CrossMark

AC electroluminescent lamps: shedding some light on their mysteries

Paul Harris[1] · Daniel den Engelsen[1] · George Fern[1] · Jack Silver[1]

Abstract AC powder electroluminescent lamps have been known and used for many years, but their mechanism of operation is still debated. Many thousands of phosphors are known, but the vast majority are not electroluminescent. A number of materials do exhibit the effect. Of these, however, ZnS doped with Cu is absolutely in a class of its own, and is the only material from which viable lamps can be made. In this work studies have been made of the performance of devices under a range of pulsed and continuous excitation conditions and new hypotheses presented which attempt to explain the behavior of this unique material.

1 Introduction

The phenomenon of electroluminescence was first discovered by Round in 1907 [1] while working on silicon carbide. Later Lossew [2] also observed the effect. The field did not really take off, however, until the pioneering work of Destriau in the thirties who worked on copper-doped zinc sulphide [3].

The 1950s and 60s saw a large number of publications in this field stimulated by interest to use the effect for displays, and there have been several reviews published [4–7]. Currently two basic types of lamps are in use, those based on thin film structures and others based upon powdered phosphors and it is this latter type which will be discussed herein.

In the last few years, however, due to the emergence of alternative light sources with improved brightness, power consumption and longevity, the applications of AC powder electroluminescent lamps ACELs have retreated into niche areas where their particular properties gives them advantages. Their main attributes are that they are simple, low cost, thin, flexible, lambertian emitting light sources that are easy to fabricate using basic equipment. These applications include throw away adverts in the form of badges, tee shirts, large scale adverts and other forms of signage, backlights for instrument panels and various military uses such as mobile landing lights and subdued cockpit lighting (making use of the none directional emission of the lamps).

ACELs can be printed onto virtually any surface [4, 8–12]. Figure 1 shows a typical structure. The precise construction details depend upon the end-use and for example for (relatively) low voltage applications and double sided ACELs the dielectric layers may not be included [9]. In Fig. 1 the substrate is indium tin oxide (ITO) coated polyethylene terephthalate (PET). One of the electrodes must be transparent to observe EL.

Since the days of Destriau in the 1930s, various materials have been found that exhibit the electroluminescent effect, but none comes close to matching the performance of the copper-doped zinc sulphide that he worked on and even today this unique material is the only phosphor used in commercial devices. Although it has been known for more than 80 years, there is still much we do not know about the operation of this material. Though, of course, its formulation and synthesis has constantly been improved, giving it a longer working life and better emission properties.

In this paper the theories of operation of ACELs will be discussed in the light of recent research findings in this laboratory.

✉ Jack Silver
  jack.silver@brunel.ac.uk; terry.ireland@brunel.ac.uk

[1] Centre for Phosphor and Display Materials, Wolfson Centre for Materials Processing, Brunel University, Uxbridge, Middlesex UB8 3PH, UK
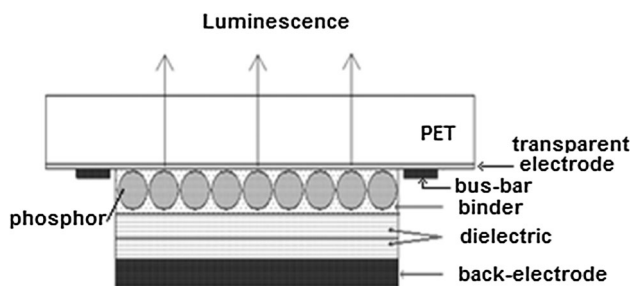
Fig. 1 Typical construction of an ACEL lamp

2 Experimental

The ACELs used in this work were made at Brunel University London using phosphor powders supplied by GTP Osram-Sylvania. Double-sided ACELs were made either using an indium tin oxide (ITO) on PET sheet as one electrode and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) from Orgacon, Kodak as the counter-electrode, or using PEDOT:PSS for both electrodes. In the latter case a two-part silicone binder was used to carry the phosphor and to stick the electrodes together. No high-k dielectric layers were incorporated into these lamps.

Quantitative measurements of radiance and luminance were made using a Jeti Specbos 1201 spectroradiometer. Cathodoluminescence (CL) images of ZnS:Cu crystals were made using a Zeiss Supra 35VP field emission scanning electron microscope (FESEM) fitted with a light pipe and photomultiplier. This measurement technique has recently been described by us [13].

