

EMISSION SPECTRA OF TRIPLE ACTIVATED SrS PHOSPHORS

A.P. RAO

B.N. College of Engineering, Pusad (M.S.), 445215, India

O.P. SINHA

SSLJ Post Graduate College, Vidisha (M.P.), 464001, India

V.G. MACHWE AND A.S. MEHTA

S.A. Technological Institute, Vidisha (M.P.), 464002, India

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Fluorescence spectra of strontium sulphide phosphors activated by three activators viz. Mn, Cu, and Gd individually and in different combinations have been discussed at length. X-ray is used as excitation source. Probable inferences are drawn regarding energy transfer phenomenon. The two channels for transfer of energy are concluded in present phosphor series. A model is also proposed.

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1. Introduction

Luminescence properties of polycrystalline powder phosphors have been studied widely so far by many researchers. The roughness of powder phosphors plays major role in the properties of emitted light which is related to trapped impurity [1]. The alkaline earth sulphide phosphors have been found more efficient if double or triple activators are used [2]. SrS has been selected as the base material because it shows sensitivity with an ability for energy storage and quick response [3-5]. Hence fluorescence emission of SrS:Mn,Cu,Gd phosphor is carried out to seek information about energy levels operative at 299 K.

2. Experiment

The purification of basic ingredients and preparation are reported in our earlier publications [6, 7]. In short, analytical reagent grade strontium sulphate mixed with appropriate amount of carbon (reducing agent), sodium thiosulphate (flux) and activators (Gd, Mn and Cu in different concentrations) is fired at 1200 ± 10 K. Using Bhawalkar's method, three series of phosphors are thus prepared (Table I). These phosphors are excited by X-rays (Philips X-ray machine type 11704) operated at 30 kV, 10 mA, using Cu target, and emission is recorded on Bellingham and Stanley spectrometer coupled with IP-21 photomultiplier tube. In each series, all the three activators are present, out of which two are kept constant and the third one is varied successively.

TABLE I

Sample details and fluorescence emission spectra at temperature 299 K.

Serial No.	Sample Nos.	Concentration of activators			Peak wavelength in nm	Peak intensity in arb. units
		Copper	Manganese	Gadolinium		
1	24	1×10^{-6}	2×10^{-2}	—	550	84
2	16	—	2×10^{-2}	—	575	225
3	22	1×10^{-6}	—	—	532	45
4	27	—	—	1×10^{-4}	532	78
5*	A1	1×10^{-6}	2×10^{-2}	1×10^{-3}	546	20
6	A2	1×10^{-6}	2×10^{-2}	5×10^{-3}	544	56
7	A4	1×10^{-6}	2×10^{-2}	5×10^{-2}	556	84
8	A5	1×10^{-6}	2×10^{-2}	7×10^{-2}	550	116
9	A'	1×10^{-6}	2×10^{-2}	9×10^{-2}	555	85
10	A7	1×10^{-6}	2×10^{-2}	1.8×10^{-1}	551	72
11	B2	1×10^{-6}	1×10^{-3}	9×10^{-2}	551	43
12	B3	1×10^{-6}	3×10^{-3}	9×10^{-2}	552	75
13	B4	1×10^{-6}	5×10^{-3}	9×10^{-2}	547	85
14	B5	1×10^{-6}	8×10^{-3}	9×10^{-2}	555	97
15	B'	1×10^{-6}	2×10^{-2}	9×10^{-2}	555	85
16	B7	1×10^{-6}	2×10^{-2}	9×10^{-2}	554	47
17	C'	1×10^{-6}	2×10^{-2}	9×10^{-2}	555	85
18	C3	5×10^{-5}	2×10^{-2}	9×10^{-2}	556	47
19	C4	1×10^{-4}	2×10^{-2}	9×10^{-2}	556	45
20	C7	5×10^{-3}	2×10^{-2}	9×10^{-2}	563	25
21	C8	1×10^{-2}	2×10^{-2}	9×10^{-2}	556	19

* Concentration of activator is per 10 g of base material.

