Characterization and XPS information of commercially Y₂O₂S:Eu³⁺ powder phosphor

JJ Dolo, FB Dejene and HC Swart*

Physics Department, University of the Free State, P.O. Box 339, Bloemfontein, 9300, South Africa

*Corresponding author: swarthc@ufs.ac.za

Abstract. Trivalent-europium doped yttrium oxysulphide phosphor (band gap $\sim 4.2-4.8$ eV) is an important phosphor system extensively applied in colour televisions, high resolution displays, memory devices, after glow phosphors, etc.. We report on the characterization of a red long-lasting phosphorescent material, $Y_2O_2S:Eu^{3+}$. The morphology and optical properties of the powder phosphor were characterized, the morphologies thereof shows that the particles differ in terms of sizes and shapes. Energy Dispersive X-ray analysis (EDX) confirms all the elements on the surface. X-ray diffraction (XRD) investigation showed a pure hexagonal phase of Y_2O_2S . All peaks have been perfectly indexed as the pure hexagonal phase. From the Photoluminescence (PL) spectrum, the main emission peaks are ascribed to the Eu^{3+} ion transition from 5D_J (J=0, 1, 2) to 7F_J (J=0, 1, 2, 3, 4). After irradiation with a wavelength of 320 nm, the phosphor emitted red long-lasting phosphorescence. X-ray photo electron spectroscopy (XPS) peaks for the $Y_2O_2S:Eu^{3+}$ have been observed for Y 3d at 156 and 158 eV, Y 3p at 298.5 and 310.5 eV, S 2p at 164.5 eV and S 2s at 228 eV, respectively.

1. Introduction

Phosphor is defined as a material that emits photons with high luminescence efficiency. The cathodoluminescent phosphors convert electron energy into visible light and are used in display devices as screen material. Trivalent rare-earth ions have usually been selected to be used as activators in line-emitting phosphors because the spectral emission lines of trivalent rare-earth ions in the host lattice are rather narrow [1,2]. Yttrium oxysulfide doped with europium $(Y_2O_2S:Eu^{3+})$ red phosphor is a high efficiency cathodoluminescent material that is used extensively in the phosphor screens. $Y_2O_2S:Eu^{3+}$ has sharper emission lines leading to better colorimetric definition and higher luminescence efficiency than the other red phosphors [3,4]. But compared with the other color persistent phosphors [5], the progress on the research of red persistent phosphors is very limited. Therefore, the development of red long-lasting phosphors with high luminescence and good chemical stability is urgently needed. Yttrium oxysulfide has been known as an excellent phosphor host material for a long time. While doped with Eu^{3+} , Eu^{3+} , and Eu^{3+} are doing-lasting afterglow phosphor that has the afterglow time of above 3h was synthesized [6]. However, the progress on the systemic research of Eu^{3+} , Eu^{3

2. Characterization

Commercially available Y_2O_2S : Eu^{3+} phosphor powders, obtained from Phosphor Technology were characterized using different techniques. Scanning Electron Microscopy (SEM) images were taken with a Gemini LEO 1525 Model to determine the particle morphology. The crystalline structure of the phosphor powders were investigated using a Burker D8 (Burker Co, German) X-ray diffractometer with Cu $K\alpha = 1.5406$ Å. The 100 μ m, 25 W, 15 kV energy X-ray beam of a PHI 5400 XPS Versaprobe was used to analyze the S 2p, O 1s, O 2s, Y 3d and Y 3p binding energy peaks (pass energy 11.8 eV, analyser resolution ≤ 0.5 eV). The possible chemical states maybe identified with the Multipak version of 8.2c computer software [7] using Gaussian-Lorentz fits.

3. Results and Discussion

Figure 1 shows the XRD pattern of the Y_2O_2S : Eu³⁺ phosphor powder. The position and relative intensity of the XRD lines are in good agreement with the data of JPCDS file No.24-1424 [8], which shows the pure Y_2O_2S hexagonal structure.

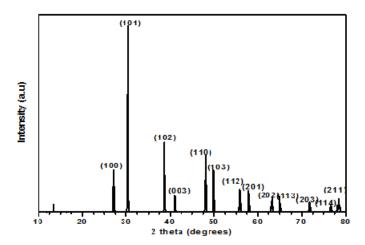
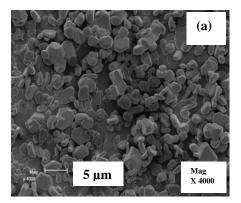
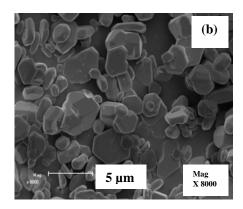


Figure 1. XRD pattern for the Y₂O₂S:Eu³⁺ phosphor powder.