Measurements of the pulsed output of ACELs were made using the apparatus layout shown in Fig. 2. The spectrometer system was supplied by Bentham Instruments
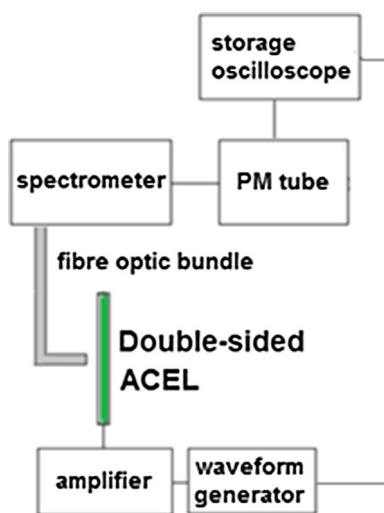
(UK), and the ACELs were energised by waveforms produced by a Tabor WW5062 Arbitrary Waveform Generator backed-up by a Newtons' 4th LPA400 amplifier.

3 Results and discussion

As mentioned above, in this work ZnS doped with copper and chlorine, was used, which in terms of its ACEL performance is a unique material, and therefore it is worthwhile discussing its complex properties and trying to understand what makes it so special. Increasing the copper concentration in this phosphor causes the emission to change in colour from blue to green. Changing the halide content also effects this transition in colour, and switching the halide from chlorine to bromine results in ACELs that are predominantly blue (see references quoted in Ref. [6]). Adding manganese to the phosphor results in initially green and orange emission until at high concentration the orange manganese emission completely replaces the green emission, suggesting an energy transfer process. Notably, however, without copper there is no ACEL activity.

Zinc sulphide can exist in both cubic and hexagonal forms and both can be made into ACEL active materials [14]. In addition to these two crystal structures various polytype structures are present with crystal structures that are intermediate between cubic and hexagonal. For example, Fig. 3 illustrates a CL image of commercial ZnS:Cu,Cl particles used for ACEL devices reported herein. The CL emission is often highly irregular with many particles having lamellar structures with alternating light and dark bands that most probably result from stacking faults introduced during the mechanical stressing stage used in the processing of the phosphor particles. The stacking faults introduce some cubic layers into the hexagonal phase made at high temperature. This leads to many different

Fig. 2 Layout of measuring system for measuring the pulse behaviour of ACELs

Fig. 3 CL image of ACEL phosphor particles

polymorphs being present in the final ACEL powder. It is also possible that at the stacking faults some segregation of dopants takes place between the structures.

This brings us onto the method of production of this material, which is singular. The process used is described in commercial patents [15] and consists of a high temperature firing at e.g. 1050–1400 °C, followed by a controlled mechanical damage process, followed by a short, low temperature firing e.g. at 500–1000 °C. It is common for phosphors to have a first firing, followed by milling (to reduce particle size and improve dopant dispersion), followed by a final, forceful high-temperature firing to ensure the lowest possible levels of crystalline defects. The mechanical damage stage in ACEL manufacture, however, is not intended to reduce particle size, and the low temperature firing is not designed to and is unlikely to remove all defects that it creates. It does not result in the transformation to the pure cubic form from the hexagonal form (which is the stable high temperature form), and commercial materials invariably contain both crystalline forms. Instead the process appears designed to ensure that controlled amounts of disorder are present in the lattices. The precise details of how best to accomplish this controlled damage stage are commercially secret, and although numerous phosphor manufacturers have attempted to make these materials, very few can compete with the performance of the best quality materials.

