Long-Lasting ZnO-P2O5-SiO2:Mn2+ Glass for Optical Information Storage

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Research

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Abstract

The optical information storage $ZnO-P_2O_5-SiO_2:Mn^{2+}$ glass was prepared by the melting method. The photoluminescence (PL), long persistence luminescence (LPL) and photo-stimulated luminescence (PSL) show the same luminescence spectra with main peaks located at 607 nm. The research shows that the color of luminescence depends on the coordination environment of Mn^{2+} in the crystal lattice and the red luminescence depends on the $^4T_1(^4G)\rightarrow{}^6A_{1g}(^6S)$ electronic transition of Mn^{2+}. PSL and LPL phenomenon can't be observed in $70ZnO-10P_2O_5-20SiO_2$ glass, which indicates that Mn^{2+} ions serve as glowing centers in PSL and LPL phenomenon. Thermo-luminescence (TL) shows that the depth of the traps in glass is as high as 0.908eV. The 254 nm ultraviolet light was used to record information in the glass and read it under 980 nm infrared light excitation. The $ZnO-P_2O_5-SiO_2:Mn^{2+}$ glass in this work is a high-security level optical information storage medium.

Introduction

In recent years, electron trapping optical storage technology attracted widespread attention for its unique advantages. Compared with traditional storage technology, electron trapping optical information storage has the advantage of high storage density (approximately 10^{12}bit/cm^2), fast access speed and information multiplexing [1, 2]. As we all know, long persistence luminescence materials and photo-stimulated luminescence materials are all electron trapping luminescent materials, the luminescent phenomenon of PSL and LPL are closely related to the property of their traps, such as density and depth [3, 4]. The trap density determines the luminescence intensity, the trap depth determines whether the photo-stimulated luminescence phenomenon can be observed [5]. Unlike LPL materials is suitable for shallower trap levels, the trap depth of PSL luminescent materials is too deep to release the energy stored without photo-stimulated. Therefore, PSL materials are one of the ideal optical information storage materials [6–9]. In order to explore the PSL phenomenon mechanism, researchers at home and abroad have made many efforts, there is still not a consensus on the mechanism of photo-stimulated luminescence.

At present, researches of electron trapping materials are mainly concentrated in powder materials such as sulfides, halides and oxides [10–12]. There are few researches on glass electron trapping materials. Powder materials are prone to aging under long-term repeated irradiation of high-energy lasers and it is difficult to combine with other equipment. Glass has its unique advantages in electron-trapping optical storage for its uniform and transparent ability and strong thermal stability. In addition, the glass is simple in preparation and low in cost [13, 14]. Choosing fluorescent glass with high thermal stability and superior luminescence performance is the future direction of high-security level optical information storage. In this work, we synthesized $70ZnO-10P_2O_5-20SiO_2:0.1Mn^{2+}$ glass with optical information storage function by high temperature melting. The TL curve shows that the trap depth and trap concentration in $70ZnO-10P_2O_5-20SiO_2:0.1Mn^{2+}$ glass are suitable for optical information storage. In addition,we measured the

PL, LPL and PSL spectra and analyzed the process of carrier capture and release. Through the mask, the patterned information can be stored inside the glass and read it under 980nm infrared light excitation.

Materials And Methods

The colorless transparent $70ZnO\text{-}10P_2O_5\text{-}20SiO_2\text{-}xMnCO_3$(x = 0.1, 0.2, 0.3, 0.5, 1) glasses were successfully synthesized by melting method. The starting materials are ZnO, P_2O_5, SiO_2, $MnCO_3$ (99.9%). In this work, we weighed 15g of raw materials and mixed all the raw materials in an agate mortar for 2 hours. First, it was melted in a furnace at 1400°C for 1 hour, then the glass was quickly poured onto a smooth copper plate and pressed into shape with another copper plate. Finally, after annealing in a box furnace at 450°C for 30 minutes, we can get $70ZnO\text{-}10P_2O_5\text{-}20SiO_2\text{-}xMnCO_3$(x = 0.1, 0.2, 0.3, 0.5, 1) samples.

All polished sample were used for the following measurements. PLE, PL, LPL and PSL spectra of $70ZnO\text{-}10P_2O_5\text{-}20SiO_2{:}0.1Mn^{2+}$ glass were measured by FLS920 fluorescence spectrometer equipped with 450W continuous xenon lamp. TL spectra of $70ZnO\text{-}10P_2O_5\text{-}20SiO_2{:}0.1Mn^{2+}$ glass was measured by 2D/3D thermoluminescence spectrometer. The optical storage phenomenon diagram is obtained from the self-made optical system.

