Photo-Electro-Luminescence of ZnS: (Cu, Ce) and ZnS: (Ag, Ce) Phosphors

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The enhancement and quenching of the prominent emission bands at 4700 Å and 5300 Å of ZnS: (Cu, Ce) and 4600 Å and 5200 Å of ZnS: (Ag, Ce) on single or simultaneous application of a sinusoidal electric field and 3650 Å UV radiation have been studied.

The enhancement of an emission band on simultaneous application of an electric field and light was first observed by Cusano [1, 2] and Cusano and Williams [3] in ZnS : Mn and has subsequently been observed in other ZnS phosphors [4, 5]. Recently we have reported the photo-electro-luminescence emission in ZnS phosphors doped with DA impurity ions like La^{3+}, Tb^{3+}, Cu^+ and Ag^+ [6, 7]. This paper deals with the enhancement and quenching of a particular emission band on single or simultaneous application of an electric field and light on ZnS: (Cu, Ce) and ZnS: (Ag, Ce).

ZnS: (Cu, Ce) and ZnS: (Ag, Ce) samples containing various concentrations of activators and coactivators were prepared by firing intimate mixtures of high purity ZnS, cerous oxalate $[Ce_2(C_2O_4)_3]$, sulphur, copper accetate $[Cu(CH_3COO)_2]$ and silver nitrate $[AgNO_3]$ in appropriate proportions in silica crucibles. The crucible was kept inside a horizontal tubular furnace maintained at 1000 °C in an inert atmosphere of argon. The firing time was 40 minutes.

The cell was a parallel plate type condensor consisting of a glass plate with a transparent conducting surface, a suspension of the phosphor in castor oil, a mica sheet (about 100 μm thick) and an aluminium plate. Sinusoidal voltage for field excitation was obtained from an audio frequency oscillator coupled to a wide band amplifier. The PL excitation was done by 3650 Å radiation from a high pressure murcury lamp operated at constant voltage. A constant deviation spectrograph was used as a monochromator for studying the spectral distribution of the luminescence emission. PEL was obtained by combining the excitation of EL and PL. The PEL intensity was measured at 4700 and 5300 Å in ZnS: (Cu, Ce) and at 4600 and 5200 Å in ZnS: (Ag, Ce). At these wavelengths the phosphors give maximum EL and PL emissions.

For detecting the integrated light output of EL, PL and PEL emission, an RCA IP21 photomultiplier tube was used. The output terminals of the photomultiplier were connected to a sensitive galvanometer whose deflections give the integrated light intensity in arbitrary units.

Figures 1 and 2 represent the variation of PL, EL and PEL emission intensities with excitation time. It is apparent that PEL first increases sublinearly with time of excitation. From a comparison of the PL, EL and PEL emission intensities it is found that in PEL both bands (4600 Å and 5200 Å) are enhanced in ZnS: (Ag, Ce) (Fig. 1), that the 5300 Å band in ZnS: (Cu, Ce) is quenched at all concentrations (Fig. 2) and that the blue band at 4700 Å is also quenched for 0.01% concentration of Cu and Ce, but enhanced at higher concentrations (0.05% and 0.1%) of impurities (Figure 2).

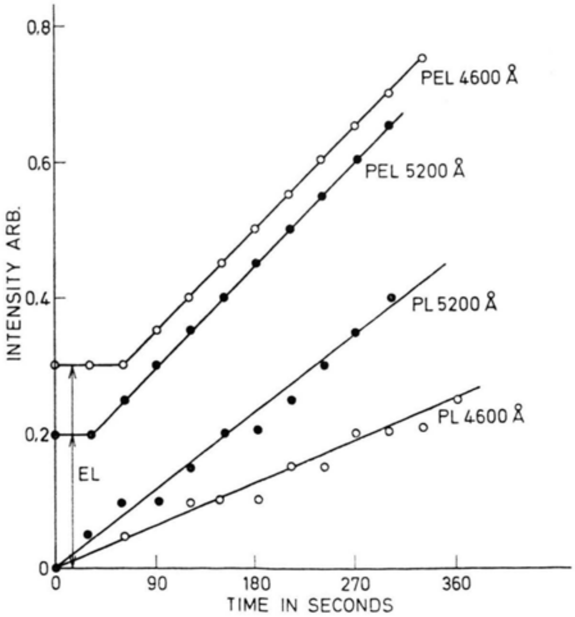

Fig. 1. Variation of PL, EL and PEL emission with time of excitation in ZnS: (Ag, Ce) for Ag=Ce=0.05% (field 2 kHz, 750 volts).

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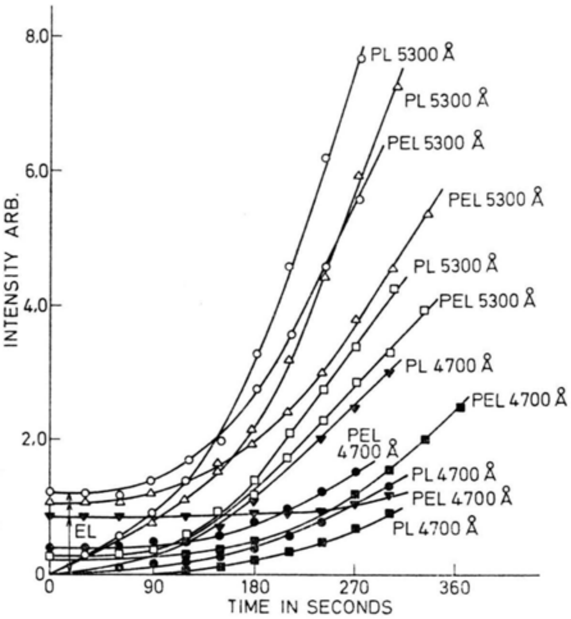

Fig. 2. Variation of PL, EL and PEL emissions with time of excitation in ZnS: (Cu, Ce) for (⊙, ▼), Cu=Ce=0.01%, (△, ●), Cu=Ce=0.05% and (□, ■), Cu=Ce=0.1% (field 2 kHz, 750 volts).

In PEL, Ce^{3+} ions and also other shallow traps are ionized due to the combined action of the electric field and the 3650 Å radiation creating a high density of conduction electrons which later on recombine with a large number of empty centers radiating more quanta of energy than they radiate under the action of the individual fields separately. In this way PL and EL effects reinforce each other. This explains the enhancement qualitatively. The quenching of the 5300 Å band in ZnS:(Cu, Ce) can be explained as arising due to further trapping of the liberated electrons at the Ce^{3+} centers or at some other deep centers. Fewer electrons are, thus, available for impact ionization with the copper centers. This does not explain why the 5200 Å band in ZnS:(Ag, Ce) is not quenched. Probably this may be due to differences of the two materials regarding their composition and structure.

The quenching of the blue band in ZnS:(Cu, Ce) at lower concentrations 0.01% and enhancement at higher concentrations (at 0.05% and 0.1%) may be qualitatively explained if it is assumed that the electric field promotes a larger number of non-radiative transitions over the radiative ones at lower concentrations, while the situation is reversed at higher concentrations of Cu^{+} and Ce^{+} ions mainly due to the participation of a large number of luminescent centers in the emission process. Further detailed investigations are necessary to substantiate the above conclusions.

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