RB-24

INSTANTANEOUS LIGHT OUTPUT AND BUILD-UP EFFECTS IN ELECTROLUMINESCENT PHOSPHORS

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This bulletin describes an investigation of the rate of build-up of light output of certain experimental electroluminescent (EL) phosphors in plastic-imbedded layers upon the sudden application of a sinusoidally varying potential. The EL light build-up can be closely approximated by an empirical relation of the following form

$$L = L_{max}(1 - e^{-f \cdot ^{9} t})$$

L = light output

f = frequency of applied a.c.

Heating the phosphors as much as 150 degrees C. did not materially change the build-up time. Cooling the phosphor to -50 degrees C. lengthened this build-up time by a factor of about two. Irradiating the phosphor with infrared for one minute before application of voltage increased this build-up time by as much as 50 percent, but the increase rapidly disappeared with either shorter time duration or less intensity of irradiation. Ultraviolet (UV) radiation had no effect on this build-up time up to levels of UV irradiation where the UV-excited luminescence was much larger than the EL. The build-up time was not voltage dependent.

Introduction

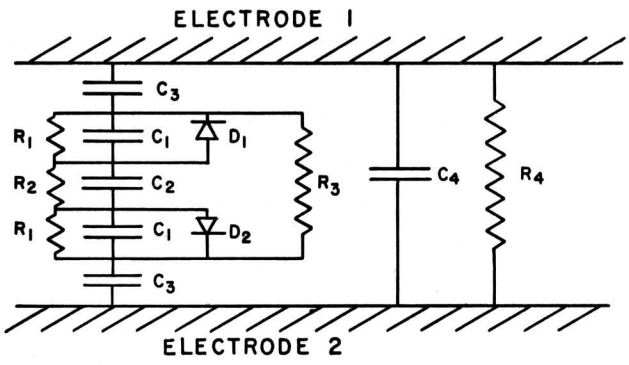
During work[1] on electroluminescent materials in connection with their application to a light amplifier type of device, it was found that a finite time of about 30 milliseconds was sometimes required for the phosphor to reach maximum light output after application of an a-c voltage. Initial investigations did not show marked effects from infrared (IR) or ultraviolet (UV) excitation. In 1954, Waymouth and Bitter[2] on the other hand did find an IR effect. In their paper on the optical and electrical response of EL phosphors dispersed in lucite to sudden changes in a d-c applied field, they stated that a sudden variation from a field, after the phosphor has reached equilibrium with the field applied, produces little or no light, while immediately returning to the steady state produces a large amount of light. Waiting a longer time and then returning to the steady state gave much less light. The interesting aspect of their work was that, when their samples were irradiated with infrared, they reached this equilibrium about 10^4 times as fast as normally. No mention was made of build-up time associated with a series of changes.

In 1954, Zalm, Diemer and Klasens[3] reported this build-up time with a.c. They attributed it to a charging up of the internal part of the EL particle, theorizing the equivalent circuit of Fig. 1. They assume that C_1, C_2, R_1, R_2, and R_3 are probably nonlinear with voltage. This circuit would allow almost any characteristics as to build-up time that one desired by merely changing the component sizes

[1] RB-14, An Electroluminescent Light-Amplifying Picture Panel

[2] Waymouth and Bitter, *Phys. Rev.*, Vol. 95, p. 941-949, (August 1954).

[3] Zalm, Diemer and Klasens, *Philips Research Reports*, Vol. 9, p. 81-108, (April 1954).



C_1 = CAPACITANCE OF SURFACE LAYER

C_2 = " OF BULK

C_3 = " OF SUSPENDING DIELECTRIC

C_4 = " OF DIELECTRIC PORES

R_1, R_2, R_3 } RESISTANCES OF BARRIER AND THE CONDUCTING LAYER AROUND THE CRYSTAL

R_4 = DIELECTRIC LOSS

D_1, D_2 } RECTIFYING ACTION OF THE BARRIER

Fig. 1 - Possible equivalent circuit for EL layer.

and characteristics. It is doubtful, though, that this type of equivalent circuit has much value other than to express the general aspect of the phenomenon.

The present bulletin describes some preliminary experiments to find the length of this build-up effect for some experimental phosphors as a factor of frequency and voltages, and to determine how this build-up time is affected by ultraviolet or infrared irradiation.

Equipment

The experimental set-up is shown in Fig. 2. When the knife switch is closed, the sweep on the cathode-ray-oscillograph (CRO) is triggered simultaneously with the voltage being applied to the sample. The electronic switch allows both the transient voltage and the light output to be observed in the proper phase and time relationship on the tube of the CRO. The applied voltage was measured on V_1, while V_2/R gave the current through the sample. A d-c microammeter (not shown) was connected in the 1P21 multiplier phototube output to measure the average level of the light output. A Hewlett Packard audio oscillator 201B and various audio amplifiers gave satisfactory sine wave output from 60 cps up to 18,000 cps, while a Tektronix 512 oscillograph was used to observe the wave-forms.

