Vol 15 No 3, March 2006
1009-1963/2006/15(03)/0526-05

Chinese Physics

© 2006 Chin. Phys. Soc.
and IOP Publishing Ltd

Estimation of luminescence lifetime in frequency domain*

Zhang Fu-Jun(张福俊)[a)b)], Xu Zheng(徐 征)[a)b)c)†], Zhao Su-Ling(赵谡玲)[a)b)],
Lou Zhi-Dong (娄志东)[a)b)], Yang Sheng-Yi(杨盛谊)[a)b)], and Xu Xu-Rong(徐叙瑢)[a)b)]

[a)] *Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing* 100044, *China*
[b)] *Key Laboratory of Luminescence and Optical Information, Ministry of Education, Beijing* 100044, *China*
[c)] *Departamento de Fisica, Instituto Superior de Engenharia do Porto,* 4200-072 *Porto, Portugal*

(Received 2 August 2005; revised manuscript received 6 December 2005)

Absorption is the origin of luminescence. But it must be noticed that the lifetime of luminescence might reversely influence the rate of absorption. In this paper, it is reported that the luminescence intensity of copper and manganese changes with the driving frequency at constant voltage. The variation of luminescent intensity depends only on the lifetime of luminescence but not on the type of quenching or other factors. Generally the rate of absorption is dominantly determined by the material property and the lifetime of luminescence centres, the absorption of shorter lifetime centre will be larger than that of the longer lifetime centre at the same excited condition.

Keywords: lifetime, electroluminescence, absorption
PACC: 2320C, 7860F, 4255

1. Introduction

There are five characteristic parameters (spectra, brightness, lifetime, polarization and efficiency) of luminescence; lifetime is the most important parameter among them. Some researches on the brightness versus the driving frequency have been done; it is only considered that the excited time increases with the increase of the driving frequency. The influence of luminescence lifetime on luminescence was ignored. Because the luminescent centres which have been excited cannot be excited again, they can absorb photons again only after their de-excitation. The luminescence lifetime has direct influence on the brightness and efficiency of electroluminescence (EL). For example, the ratio of singlet states density to triplet states density is 1:3 in organic electroluminescence (OEL). It was inaccurately considered in previous studies that the luminescence efficiency is limited to 25% due to the forbidden transition from triplet states to ground states. And it is ignored that the lifetime of electrons in the triplet states is much longer than that of electrons in the singlet state in OEL. When electrons still stay in the triplet state, the electrons in singlet state may give several times the luminescence. Indeed, the fluorescence efficiency of certain polymers that has been measured was greater than 50%.[1] Luminescence lifetime is ordinarily measured by transient spectra, i.e. the transient intensity dependence on time. For such measurements, it is necessary to use the technique of measuring transient intensity at different time domains. The detector must be adjusted corresponding to different time intervals. Now we want to find a new method to measure lifetime by the measurement of steady intensity at different frequencies instead of transient intensity. In this paper we begin our study on the estimation of lifetime and limit to the preliminary experiment on dynamic equilibrium in frequency domain.

2. Background

In inorganic EL we have calculated the differential cross-section ($\mathrm{d}\sigma/\mathrm{d}\Omega$) of excitation.[2,3] It is inversely proportional to the luminescence lifetime and explic-

*Project supported by the National Natural Science Foundation of China (Grant Nos 10374001, 10434030 and 60576016), State Key Development Program for Basic Research of China (Grant No 2003CB314707), the Excellent Doctor's Science and Technology Innovation Foundation of Beijing Jiaotong University (48011) and Beijing Jiaotong University Paper Foundation (PD296).
†Corresponding author. E-mail: Zhengxu@center.njtu.edu.cn

itly expressed as:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \propto \frac{1}{n(\varepsilon_{\mathrm{eff}}/\varepsilon_0)^2\varepsilon^2}\frac{1}{\tau_{\mathrm{e}}}A. \qquad (1)$$

Here n is the refractive index, $\varepsilon_{\mathrm{eff}}/\varepsilon_0$ is the effective field ratio, τ_{e} is the lifetime of luminescent centre, ε is the energy of hot electrons and A is related to the materials used and is unrelated to the driving conditions. The shorter the lifetime of luminescent centre, the larger the differential cross-section or the larger the probability of excitation of centres. Hence the luminescence intensity is inversely proportional to the luminescence lifetime.

