



Microwave-assisted synthesis and photoluminescence properties of ZnS:Pb²⁺ nanophosphor for solid-state lighting

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MS received 1 July 2016; accepted 14 March 2017; published online 11 November 2017

Abstract. Nanocrystalline ZnS:Pb²⁺ phosphor was synthesized by microwave-assisted co-precipitation method. The phase purity and surface morphology of prepared material were investigated using an X-ray diffractometer (XRD) and a scanning electron microscope. The photoluminescence property was studied by near-UV (nUV) excitation. The XRD pattern of prepared phosphor matches well with that of an ICDD (International Center for Diffraction Data) file. Surface morphology of prepared phosphor was found to be in submicron range. As-prepared ZnS:Pb²⁺ phosphor shows a green emission under nUV excitation. As Pb²⁺ ions are located on a regular Zn²⁺ site they produce a green emission band in the range of 400–650 nm, centred at 500 nm, under excitation wavelength of 357 nm, exhibiting luminescence properties typically observed for Pb²⁺. Effect of concentration of Pb²⁺ ions on emission intensity was studied. The colour co-ordinates of prepared phosphor were calculated and found to lie in the green region of Commission Internationale de l'Eclairage diagram.

Keywords. ZnS; Pb²⁺; nanophosphor; microwave assisted; photoluminescence; co-precipitation.

1. Introduction

ZnS exhibits direct bandgaps of 3.83 eV for the cubic zincblende (ZB) phase and 3.91 eV for the hexagonal wurtzite (WZ) phase [1]. Although much research has been devoted to the photoluminescence (PL) properties of 1D ZnS nanostructures, very few studies have reported possible UV bandgap emission at room temperature. This is mainly due to high sensitivity of the 1D ZnS nanostructure optical properties to the synthesis conditions, its crystal size and shape, and intrinsic defects such as vacancies and interstitials.

The emission wavelength strongly depends on the synthesis conditions, suggesting the presence of multiple optically active centres [2,3]. In the middle of 1980s it became clear that rare-earth doping of ZnS would not lead to sufficiently bright PL materials. As a result, several new activator–host combinations were tested and found to yield bright emission, CaS:Ce (green) [4], SrS:Ce (blue-green) [5], CaS:Eu (red) [6] and SrS:Eu (orange) [7] being the most successful combination.

Nanometre-sized semiconductor particles are currently investigated in many laboratories over the world. Due to spatial confinement of electrons and holes, the chemical and physical properties of these particles strongly differ from those of the bulk solids (size quantization effect) [8–11]. They form a totally new group of materials with potentially valuable applications [9]. Nanocrystals doped with

optically active luminescence centres create new opportunities for luminescence study and applications of nanometre scale materials [12,13]. ZnS is the most typical and important crystalline phosphor both for application and basic science [14].

Doped ZnS nanocrystals have changed properties; especially, ZnS nanoparticles activated by the transition metallic ions form a new group of luminescent materials. Sulphide phosphors could be the phosphors in future for colour conversion in white LEDs. Here we present PL characteristics of ZnS nanoparticles doped with Pb²⁺. New luminescence characteristics like strong and stable broad band emission covering entire spectrum of visible light have been observed in ZnS:Pb²⁺.

2. Experimental

2.1 Sample preparation

Pb²⁺ (0.001, 0.003, 0.005, 0.01 and 0.02 mol)-doped zinc sulphide nanophosphors have been prepared by microwave-assisted co-precipitation method. All ingredients used were of AR grade. ZnS:Pb²⁺ was first synthesized through the co-precipitation method by the reaction of freshly prepared solution of Zn(NO₃)₂ · 6H₂O and Pb(NO₃)₂ in stoichiometric amount with dropwise addition of freshly prepared and

filtered greenish solution of sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) [15].

The precipitate was washed repeatedly by double-distilled water and then dried slowly at 40°C . The dried precipitate was then heated in a slightly reducing atmosphere in the presence of charcoal in a closed crucible (in order to avoid formation of sulphate) at 700°C for 4 h in a microwave furnace and then allowed to cool very slowly to room temperature. Thus, greenish yellow colour fine powder of ZnS:Pb^{2+} phosphor was obtained.