Figures 4, 5 and 6 show typical performance characteristics of ACELs. Generally, as the voltage is increased there is a voltage threshold below which ACEL emission does not appear to occur. However if the ACELs are turned on in absolute darkness then traces of light emission can be detected using photomultiplier tubes at about 11 Volts [16], below this voltage any light emission is lost in the noise but cannot be ruled out. However to see the light by
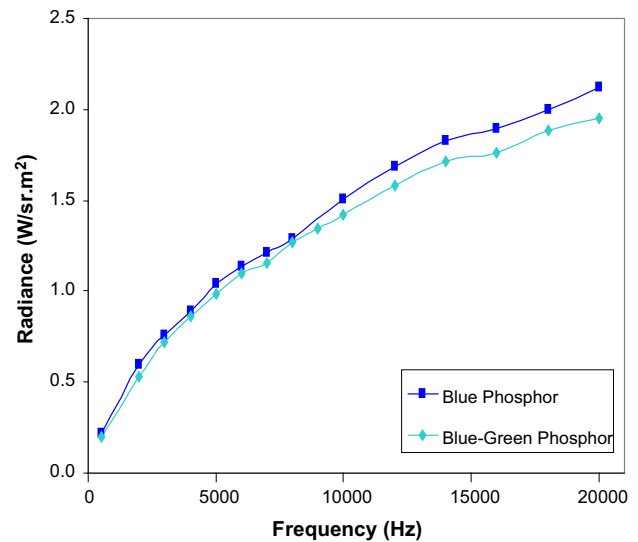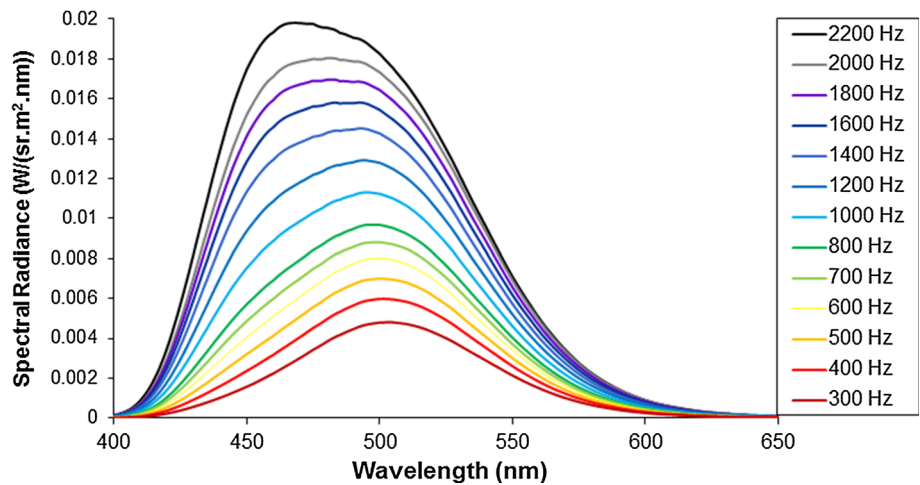

Fig. 5 Effect of frequency on the radiance of ACELs with *blue* and *blue–green* phosphors, (symmetrical, bipolar square wave excitation)
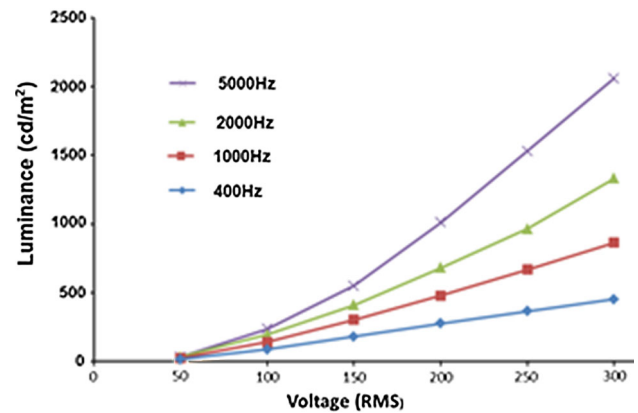

Fig. 6 Effect of voltage and frequency on the luminance of a *blue–green* ACEL (symmetrical, bipolar square wave excitation)

Fig. 4 Effect of frequency on the luminescence spectrum from a *blue–green* phosphor, (symmetrical, bipolar square wave excitation)

eye it is necessary to pass the threshold voltage, and once this happens there is a steady increase in radiance and luminance with voltage. Increasing the frequency also increases the radiance in a near linear way, but also results in a shift in emission colour from the green line to the blue. The frequency threshold of this colour shift depends on the dopant content with low levels of Cu favouring blue emission and high levels green. Microscopic examination of ACELs indicates that particles of all sizes undergo this transition, although it is unclear as yet whether the spectrum emitted from each particle is identical.

Various theories have been proposed to explain the ACEL mechanism (see for example discussions in [5, 6]). Most involve a two-stage process with the introduction of carriers (electrons and holes) from specific initiation sites, followed by their recombination at luminescent centres. Zalm [14] suggested the initiation sites were copper sulphide precipitates on the surfaces of the crystals. More recently, however, it has been demonstrated that the material does not lose its ACEL activity even if the particles are aggressively etched to a fraction of their initial diameters [17].

