

EXCITATION AND EMISSION CHARACTERISTICS OF PRESSURE PRETREATED SrS : Mn : Ce PHOSPHORS

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ABSTRACT

Excitation and emission spectra of SrS : Mn : Ce phosphors have been studied in detail at various Mn and Ce concentrations. In order to study the effect of external pressure on phosphors, the samples were pretreated under various pressures. Four bands around 470 nm, 530 nm, 310 nm and 620 nm were observed, when the samples were excited with 265 nm radiation. The effect of pressure is to reduce the fluorescence ability of the phosphors, and the luminescence vanishes above 0.1 ton m^{-2} pressure. The fluorescence ability, however, can be regained on re-firing the sample. The emission mechanism has been attributed to two luminescent centers in the forbidden gap. An appreciable amount of photocurrent has also been observed for the sample.

1. INTRODUCTION

THE presence of divalent and trivalent cation impurities in alkaline earth sulphides modify their properties, in particular, the electrical and optical properties. The nature and energy states of the luminescence centers involved in the fluorescence emission can be understood well by studying the effect of the activator doped in the matrix. Although much work has been done on the fluorescent emission of CaS and SrS phosphors doped with transition and rare earth elements, the exact nature of the luminescence centers has not yet been clearly understood¹⁻³.

Sivaraman and Sinha² explained the observed bands at 470 nm and 560 nm for SrS : Zr phosphors by assuming the formation of a level in the forbidden band due to sulphur ion vacancies. Niranjana Bhat *et al.*³ reported two bands at 580 nm and 640 nm for SrS : Mn : Zr phosphors and attributed the emission process to the excitation and recombination taking place in a complex centre in the forbidden band. The model proposed by them was in accordance with their observation of the non-existence of photocurrent in SrS : Mn : Zr phosphors. However, a study of SrS : Mn : Ce phosphors in our laboratory revealed the existence of an appreciable amount of photocurrent, which, necessitates the proposal of a different model for interpreting the excitation and emission processes in these phosphors. In this paper we report the results of the excitation and fluorescence studies of SrS : Mn : Ce phosphors. Detailed work on the photoconductivity of SrS : Mn : Ce phosphors will be published elsewhere.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of the Phosphor

All the raw materials used for the preparation of SrS : Mn : Ce phosphors were of analar grade.

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Strontium sulphate mixed with sodium thiosulphate (flux), required amount of activated carbon (reducer) and aqueous solutions of ceric ammonium sulphate and manganese chloride provided the charge which was fired in covered crucibles of silica at 900°C for half an hour. The powder thus obtained was pelletised into circular discs at 0.01 ton m^{-2} and 0.03 ton m^{-2} pressure in a hydraulic press. One set of these pelletised samples was re-fired at 900°C . The samples were prepared with Mn concentration at 0.01% by weight, and Ce concentration at 0, 0.0025, 0.004, 0.005, 0.0075 and 0.01% by weight, and Ce concentration at 0.005% by weight and Mn concentration at 0, 0.005, 0.0075, 0.015 and 0.02% by weight. These samples were designated S-1, S-2, S-3, S-4, S-5, S-6, S-7, S-8, S-9, S-10, S-11 and S-12. S-1 is a self-activated sample (Mn 0%, Ce 0%).

2.2. Fluorescence and Excitation Spectra

The fluorescence and excitation spectra of SrS : Mn : Ce phosphors have been studied at room temperature using the Aminco Bownan spectrophotofluorometer, and Xenon lamp as the source. Corrections in the spectra, due to spectral sensitivity of the photomultiplier tube and dispersion of the monochromators, have been applied. The slit widths of the exciting and analysing monochromators were kept at 0.15 mm to avoid the effect of the other wavelengths present.

