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# Time resolved microscopic cathodoluminescence spectroscopy for phosphor research

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## ABSTRACT

In impurity doped inorganic luminescent materials, there is often a close relation between the structural and optical properties. When a phosphor shows a distribution of structural properties (such as local variations in composition, dopant concentration, crystalline phase or particle size), the luminescence properties can show a similar distribution. When evaluating the synthesized phosphors at the macroscopic scale only, these properties are averaged out, which can lead to a broadened emission spectrum or a luminescence decay curve consisting of several exponentials.

This paper discusses cathodoluminescence detection inside a scanning electron microscope (SEM-CL) for the study of local emission characteristics in phosphors. In this type of instrument, imaging, local element identification as well as cathodoluminescent spectral mapping can be performed. It is shown that with the aid of a beam blanker, local decay time analysis and spectrally resolved decay time mapping can be performed. By correlating simultaneously obtained structural, compositional and luminescence properties, a profound understanding of a phosphor's behavior can be obtained. This is illustrated on  $\text{Ca}_2\text{SiS}_4\text{:Eu}$ , a red-emitting phosphor material of current interest for white light emitting diode (LED) wavelength conversion.

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## 1. Introduction

Inorganic luminescent materials (commonly called phosphors) have been investigated and used for a very long time. The development of suitable phosphors has been crucial for the success of fluorescent lighting and CRT (cathode ray tube) color television starting from the 1970s. In more recent times, new phosphor applications have emerged, notably for plasma displays and white light emitting diodes (LEDs) for lighting. In the latter application, the emission from a blue LED is partially converted to longer – green and red – wavelengths using one or more phosphors, and the combination of these yields an overall white impression [1,2].

White light sources for lighting should reproduce the color of illuminated objects as faithfully as possible, a property which is quantified by a color rendering index (CRI) or a similar metric [3,4]. In order to obtain a good color rendering, the white spectrum should resemble as closely as possible a black body radiator. In the case of wavelength converted LEDs, this can only be achieved with luminescent materials showing broad emission bands. Impurity doped

inorganic luminescent materials can roughly be divided into two groups. One group consists of compounds where the luminescence originates from  $4f^n-4f^n$  transitions within a trivalent luminescent lanthanide ion. Such transitions are characterized by narrow absorption and emission bands and generally relatively long decay times. In addition, these transitions have characteristic wavelengths which are hardly influenced by the type of host material.

In the second group of materials, using  $\text{Ce}^{3+}$ ,  $\text{Eu}^{2+}$  or a number of transition metal ions [5], both excitation and emission spectra have broad bands due to level splitting and interactions between the impurity ions and the host lattice vibrations. The latter effect implies a 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, particle morphology and size, this generally leads to a broadening of the observed spectra when a large ensemble of particles is measured using, for instance, common 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.

Scanning electron microscopy (SEM) is a common technique for imaging the morphology of particles. In luminescent materials [6], and many semiconductors [7] the incoming electron beam in

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addition 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. By detecting secondary electrons (SE) or backscattered electrons (BSE) for imaging, energy dispersive X-ray (EDX) analysis for elemental analysis and CL for light emission, the relation between morphology, composition and luminescent emission spectra can be studied on a submicron scale, without the need for any specific sample preparation [7–10].

Since the electron beam excitation is very local, SEM-CL is ideally suited to excite a luminescent particle in a very specific spot. If particles have well-defined faces and a geometrical shape, light can remain trapped within the particles and give rise to whispering gallery modes [11,12], which are visible as periodic modulations in the luminescence spectrum. From the characteristics of these modes, the size of the luminescent particles can be calculated in a very precise way. This type of information is completely lost when ensembles of particles are excited simultaneously.

SEM-CL has been applied to a wide range of materials. It has been used for natural samples: to study local impurities in minerals [13,14], bacteria with luminescent labels in minerals [15], natural sea shells containing luminescent markers [16], synthetic and natural dental materials [17], cellular structures [18] and animal tissues [19]. In materials science, it was used for the study of luminescent materials [20–22] and storage phosphors [23]. In addition, SEM-CL has proven to be extremely useful in the location and identification of defects in semiconductor structures [24–26]. In semiconductor quantum wells [27,28], nanorods [29] and quantum dots [30] and other low-dimensional structures, the spread of electrons is limited in a natural way by the surfaces of the structures, and extreme resolutions below 50 nm have been obtained [31,32].

