VNU Journal of Science, Mathematics - Physics 24 (2008) 181-187

The role of color luminescence centers Mn, Cu, Co in the semicondutors with wide band gap ZnS, ZnO and their applications

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Received 22 May 2008; received in revised form 15 December 2008

Abstract. In this paper, materials of ZnS:Cu, ZnS:Mn and ZnO:Co were prepared by ceramic method and co-precipitated method. The presence of transition metals such as $Cu^{2+}(3d^9)$, $Mn^{2+}(3d^5)$ in ZnS and $Co^{2+}(3d^7)$ in ZnO make blue bands at around 476 nm, 486 nm and green band at around 514 nm disappeared. Simultaneously, there are luminescence bands at around 533 nm, 582 nm, 693 nm for bulk samples of ZnS:Cu, ZnS:Mn, ZnO:Co and 603 nm for nanocrystalline sample of ZnS:Mn. These bands are characterized by Cu^{2+} ions, Mn^{2+} ions: $[^4T_1\text{-}^6A_1]$ and Co^{2+} ions: $[^4T_1\text{-}^4A_2]$ in ZnS:Cu, ZnS:Mn and ZnO:Co, respectively. Time-resolved luminescence spectra of these samples show that lifetime of electrons at excited states is 1.90 ms, 0.79 ms and 8.60 μs corresponding to bulk sample ZnS:Mn, nanocrystalline sample ZnS:Mn and bulk sample ZnS:Cu. The luminescence material of ZnS:Cu has been tested in off-set print for anti-imitated stamps.

Keywords: ZnS, ZnO, photoluminescence (PL), time-resolved PL spectra.

1. Introduction

ZnS, ZnO are semiconductors with wide band gap (E_g = 3.70 eV and 3.37 eV for ZnS, ZnO at 4.2K, respectively). These materials were applied widely in the field of electroluminescence displays such as luminescence diodes, cathode ray tube, transparent windows… [1-4]

In visible region, the photoluminescence (PL) spectra of ZnS materials include two wide luminescence bands at around 460 nm (blue band) and 515 nm (green band). These bands are characterized by the vacancies of Zn bonding to Cl (V_{Zn}-Cl) and some impurities in ZnS crystal [5]. PL spectra of ZnO include luminescence bands at around 380 - 410 nm, 500 - 530 nm and 590 - 620 nm... These bands are characterized by the radiation of free excitons, donor-acceptor pairs relating to vacancies of oxygen, zinc and some impurities in ZnO crystal [6].

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When doping Cu, Mn in ZnS and Co in ZnO, the self-activated luminescence bands characterized by vacancies of zinc and oxygen are extinguished or their intensities decrease. In PL spectra of ZnS:Cu, ZnS:Mn and ZnO:Co appear luminescence bands at around 533 nm, 582 nm and 693 nm, respectively. These luminescence bands are characterized by Cu^{2+}, Mn^{2+}, Co^{2+} ions [7-11]. In this paper, we study the role of color luminescence centers Cu, Mn, Co in the semiconductors with wide band gap of ZnS, ZnO and test application of ZnS:Cu material.

2. Samples and experimental devices

Bulk samples of ZnS, ZnS:Cu (x_{Cu} = 0÷5.10^{-4} mol%), ZnS:Mn (x_{Mn} = 0÷1.2.10^{-2} mol%) were prepared by the solid state reaction method in argon and ZnO:Co (x_{Co} = 2.10^{-2}÷2.10^{-1} mol%) in air enviroment. Annealing temperature and time were varied in range from 700°C to 1250°C and from 15 minutes to 36 hours [12-14]. Nanocrystalline sample ZnS:Mn (x_{Mn} = 10^{-3}÷10^{-2} mol%) was prepared by the co-precipitated method with initial chemical $ZnCl_2$, Na_2S and $MnCl_2$ and annealed in argon[15].

The crystalline structure of these samples was investigated by X-Ray diffraction (XRD) patterns on D8-Advance Brucker equipment using CuK_α radiation (λ_α = 1.5056 A^0, $2\theta = 10^0 - 70^0$). The scanning electron microscopy (SEM) image measurement is carried out on JEOL5410-VL equipment. PL spectra of these materials at 300 K were excited by the wavelengths of 325 nm from He-Cd laser, 632.8 nm from He-Ne laser and recorded on Microspec 2300i, Varian 100 spectrometer. Time-resolved PL spectra measurements were excited by the wavelength of 337 nm from N_2 laser and recorded on Jobin Yvon HRD1, GDM-1000 spectrometer using boxca technique.

