

# Quenching Problems in Inorganic Luminescent Materials

U. Vater,<sup>1</sup> G. Künzler,<sup>1</sup> and W. Tews<sup>1</sup>

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Quenching problems were investigated on inorganic luminescent materials for fluorescent lamps. It could be shown that the decrease of luminescence intensity under the influence of short-wave UV radiation is not only a function of the irradiation time but also depends strongly on the activator concentration and a mechanical treatment. The photochemical luminescence quenching represented by the intensity loss as a function of the irradiation time can be expressed as a sum of three exponential terms, constants and exponents of which contain the concentration of virgin and UV induced lattice defects in both the bulk and the surface. To explain the complex quenching process the theory of radiationless energy transport was used.

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**KEY WORDS:** Quenching; inorganic luminescent materials; luminophors.

## INTRODUCTION

In the application of inorganic luminescent materials such as oxides or oxygen-dominated compounds, doped by so-called activator ions, quenching problems play an important role. In particular, the use of luminescent materials for fluorescent lamps is restricted by the luminescence quenching under the influence of short-wave ultraviolet radiation, with the luminescence intensity continuously decreasing as a function of the irradiation time [1,2]. For a given luminophor the whole complex photochemical quenching process strongly depends on the external conditions such as irradiation intensity, temperature, and pressure as well as on the nature of the surrounding gas atmosphere [1,2]. Furthermore, on a large scale it is determined by the activator concentration [3] and the particle size [4] of the luminophors to be investigated. Examples of a few quite different luminescent materials, some experimental results, and their brief interpretation are given here.

<sup>1</sup> Department of Chemistry, E.-M.-Arndt-University of Greifswald, Soldtmannstraße 23, D-17487 Greifswald, Germany.

## EXPERIMENTAL

The experimental device for photochemical quenching is shown in Fig. 1. The powdered samples are pressed into small copper holders positioned in a glass tube with a quartz lamp HNS 10 in the axis. The tube can be evacuated or filled with gases by means of a common pumping device as described in detail previously [1]. For measuring luminescent-optical properties the samples were removed from the tube and then put into spectrometers for investigating changes in emission or reflectance [1-4]. The phosphor sample material was prepared by solid-state reactions at high temperatures [1,3] or commercial products were used. The milling process for decreasing the particle size was carried out in a drum mill with distilled water as medium.

## RESULTS

On the left in Fig. 2 typical curves of the photochemical quenching of the emission intensity are shown for five phosphors. The emission intensity decreases continuously, with the rate of the reaction becoming lower with increasing irradiation time. Simultaneously the

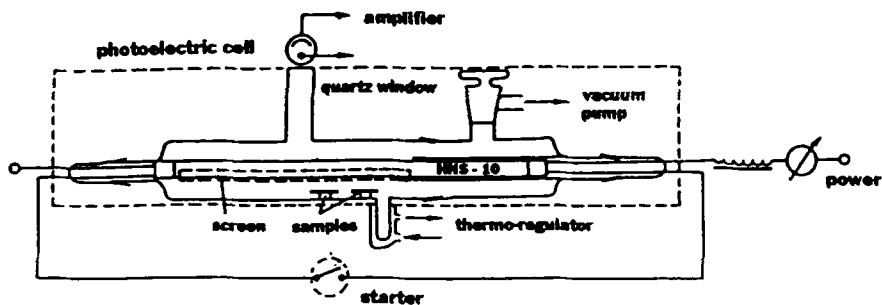


Fig. 1. Device for the aging with Hg low-pressure radiation. HNS-10, Hg-low-pressure lamp with quartz bulb;  $T_{\text{sample}} = -100^{\circ}\text{C}$  to  $+200^{\circ}\text{C}$ ;  $E_{185} = 0.86 \text{ mW}\cdot\text{cm}^{-2}$ ;  $I_{254}/I_{185} = 5.25$ ;  $p_{\text{vacuum}} = 1.3\cdot 10^{-3} \text{ Pa}$ ; discharge current = 250 mA).

