

Synthesis and photoluminescence properties of Tb³⁺- doped Sr_{0.5}Zn_{0.5}Al₂O₄ nanocrystal phosphor prepared via combustion process

S.K K. Shaat¹, F. Roelofse², H.C. Swart¹ and O.M. Ntwaeaborwa^{1,3}

Department of Physics, University of the Free State, P. O. Box 339, Bloemfontein, ZA9300, South Africa

Department of Geology, University of the Free State, P.O. Box 339, Bloemfontein, ZA9300, South Africa

³Corresponding author: ntwaeab@ufs.ac.za or samyshaat@yahoo.com

Abstract. Tb³⁺ doped Zn_{0.5}Sr_{0.5}Al₂O₄ (ZSAO) nanocrystalline phosphor was successfully synthesized by a combustion method at a relatively low temperature (500°C), using metal nitrates as precursors and urea as a fuel. The samples were annealed in air at 700°C for 4 hrs. The X-ray diffraction patterns showed phases associated with both ZnAl₂O₄ (ZAO) and SrAl₂O₄ (SAO) as referenced to standard JCPDS data files No. 05-0669 and 74-794, respectively. As confirmed from the scanning electron microscopy images, the characteristic platelet-like particles of the combustion method were formed. The photoluminescence emission and excitation spectra of Zn_{0.5}Sr_{0.5}Al₂O₄:Tb³⁺ before and after annealing were recorded and compared to those of ZnAl₂O₄:Tb³⁺ and SrAl₂O₄:Tb³⁺. In all cases, PL emissions were due to ⁵D₄ - ⁷F_J (J = 0,1,2,3,4,5,6) transitions of Tb³⁺. The PL emissions of ZnAl₂O₄:Tb³⁺ and SrAl₂O₄:Tb³⁺ were more intense than that of Zn_{0.5}Sr_{0.5}Al₂O₄:Tb³⁺. The objective of the study was to prepare a new aluminate host for Tb³⁺ consisting of Zn and Sr and evaluate its luminescent properties and chemical study for application in lighting.

1. Introduction

In recent years, interests have been focused on the development of new luminescent materials (phosphors) such as lanthanide-doped nanomaterials. Among the known luminescent materials, lanthanide (Ln) ions doped inorganic materials offer a range of compounds with unique versatility. In particular, oxide matrices are attractive host materials for the study of development of advanced phosphors due to their ease of synthesis and chemical stability [1]. Among various host oxide matrix materials, aluminates are considered to possess high energy efficiency, wide excitation wavelength range, and high quenching temperature. Aluminium-based spinels are an intriguing class of oxide ceramics with important technological applications. Rare earth ions (RE) doped aluminates serve as an important class of phosphor for fluorescent lamp and plasma display application and phosphorescence. As one of the most promising phosphors, strontium aluminate spinel, SrAl₂O₄ (SAO), has been found

