

Europium-doped phosphors for lighting: the past, the present and the future

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The past

Europium, the 63rd element of the periodic table, was isolated and identified as one of the last in the rare earth series by Eugène-Anatole Demarçay in 1901, and named after the European continent. Europium does not occur as a metallic element in nature, as it readily oxidizes. It is found in small quantities (of the order of 1 ppm) in the earth crust. It is mined from a few minerals, where the Eu-content can reach a few tenths of % [1].

Fluorite (CaF_2), a mineral which is widely found in nature, has been known to be luminescent since early times, and gave its name to the process of fluorescence. A specific mine in England, the Blue John Cavern, was known for its blue fluorescing fluorite crystals [2]. Later, it was found that not the CaF_2 itself is luminescent, but rather the Eu^{2+} ions which are incorporated as impurities in the crystals are responsible for the blue fluorescence. Therefore, the history of Eu-doped phosphors dates back thousands of years.

When in the 1960s, europium-doped yttrium orthovanadate ($\text{YVO}_4:\text{Eu}^{3+}$) was developed as a red phosphor, this formed the breakthrough of color television: until then, no bright phosphors were available for the red component of CRTs. Using $\text{YVO}_4:\text{Eu}^{3+}$ as the new material for red cathodoluminescence meant a giant leap in performance and the start of a worldwide spread of color CRTs for television screens and computer monitors [3].

About a decade later, tri-phosphor fluorescent tubes with decent white color and good color rendering were developed, again using a europium-doped phosphor ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$) as the red component. This kind of lamps has dominated the market of efficient indoor lighting for decades, followed by a trend towards compact fluorescent tubes (CFLs) ... using europium. Completely in line with its name, europium is also the dopant in the materials that are used as fluorescent safety markers in all Euro bank notes [4].

While Eu can be used for any color of visible emission (see further), it is one of the few ions which can yield efficient and saturated red emission. Therefore, we will focus on red Eu-based phosphor materials.

The present: Eu^{2+} versus Eu^{3+}

Most of the lanthanides occur in a 3+ valence state. The lowest lying occupied state is a $4f^n$ ground state, with n the number of valence electrons of the ion. Except in the case of Ce^{3+} and - in some cases - Pr^{3+} , the first excited state in these ions is also a $4f$ -level, and the relevant optical transitions are $4f$ - $4f$ transitions. As the $4f$ levels are very well shielded from the surrounding matrix, these $4f$ - $4f$ transitions are composed of sharp excitation and emission lines which are hardly influenced by the surrounding matrix. The ratio of the different emission lines are, however, highly sensitive to the symmetry of the site of the dopant. For Eu^{3+} , this is illustrated in figure 1: In $\text{SnO}_2:\text{Eu}$, where the europium ions occupy centrosymmetric sites, the reddish-orange emission is dominated by the transitions terminating at the 7F_1 levels. In $\text{Y}_2\text{O}_3:\text{Eu}$, lattice sites without inversion symmetry are also present, leading to the more

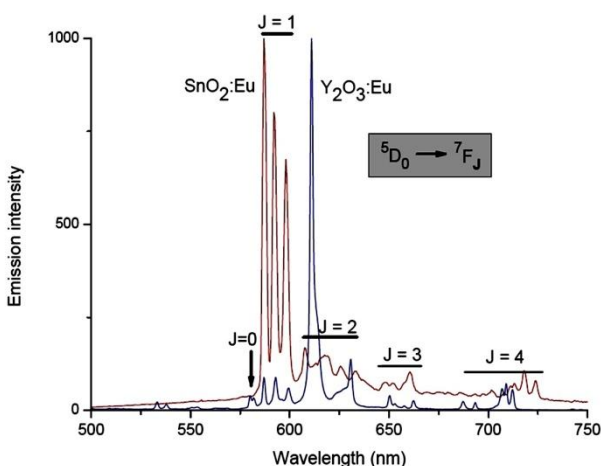


Figure 1: Photoluminescence spectrum of Eu^{3+} in SnO_2 and Y_2O_3 .

