

Spectral and surface investigations on $\text{SrZnO}_2:\text{Tb}^{3+}$ nanophosphorsVinay Kumar^{a,b,c}, A. K. Bedyal^a, O. M. Ntwaeaborwa^b and H. C. Swart^b^aSchool of Physics, Shri Mata Vaishno Devi University, Katra-182320 (J&K) India.^bDepartment of Physics, University of the Free State, P.O. Box 339, Bloemfontein 9300, South Africa.

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ABSTRACT

$\text{SrZnO}_2:\text{Tb}^{3+}$ nanophosphor was synthesized through a combustion process using metal nitrates as precursors and urea as fuel. The nanocrystals have sizes ranging from 25 nm to 30 nm. X-Ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) and cathodoluminescence (CL) spectra were utilized to characterize the present samples. Under UV excitation, it shows several bands centered at 487, 544, 588 and 624 nm, which result from $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j = 6, 5, 4$ and 3) transitions of Tb^{3+} , and the green emission band ($^5\text{D}_4 \rightarrow ^7\text{F}_5$) located at 544 nm is dominant. X-ray Photoelectron Spectroscopy (XPS) technique was used to study oxygen related defects and the surface chemical composition. Surface chemical study suggests that oxygen vacancies may be generated by surface shrinkage due to the size reduction. A surface sensitive analytical technique namely time of flight-secondary ion mass spectroscopy (TOF-SIMS), respectively was used for imaging which shows an uniform distribution of Tb^{3+} in the SrZnO_2 .

Keywords: Nanophosphors, Luminescence, XPS, ToF-SIMS.

Introduction

In recent years, nanophosphor research has been widely conducted because of their potential applications in different types of panels, displays and lighting devices^{1, 2}. Inorganic light-emitting diodes (I-LEDs) are currently promising option to replace conventional discharged and incandescent lamps due to their low energy consumption that can solve the global energy crisis. Many efforts have been made to search for novel, highly efficient phosphors to improve the efficiency of the current white light LEDs. LED phosphors normally absorb strongly in the near UV or blue region to down-convert the light emitted by LEDs. Mixed oxide compounds are resistant to high-density electron irradiation and they can maintain their stability and luminescent efficiency compared to their sulfide counterparts. Trivalent Tb ions have been expected as one of the promising species that provide optical devices in blue and green color regions and many investigations have been conducted in various compounds³⁻⁷.

Since the first report by Kubota et al.⁸ on the $\text{SrZnO}_2:\text{Ba}^{2+}$ and Mn^{2+} -doped systems as new luminescent material prepared by solid state reaction process, the host has attracted the attention of the scientific community who are investigating its suitability as an efficient⁹⁻¹². Our general strategy is to focus on materials that exhibit broad and intense charge-transfer (C-T) absorption bands in the UV regime to capture the emission from an AlGaIn or InGaIn UV based LEDs over a range of wavelengths. For the application in displays and lamps, it is desirable to have controlled morphology, a fine size and narrow size distribution for high resolution¹³.

In this paper, $\text{SrZnO}_2:\text{Tb}^{3+}$ nanophosphors were synthesized by combustion method, and their spectral (PL and CL) and surface chemical properties have been studied for fundamental interest and applications. The same host has also been studied on their utility as low voltage field emission display (FEDs) phosphor and the chemical states of the metal ions in this matrix were also investigated.

Experimental Details

The starting materials for the synthesis of the SrZnO_2 nanoparticles were Zinc Nitrate Hydrate [$\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$], Strontium Nitrate [$\text{Sr}(\text{NO}_3)_2$], and Terbium (III) Nitrate Tetrahydrate [$\text{Tb}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$] from Merck Chemicals, India. In present study, Urea (H_2NCONH_2) was used as fuel as it is cheapest and easy available fuel used to supply fuel and provide a good reducing valency (+6). It is well reported¹⁴ that compounds containing N-N bonds in their moieties are particularly found to assist the combustion better. They form complexes with the metal ions facilitating homogenous mixing of cations in solution. They break down into components from

Address:

Dr. Vinay Kumar
School of Physics,
Shri Mata Vaishno Devi University,
Katra-182320 (J&K) India

Tel: +91-1991-285699

Email: vinaykumar@smvdu.ac.in

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which they are formed. These components in turn decompose to produce combustible gases like NH_3 which ignite with NO_x . Evolve large amounts of gases that are of low molecular weight and harmless during combustion. The details of nanophosphors synthesis with combustion method has already been reported recently¹⁵.

