ZnO: Cu, Sn electroluminescent phosphor

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MS received 16 October 1980; revised 5 March 1981

Abstract. The a.c. electroluminescent characteristics of ZnO:Cu, Sn powder phosphor have been investigated in audio frequency range. A simple preparative method for this phosphor has been described. The detailed variation of light output during one cycle of the applied sinusoidal voltage has been studied and discussed. In addition to the two primary peaks, the two secondary peaks have also been observed in each cycle of the applied field. The voltage and frequency dependence of the time-averaged electroluminescent brightness have been found to follow the Alfrey-Taylor relation over a wide range of frequencies. The constants of this relation have been determined. The spectral energy distribution of this phosphor shows that the peak-shift depends upon the a.c. frequency and is independent of the magnitude of applied field.

Keywords. Electroluminescence; voltage and frequency dependence; brightness waves; spectral distribution; ZnO:Cu, Sn Phosphor.

1. Introduction

While the EL phosphors of sulphur dominated base lattices (Homer et al 1953; Lehmann 1957), activated by suitable activators and co-activators have been the subject of numerous investigations, the phosphors having ZnO as the host matrix have drawn comparatively less attention. Literature survey has revealed that the binary systems having ZnO as one of the matrices have not been studied adequately (Schwager 1961, Singh and Mohan 1968, 1969; Maheshwari and Khan 1975). Studies on single base ZnO phosphors have also been scarce (Bhushan and Pandey 1978; Dingle 1969; Meyer et al 1965, Vereshchagin and Drakak 1962). The present paper reports the results of the investigation on the new electroluminescent ZnO:Cu, Sn phosphors.

2. Experimental

For the preparation of this phosphor, pure (luminescent grade) ZnO obtained from M/s. Derby Luminescence, England was taken as the starting material. Copper and tin were added to it in the form of copper acetate and stannous chloride respectively. The mixture containing 5 g ZnO (luminescent grade), 0.05 g (CH₃COO)₂ Cu.H₂O (AR grade), 0.25 g SnCl₂.2H₂O (AR grade), 0.0092 g NH₄Cl (AR grade) and 0.025 g pure sulphur was fired in a loosely-capped silica crucible kept inside a tubular furnace at a temperature of 950°C in a continuous flow of pure nitrogen gas. The firing time was 90 minutes.
After firing, the fired content was suddenly cooled in air to room temperature and was finely powdered. It was then washed with sodium thiosulphate solution and with dilute acetic acid to remove unreacted copper and zinc oxide. The phosphor was finally washed with alcohol and double distilled water. Then it was dried at 120°C and sieved to 200 mesh size. Phosphors having the same colour composition, were also prepared without using sulphur, but the EL emission was enhanced by the incorporation of sulphur in the phosphors. Perhaps sulphur helps the formation of copper sulphide segregations, which are believed to be essential for good EL. These findings agree with those of Lehmann (1961, 1968).

A permanent type of EL cell was used, in which a plane-polished aluminium plate served as the back electrode and the transparent conducting glass plate (resistance of the order of 100Ω/cm²) served as the front electrode. A thin mica sheet was put on the front side of the aluminium plate. The finely-sieved phosphor was mixed in araldite and was pressed between the two electrodes. The thickness of the air free phosphor layer was 60 μ. The EL cell was excited with AC voltages in the audio frequency range obtainable from an audio frequency oscillator-cum-wide band amplifier (range from 0 to 750 V (r.m.s.)). The electroluminescent spectrum was measured with the constant deviation spectrometer. The light output signal was measured by an RCA-IP21 photomultiplier tube operated with a stabilized D.C. power supply and a multiflex-galvanometer (sensitivity 6 × 10⁻¹⁰ A/mm). The photomultiplier tube was calibrated with tungsten filament lamp of known colour temperature.

3. Results and discussion

The oscillograms of the integrated light output of the electroluminescent cell and the applied sinusoidal electric field versus time at different frequencies and voltages have been shown in figure 1. It is evident from these oscillograms that (a) there exist one primary and one secondary peak in each half cycle of the applied sinusoidal voltage, (b) the primary peak lags inphase with the applied voltage, (c) the phase lag of the primary peak decreases with increase of frequency of the applied field (d) the secondary peak becomes more prominent at higher voltages and lower frequencies. These observations can be explained on the basis of the relation \( \tan \phi = \frac{4\pi K_p \omega}{2 K_p f} \) derived by Destriau (1954) where \( K \) is the dielectric constant of the phosphor and \( \rho \) is its specific resistance.

The existence of the secondary peaks is attributed to the delayed transition of electrons from the deeper trap levels to the fundamental Cu level. These transitions will require more excitation energy. Hence they are more prominent at higher voltages.

The variation of time-averaged EL emission with \( \frac{100}{\sqrt{V}} \) at different frequencies of the field ranging from 60 to 10 kHz is shown in figure 2. It is evident that the light intensity \( B \) follows the relation \( B = B_0 \exp \left( -\frac{b}{\sqrt{V}} \right) \) over the entire frequency range. The close agreement of this relation with our experimental observations suggests the existence of an exhaustion barrier in this phosphor, the width of which varies as \( \sqrt{V} \). Therefore, the mechanism of electroluminescence in the phosphor studied is of acceleration-collision type (Zaln et al 1954). From the variations of the constants \( b \) and \( B_0 \) with the frequency of the applied field (as shown in figure 3), we
Figure 1. Wave shapes of the EL brightness of ZnO:Cu, Sn electroluminor and the applied sinusoidal voltage versus time.

