DETAILED SPECTROSCOPIC INVESTIGATION ON BINARY GAS MIXTURES AS A FILLING GAS FOR MERCURY-FREE FLUORESCENT LAMPS

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Abstract

Experimental investigations were performed on the fluorescence of phosphors when excited by discharges in binary rare gas mixtures as a possible candidate for mercury-free signs. Special tubular discharge lamps were built that contain a pumping port. The port permits the shelling, the filling and the evacuation of the discharge vessel as well as the spectroscopic diagnostic of the glow discharge in the VUV wavelength region. The spectroscopic results directly in the positive column of the discharge and through the glass with the phosphor coating indicated that the resonance lines are the principal agent in producing fluorescence. The illuminance results and those of the chromatic coordinates given by a luximeter complemented the spectroscopic ones.

1. Introduction

Already many years ago, several investigations were carried out in an endeavour to use pure inert gases or mixtures of them as a substitute for mercury in fluorescent signs [1,2]. For discharges in pure inert gases, the highest efficiency is attained with neon gas but the light is predominately the orange-red glow from neon. Neon is a competitor of mercury but only in pink fluorescent lamps. Nowadays, the studies of some binary rare gas mixtures showed that a significant fraction of the input power delivered to the plasma can be converted into VUV radiation. The lighter gas (buffer gas) is used to favour the operating conditions, the heavier one (active gas) is the active source of VUV photons. While high pressure discharge have already found application in the plasma display panel (PDP) technology [3,4], low pressure ones appear as a potential candidate for mercury-free signs.

Herein, we report experimental investigations on binary inert gas mixtures in a cylindrical axially homogenous positive column at low pressure. Special tubular discharge vessels were built that permit the spectroscopic diagnostics on the glow discharge not only in the visible but also in the VUV and UV wavelength region. The spectroscopic study of the positive column of the discharge and of the phosphor fluorescence indicated that the resonance lines are the principal agent in producing the phosphor fluorescence. These results were completed by those of the illuminance and the chromatic coordinates (X and Y) measured by a luximeter.

2. Experimental details

2.1. Experimental conditions

Figure 1 shows the set-up of this experiment. It consists of three principle devices. The discharge tubes with special design, the spectroscopic detection tools with data acquisition devices and a neon tube bombarder device. Every tube is equipped with a pair of hollow electrodes and a pumping port. Through this port, the tube is connected to the neon tube bombarder device, to the gas handling system and to the spectrometer. It permits the bombarding, the filling and the evacuation of the discharge vessel as well as the spectroscopic diagnostic of the glow discharge in the VUV wavelength region. The gas handling system enables us to fill the tube with a selected mixture of two high purity gases, with adjustable proportions using two gas flow controllers.
The mixture pressure can be varied from a few hundreds of mTorr to a few tens of Torr using a diaphragm valve connected to a vacuum pump. Due to the constant gas flow, the gas mixture is permanently renewed inside the tube and all the assemblies directly connected to it. This procedure allows us easily to vary in a large range the gas mixture pressure and the proportion of the gas components of this mixture. Otherwise, parametric study of gas mixtures would involve the use of tremendous number of sealed tubes.

The tube is connected to a vacuum ultraviolet spectrometer through a MgF$_2$ window. The spectral measurements are performed from 115 nm to 800 nm using two different gratings. The radiation is detected with either R 955 (160 - 900 nm) or solar blind R 1080 (115 - 320 nm) and R 1220 (115 - 320 nm) Hamamatsu photomultiplier tubes (PM). The signals are then collected with a transient analyzer (Tektronix TDS220) connected to a personal computer for data acquisition. The power supply consists of a 70mA, high voltage (3.5kV) AC transformer operating at 50 Hz. Electrical measurements have been performed using a high voltage probe (Tektronix P6015A) and a current probe (Tektronix TCP202).

2.2 Experimental results

2.2.1 Pure neon discharge

For pure rare gas discharge, the highest efficiency is attained with neon gas. Fonda [2] has estimated that about 30 percent of the energy supplied to the neon discharge is converted to the resonance radiation at 74 nm which permits the fluorescence of the phosphor. Figure 2 gives the phosphor excitation spectrum of a tube with an ordinary green phosphor coating and filled at few mbars with a pure neon gas. Neon discharge contributes such a large amount of the orange-red color to the light from the phosphor that the fluorescent colors are masked and become quite ineffective. In these conditions, the intensity at the maximum of the phosphor excitation spectrum is about 50 times less than the one of the neon line at 585,3nm. The illuminance and the chromatic coordinates (X and Y) were measured through the glass with the phosphor. The abscissa X and the ordinate Y compared to the CIE standard, show a yellowish orange phosphor which can change slightly by varying some discharge parameters. Hence, the fluorescence due to neon and the significant advance in phosphor technology, permit to build on lamps with new chromatic coordinates [5].
2.2.2 Neon-xenon discharge

The use of two rare gases, a buffer and an active gas, permits to expect the energy transfer processes. Actually, this type of transfer was demonstrated in rare gas mixtures a long time ago (see for example Gerdenken and al [6] in 1972). The energy transfer processes occur from the lighter rare gas towards the heavier one. In the neon-xenon mixtures, the lowest excited states of neon (16.6 eV) are situated above the ionization potential of xenon. The various radiative or collisional cascades must take into account the ionized state of Xe⁺. Nevertheless, this type of mixture remains easier to study as there is no overlap between the atomic emissions characteristic of each gas. As soon as the xenon concentration reaches a few percent, the emission is almost identical to that of pure xenon showing the efficiency of the energy transfer processes in populating the lowest atomic excited states of the xenon (^3P₁) and (^3P₂).