Figure 2 (a) and (b) shows the SEM image of the $Y_2O_2S:Eu^{3+}$ phosphor powder at different magnifications. The particles are polyhedron in shape and agglomerated, showing relatively good close packing which is one requirement for the cathode ray display (CRT) or X-ray intensifying screens and the particles differ in sizes and shapes. Figure 2 (c) shows the EDS data which confirms the presence of all the elements in the matrix, i.e (Y, O and S) together with the adventitious C. Eu^{3+} ions were not detected probably due to their relatively low concentration in the $Y_2O_2S:Eu^{3+}$ matrix.





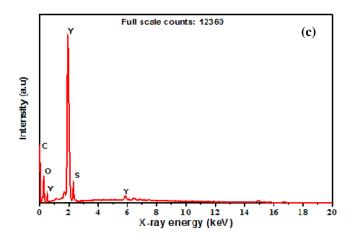


Figure 2. (a) and (b) SEM image at different magnifications and (c) EDS spectrum of the $Y_2O_2S:Eu^{3+}$ phosphor powder.

Figure 3, shows the PL spectra of $Y_2O_2S:Eu^{3+}$ phosphor powder with excitation energy (λ_{ex} = 320 nm). The main emission peaks are due to the Eu^{3+} transition ${}^5D_j \rightarrow {}^7F_j$. The stronger red emission peaks lines at 618 and 627 nm are due to the transition ${}^5D_0 \rightarrow {}^7F_2$. The shorter wavelength line at 595 nm corresponds to the transitions ${}^5D_0 \rightarrow {}^7F_1$. The PLE (Photoluminescence excitation) spectra consist of extremely broad bands that extend well into the near-UV region. Therefore, $Y_2O_2S:Eu^{3+}$ can be used as a red emitting phosphor in a three-band white LED excited by near-UV LEDs.

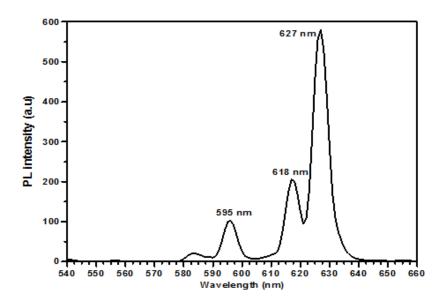


Figure 3. PL spectra for Y₂O₂S:Eu³⁺ phosphor powder.

Figure 4, shows the XPS surface measurement of the Y₂O₂S:Eu³⁺ phosphor after sputtered clean (sputtering done with Ar^+ , 2 kV, 2 μA , 1x1 mm raster). The XPS spectra of the $Y_2O_2S:Eu^{3+}$ shown in figure 4, reveals the presence of yttrium and sulphur in the expected stoichemistry Y:S). The spectra showed no extraordinary features.

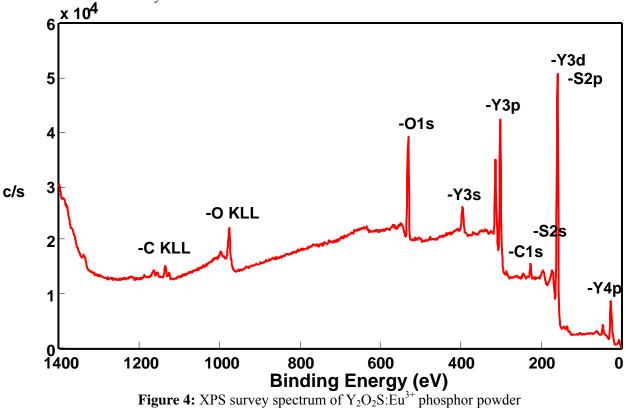


Figure 5 (a), shows the XPS measured spectra of O 2s, Y 4p as well as the S 3s and Eu 5d peaks. The Y 4p lines are located at about 23.7 eV (Y4p_{3/2}) and 24.8 eV (Y4p_{1/2}), O 2s around 23 eV, S 3s at 18 eV, Eu 5p at 19 eV [9]. The Eu 3d peaks are shown in figure 5 (b). It is clear that both Eu²⁺ and Eu³⁺ are present in the Y₂O₂S. The Eu³⁺ species are, however, much more then the Eu²⁺.

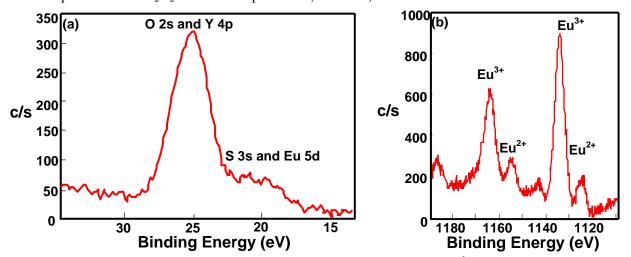


Figure 5. (a) XPS measured spectra of the O2s and Y4p of Y₂O₂S:Eu³⁺ phosphor powder and (b) the spectra of Eu 3d.