Instantaneous Light Output

Six experimental EL phosphors were excited with a.c. to observe the light output waveshape. In all six phosphors the reported[4] double peaks per half cycle applied a.c. were observed to a

[4] Destriau, M., Phil. Mag., Vol. 38, p. 700, 774, 880, (1947).

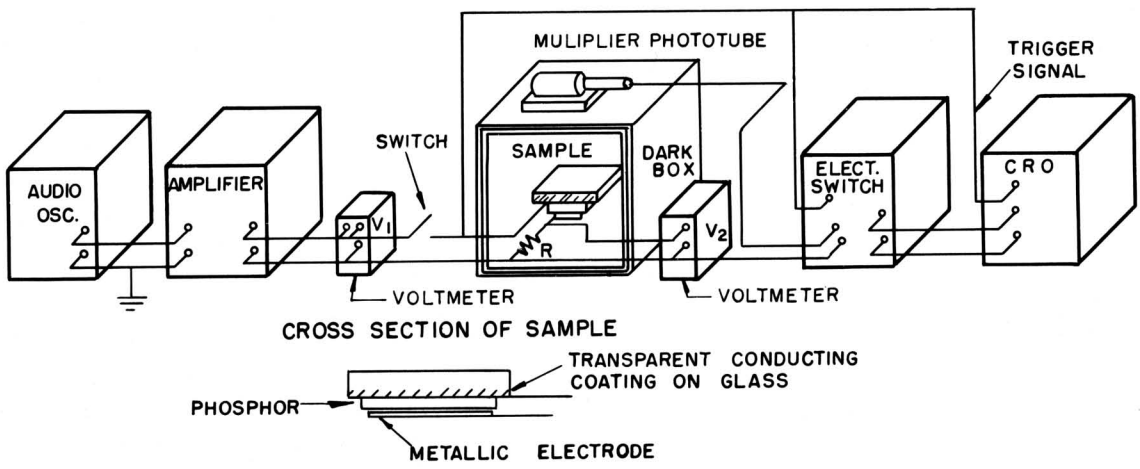


Fig. 2 - Block diagram of equipment.

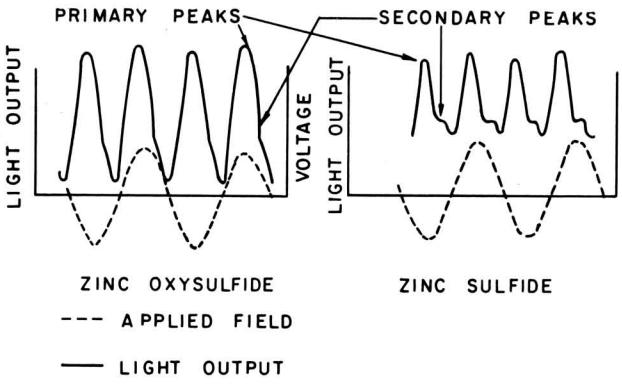


Fig. 3a - Extremes of magnitude of secondary peaks for different samples.

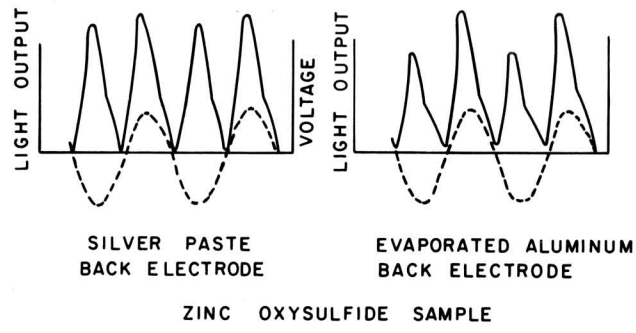


Fig. 3b - Effect of back electrode on symmetry of light output on alternate half cycles of applied field.

varying extent. Fig. 3 represents the extremes of the magnitude of this secondary peak.

Nudelman and Matossi[5] demonstrated that in their samples the spectral distribution of the secondary peaks was different from that of the main peak which indicates a different emission mechanism. These secondary peaks were observed both in samples with two emission bands (zinc oxysulfides and zinc sulfides) in which the spectral distribution of the two peaks differed as well as in samples with one broad emission band with perhaps only one emission mechanism.

The main peak leads the applied voltage slightly while the secondary peak trails the main peak by about 90 degrees. If it is assumed that the main light peak is associated with the maximum effective field *on the particles*, this secondary peak would occur when this effective field passes through zero.