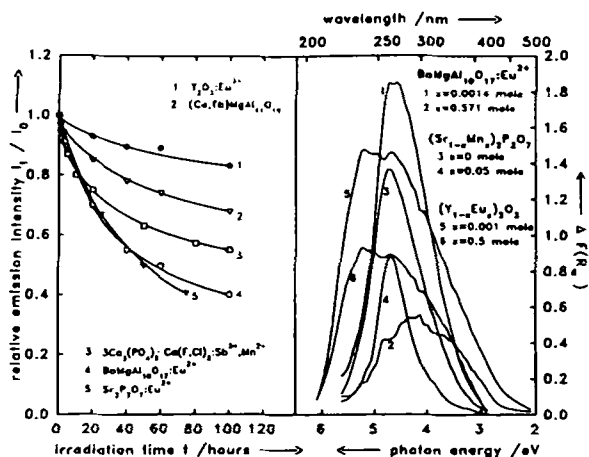


Fig. 2.  $I(t)$  curves (emission) and changes in the remission function  $\Delta F(R_z)$  after UV irradiation in vacuum for some phosphors.  $\Delta F(R_z) = F(R_z \text{ after irr.}) - F(R_z \text{ before irr.})$ .

samples become yellow-brownish discolored as demonstrated on the right in Fig. 2. The changes in the remission functions after and before irradiation result in broad bands with points of gravity in the UV region at wavelengths between about 240 and 290 nm and shoulders reaching widely into the visible spectral region, overlapping the phosphor emission.

These processes are influenced by the activator concentration as can be seen in Figs. 2 and 3 as well as Fig. 4, the latter showing typical curves of the concentration quenching of original and irradiated samples.

By milling the phosphor samples both the emission intensity and the UV stability are decreased (Figs. 5 and 6). Especially in the first 10 h of irradiation the depreciation proceeds faster if the luminophor samples have been milled. Moreover, Fig. 6 shows, for two phos-

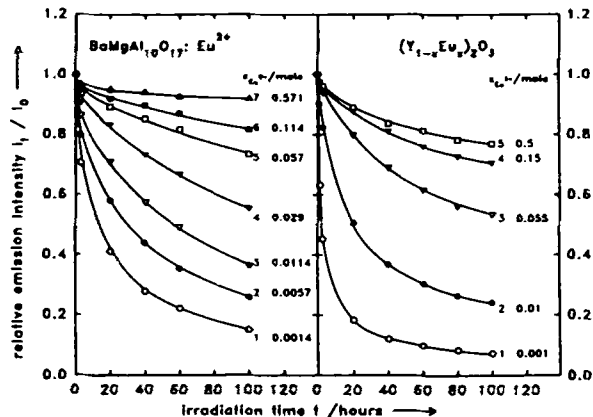


Fig. 3. UV-induced depreciation of  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$  and  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  as a function of activator concentration  $I_t$  and  $I_0$ , relative intensities after and before UV irradiation in vacuum.

phors, that the emission intensity is strongly dependent on the specific surface.

## DISCUSSION

All depreciation curves shown can be expressed by a sum of two or three exponential terms, with the constants and exponents depending on the activator concentration and the number of original defects occurring in the phosphor matrix [2,3]. The energy of the damaging radiation must be high enough to create quasi-free conduction electrons or electron-hole pairs which become trapped by defects, e.g., oxygen vacancies in the bulk and at the surface under the formation of deep color centers.

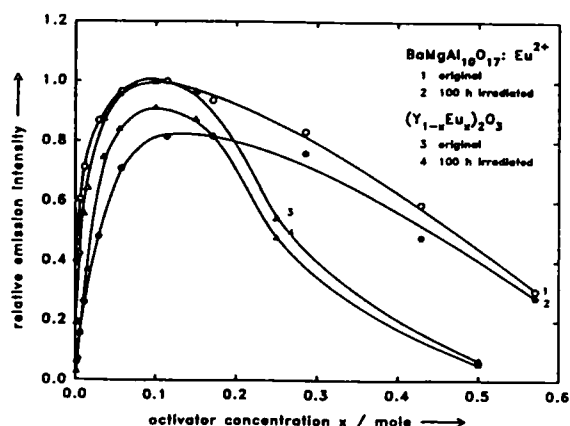


Fig. 4. The relative intensity of the emission maximum of BaMg-Al<sub>10</sub>O<sub>17</sub>:Eu<sup>2+</sup> and Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>, dependent on the activator concentration before and after UV irradiation.