Results And Discussion

Fig.1 exhibits the excitation and emission spectra of $70ZnO\text{-}10P_2O_5\text{-}20SiO_2{:}0.1Mn^{2+}$ glass. As we can see in Fig.1(a), when the monitoring peak is at 607 nm, the excitation peak of $70ZnO\text{-}10P_2O_5\text{-}20SiO_2{:}0.1Mn^{2+}$ glass is around 254nm. In addition, PL spectra of $70ZnO\text{-}10P_2O_5\text{-}20SiO_2{:}0.1Mn^{2+}$ glass is shown in the Fig.1(b), under 254 nm ultraviolet light irradiation, $70ZnO\text{-}10P_2O_5\text{-}20SiO_2{:}0.1Mn^{2+}$ glass emits bright red luminescence. The emission shows a wide band and concentrates at 607 nm.
These results suggest that the broad band emission near 607nm is originated from $^4T_1(^4G)\rightarrow{}^6A_{1g}(^6S)$ of Mn^{2+} [15,16], so we can see bright red fluorescence. Meanwhile, the color of luminescence depends on the coordination environment of Mn^{2+} in the crystal lattice. When Mn^{2+} exists in the crystal lattice with four coordination (CN=4), the luminescence color is green; when CN=6, it's red [17,18]. From this, we can judge that Mn^{2+} exists in the form of six coordination in $70ZnO\text{-}10P_2O_5\text{-}20SiO_2{:}0.1Mn^{2+}$ optical storage material.

Fig.2 exhibits the LPL emission spectra of $70ZnO\text{-}10P_2O_5\text{-}20SiO_2{:}0.1Mn^{2+}$ glass. Apart from PL phenomenon, we can also observe the obvious red LPL phenomenon of $70ZnO\text{-}10P_2O_5\text{-}20SiO_2{:}0.1Mn^{2+}$ glass after 254 nm ultraviolet light irradiation. Fig.2(a) shows the LPL spectra of $70ZnO\text{-}10P_2O_5\text{-}20SiO_2{:}0.1Mn^{2+}$ glass is same as the PL spectra, which the main peak values all located at 607 nm. Combined with the analysis of fluorescence spectrum, the emission of PL and LPL are all originated from $^4T_1(^4G)\rightarrow{}^6A_{1g}(^6S)$ of Mn^{2+}. From Fig.2(b), it can be seen that the LPL exhibits two processes of initial fast decay and subsequent slow decay. From this we can get the attenuation of the signal light when the material is reading out. Different from other rare earth doped ions, Mn^{2+}doped $70ZnO-10P_2O_5-20SiO_2$ glass has suitable trap depths and laid the foundation for LPL and PSL. The long persistence luminescence intensity attenuation can be described by the following equation:

$I=A_1 \exp(-x/t_1)+ A_2 \exp(-x/t_2)+y_0$

All data are in the second order exponential curve graph of the afterglow attenuation spectrum and the fitted correlation coefficient is 99.64%. The total decay lifetimes can be described by the following formula: [19]

$t=(A_1t_1^2 + A_1t_2^2)/(A_1t_1 + A_1t_2)$

from this, we can know the average decay lifetimes is 66.39s.

Fig.3 exhibits the PSL emission spectrum of $70ZnO-10P_2O_5-20SiO_2:0.1Mn^{2+}$ glass. After pre-irradiating with 254 nm ultraviolet light for 10 minutes and wait until the afterglow is disappeared, re-exciting with 980 nm infrared light can obtain the red PSL phenomenon. Combined with fluorescence spectrum analysis, the emission of LPL and PSL originated from $^4T_1(^4G)\rightarrow{}^6A_{1g}(^6S)$ of Mn^{2+}. However, PSL phenomenon cannot be obtained in $70ZnO-10P_2O_5-20SiO_2:0.1Mn^{2+}$ glass if without pre-irradiating with 254 nm ultraviolet light for 10 minutes. This indicates that 980nm re-excited $70ZnO-10P_2O_5-20SiO_2:0.1Mn^{2+}$ glass luminescence originated from the energy stored in deep trap levels rather than up-conversion luminescence. Besides, the PSL and LPL phenomenon can't be observed in $70ZnO-10P_2O_5-20SiO_2$ glass, which indicates that Mn^{2+} ions serve as glowing centers in PSL and LPL phenomenon. As we all know that LPL and PSL property are related to doped ions and trap depth. Doped ions determine the luminescence colour, the trap depth determines whether the photo-stimulated luminescence phenomenon can be observed. In this work, since the luminescence centers are all Mn^{2+} ions, the spectra of LPL and PSL are the same. The difference is that LPL and PSL are derived from different trap energy levels in $70ZnO-10P_2O_5-20SiO_2:0.1Mn^{2+}$ glass. PSL decay also exhibits two processes of initial fast decay and subsequent slow decay. Compared with LPL decay, the electron transition process is similar to the emission process, but the intensity of the excitation energy and the source of the released electrons are different. In this work, the emission of LPL and PSL are all originated from $^4T_1(^4G)\rightarrow{}^6A_{1g}(^6S)$ of Mn^{2+} and the attenuation curves of LPL and PSL are similar. Due to the unique advantages of glass, the $70ZnO-10P_2O_5-20SiO_2:0.1Mn^{2+}$ glass is a high-security level optical information storage medium.

Fig.4 shows the relationship of Mn^{2+} contents and relative Intensity of $70ZnO-10P_2O_5-20SiO_2:xMn^{2+}$ (x=0.1, 0.2, 0.3, 0.5, 1) glass. The spectra show that the luminescence intensity decrease as the Mn^{2+} contents increase. When the Mn^{2+} doping content reaches 1 mol%, LPL and PSL disappear due to the concentration quenching. With the increase of Mn^{2+} content, its distribution tends to be dense. Due to the same energy level structure between adjacent Mn^{2+}, the outer electron orbits will connect to form an electronic bridge. This electronic bridge makes the motion interval of the excited electrons of adjacent Mn^{2+} emission center overlap, and the electrons move back and forth between the two emission centers. Even if there are oxygen vacancies with a suitable depth around, electrons will not fall into them with a high probability (that is, concentration quenching occurs), so that the charge density trapped by the traps decreases.

