



1. Introduction

In the last several decades, we have witnessed unprecedented changes to people's way of life which were possible through rapid advances in science and technology. Undoubtedly, miniaturization of solid-state electronic devices provided the biggest contribution to the onset of a new era both in scientific research and in development of novel consumer goods.

The beginning of the nano-age can be dated back to 1959, the year when the first integrated electronic circuits were patented and Richard Feynman gave his talk "There's plenty of room at the bottom" introducing the field of nanotechnology. It was, however, not until 1990s, that actual nanotechnologies were developed and today, 50 years after the invention of ICs and Feynman's lecture at Caltech, there is still a lot of unexplored space not only "at the bottom" of electronics but also in other scientific areas, for example, in solid-state luminescence.

Research on inorganic light-emitting materials was initially focused on properties of phosphor powders consisting of particles significantly larger than the wavelengths of visible light. Most of the phosphors in use nowadays consist of particles with the sizes ranging from several micrometers to several tens of micrometers. However, down-scaling of phosphor particle size into the sub-micrometer and nano-range could be advantageous for numerous applications, e.g., digital imaging in the ultraviolet spectral range.

The first semiconductor imaging integrated circuits called charge-coupled devices (CCDs) were invented in October 1969, just ten years after the invention of electronic ICs. (It must be mentioned that the authors of CCDs were awarded with the Nobel Prize in physics in 2009 because of the high impact of their invention on modern society.) Since then, the performance of image sensors has been constantly pushed to its physical limits. As of 2011, pixel size of the state-of-the-art CCDs and their successors based on CMOS-technology is below 2 μm . Main global vendors already have a 0.9 μm technology node on the roadmap for the nearest future (for back-side illuminated CMOS chips). Following the progress in fabrication of integrated circuits, resolution of image sensors could relatively soon reach the diffraction limits for visible light (0.2-0.3 μm).

Advances in digital imaging do not merely rely on the ongoing development in the field of manufacturing of semiconductor ICs but also support it. CCDs are widely utilized in photolithography (the predominant method of material structuring in IC-industry), e.g., in systems for mask inspection or adjustment of laser beams. At the current stage of development of IC-manufacturing technology, the market of lithography tools is dominated by 248 nm and 193 nm wavelength optical systems. There are several next-generation lithography candidates: extreme ultraviolet lithography, nano-



imprint, and multi-beam e-beam maskless patterning. However, they are still far away from being commercialized. UV lithography will continue to be the mainstream technology for at least next 10 years or more and the requirements imposed on mask inspection tools and excimer laser adjustment systems will become considerably more stringent, because there will be a demand for the highest achievable resolution and high sensitivity to radiation in a range of deep UV (DUV: $\lambda < 300$ nm) at the same time.

Sufficient sensitivity of solid-state detectors to UV-light may be acquired via special device architecture of the image sensor, choice of material, etc. However, it is also possible to enhance the UV-performance of standard front-illuminated silicon CCDs by introducing a phosphor plate in front of it, which would convert the UV radiation into the visible light. This approach could substantially lower the prices of lithography mask inspection systems and laser beam profilers for the cases where sub-optical resolution is not necessary. However, it may appear critical to be able to produce phosphor screens with extremely high resolution (as close to diffraction limits as can be).

Inorganic crystalline phosphors are known for their photostability and high efficiency. Usually, phosphor coatings are applied in the form of a porous particulate layer, which has higher brightness of luminescence (as compared to single crystals). The resolution of powder screens is limited by the size of the phosphor particles. Performance of the screens can be improved by reduction of the phosphor particle size. Along with high-resolution digital imaging in the UV range, applications of inorganic phosphors which could benefit from a decreased particle size of phosphors include CCD-based X-Ray imaging, plasma display panels, field emission displays, phosphor-converted white light-emitting diodes, and electroluminescent displays.

Synthesis and further processing of phosphor powders with reduced particle size are quite challenging and although the nano-age for inorganic phosphors was entered in the late 1990s, high-throughput low-cost techniques for fabrication of screens from sub-micrometer-sized phosphors are still in great demand. Performance of such screens should be thoroughly investigated because it can be strongly affected by various effects of decreased particle size.