3. EXPERIMENTAL RESULTS

Fluorescence spectra of the phosphors were recorded at 265 nm and 365 nm excitation. The 265 nm excitation revealed a peak at 310 nm and two prominent peaks at 470 nm and 530 nm. The long wavelength tail of 530 nm band is enhanced in emission and, for a number of samples, a peak centred around 620 nm is also observed (Figs. 1 and 2 show the emission spectra of samples S-1, S-2, S-5, S-6, S-8, S-9 at 265 nm excitation). The 265 nm excitation favours emission at 470 nm and 530 nm while the 365 nm excitation favours 530 nm emission only. It was

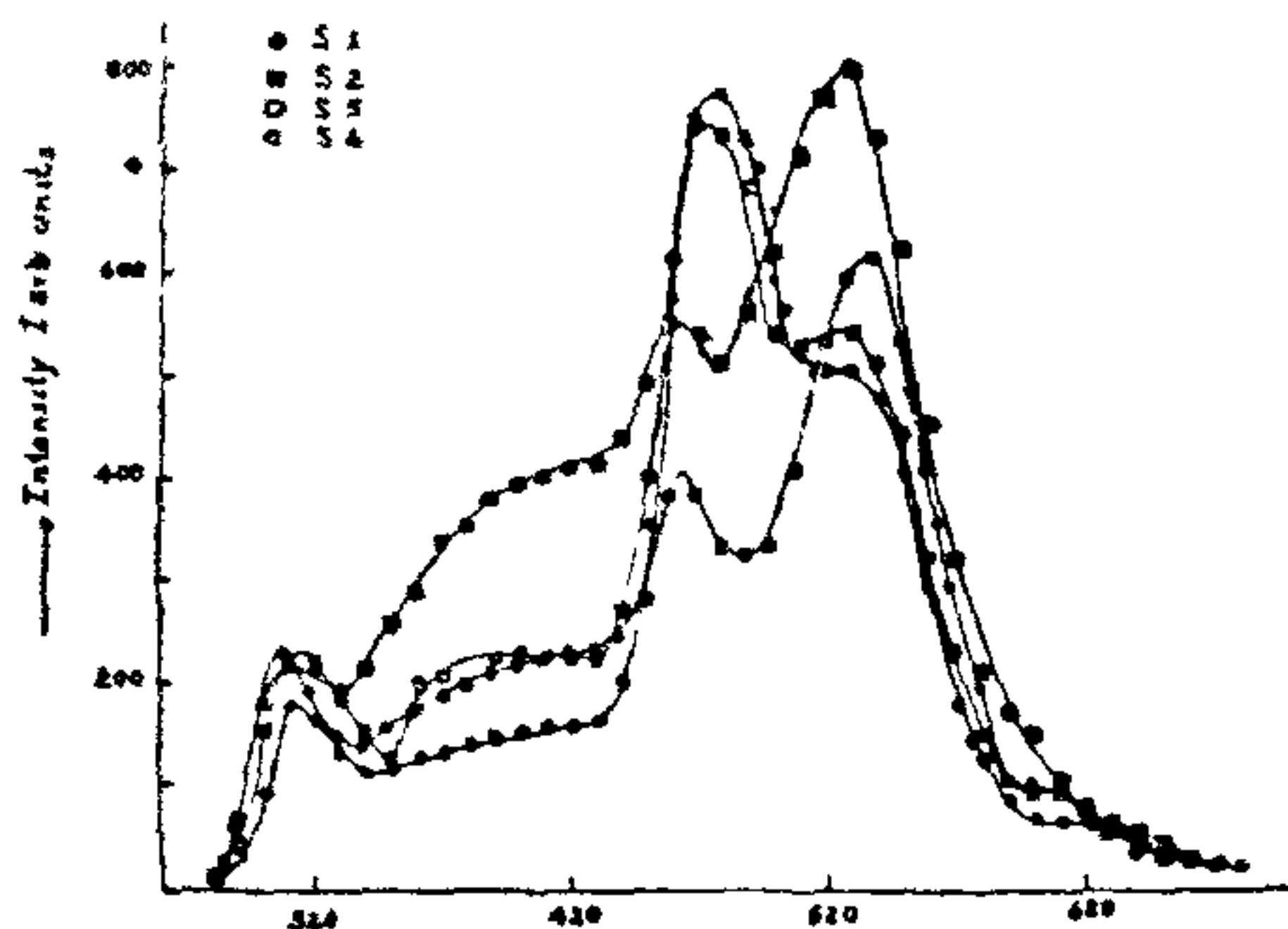


FIG. 1. Fluorescence emission spectra of SrS : Mn : Ce phosphor samples at 265 nm excitation : (1) S-1; (2) S-2; (3) S-5; (4) S-6.

