

Photoluminescence Study of Solid-State Synthesized Nanophosphor

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ABSTRACT

In the present work the nanophosphor BaS:Bi was prepared by solid state diffusion method which shows high intensity PL excitation and emission at 425 nm and 575 nm which corresponds to green color. However, for bulk phosphors emission peak is obtained at 608 nm corresponding to red color. Hence, a blue shift is observed in the spectrum. The optimize amount of activator (Bi) was found to be 0.3 mole% of BaS. The nature and amount of flux has a considerable effect on the peak intensity of the luminescence spectrum. The crystal phase was confirmed by XRD technique and mean size of the particles was determined by using Debye-Sherrer equation and found to be 20 nm, which was nearly same as observed in TEM. The SEM image shows the agglomeration of constituting particles.

Keywords : PL, nanophosphor, XRD, SEM, TEM.

I. INTRODUCTION

Alkaline earth sulphides provide a unique host because of their wide band gap and high insulating nature. These phosphors belong to very old group called Lenard phosphors. AES are the divalent counterpart of alkali halides in the sense that the constituents II B – VI A ions have close shell electronic configuration and crystallize into NaCl type structure. Their luminescence and the related properties have been reviewed from time to time.

Luminescence and related properties of AES phosphors [1,2] activated with various impurities have been widely studied. BaS is a crystalline solid of white color, oxidizes in air to produce yellowish color, having an indirect band gap of 3.8 eV in bulk,

fcc rock salt structure (NaCl type) belonging to same family.

For many years, wide band gap II-VI compounds (the compounds formed from the elemental group II and VI of periodic table such as CdS, ZnTe, ZnSe and ZnS) have been of great interest since they exhibit excellent luminescence properties. Most of them possesses high carrier mobilities and are known to be good photoconductors. Their spectral sensitivity ranges from ultraviolet (ZnS) to infrared (CdHgTe). Recently with tendency of optoelectronics towards the ultraviolet and near infrared region, impurity doped CaS, CaSe and BaS have been studied extensively because they are wide band gap semiconductors; this gives importance in the context of development of display devices, radiation detection, lamp industry,

in digital radiography as storage phosphors and also will be helpful in understanding the effect of crystal field in free ions energy levels. Amongst the class of sulphide phosphors CaS [3,4] has been extensively studied. Due to unique properties and applications, materials made up of particles with diameter less than 100 nm termed as nanomaterials have attracted a great deal of attention [5]. The stability, durability and higher efficiency of these luminescence nanocrystallites have replaced all existing bulk phosphors.

Just like CaS; BaS is also wide band gap material belonging to AES family which exhibit excellent and efficient properties. It has been found that there is no report of BaS nanophosphors; which stimulated to prepare BaS:Bi nanophosphors and to explore this area further.

II. SYNTHESIS OF BAS NANOPHOSPHORS

Solid state method is one of the methods [6,7] which is used for the preparation of nanophosphors. According to this method, two reactions are assumed to take place at higher temperature of firing:

- ✓ Reduction of the alkaline earth sulphides to its sulphide by a reducing agent.
- ✓ Incorporation of the activator in the presence of suitable flux.

Initially sulphate of required lattice ($\text{BaSO}_4 \cdot 2\text{H}_2\text{O}$), reducing agent (C, H_2 or CS_2) and flux ($\text{Na}_2\text{S}_2\text{O}_3$) are mixed in a clean and dry mortar and pestle. The required amount of activator ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) and few drops of rectified spirit was added so as to mix activator in the entire charge. This mixture is transferred to a graphite crucible and it is covered by another crucible to form a clean atmosphere. It is then fired at a temperature of 900°C for 2 hours and a muffle furnace with automatic temperature control. This charge was transferred to mortar after firing and pulverized while red hot. The resultant powdered sample so obtained is collected in clean

and dry sample tube for characterization. Various characterization techniques such as XRD, TEM, SEM and PL were performed to get information regarding structural and luminescence properties of BaS:Bi nanophosphors.

III. RESULTS AND DISCUSSION

Photoluminescence Properties

The observed excitation and emission spectrum is shown in figure 1. BaS:Bi nanophosphors were excited at wavelength of 425 nm at room temperature and the sample provided an emission peak at a wavelength of 575 nm which corresponds to green color. However the bulk phosphors give emission at 608 nm which corresponds to red color [8]. The result obtained can be explained on the basis of size effect. The excitation spectra of these phosphors show two peaks at 350 nm and 425 nm corresponding to host (BaS) and dopant (Bi) absorption respectively. It is clear that these phosphors can be excited by blue-violet light