The most widely accepted theory of operation is that due to Fischer [18, 19], who suggested that the initiation sites were copper sulphide precipitates, which injected carriers into the matrix via a field emission process. Certainly, the voltage threshold supports a field emission mechanism. In addition the presence of precipitates is very controversial. Several groups, including our own, have searched at length for these precipitates using, for example, scanning and transmission electron microscopy, but without success [20].

Perhaps a more fundamental consideration is that precipitates should form from a ZnS solution saturated with copper, and that being the case it is hard to understand that increasing the copper concentration changes the colour of the fluorescence, indicating that the quantity of copper in solution within the matrix is changing. This suggests that in fact the matrix is not saturated with copper and that therefore no precipitates would be expected.

Given the unique production process in which defects are deliberately introduced and are apparently essential, together with the need for copper, we would like to suggest that the initiation sites could be where copper has diffused into defect sites such as dislocations and grain boundaries. Such segregations are well known in materials science [21, 22] and are driven by the need to minimise interfacial energy. They can occur at solute concentration well below saturation levels. The final low temperature firing then can be understood in terms of facilitating this segregation, without causing wholesale recrystallization of the matrix. Such segregation would form structures of a fraction of a single monolayer and would be very difficult to detect, for

example by microscopy or X-ray diffraction. Relatively, small amounts of copper need be used for this purpose leaving the remainder free to form luminescent centres.

The apparent near linear shape of the voltage-radiance curves has been explained in terms of space charge limitation [6]. In essence the carriers injected create space charges that shield the initiation sites from the field and cut off further carrier injection. In support of this theory, in this work it was noted that irradiation of working ACELs with 365 nm ultraviolet radiation (at ACEL voltages and UV intensities well below that required for phosphor saturation) resulted in complete suppression of ACEL activity. It appears that the carriers generated by the ultraviolet radiation very effectively shield the initiation sites from the field.

As can be seen from Fig. 5, the radiance is near linearly related to the number of cycles per second even up to 20 kHz, suggesting that the carrier injection stage is terminated very quickly.

The light output of conventional ACELs is not continuous but shows a series of pulses, at low frequencies, although these run together at higher frequencies. The magnitude of successive pulses shows a very slight polarity dependence. This effect is greatly enhanced if the output of a double sided ACEL is monitored, as shown in Fig. 2, because in this case light emitted in the reverse direction is not reflected back to the viewer. Figure 7 shows a typical plot. The most intense pulses occur when the side that is in its positive cycle is monitored. The asymmetry increases with voltage, as indicated in Fig. 8. In this work such behaviour was observed when both electrodes were PEDOT:PSS, or ITO on glass, or mixtures of the two. Hence it does not appear to be related to the nature of the electrode material.

Figure 9 is an attempt to illustrate schematically what is likely to be happening. In the first half-cycle electrons and holes are emitted in opposite directions, and no light is
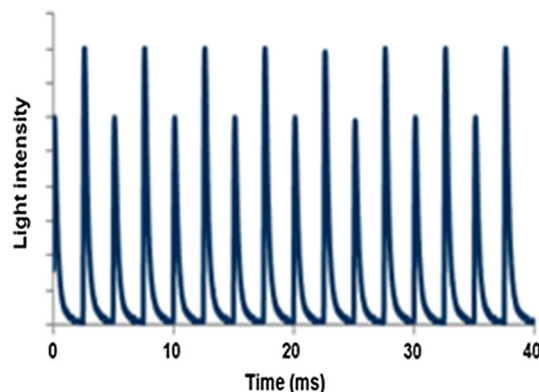

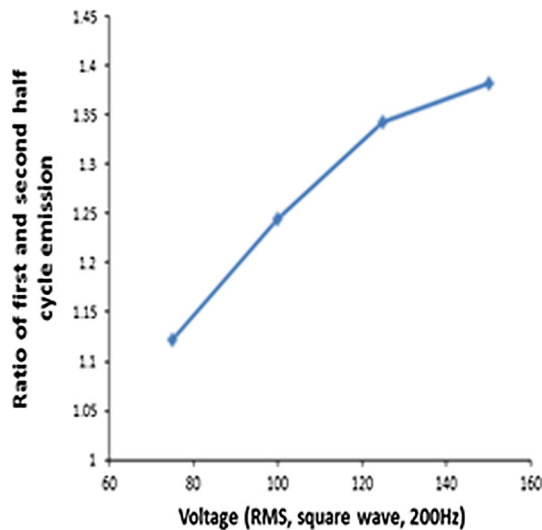Fig. 7 Asymmetric light pulses from double-sided ACELs, 200 Hz operating frequency

