PHOTOLUMINESCENCE OF OXYGEN DOMINATED PHOSPHORS

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ABSTRACT

The mechanism of fluorescence in (a) $CaWO_4$, (b) Zn_2SiO_4:Mn, (c) 3.5 MgO + 0.5 MgF_2 + GeO_2 : Mn, and (d) $3Ca_3(PO_4)_2$ Ca(F, Cl)$_2$:Sb^{3+}, Mn^{2+} under excitation by shortwave ultraviolet is explained by the electronic transitions involved in the activators. To get a daylight phosphor conforming to 6500°K, a blending of a Sb^{3+} activated halophosphate blue phosphor and a Sb^{3+} and Mn^{2+} activated warmwhite phosphor is essential and the successful preparation of the same is presented.

Key Words: Photoluminiscence, Phosphors.

INTRODUCTION

' **L**uminescent materials' or phosphors generally include all solid and liquid inorganic and organic materials which are able to convert absorbed (invisible) energy in the form of moving particles or quanta of radiation into visible light: an example is conversion of photons of energy about 1.5–3.0 eV corresponding to 700–400 nm. These materials store the energy for times between 10^{-9} to more than 10^7 sec which results in a certain persistence of illumination (decay time). Roughly speaking, the phenomena are described as 'fluorescence' if decay occurs immediately after termination of excitation and as phosphorescence if decay times extend to minutes or days after excitation has ceased.

Phosphors have achieved ever increasing importance in optical technology since 1938. Mercury discharge lamps are well-known for their excellent light yield (30–75 lumens/watt). Low pressure mercury discharge lamps produce a large amount of short wave uV. It is an obvious step to transform the spectrum of these lamps by phosphors from uV to light of a colour emission that would both be transmitted by glass envelopes and suit the peak sensitivity of the human eye (540 nm).

CLASSES OF PHOSPHORS

Phosphors may be divided broadly into two classes according to the distinction between the types of chemical bonding of the matrix lattice: sulphide phosphors with mainly covalent bonding and oxygen-dominated phosphors of a more ionic character [1]. Although the distinction between the two classes is by no means rigid, there are differences in behaviour which can be theoretically explained. Sulphide phosphors behave as photoconductors under the influence of an electric field and a suitable source of radiation, whereas oxygen-dominated phosphors are more nearly insulators under these conditions. The mechanism of process in sulphide phosphors is based on the well-known energy band model and applied successfully to modern semiconductor materials.

Phosphors containing oxygen, such as silicates, phosphates and borates are mainly ionic in character and have properties more closely associated with the activator centre than with the host lattice. In these phosphors, it is assumed that excited electrons remain within the field of the activator centre and consequently little or no photoconduction is observed.

Calcium tungstate blue phosphor

In calcium tungstate crystal phosphor which has the structure and composition of the mineral 'Scheelite' luminescence without external activators is due to the complex tungstate ions WO_4^{2-} in the lattice. The tungstate ion is coordinated by four oxygens having predominantly a covalent bond. The calcium is coordinated by six oxygen ions having predominantly an ionic bond [2]. In WO_4^{2-} centres, absorption and emission occur. A qualitative description of the optical process in such luminescence centres is given by the configurational coordinate model (figure 1). The ordinate is the total energy of the system for the ground and excited states of the centre. The abscissa is a configurational coordinate which specifies the configuration of the ions around the centre, the coordinate describing the positions of the nearest neighbour ions. The equilibrium positions at the ground and excited states are not the same [3]. Figure 2 gives the spectral energy distribution (SED) of the $CaWO_4$
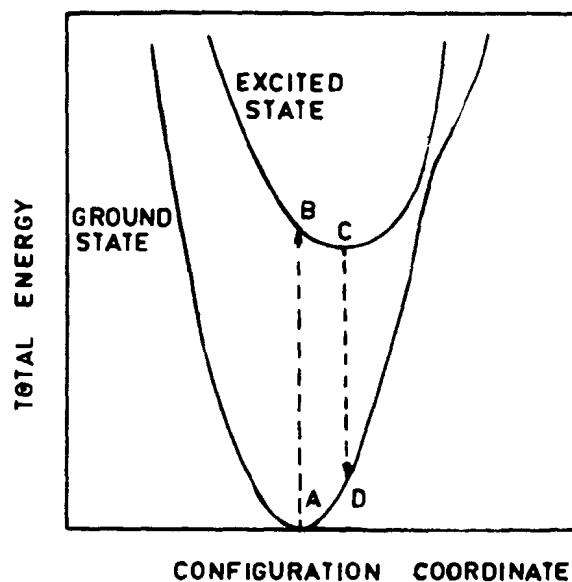

