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Effect of Various Additives on Color Center Formation and Brightness Depreciation of Calcium Halophosphate Phosphors

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Color center formation and brightness depreciation by 185 nm radiation were studied in calcium halophosphates containing various additives. Partial bleaching experiments show that the depreciation of plaque brightness is due to the absorption of 254 nm radiation by color centers, the reabsorption of luminescence by color centers being unimportant. In unactivated Ca halophosphates, the stronger the 185 nm absorption of additives, the weaker the color center formation. In Sb- and Mn-activated Ca halophosphates, however, no clear relation is found between the 185 nm absorption of additives and the brightness depreciation. The effect of cesium on improving lamp performance is described.

A great deal of information has been accumulated on the color centers of calcium halophosphate.[1–17] In fluorescent lamps, color centers are formed in halophosphate phosphors by exposure to 185 nm Hg radiation. It has been established that the decrease of lumen output in the first several minutes of lamp operation is closely related to the formation of color centers.[6,8] These centers are assumed to absorb a part of 254 nm exciting radiation and/or emitted luminescence energy in the visible region. It would be of great practical meaning to suppress, if not to prevent, the formation of color centers in halophosphate phosphors.

Aia and Poss[18] found that the initial light output of a fluorescent lamp is increased when a few percent of Cd is incorporated in halophosphate phosphors. Apple[6] explained the effect of Cd as follows. By introducing Cd, a strong absorption band appears in the wavelength region shorter than 200 nm in Ca halophosphate, which, in its pure state, is transparent down to 150 nm. In this manner, Cd provides a new process by which a considerable part of the deleterious 185 nm radiation is absorbed and dissipated without creating color centers. The major part of color centers is created in the first several minutes of lamp operation. It is, therefore, understandable why the "initial" lamp efficiency, which is usually measured after several tens of minutes of stabilization, appears to be increased.

If one follows Apple's explanation, other elements which would equal or surpass Cd in improving lamp efficiency might be found by examining whether the elements in question fulfill the following two conditions.

(I) In order to suppress the formation of color centers, such elements that give rise to strong absorption in the 185 nm region in the halophosphate matrix would be effective.

(II) The elements mentioned above should have little or no absorption at 254 nm and in the visible region, so that they absorb neither 254 nm exciting radiation nor the emitted fluorescence.

In this work, diffuse reflection spectra of Ca halophosphates with various metal additives were measured between 180 and 650 nm. Then it was checked whether any additive exists which satisfies the above conditions, and whether the element selected in this manner really brings about the expected decrease of depreciation.

Experimental

Materials. Samples prepared were: (1) Sb- and Mn-activated halophosphate $Ca_{9.5}Sb_{0.1}Mn_{0.2}(PO_4)_6(F_{0.9}Cl_{0.1})_2$, which has a composition close to that of commercial 4200 K phosphor (hereafter referred to as "Standard"), (2) unactivated halophosphate $Ca_{9.8}(PO_4)_6(F_{0.9}Cl_{0.1})_2$ ("Matrix"), (3) unactivated halophosphates with additives $Ca_{9.7}M_{0.1}(PO_4)_6(F_{0.9}Cl_{0.1})_2$ where M represents metal additives ("Series A" samples), and (4) $Ca_{9.4}M_{0.1}Sb_{0.1}Mn_{0.2}(PO_4)_6(F_{0.9}Cl_{0.1})_2$ ("Series B" samples). The raw materials ($CaHPO_4$, $CaCO_3$, CaF_2, $CaCl_2$, Sb_2O_3, $MnCO_3$ and a suitable compound of the desired metal M) were dry-mixed, ignited at 1150 °C for 30 min in air, ground thoroughly and ignited again under the same conditions.

Formation and Bleaching of Color Centers. Color centers were formed by 185 nm radiation from a 10 W, low pressure mercury lamp with a quartz envelope. Phosphor plaques were placed about 1 cm below the lamp. All the irradiation experiments were carried out in a vacuum. In order to bleach the color centers, samples were irradiated with a germicidal lamp or a 500 W Xenon arc lamp coupled with appropriate filters.

