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Changchun Institute of Physics, Chinese Academy of Sciences, Changchun¹⁾

Temperature Effect on AC EL Characteristics in ZnS:ErF₃ Thin Films

By

LIJIAN MENG and CHANGHUA LI

The temperature effect on ac EL characteristics in ZnS:ErF₃ thin films is studied. By measuring EL spectra and EL decay curves at different temperatures, the temperature effect on the cross-relaxation processes occurring between Er ions is discussed. In addition, primarily the temperature effect on the decay time of ⁴S_{3/2} and ⁴F_{9/2} energy levels is discussed.

Es wird der Temperatureinfluß auf die Wechsellspannungs-Elektrolumineszenz(EL)-Charakteristiken in dünnen ZnS:ErF₃-Schichten untersucht. Die EL-Spektren und EL-Abklingkurven bei verschiedenen Temperaturen sowie der Temperatureinfluß auf die Kreuzrelaxationsprozesse, die zwischen den Er³⁺-Ionen auftreten, werden diskutiert. Zusätzlich wird der Temperatureinfluß auf die Abklingzeit der ⁴S_{3/2}- und ⁴F_{9/2}-Energieniveaus diskutiert.

1. Introduction

Trivalent rare earth ions are efficient luminescent centers for electroluminescence (EL) of ZnS thin films which are promising display materials and attract more and more attention [1 to 3]. In most cases, ZnS thin films doped with Er ions show green ac EL [2, 3]. However, some research results have shown that the red component of emission spectra increases obviously with increase of Er ion concentration in ZnS thin films. This is due to the cross-relaxation processes between Er ions [4]. In this paper, we discuss the effect of temperature on the cross-relaxation processes occurring between Er ions.

2. Experimental Details

The fabrication method of the samples is similar to that of [4]. In order to cut down the drive voltage, we fabricate the device with single insulating layer, ITO–Y₂O₃–ZnS:ErF₃–Al. The EL characteristics of single insulating layers are similar to those of double insulating layers [5]. To observe obviously cross-relaxation processes, the Er ion concentration in ZnS thin film is as high as 20 mol%.

The EL emission is detected using a 44 W monochromator in combination with an R456 photomultiplier. To record the EL decay curves, a BX-530A boxcar is used.

3. Results and Discussions

We have measured the ac EL spectra at different temperatures; the temperature varies from 77 K to room temperature, as shown in Fig. 1. We define the emission intensities from ²H_{11/2}, ⁴S_{3/2}, and ⁴F_{9/2} to ⁴I_{15/2} as I₁, I₂, and I₃, respectively. Fig. 2 shows I₃/(I₁ + I₂)

¹⁾ P.O. Box 1035 (14), Changchun, Jilin, People's Republic of China.

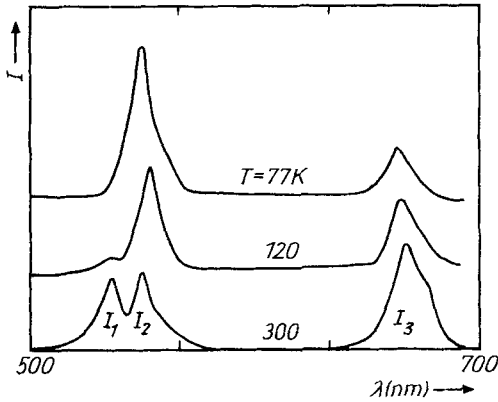


Fig. 1

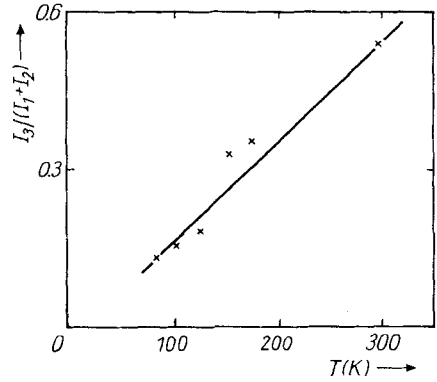


Fig. 2

Fig. 1. The ac EL spectra of ZnS:ErF₃ thin films at various temperatures

Fig. 2. $I_3/(I_1 + I_2)$ vs. temperature

versus temperature. It is found that the ratio increases with rising temperature. The experimental results have shown that the ratio increases with the increase of Er concentration, because the cross-relaxation rate increases with the increase of Er concentration and results in an increase of the ratio. Fig. 3 shows the cross-relaxation processes between Er ions [4]. Therefore, we may suppose that the cross-relaxation rate increases with the increase of temperature. To obtain quantitative results, we measure the EL decay of $^4S_{3/2}$ and $^4F_{9/2}$ energy levels at different temperature, as shown in Fig. 4. It is seen from Fig. 4 that the EL decay of the $^4S_{3/2}$ level consists of fast and slow components. The fast component becomes the predominant component in EL decay with rising temperature as shown in Fig. 5, besides the EL decay time of the slow and fast components of the $^4S_{3/2}$ level decrease

