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1994 J. Phys.: Condens. Matter 6 3279

(http://iopscience.iop.org/0953-8984/6/17/018)

J. Phys.: Condens. Matter 6 (1994) 3279–3290. Printed in the UK

A quantitative evaluation of the excitation mechanism of Tm^{3+} in a ZnS thin film

Jiang Xu-Yin, Zhang Zhi-Lin, Zhao Wei-Ming, Lui Zu-Gang and Xu Shao-Hong

Department of Material Science, Shanghai University of Science and Technology, Shanghai 201800, People's Republic of China

Received 13 July 1993, in final form 27 January 1994

Abstract. The impact excitation rates, and consequently the emission intensities, of various energy states of Tm^{3+} in ZnS thin-film electroluminescence (TFEL) have been quantitatively evaluated by calculating the radiative transition rates and the impact cross section, together with a Baraff distribution function of hot-electron energy. The results show that the direct impact excitation rate of the $^1G_4$ state of Tm^{3+} is very small, while that of the $^3F_4$ state is fairly large, resulting in a weak blue light intensity relative to the IR light in TFEL. Different theories of the electron distribution function are compared and discussed.

1. Introduction

ZnS:Tm is a very efficient photoluminescence (PL) and cathodluminescence (CL) blue phosphor. It has been considered as an important candidate for blue emitting thin-film electroluminescence (TFEL). Much effort has been made in the last decade to obtain a sufficiently intensive EL blue emission in ZnS:Tm thin films. Unfortunately, only weak blue light has been acquired so far. If this situation remains unchanged, there would be no hope of employing the blue emitting ZnS:Tm film for colour display. Thus to find out the cause of the weakening of blue emission is a problem challenging scientists working in this field.

Ma *et al* [1] investigated the excitation mechanism of ZnS:Tm TFEL by measuring the time resolved spectra and showed that the excitation in ZnS:Tm is due to the energy transfer from the excited host to the luminescence centre. Tanaka *et al* [2] reached a different conclusion after analysing the decay curves of the lower-lying state. He argued that the excitation of Tm^{3+} in EL is due to direct impact excitation by hot electrons, and the excitation of the $^3F_4$ state (the initial state of the IR emission) is dominant compared with that of the higher-lying state $^1G_4$ (the initial state of the blue emission).

The impact excitation and energy transfer through the ionization host should be considered as two coexisting excitation processes. In general, the energy transfer probability by ionized electrons and holes under a high electric field must be very small because the electrons and holes rapidly separate under the action of the field unless they are trapped in a localized centre [3], so the probability of the impact excitation appears to be the key factor determining which mechanism is the more important. When the impact excitation probability of an energy state is large, the excitation is dominated by impact excitation. On the other hand, when the impact excitation probability is small, the excitation by energy transfer becomes important.

0953-8984/94/173279+12$19.50

Thus the excitation mechanism of ZnS:Tm TFEL and the cause of the weakening of the blue emission of ZnS:Tm TFEL become two very important questions for display applications and are urgently in need of interpretation. In this paper, we try to give an explanation of these questions by performing a quantitative evaluation of the excitation mechanism of Tm^{3+} in a ZnS thin film.

2. Theory

The luminescence intensity, in terms of photon flux, can be expressed as follows:

$$L_{if} = n_f A_{if} \tag{1}$$

where n_f is the number of excited centres and A_{if} the radiative transition rate. n_f is related to the mode of excitation; A_{if} is determined by the wave function of relevant states and the crystal field at the site of the luminescence centre. For a rare earth ion, Judd–Ofelt (JO) theory provides a convenient and satisfactory method for calculating the radiative transition rate. On the basis of this theory the radiative transition rate is

$$A_{if} = [64\pi^4 e^2/3h(2j+1)]\chi \nu_{if}^3 \Sigma \Omega_\lambda \langle i|U^\lambda|j\rangle^2 \tag{2}$$

where Ω_λ are intensity parameters, $\langle i|U^\lambda|j\rangle^2$ the reduced matrix elements, h the Planck constant, $(2j+1)$ the degeneracy of the excited state, $\chi = n(n^2+2)^2/9$, n is the refractive index and ν_{if} the wavenumber. The radiative transition rate A is related to measured lifetime τ_{obs} by