³ Corresponding author: email address: ntwaeab@ufs.ac.za

to be an efficient host material with a wide band gap, which offers the possibility of generating broad band emission [2] and much attention has been paid to it owing to its higher radiation-resistance and thermal stability [3]. SAO is considered as an ideal host material for long-lasting phosphorescence. The synthesis and optical properties of SAO, in bulk form, or as films or nanoparticles, have been extensively explored during the past decades [1]. Zinc aluminate, ZnAl_2O_4 (ZAO), is a well-known wide-band gap semiconductor and due to its transparent and electro-conductive properties, it can be used for ultraviolet (UV) photoelectronic devices. Recently, ZAO has been extensively studied as a phosphor host material for application in thin film electroluminescence displays, mechano-optical stress sensors, and stress imaging devices [4]. It has a unique combination of attractive properties such as high thermal stability, better diffusion and ductility. Due to these unique properties, it is used as high temperature material and optical coating. In addition, ZAO is also widely used in many catalytic reactions, cracking, dehydration, hydrogenation and dehydrogenation, ceramic and electro-conductive materials because of its high thermal stability, high mechanical resistance, low surface acidity, and excellent optical properties [5]. The understanding of optical properties of Tb^{3+} in inorganic compounds is of great importance because these compounds have potential technological applications as functional photonic materials such as optical fiber amplifiers, lasers, and wavelength converting devices [6]. Tb^{3+} is a well known activator for green luminescence emitting materials and has been used widely in tricolor energy saving fluorescent lamp. The green emission of Tb^{3+} mainly originates from $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($J=0-6$) transitions [7], and the blue emission and UV-light correspond to the $^5\text{D}_3 \rightarrow ^7\text{F}_j$ [3]. The luminescent properties of phosphors dependent strongly on the particle size, crystal structure, and uniform distribution of activators in the host lattice [8]. In recent years, a variety of synthesis technique routes have been used successfully to prepare pure spinel powders [4], such as precipitation [9], solid-state reaction [10], hydrothermal synthesis [11], sol-gel [12], sol-gel-microwave process [13], co-precipitation [14], and combustion reaction [15-17] or microwave combustion methods [18]. Among the aforementioned different synthesis techniques, combustion reaction can be used to prepare complex oxide ceramics, such as aluminates, ferrites and chromites [19]. The combustion reaction has been widely used to fabricate aluminates, due to its success in producing homogeneous and nanocrystalline aluminate phosphors with fine particles. In addition, the synthesis can be carried out at relatively low temperatures in a short processing time [20]. In comparison with other methods, combustion synthesis is the most feasible choice because it can guarantee high purity, compositionally uniform, single phase and small and uniform particle sizes [21]. Previously, Kingsley et al.[22,23] obtained aluminates with uniform small size and good dispersity at 500 or 350 °C by the combustion reaction of the relevant metal nitrates and urea. In this study, the combustion method was used to prepare a new aluminate matrix consisting of 1:1 ratio of Zn to Sr and was used as host for Tb^{3+} resulting in a green emitting $\text{Zn}_{0.5}\text{Sr}_{0.5}\text{Al}_2\text{O}_4:\text{Tb}^{3+}$ phosphors, which was evaluated for application in different types of light emitting devices. The samples prepared were characterized by X-ray diffraction, scanning electron microscopy (SEM), and a photoluminescence (PL) property of doped sample was investigated.

2. Experimental

Tb^{3+} 1.0% mol doped $\text{Zn}_{0.5}\text{Sr}_{0.5}\text{Al}_2\text{O}_4$ (ZSAO) nanocrystalline phosphor was successfully prepared by combustion method at an initiating temperature of 500°C. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2$ precursors of AR grade purchased from Merck, South Africa were used as precursors and were used as obtained without further purification. The precursors were dissolved in distilled water and stirred at 65°C for 5hrs and a transparent solution was obtained. The resulting solution was introduced into a muffle furnace maintained at 500°C. Initially, the solution boiled and underwent dehydration, followed by decomposition with escaping large amounts of gases (oxides of carbon, nitrogen and ammonia) and then spontaneous ignition occurred and underwent smouldering combustion with enormous swelling, producing white foamy and voluminous ash, the whole process was over within 5 minutes. The product was cooled to room temperature and the ashes

were ground gently. The resulting powders were annealed at 700°C for 4 hrs. The amount of Zn and Sr in the powder was 0.5 mol% each and Tb^{3+} was 1 mol%. Using the same procedure, $ZnAl_2O_4:Tb^{3+}$ and $SrAl_2O_4:Tb^{3+}$ were also prepared. The crystalline structure and phase composition of the $Zn_{0.5}Sr_{0.5}Al_2O_4:Tb^{3+}$ were analysed by X-ray diffraction (XRD) using a Siemens D5005 diffractometer with Cu K radiation, $\lambda = 1.5406 \text{ \AA}$. Scanning electron microscopy pictures were collected using JEOL JSM-6610 Scanning electron microscopy, Energy dispersive X-ray (EDS) measurements were performed using energy dispersive X-ray spectrometer attached to JEOL JSM-6610 (SEM). Photoluminescence (PL) excitation and emission measurements were carried out at room temperature using the Varian Cary Eclipse fluorescence spectrophotometer.

