

LETTERS TO THE EDITOR

ELECTROLUMINESCENCE IN ZnO : Sm,

ZnO : Sm, Cu AND ZnO : Sm, Ag PHOSPHORS

In continuation of our plan to study the optical properties of ZnO phosphors doped with rare-earth ions¹, we have prepared ZnO : Sm, ZnO : Sm, Cu and ZnO : Sm, Ag phosphors at different concentrations of Sm, Cu and Ag ions. This paper reports the photo and electroluminescence of these phosphors.

Calculated quantities of ZnO and Sm₂O₃ were well mixed in the desired proportions. Requisite amounts of Cu₂Cl₂ and AgNO₃ were added to get ZnO : Sm, Cu and ZnO : Sm, Ag. The mixture was finely ground and fired in a silica crucible at 1050°C for 1.5 hours. It was then cooled and the phosphor finely powdered.

The photoluminescence spectra was obtained by exciting the phosphor by N₂ Laser having a wavelength of 3371 Å. The spectrum of ZnO : Sm consists of a broad and featureless band with maxima around 5150 Å and long tail on both sides extending from 4000 Å to 6500 Å. It is observed that brightness first increases with an increase of the concentration of Sm ions (Fig. 1), reaches maximum near 5150 Å at a concentration of 1.724% of Sm and then goes on decreasing with the increase of Sm concentration. The peak of the intensity shifts to low wavelength side as concentration increases from 0.035% to 1.724% and then shifts to high wavelength side with concentration from 2.586% onwards. Similar results were observed in the case of ZnO : Sm, Ag. The ZnO : Sm, Cu was found to be non-photoluminescent.

The phenomenon could be explained on the basis of donor acceptor model²⁻⁴ of luminescence. Sm forms the donor levels near the conduction band while Ag ions form acceptor levels close to valence band. When the electron in the donor level captures hole in the acceptor level the light is emitted. The electronic transition is strongly affected by interaction with lattice phonons, which accounts for the broadening.

The EL brightness of the above phosphors has been studied by applying an alternating electric field on the EL condenser. The integrated light output was detected by RCA IP 21 photomultiplier tube. The EL brightness (B) and a.c. voltage (V) was found to follow the relation $B = B_0 \exp(-b/\sqrt{V})$, where b and B_0 are constants. The mechanism of excitation of luminescence is therefore assigned as the acceleration collision type. An interesting aspect of such oxide phosphors with high concentration of impurities is that there is a deviation in straight line behaviour between 250 and 400 volts. An attempt has been made to explain this deviation on the basis of particle size⁵.

