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VUV-extended measurements of quantum efficiency of sodium salicylate and of some NBS standard phosphors

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Abstract

Phosphors play a key role in the performances of display and lighting systems, their quantum efficiency needs to be investigated and improved. That is particularly true in plasma display panels (PDP) because of vacuum ultra violet (VUV) nature of the excitation. It is well established now that a good phosphor for electronic or ultraviolet excitation, is not necessarily a good choice for excitation in VUV. In order to study the behaviour of phosphors, it is necessary to record excitation and absorption spectra and to know precisely the spectral repartition of the excitation source. In the VUV energy range, sodium salicylate is very often used as a reference because of its constant quantum efficiency. In this paper we analyse this quantum efficiency in the near VUV energy range (below 10 eV) and its evolution over time. We show that it is far from being constant at these energies and that it decreases in a non-homogeneous manner over time. We also determined the quantum efficiency, in the VUV range, of several NBS standard phosphors and $BaMgAl_{10}O_{17}:Eu^{2+}$.
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1. Introduction

Up to now, to produce light with a fluorescent lamp we put mercury inside the lamp to generate ultraviolet photons at $\lambda = 254$ nm in order to excite the phosphor coated lamp inner surface. But in a near future we will be obliged to suppress mercury in any lighting device because it is very harmful for the environment. It should be replaced by a mixing of rare gas (Xenon and Neon) which emit vacuum ultraviolet (VUV) photons from 147 nm to 190 nm. Therefore the fluorescence properties of phosphors induced by such VUV photons, has to be studied and improved if efficacy decreases. The same kind of gas discharge is used in plasma display panels (PDP) which are a very promising technique for large-screen television sets and were the object of huge improvements in the ten past years. Further progresses are needed for a wider acceptance by consumers. Among the various aspects that are subject to present R&D effort, luminous efficacy and lifetime have 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. That is particularly true in PDPs because of VUV nature of the excitation. 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 and also because the penetration depth of the VUV photons is extremely small inducing a large contribution of the surface of the phosphor. Then it is of the first importance to study the fluorescence properties of phosphors under VUV excitation in between 5 and 10 eV, and to determine their fluorescence efficiency in this energy range. In order to calculate the quantum efficiency it is necessary to record

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excitation spectra and absorption spectra, so you need to know precisely the spectral distribution of your source of excitation, i.e. the spectrum of your lamp and the transmitting coefficient of your dispersive apparatus. In the visible part of the spectrum, in the atmosphere of the laboratory, this can be easily obtained by measuring the energy at the output slit of the monochromator with a thermopile detector which is characterized by a flat response as a function of wavelength. But in the VUV energy range, in vacuum, it is impossible to use such a detector. Researchers working with synchrotron radiation at very high energy (above 10 eV) used to measure the spectral distribution of the exciting source by recording the variation of the fluorescence intensity of sodium salicylate which was known since many years as a blue phosphor with a high and constant quantum efficiency on a large energy range. Sodium salicylate emits a broad blue band centred at 420 nm with a very fast fluorescence decay time which is approximately equal to 10 ns. The earliest investigation of the fluorescence yield of sodium salicylate was carried out by Déjardin in 1934 [1]. He reported a constant fluorescent efficiency between 220 nm and 340 nm. Slavin et al. have found the same result for wavelength longer than 200 nm [2]. Several observers described a decrease in fluorescence efficiency for wavelengths between 160 and 100 nm, and a constant fluorescence efficiency below 100 nm down to 300 nm [3,4]. For the research of new phosphors with a high fluorescence efficiency excited by plasma discharge of Xenon, i.e. excitation with wavelengths between 140 and 190 nm, it is necessary to know the intensity variation of the exciting source in this area. The correction appears to be drastic if you use a deuterium lamp equipped with a MgF_2 output window because the emission spectrum of this kind of lamp is made of very intense and numerous lines below 170 nm and of a weak continuum above 170 nm. Sodium salicylate is nevertheless widely used in this wavelength range by authors arguing than its fluorescence yield is constant. We will show that this is not true and that correcting spectra in such a way may induce mistakes. Furthermore the efficiency of sodium salicylate under VUV irradiation decreases with time differently as a function of wavelength, what may also induce errors in measurement of fluorescence efficiencies of phosphors.