At present, we usually use TL spectroscopy to gain insight into internal defect structure of electron trapping optical storage materials. In order to understand the trap properties of 70ZnO-10P_2O_5-20SiO_2:0.1Mn^{2+} glass such as trap depth and trap density, TL curves of the glass are measured and shown in Fig.5(a). The TL curve of 70ZnO-10P_2O_5-20SiO_2:0.1Mn^{2+} shows a wide band from 300K to 600K, so we can see obvious LPL phenomenon and PSL phenomenon. As shown in the Fig.5(b), the TL curves were concentrated at 454K after Gaussian fitting. The TL curve of 70ZnO-10P_2O_5-20SiO_2:0.1Mn^{2+} shows a wide band with a concentration at 454 K, from this we can assess the depth of the electronic trap. We can get the depth of the electronic trap by the following formula: [20]

$E=T_m/500$

Where, T_m is the Thermo-luminescence peak. The activation energy is 0.908eV for the result of 70ZnO-10P_2O_5-20SiO_2:0.1Mn^{2+} glass. Electron trapping materials with stable optical properties require the matrix to have concentrated distribution of high-concentration deep trap energy levels (trap energy level depth>0.8eV) [21]. In fact, PSL is suitable for deep traps because deep traps can permanently fix the carriers. In this work, the emission of LPL and PSL are all originated from $^4T_1(^4G)\rightarrow{}^6A_{1g}(^6S)$ of Mn^{2+} and the spectrum of LPL and PSL are similar. The difference is that the intensity of the excitation energy and the source of the released electrons are different. It shows that under 980 nm infrared light and high temperature heat stimulation, the intensity of TL curve of deep traps is significantly reduced.

After irradiating 254 nm ultraviolet light through the photomask, the specific information pattern is stored in colorless transparent glass, and there is almost no afterglow after the sample is placed 12 hours at room temperature. When the colorless transparent glass was heated to 180°C, as shown in the Fig.6, the image “NJUPT” and the horse pattern are clearly displayed in the dark. Information can be written and read in colorless transparent glass due to the thermal stability and high transparency of the glass, which means that not only the service life can be greatly increased, but also the data security can be improved by changing the laser focus depth. Similarly, 980 nm infrared light can be used to read the information in the colorless transparent glass. Experiments show that after 24 hours of irradiating with 254 nm ultraviolet light, the red bright spot can be still observed by irradiating the colorless transparent glass with 980nm infrared light. If the area illuminated by high-energy photons is defined as“1”in the binary information and the area not illuminated by high-energy photons is defined as“0”in the binary information, the storage of digital information can be recorded. Different from high temperature heat stimulation, the readout of optical information under 980 nm infrared light stimulation provides a remote control method, which suggested a different application for future optical information storage.

In order to explore the PSL and LPL phenomenon mechanism, we put forward the possible explanations. According to TL analysis, 70ZnO-10P_2O_5-20SiO_2: Mn^{2+} glass samples have a wide continuous trap depth distribution from 300K to 600K. The TL peak of Mn^{2+} doped 70ZnO-10P_2O_5-20SiO_2 glass samples was 454 K (trap depth was 0.908eV). As we can see in the Fig.7, After irradiating 254 nm ultraviolet light, the electrons located at Mn^{2+} $^4T_1$ (^4G) will be excited to a higher excited state of $^6A_{1g}$ (^6S), so we can see bright red PL. Mn^{2+}doped 70ZnO-10P_2O_5-20SiO_2 glass has suitable trap depths and laid the foundation for LPL and PSL. After pre-irradiating with 254 nm ultraviolet light for 10 minutes, electrons can be captured by different trap levels and we can see obviously LPL and LPL exhibits two processes of initial fast decay and subsequent slow decay. LPL is suitable for shallow traps because shallow traps cannot permanently fix the carriers. By applying external 980 nm light stimulation, electrons captured by deep trap levels re-excited and recombine with the luminescence center Mn^{2+} to emit light. In this work, the emission of LPL and PSL are all originated from $^4T_1(^4G)\rightarrow{}^6A_{1g}(^6S)$ of Mn^{2+}.

Conclusion

In this work, the colorless transparent 70ZnO-10P_2O_5-20SiO_2:0.1Mn^{2+} glass was successfully synthesized by melting method. After pre-irradiating with 254 nm ultraviolet light for 10 minutes and the afterglow is disappeared, re-exciting with 980 nm infrared light can obtain the PSL phenomenon. When the Mn^{2+} doping content reaches 1 mol%, LPL and PSL disappear due to the concentration quenching. With the increase of Mn^{2+} content, its distribution tends to be dense. The TL curve shows that the trap depth and trap concentration in 70ZnO-10P_2O_5-20SiO_2:0.1Mn^{2+} glass are suitable for optical information storage. Compared with the PL spectrum, the LPL and PSL spectrum are both attributed to $^4T_1(^4G)\rightarrow{}^6A_{1g}(^6S)$. Experiments show that 70ZnO-10P_2O_5-20SiO_2:0.1Mn^{2+} colorless transparent glass is a high-security level optical information storage medium.

Declarations

Acknowledgments

Not applicable.