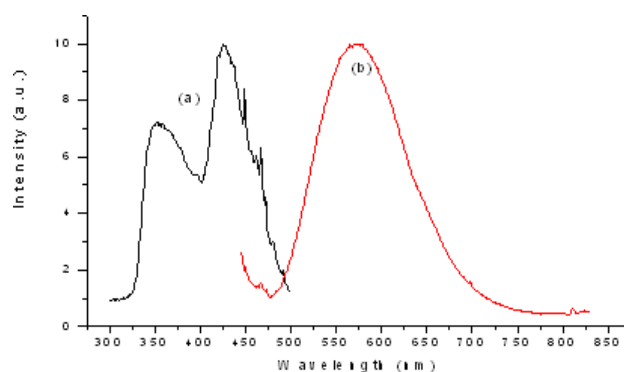


Figure 1. Emission and Excitation spectra of BaS : Bi ($\lambda_{\text{ex}} = 425 \text{ nm}$ and $\lambda_{\text{em}} = 575 \text{ nm}$)

Effect of Amount of flux

The amount and nature of flux is one of the parameters on which PL intensity depends. It is observed that intensity of nanophosphors increases continuously as the amount of flux varies from 0 to 30% of BaS beyond which it again falls as shown in figure 2. However, peak position does not shift due to variation in amount of flux. It was also observed

that emission intensity depends on nature of flux. The emission intensity of phosphors prepared by using sodium thiosulphate as flux was three times more as compared to phosphors prepared by using sodium chloride as flux as shown in figure 3.

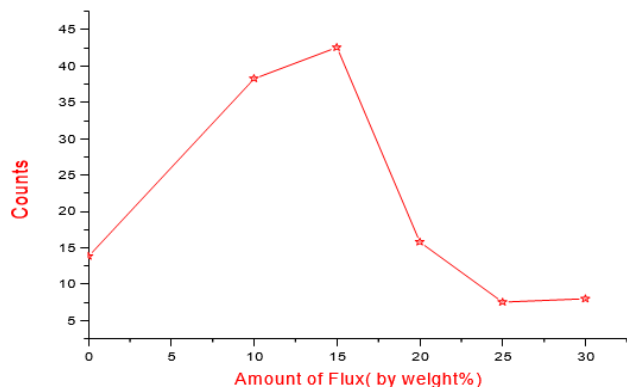


Figure 2. Effect of amount of flux on PL intensity

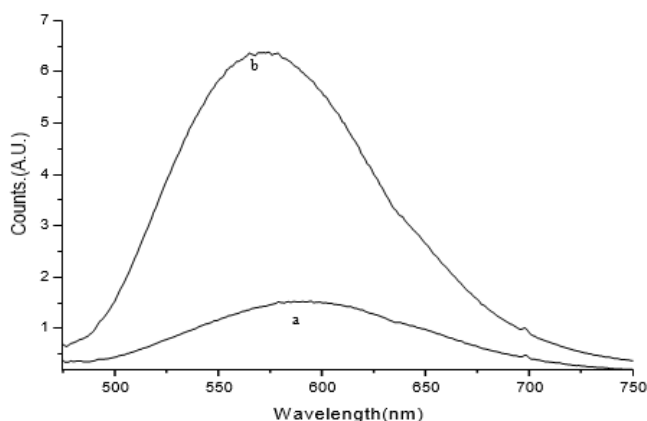


Figure 3. The effect of nature of flux on PL intensity a.Sodium Thiosulphate b. Sodium chloride.

Effect of concentration of dopant

Figure 4 shows the dependence of emission intensity of BaS:Bi nanophosphors with different concentration of Bi. It was found that with increase in dopant concentration, the intensity increases, reaches maximum value at 0.3 mole% and then decreases due to concentration quenching.

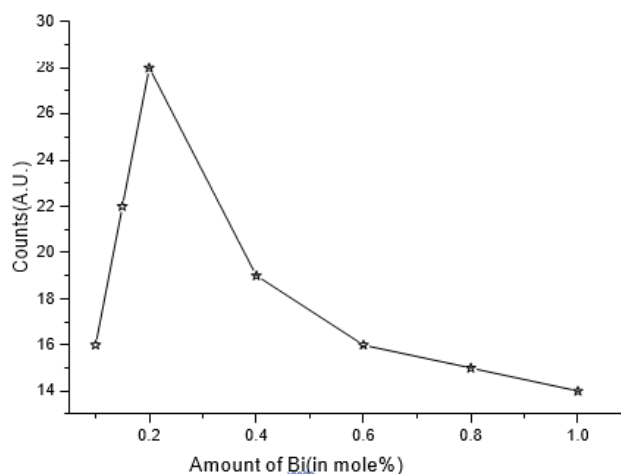


Figure 4. Effect of concentration of dopant Bi on PL intensity.

Figure 5 shows the XRD pattern of the BaS:Bi nanophosphors. All the peaks of XRD matched well with JCPDS card file no. 748, which indicates the rock salt structure of sample without any trace amount of impurities. The average grain size can be determined from the full width of half maximum using Debye- Scherrer equation, $d=0.89\lambda/\beta \cos \theta$. Using this formula the average size of the nanoparticles was calculated to be 20 nm which is approximately same as observed by TEM.