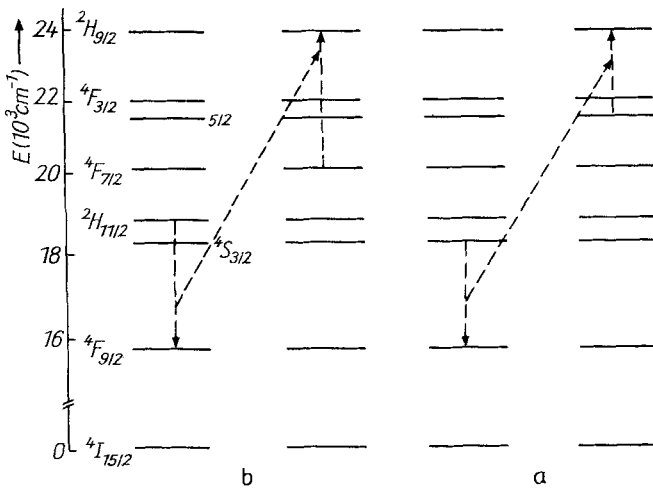


Fig. 3. Possible cross-relaxation processes

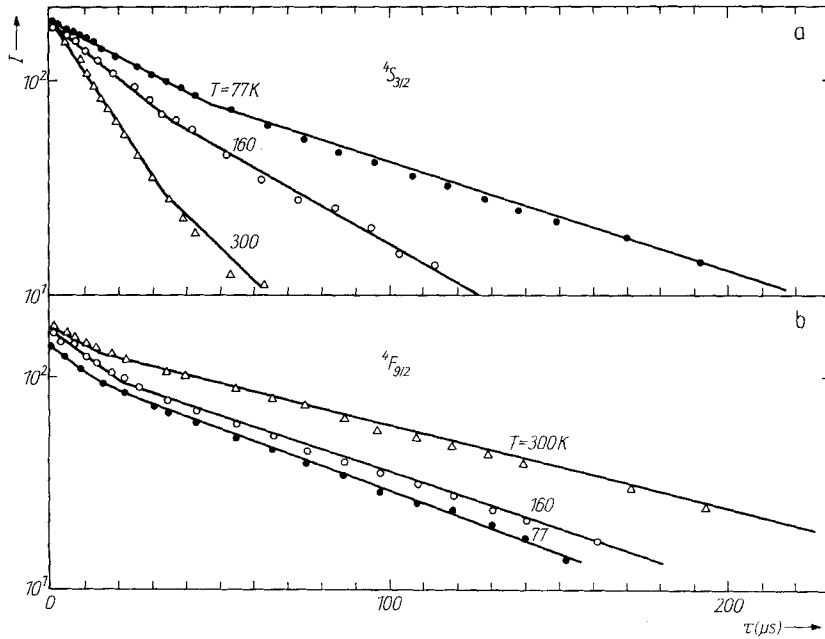


Fig. 4. The EL decay curves of the a) $^4S_{3/2}$ and b) $^4F_{9/2}$ energy levels at three different temperatures

with rising temperature as shown in Fig. 6a. However, the EL decay time of the $^4F_{9/2}$ level increases with rising temperature as shown in Fig. 6b.

To explain the decay properties of $^4S_{3/2}$ level we set up a three-level model of the Er ion, as shown in Fig. 7. Here P_{21} is the cross-relaxation rate; P_{20} and P_{10} are the radiative transition probabilities from $^2H_{11/2} + ^4S_{3/2}$ and $^4F_{9/2}$ to the ground state; n_1 and n_2 are the number of centres being in $^4F_{9/2}$ and $^2H_{11/2} + ^4S_{3/2}$ levels, respectively. Because the $^2H_{11/2}$ and $^4S_{3/2}$ levels are in thermal equilibrium, we can study their properties as a whole. The results show that the decay law of $^2H_{11/2}$ and $^4S_{3/2}$ levels is the same. At lower temperature, emission of the $^2H_{11/2}$ level disappears. Therefore, we still call $^2H_{11/2} + ^4S_{3/2}$ levels as $^4S_{3/2}$

