

# Cathodoluminescence studies of phosphors in a scanning electron microscope

**Paul Harris, Daniel den Engelsen, Terry Ireland, George Fern and Jack Silver**

Centre for Phosphor and Display Materials, Wolfson Centre for Materials

Processing, Brunel University, Uxbridge, Middlesex, UB8 3PH, UK

E-mail: [jack.silver@brunel.ac.uk](mailto:jack.silver@brunel.ac.uk); [terry.ireland@brunel.ac.uk](mailto:terry.ireland@brunel.ac.uk)

**Abstract.** Cathodoluminescence studies are reported of phosphors in a field emission scanning electron microscope (FESEM). A number of phosphor materials have been studied and exhibited a pronounced comet-like structure at high scan rates, because the particle continued to emit light after the beam had moved onto subsequent pixels. Image analysis has been used to study the loss of brightness along the tail and hence to determine the decay time of the materials. This technique provides a simple and convenient way to study the decay times of individual particles.

## 1. Introduction

The detection of cathodoluminescence (CL) is a standard technique in many scanning electron microscopes (SEM). Important applications of CL microscopy are in the field of mineralogy, studies of defects in luminescent crystalline materials and characterization of nanostructures [1-4]. CL studies of phosphor particles, however, have received surprisingly little attention in the literature. Poelman and Smet have recently published results on time-resolved CL spectroscopy of phosphor particles by blanking a static electron beam [5].

The objective of this investigation was to study the decay behaviour of phosphor particles in a conventional SEM.

## 2. Microscope and materials

A Zeiss Supra 35VP was used in this work. The system was equipped with four detector systems. The first is an Everhart-Thornley (ET) secondary electron (SE) detector, which detects SEs plus a contribution from backscattered electrons (BSE). There is also an in-lens SE detector, for use when very short working distances are required, and this detects only SEs. An annular (retractable) Robinson<sup>TM</sup> solid state BSE detector is mounted immediately above the sample.

The microscope has the facility to operate in high nitrogen pressures (<133Pa) and an additional detector is fitted to facilitate this, which operates by using a photomultiplier to detect the fluorescence generated when low-energy SEs, emitted from the surface (under bombardment from the primary electron beam), excite the gas (nitrogen) in the chamber. If this detector is used under high vacuum conditions, then these signals are absent, and it is capable of generating high quality CL images from suitable phosphor materials. Image analysis of the panchromatic CL-micrographs was performed using ImageJ (Public Domain) software.

ZnO:Zn phosphor was obtained from Kasei Optonix (Japan), with particle sizes of 0.2-1.5 $\mu$ m. Monosized Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> has been synthesized in this laboratory with an average size was 330nm. The synthesis has been described in detail in our previous work [6]. Commercial Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> and Gd<sub>2</sub>O<sub>2</sub>S:Tb<sup>3+</sup> samples (micrometer sized) were obtained from Nichia, Japan. Zn<sub>2</sub>SiO<sub>4</sub>:Mn<sup>2+</sup> was supplied by Sylvania, USA. Finally, InBO<sub>3</sub>:Tb<sup>3+</sup> and SrGa<sub>2</sub>S<sub>4</sub>:Eu<sup>2+</sup> were obtained from Phosphor Technology Ltd., UK. All commercial samples were analyzed without further treatment.



Two types of substrates were used in this work, conductive graphite loaded pads and aluminium stubs. The graphite loaded pads were obtained from Agar Scientific and were slightly sticky. Phosphor powder was deposited either by a dusting technique or by dispensing a diluted phosphor suspension in ethanol. In the first case layers with 1-5 particles on top of each other were obtained, in the second case isolated particles could be deposited. In the case of aluminium substrates phosphor was applied by the alcohol dispensing technique.

### 3. Decay

Figure 1 shows micrographs of a cluster of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  particles and a single  $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}^{3+}$  particle on a graphite-loaded pad. The SE-micrograph is a clear picture and shows details of the particles, whereas the CL-micrograph is smeared out. The reason for this blurring is the rather long decay times of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  and  $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ . In other words, smearing of CL-images offers the opportunity to measure decay times of CL-phosphors.

