Relationships between the Photolysis and Crystallinity of Zinc Sulfide Phosphors

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Introduction

Zinc sulfide phosphors are known to be photodecomposed and blackened under the irradiation of strong ultraviolet rays, a phenomenon usually called "blackening". The blackness is attributed to the metallic zinc formed as a result of the photolysis and deposited in the colloidal form. Previously one of the present authors, Shionoya[1], studied this phenomenon, extensively and discussed conclusively the mechanism of the process by which the blackening is caused. Here it was investigated how the blackening characteristics are influenced by the variation of the crystallinity, i. e. the degree of crystal growth, of zinc sulfide.

The results of Shionoya's previous work are briefly summarized here. (1) The spectral region efficient for causing the blackening coincides with the fundamental absorption region of zinc sulfide. (2) The adsorbed water is necessary for the occurrence of the blackening, the amount of which is less than the order of 0.0x wt.%. (3) Under a constant humidity and temperature the blackening proceeds according to the following equation after the lapse of the induction period of several or several ten minutes,

$$D^3=kt+l, \tag{1}$$

where D is the blackening density, k the rate constant, t the time, and l a constant. The reciprocal of the induction period is proportional to the humidity. (4) It is suggested that the mechanism of the blackening is as follows. The adsorbed water reacts photochemically on the crystal surface and the nucleus of zinc is formed. This nucleus trapps the electron in the conduction band, attracts the interstitial zinc ion from within the host crystal, and grows to the colloidal zinc. Eq. (1) corresponds to this stage of the blackening reaction, and is explained by an assumption that the migration of the interstitial zinc ion is the rate-determining step for this stage.

Experimental

Sample.—Copper-activated zinc sulfide phosphors having different crystallinities, i. e. degrees of crystal growth, were prepared by changing the time of the firing. They were fired with the flux of 4 wt.% NaCl at 1100°C for 5-90 min. Copper content was 0.003 wt.%.

The crystallinity seems to be indicated by the particle size. By means of Blaine's air permeability method[2] the specific surface area of these samples was measured, and the mean volume surface diameter, d_{vs}, was calculated by the following equation, assuming that all the particles are spheres,

$$d_{vs}=\sum_i n_i d_i^3/\sum_i n_i d_i^2=6/\rho S_w, \tag{2}$$

where ρ is the density of the particle and S_w the specific surface area per unit mass. The values of the time of the firing and d_{vs}'s are given in Table I.

TABLE I

THE TIME OF THE FIRING AND THE MEAN VOLUME SURFACE DIAMETER, d_{vs}, OF THE SAMPLES

No.	1	2	3	4
Time of the firing (min.)	5	20	30	90
d_{vs} (μ)	3.0	4.4	6.3	8.2

Measurement of the Blackening.—(1) Method.—A high pressure mercury discharge lamp made of quartz and having the capacity of 650W. was used to blacken the phosphors. The blackening density, D, was measured by means of Yamabe's type photographic densitometer using the diffuse reflected light. The dencity, D, is defined by

$$D=\log_{10}I_0/I, \tag{3}$$

where I_0 and I are the light intensities thrown on and reflected back from the sample, respectively.

The rate of the blackening was measured under several humidities and at 20°C in the way similar to that mentioned in the previous

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[1] S. Shionoya, *J. Chem. Soc. Japan (Ind. Chem. Sect.)*, **52**, 79 (1949) ; **53**. 55 (1950). *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **71**, 461, 584 (1950). *Bull. Fac. Eng., Yokohama Natl. Univ.*, **5**, 129 (1956).

[2] R. L. Blaine, *A. S. T. M. Bull.*, No. 123, 5 (1948).

paper[1]. The samples were washed thoroughly by distilled water so as to remove completely the chlorides of sodium and zinc contained in them. Zinc chloride formed by the reaction of flux on zinc sulfide influences the blackening characteristics because of its strong tendency to absorb water, so that the removal of this is needed previous to the measurement of the blackening. Then the samples were packed in small containers after being dried by heating, and placed in closed quartz tubes in which the humidity was kept constant by means of sulfuric acid of the appropriate concentration. These tubes were sunk into the circulating water to keep the temperature in them constant, and ultraviolet light from the mercury lamp set above the water surface was thrown onto the samples through the water. Thus the curves of the blackening density vs. the time of irradiation were measured under the pressure of water vapor of 6.2–13.2 mmHg.

(2) **Results.**—Results under 7.2 and 6.2 mmHg are shown in Fig. 1 and 2 as examples. Under 6.7–13.2 mmHg all the samples were remarkably blackened, whereas under 6.2 mmHg the samples, except in the case of No. 2, could hardly be blackened at all.