$$1/\tau_{obs} = A + W \tag{3}$$

where W is the non-radiative transition rate. As an approximation, the reciprocal of τ_{obs} may sometimes be taken to be the radiative transition rate. The excitation for TFEL depends both on the rate of impact excitation by hot electrons and the energy distribution function of the electrons. Allen and Aying [4] showed that the excitation rate for the impact excitation process is given by

$$R = n_e N \int \sigma(E) V(E) f(E) \mathrm{d}E \tag{4}$$

where $\sigma(E)$ is the impact cross section, $V(E)$ the velocity of the electrons, $f(E)$ the energy distribution function of the electrons, n_e the carrier density and N the number of unexcited luminescence centres. Assuming $N \gg n_f$, the rate equation is

$$\frac{\mathrm{d}n_f}{\mathrm{d}t} = n_e N \int \sigma(E) V(E) f(E) \mathrm{d}E - n_f A. \tag{5}$$

For the stationary state, $\mathrm{d}n_f/\mathrm{d}t = 0$, the luminescence intensity L can be written as follows:

$$L = n_e N \int \sigma(E) V(E) f(E) \mathrm{d}E. \tag{6}$$

The first approximated expression for impact cross section was given by Allen and Aying [4]. Yu *et al* [5] derived the analytical expression based on the Born approximation:

$$\sigma(E) = \frac{18\pi^2 m e^2 h^2 c^3}{n(n^2+2)^2} \frac{1}{E_{if}^3} \frac{1}{E} \ln \frac{\sqrt{E} + \sqrt{E - E_{if}}}{\sqrt{E} - \sqrt{E - E_{if}}} \frac{g_f}{g_i} A_{if} \tag{7}$$

where m is the electron mass, g_i and g_f are the degeneracies of the initial and final states, respectively, E_{if} is the energy gap between the initial and the final states, E the energy of incident electrons, n the refractive index and A_{if} the electric dipole transition rate. It is seen that the impact cross section is a product of two parts: the first is a function of the carrier energy E; the second depends only on the properties of the centre. It should be pointed out that this formula is derived on the basis of the Born approximation which is valid only at large E, i.e. $E \gg E_{if}$. To the best of our knowledge, there is no quantitative expression given for $\sigma(E)$ at energy values near to the threshold E_{if}, so formula (7) is used for all values of E. It is believed that the error introduced in L (formula (6)) would be relatively small due to improper application of this formula in the neighbourhood of E_{if}, since the calculation involves integration covering a large range of values of E (from $E = E_{if}$ to $E = \infty$).

According to formula (7), if we know the radiative transition rate of a certain state, we can obtain the impact cross section of this state as a function of the incident electron energy. The radiative transition rates are readily obtained by applying JO theory. In order to evaluate the luminescence intensity L, the energy distribution of the electrons $f(E)$ should be known. As to this function a survey of various theories has to be made before choosing an appropriate one.

A hot-electron energy distribution function was first proposed by Baraff [6, 7] in the early sixties. His result covers two early works by Shockley [8] and Wolff [9]. Krupka [10] used Baraff's theory for ZnS:Tb ACTFEL, considering the energy loss produced by inelastic scattering of low-lying levels of the Tb^{3+} ion. Recently, a lucky drift model has been presented by Ridley [11], in which energy loss was considered to be dominated by optical phonon scattering. Bringuier [12] used the lucky drift model to calculate impact excitation luminescence for ZnS:Mn. Recently, Monte Carlo simulation has been widely used to investigate electron distribution. However, different views have been presented by different authors. Brennan [13] suggested that very few electrons are available with sufficient energy to excite the Mn luminescence centre, while Muller and coworkers [14, 15] concluded that the electrons undergo loss free transport resulting in extremely high-energy electrons. An intermediate view given by Bhattacharyya [16] seems more realistic. In any case, the investigation of the electron distribution function is still in progress.

In this paper we use Baraff's distribution for our purpose, since this theory can describe different extreme cases by selecting an adjustable parameter. According to Baraff's theory the hot-electron distribution is expressed as follows:

$$f(E) = E^{-a+0.5}\exp(-bE) \qquad a = (E_0 - e\varepsilon\lambda)(2E_0 + e\varepsilon\lambda)^{-1}$$
$$b^{-1} = \tfrac{2}{3}e\varepsilon\lambda + \tfrac{1}{3}(e\varepsilon\lambda)^2/E_0 \tag{8}$$

where ε is the electric field, λ the mean free path of the electron and E_0 the low-energy loss parameter. With different values of E_0, 'cold'- or 'hot'-electron distribution can be obtained.

