

Microscopic cathodoluminescence spectroscopy for phosphor research

Dirk Poelman, Philippe F. Smet

*LumiLab, Ghent University, Belgium
Center for Nano- and Biophotonics (NB-Photonics), Ghent University, Belgium
Corresponding author e-mail address: dirk.poelman@ugent.be*

1. Introduction

Impurity doped inorganic luminescent materials can basically be divided into two groups. One group consists of compounds where the luminescent transition is a 4f-4f transition within a luminescent lanthanide ion. Such transitions are characterized by narrow absorption and emission lines and relatively long decay times. In addition, these transitions have characteristic wavelengths which are hardly influenced by the host material. In the second group of materials, using Ce^{3+} , Eu^{2+} or a number of transition metals [1], both excitation and emission spectra are broad due to level splitting and interactions between the impurity ions and the host lattice vibrations. The latter effect implies that there is a very strong correlation between the composition and the structure of these phosphors on the one hand and their optical properties (emission spectrum and intensity, decay time) on the other hand. As most synthesized phosphor materials have a certain distribution in composition and particle morphology and size, this leads to a broadening of the observed spectra when a large ensemble of particles is measured in, for instance, photoluminescence spectroscopy. The purpose of the technique presented here is to study the relation between morphology, composition and optical properties on a single particle level, excluding all averaging effects.

2. Results

In scanning electron microscopy (SEM), an electron beam is focused on the sample in a spot of the order of a few nm. Upon scanning the electron beam over the sample surface, secondary electrons (SE) or backscattered electrons (BSE) are used as a measure of the morphology of the surface. Due to the excitation of electronic states in the sample, fluorescent x-rays are produced; their analysis (by means of energy dispersive x-ray analysis or EDS), provides a semi-quantitative elemental composition of the sample.

In luminescent materials, we can go one step further, as the incoming electron beam also yields cathodoluminescence (CL) from the sample. Since the CL emission spectrum usually is very similar to the photoluminescence (PL) spectrum, this analytical tool is a perfect add-on for the study of luminescent materials. Using the combination of SE-BSE for imaging, EDS for elemental analysis and CL for light emission, the relation between morphology, composition and luminescent emission can be studied on a submicron scale, without the need for any sample preparation [2,3].

Due to the flexibility of standard SEM microscopes and the large number of available extensions, a wealth of information can be obtained:

- Using a sample heating/cooling stage, thermal quenching of individual particles can be studied [4]
- Using a beam blanker (switching the electron beam on and off on a picosecond time scale), the luminescent decay time of particles can be related to their morphology and composition
- By changing the acceleration voltage of the primary electron beam, its interaction volume and thus the spatial resolution of the CL signal can be influenced [5].
- Thanks to the excitation with a nanometer-size beam, particles can be excited locally, and resonance modes can quite easily be excited in regular structures [6].

A number of examples of these techniques will be illustrated on contemporary phosphor materials, currently investigated for wavelength conversion for LEDs [4].

3. References

- [1] G. Blasse, B.C. Grabmaier, *Luminescent Materials*; Springer: Berlin, Germany (1994)
- [2] D. Poelman, J. Doerschel, P. F. Smet, Cathodoluminescence study of the activator distribution in SrS:Cu,Ag thin luminescent films, *Spectrochimica Acta B* **59** 1775-1780 (2004)
- [3] P.F. Smet, J.E. Van Haecke, D. Poelman, High resolution cathodoluminescence mapping of luminescent materials using an EDX detector, *J. Microscopy Oxford* **231** 1-8 (2008)
- [4] P.F. Smet, J. Botterman, A.B. Parmentier, D. Poelman, Thermal quenching at the microscopic level in multi-phase thiosilicate phosphors, *Optical Materials*, in press (<http://dx.doi.org/10.1016/j.optmat.2012.10.051>)
- [5] K. Korthout, P.F. Smet, D. Poelman, Rare earth doped core-shell particles as phosphor for warm-white light-emitting diodes, *Appl. Phys. Lett.* **98**, art. 261919 (2011)
- [6] K. Korthout, P.F. Smet, D. Poelman, Whispering Gallery Modes in micron sized SrS:Eu octahedrons, *Applied Physics Letters* **94** art. 051104 (2009)