This thesis is dedicated to a study and further development of flame spray pyrolysis – a method which combines the synthesis of fine or ultrafine phosphor powders (with particle size ranging from approximately 1 μm down to 10 nm) and their deposition onto phosphor screens in a single processing step. The scope of the present investigation is further limited to photoluminescence (PL) of non-patterned phosphor screens made of rare earth-doped oxide phosphors, although many conclusions are also valid for luminescence excited by X-rays and cathode rays as well as for other types of phosphors.



2. Potential of phosphor coatings with decreased particle size

2.1. Phenomenon of luminescence: theory and related terminology

The word *phosphor* was coined in the 17th century and means “light bearer” in Greek.¹ This term is commonly used for any solid material exhibiting light emission due to *luminescence*. It should be added that contrary to popular belief, most of the phosphors do not contain the chemical element *phosphorus*.

Luminescence is defined as a phenomenon in which the electronic state of a substance (i.e., of a phosphor) is excited by some kind of external energy and the excitation energy is given off as light.¹ Depending on the type of the involved external energy, luminescence is further subdivided into *photoluminescence* (excited by photons), *cathodoluminescence* (excited by incident electron beam), and *electroluminescence* (excited by applied electrical field), to name a few. Heat can also participate in excitation of luminescence (e.g., thermoluminescence); however, the latter should not be confused with the thermal radiation from heated objects (incandescence, i.e., a part of blackbody radiation emitted in the visible range).² Light emission taking place simultaneously with excitation is usually referred to as *fluorescence*, whereas an *after-glow* observed after the excitation has been interrupted is called *phosphorescence*.¹

There is a substantial difference between mechanisms of luminescence in inorganic and organic compounds.¹ For inorganic materials, one further distinguishes luminescence due to band-to-band electronic transitions in semiconductors (*band-gap luminescence*) and emission from localized centers (e.g., impurity atoms) in insulating hosts (*characteristic luminescence*).^{1,3,4} Most of the currently applied phosphors are polycrystalline inorganic materials consisting of a transparent host (*matrix*) intentionally doped with small amounts of impurities (*activators*, which emit light, and *sensitizers*, which improve the efficiency of excitation).^{1,5} The present study is devoted to phosphors of this type.

2.1.1. Efficiency of phosphors and luminescent devices

In practically any application of phosphors, the objective is to obtain a sufficient brightness of emission at the lowest possible energy consumption. Obviously, the efficiency of conversion of the excitation energy into the visible light is the most important property of a phosphor.

The most general measure of the phosphor performance is the *energy efficiency*. This quantity is defined as the ratio of the energy of emitted light quanta and the required excitation energy. For cathodoluminescence, the average energy of an



emitted photon is divided by the energy needed for generation of a thermalized electron-hole pair in the phosphor (taking backscattering into account),⁵ which is equivalent to the ratio of the total emitted radiant power and the total energy of the electrons impinging on the surface of the phosphor within unit time. In the case of photoluminescence, the energy efficiency is represented by the ratio of energies of the emitted and absorbed photons multiplied by the *quantum efficiency* (QE) of the phosphor. Quantum efficiency (also called *quantum yield*) is the number ratio of the emitted and absorbed photons, i.e., it is another indicator of the performance of photoluminescent phosphors. For cathodoluminescence, QE is obtained by dividing the number of emitted photons by the number of generated electron-hole pairs. Typical figures of QE for the phosphors applied in the fluorescent lamps and plasma display panels (PDPs) are quite close to 100 % and, sometimes, may even exceed it (i.e., *multiphoton emission* takes place).^{3,5} The performance of cathode ray phosphors is not much different in this aspect and also approaches a QE of unity.⁵ A comparison of energy efficiency, however, reveals a difference between these types of luminescence. The energy efficiency of common photoluminescent phosphors is on the order of 50 %. For the cathodoluminescent phosphors, the values of energy efficiency are usually below 25 %.⁵

The complete performance analysis of luminescent devices must include the efficiency of the excitation sources (e.g., generation of the cathode rays in the cathode ray tubes (CRTs) or ignition of gas discharges in the fluorescent lamps and PDPs) and other inherent energy losses. The overall energy efficiency of luminescent displays is usually in the range of several percent. For applications in lighting, such values would not suffice. Fluorescent lamps have an energy efficiency of 15-25 %.⁵ Semiconductor light emitting devices (LEDs) which are based on electroluminescence can achieve higher energy efficiency. It is expected that they will replace fluorescent lamps in the future. The high energy efficiency, however, is not the only requirement imposed on general light sources.