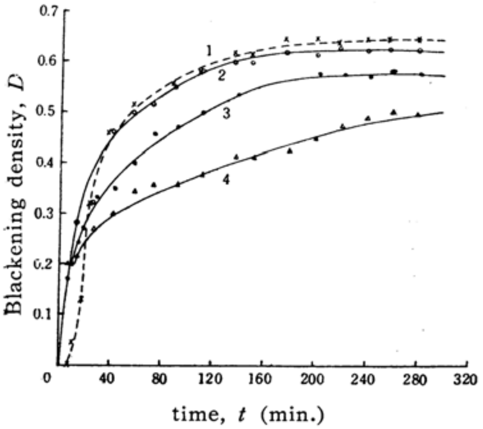

Fig. 1. Blackening curves under the pressure of water vapor of 7.2 mmHg for four samples cited in Table I.

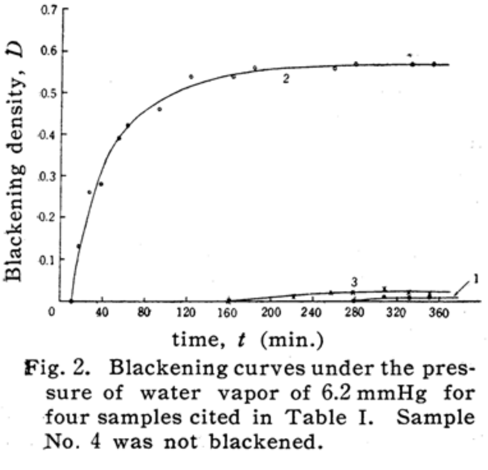

Fig. 2. Blackening curves under the pressure of water vapor of 6.2 mmHg for four samples cited in Table I. Sample No. 4 was not blackened.

The build-up parts of the blackening curves satisfy Eq. (1) and then the rate constants are calculable. After the long irradiation the blackening curves became rather flat. This effect is attributed to the simultaneous occurrence of the bleaching of blackened samples. The bleaching takes place even when the blackening is proceeding, and its rate increases with the increase of blackening density as mentioned in the previous papers[1]. Therefore, after the long irradiation, the rates of the blackening and bleaching become equal to each other, and a state of equilibrium state is reached. In Fig. 3 the rate constants for the blackening under several humidities are plotted against the particle sizes. The rate constant decreases with the growth of the particle size.

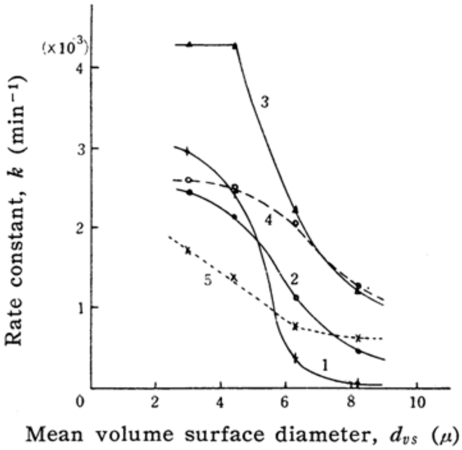

Fig. 3. Rate constants for the blackening against the particle sizes, the mean volume surface diameters, for four samples cited in Table I. The pressures of water vapor are (1) 6.7, (2) 7.2 (3) 8.1, (4) 10.0 and (5) 13.2 mmHg.

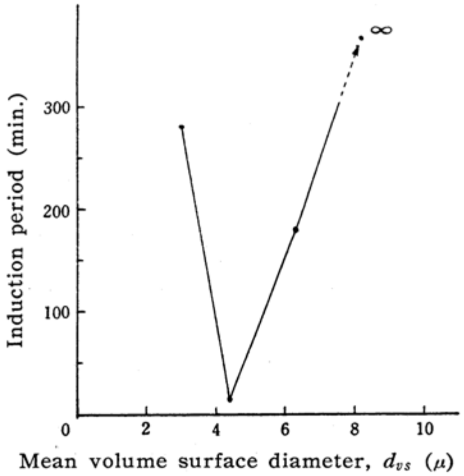

Fig. 4. Induction periods under the pressure of water vapor of 6.2 mmHg the against particle sizes, the mean volume surface diameters, for four samples cited in Table I.

Under low humidities long induction periods are observed in the beginning of the blackening reaction. In Fig. 4 the induction periods under 6.2 mmHg are plotted against the particle sizes. The induction period shows a minimum value at sample No. 2 with the diameter of 4.4 μ.

Luminescence and Blackening.—These samples emit a yellow green luminescence due to the copper activator. The relative brightness of the copper luminescence under the excitation by a high pressure mercury discharge lamp is plotted against the particle size in Fig. 5. Sample No. 2 which shows the minimum induction period has the maximum brightness.