On the other hand, in the case of discrete luminescent centres, the density of luminescent centres in the excited state $N(t)$ decreases with time as

$$N(t) = N_0\exp\left(-\frac{t}{\tau R}\right), \qquad (2)$$

where N_0 is the initial density, τ is the luminescence lifetime, τR is the decay time as denoted by the density of the excited states that has decreased to $1/e$ after $t = \tau R$. If the luminescent centre is excited periodically and is assumed to restitutes its previous state before the next half period, then the relationship of the transient density of excited states $N(t)$ with time and that of the averaged excited states $N(f)$ with the driving frequency can be calculated for luminescent centres with different lifetime (τ). The curves of transient density versus time and the averaged density versus frequency are plotted by using the mathematic calculation software.

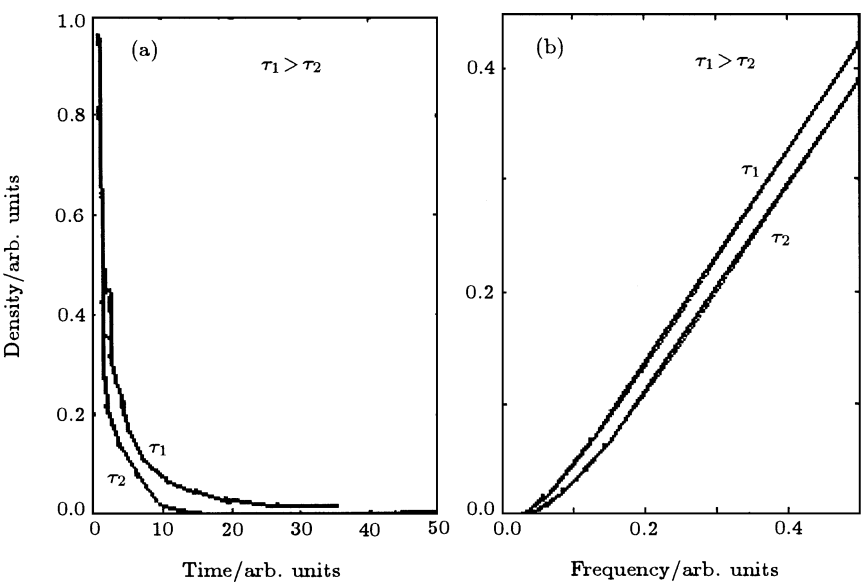


Fig.1. (a) Relationship between transient density of the excited states and time, (b) relationship between averaged density of the excited states and the driving frequency.

From Fig.1, the transient density of excited states decreases much quicker for the shorter lifetime of luminescent centre, and the averaged excited state density increases with the increase of the driving frequency.

3. Experiments

Since the luminescence lifetime of Mn ion is longer than that of Cu ion, these ions were doped into ZnS powder with the same weight ratio (1%). They were whetted about 1h and sintered at 1000° for 1h in the atmosphere of sulfur. All the powdered phosphors were sintered simultaneously so as to keep the sintering conditions completely constant. These sintered powders were dissolved into a certain solvent separately, then these colloidal powders were smeared separately on the indium tin oxide (ITO) coated glass substrate (with a sheet resistance of 80Ω/□) which was cleaned effectively. Another cleaned ITO coated glass substrate was put on the film of these powders as the top electrode. These devices were loaded with a heavy object in order to obtain a compact film. After 20h the spectra of the films were measured by Spex Fluorolog-3 Spectrometer at room temperature.

4. Results and analysis

4.1. Excitation at different voltage with constant frequency

Microcrystalline ZnS is subjected to a high electric field. The number and energy of hot electrons increases with the increase of driving voltage.[4,5] The luminescence centre is excited by hot electrons accelerated in the electric field. The higher the driving voltage, the higher the density of excited states. However, the density of excited states will be saturated when the voltage reaches a certain value.

The relationship between luminescent intensity and voltage is shown as

$$B = B_0 \exp[-(V_0/V)^{\frac{1}{2}}]. \quad (3)$$

Here, B stands for EL intensity, V is the driving voltage, B_0 and V_0 are their initial values related to the luminescent material.

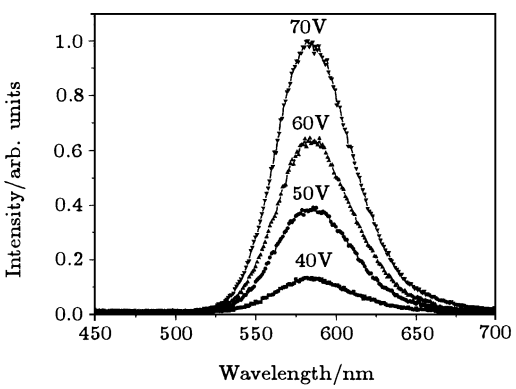


Fig.2. Emission spectra of ZnS: Mn at various voltages.