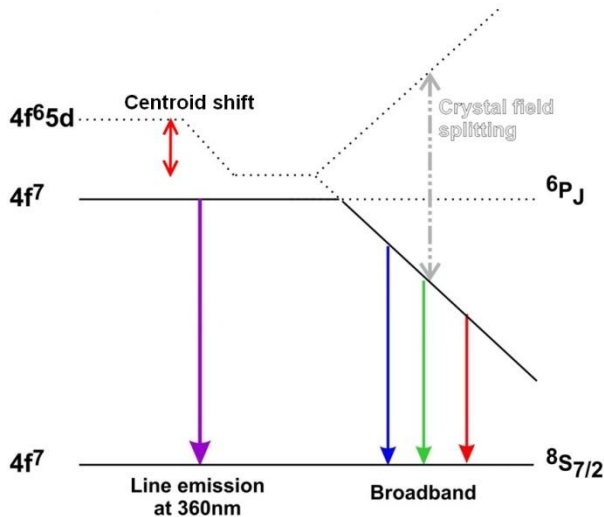


Figure 2: Schematic representation of the influence of the centroid shift and the crystal field splitting on the emission energy in Eu^{2+} .

substitutionally in a semiconductor host, these 4f-levels remain essentially unchanged, but the next higher level, a $4f^65d^1$ configuration, is decreasing in energy and drops below the first $4f^7$ excited state, as illustrated in figure 2. Depending on the crystal the center of gravity of the $4f^65d^1$ level decreases (called the centroid shift), and the level splits into several states due to the crystal field. In case of an octahedral field, the level splits into two levels (see figure 2).

The typical broadband luminescence which is observed in most Eu^{2+} -doped phosphors stems from a transition from the lower $4f^65d^1$ state to the $4f^7$ ground state. The combination of the crystal field splitting and the centroid shift leads to an overall red-shift of this emission compared to the free-ion transition. The excited state is broadened, and interacts strongly with the host lattice; therefore the typical emission from Eu^{2+} is a single broad band. The wavelength at which this band peaks is determined by the red-shift. For a number of classes of phosphor materials, the attainable wavelength range is illustrated in figure 3 (data taken from [5] and [6]). It is seen from this figure that in fluorides (including the famous $\text{CaF}_2:\text{Eu}$ phosphor), bromides and iodides, the red-shift is small, leading to UV or blue emission. Oxides, which have been the materials of choice in fluorescent tubes and CRTs because of their stability, usually have a too small red-shift to allow red emission from Eu^{2+} . The isolated points in figure 3 at 625 nm and 738 nm correspond to $\text{SrO}:\text{Eu}$ and $\text{CaO}:\text{Eu}$ respectively, but neither of these compounds are stable under ambient conditions nor yield efficient Eu^{2+} luminescence [7].

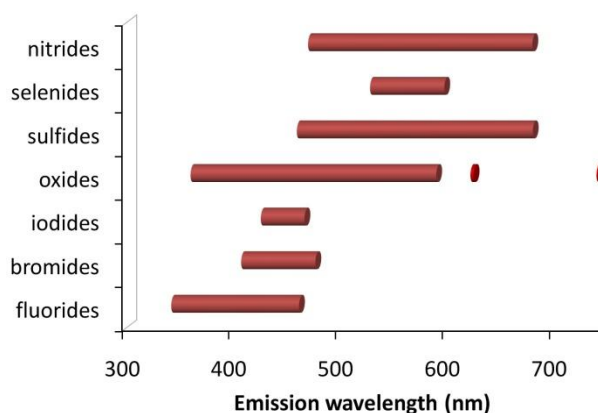


Figure 3: Range of peak emission wavelengths obtained from Eu^{2+} ions in different classes of host materials.

saturated red emission being determined by 5D_0 to 7F_2 transitions. This effect has also been used to probe the local symmetry of the europium ions. Though the details of the emission spectrum in Eu^{3+} -doped phosphors can be changed by a careful choice of host (just as in figure 1), the overall spectrum is mainly situated around 600 nm in all cases. It is one of the most popular red phosphors in cathode ray tubes and fluorescent tube lamps. For other applications (such as phosphor-converted light emitting diodes), however, these materials are not useful, as they cannot be excited efficiently using near UV or blue light. In addition, the decay time of the luminescence is quite long (of the order of a few ms), which can give rise to saturation effects in high intensity light sources. In these cases, we have to turn to its closest relative, Eu^{2+} .

