Colour cathodoluminescence of display materials

Michael Nazarov **(1)**, **Tatiana Nazarova (2)**, **Petr Ivannikov (3)**, **Gennadii Saparin (3)**

(1) Samsung Electro-Mechanics Co, LTD.314, Maetang3-Dong, Yeongtong-Gu, Suwon, Gyunggi-Do, Korea
(2) Centre of Advanced physical research, Chisinau, Moldova
(3) Moscow State University, Moscow, Russia

Phone: +82-31-210-6278, E-mail: nazarov.mihail@samsung.com

Abstract

We report simple new techniques to express analysis of display materials. Colour Cathodoluminescence combined with scanning electron microscopy and spectroscopy is a powerful, non-destructive, high-resolution method for investigation luminescent materials. Some applications of this method to powder phosphors used in display are demonstrated.

1. Introduction

There is a long interest in new methods of investigation luminescent materials. Such traditional methods as photoluminescence (PL), cathodo-luminescence (CL), scanning electron microscopy (SEM), X-ray diffraction and others are well known. But no single method can supply the necessary depth of information, which is now required by companies involved in materials development or product manufacture

The aim of this work is to propose a new technique for studying luminescent materials. The (CL) modes being incorporated into SEM give both the spectral and spatial information with high resolution. CL spectral analysis together with the colour cathodoluminescence (CCL) was applied to examination of display phosphors in powder form.

2. Experimental details

Here we used a special attachment for CCL-SEM described in previous paper for the CL examinations of powder samples.[1] We used both the monochromatic and panchromatic CCL-SEM modes. At the monochromatic mode the CL emission was detected at definite wavelength. At the panchromatic CL-mode the CL was recorded at all the visible emission spectrum. By this way, monochromatic CL corresponds to definite transitions between the defect levels attributed to the activator. Spatial distribution of the monochromatic or panchromatic CL on the surface under study was recorded in forms of corresponding CCL-maps. A variety of colours observed in panchromatic CCL-map shows, therefore, a spatial distribution of all the luminescent centres that occurred by nature or design on the surface of investigated phosphors.

We applied the elaborated method of CCL for investigation of phosphors that used as display materials or in other optoelectronic devices.[2-6]

Among the samples were self-activated $CaWO_4$:W phosphor as well as Eu- and Tb-activated phosphors, respectively, $CaWO_4$:Eu^{3+} and $CaWO_4$:Tb^{3+}. Also there is a long interest in red emitting europium-activated yttrium oxide (Y_2O_3:Eu) both as a commercial phosphor, and as a model system for the study of the effect of the interplay of radiative and nonradiative processes on phosphor efficiency. However, this CCL method can be applied for other phosphors using as display materials.

Phosphor samples were characterized by crystalline structure and luminescence properties.

Optical spectroscopy and PL characteristics were estimated on the basis of emission and excitation spectra registered at room temperature (Xe 500 W lamp) with DARSA PRO 5100 PL System (Professional Scientific Instrument Co, Korea). The excitation was performed with 254 nm and 365 nm UV radiation. Low voltage (0.5-1 keV) CL was performed with the beam current density of 100 $\mu A/cm^2$ by using a Kimball Physics FRA2X1-2/EGPS-2X1 electron gun system.