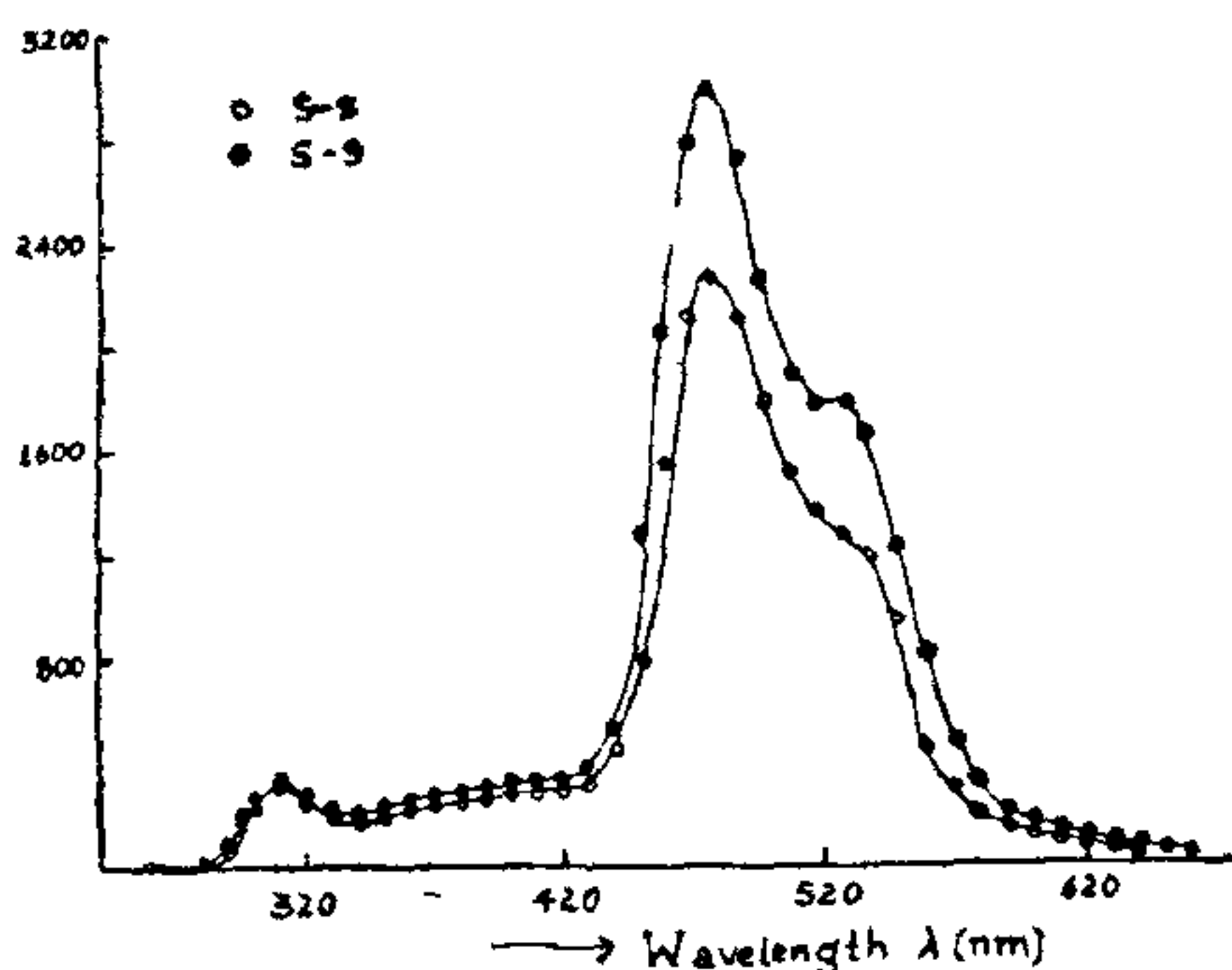


FIG. 2. Fluorescence emission spectra of SrS : Mn : Ce phosphor samples pretreated at 0.01 ton m^{-2} pressure at 265 nm excitation : (1) S-8; (2) S-9.

