J]. *Optics Express*, 2005, **13** (5): 1628-1634.
- [9] MENG Xian-geng, QIU Jian-rong, PENG Ming-ying, et al. Infrared broadband emission of bismuth-doped barium-aluminum-borate glasses[J]. *Optics Express*, 2005, **13** (5): 1635-1642.
- [10] REN Jin-jun, CHEN Dan-ping, YANG Guang, et al. Near infrared broadband emission from bismuth-dysprosium codoped chalcogenide glasses [J]. *Chinese Physics Letters*, 2007, **24**(7): 1958-1960.
- [11] YANG Guang, CHEN Dan-ping, REN Jin-jun, et al. Effect of melting temperature on the broadband infrared luminescence of Bi-doped and Bi/Dy co-doped chalcogenide glasses[J]. *Journal of the American Ceramic Society*, 2007, **90**(11): 3670-3672.
- [12] RUAN Jian, SU Liang-bi, QIU Jian-rong, et al. Bi-doped BaF₂ crystal for broadband near-infrared light source [J]. *Optics Express*, 2009, **17**(7): 5163-5169.
- [13] CHI Guang-wei, ZHOU Da-cheng, SONG Zhi-guo, et al. Effect of optical basicity on broadband infrared fluorescence in bismuth-doped alkali metal germanate glasses [J]. *Optical Materials*, 2009, **31**(6): 945-948.
- [14] SHANG Ji-hua, YANG Zheng-wen, LIU Zhi-liang, et al. Ultra broadband near infrared emission properties of bismuth doped Al₂O₃-MgO-SiO₂ glasses[J]. *Journal of the Chinese Ceramic Society*, 2010, **38**(11): 2129-2132.
- [15] PENG Ming-ying, QIU Jian-rong, CHEN Dan-ping, et al. Superbroadband 1310 nm emission from bismuth and tantalum codoped germanium oxide glasses [J]. *Optics Letters*, 2005, **30**(18): 2433-2435.
- [16] DENKER B, GALAGAN B, OSIKO V, et al. Absorption and emission properties of Bi-doped Mg - Al - Si oxide glass system[J]. *Applied Physics B*, 2009, **95**(4): 801-805.
- [17] SOKOLOV V, PLOTNICHENKO V, DIANOV E. Origin of broadband near-infrared luminescence in bismuth-doped glasses[J]. *Optics Letters*, 2008, **33**(13): 1488-1490.
- [18] DUFFY J, INGRAM M. An interpretation of glass chemistry in terms of the optical basicity concept[J] *Journal of Non-Crystalline Solids*, 1976, **21**: 373-410.
- [19] QI Ji, WANG Cheng-yu, NING Gui-ling. Application of optical basicity in glasses and its relationship with element properties[J]. *Journal of the Chinese Ceramic Society*, 2009, **28**: 1018-1023.
- [20] ROMANOV A, FATTAKHOVA Z, ZHIGUNOV D. et al. On the origin of near-IR luminescence in Bi-doped materials (I). Generation of low-valence bismuth species by Bi³⁺ and Bi⁰ synproportionation[J]. *Optical Materials*, 2011, **33**(4): 631-634.
- [21] SANZ O, HARO-POINATOWSKI E, GONZALO J, et al. Influence of the melting conditions of heavy metal oxide glasses containing bismuth oxide on their optical absorption [J]. *Journal of Non-Crystalline Solids*, 2006, **352**(8): 761-768.
- [22] KHONTHON S, MORIMOTO S, ARAI Y, et al. Redox equilibrium and NIR luminescence of Bi₂O₃ - containing glasses[J]. *Optical Materials*, 2009, **31**(8): 1262-1268.
- [23] MENG Xian-geng, QIU Jian-rong, PENG Ming-ying, et al. Near infrared broadband emission of bismuth-doped aluminophosphate glass[J]. *Optics Express*, 2005, **13** (5): 1628-1634.
- [24] PENG Ming-ying, DONG Guo-ping, WONDRAKZEK L, et al. Discussion on the origin of NIR emission from Bi-doped materials[J]. *Journal of Non-Crystalline Solids*, 2011, **357** (11-13): 2241-2245.