Measurements. Reflection spectra were measured with a Jarrel-Ash vacuum monochromator of Seya-Namioka type (model 78—660) in vacuum ultraviolet, and with a Perkin-Elmer monochromator (model E1) in the UV and visible regions.

Brightness of phosphor plaques was obtained by integrating the emission spectra. For this purpose, a ZV-1 spectroradiometer[19] equipped with a Perkin-Elmer printing integrator was used. The 254 nm exciting radiation was made as weak as possible to prevent the bleaching of color centers during the course of brightness measurements. It was confirmed that the emission spectra of investigated samples change little with the 185 nm irradiation.

Results and Discussion

Correlation between Plaque Brightness and 254 nm Absorption by Additives. Wachtel investigated thoroughly the relation between the concentration of various impurities and plaque brightness of a 3000 K Ca halophosphate phosphor.[20] In order to examine the above-mentioned condition II more quantitatively, an attempt was made to correlate the plaque brightness of Series B phosphors with the 254 nm absorption due to additives.

In the calculations described below, the following assumptions are made:

(1) Additives absorb the exciting 254 nm light and dissipate it nonradiatively.

(2) They do not sensitize nor quench the luminescence of the activators.

(3) They do not absorb the visible emission.

The plaque brightness of Series B samples, I, is given by

$$I = cE_e(1-R_B(\lambda_e))\frac{k_{ac}(\lambda_e)}{k_{ac}(\lambda_e)+k_m(\lambda_e)+k_{ad}(\lambda_e)}, \quad (1)$$

where c is a constant, E_e the energy of 254 nm exciting radiation and $R_B(\lambda_e)$ the diffuse reflectance at 254 nm, while $k_{ac}(\lambda_e)$, $k_m(\lambda_e)$ and $k_{ad}(\lambda_e)$ are the 254nm absorption coefficients of activators, pure halophosphate matrix, and metal additives, respectively.

The plaque brightness of Standard, I_0, is given by

$$I_0 = cE_e(1-R_0(\lambda_e))\frac{k_{ac}(\lambda_e)}{k_{ac}(\lambda_e)+k_m(\lambda_e)}, \quad (2)$$

where $R_0(\lambda_e)$ is the diffuse reflectance of Standard at 254 nm.

The absorption coefficients are correlated with diffuse reflectance by the Kubelka-Munk formula[21]

$$\frac{k}{s} = \frac{(1-R)^2}{2R}, \quad (3)$$

where s is scattering coefficient. The ratio k/s is called remission function. It is assumed that s is constant for all the samples. The ratio $(1-R_B(\lambda_e))/(1-R_0(\lambda_e))$ is close to unity in the presence of strong absorption of activators. Thus, the relative plaque brightness of Series B phosphors compared to Standard, I/I_0, is given by

$$\begin{aligned}\frac{I}{I_0} &\fallingdotseq \frac{k_{ac}(\lambda_e)+k_m(\lambda_e)}{k_{ac}(\lambda_e)+k_m(\lambda_e)+k_{ad}(\lambda_e)} \\ &= \frac{(1-R_0(\lambda_e))^2/2R_0(\lambda_e)}{\begin{aligned}\{(1-R_0(\lambda_e))^2/2R_0(\lambda_e)+(1-R_A(\lambda_e))^2/2R_A(\lambda_e) \\ -(1-R_m(\lambda_e))^2/2R_m(\lambda_e)\}\end{aligned}} \quad (4)\end{aligned}$$

where $R_A(\lambda_e)$ and $R_m(\lambda_e)$ are diffuse reflectance of Series A samples and Matrix at 254 nm, respectively.