3. Result and discussion

The result of representative samples are shown in graph (Fig. 1) and the numerical values are tabulated in Table I. In series *A*, Gd alone varies while Cu and Mn are kept constant. The wavelength of emission peak lies between 544 nm and 556 nm for various concentration of Gd. However, change in peak intensity has been observed in series *A*. In series *B*, in which Mn alone varies while Cu and Gd are constant, the peak wavelength varies between 547 nm and 555 nm. A small but slight shift towards higher wavelength side can be seen with rise of concentration of Mn. While in series *C*, in which Cu alone varies, the peak wavelength of emission intensity is obtained between 547 nm and 563 nm with irregular variation of shift of peak wavelength with change in concentration of copper. In general, only one emission band is observed for all the three series *A*, *B* and *C* (refer Table I). The concentration of activator seems to play interesting role in present series of phosphors. When the peak intensity of emission reduces with increase in concentration of activators (other than concentration quenching), it is attributed to the defect of matrix or host. This has not been observed in present case. The prepared phosphors do not show presence of SrO as tested by X-ray diffraction method and hence do not contribute to luminescence [8]. Thus, it seems reasonable to associate the observed band to the impurity rather than defects. The pointwise discussions are given below.

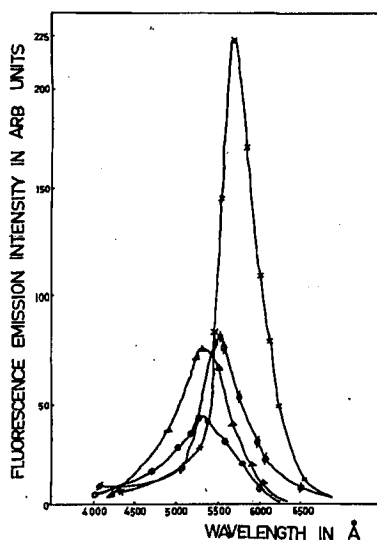


Fig. 1. Variation of fluorescence emission intensity with wavelength of SrS:Cu,Mn,Gd phosphors at 299 K: \times — 16, ϕ — A4, Δ — B3, \circ — C4.

3.1. Gadolinium impurity

The emission due to Gd is reported [9]. Aterkar et al. [10] reported four lines of Gd in CaS lattice doped simultaneously with Sm. Instead of lines, a band emission has been reported by Laud and Kulkarni [11] in SrS:Gd when doped simultaneously with Cu at 553 nm. It is attributed to Gd by the same author. Pringsheim [12] reported that Gd alone is not fluorescent in SrS. In present case no emission line is observed. A band in the region of 548 nm is observed in series A, where Gd alone varies. This may be due to sensitization by other activators present. According to Laud and Kulkarni, the increase in concentration of Cu enhances peak intensity and shifts the band from 548 nm to 553 nm. Kingsley [13] reported that no energy transfer is possible to Gd from Cu in ZnS:Cu,Gd phosphors because of the fact that lowest excited state of Gd^{3+} is greater than band gap of ZnS. But this compatibility is not faced by SrS because of its wider band gap. Therefore, energy transfer is possible to Gd from copper in this case. The strong phosphorescence of the present phosphor also favours such transfer of energy. The luminescence of Gd^{3+} ion arises from transition due to excited ${}^6P_{7/2}$ state to the ground ${}^8S_{7/2}$ state. It becomes possible for Gd to be sensitized, if emission of some other activator overlaps the absorption edge of Gd. The energy transfer from Gd^{3+} ion to activator is subjected strongly on the nature, site and concentration of other activators incorporated in addition to Gd. In the present case Gd^{3+} with Na^+ as a charge compensator may be substituting for two Sr^{2+} ions. This model of charge compensation gets supported by observing the shift of band-peak wavelength towards higher wavelength side with increase in concentration of Gd^{3+} ions (series A). In CaF:Gd,Mn intracentric energy transfer due to non-cubic centres of Gd^{3+} is reported [14] and concluded that Gd centres do not exhibit emission themselves. However, the observed variation of emission intensity in present series of phosphors can be attributed to Gd and can help in deriving conclusion that it acts as an activator. After increasing the concentration of Gd from 7×10^{-2} g the decrease in intensity may be attributed to concentration quenching due to dense ion packing that in turn give rise to nonradiative transitions and favours sensitization of ions.