Luyckx and Stokkink[6] have shown that secondary peaks of considerably varying size can be obtained by slightly changing the waveshape of the applied sinosoidal field and attribute the secondary peaks observed by other workers to assymmetry in their sine waves.

To preclude difficulties due to assymmetry in the measurements here, the voltage output of the amplifier was checked visually on CRO and found to be a smooth sine wave. In order to insure that the applied waveshape did not change from sample to sample, the light output waveshape of a particular sample has observed with various loads on the amplifier and was found to retain the same shape.

[5] Nudelman and Matossi, *Journal of Electrochemical Society*, Vol. 101, p. 546, (1954).

[6] Luyckx and Stokkink, *Brit. Jour. of Appl. Phys.* Supp. No. 4, p. 57, (1954).

Increasing frequency of the applied field has two effects on this waveshape. (1) Higher frequencies tend to cause the main peak to overshadow the secondary peak, possibly due to the finite time which is thought necessary for the emission phenomena causing this second peak. (2) At high frequencies the light output no longer returns to zero between alternate half cycles of the applied field. The frequency where this minima becomes measurably different from zero depends also on this secondary peak with samples having the largest secondary peaks (zinc oxysulfides) no longer returning to zero light output between half cycles at as low as 60 cps.

A marked difference was found in the height of the light output peaks for alternate half cycles of the applied field when observed through the transparent conductive coating. This was correlated to two facts.

1. The individual crystals emit light only on the side towards the positive electrode. This gives the maximum light output on the half cycle when the transparent electrode is positive.

2. On the opposite half cycles the light is emitted mainly towards the metallic back electrode and reflected back with some absorption in the EL material and the dielectric binder.

To demonstrate the effect of the metallic back electrode on a sample, one half was made of silver paint while the other was evaporated aluminum. As can be seen from Fig. 3, there was a marked difference in the light output with the silver paint reflecting better and thus emitting more light in this particular case.

Variation of Build-up Time with Frequency

The build-up time varied only slightly from phosphor to phosphor and was shortest in the case of one oxysulfide sample. Due to a random variation in the phase of the applied a-c field when the sample was pulsed, there is some uncertainty in the exact time measurements. The light output during the build-up time of all of the phosphors can, however, be expressed by an empirical relation of the type:

$$L = L_{max}(1-e^{-f \cdot \theta t})$$

L = light output

L_{max} = steady state light output

f = frequency of applied a.c.

t = time

Some representative measured build-up times (to 90 percent L_{max}) are:

Frequency	*Build-Up Time*	*No. of a-c Cycles*
60	45 ms	3 cycles
400	9 ms	4 cycles
1000	5 ms	5 cycles
10000	0.6 ms	6 cycles

Dependence of Build-up Time on Voltage

No variation was found over the limits of the voltage range between the point where light was first emitted and where the samples broke down.

Furthermore, a small steady a-c voltage was applied to the sample so that it was just on the threshold of emitting light and then the higher voltage of the same frequency pulsed on. No change in build-up time was noticed over that for the same sample with no steady state a.c. on it.

Light Output vs. Voltage

The light output increases rapidly with voltage. If it is expressed as a power law $L = AV^n$, n will vary from 3 to 4 except at very low voltages.

Destriau[4] proposed the relation $L = AV^n e^{-b/V}$ which fit his experimental values quite well. In 1954, Alfrey and Taylor[7] published the relation $L = AVe^{-n/\sqrt{V}}$ as more closely matching their empirical voltage-light output curves. Several samples were measured to check this as opposed to Destriau's formula and it was found to match the present data better. One exception was the light vs. voltage data published for a single small emitting point which was closer to linear than of the proposed form[2].

Current and Voltage Measurements during Build-up Time

The voltage across the sample and the current through the sample were both observed on an oscilloscope during the build-up time. No visible changes in either current or voltage were noticed, because most of the current is capacitive. A small change in the resistive current through the phosphor particles would not have been observable on the oscilloscope.

Temperature Studies

The build-up time of the various phosphor samples was measured from -50 degrees to 150 degrees C. No effect on the build-up time was noticed on heating although the higher temperatures tended to reduce the height of the secondary peaks. Cooling the phosphors tended to lengthen the build-up time with different effects on the main peaks and secondary peaks of one phosphor. In one sample at room temperature, the build-up time at 400 cps was 8 ms with the waveshape remaining constant and the magnitude increasing. At -50 degrees C. the secondary peaks reached full height in 6 ms, but the main peaks did not reach the height of the secondary peaks until 10 ms and did not reach full height until 22 ms.

This phenomenon leaves some doubt that the build-up is caused by internal storage of charge as suggested by Zalm et al.[3], unless the main mechanism is dependent on a supply of excess electrons and the secondary is not. This does not, however, agree with postulated emission mechanisms.[1,8]

[7] Alfrey and Taylor, *British Journal of Appl. Phys.*, No. 4, p. 44, (1954).