3. Results and discussion

3.1. Study of structure properties

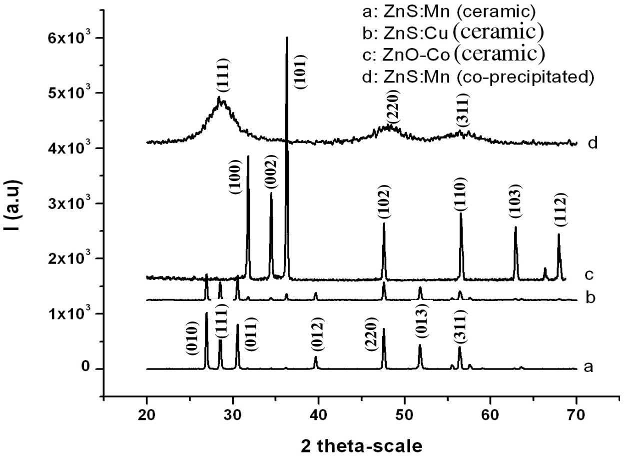

Fig. 1. XRD patterns of bulk samples ZnS:Mn (a), ZnS:Cu (b) ZnO:Co (c) and nanocrystalline ZnS:Mn (d).

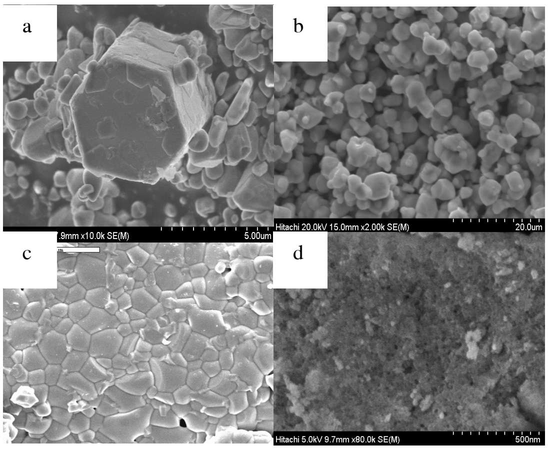

Fig. 2. SEM images of bulk samples ZnS:Mn (a), ZnS:Cu(b), ZnO:Co (c) and nanocrystalline sample ZnS:Mn (d).

XRD patterns of bulk samples ZnS:Mn, ZnS:Cu show that they have hexagonal structures with main diffraction planes (010), (111), (011), (012), (220), (013), (311) (Fig.1a,1b). As changing concentration of Cu ($0 \div 5.10^{-4}$ mol%), Mn ($0 \div 1.2.10^{-2}$ mol%), the position of peaks and lattice constants of bulk samples of ZnS:Mn and ZnS:Cu almost do not change. Fig.1c shows XRD pattern of ZnO:Co with main peaks corresponding to the (100), (002), (101), (102), (110), (103), (112) planes. The lattice constants a, c decrease gradually when concentration of Co increases. This is due to the fact that ionic radius of Co^{2+} (0.83 A^o) is smaller than that of Zn^{2+} (0.88 A^o). The XRD pattern of nanocrystalline sample ZnS:Mn concludes three broad bands corresponding to the (111), (220) and (311) planes (Fig.3d). The average crystalline size calculated by using the Scherer's formula is about 5 nm. Values of average crystalline size do not show any systematic change with Mn content variation in range of $10^{-3} \div 10^{-2}$ mol%. The reported Bohr's radius value for ZnS is about 10 nm [16]. Obviously, the particle size of our samples is within this range.

Fig.2 shows SEM images of bulk samples of ZnS:Mn (a), ZnS:Cu (b) and ZnO:Co (c) and nanocrystalline sample ZnS:Mn (d). In general, distribution of particles is quite properly. For bulk samples of ZnS:Mn, ZnS:Co and ZnS:Cu, the particle size is about 3 μm.

