LUMINESCENCE OF CALCIUM HALOPHOSPHATE PHOSPHORS

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ABSTRACT

Details of preparation of two component calcium halophosphate daylight phosphor 6500° K doped with antimony and manganese by high temperature solid state reaction between $CaHPO_4$, $CaCO_3$, CaF_2, $SrCl_2$, Sb_2O_3 and $MnCO_3$ are reported. The effects of varying the activator concentration, metal to phosphorus ratio and chlorine to fluorine ratio on the photoluminescence of the light blue and warmwhite phosphors are discussed. Optimum values of the above parameters in the preparation of the two components, the blending of which leads to a daylight phosphor 6500° K are given.

Key words: Calcium halophosphate, phosphors, luminescence, doping with Sb and Mn

INTRODUCTION

Calcium halophosphate phosphors doped with antimony and manganese are widely used in fluorescent lamp industries. This phosphor is constituted of a non-fluorescing host lattice into which the specific impurities are purposely doped in order to absorb the 254 nm uV radiation of the low pressure mercury discharge and emit it as visible radiation. It has the special distinction of having the emission spectra of both activators in the visible region, thus enabling the colour rendition possible. Halophosphate phosphors activated by Sb^{3+} alone give a light blue luminescence. Addition of manganese as a second activator gives a luminescence spectrum in green-red region by absorption of uV transferred from antimony by a resonance process [1]. By varying the amounts of manganese and to some extent the halogen ratio, colour ranging from light blue to warmwhite can be obtained. In order to obtain a daylight phosphor of colour temperature 6500° K, it is essential to blend in proper ratio, a light blue phosphor activated by Sb^{3+} alone and a warmwhite phosphor activated by both Sb^{3+} and Mn^{2+}

In the calcium halophosphate lattice, both Sb^{3+} and Mn^{2+} substitute Ca^{2+} in one or other of the two inequivalent Ca^{2+} sites. The Ca (I) site is on a trigonal symmetry axis in the centre of a slightly twisted prism of six oxygen ions and Ca (II) is in a reflection plane containing an adjacent fluoride ion also in the reflection plane. 40% of the Ca^{2+} ions are on the Ca (I) sites and the remainder on Ca (II) sites. In the chloro-fluoro phosphate Cl^- ions are in between the reflection planes [2].

The main parameters involved in the preparation of the phosphors are the concentration of activators, metal to phosphorus ratio, Cl^-/F^- ratio, temperature and duration of firing. In the calcium halophosphate [formula $3Ca_3(PO_4)_2 \cdot Ca(F,Cl)_2$], the theoretical ratio of metal to phosphorous is 5 : 3. It has been reported that for maximum phosphor brightness, metal must be slightly less than 5 [3]. As part of a programme of work on indigenous development of phosphors for use in fluorescent tubes, studies have been made on the luminescence characteristics of both light blue and warmwhite phosphors by varying the different parameters.

EXPERIMENTAL

In the preparation of light blue halophosphate phosphor, an intimate mixture of $CaHPO_4$, $CaCO_3$, CaF_2, $SrCl_2$ and Sb_2O_3 (all luminescent grade) in proper proportions is heated in closed silica crucibles in the temperature range 1100-1180°C for a duration of time depending on the quantity of material started with. The composition of the reaction mixture corresponds to the formula $3Ca_3(PO_4)_2 \cdot Ca(F,Cl)_2$. The metal/phosphorous ratio lower

than 5/3 is required in order to make the incorporation of Sb^{3+} into the host lattice possible. After firing, the product is quenched to room temperature, pulverized and sieved through 300 mesh. In the preparation of warmwhite phosphor, activator manganese is added in the form of carbonate. A small percentage of cadmium in the form of carbonate added to the reaction mixture helps in reducing the lumen depreciation in the finished phosphor [4, 5]. The spectral energy distribution (SED) of the phosphor samples in the visible region is measured under excitation by 254 nm uV radiation obtained from a UVL-54 lamp with a Beckman DU Spectrophotometer. The amounts of antimony and manganese retained in the finished product after firing are estimated by atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Light Blue Phosphor