3. *Experimental details and results*

ZnS,Tm_2O_3 and Li_2SO_4 were mixed with the appropriate ratio and fired at 1100 °C for 1 h in a reducing atmosphere. The TFEL sample is of a double insulating sandwiched structure (MISIM). The emission and excitation spectra were measured by a Hitachi 850 Fluorescence Spectrophotometer. The lifetime of the excited state was measured by a GD 50-15 double

monochrometer together with a DSS 6521 digital storage oscilloscope. For PL, an N_2 laser was used as the excitation source and for EL a pulse voltage source with 20–50 μs pulse width and an alternate polarity of 1 kHz was used. The temperature of the sample was controlled by the DE202 chamber of a cryogenic refrigeration system between 10 K and 300 K.

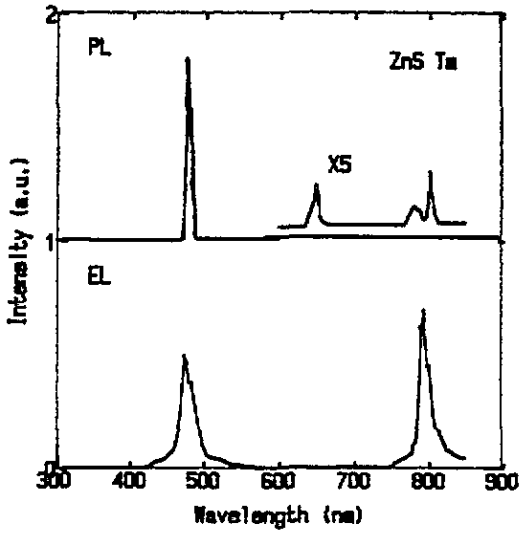

Figure 1. The emission spectra of ZnS:Tm^{3+} for PL and EL.

The emission spectra of ZnS:Tm are shown in figure 1. In PL there are four emission lines. In EL the blue emission is very much weakened and the 650 nm and 780 nm lines were too weak to be observed. The transitions corresponding to these emission lines have been identified by Tanaka *et al* [2]: the 475 nm, 650 nm and 780 nm emissions originate from the same state, $^1G_4$, while the 800 nm emission is from $^3F_4$. The relative luminescence intensities of the observed lines for both PL and EL as well as the corresponding transitions are listed in table 1.

Table 1. The relative luminescence intensities of the emission lines for PL and EL and the corresponding transitions.

Emission	Transition	Intensity (PL)	Intensity (EL)
475 nm	$^1G_4$–$^3H_6$	12.3	0. 6
650 nm	$^1G_4$–$^3H_4$	0.67	—
780 nm	$^1G_4$–$^3H_5$	1	—
800 nm	$^3F_4$–$^3H_6$	1	1

The excitation spectra for PL are shown in figure 2. It is obvious that the excitation of the host can be efficiently transferred to $^1G_4$ as well as to $^3F_4$. $^3F_4$ can also be populated via excitation to $^3F_3$.

The lifetimes of the $^1G_4$ state and the $^3F_4$ state at different temperatures are indicated in table 2. It is seen from this table that the lifetimes of $^1G_4$ and $^3F_4$ in EL were nearly the same as those in PL (at room temperature). This implies that the rate of radiative transition remains the same for PL and EL; the luminescence intensities corresponding to different states, however, are quite different.

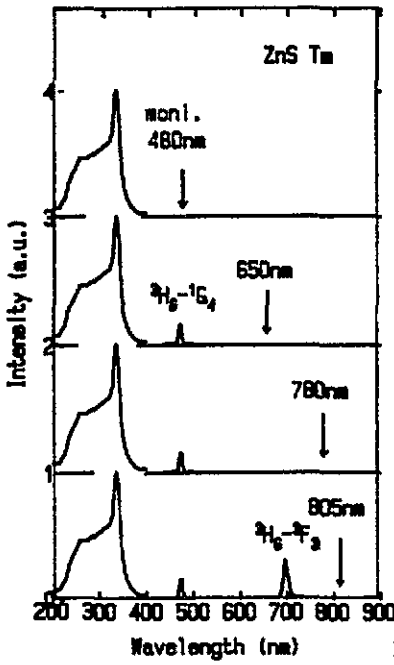

Figure 2. The excitation spectra of ZnS:Tm^{3+}.