PL-SPECTRA

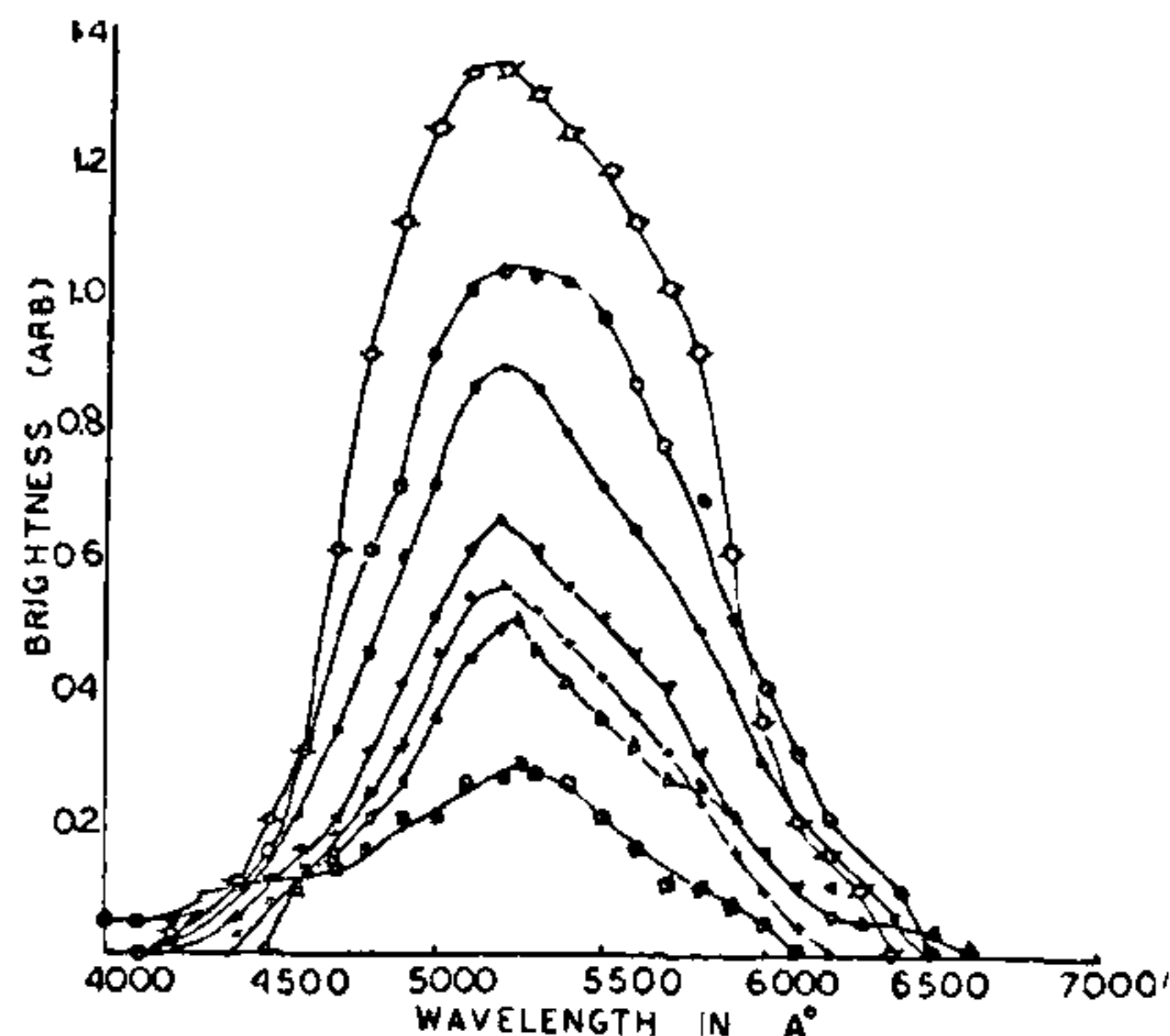


FIG. 1 Photoluminescence Spectra of ZnO : Sm and ZnO : (Sm, Ag) phosphors.

PHOSPHORS

ZnO : Sm {
 ▲ Sm = 2.586 %
 ◇ Sm = 1.724 %
 ○ Sm = 0.862 %
 △ Sm = 0.039 %

ZnO : Sm Ag {
 □ Sm = 3.448 %
 Ag = 0.015 %
 ● Sm = 1.724 %
 Ag = 0.015 %
 + Sm = 0.034 %
 Ag = 0.101 %

Frequency dependence of light output has been studied. In general the brightness increases with the increase of frequency, approximately linearly in the range 200 Hz to 3 KHz. Discrepancies in the linear relation has been found in the range 3 KHz to 5 KHz. The light output decreases abruptly from 3 KHz to 5 KHz to a low value and then again shows rising trend. At present we are not in a position to offer

any explanation to this anomalous behaviour of the EL cell. A detailed analysis will be published elsewhere.

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AN ALTERNATIVE SYNTHESIS OF 7-O-METHYL GLABRANINE

GLABRANINE m.p. 154–55° was isolated from *Glycyrrhiza glabra*¹ and has been assigned the structure 8-C-prenyl-5, 7-dihydroxy flavanone from its spectral studies and synthesis². Synthesis of 5-hydroxy-7-methoxy flavanone was accomplished *via* isomerisation of 2'-hydroxy-4'-methoxy-6'-benzyloxy chalcone and its nuclear prenylation with 2-methyl-but 3-en-2-ol and boron trifluoride etherate in dry dioxan medium gave 7-O-methyl glabranine.