2.2 Instruments

A microwave muffle furnace of CEM corporation, Phoenix Standard Unit (a high-capacity model, maximum temperature 1000°C), working at nominal line voltage of 220–240 V_{AC} , 50 Hz, 10 A and magnetron frequency 2455 MHz with power output of 1350 W (± 50 W) was used for heating the samples during the synthesis process. The phase purity of the prepared phosphors was investigated using a Rigaku Mini-flex II X-ray diffractometer (XRD) with Cu $\text{K}\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$) at 40 kV and 30 mA. The XRD pattern was recorded in the range of $10^\circ \leq 2\theta \leq 70^\circ$. PL measurement at room temperature was performed on a Hitachi F-7000 spectrofluorimeter equipped with a 450-W Xenon lamp, in the range of 200–700 nm, with spectral width of 2.5 nm, and spectra were corrected using Rhodamine B standard following the procedure prescribed by Hitachi. Effect of dopant concentration on emission intensity of prepared phosphor was studied and chromaticity coordinates for optimum concentration were also calculated. Surface morphology and elemental composition of phosphors were studied by scanning electron microscopy (SEM) using a JEOL's model JSM-6360A fitted with EDS facility.

3. Results and discussion

3.1 XRD analysis

XRD pattern of the synthesized ZnS:Pb^{2+} phosphor is shown in figure 1. The peak positions in the diffraction pattern of the synthesized material when compared to the standard data available with International Center for Diffraction Data were found to match with those of ICDD file 01-072-4841, confirming the formation of the material. The crystallographic data are given in table 1. No additional peaks corresponding to any impurity phase were reported in the XRD pattern, showing that the dopant has a good solubility in the host matrix for this range of concentration. The average crystalline size of this prepared phosphor was found to be 45.36 nm when estimated from XRD information using the Debye–Scherrer formula [16]

$$D = \frac{K\lambda}{\beta \cos \theta},$$

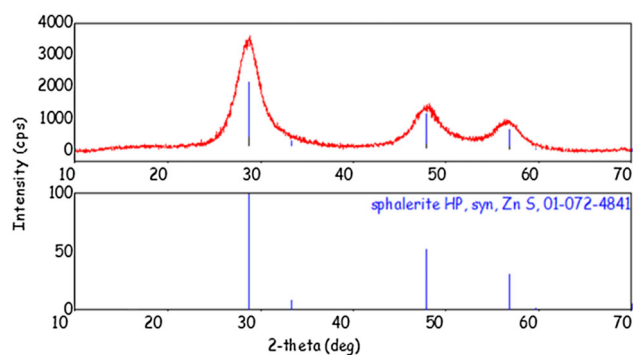


Figure 1. XRD pattern of prepared ZnS:Pb phosphor with ICDD file.

Table 1. The crystallographic data of ZnS:Pb^{2+} phosphor.

Chemical formula	ZnS:Pb^{2+}
Crystal structure	Cubic
Space group	F-43m (216)
a (\AA)	5.3829
b (\AA)	5.3829
c (\AA)	5.3829
α ($^\circ$)	90.000
β ($^\circ$)	90.000
γ ($^\circ$)	90.000
V (\AA^3)	155.973
Z	4

where θ is the Bragg angle of diffraction lines, K is a shape factor taken as 0.90, λ is wavelength of incident X-rays ($\lambda = 0.154 \text{ nm}$) and β is full-width at half-maximum (FWHM in radians).

3.2 Surface morphology study of as-synthesized phosphor

The morphological structures of the prepared ZnS:Pb^{2+} phosphor characterized by SEM are shown in figure 2. Though exact dimensions are difficult to measure, the particles can be approximately considered, from the resolution scale, as micro–nanostructures (submicron), i.e., mix-up of nanoparticles 200–400 nm (0.2–0.4 μm) in diameter (figure 2a) and nanorods of diameter 300–500 nm (0.3–0.5 μm) and 0.5–1 μm length (figure 2b). The SEM images also reveal that some of the crystals of prepared phosphor are almost similar to nanoawls, i.e., nanorods with needle-shaped tips, having tips of length 1–5 μm , as shown in figure 2c.

The EDS pattern of prepared phosphor shown in figure 3 contains prominent peaks of Zn and S along with small peaks of Pt, as platinum was used during sample preparation for SEM. From the EDS pattern, it was observed that Zn and S are not in appropriate proportion of elemental