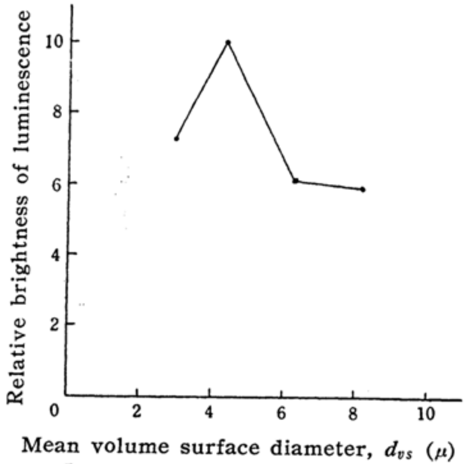

Fig. 5. Relative brightnesses of luminescence against the particle sizes, the mean volume surface diameters, for four samples cited in Table I.

Discussion

Zinc sulfide is made luminescent by the firing, during which the particle size of crystal grows owing to the sintering of small particles, and the activating impurity is incorporated by the diffusion. The result, namely, that the luminescent brightness of sample No. 1 with the smallest diameter is lower than that of sample No. 2 may be attributed to the incompleteness not only of the activator incorporation but of the crystal growth. The lowering of the brightness in the samples with larger diameters seems to be predominantly due to the oxidation of the samples caused by the over-firing.

Comparing Fig. 4 with Fig. 5, it is seen that the sample with the minimum induction period shows the maximum luminescent brightness. Since earlier days it has been known that zinc sulfide phosphors with bright luminescences are apt to be blackened. Recently Gobrecht and Kunz³⁾ studied the relationship between the luminescent brightness and blackening, and found that the blackening is nearly proportional to the brightness. However, this is not exactly true according to the present results. As seen from Figs. 3, 4 and 5, the reciprocal of the induction period, i. e. the reaction rate during the induction period, is nearly proportional to the brightness, but the rate constant for the blackening is not. Therefore, as seen by comparing Fig. 1 with Fig. 5 the blackening density is not always proportional to the luminescent brightness after long irradiation. The relationship between the luminescence and blackening should be discussed using the induction period.

This relationship is explained as follows, based on the mechanism of the blackening presented in the previous papers¹⁾. It was found that the reciprocal of the induction period is propotional to the amount of adsorbed water. From this result it was suggested that the adsorbed water reacts on the sulfur atom formed momentarily as a result of the photoabsorption and consequently it disappears from the crystal. This is the starting reaction of blackening and determines the reaction rate during the induction period. Therefore, it is said that the rate of this surface photochemical reaction is proportional to the luminescent brightness. This photochemical reaction would be accelerated by the condition that the conduction electron produced by the photoabsorption can move freely over the wide range through the whole crystal. As understood from the fact previously found that the blackening occurs in the spectral region of the fundamental absorption of zinc sulfide, but does not in the region of the absorption of activating impurities, such as copper, the existence of activating impurities which form the luminescent center does not contribute essentially to the occurrence of the blackening. In other words, the blackening and luminescence do not essentially correlate to each other. However, the condition of free moving of the photoelectron would also intensify the luminescence, especially in the case of the excitation by host crystal absorption. Then this condition would be necessary for both the luminescence and blackening, and this fact seems to be the reason for the fact that phosphors with bright luminescences are apt to be blackened.

The result that sample No. 1 has a long induction period is attributed to the in-

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3) H. Gobrecht and W. Kunz, *Z. Phys.* **136**, 21 (1953).

sufficiency of the above condition. In this sample, a photoelectron will not be able to move through the whole crystal as freely as in the other samples because of the incompleteness of the crystal growth. Sample No. 3 and 4 have long induction periods, although it appears that they have more complete lattices than sample No. 2. Then the circumstances would be different in these samples. Surface oxidation caused by the over-firing would prevent the occurrence of the surface photochemical reaction, so shat this would explain the reason for the long induction periods of these samples.

Furthermore, the variation of the water-adsorbing power with the particle size would also have influence on the induction period. It appears reasonable that the water-adsorbing power decreases with the growth of the particle size, because the crystal surface becomes flat and perfect as the crystal grows larger. Then the induction period would become longer with the growth of the particle size. This suggestion may be responsible for the results shown in the light half part of Fig. 4.

The decrease of the rate constant for the blackening with the growth of the particle size is also explained. It was inferred that the migration of the interstitial zinc ion determines this reaction rate, and further that the migration occurs, not through the perfect lattice, but along the internal imperfections in the crystal, such as internal surface, grain boundaries and dislocations. As the particle size grows larger the phosphor crystal would approach the perfect one, and the number of the internal imperfections would be decreased. This would make it difficult for the migration of the zinc ion to occur, and thus would cause the decrease of the rate constant.

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