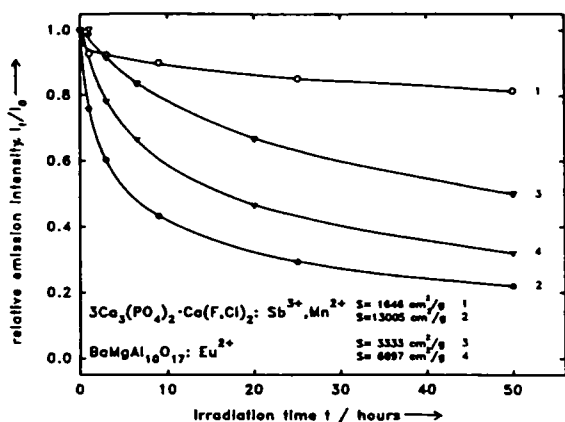


Fig. 5. UV-induced depreciation of lamp phosphor samples with different specific surfaces S. I<sub>t</sub> and I<sub>0</sub>, relative emission intensities after and before t hours of UV irradiation in vacuum.

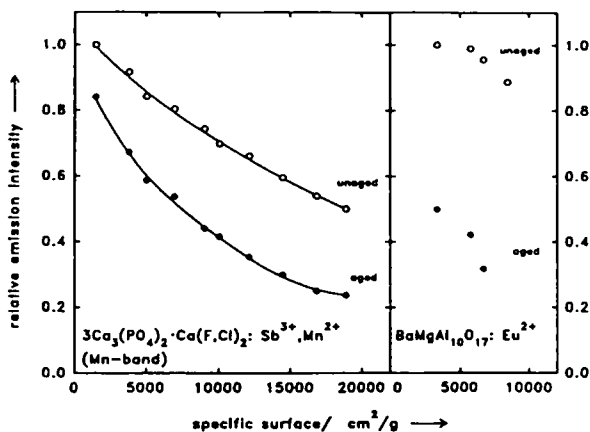


Fig. 6. The relative emission intensity of lamp phosphor samples before and after aging under UV irradiation in vacuum, respectively, dependent on the specific surface.

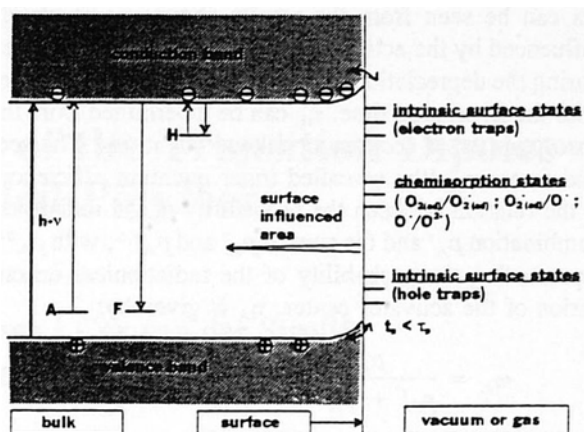


Fig. 7. Schematic representation of depreciation processes in the bulk and at the surface. A, activator; F, color center; H, electron trap; t<sub>p</sub>, transit time of holes to reach the surface; τ<sub>p</sub>, recombination lifetime of holes.

The very complex reaction should proceed over oxygen surface states as shown schematically in Fig. 7. Thus an increase in the surface-bulk relation by the milling process leads to a higher depreciation (Figs. 5 and 6). The negative effect of the color centers, produced by original and induced defects, on the phosphor efficiency is influenced by the activator concentration as well as by the particle size and can be explained in the following way: The quantum efficiency, given by the relation of the number of photons emitted to the number of photons absorbed, can be expressed as the product of some factors:

$$\eta_{\text{overall}} = \frac{N_{\text{emitted}}}{N_{\text{absorbed}}} = \eta_E \cdot \eta_A \cdot \eta_T \cdot \eta_R \quad (1)$$

where

$$\eta_E = \text{the efficiency of the absorption of exciting radiation by activator centers} \\ = \frac{A_A}{A_A + \Sigma A_D} \quad (2)$$

where A is the absorption cross section of activators and defects (ΣA<sub>D</sub> = A<sub>D,O</sub> + A<sub>D,ind.</sub>),