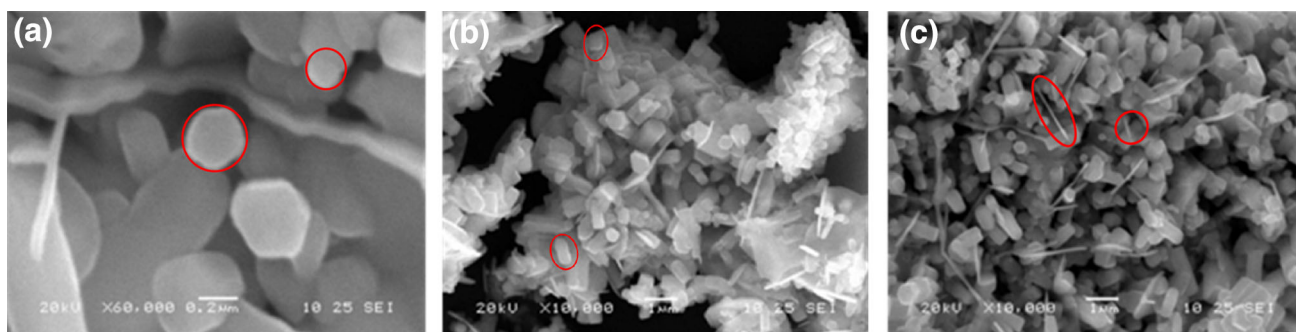


Figure 2. SEM images of as-synthesized ZnS:Pb²⁺ phosphor.

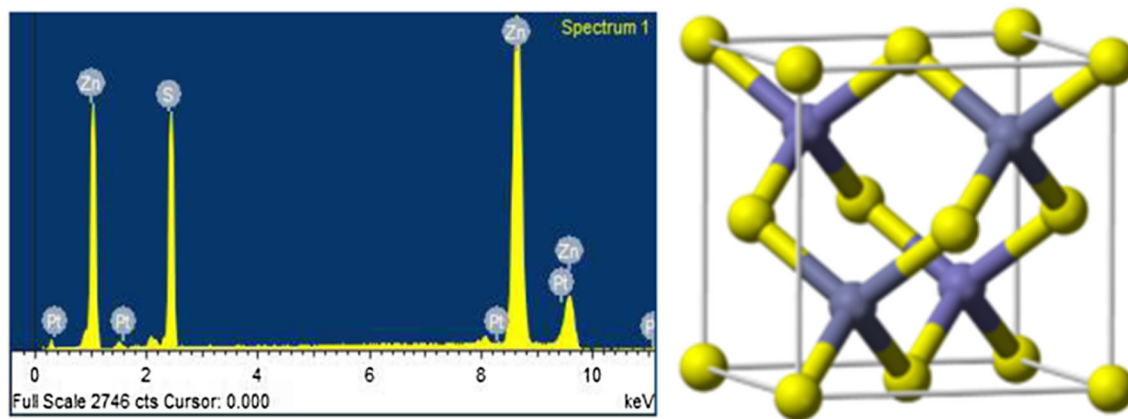


Figure 3. EDS pattern of prepared ZnS nanophosphor doped with Pb²⁺ ions along with Sphalerite-unit-cell-3D-ball model of ZnS host.

composition; instead, sulphur deficiency is indicated, as reported in other papers [17]. In the ZnS lattice, the Pb²⁺ cation has an oxidation state of +2 and on doping it is located on a tetrahedral site with replacement of Zn²⁺ (purple balls), where it is coordinated by four S²⁻ anions (yellow balls) as shown in figure 3.

3.3 PL study of synthesized phosphor ZnS:Pb²⁺

A combined excitation and emission spectrum of ZnS:Pb²⁺ studied at room temperature is shown in figure 4a. The excitation monitored at 500 nm shows broad excitation band with the highest intensity peak at 280 nm along with a broad and flat region with a maximum at 357 nm. Some low-intensity peaks as compared with these were also observed on smaller wavelengths side, indicating direct transition from valence band to conduction band associated with the peculiar nanostructure of the host ZnS lattice (figure 4b).

The curve representing emission spectrum of the synthesized ZnS:Pb²⁺ phosphor monitored at 357 nm shows a broad emission band in the wavelength range 400–650 nm (covering

almost the entire visible spectrum) centred at 500 nm exhibiting green emission with FWHM of around 100 nm having a slight shouldering at 475 nm (figure 4a). The stable and wide green emission band centred at 500 nm is attributed to a characteristic transition between Pb²⁺ levels and the slight shouldering at 475 nm, blue–green emission, could be ascribed to the transitions involving self-activated centres, vacancy states or interstitial states associated with the peculiar nanostructure (figure 4b).

3.4 Effect of Pb²⁺ concentration on emission intensity of ZnS:Pb²⁺ phosphor

Emission spectra for different concentrations of Pb²⁺ ions are shown in figure 5. When the molar concentration of Pb²⁺ ions was increased from 0.1 to 2% it was observed that 1 mol% concentration was the optimum for the prepared phosphor, showing the maximum emission intensity. Thereafter, emission intensity decreased due to the well-known phenomenon of concentration quenching [18].