Figure 1 shows diffuse reflection spectra of Matrix, Standard and selected Series A samples. The $R_A(\lambda_e)$ values of all of Series A samples and the I/I_0 values of the corresponding Series B phosphors are given in Table 1. The same data are plotted also in Fig. 2. Using the observed values of $R_0(\lambda_e)=0.228$ and $R_m(\lambda_e)=0.865$, the dependence of I/I_0 on $R_A(\lambda_e)$ was calculated by Eq. (4) (solid line curve, Fig. 2).

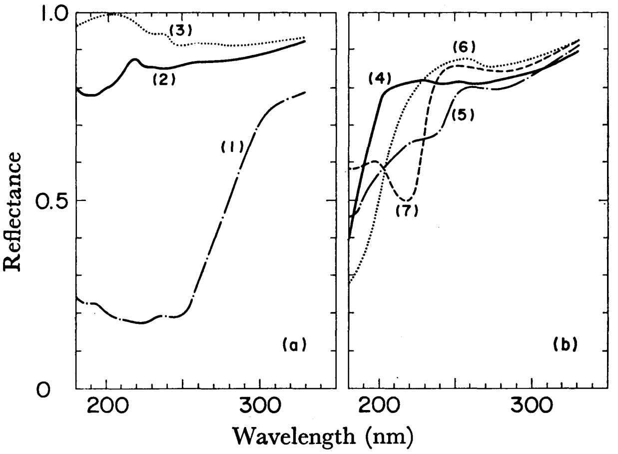

Fig. 1. Diffuse reflection spectra of Standard, Matrix and selected Series A samples (Additives are specified below).
(1) Standard. (2) Matrix. (3) Cs. (4) Cd. (5) Zr.
(6) Ge. (7) Tb.

TABLE 1. SUMMARY OF REFLECTANCE AND BRIGHTNESS DEPRECIATION DATA

Additive	$R_A(\lambda_e)$	I/I_o	$R_A(\lambda_i)$	$k_c(\lambda_e)/s$	I_i/I	$(I/I_o)\times(I_i/I)$
Standard	0.865	1.000	0.782	0.936	0.800	0.800
Li	0.700	0.907	0.702	1.02	0.821	0.745
Na	0.690	0.894	0.762	0.66	0.839	0.750
K	0.782	0.959	0.904	0.84	0.829	0.795
Rb	0.782	0.971	0.866	0.92	0.819	0.795
Cs	0.911	1.005	0.976	0.90	0.844	0.848
Cu	0.191	0.291	0.251	0.60	0.789	0.229
Ag	0.749	0.920	0.637	0.79	0.820	0.755
Au	0.798	0.787	0.848	0.74	0.755	0.594
Mg	0.860	0.952	0.875	0.86	0.780	0.743
Sr	0.811	0.993	0.804	0.85	0.800	0.795
Ba	0.821	0.971	0.735	0.96	0.806	0.782
Zn	0.780	0.866	0.476	0.96	0.816	0.706
Cd	0.815	0.999	0.500	0.66	0.834	0.833
Hg	0.824	1.018	0.799	0.82	0.809	0.824
Sc	0.766	0.948	0.789	0.86	0.765	0.725
Y	0.801	0.975	0.793	0.82	0.796	0.776
B	0.760	0.985	0.748	0.86	0.811	0.799
Al	0.831	1.001	0.829	0.86	0.795	0.796
Ga	0.719	0.758	0.482	0.76	0.776	0.588
In	0.481	0.831	0.204	0.68	0.744	0.618
Tl	0.829	0.986	0.666	0.86	0.797	0.786
Ti	0.252	0.259	0.139	0.44	0.799	0.207
Zr	0.789	0.971	0.469	0.60	0.820	0.797
Hf	0.618	0.894	0.466	0.60	0.860	0.768
Si	0.880	0.989	0.845	0.69	0.796	0.787
Ge	0.870	0.968	0.198	0.53	0.786	0.761
Sn	0.536	0.616	0.451	0.66	0.815	0.502
Pb	0.450	0.716	0.345	0.48	0.858	0.614
V	0.149	0.180	0.140	0.18	0.835	0.150
Nb	0.160	0.417	0.178	0.70	0.792	0.330
Ta	0.441	0.707	0.345	0.60	0.811	0.574
As	0.820	0.852	0.440	0.56	0.809	0.690
Bi	0.125	0.572	0.170	0.73	0.881	0.504
Cr	0.408	0.593	0.214	0.40	0.773	0.459
Mo	0.299	0.255	0.307	0.26	0.660	0.168
W	0.380	0.431	0.262	0.86	0.838	0.361
Fe	0.208	0.435	0.192	0.16	0.898	0.391
Co	0.802	0.158	0.190	0.18	0.850	0.134
Ni	0.631	0.347	0.242	0.22	0.857	0.297
La	0.830	0.966	0.793	0.86	0.784	0.757
Ce	0.502	0.814	0.618	0.61	0.815	0.663
Pr	0.850	0.799	0.411	0.42	0.797	0.637
Nd	0.842	0.599	0.366	0.47	0.801	0.480
Sm	0.780	0.885	0.364	0.43	0.779	0.689
Eu	0.441	0.785	0.445	0.48	0.775	0.609
Gd	0.838	0.945	0.950	0.70	0.798	0.754
Tb	0.859	0.969	0.601	0.56	0.790	0.765
Dy	0.850	0.909	0.623	0.67	0.776	0.703
Ho	0.820	0.765	0.581	0.65	0.795	0.608
Er	0.800	0.787	0.756	0.65	0.805	0.633
Tm	0.838	0.872	0.744	0.60	0.811	0.707
Yb	0.763	0.874	0.620	0.63	0.801	0.700
Lu	0.838	0.963	0.742	0.72	0.796	0.766