3. Results and discussion

CCL-SEM image analysis of powders

An image analysis of the CCL-SEM maps taken from the powders must account the peculiarities of CL-contrast, which have not been observed in the maps for solid specimens. The mixed CL-spectrum image formation for two particles is schematically shown in Fig 1(a). Both the scattered and secondary electrons excite the CL emission of the surrounding particles. The CL from irradiated particle A is referred to as true CL. The CL from the particle B corresponds to the background. In the case of three particles, shown in Fig.1(b) the CL-background signal is formed by photons of excited particle "1" as well as by photons knocked-on by backscattered electrons (BSE) getting into the irradiated volume. For example, in Fig.3 the CCL-map of powder (F56), displayed with higher magnification than another maps, reveals that background CL corresponds to the green emission.
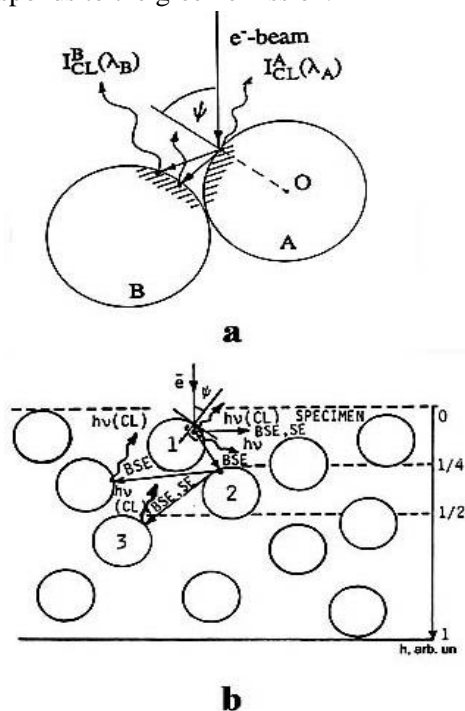

a

b

Fig. 1. (a) The excitation of two neighboring particles. (b) Vertical section of an ideal powder. Particles "1", "2", and "3" lie at depth $h_1 = 0$, $h_2 = 1/4$, $h_3 = 1/2$ arbitrary units, respectively. Ψ-electron beam incidence angle; CL- local CL emission; SE-secondary electrons; BSE- backscattered electrons.

To reveal physical mechanisms of the CL-image formation for the processes described above a computer model has been made by the Monte-Carlo method. Topographical component of a contrast $C(\Psi)$ observed in the CCL-map have been calculated by using a normalized integral CL intensity (I_n). Dependencies of the $I_n(\Psi)$ upon the electron beam incident angle Ψ have been calculated for the case of three particles, shown in Fig 1(b). Three corresponding plots of $I_n(\Psi)$ are presented in Fig. 2(a). On the basis of these results the angular contrasts $C(\Psi)$ for three particles of a powder have been obtained. Their plots are shown in Fig. 2(b), where an angular contrast for the secondary electron emission (SEE) mode is also presented. It had to note that in common sense a SEM -image presents a topographical map of surface under study obtained by means of the SEE-mode.

It would be interesting to compare calculated angular values $C(\Psi)$ for the SEE with a topographical component of contrast observed in the CCL-map. The plots in Fig. 2(b) show that the maximal topographical component of contrast $C(\Psi)$ observed in the CCL-maps correspond to the particles laying at the depth $h = 0$. For example, in Fig 3 the surface particles corresponding to $h = 0$ are seen as the brightest blue ones. One can see that in case of normal incidence ($\Psi \approx 0$) for all the depth of particles the corresponding values of the CL-contrasts (plots 1,2,3) prevail the SEE ones. Moreover, for the surface particles ($h = 0$, curve "1") the value of the CL- contrast for powder may exceed by several orders of magnitude the topographical contrast value of the SEE. Hence, the CCL-SEM are more sensitive than the traditional SEE ones.
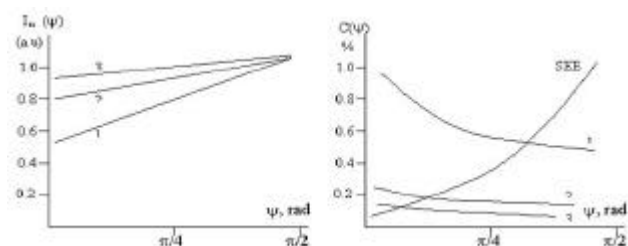