CONFIGURATION COORDINATE

FIG 1

Fig. 1: Schematic configuration coordinate curves

phosphor developed. The effect of dopants like Cd^{2+}, In^{3+}, Sb^{3+} and Pb^{2+} in $CaWO_4$ has also been studied [4].
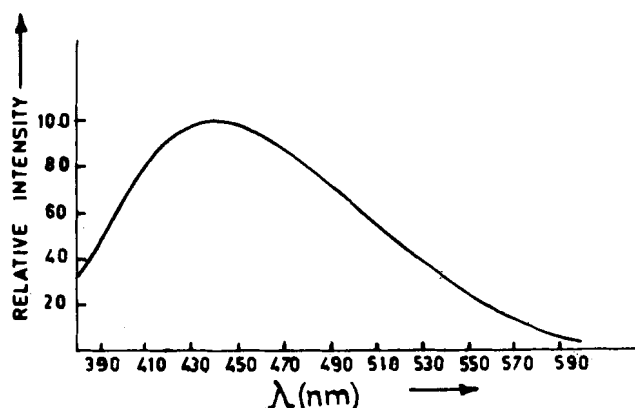

Fig. 2: Spectral energy distribution of calcium tungstate blue phosphor

Zinc silicate green phosphor

Zinc silicate matrix is known to be rhombohedral in its structure. The configurational coordinate diagram for Zn_2SiO_4: Mn has been worked out by various workers. The emission transition is attributed to a spin reversal of one of the 3d electrons of the Mn^{2+}-ion. The mode of vibration is a radial one for the four oxygen ions surrounding the manganese ion. Depending on the interaction between the Mn^{2+} ion and the host lattice, the luminescence peak is at 520 nm, the mechanism being explained by a configurational coordinate scheme. The green fluorescence of Zn_2SiO_4: Mn is readily and explicitly accounted for by the direct substitution of Mn^{2+} for Zn^{2+}. Since Zn^{2+} ions in Willemite are surrounded by four oxygens, this substitution gives rise to MnO_4 groups responsible for the green emission. In this background the effects of Cd^{2+}, Pb^{2+}, Tl^{1+} and Sb^{3+} have been studied [5]. As can be seen from figure 3 Cd^{2+} and Tl^+ have very little effect on SED in comparison with a commercial phosphor plotted alongside and in all the cases, there is no new band appearing [5].
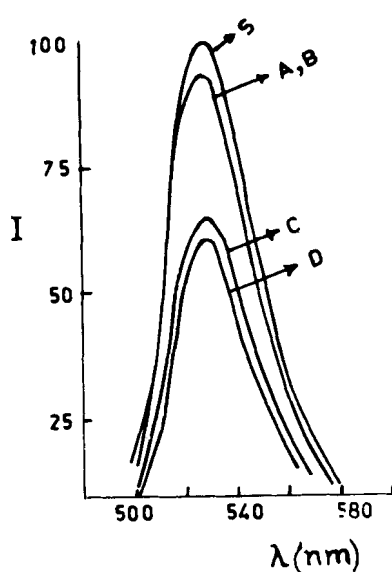

Fig. 3: Spectral energy distribution of
(S) Zn_2SiO_4: Mn, (A) Zn_2SiO_4: Mn + Cd, (B) Zn_2SiO_4: Mn + Tl (C) Zn_2SiO_4: Mn + Pb, (D) Zn_2SiO_4: Mn + Sb

Magnesium fluogermanate red phosphor

In the magnesium fluogermanate red phosphor, the activator centre is Mn^{4+} ($3d^3$ configuration) subjected to an octahedral field of oxygen. The effects of activator concentration and the luminescence spectra at various temperatures ranging from room temperature to 300°C were studied on the magnesium fluogermanate phosphor of matrix composition 3.5 MgO, 0.5 MgF_2, 1.0 GeO_2 with manganese as activator [6]. It was found that the temperature dependence of the SED of emission of magnesium fluogermanate is a function of both matrix composition and manganese content.