X-ray diffraction (XRD) patterns were recorded with scanning step of 0.01° , scanning time at each step 20 s from a Bruker D8 Advance diffractometer to examine the purity and the phase homogeneity of the nanocrystalline phosphors. The morphology of the product were cross verified by scanning electron microscopy (SEM) carried out by an Shimadzu *SSX superscan*. The spectral features like photoluminescence excitation and emission (in phosphorescence mode) spectra were measured at room temperature by using a Cary-Eclipse spectrofluorometer equipped with a Xenon lamp used as an excitation source. For Cathodoluminescence (CL) measurements, a vacuum chamber from PREVAC equipped with an ES40C electron gun power supply unit and USB2000+ spectrometer under different accelerating voltages and emission currents at a base pressure of $\sim 2 \times 10^{-8}$ Torr was used.

For chemical states and surface examination, X-ray photoelectron spectroscopy (XPS) using a PHI 5000 versa probe equipped with monochromatic Al $K\alpha$ radiation ($h\nu=1253.6\text{eV}$) was conducted. For higher resolution spectra, the hemispherical analyzer pass energy was maintained at 11.3 eV. Measurements were performed using a 1 eV/step (or 45 min acquisition times) binding energies for survey scans from 0–1400 eV and 1 eV/step and 20–30 min. times for the high resolution scans. A low energy electron beam was used to achieve charge neutrality on the sample surface. All the absolute binding energies of the photoelectron spectra were corrected with C 1s signal at 284.6 eV.

Results and Discussion

The XRD pattern of all the samples was nearly the same and hence only one pattern is shown in figure 1. The average size of the nanoparticles was estimated from the line broadening of the XRD peaks and well-known Scherrer's equation¹⁶. The average particle sizes were found to be in the range of 25 nm to 30 nm. The structure of the host material is of orthorhombic type with space group *Pnma*. The XRD pattern was compared with JCPDS card No. 41-0551. The marginal broadening of the diffraction peaks in the patterns indicates small crystalline size¹⁷.

The morphology of the as prepared nanophosphors was investigated using a SEM image. Fig. 2 shows a SEM image of the SrZnO_2 nanoparticles. The leafy like morphology were observed and also some traps and voids were seen due to the evolution of gases during combustion synthesis.