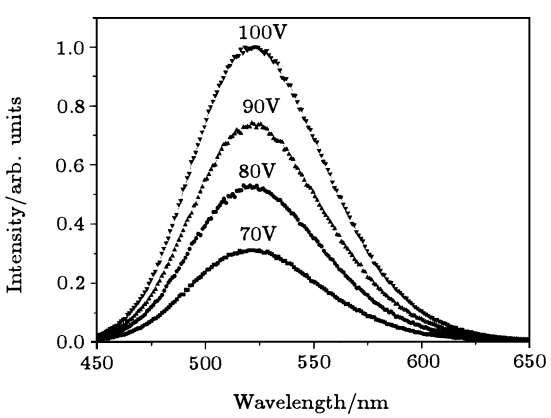


Fig.3. Emission spectra of ZnS: Cu at various voltages.

From Figs.2 and 3, the EL intensity increases with the increase of the driving voltage, but the EL emission peak of each luminescent centre remain unchanged.

4.2. Excitation at constant voltage with different frequencies

There is one luminescence peak in each half period of excitation under alternating current (AC). The number of excitations increases with the increase of the driving frequency, and the permitted time for electrons to transit from their excited states to ground states becomes shorter. If the de-excitation of a certain centre is not completed in the first half period, this centre will not be excited in the next half period. In this case the luminescent lifetime must obviously influence the EL efficiency and intensity.

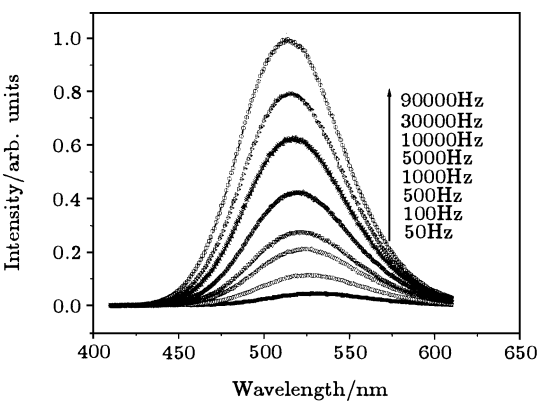


Fig.4. Emission spectra of ZnS: Cu at various frequencies.

The energy level of luminescent centres determines the peak and shape of the emission spectrum. There are two kinds of luminescent centres in ZnS:Cu. One is the blue emission centre (B-Cu), the other is the green emission centre (G-Cu).[6,7] The EL spectra of ZnS: Cu is jointly determined by the green centre and the blue centre of Cu.

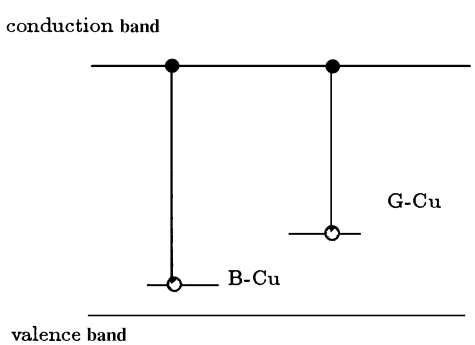


Fig.5. Energy level of ZnS: Cu.

The EL intensity corresponding to the emission of B-Cu and G-Cu centres is enhanced by the increase

of the driving frequency. But the luminescent intensity of G-Cu is enhanced with a smaller factor. So the measured EL peak shifts to shorter wavelength (higher energy) with the increase of the driving frequency, as shown in Fig.4. Why is the enhanced factor of B-Cu emission bigger than that of G-Cu with the increase of frequency? We analyse the energy levels of B-Cu and G-Cu centres in ZnS. The B-Cu energy level is much closer to the valence band of ZnS than the G-Cu energy level, as shown in Fig.5. Thus the hole on the G-Cu acceptor energy level is more stable than that on the B-Cu one: i.e., the lifetime of the G-Cu luminescent centre is longer than that of B-Cu centre. The luminescence intensity ratio between B-Cu and G-Cu increases with the increase of the driving frequency. The luminescence peak shifts from 528 to 513nm due to the different enhancing factor of EL intensity between B-Cu and G-Cu centres.

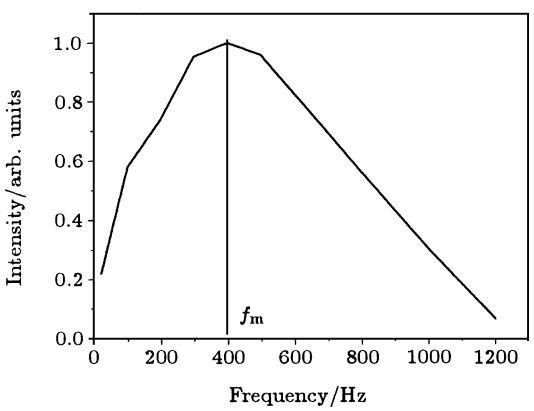


Fig.6. The relationship between EL intensity and the driving frequency.