Authors' contributions

Tao Zheng is responsible for data collection and article writing. Haoran Xu is responsible data collection, Xiangfu Wang and Xiaohong Yan are responsible for the guidance of data articles.

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Availability of data and materials

All details have been provided in the article.

Competing interests

The authors declare that they have no competing interests.

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Figures

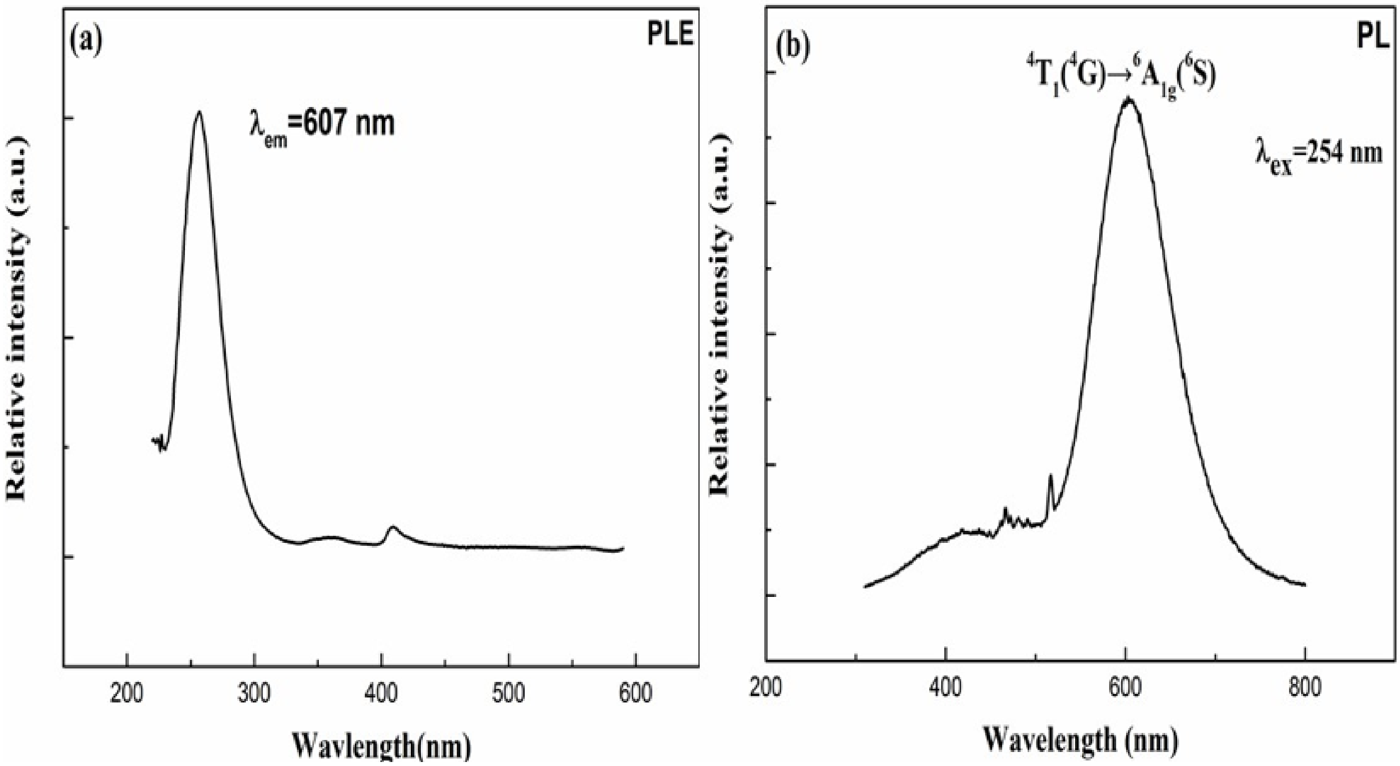

Figure 1

The PLE and the PL spectra of 70ZnO-10P2O5-20SiO2:0.1Mn2+ glass

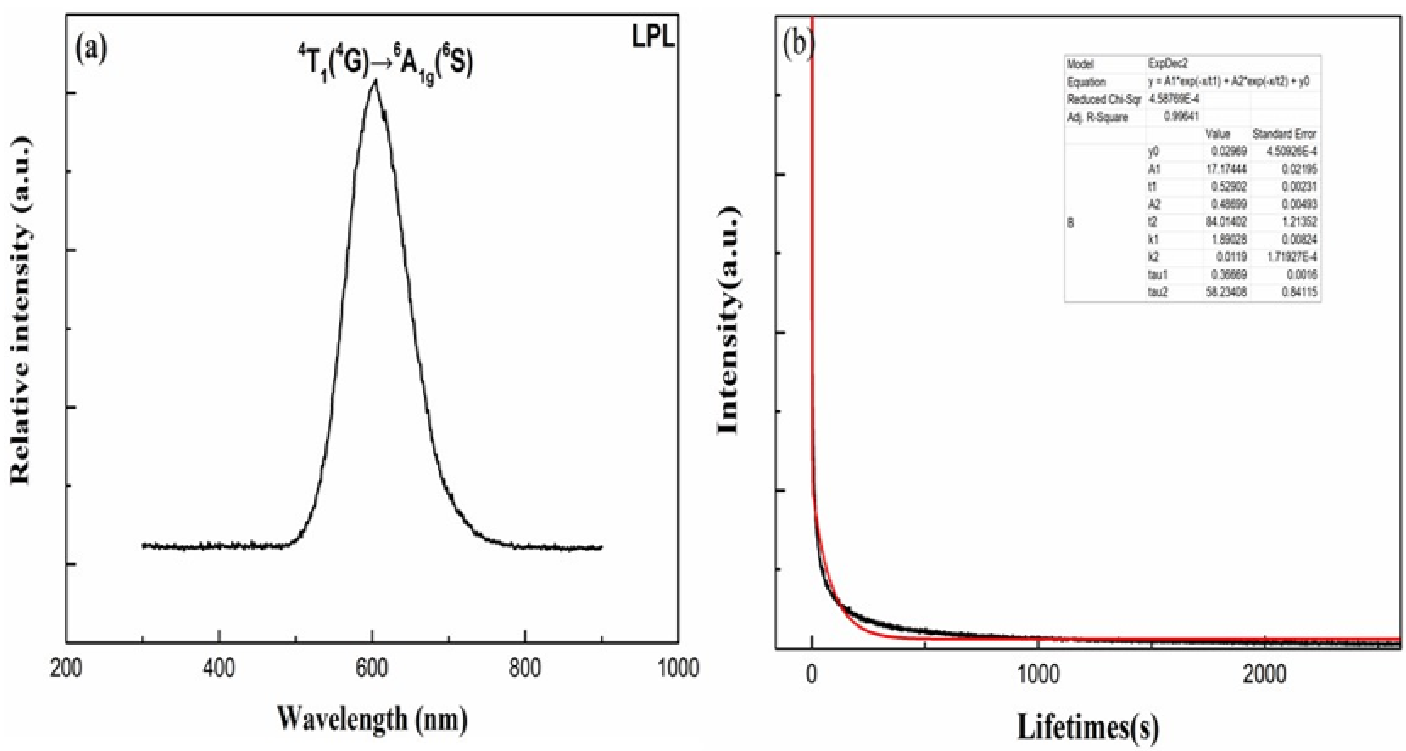

Figure 2

The LPL spectra and LPL decay curves of 70ZnO-10P2O5-20SiO2:0.1Mn2+ glass after pre-irradiating under UV (254 nm)