Some of the factors determining the perceived brightness of luminescence do not belong to the physics of luminescence. For example, human eyes have unequal sensitivity to different wavelengths of light. Spectral luminous efficiency function of the eye under conditions of *photopic vision* (i.e., in bright environments, which allow for perception of colors) has a maximum at a wavelength of 555 nm and gradually decreases towards both ends of the visible range (380-760 nm).¹ As a consequence, for the equal radiant intensities, blue or red light sources will appear noticeably fainter than green ones.

The color of light emitted by doped phosphors is to a large extent determined by the nature of activator. In many cases, it is possible to obtain luminescence of different colors for the same host material doped with various impurity ions. Furthermore, particular activator ions quite often produce luminescence of the same color in

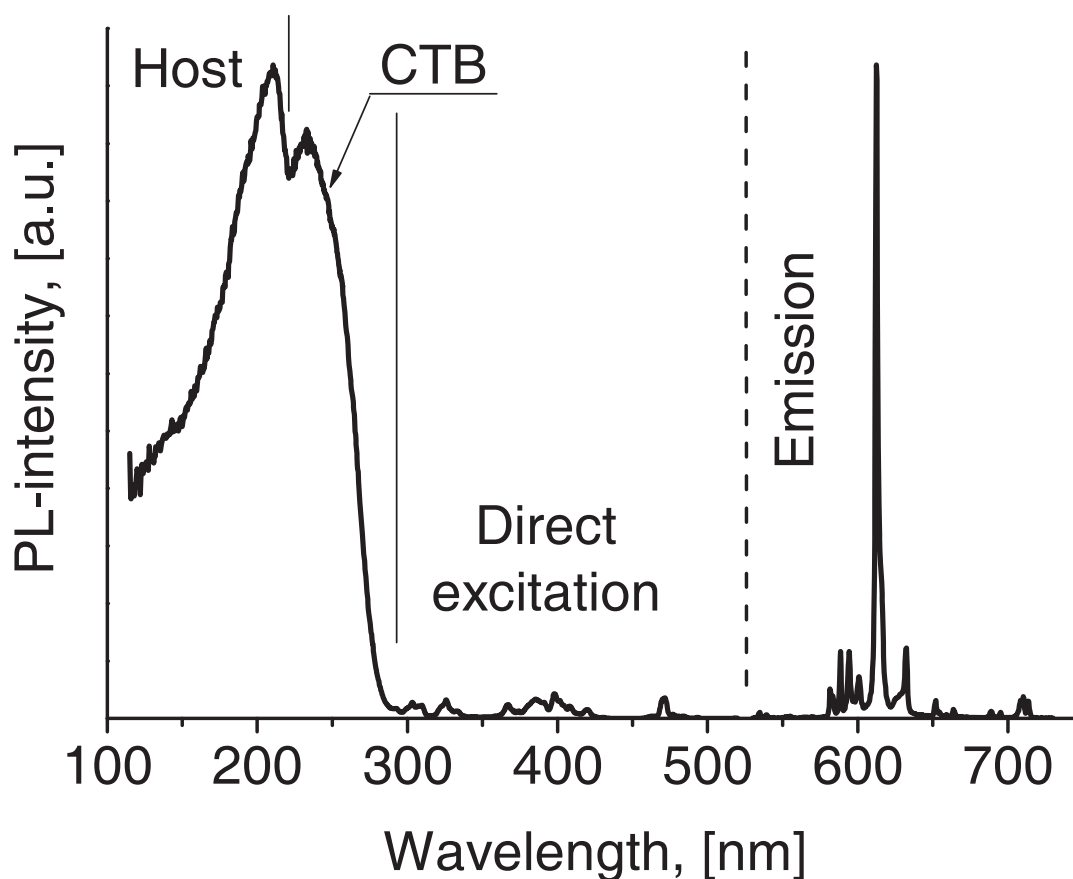


Figure 2.1 – Example of the emission and excitation spectra (for a commercial $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor).

different hosts. However, in general, the exact spectral distribution of emission (usually presented in an *emission spectrum* of the phosphor, see Figure 2.1) depends on the chemical environment of the luminescence centers.