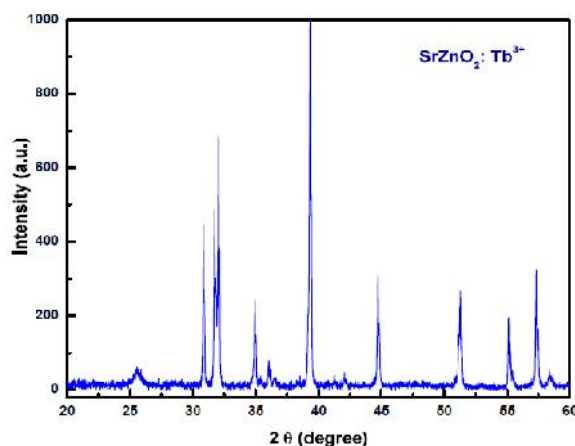


Figure1: XRD pattern of the $\text{SrZnO}_2:\text{Tb}^{3+}$ nanoparticles

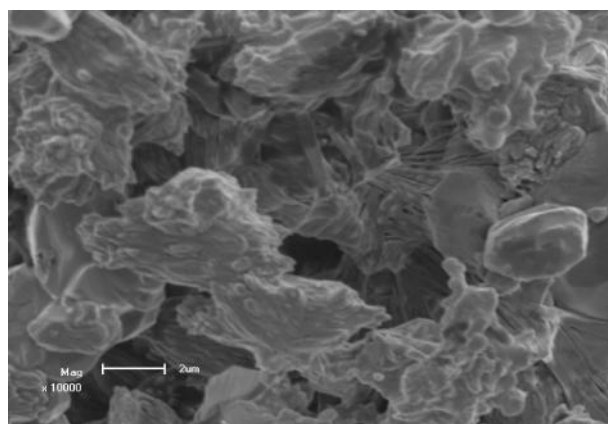


Figure 2: SEM image of the $\text{SrZnO}_2:\text{Tb}^{3+}$ nanoparticles

Figure 3 shows the photoluminescence excitation and emission spectra of the $\text{SrZnO}_2:\text{Tb}^{3+}$. Under 237 nm UV excitation, the photoluminescence emission spectra shows well-known characteristics of Tb^{3+} emission including the transition from $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($J = 6, 5, 4$ and 3) transitions of Tb^{3+} , and the green emission band ($^5\text{D}_4 \rightarrow ^7\text{F}_5$) located at 544 nm is dominant.

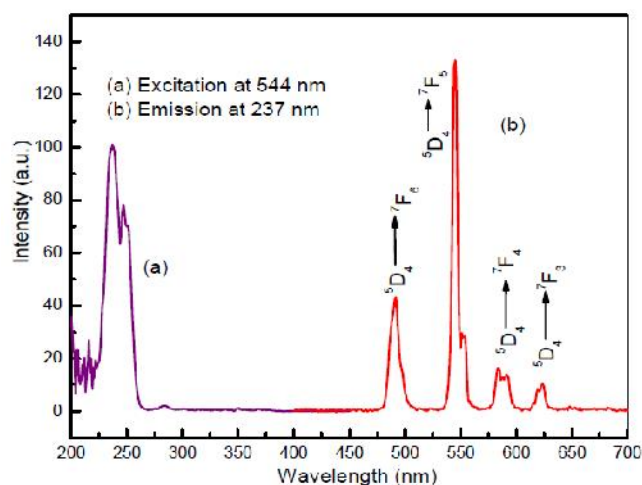


Figure 3: (a) PL excitation and (b) emission spectra of the $\text{SrZnO}_2:\text{Tb}^{3+}$ nanoparticles

The CL emission intensities of the $\text{SrZnO}_2:\text{Tb}^{3+}$ sample have been investigated as a function of the accelerating voltage and the emission current, as shown in figure 4.

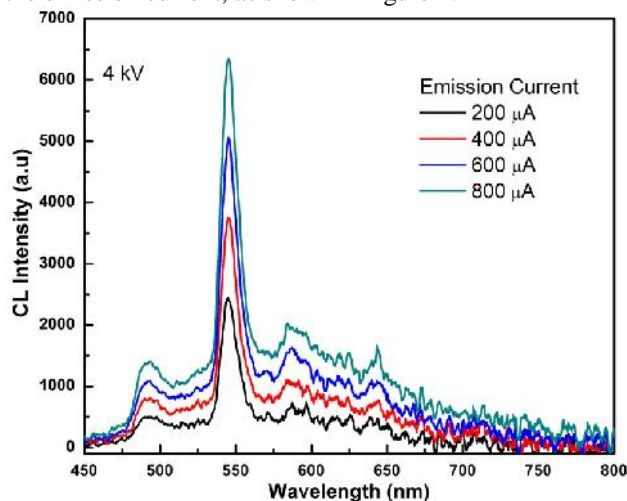


Figure 4: CL spectra of the $\text{SrZnO}_2:\text{Tb}^{3+}$ at an accelerating potential of 4 keV with different emission current as indicated.