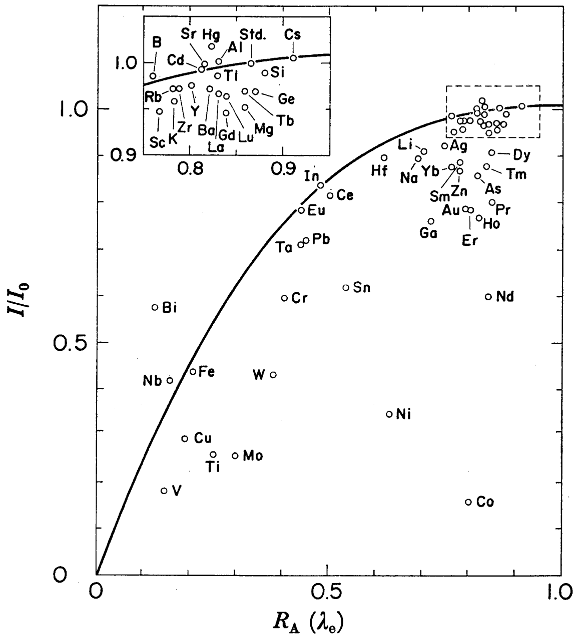

Fig. 2. Relation between 254 nm reflectance of Series A samples ($R_A(\lambda_e)$) and relative plaque brightness of corresponding Series B samples (I/I_0). Names of additives are indicated in the figure.

We see that the experimental I/I_0 values of such Series B samples as those containing K, Rb, Cs, Mg, Sr, Ba, Cd, Hg, Sc, Y, B, Al, Tl, Zr, Si, Ge, La, Gd, Tb, Lu, In, Eu, Fe and Nb are close to the calculated values. Of these, the first twenty additives might be of practical value, since their I/I_0 values are high. For the additives not mentioned above, I/I_0 is much lower than expected from Eq. (4), indicating that assumptions (2) and (3) are more or less invalid.

Change of Plaque Brightness due to Color Center Bleaching. As the absorption due to the color centers of Ca halophosphate extends from UV to visible region, both the 254 nm exciting radiation and the emission in the visible region may be absorbed by the color centers. In order to determine which of these two absorption processes is dominant in brightness depreciation, the effect of partial bleaching on plaque brightness was investigated.