Table 2. The lifetimes (μs) of $^1G_4$ and $^3F_4$ states at different temperatures.

State	9 K	120 K	283 K	EL (room temperature) [1]
$^1G_4$	54	50	35	~ 30
$^3F_4$	73	73	70	~ 70

4. Calculation and discussion

In order to calculate the impact cross section, the radiative transition of various energy states should be known.

4.1. Radiative transition rates

According to Huang [17], if the luminescence intensities of three or more emission lines originating from the same excited state are known, the three intensity parameters Ω_2, Ω_4, Ω_6 or their ratios can be obtained by solving three or more linear equations. Thus by measuring the relative luminescence intensities of the three emission lines from the $^1G_4$ state in ZnS:Tm listed in table 1 and the corresponding reduced matrix elements of the Tm^{3+} ion given in [18], we obtained the ratio of the three intensity parameters as follows:

$$\Omega_2 : \Omega_4 : \Omega_6 = 4.1 : 7.5 : 1.$$

In order to obtain the absolute values of Ω_2, Ω_4 and Ω_6, the radiative transition rate of a state, for example $^1G_4$, is needed. By assuming the reciprocal of τ_{obs} of the $^1G_4$ state at 9 K to be the radiative transition rate of this state, then $A(^1G_4)$= 18 519 (s^{-1}). Since the gap between $^1G_4$ and the next lower level is approximately ten times the phonon energy of

the ZnS host, it is reasonable to assume that multiphonon non-radiative transition may be neglected. Consequently the intensity parameters were calculated to be

$$\Omega_2 = 6.6\times10^{-20}\,\mathrm{cm}^2 \qquad \Omega_4 = 12\times10^{-20}\,\mathrm{cm}^2 \qquad \Omega_6 = 1.6\times10^{-20}\,\mathrm{cm}^2.$$

After obtaining the Ω_λ parameters, the radiative transition rates of the various energy states of ZnS:Tm could be calculated and the results are listed in table 3.

Table 3. The radiative transition rates of various energy states in ZnS:Tm.

Energy state	Wavenumber (cm^{-1})	Energy (eV)	A (s^{-1})	τ_r (μs)
$^3H_4$	5811	0.72	2928	341
$^3H_5$	8390	1.04	2626	381
$^3F_4$	12720	1.58	10038	100
$^3F_3$	14510	1.80	27122	37
$^3F_2$	15116	1.87	3033	329
$^1G_4$	21374	2.65	18519	54

τ_r is the reciprocal of the radiative transition rate, τ_r of $^3F_4$ and $^1G_4$ are 100 μs and 54 μs respectively and the quantum efficiencies τ_{obs}/τ_r of $^1G_4$ and $^3F_4$ were determined to be 65% and 70% at room temperature respectively.

4.2. Impact cross section

The expression for the impact cross section in formula (7) may be written as follows:

$$\sigma(E) = \sigma_0 \frac{1}{E} \ln \frac{\sqrt{E} + \sqrt{E - E_{if}}}{\sqrt{E} - \sqrt{E - E_{if}}}$$

where the coefficient

$$\sigma_0 = \frac{18\pi^2 m e^2 h^2 c^3}{n(n^2+2)^2} \frac{1}{E_{if}^3} \frac{g_f}{g_i} A_{if} \tag{9}$$

is a parameter depending only on the nature of the luminescence centre in ZnS. By using the radiative transition rates given in table 3, the σ_0 of various energy states of ZnS:Tm were calculated and are listed in table 4.

Table 4. σ_0 of various energy states of Tm^{3+} in ZnS.

State	Energy (eV)	σ_0 (10^{-16} cm^2 eV)
$^3H_4$	0.72	2.73
$^3H_5$	1.04	0.99
$^3F_4$	1.58	0.88
$^3F_3$	1.80	1.25
$^3F_2$	1.87	0.09
$^1G_4$	2.65	0.45

Table 5. σ_0 of the various energy states of Er^{3+} in ZnS.

