Journal of Luminescence 18/19 (1979) 913–916

EXCITATION MECHANISM IN DC ELECTROLUMINESCENCE OF Y_2O_3·Eu SINTERED SLICE AND ZnS·Cu, Er, Cl THIN FILM AGEING AND FORMING PROCESSES

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Some remarks on the impact excitation process in ZnS·Cu, Er, Cl thin film and the origin of initial electrons in Y_2O_3·Eu sintered slice are given. The ageing and forming processes are examined from the viewpoint of field strength changes in the high field region.

The wide bandgap materials are of great interest in luminescence, but it is difficult to make type conversion owing to the self-compensation effect. As a result, high electric field is often indispensable to produce electroluminescence (EL) in such materials. For this reason we have paid special attention to the high field effect, e.g., we proved the existence of impact ionization in ac EL of ZnS powder immersed in dielectric medium by means of the short photoexciting pulse perturbation method [1], we studied the influence of the electric field strength on the recombination cross sections of conduction band electrons with ionized luminescent centres in ZnS powders [2].

In this paper, some experimental results on the excitation mechanisms of dc EL under high electric field are given. We investigated the role and origin of initial electrons in dc EL of Y_2O_3·Eu and proved the existence of impact excitation in dc EL of ZnS thin films. On the basis of these results, a preliminary analysis of the ageing and forming process in the dc EL of thin films was carried out.

First of all, we examined the local character of the region from which luminescence originated. From the microscopic observations, it was shown that the light emitted by the slice of Y_2O_3·Eu was limited to a thin layer closely adjacent to the cathode (the slice was sandwiched between two SnO_2 coated glass plates). The higher the applied voltage was, the wider the luminescent region. The maximum width of the luminescent layer extended up to 200 μm when the applied voltage increased to 1500 V. The electric field distribution along the direction perpendicular to the surface of the slice was investigated by means of the scanning electron microscope. The micrograph of the distribution of secondary electrons emitted from the profile of a slice under dc bias shows that the voltage drops abruptly in the vicinity of the cathode where a high field region is established.

For the thin film of ZnS·Cu, Er, Cl, a similar micrograph was obtained.

Electrical measurements indicated that the current–voltage characteristics were not symmetrical; a potential barrier should exist. The existence of this barrier was also examined from capacitance measurements. Without a potential barrier in the film, the capacitance of pure ZnS film at a thickness of 1.5 μm should be about 0.05 $\mu F/cm^2$. The capacitance of this doped film at the same thickness is found to be about 0.1 $\mu F/cm^2$. This is considered as an evidence for a potential barrier in this film.

These facts indicate that excitation processes take place in high electric field in both cases.

When dc or rectangular pulses are applied to the sintered $Y_2O_3 \cdot Eu$ slice sample, a series of peculiar and interesting properties can be detected. The most important one seems to be the existence of a threshold voltage for light emission. Both the current and light intensity depend on the applied voltage according to power laws:

$$I \propto V^n \quad \text{and} \quad J \propto V^m,$$

where $n \cong 1.2$ and $J \cong 0$ at low voltage, $n \cong m > 5$ at high voltage.

We examined the threshold as a function of humidity of the surrounding atmosphere and found that the threshold value increased rapidly when the relative humidity was decreased. If we put the sample into a vacuum chamber and kept the applied voltage constant, when the pressure decreased by pumping, the light intensity increased at the very beginning, surpassed a maximum at about 4×10^2 Torr, and then went down to zero [3].

On the other hand, if we excited the sample with an increasing voltage, the instantaneous light intensity and current both increased correspondingly. But, when we kept the voltage constant at a definite value, the light intensity and current both dropped down to a lower stable value (see fig. 1). This phenomenon could be demonstrated as being a result of electron accumulation.