In the free Eu^{2+} ion, both the ground state and the first excited state are $4f^7$ configurations, with a transition energy corresponding to about 360 nm, in the near UV. When the Eu^{2+} ion is incorporated

From figure 3, we see that currently sulfides and nitrides are the materials of choice for red emission using Eu^{2+} doping. Until a few years ago, most research was focused on sulfides, which has led to a large series of phosphors for lighting applications [8]. Among these, $\text{CaS}:\text{Eu}$ (red emission at 650 nm), $\text{SrS}:\text{Eu}$ (orange emission at 620 nm) and their solid solutions are notable. In the 1980's and 1990's, these phosphors were introduced in thin film electroluminescent devices. Later, when bright blue LEDs became available, they were the first materials to obtain high color rendering white LEDs. Indeed, a typical white LED is based on a blue LED, together with one or two phosphor materials, converting part of the blue into green and red, to obtain an overall white emission. Early white LEDs used YAG:Ce (having a very broad yellow spectrum) as the only phosphor,

but this yields a white color with mediocre color rendering, due to the lack of a sufficient amount of green and red in the spectrum. Existing red phosphors, based on Eu^{3+} , could not be used for this purpose, as they cannot be excited efficiently using blue light (typically 460 nm). CaS:Eu and SrS:Eu have an excitation spectrum which perfectly overlaps with the blue spectrum from exciting LEDs, and were used in a number of commercial high color rendering white LEDs. Unfortunately, these sulfides suffer from two disadvantages. Firstly, depending on the material purity and the dopant concentration, the thermal quenching of the emission is quite considerable. This makes it difficult to apply the material directly on an LED chip for wavelength conversion, as the chip can reach temperatures of the order of 150°C during operation. Secondly, the sulfides are sensitive to moisture. This effect can be tackled – albeit at added cost and complexity – by encapsulating the phosphor particles in an inert matrix [9,10].

These two disadvantages can be avoided to a large extent by using nitrides (see figure 3). Research into this class of materials only started quite recently; an excellent review on their synthesis and properties can be found in [11]. Nitrides and oxynitrides studied for red (broadband) emission include $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) and $\text{CaAlSiN}_3\text{:Eu}^{2+}$. Both phosphors show red emission at around 615 to 650 nm, a broad excitation spectrum, high chemical stability and decent thermal quenching behavior. Due to these highly promising properties, they are actively investigated and used for high-end high-power LED applications. Currently, the main drawback of this class of materials is their difficult preparation: typically, very high processing temperatures of the order of 1500-1800°C are needed to obtain bright phosphors. Efforts in decreasing this temperature have been partly successful: synthesis at 800°C proved possible, albeit under a 100 MPa ammonia atmosphere.

The future

During the last decades, europium has played a major role in the development of new phosphor materials. While many materials have been fully optimized for use in – now mostly obsolete - CRTs and fluorescent lamps, there is ample room for improvement of materials for other applications. Phosphor converted white LEDs are now a mature technology, showing efficacies well over 100 lum/W. For good color rendering devices, Eu is essential as a dopant for red emission, and improvements in materials processing are expected to yield close to optimum phosphors in the next few years. This research runs in parallel with a more fundamental approach: several research groups investigate the details of the structural incorporation of the Eu-ions in semiconductor lattices. A better knowledge of these details should indeed lead to a more focused research of materials technology. The problem of thermal quenching of the phosphor emission in white LEDs could be solved using a ‘remote phosphor’ approach: the phosphor is then incorporated in a plate at some distance from the LED chip(s), for example in the lamp shade, where temperatures are much lower than on the LED chip itself.

Another recent application of europium in phosphors is persistent luminescence [12]. Since the development in 1996 of the very bright and long lifetime persistent phosphor $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$, emitting in the green, there is a strong renewed interest in persistent luminescence. Potentially, these materials cover a wealth of applications, ranging from emergency illumination, road markings, background lighting and household applications to medical imaging. Currently, the main problem is the lack of other colors than green, and undoubtedly, europium will play a major role in the development of red emitting persistent phosphors [13].

As europium is quite abundant in the earth crust, there is no danger we will run out of the element in the foreseeable future. However, there are only few mines with sufficiently high Eu-concentrations to make mining profitable. Therefore, europium is relatively expensive, and its cost is highly dependent on political decisions regarding export regulations [1]. This might be a reason to try and find alternative doping elements (or combinations of elements) outside of the rare earth series, such as the so-called s^2 -ions Sn^{2+} , Pb^{2+} and Bi^{3+} . Unfortunately, these efforts have not led to equally performing devices so far.

Acknowledgments

This work was conducted in the framework of the interdisciplinary research platform NB-photonics at Ghent University, Belgium and the Interuniversity Attraction Pole programme IUAP VI/17-INANOMAT funded by the Belgian Science Policy.

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