found that the 265 nm excitation was favoured when the excitation spectrum of the samples were recorded at 470 nm, 530 nm and 630 nm emission. On analysing the intensity curves it is found that the intensity of the 470 nm band increases at the cost of the 530 nm band. Fluorescence efficiency is diminished by the application of pressure during pelletisation of the phosphor samples. On refiring the efficiency is regained. However, the spectra of refired samples show an increase in intensity of the 540 nm band at the cost of the 470 nm band (Fig. 3). Almost all samples show appreciable photocurrent.

4. DISCUSSION

The energy distribution of the fluorescence spectrum obtained depends only slightly on the nature of the activator ions as is evident from Figs. 1 and 2. This

indicates that the activator ions themselves are probably not the luminescence centers. The activator ions disturb the host lattice in the immediate vicinity in such a manner that the transition probability is increased as is evident from the increase in the intensity of emission.

Luminescence of self-activated SrS indicates the presence of luminescence centers which may arise due to the defects in the lattice giving rise to localised levels in the normally forbidden range. The lattice defects may possibly occur due to anion and cation vacancies⁴. The presence of the 470 nm and 540 nm bands may be attributed to the presence of two compounds SrS and SrO, but this possibility is ruled out as X-ray diffraction studies indicate that SrO is not formed with SrS during heat treatment. The intensities of both the bands increase and decrease together and the total energy of the emission bands (2.34 eV, 2.64 eV) is greater than the band gap of SrS (4.8 eV)⁵. A close observation of the change (increase or decrease) in the relative intensities of the bands indicates that the intensity of the 470 nm band increases at the cost of the 530 nm band. Also, an appreciable amount of photocurrent has been observed in the SrS : Mn : Ce phosphors which calls for a different model. The fact, that the intensity of the 470 nm band increases at the cost of the 530 nm band, as the activator concentration is varied indicates that two luminescence centers (class I and class II) exist in the forbidden, energy region (Fig. 4). Class I centers may be associated with the 470 nm emission and class II to the 530 nm emission.

The fluorescence band observed at 310 nm may be attributed to an exciton (transition 1 in Fig. 4). The weak emission in the orange-red region can occur due to the interaction between Mn^{2+} ions and excitons, which will be confirmed later by a study of fluorescence spectra of the phosphors at low temperatures. Such results have been obtained in the case of CaS : Mn : Ce phosphors for Mn emission in the 580 nm region⁶.

The presence of photoconductivity suggests that the excitation process involves the motion of free electrons and holes. Free electrons and holes are formed as follows :

Transition 2 corresponding to absorption, raising an electron from the valence band to an unoccupied imperfection level, producing a free hole and an electron bound in the neighbourhood of the imperfection for each photon absorbed (Fig. 4).

Transitions 3 and 4 corresponding to absorption at localised imperfections in the crystal, producing a free electron and a hole bound in the neighbourhood of the imperfection for each photon absorbed.