Figure 2. Variation of time-averaged EL brightness of ZnO:Cu, Sn electroluminor with 100/√V at different frequencies of the applied field.
observe that $b$ varies slightly with increase of the frequency whereas log $B_0$ is more sensitive to the frequency.

The variation of time-averaged EL emission intensity of the cell with the frequency of the applied field at a constant voltage (figure 4) shows that EL brightness increases.

![Figure 3](image)

**Figure 3.** Variation of $b$ and log $B_0$ with frequency.

![Figure 4](image)

**Figure 4.** Variation of time-averaged EL brightness of ZnO:Cu, Sn electroluminor with frequency of the applied field at different voltages.
linearly with increase of frequency from 60 to 5 kHz whereas it tends to saturate or passes through a maxima at higher frequencies (Lehmann 1956; Haake 1956). This behaviour of integrated light output with increasing frequency is similar to that observed in related phosphors and conforms to the theory of hyperbolic recombination process given by Curie (1963) on the assumption of the bimolecular law of recombination of electrons with luminescent centres. Accordingly

$$B = C \frac{n_0^2 \alpha}{1 + \frac{n_0 \alpha}{2f}},$$

where $n_0$ is the number of electrons initially excited, $\alpha$ is the recombination coefficient and $C$ is the constant of proportionality. At low excitation frequency

$$B = C 2n_0 \cdot f \text{ since } 1 \ll \frac{n_0 \alpha}{2f}.$$  

It implies that the brightness increases linearly with increase of the frequency. At high excitation frequencies,

$$B = C \alpha n_0^2 \text{ since } 1 \gg \frac{n_0 \alpha}{2f}.$$  

i.e. the brightness is independent of frequency. This satisfactorily explains our experimental findings. The decrease in light output at higher frequencies, and higher voltages may be due to the dielectric heating of the sample or voltage losses in the transparent conducting electrode (Destriau and Ivey 1955).

The spectral energy distribution of electroluminescent brightness of ZnO: Cu, Sn electroluminor at various frequencies ranging from 200 to 10 kHz at 400 V (r.m.s) is shown in figure 5. It is observed that the electroluminescent emission of this phosphor extends from 4400 to 6200 Å. The phosphor shows only one distinct maxima at each frequency of the applied field. The peak of the EL emission shifts towards shorter wavelength side with increase of the field frequency, whereas it remains unchanged with increase or decrease of the applied voltage at a fixed frequency as is evident from figure 6.

The main features of this phenomenon can be accounted within the framework of the Schon-Klasen's model (Waymouth and Bitter 1956). Accordingly, when the field is applied, luminescent centres are ionized. The released electrons will try to occupy the lowest empty centres for stability. If the frequency of the excitation is low, the lowest centres will be fully occupied and recombination will take place at higher centres. This means the emission will involve less energy i.e. higher wavelengths. Now if the frequency of the excitation is increased, the electrons will not have sufficient time to redistribute themselves. Consequently, the recombination will occur at low lying centres which means higher energy i.e. shorter wavelengths. This explains the shift of the spectrum towards the shorter wavelength side on increasing the frequency of excitation.
Figure 5. Spectral energy distribution of ZnO:Cu, Sn electroluminor at different frequencies.

Figure 6. Spectral energy distribution of ZnO:Cu, Sn electroluminor at different voltages.
The current-voltage characteristics of the electroluminescent cell are shown in figures 7 and 8. From semilog plot (figure 7) it is evident that the current varies as \( \exp(a V^{1/2}) \) for voltages up to 250 V (r.m.s.). Above this voltage (figure 8) it deviates from this relation and varies as \( \exp(a V) \). These observations further confirm the existence of exhaustion barrier in the phosphor, the width of which varies as the square root of the applied voltage. The deviation of the current voltage characteristic from \( \exp(a V^{1/2}) \) type to \( \exp(a V) \) type of variation at higher voltages can be explained by considering the specks of Cu$_2$S to act as electrodes upon the phosphor grains. When the field is applied, electrons from one side of the phosphor grains move towards the other side, leaving behind positive holes near the negative electrode.

![Figure 7](image1.png)

**Figure 7.** Variation of the current across the EL cell with square root of the applied voltage (at 500 Hz) for ZnO:Cu, Sn electroluminor.

![Figure 8](image2.png)

**Figure 8.** Variation of the current across the EL cell with the applied voltage (at 500 Hz) for ZnO:Cu, Sn electroluminor.
due to the ionized centres. Thus, it is obvious that there exists an exhaustion-barrier, the length of which is being reduced at higher voltages, since the effective field across the barrier increases at higher voltages. Consequently, the current through the EL cell follows the relation $\exp (aV)$ at higher voltages.

Acknowledgements

The authors gratefully acknowledge the financial assistance provided by C S I R, New Delhi to one of us (MHK). They are also thankful to Sri R K Tripathi for assistance.

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