State	Energy (eV)	τ_{obs} (μs)	A (s^{-1})	σ_0 (10^{-16} cm^2 eV)
$^4F_{9/2}$	1.90	75 [a]	1.3×10^4	0.6
$^4S_{3/2}$	2.28	50 [a]	2.0×10^4	0.2
$^2H_{11/2}$	2.38	5.9 [5]	1.75×10^5	4.9

[a] Our measured data.

For comparison, the σ_0 values of some energy states of ZnS:Er were calculated, where as an approximation the reciprocal of measured lifetimes τ_{obs} was taken as the radiative transition rate. The results are listed in table 5.

It is seen from table 4 and table 5 that σ_0 of the high-lying state $^1G_4$ is smaller than that of the lower-lying state $^3F_4$ in ZnS:Tm. In contrast, σ_0 of the high-lying state $^2H_{11/2}$ is much larger than that of the lower-lying state $^4F_{9/2}$ in ZnS:Er. Although σ_0 of the state $^4S_{3/2}$ is small, it can be efficiently populated via the $^2H_{11/2}$ state due to their small energy difference, so we can take the σ_0 value of $^2H_{11/2}$ for that of the $^4S_{3/2}$ state. In comparing Tm^{3+} with Er^{3+}, we noticed that the difference of σ_0 between the states $^3F_4$ of ZnS: Tm and $^4F_{9/2}$ of ZnS:Er is not large, but σ_0 of $^2H_{11/2}$ of Er^{3+} is an order of magnitude higher than that of the $^1G_4$ state.

After obtaining σ_0 of the energy states in ZnS:Tm and in ZnS:Er, the function $\sigma(E)$ can be calculated, as shown in in figures 3 and 4.

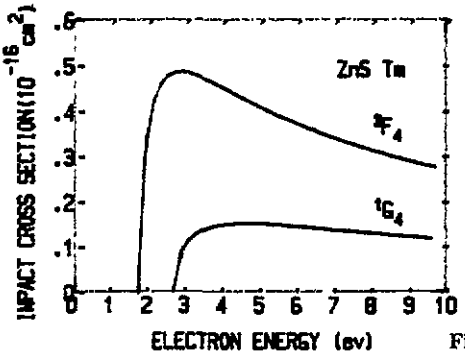

Figure 3. The dependence of impact cross section of $^3F_4$ and $^1G_4$ on hot-electron energy in ZnS:Tm.

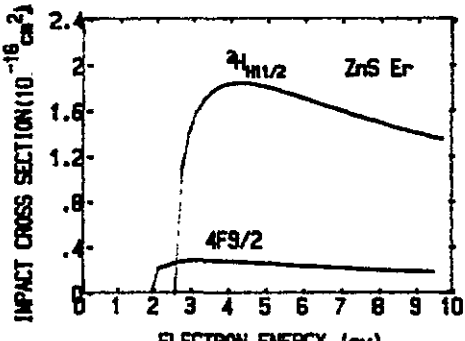

Figure 4. The dependence of impact cross section of $^2H_{11/2}$ and $^4F_{9/2}$ on hot-electron energy in ZnS:Er.

The figures show that the $^1G_4$ state of Tm^{3+} not only has a high energy above the ground state but also has a small impact cross section in ZnS. These two characteristics are both unfavourable to impact excitation, thus resulting in the low intensity of the blue emission.

Table 6. The ratios of U values and the luminescence intensities for the blue and infrared emissions of Tm^{3+} in ZnS for different $e\varepsilon\lambda$, setting E_0= 0.36 eV.