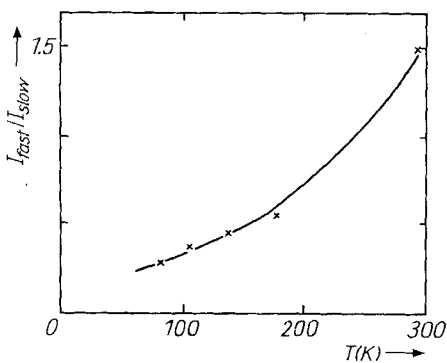


Fig. 5. I_{fast}/I_{slow} vs. temperature

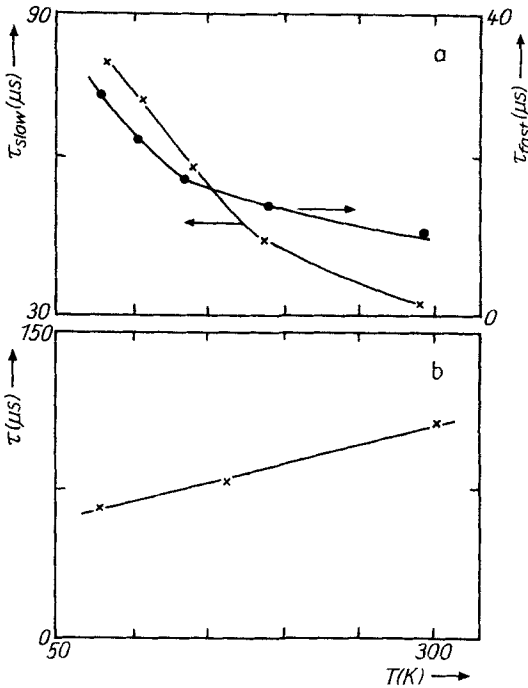


Fig. 6. a) The EL decay time of the fast (●) and slow (×) components of the $^4S_{3/2}$ energy level vs. temperature. b) EL decay time of the $^4F_{9/2}$ energy level vs. temperature

level. Neglecting nonradiative multiphonon transitions, the rate equations for the populations of $^4S_{3/2}$ and $^4F_{9/2}$ levels after excitation are

$$\dot{n}_2 = -P_{21}n_2 - P_{20}n_2, \quad (1)$$

$$\dot{n}_1 = P_{21}n_1 - P_{10}n_1. \quad (2)$$

From (1) it is clear that decay of the $^4S_{3/2}$ level should be single exponential,

$$n_2(t) = n_{20} \exp(-P_{20} + P_{21})t) = n_{20} \exp(-P_2t). \quad (3)$$

However, from Fig. 4a it follows that the decay curves are not single exponential. The discrepancy between the experimental decay curves of the $^4S_{3/2}$ level and the theoretical curves described by (3) is ascribed to the fact that the cross-relaxation processes only occur between Er ions located in proper positions (proper position means there is an Er ion excited to the $^4F_{7/2}$ or $^4F_{5/2}$ level which is near an Er ion excited to the $^2H_{11/2}$ or $^4S_{3/2}$ level [4, 6]. Not all Er ions are located in proper positions. Equation (3) only indicates the decay of Er ions occurring in the cross-relaxation processes. However, because of the presence of Er ions without cross-relaxation processes, the expression for the population of the $^4S_{3/2}$ level at time t after the excitation pulse becomes

$$n_2(t) = n_{20} \exp(-P_2t) + n_{20}^0 \exp(-P_{20}t), \quad (4)$$

where n_{20} is the population of the $^4S_{3/2}$ level of Er ions at $t = 0$ after excitation in which the cross-relaxation will occur; n_{20}^0 is also the population of the $^4S_{3/2}$ level of Er ions at

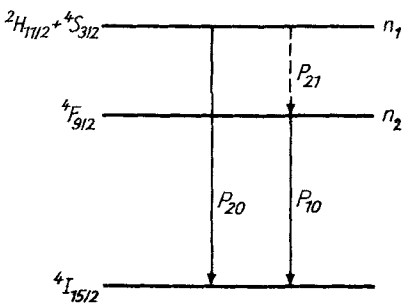


Fig. 7. The three-level model of the Er ion

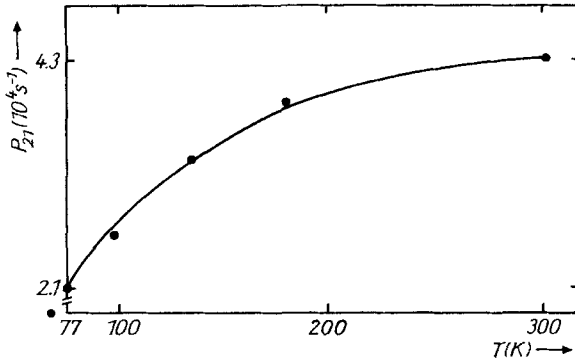


Fig. 8. The cross-relaxation rate vs. temperature. ● Experimental values, — fitted curve

$t = 0$ after excitation but in which the cross-relaxation will not occur. We have obtained the cross-relaxation rate P_{21} at various temperatures by the fit according to (4) of the decay curves of the $^4\text{S}_{3/2}$ level, as shown in Fig. 8. It is seen from Fig. 8 that the cross-relaxation rate increases with rising temperature and results in the increase of the emission intensity of the $^4\text{F}_{9/2}$ level.