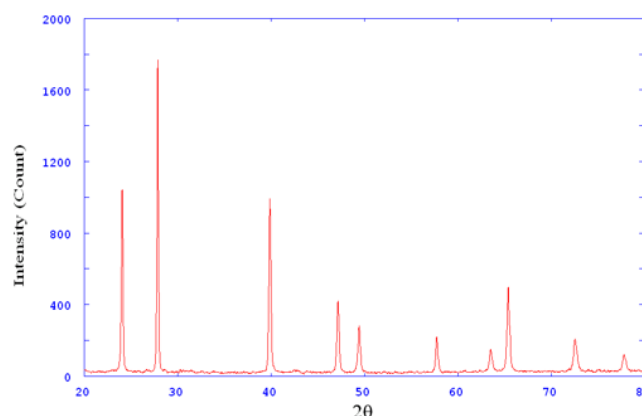


Figure 5. XRD pattern of powdered BaS:Bi nanophosphor.

TEM confirmed the nanostructured form of prepared sample. Figure 6 shows the TEM image of BaS:Bi nanophosphors annealed at 9000C. The average size of the nanoparticles was found to be 15-

18 nm which confirm the nanostructured form of prepared sample.

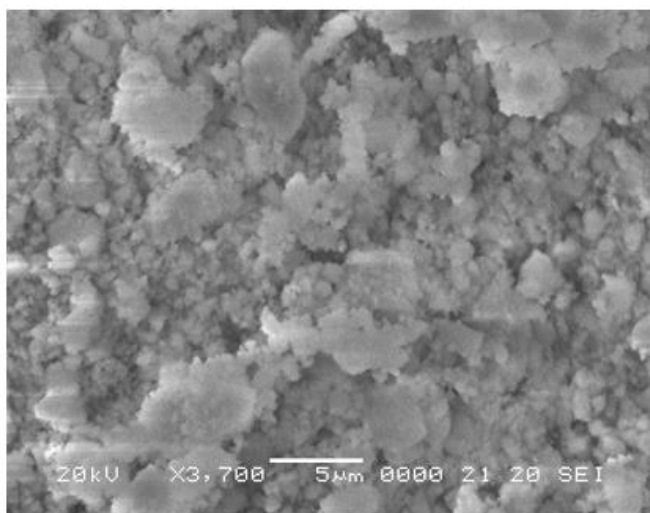


Figure 6. TEM image of BaS:Bi nanophosphor annealed at 9000C

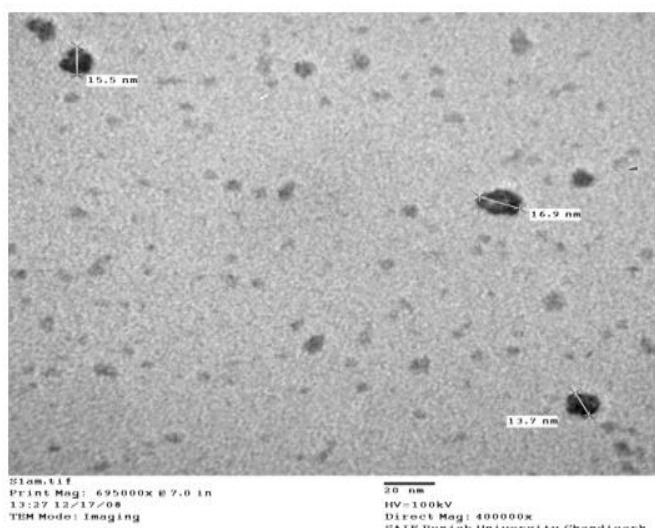


Figure 7. SEM image of BaS:Bi nanophosphor annealed at 9000C

SEM was employed for surface characterization (topographic information, shape, size and arrangement of particles constituting the sample) of nanomaterials and nanostructures. Figure 7 shows the SEM image of BaS : Bi nanoparticles annealed at 9000C. This image shows the agglomeration of nanoparticles because at high temperature agglomeration of particles is unavoidable.

IV. CONCLUSION

The objective of reported study is to conduct an indepth study on luminescence properties, synthesis and characterization of BaS:Bi nanophosphors. The nanophosphor BaS:Bi was prepared by solid state diffusion method which is simple, cheaper and convenient and nevertheless involve less solvent and reduce contamination; gives high yields and good reproducibility. The prepared nanophosphor PL excitation and emission at 425 nm and 575 nm which corresponds to green color. However, for bulk phosphors emission peak is obtained at 608 nm corresponding to red color. Hence, a blue shift is observed in the spectrum. The optimize amount of activator (Bi) was found to be 0.3 mole% of BaS. The nature and amount of flux has a considerable effect on the peak intensity of the luminescence spectrum. The crystal phase was confirmed by XRD technique and mean size of the particles was determined by using Debye-Sherrer equation and found to be 20 nm, which was nearly same as observed in TEM. The SEM images show the agglomeration of constituting particles.

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