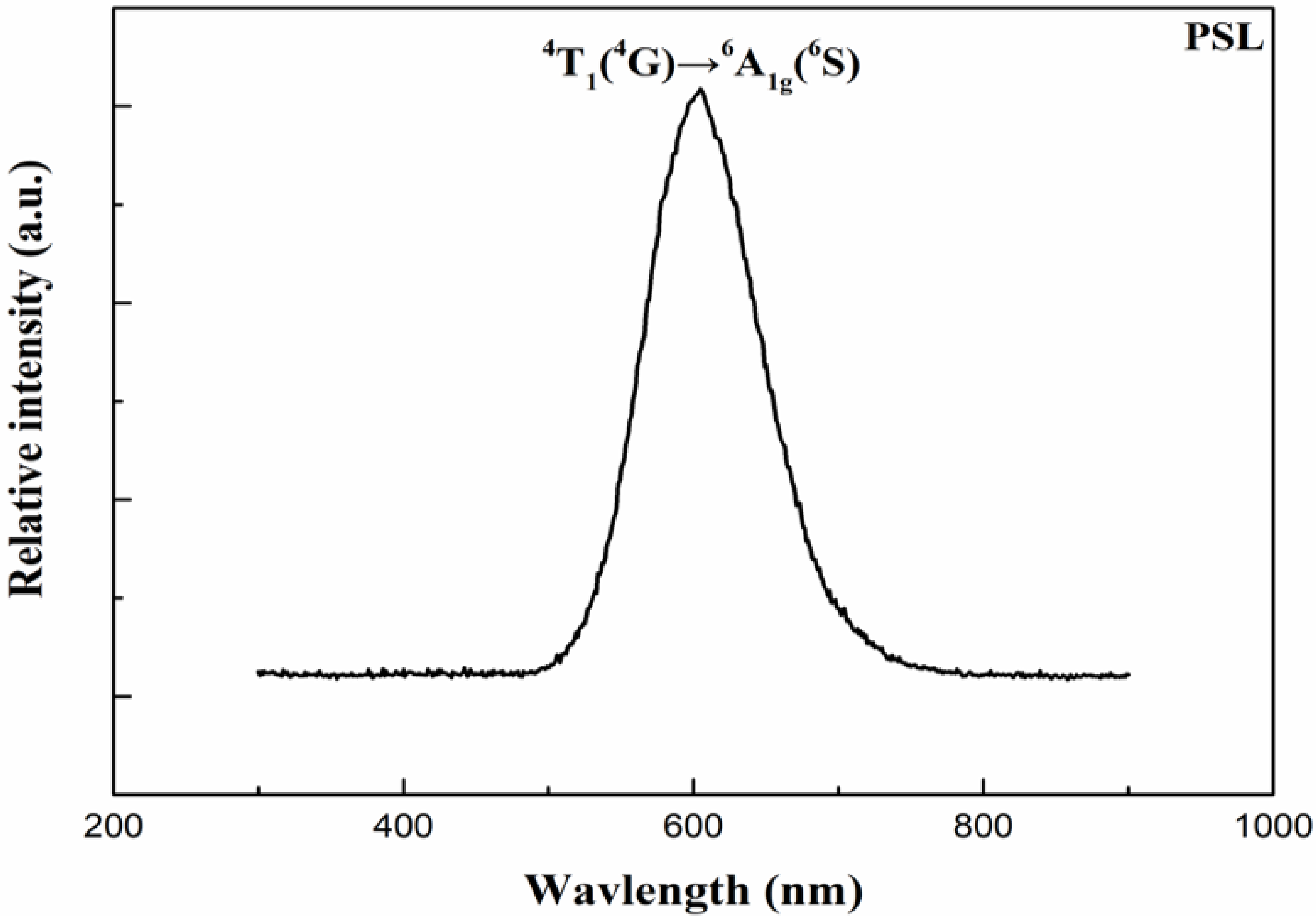

Figure 3

The PSL spectra of 70ZnO-10P2O5-20SiO2:0.1Mn2+ glass under 980 nm stimulation after pre-irradiating under UV (254 nm)