Calcium halophosphate daylight phosphor

One of the many oxygen-dominated phosphors is halophosphate phosphors. They have the chemical composition $M_5(PO_4)_3X$ where M is Cd or an alkaline earth and X is halide, usually F^- and/or Cl^- and their structure is similar to that of the apatite. The principal activators are Mn^{2+} and Sb^{3+}

The earliest single component phosphor was $(ZnBe)_2 SiO_4$:Mn^{2+}. It was found that Zn-beryllium silicate phosphor exhibits a toxicity common to beryllium and its compounds so that its continued use in fluorescent lamps was undesirable. By the year 1949, the single component calcium halophosphate phosphor, with no toxicity characteristics was discovered [7]. Good control over colour is possible by variation of the ratio (Cl^-/F^-) and concentrations of Mn^{2+} and Sb^{3+}

When the calcium halophosphate is activated by antimony alone, the emission has a principal band in the visible spectrum peaking at 480 nm. The inclusion of manganese depresses the blue band and produces a second principal band with a peak at 585 nm [8]. The manganese content and to a lesser degree the ratio of the fluoride: chloride, can be varied to produce a range of phosphors, giving near-white colours from light blue to orange; or in terms of fluorescent lamp colours, light blue, colour matching white, daylight and warm white can be prepared with a single halophosphate in each case.

Activators

Antimony is the primary or sensitizing activator and is usually added as trioxide. For the optimum phosphor brightness, the antimony content should be about 1.8% by weight of the basic raw materials. The antimony is present in the phosphor in the trivalent state. In the calcium halophosphate daylight phosphor antimony is added as sensitizer. This introduces an absorption band in the blue region for the manganese as well as its own luminous emission. The trivalent state of Sb^{3+} has three excitation states, ie. 1_{p1}, 3_{p2} and 3_{p1}, the transition of the Sb^{3+} ion being from its ground state $1_{So} \rightarrow 3_{p1}$ (250 nm). The absorption of ultraviolet produced by the mercury discharge mainly takes place because of the above transition.

The manganese is present in the halophosphate phosphor as Mn^{2+} The various excited states for Mn^{2+} are 4_G 4_D, 4_P and 4_F and the ground state is 6_S. The excitation spectrum for Mn^{2+} in calcium halophosphate shows the bands at about 400 and 404 nm and they are assigned to the 4_A, 4_E (4_G) level and five bands at longer wavelengths to the split 4_{T2} (4_G) and 4_{T1} (4_G) levels.

The antimony absorbs 254 nm radiation and its two emission bands are at 487 nm and 396 nm. The excitation bands of Mn^{2+} and transition from $6_S \rightarrow 4_G$ level leads to absorption of the bands produced by the antimony. As manganese is present in various centres in Ca halophosphate phosphor, these could receive the energy transferred from the antimony.

The main parameters involved in the preparation of halophosphate phosphor are metal to phosphorus ratio, F:Cl ratio and the concentration of antimony and manganese. A small percentage of Cd added to the halophosphate matrix helps to reduce lumen depreciation of the finished product [9].

The halophosphate phosphor used in tubes at present is of the daylight colour 6500°K and has the colour-coordinates x = 0.314 and y =

0.342. Any daylight phosphor prepared must lie within the tolerance ellipse of 6500°K. The luminous spectrum of single halophosphate phosphor is always deficient in the red region and does not correspond to 6500°K. So a blue halophosphate phosphor activated by antimony alone is first prepared. Another phosphor activated by antimony and a higher concentration of manganese is prepared. This gives a higher intensity in the red region, i.e. warm white tint. This blue phosphor and warm white phosphor are blended in a proper ratio so that the luminous spectrum corresponds to daylight colour of 6500°K. The SED of daylight phosphor as measured by IP 28 photomultiplier is given in figure 4.
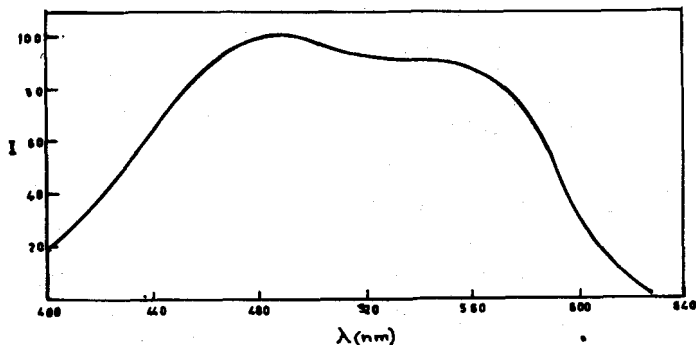

Fig. 4: Spectral energy distribution of daylight phosphor

The excellent qualities of efficiency and maintenance and the low cost make it a safe rule that wherever possible halophosphates should be used in fluorescent lamps. However, if desired, they can be admixed with other phosphors to obtain intermediate efficiencies and colours. The most obvious case for an admixture of phosphors is to improve the red emission from the lamp. Two phosphors which technically are almost ideal are light blue phosphor and warm white phosphor in a proper ratio blended, so as to give a luminous spectrum corresponding to daylight colour of 6500°K.

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