ZnS:Sm and ZnS:Cu, Sm electroluminescent phosphors

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Abstract. Electroluminescent ZnS: Sm and ZnS: Cu, Sm phosphors have been prepared and their electroluminescent (EL) characteristics have been studied. The time-averaged EL brightness follows the Alfrey-Taylor relation over a wide range of frequencies. The constants of this relation have been determined. The EL emission shows one main and one auxiliary peak during each half cycle of the applied voltage. Variation of current with applied voltage has also been investigated.

Keywords. Electroluminescence; brightness-waves; ZnS: Sm and ZnS: Cu, Sm electroluminors; Alfrey-Taylor relationship.

1. Introduction

Electroluminescence (EL) can be studied by their luminescence characteristics or electrical properties or the absorption of energy of external excitation. Studies on brightness waves, emission spectra and the time-averaged brightness as a function of applied voltage and frequency have helped in understanding the mechanism of luminescence. The study of rare-earth doped (Chase *et al* 1969; Waite and Vecht 1971) zinc sulphide type lattices is interesting for several reasons and has been done in conjunction with a wide variety of luminescent phenomena. The common feature of all such investigations is that they exhibit emission lines corresponding to $(4f)^n$ configuration of the trivalent ion. The rare-earth emission lines appear under both types of excitations *i.e.* PL and EL. Usually they are suppressed on the background emission due to copper which was added to make the phosphor more electroluminescent. These phosphors are of interest from the viewpoint of their application to fast-type colour displays.

The present paper reports such investigations on the newly synthesized ZnS: Sm and ZnS: Cu, Sm electroluminors in the form of fine crystalline powders of particle size of about 10 μ .

2. Experimental

The electroluminors were prepared as described earlier (Maheshwari and Khan 1975). The following compositions were used:

Figure 1. Block diagram of the experimental arrangement for determining the spectral distribution of EL emission M, monochromator; T, photomultiplier tube; G, galvanometer; P, power supply; S, voltage stabilizer; M, AC mains; O, oscillator; A, wide band amplifier; E, EL cell.

- (a) 0.702×10^{-3} Sm per g ZnS.
- (b) $(0.702 \times 10^{-3} \text{ g Sm} + 3.00 \times 10^{-3} \text{ g Cu})/\text{g ZnS}$

The firing was carried out at a temperature of about 1000°C for approximately 1 hr in a continuous flow of pure argon gas. The phosphors were dried at 120°C and sieved to 200 mesh size. EL cells were prepared from these powders using castor oil as dielectric. One volume of phosphor powder was used with two volumes of castor oil. The suspension was placed over a conducting glass plate, which formed one electrode of the cell and a metallic electrode was applied from above. The layer was of constant thickness of about 60μ . A thin mica sheet was introduced between the phosphor and the metallic electrode. The sinusoidal a.c. voltages used were generated by an audio frequency oscillator-cum-wide band amplifier as shown in figure 1. Light was detected by an RCA IP21 photomultiplier tube. The time-varying light output wave forms were studied using a dual trace oscilloscope (OS 785, ECI). The current through the EL cell was measured with a digital multimeter. Spectral measurements were made with a prism monochromator with RCA IP21 detector coupled with a multiflex galvanometer (sensitivity of the order of 6×10^{-10} A/mm) at the exit slit. Resolution was about $10 \text{ \AA}$. Because of the low brightness magnitude of ZnS: Sm phosphor, its EL spectrum was measured using Zeiss interference filters. The photomultiplier tube was calibrated with a tungsten filament lamp of known colour temperature. Throughout the measurements the geometry of the arrangement was kept identical.

Figure 2. Oscillograms of ZnS: Sm electroluminor showing the phase relations of emitted light with applied a.c. voltage (a) at 400 V of different frequencies (b) at different voltages of 2 kHz frequency.

3. Results and discussion

3.1 Brightness-wave shapes

Figure 2 shows the oscillograms of the voltage and brightness waves. There are two main and two auxiliary peaks in each cycle of the applied voltage. The main peaks lag in-phase with the applied voltage. The auxiliary peaks become more pronounced with increase in the applied voltage of constant frequency. They are also better developed at lower frequencies keeping the voltage constant.

The field E_d in the dielectric lags in-phase with the applied field E_p in the phosphor by an angle ϕ which according to Destriau can be written as

$$\tan \phi = \frac{2}{K\rho\nu}$$

where ν is the frequency of the applied field, ρ is the specific resistance of the phosphor and K is the dielectric constant of the phosphor.

According to Ivey (1963) and Destriau (1954) the field E_d in the dielectric also lags in-phase to the voltage V applied across the EL cell (Singh and Mohan 1969). If the phosphor used is much less than that of the dielectric, then the phase difference between the field E_p in the phosphor and applied voltage V is ϕ . This means that the ϕ phase difference exists between the EL output and the applied a.c. voltage (Bhushan *et al* 1979). Thus the phase difference decreases with increase in frequency. But at higher voltages, the resistivity ρ decreases and finally at very high voltages dielectric breakdown occurs, thus ϕ increases. Our experimental results are in close agreement with the above findings. The phase difference between the brightness waves and applied higher a.c. voltages of lower frequencies is greater than that of low applied voltages of higher frequencies as shown in figure 2.

The auxiliary peaks are attributed to the return of trapped charges, under the influence of a residual polarization field when the external voltage decays to zero. These transitions require greater excitation energy and therefore appear at higher voltages.

Figure 3. Variation of time averaged EL brightness of ZnS: Sm electroluminor with voltage at different frequencies of the applied field.