(a) Antimony concentration

Figure 1 gives the SED of lightblue phosphor for various concentrations of Sb^{3+}. Table I gives the percentage of Sb^{3+}; the number of calcium ions per antimony ion, the absorption and the peak intensity for the range of Sb^{3+} concentrations studied.
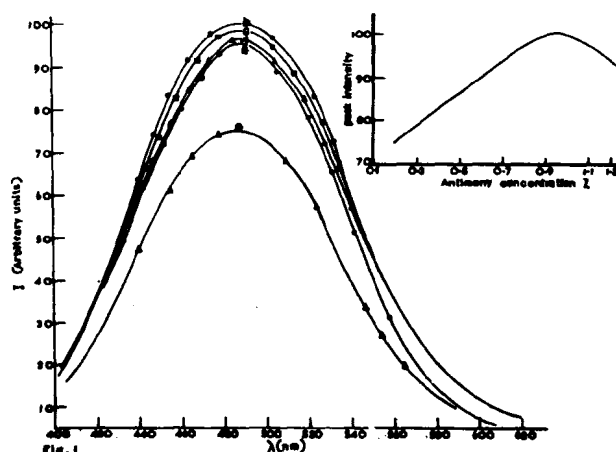

Fig. 1 : Effect of antimony concentration on the spectral energy distribution of light blue phosphor with (a) 1.168% (b) 0.92% (c) 0.862% (d) 0.77% and (e) 0.204%

Table I : Effect of antimony concentration on spectral energy distribution of light blue phosphor

Sb^{3+} %	Ca^{2+}/Sb^{3+}	Absorption % at 254 nm	Peak intensity at 480 nm
1.168	95	87	95
0.92	127	84	100
0.862	135	81	98
0.77	152	78	96
0.204	580	52	75

It is clear from the figure that although the shape of the SED curve is the same in all the samples, the maximum intensity is obtained for the sample with 0.92% antimony, corresponding to about 125 calcium ions per antimony ion. Though the absorption of uV increases with Sb^{3+} concentration the luminous intensity is found to decrease beyond a critical value of $Ca + Sr/Sb^{3+}$. The uV energy absorbed by Sb^{3+} can be released in the following three ways : (i) by direct conversion into visible radiation (ii) by resonance transfer between Sb^{3+} ions themselves and (iii) by radiationless transition. The decrease in intensity with Sb^{3+} concentration may be explained by the high probability of transfer of energy due to their nearness by resonance transfer between Sb^{3+} centres which is generally termed as concentration quenching [6]. The decrease in intensity in the case of low concentration of Sb^{3+} is due to the decrease in the absorption of uV due to decrease in activator centres.

(b) Halogen ratio

Figure 2 gives the SED of antimony emission for different values of Cl^-/F^-. It is evident from the figure that the λmax of the antimony emission is independent of halide composition. This shows that Sb^{3+} ions can occupy both the Ca^{2+} sites. In Ca(I) position, Sb^{3+} ions replace Ca^{2+} in two adjacent Ca(I) positions and the charge compensation is accomplished by the presence of an interstitial O^{2-} near the two substituents [7]. In the substitution of Sb^{3+} for Ca^{2+} in Ca(II) position, the charge compensation is effected by substituting O^{2-} ions for the adjacent halide ions leaving the Sb^{3+} environment independent of halide [8].
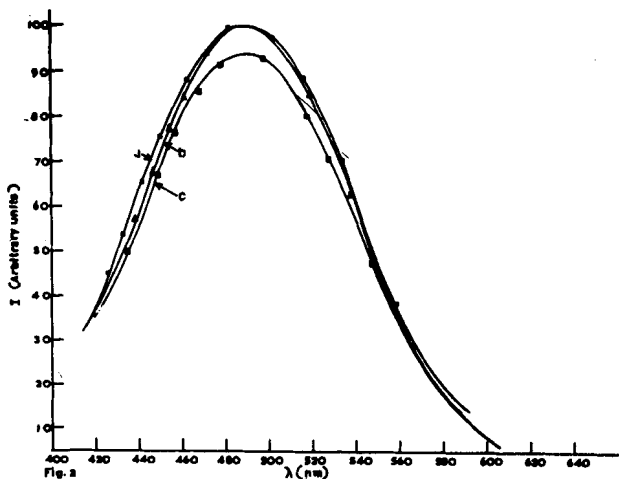

Fig. 2 : Effect of halogen ratio on the spectral energy distribution of light blue phosphor with Cl^-/F^- (a) 0.01442 (b) 0.02885 (c) 0.0577