Reproduction of different colors in the information displays and lighting is facilitated by simultaneous emission at several wavelengths. Usually in such cases, two or more different phosphors are blended together based on the concept of human *color vision*.^{1,3,6,7} Photometric quantities such as luminous intensity, luminous flux, illuminance, and luminance are obtained by integrating the energy of the optical radiation at different wavelengths over the standard spectral efficiency function for photopic vision.¹ It is convenient to characterize the performance of a light source by its *luminous efficacy* defined as a ratio of the total luminous flux to the consumed electric power (i.e., measured in units of lm/W). Another important characteristic derived from the spectral distribution of emission is the *color rendering index*, which measures the ability of a light source to reproduce colors of various illuminated objects.⁵



2.1.2. Photoluminescence performance of doped phosphors

The optimization of excitation conditions allows for increasing the intensity of emission and/or decreasing the amounts of the consumed phosphors. The photoluminescent performance of any phosphor can be characterized with an *excitation spectrum* (Figure 2.1), which shows the dependence of the intensity of emission upon the excitation at different wavelengths.

In general, excitation spectra of doped phosphors include three wavelength ranges corresponding to different mechanisms of excitation of the optically active ions. In the range of *direct excitation*, which is the closest to the emission bands, luminescence takes place if the energy of incident photons equals the energy of transition from the ground state of the ions to some of the excited states (i.e., they directly absorb exciting light). For shorter wavelengths, the energy of exciting light quanta increases and at some point, excitation of the luminescent ion by charge transfer from the top of the valence band of the host material becomes possible. The corresponding wavelength range is referred to as the *charge transfer band* (CTB). For even shorter wavelengths, in the *range of host absorption*, the energy of absorbed photons becomes sufficient for band-to-band transitions between the valence band and conduction band. The free charge carriers generated in this process can recombine at the activator ions resulting in intensive emission of light.

Low efficiency of the direct excitation is mostly due to a weak absorption of photons in the corresponding wavelength range. A substantial part of the exciting radiation is either reflected by the phosphor or transmitted through it. An increase in the concentration of the activator ions leads to more efficient absorption and thus can improve the performance of the phosphor. As it can be seen from the curves in Figure 2.2,⁸ the dependence of the intensity of emission on the dopant concentration is pronounced for all three mechanisms of excitation. In each case, there is a limit on the PL-brightness that can be achieved by increasing the amount of luminescent centers. If their concentration exceeds the limit, the light output decreases. This phenomenon is referred to as the *concentration quenching* of the phosphor. For increasing concentration of the optically active ions, the average distance between the neighboring ions decreases and they start to interact with each other. The rate of energy transfer between the ions increases so that the excitation energy can migrate from one ion to another until it is lost non-radiatively at a quenching site (a *killer*), e.g., at non-luminescent impurity ions or some other defects, which are inevitably present in the crystalline structure. The values of the optimum activator concentration corresponding to the maxima of the *concentration dependence* (CD)-curves can be quite different. For example, the concentration of luminescence centers in the ZnS-based phosphors, which have been used in the cathode ray tubes, never exceeds 1%. The dopant concentration in the rare earth based phosphors is typically