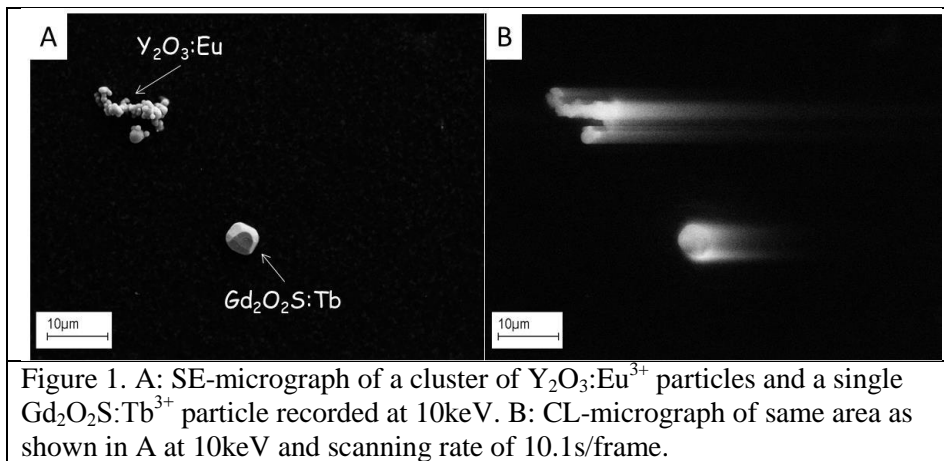


Figure 1. A: SE-micrograph of a cluster of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  particles and a single  $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}^{3+}$  particle recorded at 10keV. B: CL-micrograph of same area as shown in A at 10keV and scanning rate of 10.1s/frame.

The decay times can be determined by analyzing the greyscales in comet-like structures as shown in figure 1B. We made these analyses with the ImageJ software; an example is shown in figure 2. The comets shown in figure 1B are represented in spatial dimensions. From the known scanning speed and the number of pixels (1024x768) the length can be converted into time, as shown in figure 2. Figure 2 shows two curves: the noisy curve has been determined with ImageJ from the CL-micrograph, while the exponential is the greyscale representation (GS) of the experimental data in terms of one exponential function:

$$GS = GS_{\max} e^{-t/\tau} + BG \quad (1)$$

where  $GS_{\max}$  is the maximum greyscale,  $t$  indicates the time, being 0 when  $GS=GS_{\max}$ ,  $\tau$  is the time constant, being the 1/e-value of the decay time ( $\tau_{1/e}$ ), and BG is the background correction. This latter correction depends on the gain setting of the photomultiplier tube that amplifies the weak CL from individual phosphor particles in the SEM chamber.

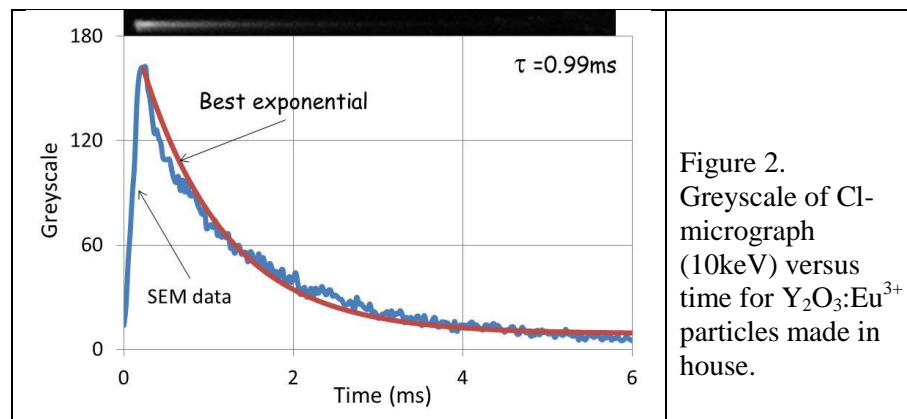


Figure 2.  
Greyscale of CL-  
micrograph  
(10keV) versus  
time for  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$   
particles made in  
house.

The comet, from which the GS curve is derived, is also indicated in figure 2. It can be seen in figure 1B that in the case of a cluster of particles it will not be possible to determine  $\text{GS}_{\text{max}}$  unambiguously. In that case the magnification can be lowered to enable an accurate determination of the start time. We have measured the decay times of various commercial phosphors to get an impression of the range of decay times that can be measured by this method. The result is shown in table 1.

**Table 1.** Decay times ( $1/e$ ) determined from CL-micrographs

Material source	$\tau_{1/e}$ (ms)		Ref.
	This work	Literature	
$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (Nichia)	1.2	1.2, 1.12, 1.1	7, 8, 9
$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (Brunel)	0.99	n.a.	
$\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ (Sylvania)	3.3	8*)	10
$\text{InBO}_3:\text{Tb}^{3+}$ (PT)	3.2	2.1	11
$\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ (PT)	0.0023	$\sim 0.0001$	12
$\text{Gd}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ (Nichia)	0.56	0.558	13

\*) This refers to  $\tau_{10\%}$ . The  $\tau_{10\%}$  of the  $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$  sample in our work is 7.6ms, which indicates that the Mn-doping is  $\sim 5\%$  according to the information in [12].