There are many EL experiments on ZnS:Mn. Now the EL mechanism of ZnS:Mn has been clarified.[8–13] The emission peak of manganese is located at about 585nm. The lifetime of Mn is about 1.5ms.[14] The EL intensity is the maximum when the half period of excitation is nearly equal to the lifetime of Mn ions, as shown in Fig.6. When the frequency of excitation is about 400Hz, that is, the half period of excitation is 1.25ms, the maximum luminescent intensity is obtained. From this result we can conclude that the luminescence lifetime of Mn is about 1.25ms.

4.3. Frequency effect on the EL intensity ratio between centres with different luminescence lifetimes

The EL intensity ratio of B-Cu to G-Cu or to Mn centre increases with the increase of driving frequency. Figure 7 shows these results.

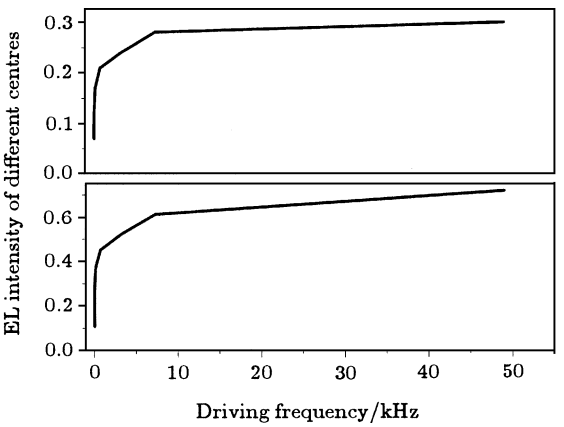


Fig.7. (a) the EL intensity of B-Cu to G-Cu as a function of driving frequency, (b) the EL intensity ratio of B-Cu to Mn versus driving frequency.

It can be concluded that with the increase of the driving frequency the EL intensity increases more quickly for the centres with shorter lifetime than for those with longer lifetime. So we can study the lifetime of luminescent centres by the variation of ratio of their EL intensities with the driving frequency.

5. Conclusion

The absorption rate of luminescent centre is controllable by changing the driving frequency, and the luminescence intensity and efficiency are determined by the energy of absorption. So the luminescence efficiency and intensity can be improved by adjusting the driving frequency. Experiments also demonstrate the correctness of the relationship between the differential cross-section and lifetime, the relationship was put forward for thin film IEL.[2] If the luminescence intensity ratio of centre B to centre A increases with the increase of driving frequency, the lifetime of centre B must be shorter than that of centre A. This result suggests that we can develop a new simple method to estimate luminescence lifetime of materials.

References

[1] Grice A W, Bradley D D C, Bernius M T, Inbasekaran M, Wu W W and Woo E P 1998 *Appl. Phys. Lett.* **73** 629

[2] Shen M Y and Xu X R 1989 *Solid State Commun.* **72** 803

[3] Ge Z M, Lu Z W and Wang Z W 2002 *Chin. Phys.* **11** 915

[4] Dai R S and Xu X R 1982 *J. Phys.* C: *Solid State Phys.* **15** 1781

[5] Zhang F J, Xu Z, Teng F and Liu L 2005 *Mater. Sci. Eng.* B **123** 84

[6] Chen Y Y, Duh J G, Chiou B S and Peng C G 2001 *Thin Solid Films* **392** 50

[7] Nathaniel E Brese, C Lane Rohrer and Gregory S Rohrer 1999 *Solid State Ionics* **123** 19

[8] Krasnov A N, Bender J P and Kim W Y 2004 *Thin Solid Films* **467** 247

[9] Vlasenkoa N A, Denisovaa Z L, Kononetsa Ya F, Kopytkoa Yu V, Veliguraa L I and Vdovenkov A A 2003 *J. Cryst. Growth.* **257** 263

[10] Wagera J F, Hitta J C, Baukola B A, Bendera J P and Keszler D A 2002 *J. Luminescence* **97** 68

[11] Lou Z D, Xu Z and Xu C X 1998 *Acta Phys. Sin.* **47** 139 (in Chinese)

[12] Zhang C G, Qiu W and Xin J L 2003 *Chin. Phys.* **12** 1395

[13] Zhang F J, Xu Z, Teng F, Yang S Y, Lou Z D, Liu L, Meng L J, Hou Y B, Wang Y S and Xu X R 2006 *J. Luminescence* **117** 90

[14] Kiichi T, Ito K, Ohyama T, Fujii K, Ishikawa T, Nakamura T and Fujiyasu H 2000 *J. Cryst. Growth.* **214/215** 405