A new red colour emitting phosphor - ZnS: Mn co-doped with Ba for electroluminescent (EL) display devices

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Abstract

We prepared a new Mn activated ZnS phosphor co-doped with Ba that showed an interesting shift in the spectral emission from amber-yellow to red colour. We believe it to be an important result to understand the underlying Physics and for display devices. To realize this, attempts were made to fine tune the band gap of ZnS with various concentrations of Ba co-doping within the concentration range of 2.50 to 10 mol%. Upon the addition of Ba 2+ into the Mn activated host lattice of ZnS, a significant shift in the emission band from amber yellow (570nm) to red (620nm) was observed. Ba co-doping in ZnS host was achieved by sintering BaSO4 with ZnS at 900°C by carbothermal reduction method.

Keywords: Phosphor, Zn(1-x)Ba_xS:Mn, Photoluminescence (PL), red emission.

Introduction

Zinc sulfide (ZnS) is an important host material for the preparation of phosphors (luminescent solids) for cathode ray tube and various display device applications. ZnS:Mn is an excellent thin film phosphor widely used in electroluminescence (EL) panels as an amber yellow colour emitting phosphor. It emits a broad band spectrum with a peak wavelength maximum at 582nm due to \(^5\)G\(^{4}\)T\(_1\) \(-\) \(^6\)S\(^{6}\)A\(_1\)) transition. For a full colour EL display application, the amber light is filtered with red filters. This process tends to decrease the intensity of emitted light. In order to avoid this problem, development of individual phosphors that emit at red and green wavelength regions is an essential step to realise full-colour-emission of EL panels with high resolution. Based on the argument, by manipulating the defect manipulation in the solid and the subsequent changes in the crystal properties in the desired host materials, essentially any colour can be represented over the entire portion of the visible spectrum viable for display device applications. Indeed for the first time, we observed red emission from Ba co-doped ZnS: Mn system. The colour tuning of ZnS: Mn phosphor emission wavelength has previously been accomplished by altering the band gap of materials. For example, a gradual increase of Mg concentration in Zn\(_{1-x}\)Mg\(_x\)S:Mn leads to shorter emission wavelengths from amber to green. Therefore, emission colour is primarily determined by the magnitude of the band gap rather than the nature of dopant atom (Mn)

In this work, we have synthesized the Mn activated Zn\(_{1-x}\)Ba\(_x\)S phosphor by carbothermal reduction in conventional solid state method. The results of powder x-ray diffraction (XRD) and structural aspects, photoluminescence (PL) and photoluminescence excitation (PLE) studies of Zn\(_{1-x}\)Ba\(_x\)S phosphors are also discussed.

2. Experimental Details

2.1 Sample preparation

Samples of composition Zn\(_{1-x}\)Ba\(_x\)S:Mn (0 < x < 10mol %), with an increment in x by 2.5 mol%, were prepared by carbothermal reduction method through solid state reaction. To begin with, chemical ingredients consist of ZnS (Central Drug House – CDH, India), BaSO\(_4\) (CDH, India), and MnSO\(_4\).H\(_2\)O were weighed in stoichiometric proportions along with excess sulfur and then mixed thoroughly in an agate mortar to form a homogeneous mixture. This step was crucial to maintain the stoichiometry of the phosphor. The powder mixture was heated at 900°C for 5h in a reducing carbon atmosphere in a muffle furnace.
2.2 Characterization

The structural aspects of the parent compound and final product was monitored by X-ray powder diffraction (XRD) using Cu K\textsubscript{α} radiation (\(\lambda = 1.5405\ \text{Å}\)). Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded at room temperature with a fluorolog spectrophotometer by scanning the wavelength from 325 to 800 nm.

3. Results and Discussion

3.1 Phase identification

The powder X-ray diffraction traces of the parent compound and phosphor compositions with varying x in Zn\textsubscript{1-x}Ba\textsubscript{x}S:Mn\textsubscript{0.01} (0<\(x<10\) mol\%) calcined at 900°C for 5h are shown in Fig.1a. The parent ZnS compound showed its wurtzite – poly phase (8H and 10H\textsuperscript{*}) hexagonal structure with a lattice constants (3.82Å, 24.96Å & 3.82Å, 31.2Å) and phase group P\textsuperscript{6}3mc respectively. Addition of 2.5 – 7.5 mol% of Ba leads to minor shift in the (hkl) lines to lower angles compared to ZnS:Mn. Moreover, as the ionic radii of Ba (1.34Å) is larger than that of Zn (0.74Å), the lattice deformation may lead to the formation of BaS phase. At this juncture, it is important to note the formation of BaS is not observed at any concentration of Ba (fig. 1b). Whereas further addition of Ba beyond 7.5 mol% resulted in the formation of a new minor phase, along with the major ZnS phase. The minor phase (+) was identified as Ba\textsubscript{2}ZnS\textsubscript{3} which has an orthorhombic structure with a lattice constants \(a = 12.025, \ b = 12.62, \ c = 4.193\text{Å}^0\) (space group Pnam). There is no marked difference in crystallinity due to the addition of Ba to ZnS:Mn.

