Luminescent Centres of T_d Symmetry in “Cold” Activated ZnS-Mn

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By coprecipitation of ZnS and MnS in excess of Na_2S, luminescent centres are built differing considerably from those in zinc salt excess. ESR data give evidence of centres of T_d symmetry.

The “cold” activation of zinc sulphide with manganese leads to a phosphor which shows other luminescent properties than ZnS-Mn prepared at high temperatures [1]. In the precipitated ZnS-Mn, “orange” centres with $\lambda_{max} = 600-615$ nm are built, whereas for the fired phosphor, yellow luminescence ($\lambda_{max} = 585$ nm) is characteristic. In this communication we report on the formation of “yellow” centres without sample firing.

According to [1], non-fired ZnS-Mn with orange luminescence, in the following designed as I, can be obtained by coprecipitation with Na_2S in excess of the zinc salt ($ZnCl_2$ or $ZnSO_4$) and heating the suspension at 100 °C. Our further investigations show that yellow emitting phosphor with band maximum at 590–595 nm (II) is formed when the “cold” activation is performed in a similar way in excess of Na_2S. The luminescence spectra of I, II and the fired ZnS-Mn (III), measured at 365 and 254 nm excitation, are shown in Figure 1. It is to be noted that in excess of $ZnCl_2$ only part of the manganese ions can be coprecipitated in the ZnS matrix; therefore the amount of $MnCl_2$ introduced was suitably adjusted to ensure incorporation of activator ions in I in a concentration nearly equal to that in II ($\approx 5 \cdot 10^{-3}$ Mol Mn/Mol ZnS).

The comparison of the emission spectra of I and II give evidence that different kinds of centres are formed in I and II. This is confirmed by ESR measurements.

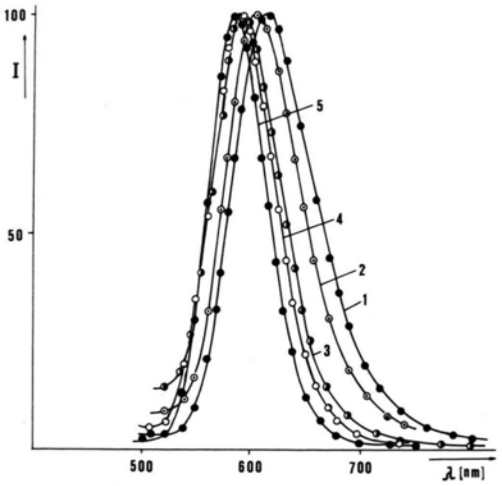

Fig. 1. Luminescence spectra of ZnS-Mn (I), prepared in excess of $ZnCl_2$ (curve 1: excitation at 365 nm; curve 2: at 254 nm), (II), prepared in excess of Na_2S (curve 3: excitation at 365 nm; curve 4: at 254 nm), and (III), prepared at high temperature (5).

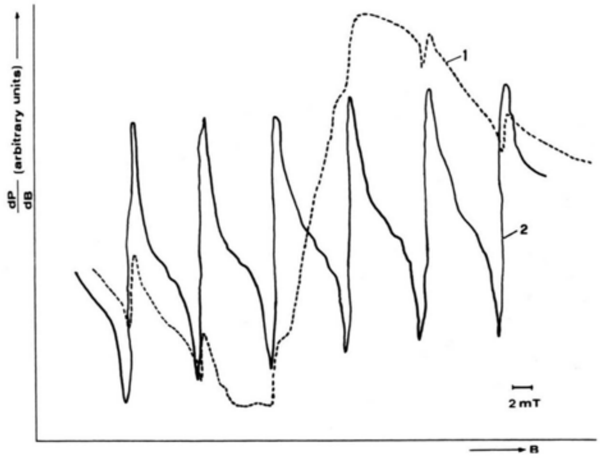

Fig. 2. ESR-spectra of the phosphors I (1) and (II) (2), plotted at room temperature in the X-band region (9.4 Gc/per sec).

For II the well known sextet due to the Mn^{2+}-ions in tetrahedral environment (T_d-symmetry) as in the fired ZnS-Mn is observed; for I a more complicated ESR spectrum is registered (Figure 2). This is in accordance with the spectral position of the luminescence band: the band of II is located nearer to the Mn band in III than the band typical for I.

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The luminescence bands of both I and II are to be considered as non-elementary – their spectral positions turn out to depend on the wavelength of the exciting light (Fig. 1); for the fired ZnS-Mn (III) the luminescence spectrum does not change with the energy of the exciting photons. To explain this observation it is reasonable to suppose the existence of at least two kinds of luminescent centres in I and II. In this case the relative intensities of the superposed elementary bands could be different on excitation with the 254 nm and 365 nm Hg-lines; at 254 nm, band-band transitions followed by energy transfer to Mn-centres occur, whereas at 365 nm, absorption in the Mn-ions should also be expected. In phosphor II, centres of T_d-symmetry located in the bulk are predominant and therefore the luminescence band of II (Fig. 1, curve 4) lies near to the emission band of III (curve 5). The fact that the emission bands of II and III do not coincide, as the ESR spectra do, is probably due to considerably more effective excitation of the longwave Mn-centres in II in spite of their low concentration. Curve 3 is displaced to longer wave lengths relative to 4 because the longwave centres are excited to a higher extent by the Hg-365 nm line. A relatively strong longwave shift takes place with curve 2 since the concentration of longwave centres in I is much higher than in II. In accordance with the assumptions made above a maximal shift to the longwave region is observed for the band of I excited at 365 nm (curve 1).

Having in mind the high dispersity of precipitated ZnS phosphors [1] and the smaller size of the primary particles of I compared to II [2], we assume that Mn centres with lower symmetry, located on the surface or near to it and therefore represented relatively strongly in I, are responsible for the longwave Mn emission. Formation of Mn-Mn associates may also contribute to the longwave shift of the activator band. According to [3], the interaction between Mn-ions in fired ZnS-Mn leads to short-wave band displacement. However, our investigations show that for I and II a considerable shift to longer waves occurs when the activator concentration increases [2, 4]. In fired ZnS-Mn a longwave band (632 nm) in reported to appear only at low temperatures [5].

[1] K. Kynev, Proc. of Intern. Conference of Luminescence, 1966, Budapest, p. 1229.
[2] S. Angelov, K. Petrov, N. Maneva, and K. Kynev, to be published.
[3] A. A. Andreev, N. D. Borisenko, F. F. Kodzhespirov, and A. Polezhaev, Zh. Prikl. Spectrosk. **36** (4), 679 (1982).
[4] K. Kynev and N. Preslavski, C. R. Acad. Bulg. Sci. **22,** 1103 (1969).
[5] N. E. Gumlich, J. Luminescence **23** (1–2), 73 (1981).