Under a constant 4 keV electron-beam excitation, an increase in the CL intensity was observed when the emission current was changed from 200 μA to 800 μA . The increase in the CL brightness with an increase in the electron energy (not shown) and emission current may be attributed to the deeper penetration of the electrons into the nanophosphor and the larger electron-beam current density¹⁸. It is worth mentioning that under UV excitation and low-voltage electron beams, the doped SrZnO_2 sample can exhibit good color purity and appropriate intensity.

Surface characterization

The elemental composition and the oxidation state of the cations were analyzed with a powerful analytical X-ray photoelectron spectroscopy (XPS) technique. In figure 5, the survey XPS scan of the $\text{SrZnO}_2:\text{Tb}^{3+}$ indicates the presence of Sr, Zn, O and Tb corresponding to their binding energies.

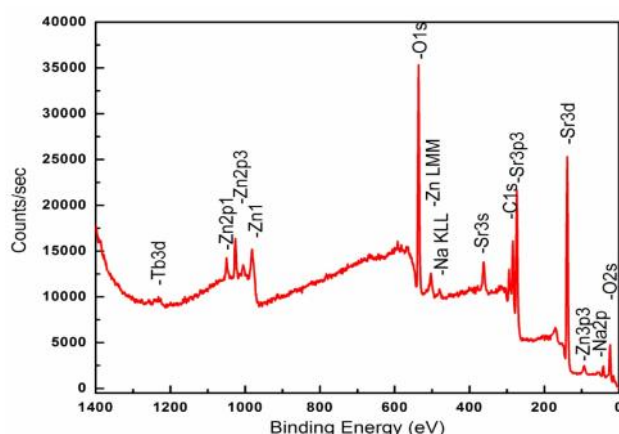


Figure 5: XPS wide scan spectrum of the $\text{SrZnO}_2:\text{Tb}^{3+}$ nanophosphors

The TOF-SIMS offers the possibility of imaging components based on the elemental or isotopic masses of their atomic and molecular ion fragments with high lateral

resolution and sensitivity, yielding information including the identification of the peak composition and the distribution of the dopant and the homogeneity of the doping in the host lattice¹⁹. Thus, we used the TOF-SIMS to analyze the composition of the elemental masses. Fig. 6 shows the chemical false colour images of an area of $200 \mu\text{m} \times 200 \mu\text{m}$ of the Sr^+ 80.9 u, Zn^+ 64 u, Tb^+ 159 u, TbO^+ 175.4 u respectively and their overlay. It was not possible to measure Tb^+ ions and therefore ions such as the $\text{Tb}(\text{NO}_3)_3^+$ and TbO^+ were measured. The relative sensitivity of the two ions is different and it is not known which ion is more favorable to be removed from the phosphor structure, therefore a difference in the amounts is expected. This confirms a successful doping with Tb^{3+} ions over the scan area of $200 \mu\text{m} \times 200 \mu\text{m}$ in the $\text{SrZnO}_2:\text{Tb}^{3+}$ host.

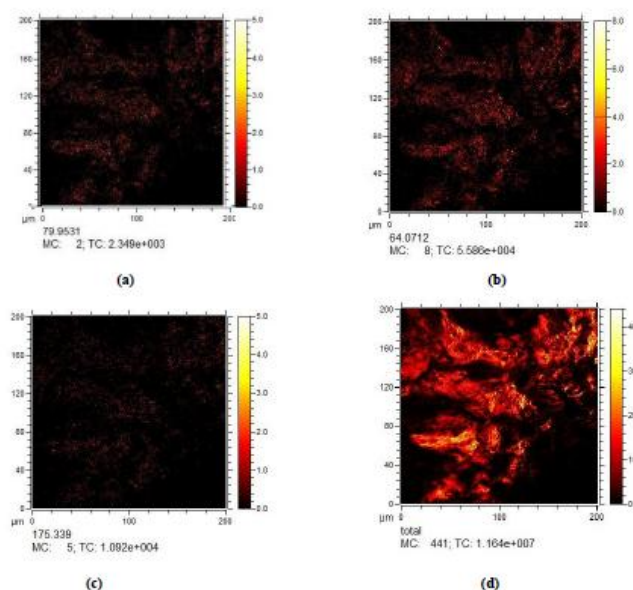


Figure 6: False colour TOF SIMS images of (a) Sr^+ (b) Zn^+ and (c) $\text{Tb}(\text{NO}_3)_3^+$ and (d) overlay $\text{SrZnO}_2:\text{Tb}^{3+}$.