Figure 4. Variation of time averaged EL brightness of ZnS: Cu, Sm electroluminor with voltage at different frequencies of the applied field.

3.2 Integrated light output with applied voltage

The variation of integrated EL output with applied voltage at various frequencies is demonstrated in figures 3 and 4 for ZnS: Sm and ZnS: Cu, Sm phosphors respectively. The functional relation which best describes these curves is identical to the Alfrey-Taylor curve

$$B = B_0 \exp \left(- \frac{b}{V^{1/2}} \right)$$

This equation is derived assuming Mott-Schottky type depletion barriers inside the phosphor where the field E varies as the square root of the voltage. These observations confirm that the mechanism of EL in the phosphors studied is of acceleration collision type (Zalm *et al* 1955). The constants b and B_0 of the above relation have been calculated using figures 3 and 4 for ZnS: Sm and ZnS: Cu, Sm phosphors

Figure 5. Variation of b and B_0 with frequency for ZnS: Sm and ZnS: Cu, Sm electroluminors.

Figure 6. Variation of time averaged EL brightness of ZnS: Sm electroluminor with frequency of the applied field at different voltages.

respectively. The dependence of these constants on frequency given in figures 5 and 6 respectively show that b varies slightly with frequency whereas B_0 increases with the frequency. These observations are in close agreement with the investigations by other workers on related phosphors.

3.3 Integrated light output with frequency of the a.c. voltage

The dependence of integrated EL output with the frequency of the applied voltage has also been studied and the experimental observations are given in figures 6 and 7 for various values of applied voltages. Measurements show that EL output increases linearly with frequency until saturation starts (Lehmann 1956; Haake 1956). The characteristic frequency of saturation, however, varies from cell to cell. These observations can be explained by considering the bimolecular law of recombination of electrons with luminescent centres which has yielded the following relation (Curie 1963)

Figure 7. Variation of time averaged EL brightness of ZnS: Cu, Sm electroluminor with frequency of the applied field at different voltages.

$$B = K n_0^2 \alpha / 1 + (n_0/2\nu),$$

where B denotes the EL brightness, K is a constant of proportionality, n_0 is the initial electron concentration in the conduction band, α is the recombination coefficient and ν is the frequency of applied voltage. If α is large compared to ν , the EL brightness will grow with ν as is usually the case. If the excitation frequency is sufficiently high $n_0/2\nu \ll 1$, a state of saturation results, again agreeing with experimental observation.

3.4 Current voltage characteristics of the EL cell

Figure 8 shows the variation of current in the EL cell with the applied voltage and figure 9 shows the variation of current with the square root of applied voltage. It is obvious that the current through the cell follows the relation $I \approx \exp -aV^{1/2}$ up to 200 V (RMS). Above this voltage the slope of the curve decreases and it follows the relation $I \approx \exp (aV)$ for the voltage up to 600 V (RMS). The change in the current voltage characteristic from $\exp (aV^{1/2})$ to $\exp (aV)$ can be interpreted by considering the specks of copper sulphide to act as electrodes upon phosphor grains. When the field is switched on, electrons from one side of the grains move towards the other, leaving behind positive holes near negative electrode due to ionised centres. These observations suggest the existence of an exhaustion barrier, the height of which reduces at higher voltages, since the effective field across the barrier increases at higher voltages (Maheshwari and Khan 1974). Consequently the current through the EL cell follows the relation $\exp (aV)$ at higher voltages.

Figure 8. Variation of current with applied voltage for ZnS: Sm and ZnS: Cu, Sm electroluminors.

Figure 9. Variation of current with square root of applied voltage for ZnS: Sm and ZnS: Cu, Sm electroluminors.

Figure 10. Spectral energy distribution of ZnS: Sm electroluminor at 600 V of 5 kHz frequency.

Figure 11. Spectral energy distribution of ZnS: Cu, Sm electroluminor at 600 V of 5 kHz frequency.

3.5 Emission spectra

The EL emission spectra of ZnS: Sm and ZnS: Cu, Sm phosphors have been recorded in the region 400–650 nm and are shown in figures 10 and 11 respectively. The EL samples, ZnS: Sm and ZnS: Cu, Sm were excited with a.c. voltage of 600 V (RMS) at 5 kHz frequency. There are indications that the spectra of both the phosphors *i.e.* ZnS: Sm and ZnS: Cu, Sm, extend beyond 625 nm towards red. Since our photomultiplier tube was not sensitive for this region, the same could not be recorded. The spectra of ZnS: Sm show two emission peaks, one at 460 nm which is presumably due to self-activated (luminescence) centres and the other at 550 nm which is due to transition $^4G_{5/2} \rightarrow ^6H_{5/2}$ of trivalent Sm ions. The spectra of ZnS: Cu, Sm show three emission peaks due to $^4G_{7/2} \rightarrow ^6H_{7/2}$ at 520 nm, $^4G_{5/2} \rightarrow ^6H_{5/2}$ at 550 nm and $^4G_{5/2} \rightarrow ^6H_{7/2}$ at 610 nm corresponding to $4f-4f$ transitions of trivalent samarium ions. In this case the peak at 460 nm has not been observed. Identification has been made by comparison with the data of Magno and

Deike (1962). ZnS: Sm phosphor is a poor electroluminescent. The EL increases by the addition of copper to the phosphor.

4. Conclusion

From the observed experimental results it is concluded that the EL of samarium centres in these phosphors occurs with impact excitation by hot electrons.

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