	$e\varepsilon\lambda$ (eV)		
	0.3	0.45	0.6
U_1 ($^1G_4$)	1.28×10^{-5}	1.67×10^{-3}	0.019
U_2 ($^3F_4$)	7.37×10^{-4}	1.86×10^{-2}	0.109
U_1/U_2	0.017	0.090	0.174
I_b/I_{IR}	0.014	0.080	0.149

4.3. The excitation rate and the ratio of the blue to the infrared emission intensities under impact excitation

Taking Baraff's function given in formula (8) as the electron energy distribution function, the excitation rate R, and hence the luminescence intensity L, can be written as:

$$R \propto \sigma_0 \int \left[\frac{1}{E}\ln\frac{\sqrt{E}+\sqrt{E-E_{if}}}{\sqrt{E}-\sqrt{E-E_{if}}}\right]\left[\sqrt{E}\right]\left[E^{-a+0.5}\exp(-bE)\right]dE. \tag{10}$$

The integral is taken from $E = E_{if}$ to $E = \infty$. The integrand consists of three parts: the first is related to the impact cross section, the second to the velocity of the electrons and the third to the distribution function of the hot electrons. Let the integral be denoted by U, then the excitation rate $R = \sigma_0 U$, where σ_0 is only related to the property of the centre and U is related to the energy level position. Thus the ratio of luminescence intensity of blue and infrared emission is

$$\frac{I_b}{I_{IR}} = \frac{\sigma_0(^1G_4)}{\sigma_0(^3F_4)}\frac{U(^1G_4)}{U(^3F_4)}\frac{\nu_b}{\nu_{IR}} \tag{11}$$

where ν is the wavenumber of the emission. In fact we have already obtained from table 4 $\sigma_0(^1G_4)/\sigma_0(^3F_4)$=0. 51 and ν_b/ν_{IR} = 1.68, once the ratio of integrals U is calculated, I_b/I_{IR} can be found. The integrals U for various states were obtained by numerical integration for different values of $e\varepsilon\lambda$ at two different values of E_0. I_b/I_{IR} was then calculated. The results are listed in tables 6 and 7.

Taking the mean free path λ to be 30 Å at room temperature as given in [12] and assuming it to be independent of the electric field, the values of $e\varepsilon\lambda$= 0.3 eV, 0.45 eV and 0.6 eV correspond to electric field ε= 1 MV cm^{-1}, 1.5 MV cm^{-1} and 2 MV cm^{-1} respectively. The two values of E_0 taken in tables 6 and 7 represent two extreme cases of electron energy distribution. E_0 = 0.36 eV represents an inelastic scattering by low-lying energy levels of the Tm^{3+} ion. This value is quite close to the value E_0 = 0.34 eV taken for Tb^{3+} [10]. With this E_0 value, Baraff's distribution shows a 'not hot' electron distribution, which approximates the Shockley distribution. For E_0 = 0.064 eV, comparable to the optical phonon energy of ZnS, 0.043 eV, Baraff's function gives a 'hot' electron distribution, which

Table 7. The ratios of U values and the luminescence intensities for the blue and infrared emissions of Tm^{3+} in ZnS for different $e\varepsilon\lambda$, setting $E_0 = 0.064$ eV.

	$e\varepsilon\lambda$ (eV)		
	0.3	0.45	0.6
U_1 ($^1G_4$)	0.022	0.58	2.92
U_2 ($^3F_4$)	0.11	1.34	5.23
U_1/U_2	0.19	0.43	0.55
I_b/I_{IR}	0.16	0.37	0.48

approximates to the results obtained by the lucky drift model or Monte Carlo simulations, where energy loss is considered to be dominated by scattering of the optical phonon.

It is seen from tables 6 and 7 that in both cases, 'hot' or 'not hot' electron distribution, the impact excitation of the blue emission of Tm^{3+} in ZnS is weak compared with the infrared emission. At high electric field, 1.5–2 MV cm^{-1}, the ratios I_b/I_{IR} are around 0.1 for $E_0 = 0.36$ eV and around 0.4 for $E_0 = 0.064$ eV. This shows that the small impact cross section of the $^1G_4$ level of the Tm^{3+} ion is the main reason for the weak blue emission.

For comparison, the ratios of U values and the luminescence intensities for the green and the red emissions of Er^{3+} in a ZnS thin film were also calculated, where $\sigma_0(^2H_{11/2})/\sigma_0(^4F_{9/2}) = 8.17$, $\nu_g/\nu_r = 1.2$ from table 5. The results are listed in tables 8 and 9.

Table 8. The ratios of U values and the luminescence intensities for the blue and infrared emissions of Er^{3+} in ZnS for different $e\varepsilon\lambda$, taking $E_0 = 0.36$ eV.