From these experimental results we can draw the conclusion, that the initial electrons are supplied by impact ionization of surrounding gaseous molecules,

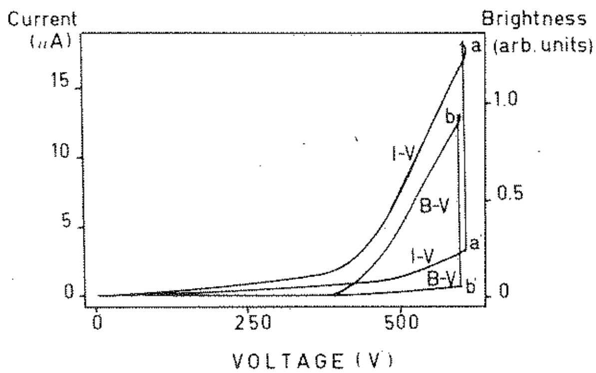

Fig. 1. Current (I) vs. voltage (V) and light brightness (B) vs. voltage relations in a sintered slice under dc excitation. Curves 0a and 0b correspond to dynamic low resistance state, curves 0a' and 0b' correspond to static high resistance state.

probably adsorbed molecules. An additional evidence for this argument serves the fact that when we brought the sample from vacuum to the ordinary environment again, it would take a long time, up to hours, to recover the brightness. Another additional evidence can be found also from the measurement of short circuit current after switching off the external electric field. This short-circuit current may persist for ten or more seconds.

In case of ZnS·Cu, Er, Cl thin film, the mechanism of excitation in dc EL was examined by studying the variation of emission spectrum with the applied voltage. With a certain reasonable assumption the conclusion of impact excitation can be reached as in the similar works given by Krupka and Kobayashi for ac EL [4, 5].

Based on these experimental results, we tried to use the ratio of green ($\lambda = 5520$ Å) to red ($\lambda = 6650$ Å) line intensities as a certain kind of indicator in order to estimate the electric field strength at which the dc EL originates. Applying this method to the analysis of ageing and forming processes, we found that this ratio decreased with ageing and increased with forming processes (see fig. 2). That is, the field intensity was decreased during ageing and increased after forming.

The capacitance measurement shows at the same time that the capacitance of the film decreased by 20% after ageing and increased by 40% after forming. This can be attributed to the variation of positive space charges in the high field region, which, in its own turn, changes the field strength.

Thus, the ageing and forming processes arise essentially with the strength change of the electric field at which the EL originates. If the operation condition was so chosen that the forming process was continuously active, the ageing process during operation might be partially compensated by the forming process. Films with a half-life more than 1000 h and a luminance higher than 34 cd/cm^2 were obtained in our laboratory.

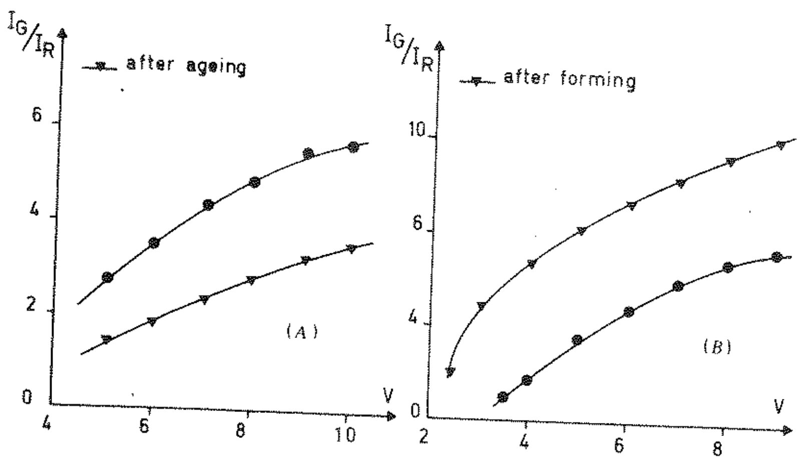

Fig. 2. Dependence of the ratio of green ($\lambda = 5520$ Å) to red ($\lambda = 6650$ Å) line intensities on the applied voltage.

Acknowledgements

The authors are indebted to Prof. Hsu Shaohung and also to Fan Hsiwu, Tai Jensung, Hsung Kuangnan for helpful discussions.

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