In these previous studies panchromatic images (without collecting any spectral information), multispectral images (using band pass filters to select wavelength ranges) and spectrally resolved images have been collected. For natural samples, measurements are usually made at room temperature. Very low temperatures (using liquid helium) are most often applied for studying semiconductor defects, in order to avoid dissociation of excitons with low binding energies and minimize thermal broadening of the transitions. In a few cases, CL decay times have been measured [22,24,26,28].

For phosphor research, several other parameters are important and are of interest in a SEM-based cathodoluminescence setup:

- Local variations in dopant concentration or stoichiometry of the host material will lead to local differences in emission intensity and emission spectrum. Thus, even in single-phase materials, these are averaged when measuring over a large volume of the sample. Therefore, the application of spatially resolved CL spectroscopy is important even in these ‘simple’ materials.
- At higher temperatures (typically well above room temperature), the luminescent emission decreases due to unwanted ionization of activator ions and cross relaxation. In order to study this thermal quenching process, a heating stage is necessary. If the material is inhomogeneous or consists of multiple phases, different thermal quenching temperatures can occur in a single sample, leading to color changes upon changing temperatures (a nightmare for manufacturers of white LEDs).
- When thermal quenching occurs, this not only influences the total emission intensity, but also leads to a decrease of the luminescence decay time [33]. Ideally, the decrease in emission intensity is correlated to the change in decay time, and both are mapped simultaneously. Also, a lower luminescence decay time

can point at the local presence of defects, providing an additional non-radiative depopulation of excited states. As it is not trivial to assess the quantum efficiency at the microscopic level in CL, due to uncertainties on the amount of absorbed energy and on the fraction of light which is collected, the decay time can provide an indirect measure of the local value for the quantum efficiency.

- In multiphase or multi-dopant luminescent materials, care has to be taken when interpreting SEM-CL spectra and maps as artifacts can sometimes occur. Short wavelength light from one emitter can be absorbed by a longer wavelength emitter at a certain distance from the excitation [5]. Since all emission is attributed to the place of excitation in SEM-CL, this can lead to false spectral information (an apparent broadening or shift of the emission spectrum), similar to effects of X-ray fluorescence in the case of EDX analysis. This effect was, however, not an issue in the present work.

The present work illustrates the use of SEM-CL on the broad band emitting multi-phase powder phosphor  $\text{Ca}_{1.5}\text{Eu}_{0.5}\text{SiS}_4$ . It is shown that the combination of surface imaging, chemical mapping and temperature dependent and time resolved cathodoluminescent spectroscopy yields a wealth of information and allows to study a broad range of material properties.

## 2. Materials and methods

### 2.1. Materials

Samples of the yellow-to-red emitting luminescent material  $\text{Ca}_2\text{SiS}_4:\text{Eu}$  were prepared by solid state synthesis from mixtures of CaS, EuS and Si (in slight excess). Preparation and basic properties of this material were described in detail and can be found in [34]. As model system for the present analyses, heavily Eu-doped powders were prepared, with a 25% substitution of the Ca-ions, yielding an intended composition of  $\text{Ca}_{1.5}\text{Eu}_{0.5}\text{SiS}_4$ .

### 2.2. Experimental setup

The CL setup was built around a tungsten filament SEM (Hitachi S-3400N). Experiments were performed in low vacuum mode (20 Pa) to avoid electrostatic charging of the phosphor samples, thus suppressing undesired image shifting during mappings. Imaging was obtained by detection of backscattered electrons. Elemental analysis was performed on a Peltier cooled dry EDS system (Thermo Scientific Noran System 7, energy resolution  $< 125$  eV). Light was collected by means of an optical fiber (400  $\mu\text{m}$  diameter), positioned at about 2 mm from the sample. Light was guided to a 500 mm spectrograph via a fiber vacuum feed through. The spectrograph was coupled to a gated intensified CCD (Andor ICCD DH720). Both individual spectra (with the electron beam on a fixed position) and decay maps were recorded, with a typical  $64 \times 46$  map size and an exposure time per point of 300 ms, yielding a full map collection time of about 15 min. Full spectra were stored at each data point for further spectral and image processing in Matlab<sup>®</sup>. A temperature stage, controlled with a Peltier-element (temperature range  $-25$  °C– $150$  °C) was used to vary the phosphor's temperature during the cathodoluminescence measurements.

Time resolved CL measurements were performed in the same SEM. The electron beam was switched using an in-column beam blanker (Kammrath & Weiss fast electrostatic beam blanker) with a time resolution of 100 ps. The beam blanker was controlled with a pulse generator, and synchronized with the optical detector, as

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