Fig. 8 Pulse asymmetry in double sided ACELs, 200 Hz operating frequency

First half-cycle

Holes emitted towards negative, electrons towards positive

Second half-cycle

Electrons now emitted into cloud of holes from previous half-cycle: light emitted

Third half-cycle

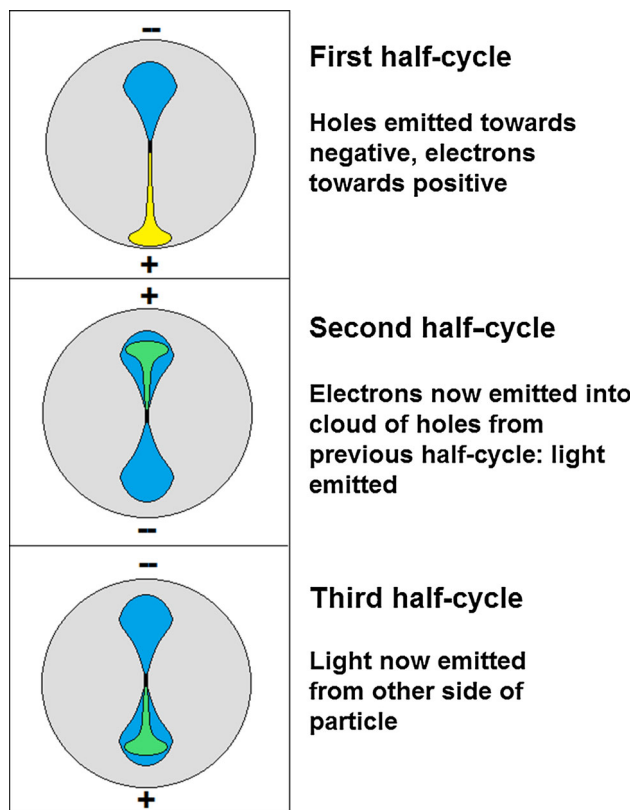**Light now emitted from other side of particle**

Fig. 9 Schematic illustrating light emission, switching from one side of a particle to the other with changing polarity

emitted. In the second half-cycle the carriers are emitted in opposite directions. The much higher mobility of the electrons allows them to be swept quickly from side to side with the field, whereas the holes are much more sluggish. As a result recombination occurs primarily on the positive

side of the particle. When the polarity again changes light emission is generated on the other side of the initiation site.

Increasing the voltage enhances hole transport and causes the light emitting zones to be spaced further apart, and thus increases the observed pulse height asymmetry. This model is in agreement with the observation from microscopic studies [23] that light emission occurs from discrete areas near to the surface of the particles. It also agrees with the observation [24] that unconfined ACEL particles rotate until their long axes are parallel to the field (in order that their positive and negative space charges can get as close to the appropriate electrode as possible).

Other workers, notably Zalm [14], have observed pulse asymmetry, and attributed it to similar mechanisms as described here. However, the dependence on voltage was not elucidated, and indeed Zalm reported that at very high voltages the asymmetry 'may' reverse, but this was not observed in our work. For simplicity in the illustration, Fig. 9, only a single initiation site is drawn. In practise there are likely to be a number of sites, in different positions around each particle, and the effect of the polarity change is to move the centre of gravity of the luminescence from one side to the other.

The reason that more of the light generated near the closest surface is able to escape to the observer, may be a combination of effects. The first, as mentioned by Zalm [14] is that there is less total internal reflection (and self-absorption losses) within the particle. The second is that luminescence that suffers multiple scattering within the powder layer (after escaping the particle) is statistically more likely to emerge on the side closest to its source than by making its way via a tortuous route through the binder and emerging on the far side. In support of this suggestion it has been found, for example [25] that when even very thin (~ 0.5–4 mg/cm^2) coatings of nano or micrometre-sized phosphor particles are excited by low energy (1–5 kV) electrons beams that substantially (<4 times) more cathodoluminescence emerges on the side which is excited, compared to that which emerges on the far side (NB no binder was present in this work). In the present case, the longer more tortuous route will also mean that the luminescence will suffer more absorption losses within the binder.