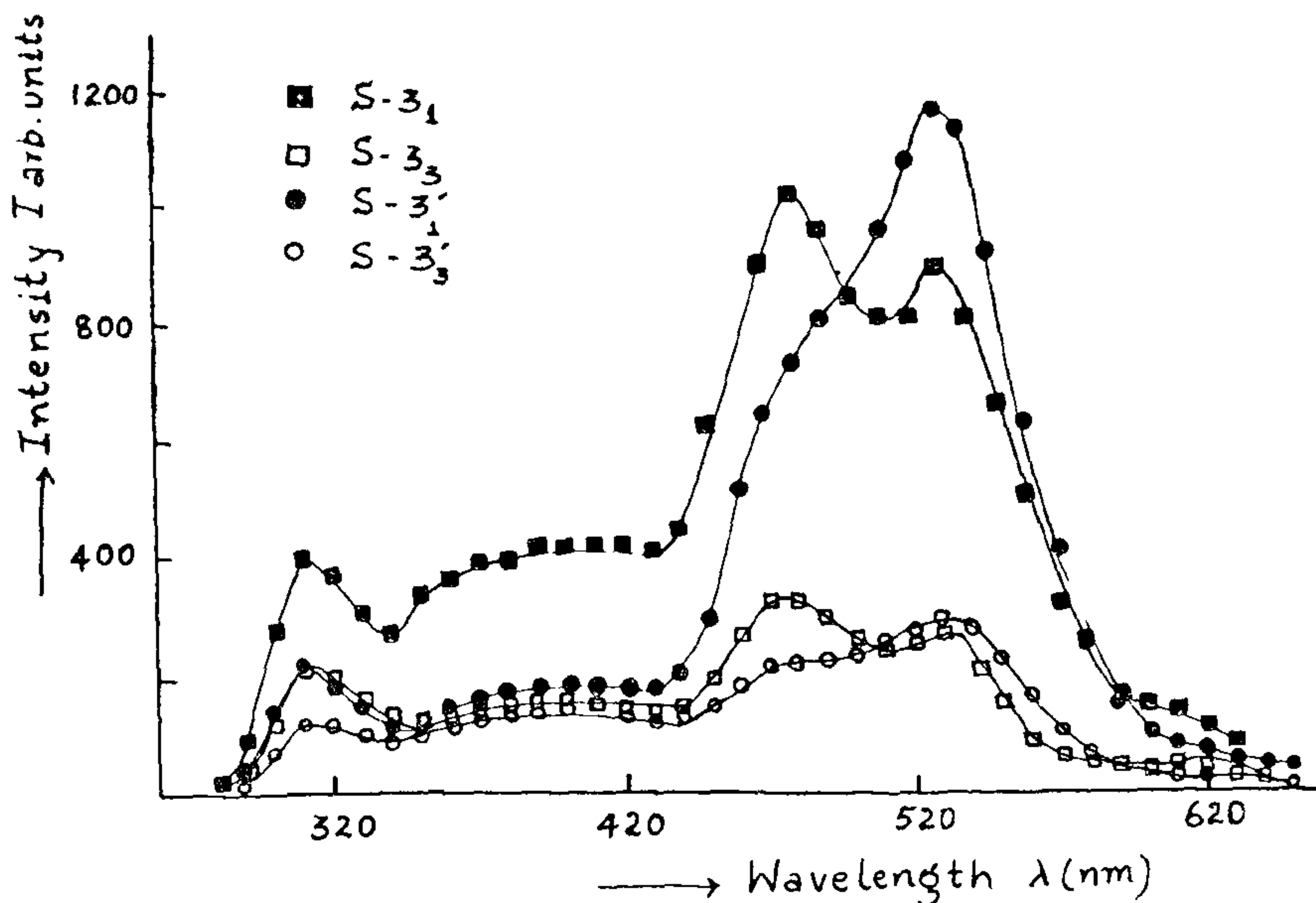


FIG. 3. Fluorescence spectra of S-3 excited at 265 nm under various conditions: (1) S-3 pretreated under 0.01 ton m^{-2} pressure ($S-3_1$). (2) S-3 pretreated under 0.03 ton m^{-2} pressure ($S-3_0$). (3) S-3 pretreated under 0.01 ton m^{-2} pressure and refired ($S-3'_1$). (4) S-3 pretreated under 0.03 ton m^{-2} pressure and refired ($S-3'_3$).