A<sub>D,O</sub> = original phosphor defects containing, e.g., vacancies, interstitials, substitutions, or foreign ions

A<sub>D,ind.</sub> = UV-induced absorbing defects as color centers or chemically changed ions

As can be seen from the results above,  $\eta_E$  is clearly influenced by the activator concentration and is changed during the depreciation process. In general,  $\eta_E$  decreases with the irradiation time.  $\eta_E$  can be determined from the absorption cross sections or related quantities. The second factor  $\eta_A$  (the so-called inner quantum efficiency) is the relation between the probability of the radiant recombination  $p_A^r$  and the sum of  $p_A^r$  and  $p_A^{n.r.}$ , with  $p_A^{n.r.}$  representing the probability of the radiationless deactivation of the activator center.  $\eta_A$  is given by:

$$\eta_A = \frac{p_A^r}{p_A^r + p_A^{n.r.}} = \frac{1/\tau_A^r}{1/\tau_A^r + 1/\tau_A^{n.r.}} \quad (3)$$

That means that  $\eta_A$  can be found by decay measurements. The next factor,  $\eta_T$ , describes the energy transfer from the activator to defects and can be expressed by

$$\eta_T = \frac{p_A^r}{p_A^r + p_{T,D,O} + p_{T,ind.}} \quad (4)$$

A valuation can be made from considerations of the radiationless resonance energy transfer from sensibilizers S to activators A according to Blasse and Bril [5]:

$$P_{SA} (DD) = \frac{3\hbar^4 c^4}{4\pi K^2} \cdot \frac{Q_A}{\tau_s \cdot r_{SA}^6} \cdot \int f_S f_A \frac{dE}{E^4} \quad (5)$$

In case of exchange interaction the equation

$$P_{SA} = \frac{2\pi}{\hbar} \cdot z^2 \int f_S f_A dE \\ = \frac{2\pi}{\hbar} \cdot K' \exp \left[ -\frac{2r_{SA}}{L} \right] \cdot \int f_S f_A dE \quad (6)$$

is valid. In the above expression  $\hbar = h/2\pi$ ,  $h$  is the Planck constant,  $c$  is the velocity of light,  $K$  is the dielectric constant of the lattice matrix,  $Q_A$  is the integrated absorption of A,  $\tau_s$  is the decay time of S in the absence of A,  $r_{SA}$  is the average distances between S and A;  $\int f_S f_A dE$  is the overlap integral,  $Z$  is the exchange integral,  $L$  is the effective Bohr radius, and  $K$  is a constant.

Because the energy transfer processes depend largely on the concentrations of activators and defects in the bulk as well as at the surface,  $\eta_T$  is strongly dependent on the concentration. On the other hand,  $\eta_T$  stands for a further deactivation process of excited activators and the decay times measured become shorter [3]. The last factor  $\eta_R$  depends on the number of absorbing defects in the emission range and can be estimated from measurements of the diffuse reflectance according to Kortüm [6]. In the case of the above phosphors  $\eta_R$  is more influenced in the blue than in the red region of the spectrum.

## REFERENCES

1. W. Tews (1983) *Z. Phys. Chem. Leipzig* **264**, 123.
2. W. Tews, W. Wetterau, G. Schmidt, and G. Herzog (1987) *Z. Phys. Chem. Leipzig* **268**, 81.
3. G. Künzler, P. Becker, and W. Tews (1992) *Phys. Stat. Solidi (a)* **130**, K 273.
4. U. Vater, W. Tews, and U. Sasum (1992) *Phys. Stat. Solidi (a)* **130**, K 221.
5. G. Blasse and A. Bril (1970/1971) *Philips Techn. Rdsch.* **31**(10), 320.
6. G. Kortüm (1969) *Reflexionsspektroskopie*, Springer-Verlag, Berlin, Heidelberg.