3. Results and Discussion

4. Structure

4.1. XRD analysis

Fig. 1 displays the X-ray diffraction patterns of ZSAO: Tb^{3+} before and after annealing. The patterns are consistent with ZAO and SAO phases referenced in the Joint Committee of Powder Diffraction (JCPDS) file No. 05-0669 and 74-794, respectively. It is noticed that there were no differences on the X-ray diffraction before and after annealing. The broadening of the diffraction peaks points to the presence of nanocrystalline domains. The result indicates that the obtained products are of high crystallinity and the small amount of Tb^{3+} doped virtually has no effect on the phase structures. Secondary phase of SrO was detected.

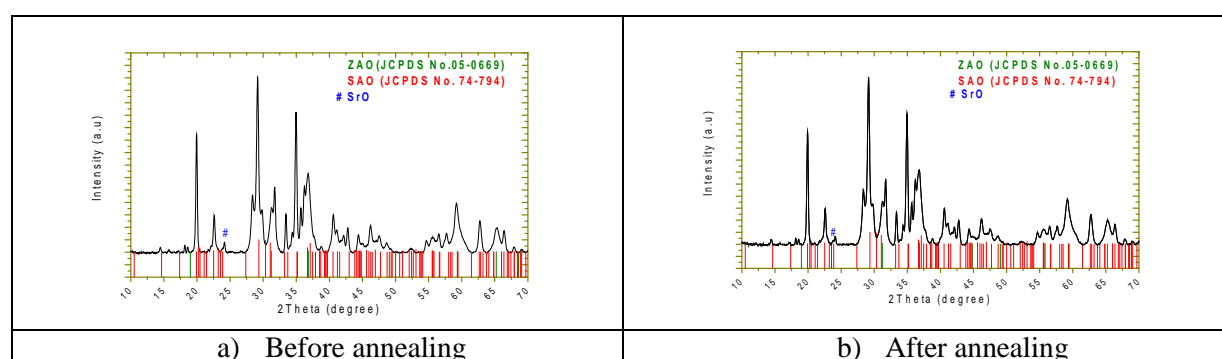


Figure 1: XRD pattern along with the standard JCPDS file of combustion synthesized ZSAO: Tb^{3+} 1.% mol phosphor.

4.2. Phosphor morphology

The morphological aspect of the resulting powders was examined by scanning electronic microscopy (SEM). The SEM images of ZSAO: Tb^{3+} before and after annealing are shown in Fig. 2a–b. The well-known semicontinuous folded dense platelet like morphology was observed and there were also voids resulting evolution and escape of large amount of gases during the combustion process. The particle shape was irregular; the surfaces of the foams show a lot of cracks, voids and pores formed by the escaping gases during combustion reaction. Compositional analysis on the nanostructures probed by EDS shows that the powders were composed of the C, Zn, Sr, Al and O elements (Fig. 2), and also, composed of a small amount of Mg and Co, which probably were incidental impurities in the precursors. Tb^{3+} was not detected due to its relatively low concentration. The results show that the doping process does not make significant changes to the morphology and size of the nanostructures.