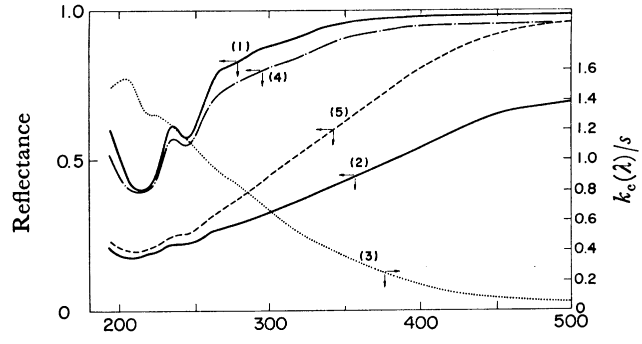

Fig. 3. Change of diffuse reflection spectrum of $Ca_{9.7}Sb_{0.03}(PO_4)_6(F_{0.9}Cl_{0.1})_2$ by 185 nm irradiation and by subsequent bleaching. (1) Before irradiation. (2) After 185 nm irradiation (6 hr in vacuum). (3) Spectrum of $k_c(\lambda)/s$ calculated from (1) and (2). (4) After bleaching by 254 nm light (1 hr). (5) After bleaching by blue light through UV 39+V-V 40 filters (10 hr).

Figure 3 shows the change of diffuse reflection spectra of a $Ca_{9.7}Sb_{0.03}(PO_4)_6(F_{0.9}Cl_{0.1})_2$ phosphor during the course of bleaching of color centers. The sample containing only a small amount of Sb was chosen because of ease of reflectance measurements. This sample has a weak absorption due to Sb in the UV region (curve (1)). The reflection spectrum after 185 nm irradiation (6 hr in a vacuum) is shown by curve (2). The remission function of the induced color centers, $k_c(\lambda)/s$, was calculated by

$$\frac{k_c(\lambda)}{s} = \frac{(1-R_i(\lambda))^2}{2R_i(\lambda)} - \frac{(1-R(\lambda))^2}{2R(\lambda)}, \tag{5}$$

where $R(\lambda)$ and $R_i(\lambda)$ are diffuse reflectance before and after irradiation, respectively. The result is shown by curve (3). The color centers were then bleached, either by 254 nm light from a germicidal lamp or by blue light from a xenon lamp coupled with Toshiba UV-39 (sharp cut-off at 390 nm) and V-V 40 (band pass with peak at 400 nm) filters. The results are shown by curves (4) and (5), respectively. Note that 254 nm irradiation bleaches the color centers almost completely, while the blue light bleaches the color centers in the visible, with little change in the 254 nm region.

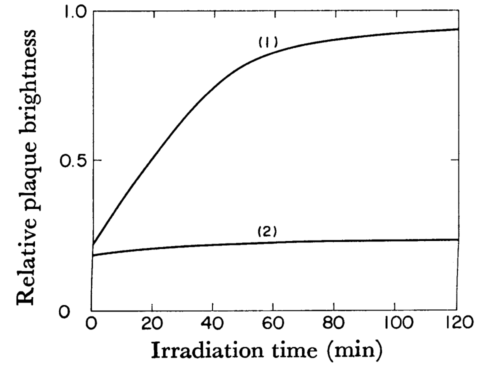

Fig. 4. Change of plaque brightness during bleaching. The sample was first irradiated by 185 nm light and then (1) by 254 nm light, (2) by blue light through UV 39+V-V 40 filters.

Figure 4 shows the change of plaque brightness of the same phosphor by bleaching. It is seen that the brightness, which has decreased to about 20% of the initial value due to 6 hr 185 nm irradiation, is almost completely restored by exposition to 254 nm light. On the other hand, little restoration of brightness is observed by blue light irradiation. It is thus concluded that the brightness depreciation is caused by the absorption of 254 nm light by color centers, the self-absorption of the emission in the visible region being unimportant. This might be due to the fact that the absorption of the color centers is very weak for the visible luminescence as compared with the absorption for the 254 nm radiation (Fig. 3, curve (3)). The same results as those shown in Figs. 3 and 4 were obtained for Standard phosphor.[22]

The nonradiative energy transfer from Sb to color centers, proposed recently by Parodi,[17)] does not seem to play a significant role in this case, since, in his concept, bleaching of color centers in the visible region should result in the recovery of brightness.