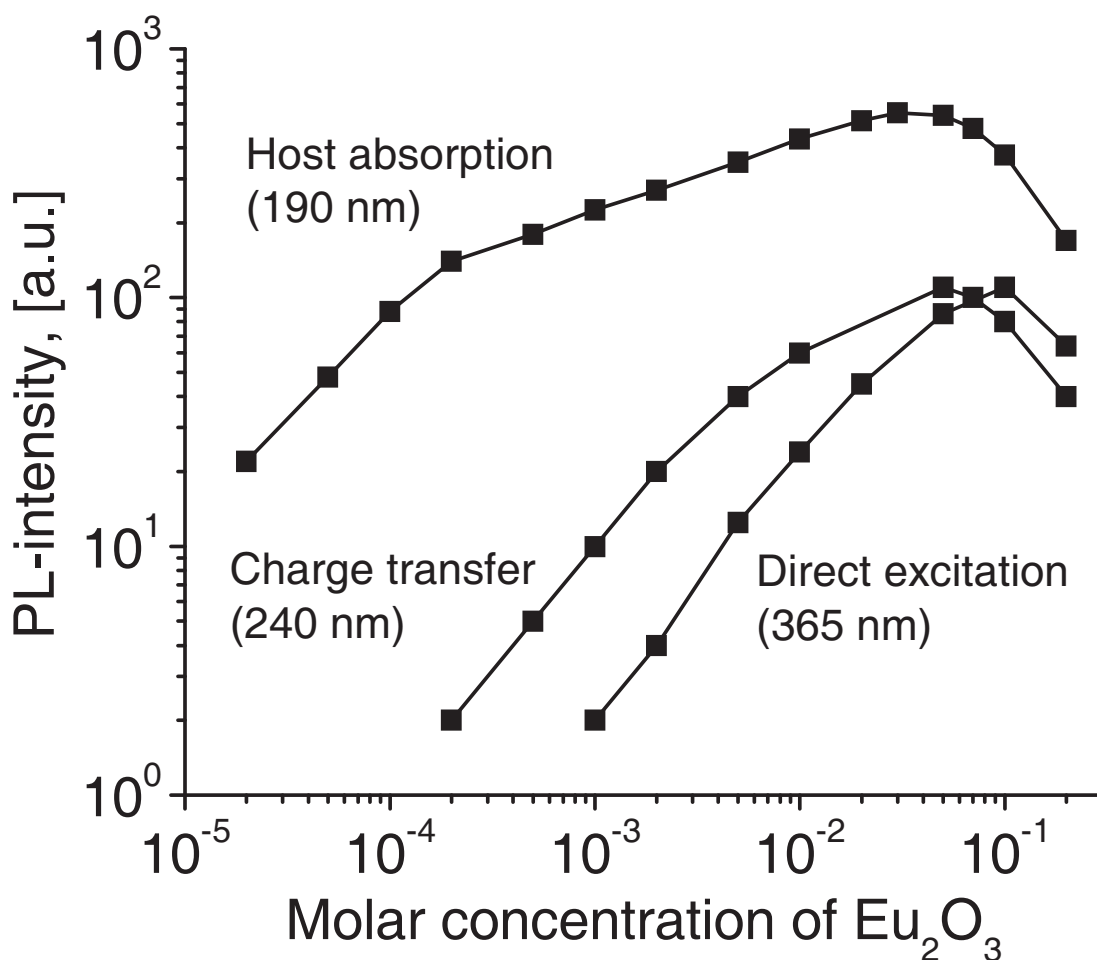


Figure 2.2 – Concentration dependence of photoluminescence intensity for the different mechanisms of excitation of the $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor (after Ozawa⁸).

noticeably higher and totals to a few percent of the cations in the compound. There are several phosphors (e.g., the CaWO_4 phosphor used in X-ray intensifying screens) which have no concentration quenching.³

In general, the presence of unintended impurities (contaminants) in the phosphor is detrimental at any concentration of the activator ions because they can act as additional absorption centers and increase the probability of non-radiative relaxation of the exciting energy. The first contribution (additional absorption) may be figured out by comparing the excitation spectra with the spectra of optical absorption (or reflection). The increased rate of non-radiative transitions can be confirmed by a decrease of the decay time constant of photoluminescence. In the simplest case, when both the radiative and non-radiative contributions can be represented by a first-order exponential decay, the emission decay time constant τ would change according to



$$\frac{1}{\tau} = \frac{1}{\tau_R} + \frac{1}{\tau_{NR}}, \quad (2.1)$$

where τ_R is the radiative decay time constant (without non-radiative processes) and τ_{NR} is the non-radiative decay time constant.⁵

If the radiative decay time is known, one can assess the degradation of the efficiency of the phosphor from the measured value of τ

$$q = \frac{\tau}{\tau_R}, \quad (2.2)$$

where q is the quantum efficiency of the phosphor.⁵

It should be noticed that quenchers can be generated in the phosphor during its use. For example, the decrease of brightness of the fluorescent lamps in the first minutes of lamp burning is attributed to *color centers* (structural defects which absorb light) generally formed in phosphors upon exposure to Hg radiation at 185 nm.¹ Generation of color centers is reversible. The long-term degradation of the inorganic phosphors is usually attributed to the ion or electron bombardment. The efficiency loss over the operational lifetime for the fluorescent lamps is relatively small (~10 %).^{1,5} In the case of CRTs, the maintenance is usually much worse (30-50 %).⁵

The probability of non-radiative recombination is not exclusively determined by the structural perfection of the phosphor material and concentration of activator. Changes of temperature also affect the quantum efficiency of a phosphor. In general, QE degrades at elevated temperatures. This process is called *thermal quenching*.