Figure 6, shows the XPS measured spectrum of Y 3d from $Y_2O_2S:Eu^{3+}$. It has been reported that the Y3d_{5/2-3/2} doublet position is at 157.2 eV and 159.7 eV [10]. Figure 6 (b) shows the XPS spectrum of O 1s with two different oxygen states. O1s peaks were located at 531.3 eV and 532.0 eV. The lower energy O1s peak is very consistent with normal Y-O bonding energy in Y_2O_2S [10].

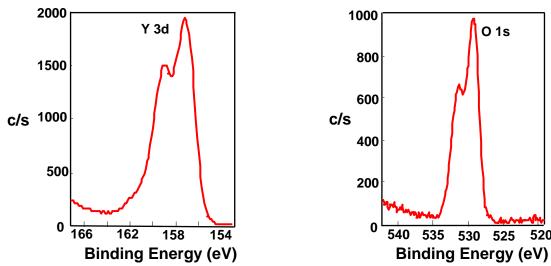
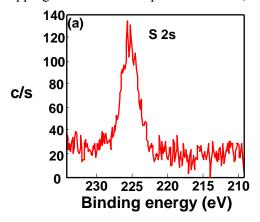


Figure 6. XPS measured spectra of the (a) Y 3d and (b) O 1s of Y₂O₂S:Eu³⁺ phosphor powder.

Figure 7 (a) and (b), show the XPS of S 2s and S 2p of Y₂O₂S:Eu³⁺ respectively. The low signal-tonoise ratio in some of the XPS spectra in the region of both S 2s and S 2p peaks made systematic quantification of the different sulphur species present in the samples difficult. However, two sulphur species can be identified in the S 2p peak, at the binding energies of 167.8 eV and 164.9 eV. In the light of the S 2p peak analyses, only minor amounts of surface sulphate were present in the reacted samples. More work is, however, needed to deconvoluted all the peaks, especially those peaks in which overlapping of the different species occurred, to determine the correct binding energy positions.



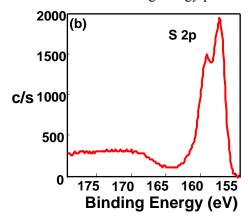


Figure 7: XPS measured spectra of the (a) S 2s and (b) S 2p of Y₂O₂S:Eu³⁺ phosphor powder.

4. Conclusion

EDS analysis confirms the presence of all elements on the surface of $Y_2O_2S:Eu^{3^+}$. The hexagonal phase of $Y_2O_2S:Eu^{3^+}$ was successfully determined by XRD. The elemental state of the surface was also determined with XPS. The SEM images with different magnifications revealed spherical particles with different shapes and sizes. CL degradation for both powders and thin films of $Y_2O_2S:Eu^{3^+}$ will be done to confirm some species on the surface.

Acknowledgement

The authors send gratitude to the National Research Foundation (NRF) for funding the project and the University of Free State (Physics department, Center for microscopy and Geology department) for the research techniques used in this study.

Reference

- [1] Yost D M, Russel T R and Garner C S, The Rare Earth Elements and their Compounds, Wiley, New York, 1950.
- [2] Taylor K N R, M I Darby M.I, Physics of Rare Earth Solids, Chapman & Hall, London, 1965.
- [3] Royce M R 1968 U.S. Patent 3, 245 418
- [4] Yocom P N 1968 U.S. Patent 3, 247 418
- [5] Wang X X, Zhang Z T, Tang Z L, Lin Y H 2003 Mater. Chem. Phys. 80 1.
- [6] Murazaki Y, Arak K and Ichinomiya K 1999 J. Rare Earth Jpn. 35 41.
- [7] Moulder F, Stickle W.F., Sobol P.E., Bombe K.D. 1995 Handbook of X-ray Photoelectron Spectroscopy, ULVAC-PHI, Inc., 370 Enzo, Chigasaki, Japan 143.
- [8] Zhou X, Xing M, Jiang T, Fu Y, PengY, Wang H and Luo H 2014 J. Alloys Compd. 585 376
- [9] Thirumalai J, Chandramohana R, Auluck S, Mahalingam T and Srikumar S R 2009 J. of Colloid Interf. Sci. **336** 889.
- [10] de Rouffignac P, Park J-S and. Gordon R G 2005 Chem. Mater. 17 4808.