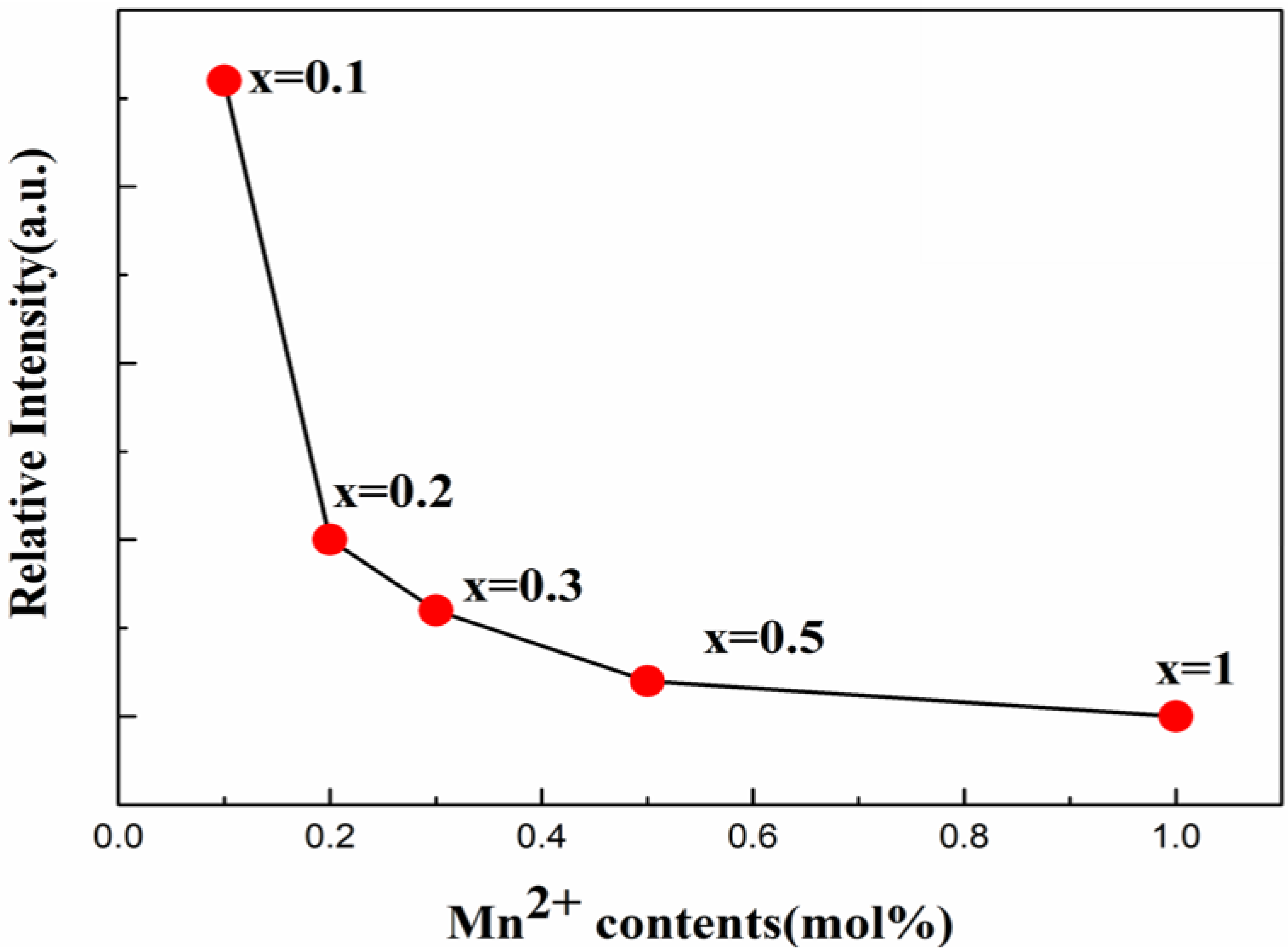

Figure 4

The relationship of Mn2+ contents and Relative Intensity of 70ZnO-10P2O5-20SiO2:xMn2+ (x=0.1, 0.2, 0.3, 0.5, 1) glass