2.1.3. Configurational coordinate diagram

A *configurational coordinate model* can be used to explain the dynamics of the luminescence process (Figure 2.3). This model represents the potential energy curves of an absorbing center as a function of a *configurational coordinate* which describes the symmetrical stretching vibrational mode of the center.^{1-3,5} This mode is assumed to be harmonic and curves corresponding to different electronic states all have parabolic shapes. Nuclei surrounding the ion very slowly accommodate to a change of the electronic state (as compared to durations of electronic transitions) and therefore electronic and vibronic transitions can be treated separately (*Born-Oppenheimer approximation*).⁹ In the terms of the model, it means that the configurational coordinate does not immediately change upon an electronic transition between different states. As a result, electronic transitions always have vertical direction in the diagram (*Franck-Condon principle*).¹ Generally, each transition is accompanied by emission of phonons (process of *thermalization*). The average amount of phonons involved in the absorption and emission processes (expressed by *Huang-Rhys fac-*

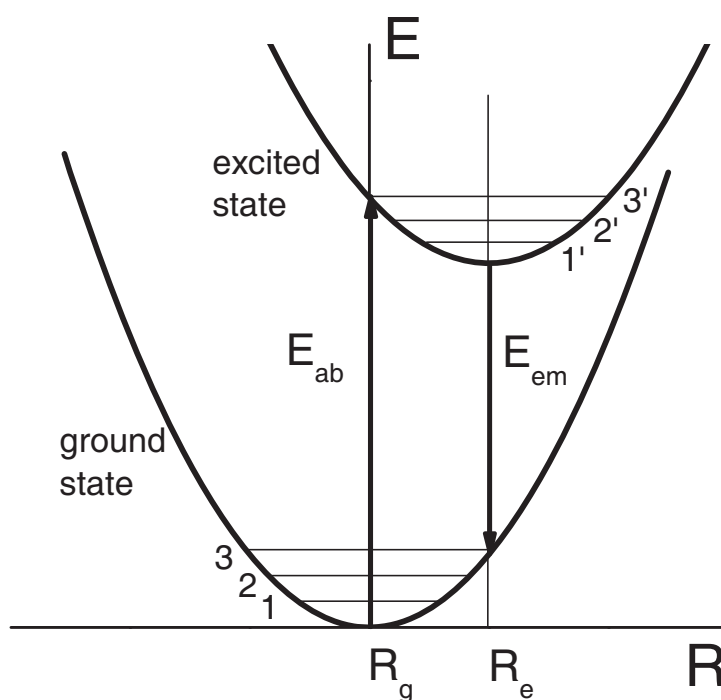


Figure 2.3 – Configurational coordinate diagram (schematically).

tors) corresponds to the difference between the energies of electronic transitions E_{ab} and E_{em} in Figure 2.3, which is termed the *Stokes shift*.^{3,5}

The diagram sketched in Figure 2.3 shows why the wavelength of light emitted by a phosphor is usually longer than that of the light, which excites luminescence (*Stokes law*). It can also be seen that the Stokes shift increases with increasing offset of parabolae along configurational coordinate axis (represented by the distance between R_g and R_e). Based on this offset, emission from luminescence centers in different materials can be classified into cases of *weak*, *intermediate*, and *strong coupling*, which determines the shape of the peaks in the emission spectra.³ The probability of thermal quenching is also determined by the mutual arrangement of the two parabolae.

The configurational coordinate model can include charge transfer states and multiple excited states of the dopant inside the band-gap of the host material. However, it delivers a somewhat oversimplified description of optical processes because more than one vibrational mode actually exists (i.e., several configurational coordinates may be needed) and thermal expansion of the host lattice is not taken into account.^{1,3,5} Furthermore, behavior of real systems often significantly deviates from harmonic approximation.³ Nevertheless, the model is very helpful for interpretation of dynamic effects and is commonly used in addition to the theory dealing with static interaction of luminescence centers with their surroundings.