Fig. 2 (a) Function $I_n(\Psi)$ in arbitrary units for $h_1 = 0$, $h_2 = 1/4$, $h_3 = 1/2$ (curves 1, 2 and 3, respectively). Where I_n is the normalised intensity of integral CL of a powder. Fig.4(b) Function $C(\Psi)$ in percentage for $h_1 = 0$, $h_2 = 1/4$, $h_3 = 1/2$ (curves 1, 2 and 3, respectively for CL-mode). SEE -for secondary electron emission mode. $C(\Psi)$ is topographical component of contrast of the CL-image.
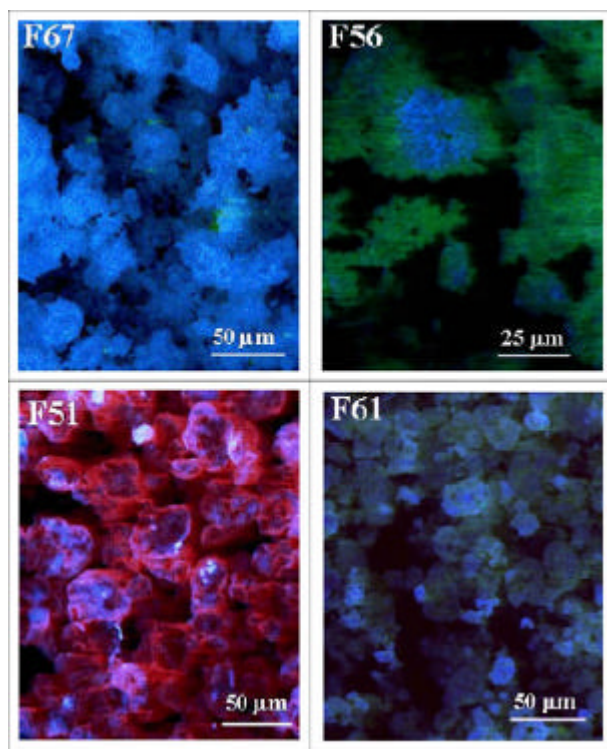
Fig.3. Panchromatic CL images of powder samples: F67 (CaWO$_4$:W); F56 (CaWO$_4$:Tb(1.0%)), F51 (CaWO$_4$:Eu^{3+}), F61 (CaWO$_4$:Tb(7.5%)).

Spectroscopic investigation of activator incorporation degree in Y$_2$O$_3$:Eu

To better understand the role of mineralizing agents and to explain the energy transfer in Eu^{3+}, the PL and CL spectra were registered. Spectroscopic measurements put in evidence the influence of thermal synthesis conditions on activator substitution efficiency when Eu^{3+} ion replace Y^{3+} or Ca^{2+} in the host lattice. If the difference in ionic radii is sufficient, the unit cell parameter could characterize an activator incorporation degree (AID) and play the role of an indicator of activator substitution. It is shown that substitution of Eu^{3+} for Y^{3+} results in an increase in the doped phase unit cell volume as the concentration in Eu^{3+} increases. Difference in the ionic radii of yttrium and europium (0.90 Å and 0.95 Å respectively) may account for this increase. Thus, the concentration dependence can be explained. In certain limits (for the same or similar particle sizes and before the concentration quenching), the term AID could be used to illustrate the phosphor performances resulting from the ratio

between the concentrations of emission centers and quenching centers. The direct correlation between the lattice parameter and luminescence properties was determined (Figs. 4,5).
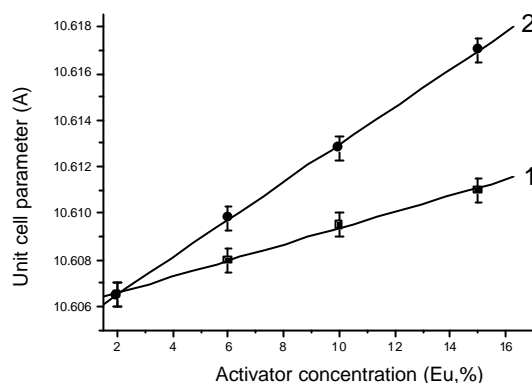

Fig.4. Lattice parameter dependence vs. activator concentration without flux (1) and with sodium tetraborate as flux (2). T=1300 ^{0} C