Thus, by adding some few percent of xenon to the tube with the neon discharge, the positive column turns from orange-red light to blue one, which corresponds essentially to the xenon transitions. Moreover, when the phosphor excitation is optimized, the plasma starts from a small spot at the cathode and goes very thinly along the positive column with a pale blue color. The green fluorescence appears uniformly bright and the color is quite pure. For more disadvantageous discharge conditions: for example, when the xenon proportion in the gas mixture is very low, the fluorescent light decreases, the spot and the plasma column are more diffuse. The plasma color turns progressively from pale blue to orange-red, the contribution from the neon increasing rapidly.

The figure 3 gives the intensity at the maximum of the phosphor excitation spectrum for a tube with a neon-xenon discharge as a function of the xenon proportion in the gas mixture at two pressures, 1 mbar and 5 mbar. The phosphor excitation at 1 mbar is about twice higher than the one at 5 mbar and the interval of suitable discharge conditions is extended in a quite large one. Thus, the phosphor excitation, the suitable xenon proportion and its extended interval are more reduced when the mixture pressure increases. The variation of the xenon partial pressure and the pressure mixture affect the efficiency of the energy transfer processes which populate the xenon resonant states. Spectroscopic diagnostics of the glow discharge in the VUV wavelength region confirmed the intense emission of the resonance line of xenon at 147 nm (^3P₁) which is mainly responsible for the phosphor fluorescence. The second xenon resonance radiation at 129.6 nm (^1P₁) is also recorded. For mixtures with low xenon concentration, the fluorescence contribution of the resonance line at 129.6 nm must not be underestimated [7]. Figure 4 gives the PM signal of the intense VUV emission at 147 nm as a function of the xenon concentration at the two pressures (1 mbar and 5 mbar). The evolution of the resonance line at 147 nm and the one of the phosphor excitation
(figure 3) are very similar. Consequently, the increase either in the xenon partial pressure or in the total pressure is unfavourable for populating excited states of xenon particularly, in this case, the \(^{1}\text{P}_1\) one.

![Figure 3: Evolution of the phosphor excitation of Ne-Xe discharge at two pressures.](image)

![Figure 4: Evolution of the xenon resonance line at 147 nm at two pressures.](image)

For a neon-xenon discharge with the same xenon proportion in the gas mixture (the same xenon partial pressure), figure 5 gives, at two pressures, the spectrum around the xenon resonance line at 147 nm. The resonance line intensity is greatly reduced by increasing the pressure. Moreover, at relatively high pressure mixture (12 mbar), figure 6 shows that an increase of the xenon proportion in the gas mixture greatly affects the intensity of the resonance line and also its distribution. The spectral line is self-absorbed. The line profile is asymmetric, the “blue” portion of the line profile is suppressed and the “red” portion is enhanced.

**2.2.3 Neon-Krypton discharge**

Almost the same type as the previous phenomena are also shown with the neon-krypton mixture. With suitable mixtures of krypton in neon, krypton reduces greatly the orange-red neon lines and
the discharge emission shows almost the krypton spectrum. The fluorescence appears uniformly bright and its spectrum includes yellow krypton lines. Doubtless, such lines modifies slightly the chromatic coordinates of the color fluorescence. Actually, for the suitable conditions, the chromatic coordinates show a yellowish-green fluorescence color ($X \sim 0.27$ et $Y \sim 0.64$). The phosphor fluorescence is reduced when the mixture pressure increases and the contribution from the neon increases rapidly with decreasing the krypton pressure. Moreover, the illuminance and the resultant color measured by a luxmeter are greatly affected by the pressure (figure 7 and 8). The color fluorescence changes progressively from yellowish-green to greenish-yellow by increasing the mixture pressure. The color fluorescence is also progressively modified by varying the krypton pressure. Such discharges permit to develop sources with a large choice of chromatic coordinates.

![Figure 7: Evolution of the illuminance of a Ne-Kr discharge](image)

![Figure 8: Evolution of the chromatic coordinates of a Ne-Kr discharge](image)

The phosphor exciting agent is the krypton resonance radiation at 123.6 nm and 116.5 nm. Thus, neon-krypton mixture shows also an efficiency of the energy transfer processes in populating the lowest atomic excited states of the krypton. Comparing to neon-xenon discharge, the kinetic processes in mixtures of krypton in neon induce similar variations as regard of both the heavier gas partial pressure and the total pressure. Nevertheless, figure 9 shows that the decreasing of the phosphor fluorescence occurred more rapidly in the case of neon-xenon discharge compared to the neon-krypton one.

![Figure 9: Evolution of the phosphor excitation of Ne-Kr discharge at two pressures](image)

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3. Conclusions
In binary rare gas mixtures, the resonance lines are the principal agent for fluorescing phosphors. In the case of neon-rare gas discharge, the active gas changes completely the positive column emission quenching the states responsible for the orange-red neon lines. The quenching is more or less efficient depending on the active gas. This might be a key function for developing signs with new chromatic coordinates. Work is in progress using new phosphors, for improving mercury-free signs efficiency.

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5. References