3.2. Manganese impurity

Gd^{3+} has preferential tendency to transfer energy to Mn^{2+} , thus Mn gets normally sensitized by Gd^{3+} in these lattices [15, 16]. The energy transfer from sensitizer to activator becomes predominant at lower concentrations. In the present case it may be inferred that Gd may be transferring its energy to Mn^{2+} and playing a role of mediator. The energy transfer from Gd to Mn^{2+} may possibly be taking place by resonance transfer. The ionic radii and ionic charges favour Gd^{3+} to be substitutional. The energy levels of Mn^{2+} are 6S , 4G , 4P , 4D and 4F where 6S is a ground state. Mn^{2+} after reaching higher excited state transfers energy nonradiatively to the adjacent lower excited state until it reaches back lowest 4G excited state. It can be assumed that emission is due to transition within Mn^{2+} ions as the gap between lowest excited state and ground state prefers radiative transfer of energy. Manganese gives fluorescence band in yellow-orange region and it is reported to be due to Mn^{2+} state having d^5 configuration [17]. Mn^{2+} is

known to be a classical acceptor in energy transfer because of $3d \Rightarrow 3d$ forbidden transition in visible and near UV region. In series *B* (concentration of Mn varies only) it has been observed that with increase in concentration of Mn, increase in intensity of the band takes place up to sample B5 beyond which decrease in intensity is observed. This can be attributed to concentration quenching.

A band in SrS phosphor is observed at 575 nm when doped only with Mn (sample No. 16). Band at 580 nm has been reported by Sivraman [18] in SrS:Mn,Zr phosphors and Bhushan [19] has reported a band at 560 nm in SrS:Mn phosphors. Resonance transfer of energy to Mn from other incorporated activators has been concluded by Bhushan [20]. Our results of series *B* are in accordance with these interpretations.

3.3. Copper impurity

For series *C*, sample *C'* exhibits maximum intensity which further decreases with increase in concentration of copper. This fact supports the idea of concentration quenching. Sample C7 indicates peak wavelength at 563 nm. However, peak wavelength of sample SrS:Cu,Mn (sample No. 24) shifts to lower wavelength side, which favours sensitization of Mn^{2+} by Cu^{2+} . The decrease in intensity may be assigned to destructive dipole-dipole interaction on account of closeness of dopant ions and probably energy transfer may be taking place by magnetic dipole-dipole interaction rather than forbidden [21] electronic dipole-dipole interactions.

Emission from Mn^{2+} seems to dominate in all the three series viz. *A*, *B* and *C*. The ionic radii of Cu (0.96 Å) and Mn (0.80 Å) favour substitutional and interstitial site, along with Gd at substitutional site.

4. Conclusion

It seems probable that energy from Cu^{2+} may be transferred directly to Mn^{2+} and also via Gd^{3+} . There may be two ways for transferring energy in present case. A cascade mechanism is expected to be involved between Cu and Gd. And finally the energy may be transferred to Mn by resonance transfer. Band spectra of Mn^{2+} may be attributed to the electronic transition, involving the outermost electrons whose resultant principal angular momentum and spin quantum number change during transitions. Usually increase in temperature of phosphor results in higher probability of radiationless transition within the activator ions and results in temperature quenching. In the present case decrease in intensity of emission is observed without shift of the peak when fluorescence is recorded at temperature 363 ± 2 K (Fig. 2 and Table II). This lowering of intensity can be attributed to interaction of thermally released and optically released carriers causing dissipation of energy to the lattice and hence lowering of peak intensity is observed.

A comparative study of phosphorescence peak of samples (Fig. 3) and its spectral shift (Table III) supports the importance of sensitization, charge compensation and concentration quenching.

Averaged out trap levels are formed almost at one depth irrespective of concentration of activators in all the series. This has been also confirmed by thermoluminescence and emission decay studies of the phosphors [22, 23].

TABLE II
Fluorescence emission spectra at temperature 363 ± 2 K.