Phloroacetophenone was converted into its ditosyl ester and the remaining hydroxyl was benzylated using benzyl chloride. The resulting product was saponified and the monobenzylphloroacetophenone was obtained as a buff coloured solid m.p. 233–35° (Found: C, 69.6; H, 5.20, C₁₅H₁₄O₄ requires C, 69.77; H, 5.42%). It was then subjected to methylation in the 4-position to yield 4-O-methyl-6-O-benzylphloroacetophenone m.p. 110–13° (Found: C, 70.30; H, 5.62 C₁₆H₁₆O₄ requires C, 70.58; H, 5.58%). On condensation with benzaldehyde in alcoholic potassium hydroxide, it gave the 2'-hydroxy-4'-methoxy-6'-benzyloxychalcone m.p. 126–27°; $\nu_{\text{max}}^{\text{KBr}}$ 1618, 1582, 1563, 1389, 1337, 1282, 1212, 1105, 1031, 816, 746 and 690 cm⁻¹; $\lambda_{\text{max}}^{\text{MeOH}}$ 337; + AlCl₃ 367 nm. NMR (δ , CDCl₃): 3.67 (s, 3H, -OCH₃), 4.88 (s, 2H, -OCH₂-C₆H₅), 5.92, 6.0 (d, J = 2 Cps, 3', 5'-protons), 7.13 (m, 1OH, -OCH₂-C₆H₅) and ring A protons), 7.50 (d, J = 15 Cps, 1H), 7.80 (d, J = 15 Cps, 1H) α and β Protons, 14.70 (s, 1H,

-OH) (Found: C, 77.0; H, 5.9; C₂₃H₂₀O₄ requires C, 76.7, H, 5.6%). Its isomerisation to 5-hydroxy-7-methoxyflavanone was carried out by refluxing with 4% H₂SO₄. The flavanone was crystallised from the mixture by petroleum ether as colourless needles m.p. 104–5°; $\nu_{\text{max}}^{\text{KBr}}$ 2941, 1626 (b), 1575, 1379, 1351, 1299, 1259, 1208, 1093, 995, 962, 891, 794, 743, 698 and 683 cm⁻¹. NMR (δ , CDCl₃), 2.80 (m, 2H, C₃-H₂), 3.70 (s, 3H, -OCH₃), 5.20 (m, 1H, C₂-H), 5.90 (s, 2H, 6, 8-H), 7.31 (s, 5H, side phenyl protons), 11.90 (s, 1H, -OH). (Found: C, 70.95; H, 5.08; C₁₆H₁₄O₄ requires C, 71.11; H, 5.18%). Nuclear prenylation of 5-hydroxy-7-methoxy flavanone with 2-methyl-but-3-en-2-ol in the presence of boron trifluoride-etherate in dry dioxan medium gave a mixture of two compounds which were separated by column chromatography over silica gel and designated as A and B. Compound A crystallised from petroleum ether as colourless needles m.p. 108–110°, $\nu_{\text{max}}^{\text{KBr}}$ 3378, 1640, 1626 cm⁻¹; $\lambda_{\text{max}}^{\text{MeOH}}$ 288, 322; + AlCl₃ 310, 370; + AlCl₃ + HCl 308, 370 nm; NMR (δ , CDCl₃): 1.60 [s, 6H, (CH₃)₂C = C<], 2.75–2.95 (m, 2H, C₃-H₂), 3.15 (d, J = 7 Cps, -CH₂-Ar), 3.80 (s, 3H, -OCH₃), 5.20 (m, 1H, C₂-H), 5.40 (m, 1H, vinylic proton), 5.90 (s, 1H, 6-H), 7.25 (s, 5H; side phenyl protons), 12.00 (s, 1H, -OH). That the prenyl unit had entered into one of the two available nuclear positions 6 or 8 in the ring A was shown by its NMR spectrum which had the expected resonance signals of one C-prenyl unit at δ 1.60, 3.15 and 5.40 and signals at 5.90 and 7.25 integrating for one and five protons respectively. No change in R_f value and other properties was observed when compound A was treated with formic acid for ½ hr. Thus the C-prenyl unit is at 8-position. Hence the structure of compound A is 8-C-prenyl-5-hydroxy-7-methoxy flavanone, which resembled in all respects with that reported by Khanna *et al*³ (Found: C, 74.40; H, 6.80; C₂₁H₂₂O₄ requires C, 74.5; H, 6.6%).

Compound B was found to be the starting material by direct comparison.

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