	$e\varepsilon\lambda$ (eV)		
	0.3	0.45	0.6
$U_1(^2H_{11/2})$	3.53×10^{-5}	3.25×10^{-3}	0.032
$U_2(^4F_{9/2})$	2.17×10^{-4}	8.90×10^{-3}	0.065
U_1/U_2	0.16	0.365	0.493
I_g/I_r	1.57	3.58	4.86

Table 9. The ratios of U values and the luminescence intensities for the green and red emissions of Er^{3+} in ZnS for different $e\varepsilon\lambda$, taking $E_0 = 0.064$ eV.

	$e\varepsilon\lambda$ (eV)		
	0.3	0.45	0.6
$U_1(^2H_{11/2})$	0.034	0.733	3.47
$U_2(^4F_{9/2})$	0.067	1.039	4.40
U_1/U_2	0.51	0.71	0.79
I_g/I_r	5.0	6.9	7.7

It is seen that in ZnS:Er although $U(^2H_{11/2})$ is also smaller than $U(^4F_{9/2})$, σ_0 of the $^2H_{11/2}$ state is much larger than that of the $^4F_{9/2}$ state. As a result, at the same electron distribution as in ZnS:Tm the green emission intensity of Er^{3+} is larger than the red emission intensity. From tables 8 and 9, at $\varepsilon = 1.5$–2 MV cm^{-1} the ratio is about four to five for $E_0 = 0.36$ eV and five to eight for $E_0 = 0.064$ eV.

In comparing the impact excitation rates of the $^3F_4$ state of the Tm^{3+} ion and the $^4F_{9/2}$ state of the Er^{3+} ion, we found that $\sigma_0(^3F_4)/\sigma_0(^4F_{9/2}) = 1.5$ from tables 4 and 5 and $U(^3F_4)/U(^4F_{9/2}) > 1$ for all values of ε and E_0 listed in tables 6–9. This implies that the $^3F_4$ state in Tm^{3+} can be efficiently excited by electron impact, just like the $^4F_{9/2}$ state in ZnS:Er. Therefore, it may be concluded that the infrared emission of the Tm^{3+} ion is dominated by impact excitation.

Now we return to the discussion of electron distribution. Although the lucky drift model and Monte Carlo simulation, where electrons are estimated to be 'hot', could be applied in ZnS:Mn ACTFEL, whether they could be used in ZnS:Tm ACTFEL is doubtful, since the efficiency of EL blue emission of ZnS:Tm is much lower than that of ZnS:Mn. The efficiency of ZnS:Tm was measured to be 0.002 lm W^{-1} by us with a Sawyer Tower circuit, about 0.003 lm W^{-1} was given by Kobayashi *et al* [19], and lower than 0. 01 lm W^{-1} was listed in the paper by Ono [20]. This means that the efficiency of blue emission of ZnS:Tm is three orders of magnitude lower than that of ZnS:Mn, which is 2–8 lm W^{-1}, also listed in [20], whereas the impact cross section of the $^1G_4$ level of the Tm ion is only an order smaller than that of the Mn ion, so by adopting the same electron distribution it is difficult to explain why the efficiency of blue emission of Tm^{3+} is so much lower than that of orange emission of Mn^{2+} in ZnS.

A rough estimation for the number of electrons with sufficient energy to excite the $^1G_4$ level of Tm^{3+} from the measured efficiency can be made. By taking the efficiency to be 0.005 lm W^{-1}, which is equivalent to a quantum efficiency of 1.6×10^{-3} photons per transfered charge (for a photon of blue emission), according to the method described by Mach and Muller [21], for $\sigma(^1G_4) = 2 \times 10^{-17}$ cm^2 (figure 3) and a concentration of centres of 1.09×10^{20} cm^{-3}(0.43 mol%) [19], the excitation yield η_{exc} for the electrons with $E \geqslant 2.65$ eV is estimated to be 2.2×10^3 cm^{-1}. If η_{lum} and η_{opt} are asummed to be 0.8 and 0.1 $\times$ 600 nm, respectively, $\eta = \eta_{exc}\eta_{lum}\eta_{opt}$ is about 10^{-2} photons per transferred electron with energy $E > E_{th}$. In comparison with the measured 1.6×10^{-3} photons per charge, the fraction of electrons with energy exceeding the threshold should be 16%.