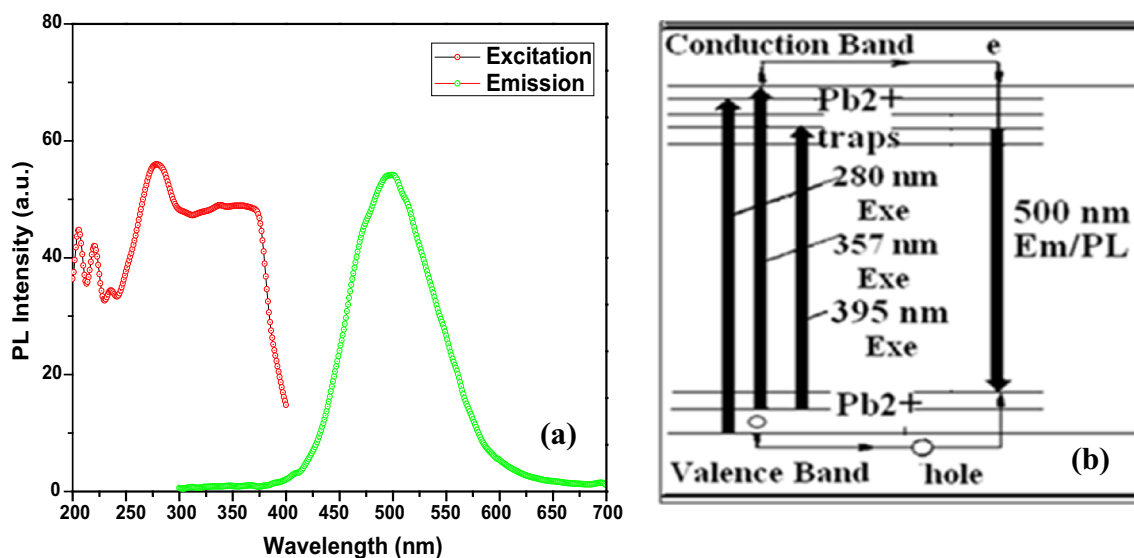


Figure 4. (a) Excitation and emission spectra of ZnS:Pb²⁺ phosphor and (b) energy band structure in Pb²⁺ ions.

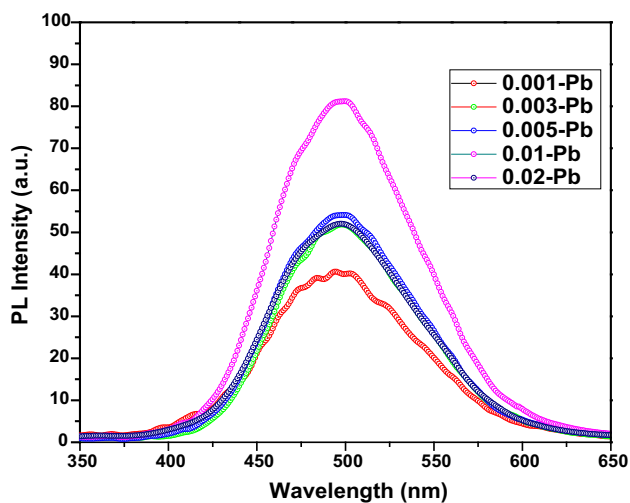


Figure 5. Emission spectra of ZnS:Pb²⁺ phosphor doped with ions at different concentrations.

3.5 Study of colour chromaticity

The chromaticity diagram established by the Commission Internationale de l'Éclairage (CIE) in 1931 is a two-dimensional graphical representation of any colour perceivable by the human eye on an x - y plot, in which colours are represented by means of colour coordinates. To confirm the chromaticity in the present case, the colour coordinates of phosphors ZnS:Pb²⁺ (Pb = 0.01 mol) have been calculated from their corresponding emission spectra. Calculated colour coordinates ($x = 0.192$, $y = 0.371$) fall in the blue–green boundary region of CIE diagram and it is closer to green than blue colour as shown in figure 6.

