

Why the quest of new rare earth doped phosphors deserves to go on

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Received 29 September 2004; accepted 30 September 2004

Available online 6 June 2005

Abstract

The scientific research on phosphors has a long history starting more than 100 years ago. But recently the appearance of new kinds of displays and lighting devices (plasma display, fluorescent lamp without mercury...) induced an increase of the research of new phosphors with better luminous efficiency than those available up to now. It has been shown that the behaviour of “classical” phosphors in a plasma display panel is quite different than in a cathode ray tube and that the vacuum ultraviolet (VUV) excitation process has to be studied with care in order to improve the phosphors efficiency. It is well established now that a good phosphor for electronic or ultraviolet excitation, is not necessarily a good choice for excitation in VUV. This is probably due to the fact that the excitation process is very different in that case. We will illustrate this difference on the well-known $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} phosphor. The penetration depth of the VUV photons is extremely small inducing a large contribution of the surface of the phosphor. We have shown that, for most phosphors, only a few tens of nanometers of the phosphor grain are really useful and we propose a way to realize phosphors powders using less than 20% of doped materials. However the traps of the material play a crucial role in the fluorescence properties due to the fact that autoionization process is likely when dopant ions absorb high energy photons. Fast aging process is one of the main drawbacks of VUV excitation. We demonstrate this effect on $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$, the blue emitting phosphor widely used up to now in Plasma Displays Panels and fluorescent lamps. Low energetic efficiency is another drawback of VUV excitation that can be solved only in the framework of fundamental studies. Quantum cutting emission may be a solution and calls new research to find good phosphors characterized by a high quantum efficiency, a high fluorescence efficiency and an adapted colorimetry.

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PACS: 78.55.Hx; 78.60.Kn

Keywords: Phosphors; Luminescence; VUV; Aging process

1. Introduction

The scientific research on phosphors has a long history starting more than 100 years ago. Why do we need new phosphors? Essentially because of the technological progress: From the early black and white television, in 1936, to the new 60 in. plasma display panels, the technology has really changed. In the domain of lighting devices, also from the first lamp made by Edison to the

compact fluorescent lamp used everywhere now, progress and improvement are obvious. We also need to continue research in this field because the excitation sources have changed and it is known that a good phosphor for electronic or ultraviolet excitation is not necessarily a good choice for excitation in vacuum ultraviolet (VUV). In a near future, we will be obliged to suppress mercury in any lighting devices because it is very harmful for the environment, and replace it by a mixing of rare gas (Xenon and Neon) which emits VUV photons from 147 nm to 190 nm instead of ultraviolet photons at $\lambda = 254$ nm in order to excite the phosphor coated lamp inner surface. Therefore the fluorescence properties of

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phosphors induced by such VUV photons, has to be studied and improved. In the domain of plasma display panel (PDP) the key factors for success are quality and longevity. Both factors depend directly on phosphors: luminous efficiency, color rendering and longevity are all properties which depend on the nature and the quality of phosphors. Another crucial characteristic of phosphors for PDP is the fluorescence lifetime: the shorter, the better in order to produce the highest number of grey levels.

2. The VUV excitation process

2.1. VUV energy is transfer

It is well established now that a good phosphor for electronic or ultraviolet excitation is not necessarily a good choice for excitation in vacuum ultraviolet (VUV). The behaviour of phosphors under VUV excitation process has to be studied with care in order to understand the excitation path and to improve the phosphors efficiency. The excitation process is very different in that case and the penetration depth of the VUV photons is extremely small inducing a large contribution of the surface of the phosphor. In order to illustrate this problem we will consider the case of LaPO_4 doped with Ce^{3+} and Tb^{3+} . This very famous phosphor has been studied in our laboratory [1,2]. It is used in fluorescent lamp and characterized by a green emission at $\lambda = 545 \text{ nm}$ corresponding to the transition ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ as soon as the terbium concentration is high enough to make the cross-relaxation mechanism process (${}^5\text{D}_3, {}^7\text{F}_6 \rightarrow {}^5\text{D}_4, {}^7\text{F}_0$) effective, i.e. ($C_{\text{tb}} > 10\%$).

In this phosphor, cerium is the sensitizer which strongly absorbs UV photons and transfers the energy to Terbium ion which plays the role of emitting center. In the VUV, the situation is different: most of the photons are absorbed by the host crystal, moving electrons from the valence band towards the conduction band. Then, either self trapped excitons (STE) or free electron–hole pairs are formed. So we need to study the energy transfer from STE to rare earth ions and the ability of these rare earth ions to capture electron–hole pairs. The ability to capture electrons or holes depends on the rare earth ion and on the energetic position of its ground state inside the energy gap of the crystal. Photoconductivity or XPS experiments help to determine this position. But both these techniques are difficult and their results sometimes ambiguous. Nevertheless it is possible, at least, to predict which ions will be good electron traps and those which will be good hole traps. In order to have a good hole trap, the ground state of the trivalent rare earth ion has to lie high in the forbidden gap of the host matrices, i.e. its ionization potential must be low; on the other hand in order to have a good electron trap,

the ground state of the corresponding divalent rare earth ion has to be deep inside the forbidden gap, i.e. the ionization potential of the divalent species must be large. Thus europium and samarium are likely good electron traps while cerium and terbium are prime candidates to create hole traps [3].

2.2. Ionization of rare earth ions

Another process well-known under VUV excitation is the ionization of rare earth ions. The autoionization process which consists of the transition of one electron from the ground state to one excited state of the rare earth ion lying in the conduction band of the crystal followed by the escape of this electron into the conduction band is the more probable. This depends not only on the relative position of the excited state of the rare earth ion and the conduction band but also on the coupling of these excited states with the conduction band. For example, Eu^{2+} in BaF_2 efficiently ionizes from its 5d band, inducing a Fano broadening of its “d” levels, but does not ionize at all from its excited “f” levels although these levels are located higher in the conduction band than the “d” band [4,5].

2.3. Fluorescence efficiency under VUV excitation

LaPO_4 doped with trivalent cerium and terbium has a high fluorescence efficiency under excitation at $\lambda = 254 \text{ nm}$ owing to the strong absorption of Ce^{3+} at this wavelength and the overlap of cerium emission and terbium absorption inducing an efficient energy transfer between both ions.

Cerium and terbium ions are good electron–hole pairs traps, but STE transfers its energy mainly to Ce^{3+} . Under VUV excitation both ions are in competition and the efficiency of the energy transfer between cerium and terbium being less than 1, it is likely that co-doped samples may be less efficient than single doped sample with terbium. The results are shown in Fig. 1.

The gain for terbium emission when the cerium concentration increases, is clear for $\lambda_1 = 254 \text{ nm}$ excitation, but for the shorter excitation wavelengths, the contribution of cerium has indeed a damaging effect.

3. Aging processes of phosphors

Plasma display panels are a new technique for large-screen television sets and were the object of huge improvements in the ten past years. Among the various aspects that need R&D effort, luminous efficacy has relatively high priority. As phosphors play a key role in these performances, their quantum efficiency and stability over time needs to be investigated and improved.

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