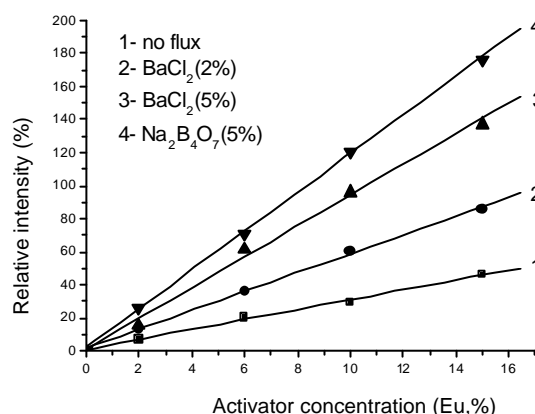Fig.5. Relative PL intensities (λ_{exc} =365 nm) vs activator concentration for different fluxes T=1300^{0}C

The europium doping level corresponds to linear intensity vs. concentration dependence (Fig.5). It should be noted that the linear dependence in Figs. 4 and 5 is determined by AID. Double role of flux is evident. BaCl$_2$ and Na$_2$B$_4$O$_7$ act as mineralizing agents that contributes to both intra- and inter-grains re-crystallization. Intra-grain re-crystallization leads to the AID improvement and as a result, to superior PL characteristics. Inter-grains re-crystallization increases the particle size that also increases PL intensity.

Less evident is dependence of lattice parameter on the annealing temperature (Fig.6). We can explain this phenomenon because an activator

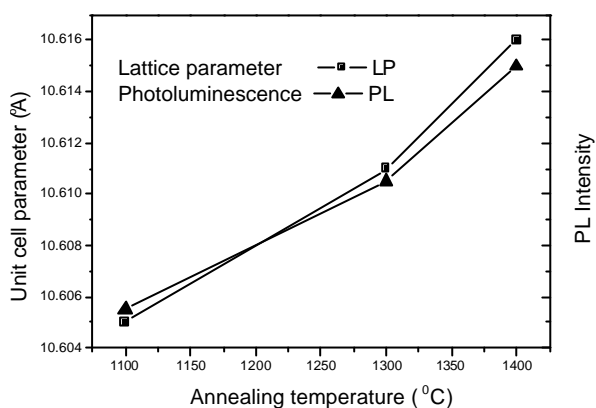substitution is more efficient with a temperature and occurs more fruitful

Fig.6. Unit cell parameter and PL intensity dependences vs. annealing temperature

Two important factors such as AID and increase of particle size intensify the luminescence enhancement. Activator substitution in general is a function of concentration, annealing temperature, flux etc, so the same replacement can be achieved by different ways: varying the concentration and flux at the same temperature, or flux and temperature at the same concentration. In any case, when we achieve the same lattice parameter and AID, the luminescence properties are very similar (it is valid, of cause, for the similar particle size).

It is found that a use of the relatively higher firing temperature and the presence of mineralizing agent contribute to both the formation of homogeneous Y_2O_3-Eu_2O_3 solid solutions and higher activator substitution efficiency for 2-15% europium into the host lattice. It has been obtained from all our measurements that the samples prepared with sodium tetraborate are more efficient than the corresponding material synthesized with barium chloride as flux and significantly better than the samples prepared without any flux. Light-emitting output of samples prepared with barium chloride and sodium tetraborate as flux exceeded the commercial ones by 20-30 %.

4. Conclusion

We have used both the PL and CCL-SEM for the complex examination of the powder luminescent materials. CL-images obtained in SEM in real colours can be used for a rapid examination of spatial and spectral characteristics of powder materials, produced by different technologies.

This method could be proposed for a complex investigation of phosphorescence and fluorescence from materials with different structures: powders, tablets and crystals.

We found that the double incorporation of Eu^{3+} and Tb^{3+} ions into $CaWO_4$ crystalline lattice modifies the luminescence spectrum due to formation of new emission centers. Depending on the activators concentration and nature, as well as on the interaction between the activators themselves, the luminescence color can be varied within the entire range of the visible spectrum. Under high excitation energy such as VUV (147 nm) radiation or electron beam in CL, white light could be observed.

The direct correlation between synthesis conditions, such as activator concentration, annealing temperature or flux and luminescence properties was established. Lattice parameter can be proposed as indicator of AID. In order to obtain high AID and consequently efficient Y_2O_3:Eu samples, flux nature and concentration, firing temperature and activator amount have to be carefully chosen.

5. Acknowledgements

6. References

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