Some hydrocarbon signals are observed across the surface of the phosphor particles that superficially arises from contamination produced during the process of sample mounting and handling. TOF-SIMS was successfully used in the past to obtain the relative distribution of the dopants in a $\text{Sr}_5(\text{PO}_4)_3\text{F}$ host matrix²⁰.

Conclusion

In summary, the $\text{SrZnO}_2:\text{Tb}^{3+}$ nanocrystalline phosphors have been successfully synthesized via a combustion process with metal nitrate as precursors and urea as fuel. The emission spectra of these phosphors are composed of several band arising due to the transition from $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j = 6, 5, 4$ and 3) transitions of Tb^{3+} . The strongest green emission appears at 544 nm. At the same time, luminescence studies showed that the $\text{SrZnO}_2:\text{Tb}^{3+}$ nanoparticles have good PL and CL performance which explore its potential as a new promising material for LEDs and FEDs. XPS studies also reveal the formation of the host matrix and confirm the incorporation of the Tb^{3+} in the host. This was also verified with surface sensitive ToF-SIMS chemical imaging data. The images suggested a uniform distribution of the Tb^{3+} ions in the SrZnO_2 .

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Vinay Kumar received his M. Sc. Degree in Physics from Jiwaji University, Gwalior in 2002. He obtained his Ph.D. from K.U., Kurukshetra in 2007. His research interests are in fluorescent nanomaterials in powder and their applications in lighting, displays, and latent finger-print development. He did his first Post-Doctoral Research from UFS, South Africa and second PDF from Panjab University, Chandigarh, India. He has published more than 38 international research articles. Currently, Dr. V. Kumar is an Assistant Professor of Physics at the Shri Mata Vaishno Devi University, India. He is also a Life member of Luminescence Society of India.



A.K. Bedyal obtained M. Sc. degree in Physics from Lovely Professional University, Punjab, India in 2010. He also received his M.Phil degree from the same University in 2011. A.K. Bedyal is presently doing Ph.D at Shri Mata Vaishno Devi University, Katra (J&K). He is currently working in the area of development of phosphors for their potential application in solid state lighting, LED'S, radiation dosimetry etc.



O. Martin Ntwaeaborwa is a Professor of Physics at the University of the Free State, South Africa. He is the President of the South African Nanotechnology Initiative. His research interests are in luminescent nanomaterials in powder and thin film forms, and their applications in lighting, displays, and organic photovoltaic cells. He has published more than 85 articles and 3 book chapters in the past 10 South African Nanotechnology Initiative. Professor Ntwaeaborwa received his B.Sc. degree in Education, B.Sc. Honours and M.Sc. degrees, all from the Mafikeng Campus of the North West University in 1997, 1998 and 2000, respectively. He received his PhD degree from the University of the Free State in 2006.



Hendrik C Swart is an international acclaimed national research foundation (NRF) rated researcher and currently a senior professor in the Department of Physics at the University of the Free State, South Africa. Over the past 18 years he has led research in the area of the degradation of phosphors for field emission displays and developing materials for nano solid state lighting. He has more than 200 publications in international peer reviewed journals, 36 peer reviewed conference proceedings and 3 book chapters and books with more than 1100 cited author references. He has received the South African National Science and Technology Forum (NSTF) award for research capacity development of students in the niche area of nanophysics in 2009. He has established a National Nano Surface Characterization Facility (NNSCF) containing state of the art surface characterization equipment. A research chair in Solid State Luminescent and Advanced Materials was awarded to him from the South African Research Chairs Initiative (SARChI) at the end of 2012.