Let us calculate the fraction of electron with energy $E \geqslant E_{th}$ (2.65 eV for ZnS:Tm and 2.1 eV for ZnS:Mn) by numerical integration for two different E_0. When taking E_0 = 0.36 eV, Baraff's distribution gives the fractions of electrons with energy exceeding 2.65 eV to be 0.3%, 1.5% and 8% for electric field 1 MV cm^{-1}, 1.5 MV cm^{-1} and 2 MV cm^{-1}, respectively, whereas these fractions become 0.2%, 4% and 16% for E > 2.1 eV. This distribution appears to be suitable for ZnS:Tm, but for ZnS:Mn it is obvious that the distribution is too 'cold' to explain its high efficiency.

If E_0 = 0.064 eV, the fractions of electrons with energy exceeding 2.65 eV were calculated to be 10% for 1 MV cm^{-1}, 46% for 1.5 MV cm^{-1} and 71% at 2 MV cm^{-1}, while the fractions of electrons with energy exceeding 2.1 eV were 19% for 1 MV cm^{-1}, 59% for 1.5 MV cm^{-1} and 79% for 2 MV cm^{-1}, which approximate to those given by the lucky drift model, where these are estimated to be 19% for 1 MV cm^{-1}, and 65% for 2 MV cm^{-1} [22]. This distribution is appropriate to ZnS:Mn, but it is too 'hot' to explain the low efficiency of ZnS:Tm. It seems that the electron distributions are not the same for ZnS:Tm and ZnS:Mn. Perhaps the inelastic scattering of the low-lying level of the Tm^{3+} ion could efficiently cool the electron distribution since these levels have large impact cross section as shown in table 4, whereas no low-lying level exists in ZnS:Mn. In this work, a definite conclusion on the electron distribution function could not be obtained; the conclusion that, whether the electrons are 'hot' or 'cold', the blue emission produced by impact excitation in ZnS:Tm is much weaker than the infrared can, however, be drawn.

Finally, it should be noted that although the radiative transition rates of Tm^{3+} were

calculated on the basis of the data taken from ZnS:Tm powder phosphor, it appears that the radiative transition rates for the thin film do not differ much from that of the powder from table 2. In fact, by using τ_{obs} of $^1G_4$ and $^3F_4$ obtained from TFEL, results near the above can be obtained. These facts imply that the structure of the luminescence centre in the thin film is the same as that in powder. Thus the weak blue emission of Tm^{3+} in ACTFEL is mainly a result of the excitation mode rather than a change of the environment of the Tm^{3+} ion in the ZnS film. According to the impact excitation theory, in the case where the radiative transition rates of $^1G_4$ and $^3F_4$ have the same order of magnitude, it appears impossible to obtain a bright blue emission.

5. Conclusion

The calculation for impact excitation rates of $^1G_4$ and $^3F_4$ states shows that the $^1G_4$ state cannot be efficiently excited by direct impact of hot electrons due to its small impact cross section and large energy gap, no matter whether the electrons are 'hot' or 'cold'. In contrast, the $^3F_4$ state is readily excited, resembling the $^4F_{9/2}$ state of the Er^{3+} ion in ZnS. It appears that the excitation of $^1G_4$ and $^3F_4$ may be through different routes. The excitation of $^1G_4$ is dominated by energy transfer of electron–hole pairs as a result of the excitation of the host, while $^3F_4$ is populated mainly by direct impact of hot electrons. Since the energy transfer rate under high field is very small compared with that under zero field, which is the case in PL, it is difficult to populate $^1G_4$ in this way. Thus the weakening of the blue emission in ZnS:Tm TFEL with the present structure seems inevitable.

As for the electron energy distribution, a definite conclusion cannot be reached, but the low efficency of blue emission in ZnS:Tm implies a 'not hot' electron distribution in ZnS:Tm. It seems that for Tm^{3+} inelastic scattering of hot electrons by low energy levels, which do not exist in Mn^{2+}, is a probable source causing some difference in hot electron distribution for ZnS:Mn and ZnS:Tm. It appears that Baraff's function with E_0=0. 36 eV is an appropriate one for ZnS:Tm.

Acknowledgment

This project was supported by the National Natural Science Foundation of China.

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