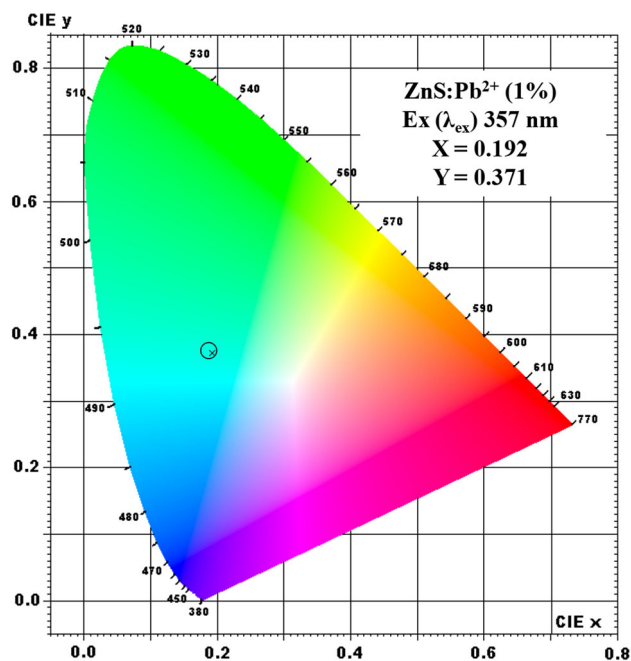


Figure 6. CIE colour coordinates of ZnS:Pb²⁺ phosphor.

4. Conclusions

Pb²⁺-doped ZnS nanocrystalline phosphor was successfully synthesized by microwave-assisted co-precipitation method. The crystal structure and phase purity of prepared phosphor was confirmed with XRD analysis. Broadening of peaks in XRD pattern and particle size calculated by the Debye–Scherrer formula signify that the prepared phosphor is in nanometre range. Also from surface morphology it was observed that the prepared phosphor is in submicron range.

The emission spectra of Pb²⁺-doped ZnS demonstrate stable broad-band green emission centred at 500 nm for nUV excitation of 357 nm. From the afore-mentioned discussion, ZnS:Pb²⁺ phosphor can be used as a green component of nUV-excited RGB tricolour LED for production of white light in solid-state lighting application.

Acknowledgements

DNG is thankful to The Chairman, FIST-DST Project, Sant Gadge Baba Amravati University, Amravati, for providing all the necessary research facilities and also to the Head, Deccan Education Society's Technical Institute, Fergusson College Campus, Pune, for constant encouragement and guidance.

References

- [1] Shionoya S 1999 in: Shionoya S and Yen W M (eds) *Phosphor handbook* (Boca Raton, FL: CRC Press) p 239
- [2] Rennie J, Takeuchi K, Kaneko Y and Koda T 1991 *J. Lumin.* **48** 787
- [3] Gruzintsev A N, Volkov V T and Pronin A N 1992 *J. Cryst. Growth* **117** 975
- [4] Shankar V, Tanaka S, Shiiki M, Deguchi H, Kobayashi H and Sasakura H 1984 *Appl. Phys. Lett.* **45** 960
- [5] Barrow W A, Coovert R E and King C N 1984 *SID Symposium Digest of Technical Papers*, San Francisco, CA, USA, p 249
- [6] Tanaka S, Shankar V, Shiiki M, Deguchi H and May K H 1985 *SID Symposium Digest of Technical Papers*, Orlando, FL, USA, p 255
- [7] Kane J, Harty W E, Ling M and Yocom P N 1985 *Proceedings of the International Display Research Conference*, San Diego, CA, USA, p 163
- [8] Alivisatos A P 1996 *Science* **271** 933
- [9] Pool R 1990 *Science* **248** 1186
- [10] Weller H 1993 *Adv. Mater.* **5** 88
- [11] Hasselbarth A, Eychmuller A and Weller H 1993 *Chem. Phys. Lett.* **203** 271
- [12] Bhargava R N, Gallagher D and Welker T 1994 *J. Lumin.* **60–61** 275
- [13] Li Y, Ding Y, Zhang Y and Quian Y 1993 *J. Phys. Chem. Solids* **60** 13
- [14] Marfunin A S 1979 *Spectroscopy* (New York: Springer)
- [15] Ingale N B, Omanwar S K, Muthal P L, Dhopte S M, Kondawar V K, Gundurao T K *et al* 2008 *Radiat. Meas.* **43** 1191
- [16] Sawala N S, Palan C B, Chauhan A O and Omanwar S K 2016 *Optik: Int. J. Light Electron Opt.* **127** 6419
- [17] Manzoor K, Vadera S R, Kumar N and Kutty T R N 2003 *Mater. Chem. Phys.* **82** 718
- [18] Palan C B, Bajaj N S and Omanwar S K 2016 *Mater. Res. Bull.* **76** 216