Serial No.	Sample Nos.	Peak wavelength in nm	Peak intensity in arb. units
1	A1	546	16
2	A2	544	40
3	A4	556	68
4	A5	550	90
5*	A'/B'/C'	555	70
6	A7	551	50
7	B2	551	30
8	B3	552	57
9	B4	547	62
10	B5	555	71
11	B7	554	25
12	B8	555	22
13	C3	556	34
14	C4	556	30
15	C8	563	17
16	C8	556	10

* Sample common to all three series.

TABLE III
Phosphorescence emission spectra at temperature 299 K.

Serial No.	Sample Nos.	Peak wavelength in nm	Peak intensity in arb. units
1	A4	570	31
2	A6	560	60
3	B3	565	29
4	B4	565	34
5*	A'/B'/C'	547	35
6	B7	560	50
7	C3	575	44
8	C7	570	31

* Sample common to all three series.

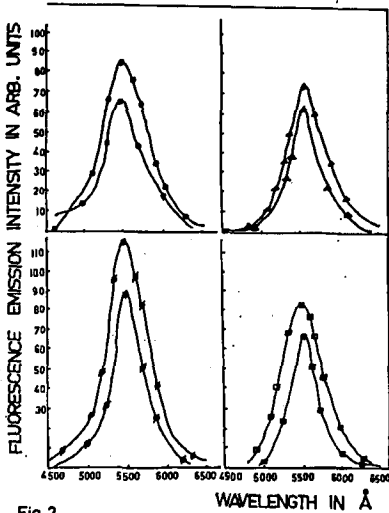


Fig. 2

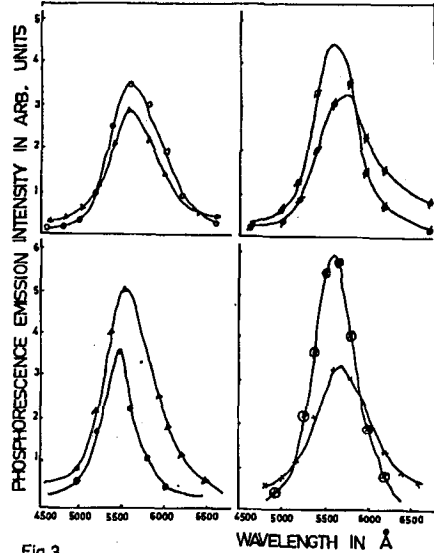


Fig. 3

Fig. 2. Comparison of variation of fluorescence emission intensity with wavelength of SrS:Cu,Mn,Gd phosphors at 299 K and 363 ± 2 K: \circ — B4, Δ — C2, ϕ — A5, \square — A4 at temperature 299 K, \bullet — B4, full Δ — C2, full ϕ — A5, \blacksquare — A4 at temperature 363 ± 2 K

Fig. 3. Variation of phosphorescence emission intensity with wavelength of SrS:Cu, Mn,Gd phosphors: \times — A4, \otimes — A6, Δ — B3, \circ — B4, \bullet — B', full Δ — B7, ϕ — C3, full ϕ — C7.

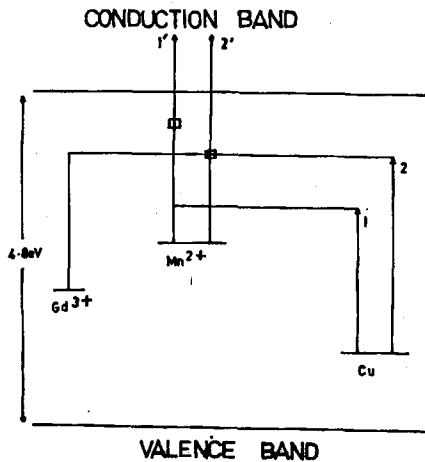


Fig. 4. Proposed model: 1 — Cu, Mn resonance transfer, 2 — Cu, Gd cascade, 1' and 2' — outcoming radiation dominated by Mn^{2+} .

The proposed model (Fig. 4) explains the observed emission as an average result of competition between two channels of energy transfer.

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