![Figure 1a: X-Ray diffractograms of Zn\textsubscript{1-x}Ba\textsubscript{x}S:Mn (0<\(x<10\) mol\%) phosphor heat treated at 900°C/5h.](image-url)
3.2 Spectral analysis – photoluminescence (PL)

The photoluminescence excitation (PLE) spectra of Zn$_{1-x}$Ba$_x$S:Mn$_{0.01}$ (0<x<0.10) phosphors (powder samples) are shown in fig 2. Photoluminescence (PL) excitation spectroscopy was carried out by fixing the emission wavelength at 582 nm for ZnS: Mn and 610 nm for Ba co-doped ZnS: Mn by varying the excitation wavelength from 250-550 nm. It was observed from the excitation spectra that the major peak obtained at 346 nm corresponds to band gap of host material (ZnS).

On addition of Ba to the host material the band gap modification was observed from excitation peak shift from 346 nm to 386, 374, 361, and 356 nm for 0, 2.5, 5.0, 7.5, and 10 mol% respectively. The composition dependence of band gap energy of host has been reduced from 3.67 to 3.23 eV which was estimated from the shift in the excitation peak. For a ZnS:Mn phosphor, multiple excitation peaks appear at higher wavelength apart from the host excitation. The excitation around 400 nm is probably due to Mn$^{2+}$ 3d transitions. It was reported that the absorption at 535, 495, 460, 425, 385 nm corresponds to transition from ground state to $^4T_1(^2G)$, $^4T_2(^2G)$, $^4A_1(^2E)$, $^4T_2(^2D)$ and $^4E(^2D)$ excited
states respectively. On Ba addition, all other peaks related to d energy levels transition diminish leading to a shift in the host excitation spectrum.

The plot of powder photoluminescence emission spectra of Zn\(_{1-x}\)Ba\(_x\)S:Mn\(_{0.01}\) (0<x<0.10) phosphors under UV excitation are shown in fig 3. The powder ZnS:Mn\(_{0.01}\) phosphor showed the amber yellow emission with the peak at 582 nm which results from \(^4\text{T}_1(4^G)\) \(\rightarrow\) \(^6\text{A}_1(6^S)\) (d-d) transition of Mn\(^{2+}\) ion. It was reported earlier that BaS:Mn emit at 541 nm. Upon Ba addition to the host material, the emission wavelength significantly shifts from 582 nm to, 610, 618, 619, and 623 nm for 0.0, 2.5, 5.0, 7.5, 10 mol\% respectively. Note that the shift in emission peak position is proportional to Ba concentration. It has been shown that in Zn co-doped MgS:Mn system, crystal field effects, changes in the bond length, and ionic fraction etc. could be responsible for the observed shifts in the emission spectra. We discuss the concentration dependence of Zn\(_{1-x}\)Ba\(_x\)S on Mn\(^{2+}\) emission on the basis of crystal field exerted by Ba ion which is assumed to play a major role changing perturbing the d orbital energy level scheme of Mn\(^{2+}\) luminescent centre. In ZnS:Mn, divalent Ba is expected to occupy the Zn site because of its positive valance state. Due to its larger ionic size, the crystal field stabilization energy (\(D_q\)) is expected to be large. Consequently this compound yields an emission to higher wavelength (lower energy) due to \(^4\text{T}_1 \rightarrow \text{A}_1\) transition of Mn\(^{2+}\) ion 3d state. Hence at x = 10 mol\% the photoluminescence emission wavelength peaked at 623 nm (red region). The Mn\(^{2+}\) ion in the host lattice site probably leads to increased phonon coupling because of higher Ba ionic size which may lead to lower energy shift of the spectrum by the number of average phonon annihilation associated in the transition, even if there is a smaller effect on the energy difference between \(^4\text{T}_1(4^G)\) and \(^6\text{A}_1(6^S)\) states. It appears that the red shift is closely related with the formation of Zn\(_{1-x}\)Ba\(_x\)S solid solution resulting in the changes in the crystal field and crystal relaxation processes. Our present work clearly demonstrates the formation of a new Ba-codoped ZnS:Mn phase that can be termed as a new ‘red-phosphor’.

**Fig 3: PL Emission spectrum Zn\(_{1-x}\)Ba\(_x\)S:Mn\(_{0.01}\) (0<x<0.10) phosphors**

**Conclusion**

We have developed Zn\(_{1-x}\)Ba\(_x\)S: Mn0.01 (0<x<0.10) as a new red emitting phosphor. This phosphor is shown to have a tunability in the emission wavelength from 583 nm to 623 nm as function of Ba concentration. The fundamental excitation and luminescent properties showed that, this composition range is best suited electroluminescent applications without any need for filter.

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