Warmwhite Phosphor

(a) Mn concentration

Figure 3 gives the SED of warmwhite phosphors for various manganese concentrations. It has been estimated that optimum concentration of Mn^{2+}

is 0.98 %. The desired ratio between the emission peaks at 565 and 480 nm is obtained only at the optimum Mn^{2+} concentration, and when the manganese is increased beyond this value, the emission spectrum gets more intense around 565 nm region with decrease in emission near 480 nm. This is due to the fact that when the distance between Mn^{2+} and Sb^{3+} is decreased, the energy transfer from Sb^{3+} to Mn^{2+} is more dominant, thereby decreasing the blue emission due to antimony.
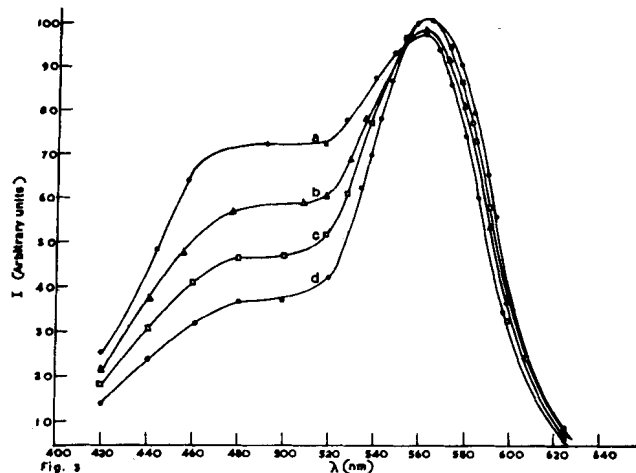

Fig. 3 : Effect of manganese concentration of the spectral energy distribution of warmwhite phosphor with Mn^{2+} (a) 0.56 % (b) 0.74 % (c) 0.98 % (d) 1.19 %

(b) Halogen ratio

Table II gives the effect of variation of Cl^-/F^- on peak wavelength of warmwhite phosphors. It has been observed that as the ratio is increased, the Mn^{2+} emission peak shifts towards longer wavelengths. The ionic radius of Cl^- is 1.81 Å and that of F^- is 1.33 Å. Due to the fact that the size of Cl^- ion is considerably larger than that of F^- ion by over 30 %, when Cl^- is incorporated in the lattice, the lattice constant increases and the Mn^{2+} energy levels are altered in such a way as to shift the emission towards longer wavelengths [9].

Table II : Effect of Cl^-/F^- on the spectral energy distribution of warmwhite phosphor

Cl^-/F^-	λ max (nm)	Sb^{3+} % retained	Mn^{2+} % retained
0.1649	560	1.012	0.92
0.1977	566	1.520	0.95
0.2373	570	1.25	1.03

(c) Metal/phosphorus variation

The effect of variation of metal/phosphorus on the SED of warmwhite phosphor is given in figure 4. Here metal refers to Ca + Sr + Mn. When the metal is increased from the optimum value of 4.89 to 5.0 mole, the incorporation of antimony is almost reduced to half resulting in poor absorption of 254 nm radiation and consequently there is overall decrease in intensity. When the metal is decreased from the optimum value to 4.77, the amount of antimony incorporated increased by about 30% for the same amount of antimony added. The decrease in intensity obtained can be attributed to concentration quenching. It has also been found that Mn^{2+} incorporation is not much dependent on the variation of metal to phosphorus ratio.
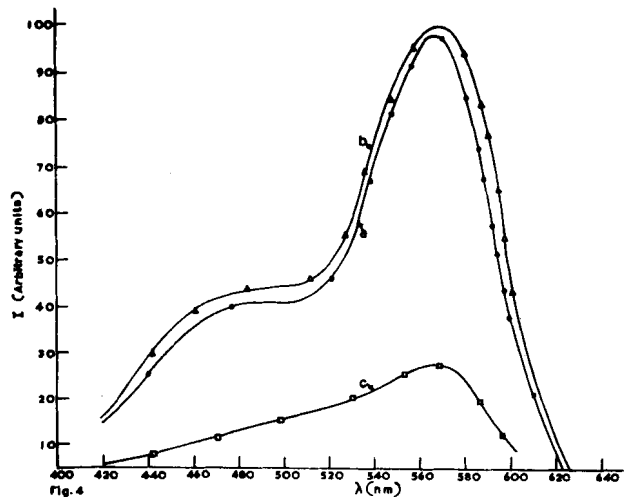
Fig. 4: Effect of metal to phosphorus ratio on the spectral energy distribution of warmwhite phosphor with metal (a) 4.776 mole (b) 4.893 mole and (c) 5.00 mole

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