3.2. Photoluminescence spectra

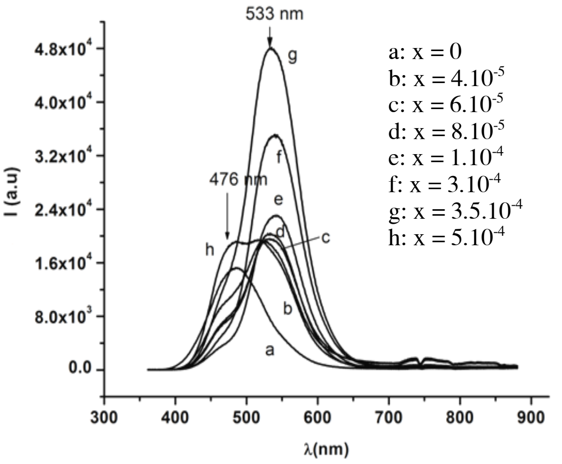

Fig. 3. The PL spectra of bulk sample ZnS:Cu at 300 K excited by the wavelength of 325 nm from He-Cd laser.

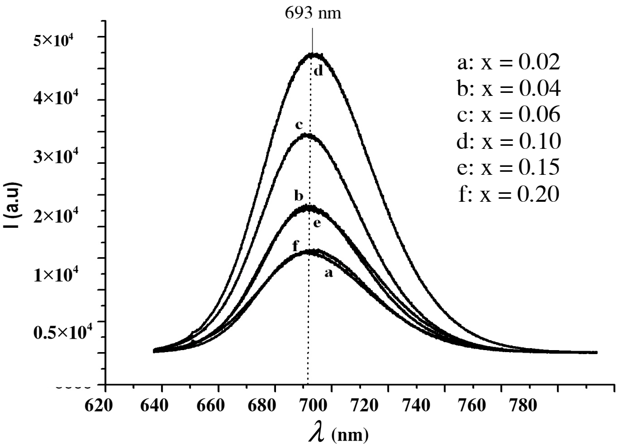

Fig. 4. The PL spectra of bulk ZnO:Co at 300 K excited by the wavelength of 632.8 nm from He-Ne laser.

When Cu ($x_{Cu} = 4.10^{-5}$ mol%) was doped in ZnS, in the PL spectrum of bulk sample ZnS:Cu except a blue band at 476 nm, there is one more green band at around 533 nm characterized by Cu^{2+} ions (Fig. 3). Intensity of the green band is greater than that of the blue band. As increasing the concentration of Cu, the intensity of the blue band decreases while the intensity of the green band increases and reaches to maximum at $x_{Cu} = 3.5.10^{-4}$ mol%. This means that Cu^{2+} ions substituted for positions of Zn^{2+} ions or vacancies of Zn in ZnS crystal. With increasing of concentration of Cu beyond $3.5.10^{-4}$ mol%, the intensity of the green band decreases. Because at high concentration of Cu, it is possible that interaction between Cu^{2+} ions and ions of the lattice and between Cu^{2+} each other make the intensity of the green band decrease. Hence, at $x_{Cu} = 5.10^{-4}$ mol% the intensities of these two bands are equal to each other and they merge into one wide band ranging from 476 nm to 533 nm. The blue and green bands are characterized by radiation transition of electrons from conduction band to acceptor levels and levels of Cu^{2+} ions in the band gap of ZnS, respectively in which acceptor is vacancies of Zn bonding to Cl (V_{Zn} - Cl)[5-7].

Fig.4 shows the PL spectra of bulk sample ZnO:Co with variation of Co concentration. When Co (x_{Co} = 2.10^{-2} mol%) was doped in ZnO, the presence of Co^{2+} ions resulted in change in the PL spectrum of ZnO. As exciting by the wavelength of 632.8 nm from He-Ne laser, the PL spectra of bulk sample ZnO:Co show red band at around 693 nm with strong intensity. When the concentration of Co increases, the intensity of the red band increases gradually and reaches to maximum at x_{Co} = 10^{-1} mol%. This means that Co^{2+} ions substituted in both positions of Zn^{2+} ions and vacancies of Zn in ZnO crystal. With the increasing of concentration of Co beyond 10^{-1} mol%, interaction can occur between Co^{2+} ions and ions of the lattice or between Co^{2+} ions each other. Thereby, the intensity of the red band decreases. The red band is characterized by radiation transition of electrons in 3d shell of Co^{2+} [$^4T_1 \rightarrow {}^4A_2$] [17]

Fig. 5 shows the PL spectra of bulk sample ZnS:Mn with variation of Mn concentration (x_{Mn} = 0÷1.2.10^{-2} mol%). Besides the blue band with small intensity, a yellow-orange band appears at around 582 nm with strong intensity. As concentration of Mn increases, the intensity of the blue band decreases while the intensity of the yellow-orange band increases gradually and reaches to the maximum at x_{Mn} = 8.10^{-3} mol%. However, the position of this band hardly changes.

