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Emission curves vs charging conditions in phosphorescent pigments embedded in sintered glass: Is there a reciprocity law?

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ABSTRACT

Applications of phosphorescent materials are derived from their light emission properties at short and long times since the end of stimulation. The enhancement of such properties affects its performance in safety signs systems. Light emission power is conditioned by the time of excitation and the illumination received by the phosphorescent material, so that the total incoming energy is the product of both. For a given spectral profile, there is at least one upper limit of storable energy, resulting in effects of saturation for high values of illumination and excitation times. This work examines the emission curves of phosphorescent pigments embedded in sintered glass, in experiments where the total incoming energy is kept constant for combinations of illumination and time, in order to analyze the existence and the degree of reciprocity between these pairs. In addition, using a simple model we simulate some of the results obtained experimentally.

1. Introduction

The term *reciprocity* refers to the dependence of some properties of photosensitive materials on the total energy received by means of radiation, regardless of the particular values taken by the irradiance, I, and the excitation time, t_{exc}, whose product is the incoming power per surface unit. In other words, there is a reciprocal relationship between illumination and time of excitation as alternative mechanisms to increase proportionally the amount of energy received by a given material. This concept was applied since the last century, and is known as the reciprocity law. Its failure, either for low or for high intensity, has been studied in film photography [1] and, more recently, in some materials like screen-film systems [2], polymeric materials [3], detectors [4], photoetching processes or CCD imaging [5]. Therefore, similar response is expected, in the absence of losses, by reducing the intensity or duration of excitation. If we define the exposure as $H=Et_{exc}$, where E is the illumination, a photometric magnitude that is proporcional to the irradiation for any given spectral profile, then the condition $H=constant$ defines all the reciprocal pairs [E, t_{exc}] whose product is H. Although invariance in the behaviour of the system is expected for the conditions specified by these pairs, it is also expected that in the extremes, i.e. t_{exc} very long with E very low and t_{exc} very short with E very high, some effects may appear that make the material behave differently, and the reciprocity fails. The fulfillment or failure of such reciprocity becomes an empirical source of information about the mechanisms going on in the system.

In the last two decades, there has been a growing interest in phosphorescent materials due to the development of new pigments [6], or *phosphors*, as they are often named. The improved performance of these phosphors has produced an impact not only in the old applications but also in the development of new ones like night-vision or solar energy [7]. Current applications include safety signals for inner and outer spaces, emergency exits and signaling for vehicles and pedestrians [8,9] and the emission parameters that appear in these standards are continuously updating – increasing – their requirements. Although the basics of the phosphorecent processes are known since a long time [10] and their decay behavior has been empirically described [11], the complexity of the internal processes that mediate between the absorption and emission in these last-generation phosphors makes it difficult to know in detail which are the storing mechanisms [12,13]. In this context, an interesting approach is the analysis of the emission decay curves associated to experiments in which the exposure is kept constant, i.e. the reciprocity analysis. In this study, we analyze the influence that the charging process has on the emitting curves, in the hope that it may give some insight into the physics involved. In order to keep a constant exposure, we must control independently the variables t_{exc} and E.

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For the first, we need an appropiate shutter system, while for the second it is possible to use apertures or filters, but a practical option is to use the inverse square law dependence of E with the source–sample distance.

In this work we will focus on highly efficient phosphors in the form of pigment grains that are embedded in a non-absorbent strong-scattering matrix formed by sintered glass. This material allows good control of the distribution and concentration of pigment. It is stable, does not affect the spectrum and allows an easy handling of the samples.

The article is organized as follows. Firstly, we describe the process of preparation of the samples of the photoluminescent vitreous tile used in the study. Then, we describe the elements of the experimental setup used for the measurement of the emission properties and outlining the sequence of conditions of exposure in the study. Finally, we show the results divided into two parts: (i) the emission values, the characteristic power-law that follows the phosphorescence, in conditions of constant exposure and (ii) the variation in the form of such emission, which has, at least, two distinct behaviour zones: short emission times (a few min) and long emission times (greater than or equal to 20 min) as it has been published [14], in such conditions of exposure.