Relation between 185 nm Absorption and Color Center Formation. The next step is to investigate whether condition I can be used as a criterion to find other additives which are effective in suppressing the formation of color centers.

As a measure of the concentration of color centers, the remission function of the color centers at 254 nm, $k_c(\lambda_e)/s$, is used, since this value determines the extent of brightness depreciation.

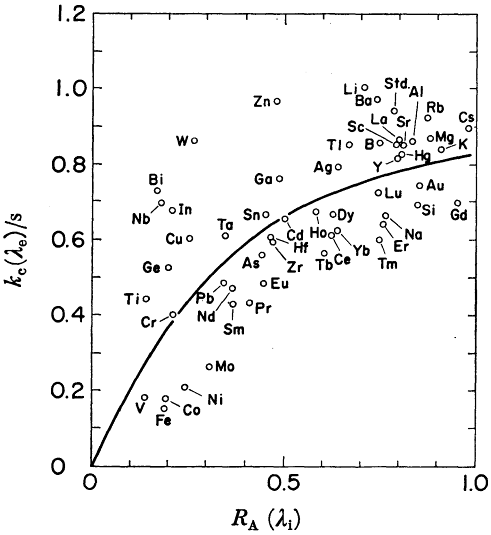

Fig. 5. Relation between 185 nm reflectance ($R_A(\lambda_i)$) and the extent of 254 nm absorption due to induced color centers ($k_c(\lambda_e)/s$) in Series A samples. Irradiation by 185 nm light was carried out for 6 hr in vacuum.

Figure 5 shows the relation between the reflectance at 185 nm ($R_A(\lambda_i)$) and the $k_c(\lambda_e)/s$ values induced by 6 hr of 185 nm irradiation in Series A samples. As expected, the stronger the 185 nm absorption due to additives, the weaker the color center formation. Of the twenty additives selected in accordance with condition II, Cd, Zr, Ge and Tb give rise to strong absorptions at 185 nm. Out of these additives, Cd, Zr and Tb suppress the formation of color centers to the extent expected for their $R_A(\lambda_i)$ values. Germanium also has such an effect, but less than expected for its strong absorption at 185 nm.

Relation between Color Center Formation and Brightness Depreciation. In order to calculate the relative brightness depreciation by color center formation, the view deduced from partial bleaching experiments is adopted. That is, a part of 254 nm light is absorbed and dissipated by color centers, the reabsorption of the emitted light being negligible. In a similar way to Eq. (4), the relative brightness in the presence of color centers, I_i/I, is given by

$$\frac{I_i}{I}=\frac{1-R_{Bi}(\lambda_e)}{1-R_B(\lambda_e)}\cdot\frac{k_{ac}(\lambda_e)+k_m(\lambda_e)+k_{ad}(\lambda_e)}{k_{ac}(\lambda_e)+k_m(\lambda_e)+k_{ad}(\lambda_e)+k_c(\lambda_e)}, \quad (6)$$

where I and I_i are the plaque brightness of Series B samples before and after 185 nm irradiation, respectively, and $R_{Bi}(\lambda_e)$ is 254 nm reflectance of Series B phosphors after irradiation.

In the first approximation, the term $k_{ad}(\lambda_e)$ is neglected, which in most cases is much smaller than the absorption coefficient of activators. Moreover, it is assumed that $k_c(\lambda_e)/s$ is related to $R_A(\lambda_i)$ by the solid line curve of Fig. 5. The values of I_i/I can then be calculated numerically as a function of $R_A(\lambda_i)$.