2. Experimental

A schematic drawing of our VUV spectroscopy experiment is shown in Fig. 1. The spectrometer allows to excite phosphors samples in the VUV–UV spectral range, to record the VUV diffused reflection and to analyse the fluorescent emission in the UV–visible range. It is essentially composed of two parts: the first one for VUV spectroscopy covering $\lambda = 110$ nm to $\lambda = 240$ nm spectral range, and the second one for UV spectroscopy covering $\lambda = 200$ nm to $\lambda = 400$ nm spectral range. The VUV part consists of a 150 W deuterium lamp equipped with a MgF_2 output window from Hamamatsu as a light source. The lamp is

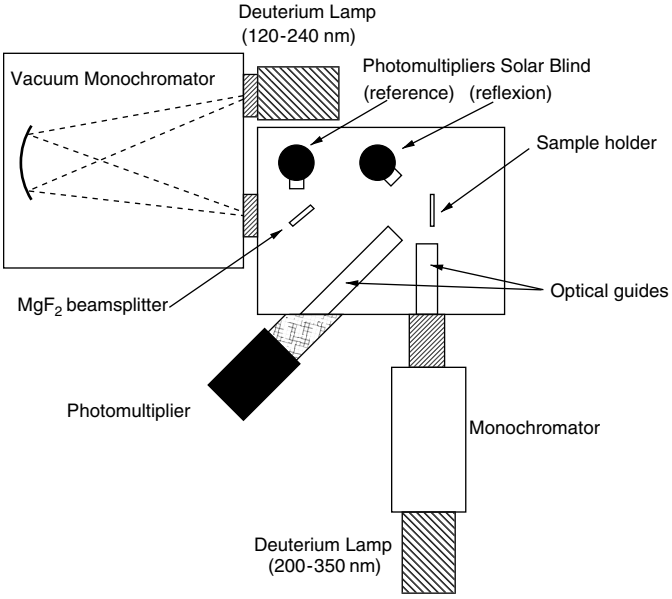

Fig. 1. Experimental set-up diagram.

directly mounted in front of the monochromator entrance slit with a special vacuum flange. The entrance slit can be isolated from the monochromator by a gate valve, allowing us to change the lamp without perturbing the vacuum inside the monochromator. The Beaudouin MVR 100 vacuum monochromator has a focal length of 1 m. Its concave grating is blazed at 800 Å and it has 1200 lines/mm giving a dispersion of 1 nm/mm and resulting in a potential resolution of the system well below 1 Å. It is continuously evacuated by a turbo pump ATP 150 from Alcatel, the pressure being less than 10^{-7} Torr. The sample chamber is directly mounted on the exit slit of the monochromator. Like the excitation source, it can be isolated from the vacuum monochromator by a gate valve. The sample chamber is equipped with its own turbo pump ATP 80 from Alcatel which allows to reach a pressure of 10^{-7} Torr in a few minutes. The pressure in our set-up cannot be adjusted to higher values, so it is impossible to study the variation of the observed effects under different pressure values. The sample holder is approximately at 20 cm from the exit slit of the monochromator, then the size of the light spot on the surface of the sample is about 4 mm wide and 8 mm high. Therefore no extra optics is necessary to focus the exciting photons on the sample. In order to have a reference of VUV intensity, a MgF_2 beam-splitter is used to pick up a small percentage of the exciting beam and to deviate it towards a solarblind PMT (Hamamatsu R1486) equipped with a housing in which a pinhole has been drilled in front of the photo-cathode. This PMT has been calibrated by Hamamatsu company and its spectral sensitivity is known. We have determined the spectral sensitivity of the other solarblind PMT used in these experiments by comparing the current intensity delivered by both PMTs in the same experimental conditions. A small difference was observed in the high energy range and was taken into

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