2. Sample description

The samples used in this study have been developed using the technical means provided by the company Hispano Italiana de Revestimientos Vitreos, HISBALIT, and correspond to a commercial product, a mosaic belonging to the StarLight series, with a square format of $l=4$ cm side [15]. The main raw material used in the manufacture of the mosaic is milled ground glass, in which a long-life phosphorescent pigment is added in an amount of 7% in weight. This pigment is based on an aluminate of alkaline earth metal dopped with rare earths ions [16,17], and is a commercial phosphor provided by the supplier LANXI MINHUI Photoluminescent, Co., with trade name MHG-4B. It has been selected by its spectral properties of emission, excitation, a proper particle size to be mixed with powder glass and by its good capacity to support the manufacturing process.

The manufacturing process consists of several stages. After grinding the glass, it is mixed in loads of 80 kg with phosphorescent pigment, while water is added in order to get good molded samples. Using mechanical presses, mosaics are molded to the desired size and shape. Finally, the glass powder conglomerates are sintered in continuous electric furnaces with a heating curve pattern of 12 min that reaches a maximum temperature of 850 °C.

3. Experiment

An outline of the experimental device is shown in Fig. 1. Both the experimental setup for the excitation of the pieces of photoluminescent glass (Fig. 1a) and that corresponding to the subsequent measurement of phosphorescent emission (Fig. 1b) are designed according to the geometries and devices recommended by the existing international standards for the measurement and classification of photoluminescent safety way guidance systems. The advantage of using this approach is that we make sure that the spectral profile as well as the excitation time and the distances involved in the experiment are within a range for the adequate excitation of pigments ensuring the saturation of the illuminated samples.

The elements of the experimental setup are:

- Illumination:
  For the illumination of the samples, we used a HAMAMATSU Super-Quiet Xenon short-arc lamp of 150 W, with high stability and long life. This lamp produces an efficient light emission with a continuous and stable spectral distribution in the range of visible, near UV and IR (see Fig. 2). The output window of the lamp housing has a diameter $\emptyset_S=20$ mm.
  The sample is placed in a holder to the same height as that of the source of illumination and at a distance from the lamp given by its position on an optical bench. The illumination received by the surface of the sample is homogeneous within 1%, according to the general photometry criterion, provided that the ratios $\emptyset_S/r$ and l/r are kept under 10^{-1}. This must be taken into account if the illumination is to be governed by the position of the sample on the bench (using the distance square -law). The illumination for each position of the sample is monitored by a photometer MINOLTA T-10M. The exposure time is controlled by a thick metal plate shutter placed very close to the lamp in order to block the illumination in the sample.

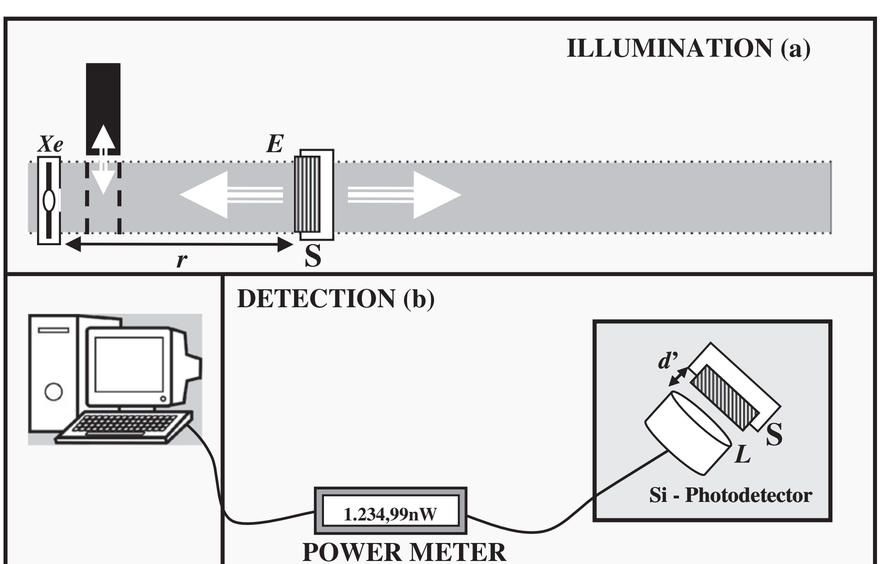

Fig. 1. Outline of the experimental device for illumination (a) and detection (b) processes.