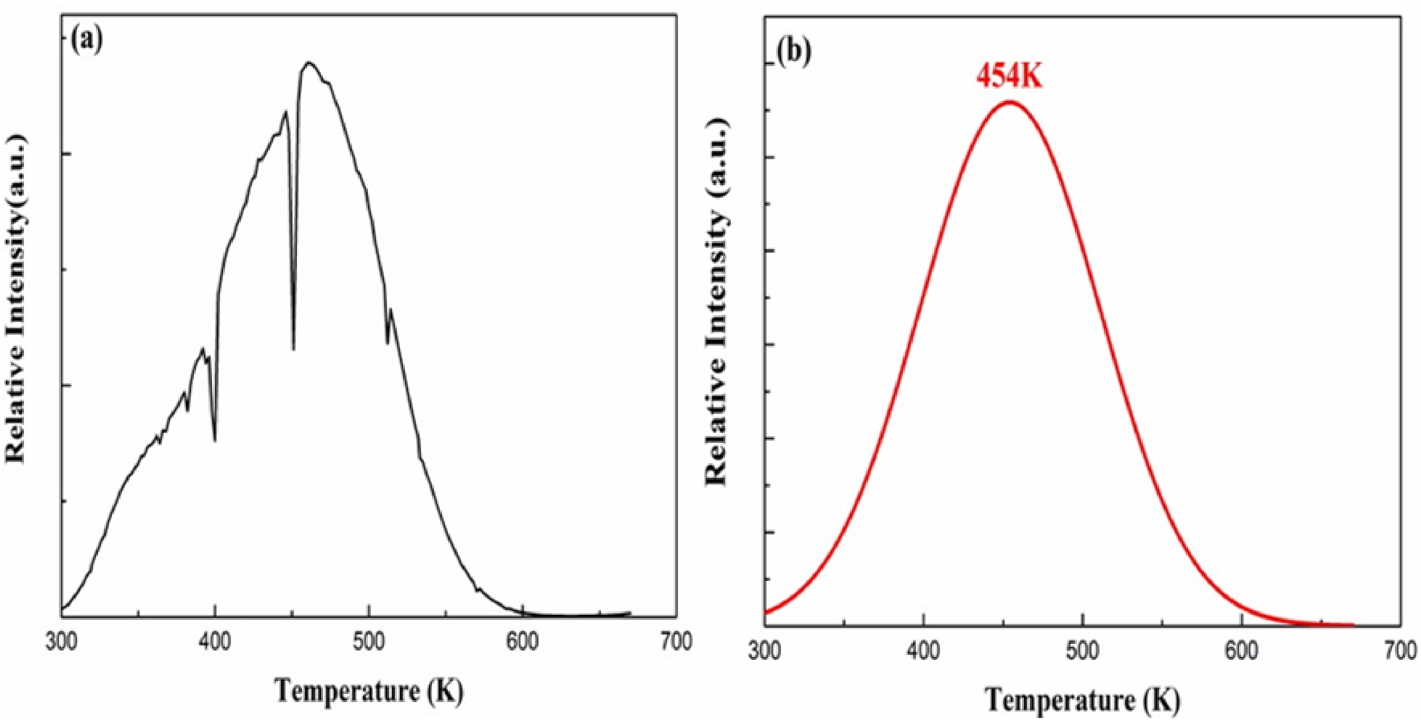

Figure 5

(a) Thermal luminescence spectrum of 70ZnO–10P2O5–20SiO2:0.1Mn2+; (b) Thermal luminescence spectrum of 70ZnO–10P2O5–20SiO2:0.1Mn2+ after Gaussian fitting