[8] Curie, D., *Journal Phys. et Radium*, 14, p. 510, 672 (1953).

Irradiation with Infrared

The effects of infrared radiation on the build-up time were investigated using various infrared filters. A tungsten light source with a Corning 2540 filter was found to have the greatest effect. With sixty seconds irradiation from the above before application of the field, the build-up time was lengthened by as much as 100 percent. This effect decreased rapidly with the duration of infrared irradiations and there were no visible effects for an irradiation of 5 seconds. No increase in this effect with greater than 60 seconds irradiation was observed.

If the sample remained in the dark after infrared irradiation before application of an a-c field, the build-up time changed back to normal. As short a time as 15 seconds was enough to remove all trace of the increased build-up time due to infrared.

Ultraviolet Irradiation

Ultraviolet was found to have no effect on the EL build-up time up to levels of UV where the UV-excited luminescence became a significant part of the output light. At these levels, the main effect was the electric field quenching the UV-excited luminescence. There were two separate effects involved in this.

1. When any field a-c or d-c was applied the UV excited luminescence was initially quenched, taking about 100 ms to return to its steady state value.

2. In the case of an a-c field, there was superimposed on this an additional varying component of the light output in phase with the applied a.c. This was not entirely quenching as the average light output did not decrease. The amplitude of these variations (measured from peak to peak) was at certain levels of field considerably more than the varying light output that would be present due to EL from the same field. The ratio of the peak to peak measurements of this varying component and the EL from the same field gives us a multiplication factor for various levels of a-c field.

Some typical values are:

a-c voltage r.m.s.	90	100	120	140
EL (relative levels of light output)	2	4	11	25
Varying component of light output with a.c. and UV	10	11	12	26
Multiplication factor	5	3	1	1

The maximum multiplication is obtained at fields just below where the EL becomes visible. The largest multiplication measured was 30 times. At higher a-c fields, the UV-excited luminescence and the EL appear to be additive. This effect is shown in Fig. 4. A through D show this multiplication for increasing a-c fields. E and F show this effect superimposed on the ~100 ms quenching due to the initial application of the field. Within the range of UV tested, the quenching was proportional to the level of UV radiation.

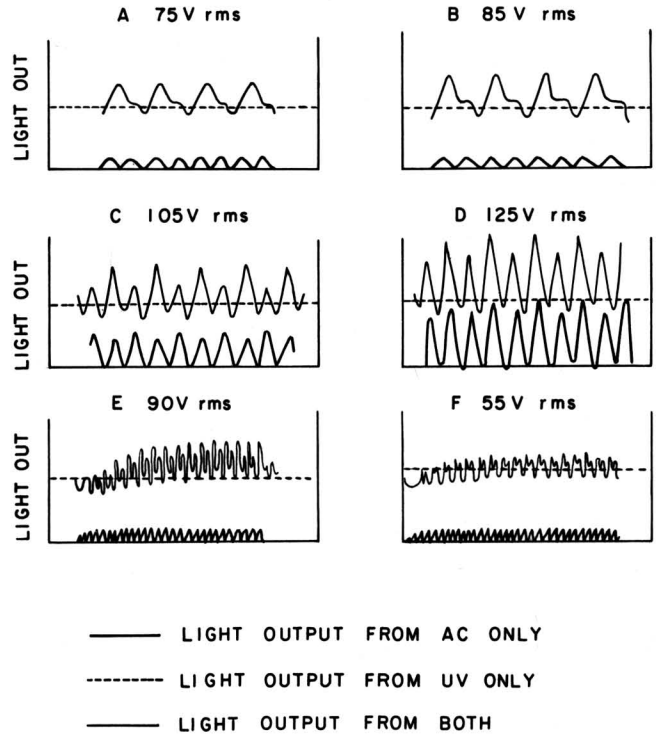


Fig. 4 - Light output for a zinc oxysulfide sample with AC and/or UV excitation.

Discussion

The materials tested exhibited almost all of the effects reported by other workers plus several new phenomena. The interaction of the UV-excited luminescence and the EL to provide a varying component of the light output larger than the EL itself is apparently new and while it does not appear to be a significant factor in these particular phosphors, it could be important in others. The most interesting thing from a theoretical point of view is the differential rate of build-up of the main and secondary peaks of light output when certain samples are cooled. This effect is more pronounced if it is measured while the sample is slowly warming up from the minimum temperature with the magnitude of the effect passing through several maxima and minima.

No drastic changes in build-up time or other measured characteristics except for the differences in emission spectra were observed that could be correlated to any given phosphor type.

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