Some results have shown that the cross-relaxation rate P_{21} obeys the $A + B \exp(-E/kT)$ relation [7]. We tried to fit the experimental data in Fig. 8 to this relation. The best fit is presented in Fig. 8 and is obtained with the parameters $A = 6100 \text{ s}^{-1}$, $B = 48500 \text{ s}^{-1}$, $E = 50 \text{ cm}^{-1}$. This suggests that the cross-relaxation rate is 6100 s^{-1} at very low temperature and remains practically constant up to $kT = 50 \text{ cm}^{-1}$ ($T = 70 \text{ K}$) above which temperature it starts to increase rapidly. Therefore, when the temperature is higher than 77 K, the cross-relaxation rate increases with rising temperature.

It is seen from Fig. 5 that the fast component becomes the predominant component in EL decay with rising temperature. This suggests that n_{20} increases with rising temperature. The result that the cross-relaxation rate increases with rising temperature does not explain this phenomenon, because the cross-relaxation rate does not depend on n_{20} . Our results have shown that the cross-relaxation processes are due to the interaction between two dipoles [8]. Inokuti and Hirayama have pointed out that the interaction has a critical distance. When the distance between ions is longer than the critical distance, the cross-relaxation rate will fall down [9]. Some results have shown that the critical distance increases with rising temperature [7]. This will result in the increase of n_{20} . Therefore, the fast component becomes the predominant component in EL decay with rising temperature.

Fig. 6a has shown that the decay times of the fast and slow components of the $^4\text{S}_{3/2}$ level all decrease with rising temperature. The change of the decay time of the fast component depends on the cross-relaxation processes. The cross-relaxation rate increases with temperature and results in decrease of the decay time of the fast component of the $^4\text{S}_{3/2}$ level.

The EL decay time of the slow component of the $^4\text{S}_{3/2}$ level does not depend on the cross-relaxation processes. The decrease of decay time shows that there are other nonradiative processes. Yokota and Tanimoto pointed out that the energy migration among donor ions would be more important when the concentration of donor ions is higher than that of acceptor ions [10]. The cross-relaxation processes occur between two excited Er ions in ZnS:ErF₃ thin films, the number of donor ions is higher than that of acceptor ions [8]. Therefore, energy migration among donor ions will appear, and the energy migration

rate will also increase with rising temperature. Hence, the decay time of the slow component will decrease with rising temperature.

Fig. 6b shows that the decay time of the ${}^4F_{9/2}$ level increases with rising temperature. This phenomenon is found for the first time. The decay time will decrease with rising temperature as a general rule. We suppose that the increase of the decay time of the ${}^4F_{9/2}$ level is not due to the direct cross-relaxation processes, because the direct cross-relaxation processes occur in a short time after the pulse (the decay time of the fast component of the ${}^4S_{3/2}$ level is $\approx 10 \mu\text{s}$), its influence on the decay time of the ${}^4F_{9/2}$ level cannot be so long ($100 \mu\text{s}$). The energy migration among the donor ions is important for the Er ion, therefore the increase of the decay time of the ${}^4F_{9/2}$ level is due to the energy migration among donor ions. After excitation, the energy of some donor ions located in proper environment will migrate. When the energy migrates to a proper position, the ion will relax from ${}^4S_{3/2}$ to ${}^4F_{9/2}$ state. The energy released will be absorbed by impurity and defect centers. The energy migration rate increases with rising temperature and results in the decrease of the decay time of the slow component of the ${}^4S_{3/2}$ level and in the increase of the decay time of the ${}^4F_{9/2}$ level. The details of energy migration will be the subject of further research work.

4. Conclusion

When the temperature varies from 77 K to room temperature, the EL decay of the ${}^4S_{3/2}$ level of Er ions can be divided into two exponential components of fast and slow decay. Their decay times all decrease with rising temperature. However, the decay time of the ${}^4F_{9/2}$ level increases with rising temperature. By analysis of the results it is found that the cross-relaxation rate increases with rising temperature and results in a decrease of the decay time of the fast component of the ${}^4S_{3/2}$ level. Besides, the energy migration among the donor ions results in a decrease of the decay time of the slow component of the ${}^4S_{3/2}$ level and an increase of the decay time of the ${}^4F_{9/2}$ level with rising temperature. Because the energy gap of ${}^4S_{3/2} - {}^4F_{9/2}$ is less than that of ${}^4F_{5/2} - {}^2H_{9/2}$, the phonons will take part in the cross-relaxation processes. We suggest that this is the reason why the cross-relaxation processes depend on temperature.

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