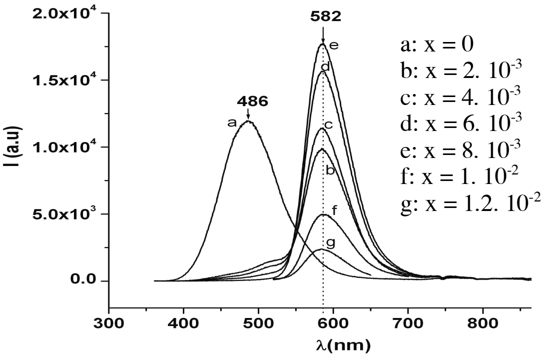

Fig. 5. The PL spectra of bulk ZnS:Mn at 300 K excited by the wavelength of 325 nm from He-Cd laser.

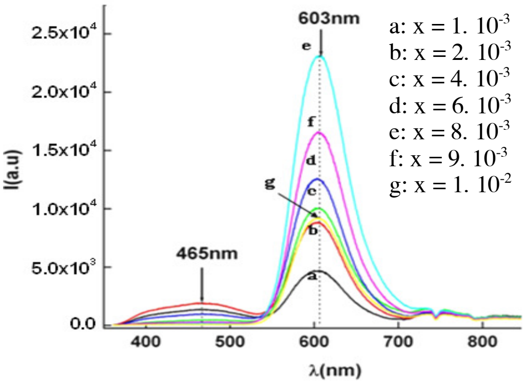

Fig. 6. The PL spectra of nanocrystalline ZnS:Mn at 300 K excited by the wavelength of 325 nm from He-Cd laser.

The yellow-orange band is characterized by radiation transition of electrons in 3d^5 shell of Mn^{2+} ions: [$^4T_1 \rightarrow {}^6A_1$][7-11].. When Mn^{2+} concentration increases over x_{Mn} = 8.10^{-3} mol%, it is possible that interaction between Mn^{2+} ions and ions of the lattice or betwen Mn^{2+} ions each other. As the result, absorption energy of ZnS:Mn crystal was transferred into thermal energy, not radiation energy [7, 8].

Fig.6 shows the PL spectra of nanocrystalline sample ZnS:Mn with different concentrations varying from 10^{-3} to 10^{-2} mol%. There are two broad bands: a orange band centered at 603 nm arises from the [$^4T_1$-$^6A_1$] radiation transition of Mn^{2+}, which is slightly red-shifted compared to the peak of bulk sample ZnS :Mn [18]. The blue band at 465 nm originates from the self-activated radiation of Zn vacancies [2,19]. As the Mn^{2+} concentration increases from 10^{-3} to 10^{-2} mol%, the change in intensity of these bands is similar to the change in bulk sample but its position is unchanged. The radiation transitions corresponding to these bands in samples of ZnS:Cu, ZnS:Mn and ZnO:Co are shown in Fig.7.

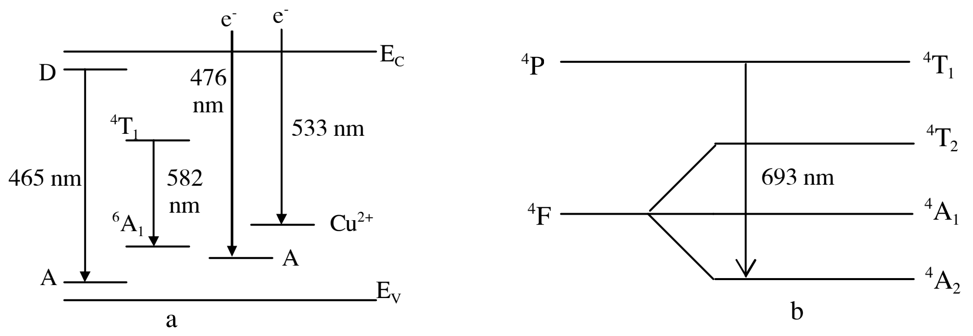

Fig. 7. Diagram of energy levels of Mn^{2+}, Cu^{2+} ions in ZnS (a); Co^{2+} ions in ZnO (b) and radiation transitions corresponding to the blue, green, yellow-orange, red bands.