Figure 10 shows the effect of exciting ACELs using widely spaced, narrow pulses. No light is detected on the first voltage transient of each pulse, only on the second transient, in line with the model. If the pulses are moved closer together then predominantly green light starts to be emitted on the first transient, presumably due to neutralisation of holes left over from the previous cycle.

The colour of the light emitted depends on the time delay between transients (half-cycles). If the second half cycle follows very rapidly after the first (e.g. because a
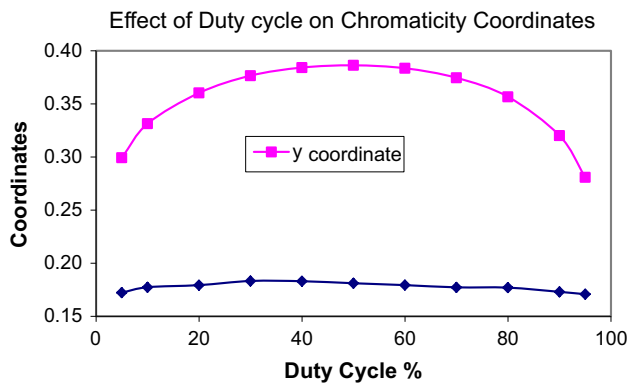
Fig. 11 Effect of duty cycle on CIE colour coordinates (*blue–green* phosphor, bipolar square wave excitation, 500 Hz)

high frequency and/or narrow pulse width is used) then the light is predominantly blue. If there is a long time delay between the transients (for example because a low frequency is used) then it is predominantly green. Figure 10 illustrates the output from a blue-green phosphor operated at 100 Hz. When operated with a 50% duty cycle the luminescence from this lamp was (as expected) green. In this case, however, because narrow pulses were used, the output was predominantly blue. Figure 11 shows what happens to the CIE coordinates if the duty cycle of the square wave (in this case at 500 Hz) is changed. When the leading and trailing edges of the square waves are close together the blue emission is enhanced. This suggests that as postulated by Ivey [6] blue sites are occupied by holes in preference to green, and if neutralised quickly give rise to blue emission. If time permits, however, the hole transfers onto green sites. Increasing the concentration of copper then makes this transfer more efficient, and hence the transition from blue emission to green occurs at lower frequencies. It appears that the transfer process is thermally activated, and does not occur at liquid air temperatures, where the emission is blue at all frequencies [6]. Whether
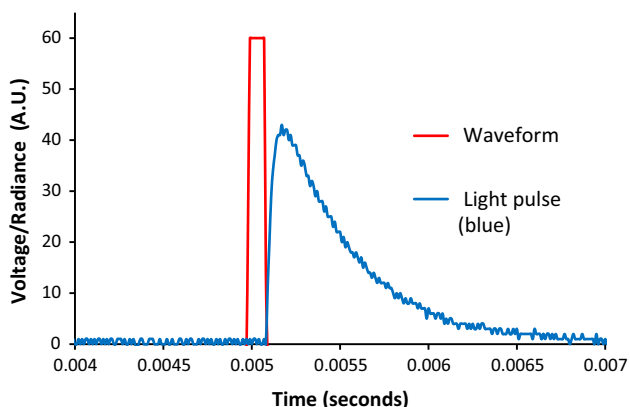
the square wave is bipolar or unipolar (in either direction) has no apparent effect on the emission colour or radiance.

4 Conclusions

Consideration of the method of manufacture and the effect of doping of ZnS:Cu electroluminescent phosphors suggests that the most likely initiation sites are copper segregated into dislocations/grain boundaries rather than as precipitates as suggested by Fischer.

Measurements of the emission from double-sided ACELs suggest that the luminescence originates on the side of the particle that is closest to the positive electrode, and oscillates from one side to the other with the changing ac polarity.

The transition from blue to green emission is governed by the length of time between voltage transients. A short time period (e.g. due to working either at high frequency or low frequency with a short duty cycle) gives rise to blue emission. If the time period is long enough (e.g. low frequency with a 50% duty cycle), then holes are transferred to a green luminescent centre and green emission results.