Figure 6 shows the result of this calculation (solid line curve) as well as experimental brightness depreciation data under 6 hr of 185 nm irradiation. The individual $R_A(\lambda_i)$ and I_i/I values are given in Table 1.

The calculation predicts that the brightness depreciation of Series B phosphors under this irradiation condition will be 15—25%. Another prediction is that the brightness would decrease, for example, by *ca.* 6% as compared to Standard, if one could find such an additive with $R_A(\lambda_i)=0.20$ with no absorption at 254 nm.

The experimental I_i/I_0 values are, as a whole, in rough agreement with the calculated one (Fig. 6). The dependence of I_i/I_0 on $R_A(\lambda_i)$ is, however, not so explicit as predicted by calculation. Some particular cases are discussed below.

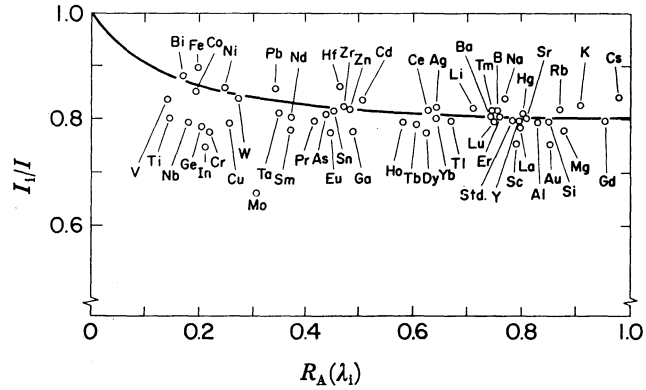

Fig. 6. Relation between 185 nm reflectance of Series A samples ($R_A(\lambda_i)$) and relative brightness after depreciation (I_i/I). Irradiation by 185 nm light was carried out for 6 hr in vacuum. Solid line curve was calculated by Eq. (6).

Considering the results mentioned in the previous section, particular attention was paid to Series B phosphors containing Cd, Zr, Ge and Tb. Cd- and Zr-containing phosphors show better performance than Standard under 185 nm radiation (Table 1 and Fig. 6). It was found, however, that Zr-containing phosphor has some disadvantages. Its initial brightness is inferior to that of Cd-containing phosphors. It tends to sinter slightly during lamp baking, thus giving an inhomogeneous phosphor layer.

Additives Ge and Tb were found, for unknown reasons, to be ineffective in improving performance. It seems that the absorption spectra of color centers in the presence of the activators differ considerably from those in the absence of activators. In short, application of conditions I and II did not lead to the finding of another additive having an advantage over Cd.

It was found unexpectedly that the addition of Cs improves not only the initial brightness, but also the maintenance. The increase of initial brightness can be understood in terms of the decreased absorption at 254 nm (Fig. 1, curve (3)). However, the reason for the brightness depreciation of the Cs-containing phosphor being even smaller than the Cd-containing phosphor (Table 1 and Fig. 6) is inexplicable, since Cs does not suppress color center formation at all (Fig. 5). Microscopic observation revealed that the Cs-containing phosphor is much more transparent or "porosity-free" than Standard. The optimum amount of Cs to be added depends strongly on the ignition conditions. In routine production, the best result was obtained when 0.03—0.1 g atom Cs was added to 1 mol phosphor. By chemical analysis, only a very small portion of the added Cs ($<$100 ppm) was found in the ignited phosphor. Moreover, the particle size of the Cs-containing phosphor was slightly greater than Standard. It is thus postulated that the added Cs compound (usually Cs_2CO_3) acts as a flux in the ignition process.

The promising outcome on the Cs-containing phosphor powder prompted a large scale lamp test using this phosphor. These lamps have 1—1.5% more initial lumen output than the reference lamps coated with Standard phosphor, and the decrease of the output after 1000 hr of operation is about 1% less than that of the reference. This result compares favorably with the Cd-containing phosphor, which gives 2% more initial lumens than the reference lamps, but no advantage in performance for long-term operation.

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