3.3. Time-resolved photoluminescence spectra

Fig. 8, 9 show the time-resolved PL spectra of the band at 582 nm for bulk sample ZnS:Mn and the band at 603 nm for nanocrystalline sample ZnS:Mn with the same concentration of Mn (x_{Mn} = 8.10^{-3} mol%). When the delay-time increases from 80 μs to 1000 μs, the intensity of yellow-orange band decreases gradually but the position of the band does not change. This is the characteristic of radiation transition in 3d shell of Mn^{2+} ions: [$^4T_1$-$^6A_1$]. The fluorescent life-time of electrons at excited state $^4T_1$ of Mn^{2+} is 1.9 ms (for the band at 582 nm) and 0.79 ms (for the band at 603 nm) calculated from luminescence decay curve fitted with first order exponential function.The milisecond life-time consists of two processes, due to transition of Mn^{2+} single ions and Mn^{2+} coupled pairs, respectively [17,18]. The difference of life-time between bulk and nanocrystalline samples could be ascribed to surface defects. There are more defects in nanocrystalline than in bulk ZnS:Mn. The energy of excited Mn^{2+} transfers to surface defects in nanocrystalline more easily than in the bulk samples, so the life-time of Mn^{2+} in nanocrystalline is shorter than that in bulk sample ZnS:Mn. The nanosecond life-time can be observed for samples of ZnS:Mn due to the blue radiation centered at 465 nm [1,2].

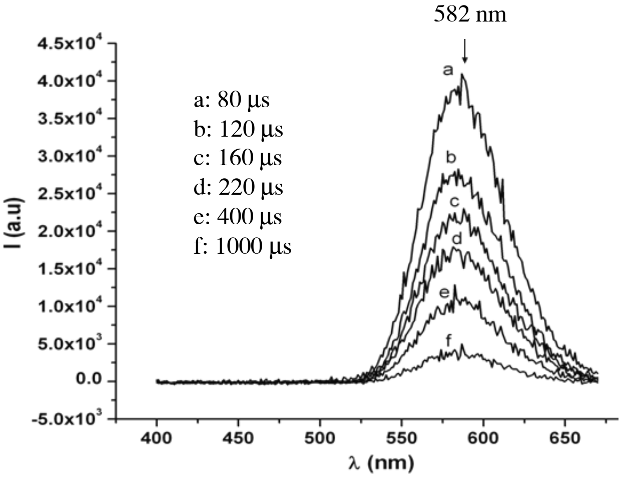

Fig. 8. Time-resolved PL spectra of 582 nm band of bulk sample ZnS:Mn (x_{Mn} = 8.10^{-3} mol%) at 300 K excited by the wavelength of 337 nm.

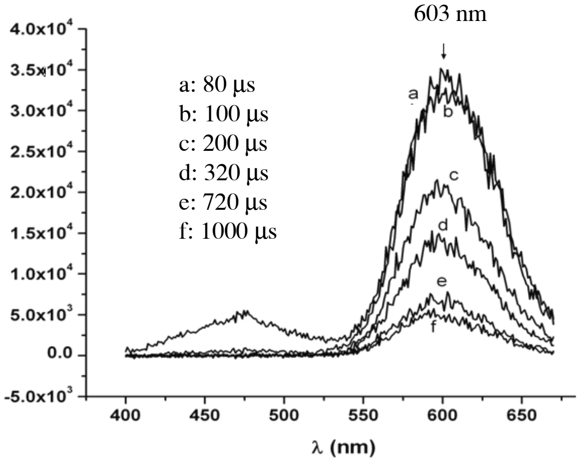

Fig. 9. Time-resolved PL spectra of 603 nm band of nanocrystalline sample ZnS:Mn (x_{Mn} = 8.10^{-3} mol%) at 300 K excited by the wavelength of 337 nm.

Fig.10 shows the time-resolved PL spectra of bulk sample ZnS:Cu with time-delay variation. When the time-delay is 30 ns, in PL spectrum of ZnS:Cu (x_{Cu} = 3.5.10^{-4} mol%), there is a band at 476 nm with strong intensity but a band at 533 nm of Cu does not appears as a sharp peak. While the time-delay increases from 30 ns to 80 ns, the position of 476 nm band does not change but the intensity of the band decreases about 2.6 times. The life time of free electrons at conduction band is about 8.6 μs that is deduced from luminescence extinguishing curve of 476 nm band.