Fig. 10 Light output from (*blue–green*) ACEL driven by 100 μsecondpulses at 100 Hz

References

1. H.J. Round, A note on carborundum. Electr. World **49**, 308 (1907)
2. O.V. Lossew, Wireless telegraphy and telephony. Telegrafia i Telefonia bez Provodor **18**, 61 (1923)
3. G. Destriau, Research on the scintillation of zinc sulphide with radiation. J. Chim. Phys. **33**, 587–625 (1936)
4. R. Withnall, J. Silver, P.G. Harris, T. Ireland, P.J. Marsh, AC powder electroluminescent displays. J. SID **19**(11), 798 (2011)
5. H.K. Henisch, *Electroluminescence* (Pergamon Press, Oxford, 1962)
6. H.F. Ivey, *Electroluminescence and related effects, advances in electronics and electron physics* (Academic Press, New York, 1966)
7. M. Bredol, H. Schulze Dieckhoff, Materials for powder-based AC electroluminescence. Materials **3**(2), 1353–1374 (2010)
8. R. Withnall, J. Silver, G.R. Fern, P.J. Marsh, T.G. Ireland, P.S.A. Evans, D.J. Southee, G.I. Hay, D.J. Harrison, K.F.B. Breen, Low cost flexible electroluminescent displays with a novel electrode architecture printed by offset lithography. SID Dig. **37**, 1491–1494 (2006)

9. P. Harris, J. Silver, S. Jones, Novel, bright, inorganic electroluminescent flexible displays comprising ink-jet printed silver back electrodes. SID Dig. **41**, 397–400 (2010)

10. R. Withnall, J. Silver, P.G. Harris, Eco-friendly AC electroluminescent lamps. Proc. IDW **1**, 1043–1046 (2012)

11. R. Withnall, J. Silver, P.G. Harris, High flexibility ACEL lamps printed directly onto cloths. Proc. IDW **2**,1719–1722 (2012)

12. D.A. Davies, A. Vecht, J. Silver, P. Titler, D.C. Morton, A novel low cost binder for flexible AC electroluminescent lamps. SID Dig. **32**(1), 395–397 (2001)

13. D. den Engelsen, P.G. Harris, T.G. Ireland, G.R. Fern, J. Silver, Contrast and decay of cathodoluminescence from phosphor particles in a scanning electron microscope. Ultramicroscopy **157**, 27 (2015)

14. P. Zalm, Ph. Res. Rep. **11**(353), 417 (1956)

15. See for example, US Patents 6248261(2001), 5711898 (1998) 7014293B2 (2006)

16. R. Withnall, J. Silver, G.R. Fern, T.G. Ireland, Brightness–voltage characteristics of powder AC electroluminescent lamps, eds. By G. Baldacchini, R.M. Montereali, M.A. Vincenti. in Proceedings 14th international workshop on inorganic and organic elecroluminescence & 2008 international conference on the science and technology of emissive displays and lighting, 435–438 (2008). ISBN: 88-8286-194-5

17. R. Withnall, J. Silver, T.G. Ireland, G.R. Fern, P.J. Marsh, Structure and morphology of ACEL ZnS:Cu, Cl phosphor powder etched by hydrochloric acid. J. Electrochem. Soc. **156**(11), 326–332 (2009)

18. A.G. Fischer, J. Electrochem. Soc. **109**, 1043–1049 (1962)

19. ibid, J. Electrochem. Soc. **110**, 773–748 (1963)

20. A.C. Wright, I.V.F. Viney, A structural evaluation of ZnS-based electroluminescent phosphors and devices: a comparison with performance. Philo. Mag. B **81**(3), 279–297 (2001)

21. D. McLean, *Grain Boundaries in Metals* (Oxford University Press, London, 1957)

22. M.P. Seah, Solute segregation at grain boundaries. J. Phys. F Metal Phys. **10**, 1043–1064 (1980)

23. N.E. Grzeskowiak, J.F. Winkel, Structure and location of electroluminescent light emission within ZnS/Cu ACEL powder phosphor particles. J. Electrochem. Soc. **154**(10), J289–J294 (2007)

24. T.G. Ireland, J. Silver, Studies on the orientation of ACEL ZnS: Cu particles in applied AC fields, ECS. J. Solid State Sci. Technol. **3**(3), R25–R32 (2014)

25. D. den Engelsen, P.G. Harris, T. Ireland, R. Withnall, J. Silver, Cathodoluminescence of powder layers of nanometer-Sized Y2O3: Eu and micrometer-sized ZnO: Zn phosphor particles, ECS. J. Solid State Sci. Technol. **2**(9), R201–R207 (2013)