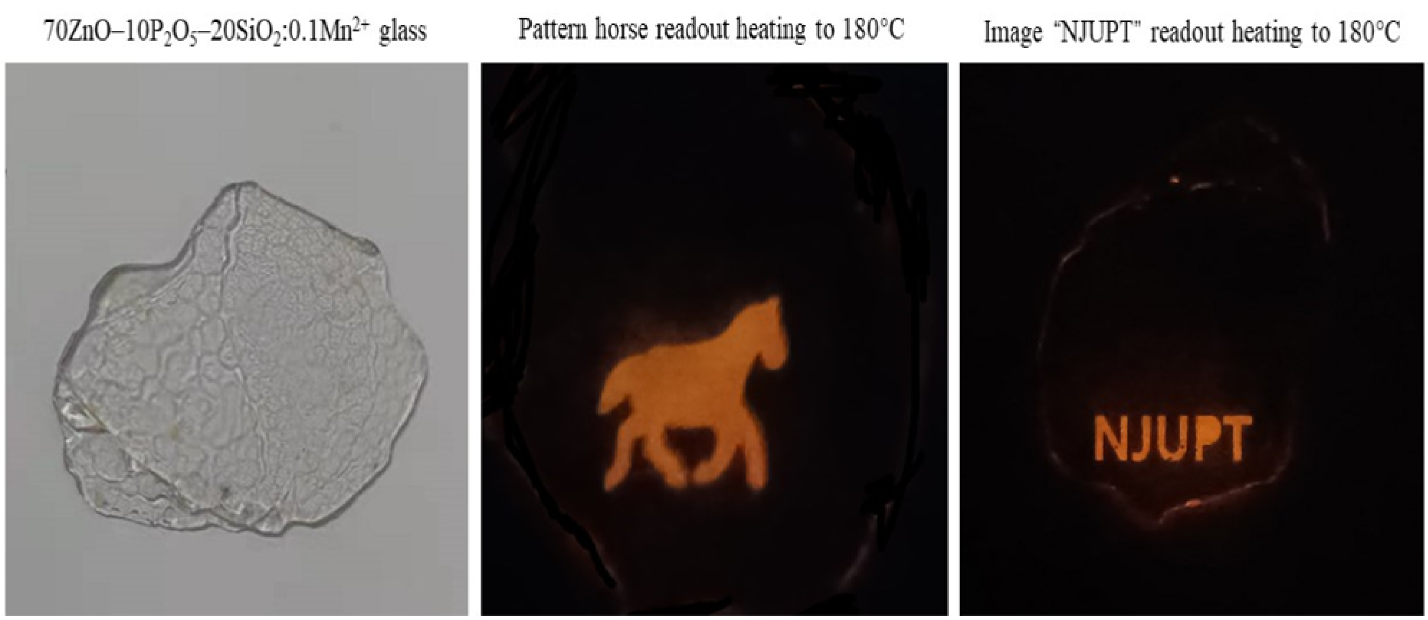

Figure 6

The write-in using UV (254 nm) irradiation and read-out (heating at 180 °C) of the image “NJUPT” and the horse pattern on the glass

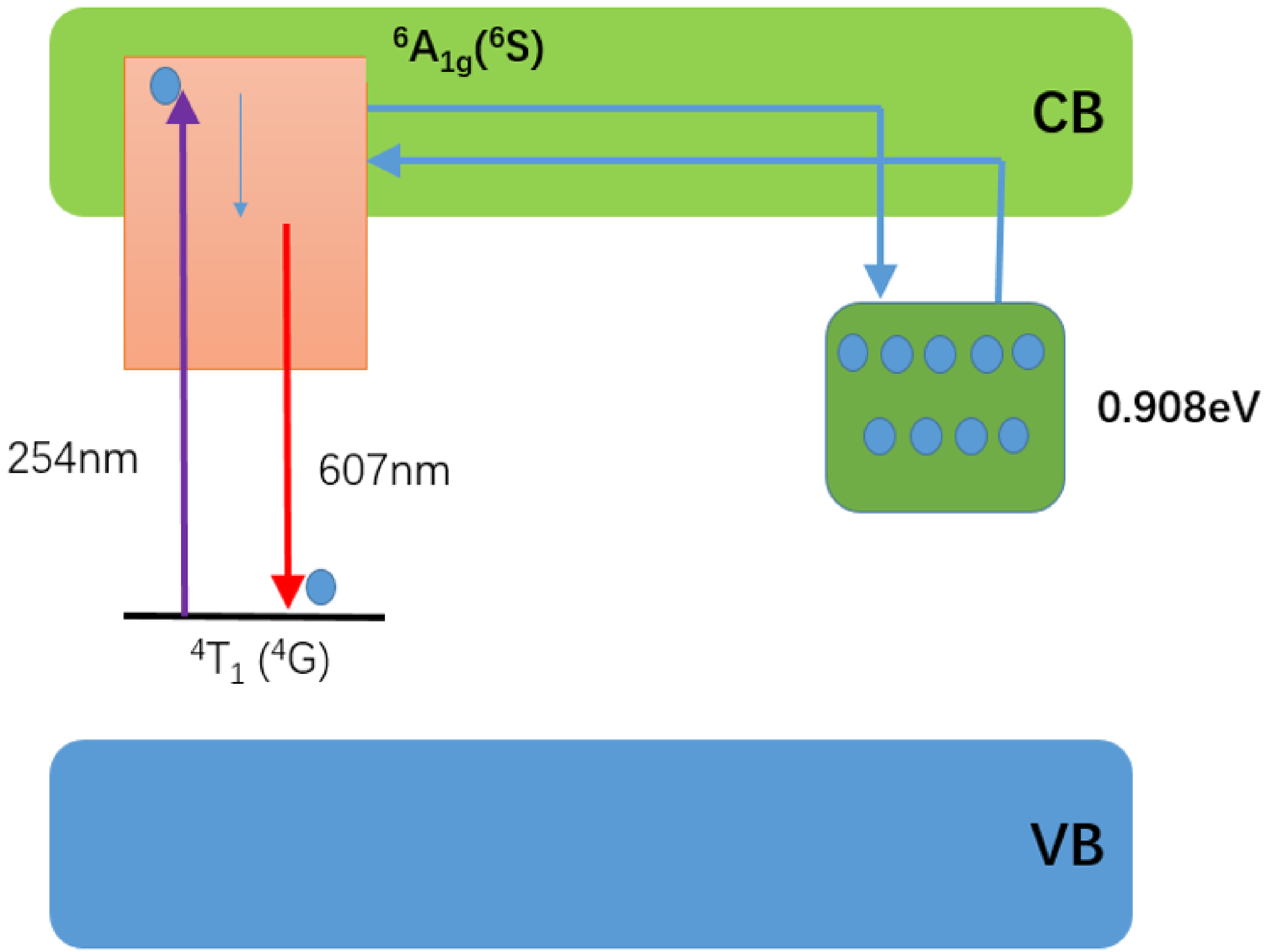

Figure 7

Schematic representation of the LPL and PSL mechanisms in 70ZnO-10P2O5- 20SiO2:0.1Mn2+ glass