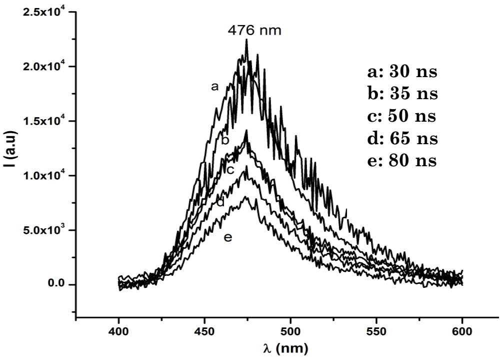

Fig. 10. Time-resolved PL spectra of 476 nm band of bulk sample ZnS:Cu (x_{Cu} = 3.5.10^{-4} mol%) at 300 K excited by the wavelength of 337 nm.

3.4 Application

We have succeeded in efforts to apply the luminescence powder ZnS:Cu (x_{Cu} = 3.5.10^{-4} mol%) for anti-imitated labels and stamps. Fig. 11a shows a real stamp when it has not been lighted yet. Fig. 11b and Fig. 11c show the stamp and a 50000 VND polymer cash under UV light, respectively. The stamp was marked at 4 certain points by ZnS:Cu luminescent powder (the points have green radiation). Here, we can see that the emission colors of the 4 points (on the stamp) and surround of 50000 number (on the polymer cash) are familiar. In the future, we are going to try doing with other materials such as ZnS:Mn (yellow-orange) and ZnS:Eu (red) in off-set printing application.

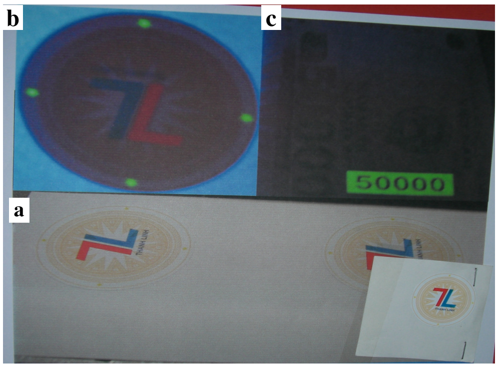

Fig. 11. A stamp sample using ZnS:Cu (x_{Cu} = 3.5.10^{-4} mol%) luminescence powder to label the certain points a.The real stamp; b. The stamp under UV light; c. The polymer cash under UV light.

4. Conclusion

By doping $Cu^{2+}(3d^9)$, $Mn^{2+}(3d^5)$ and $Co^{2+}(3d^7)$ in ZnS, ZnO we have prepared successfully materials radiating at different wavelengths in visible region (different color from blue to red). The yellow-orange band at around 582 nm and 603 nm corresponding to bulk sample ZnS:Mn and nanocrystalline sample ZnS:Mn are characterized by the radiation transition of electrons in 3d shell of Mn^{2+} ions: [$^4T_1$-$^6A_1$]. The 603 nm band of nanocrystalline sample ZnS:Mn is slightly red-shifted compared to bulk sample ZnS:Mn due to strong quantum confinement regime. The 476 nm and 533 nm bands of bulk sample ZnS:Cu are characterized by the radiation transition of electrons being from the conduction band down to acceptor levels and levels of Cu^{2+} ions in the band gap of ZnS, respectively in which acceptor is vacancies of Zn bonding to Cl (V_{Zn} - Cl). The 693 nm band of bulk sample ZnO:Co is characterized by the radiation transition of electrons in 3d shell of Co^{2+}: $[^4T_1 \rightarrow {}^4A_2]$.

ZnS:Cu, ZnS:Mn samples reveal the extend luminescence. The lifetime of electrons at excited states $^4T_1$ is about 1.90 ms, 0.79 ms corresponding to bulk, nanocrystalline samples ZnS:Mn. For bulk sample ZnS:Cu, the lifetime of electrons in conduction band is about 8.60 μs .

These results can be open widespread applications in display devices, luminescent labels, transportation...The luminescence material of ZnS:Cu which we prepared was tested in off-set print for anti-imitated stamps.

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