The shortest decay time determined was  $2.3\mu\text{s}$  for  $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ . In this case, the fastest scan rate of the SEM (90ms per frame) was used. At this high scan rate it was necessary to use frame averaging to achieve good signal to noise ratios. It appears that the minimum decay time that can be determined with the SEM used in this work is  $\sim 1\mu\text{s}$ . The longest decay time that could be determined is about 0.1s; so, the range of decay times that can be determined with this method is about 5 decades. It should be noted that the decay time of the nano  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  made in-house is shorter than that of the coarser commercial sample and shorter than values reported in the literature [7-9]. We also tried to measure decay times of phosphors deposited on Al substrates. Figure 3 is a CL-micrograph of monosized  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  (2%Eu) spheres with a diameter of 300nm on an Al substrate.

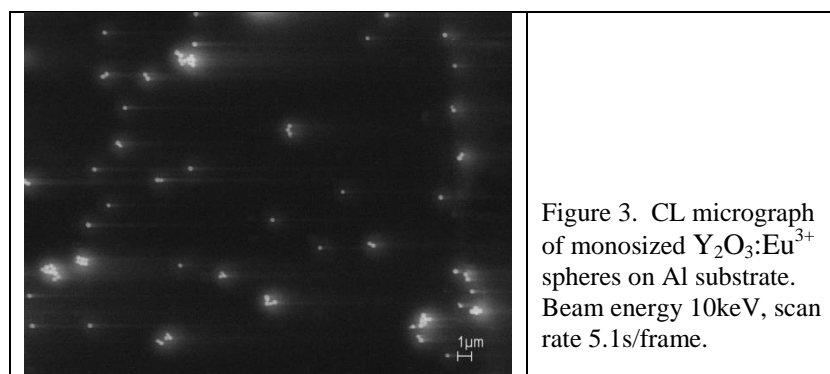


Figure 3. CL micrograph of monosized  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  spheres on Al substrate. Beam energy 10keV, scan rate 5.1s/frame.

Unlike the CL micrographs of phosphors on the graphite-loaded pads, the CL micrograph shown in figure 3 has a noticeable halo effect surrounding each particle that is of similar intensity to the comet tails. What appears to be happening is that a fraction of the electrons striking the substrate immediately around each phosphor particle are backscattered onto the particle, causing it to emit light. The reason that we can see this more clearly from an aluminium substrate rather than the graphite-loaded polymer substrate is the much larger backscatter coefficient of aluminium  $\sim 13\%$  at 10keV, as compared to that on graphite-loaded polymers of  $\sim 2.2\%$  at 10keV. Although it is possible to evaluate decay times from CL micrographs as presented in figure 3, the accuracy is reduced and the preferred measuring method is to use substrates with low backscatter coefficients, such as graphite-loaded pads or Formvar-coated TEM grids.

#### 4. Conclusions

CL-microscopy is found to be well suited for measuring decay times in the range between  $1\mu\text{s}$  and  $0.1\text{s}$  for individual phosphor particles that may have micrometer or nanometer dimensions. No additional investments are needed to make these analyses with a SEM that is equipped with a CL-sensor. For this measuring method substrates with low backscatter coefficients are recommended. We believe that our new measuring method of analyzing the temporal information in CL-micrographs can be applied simply in studies of individual micro and nano luminescent particles.

#### 5. References

- [1] Yacobi B G and Holt D B 1986 *J. Appl. Phys.* **59** R1.
- [2] Götze J 2002 *Anal. Bioanal. Chem* **374** 703
- [3] Maestre D, Cremades A and Piqueras J 2004 *J. Appl. Phys.* **95** 3027
- [4] Dierre B, Yuan X and Sekiguchi T 2010 *Sci. Technol. Adv. Mater.* **11** 043001
- [5] Poelman D and Smet P F 2014 *Physica B* **439** 35
- [6] den Engelsen D, Harris P G, Ireland T G, Withnall R and Silver J 2013 *ECS J. Solid State Sci. Technol.* **2** R201
- [7] Chung Y, Park S, Jang K, Kim I, Lee Y I and Seo H J 2003 *J. Korean Phys. Soc.* **42** 543
- [8] Tallant D R, Seager C H and Simpson R L 1999 *Extended Abstracts of The fifth International conference on the science and technology of display phosphors*, November 8-10, San Diego, CA, 325-328
- [9] Thomes J, Seager C, Tallant D and Holloway P 2000 *Extended Abstracts of The sixth International conference on the science and technology of display phosphors*, November 6-8, San Diego, CA, 249-251
- [10] Taghavinia N, Lerondel G, Makino H, Yamamoto A, Yao T, Kawazoe Y and Goto T 2001 *Nanotech.* **12** 547-551
- [11] Chiu Z W, Fang T H and Hsiao Y J 2012 *J. Lumin.* **132** 2608
- [12] Talin A, Dean K A and Jaskie J E 2001 *Solid-State Elect.* **45** 963
- [13] Glendinning A G, Hunt S G and Bonnett D E 2001 *Phys. Med. Biol.* **46** 517