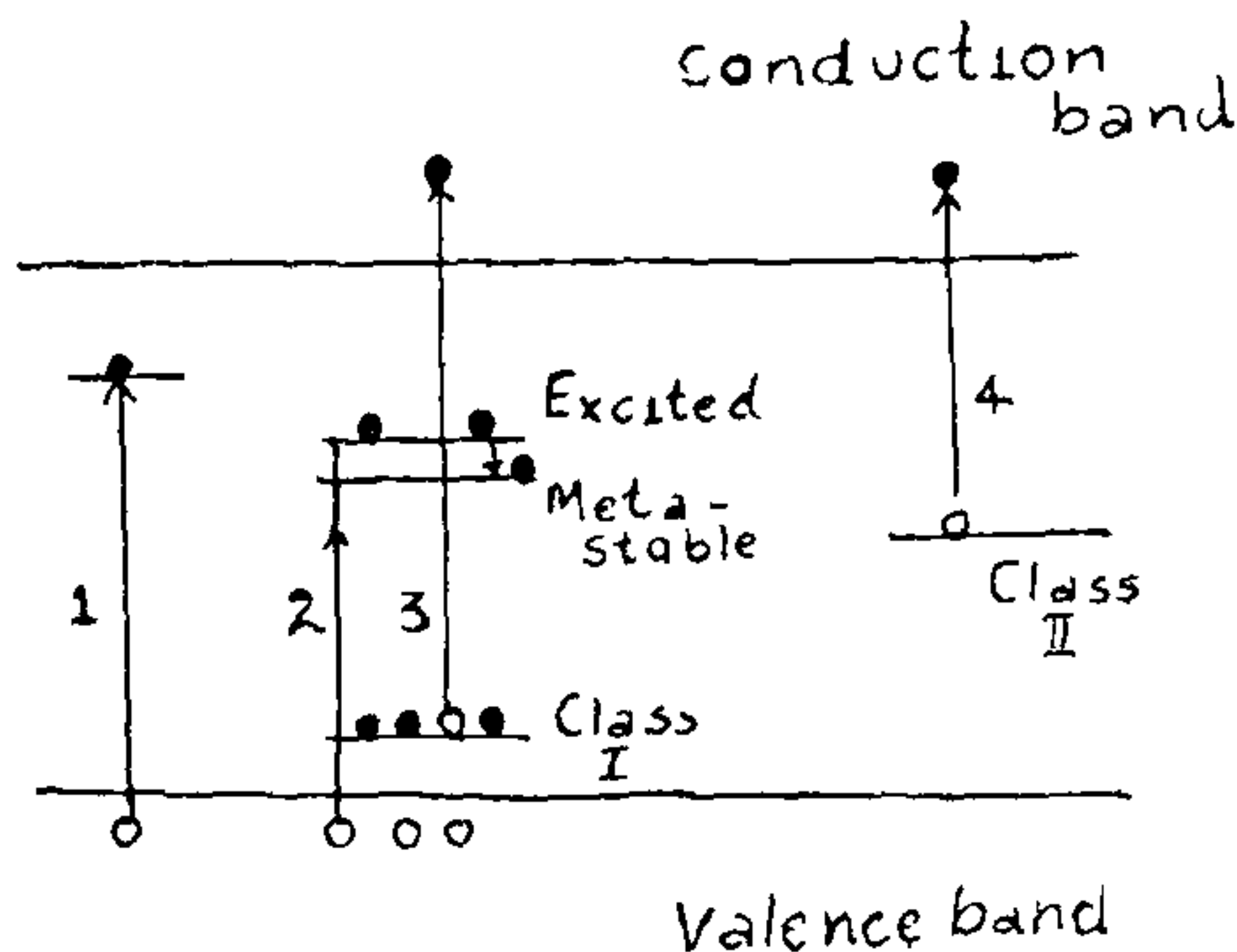


FIG. 4. Proposed model for fluorescence emission in SrS : Mn : Ce phosphor.

The luminescence property of the phosphor is completely destroyed when the samples are pretreated under high pressures. Above 0.1 ton m^{-2} pressure, the samples do not show any luminescence at all. At intermediate pressures of 0.01 ton m^{-2} and 0.03 ton m^{-2} samples regain the luminescence property on refiring, with the band at 530 nm being more intense

than that of the 470 nm band. From this, it is evident that, external pressure changes the nature and distribution of the luminescence centers.

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