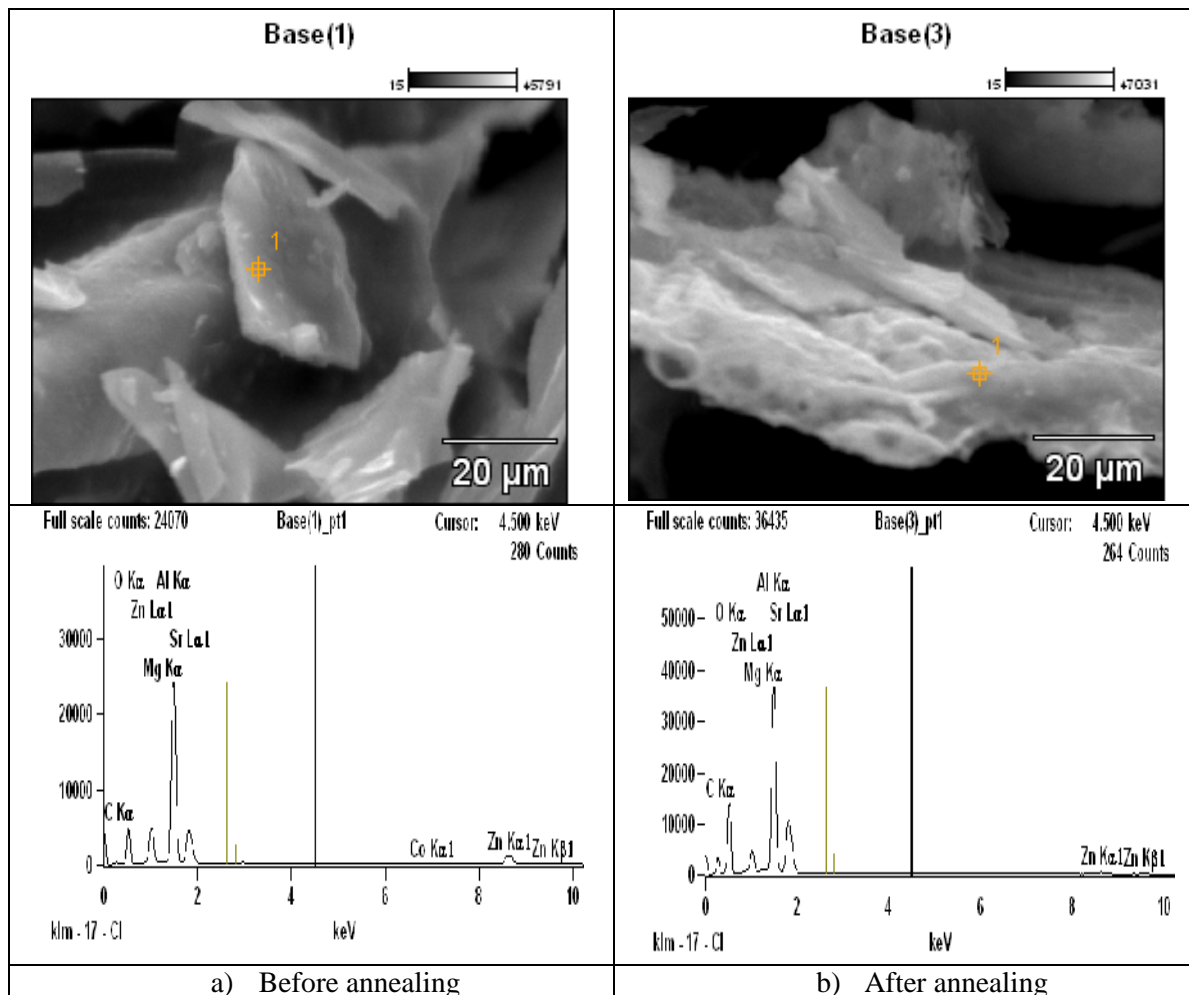


Figure 2: SEM micrographs of ZSAO:Tb³⁺ 1.0% mol , and the EDS spectrum of the combustion.

5. Photoluminescence properties

Photoluminescence (excitation and emission) spectra of Tb³⁺ in nano sized ZSAO, SAO and ZnO powder phosphors are shown in Fig 3a- b, before and after annealing. The excitation peak at 230 nm is attributed to the 4f⁸ 4f⁸5d¹ transitions of Tb³⁺ [15]. Fig.3a depicts the emission spectra (excitation = 230 nm) before annealing which consists of eight line emission bands. The 378, 410, 434 and 447 nm bands originate from the ⁵D₃-⁷F_J (J= 6,5,4,3,2) transitions, whereas 487, 544, 584 and 619 nm bands come from ⁵D₄-⁷F_J (J=6,5,4,3,2) transitions of Tb³⁺. The emission spectra after annealing also consists mainly of eight broad band (Fig.3b). The PL intensity of the annealed sample in Fig 3b was considerably more intense than that of the as prepared sample. The highest intensity before and after annealing was observed from SrAl₂O₄:Tb³⁺ and the least intensity was observed from Zn_{0.5}Sr_{0.5}Al₂O₄:Tb³⁺. Although the PL emission from Zn_{0.5}Sr_{0.5}Al₂O₄:Tb³⁺ was less intense than those from SrAl₂O₄:Tb³⁺ and ZnAl₂O₄:Tb³⁺, this preliminary data suggest that Zn_{0.5}Sr_{0.5}Al₂O₄, as a possible future host for rare-earths to prepare phosphors. This study is in progress and the effects of Zn and Sr concentration of the PL intensity will be evaluated in future experiments.

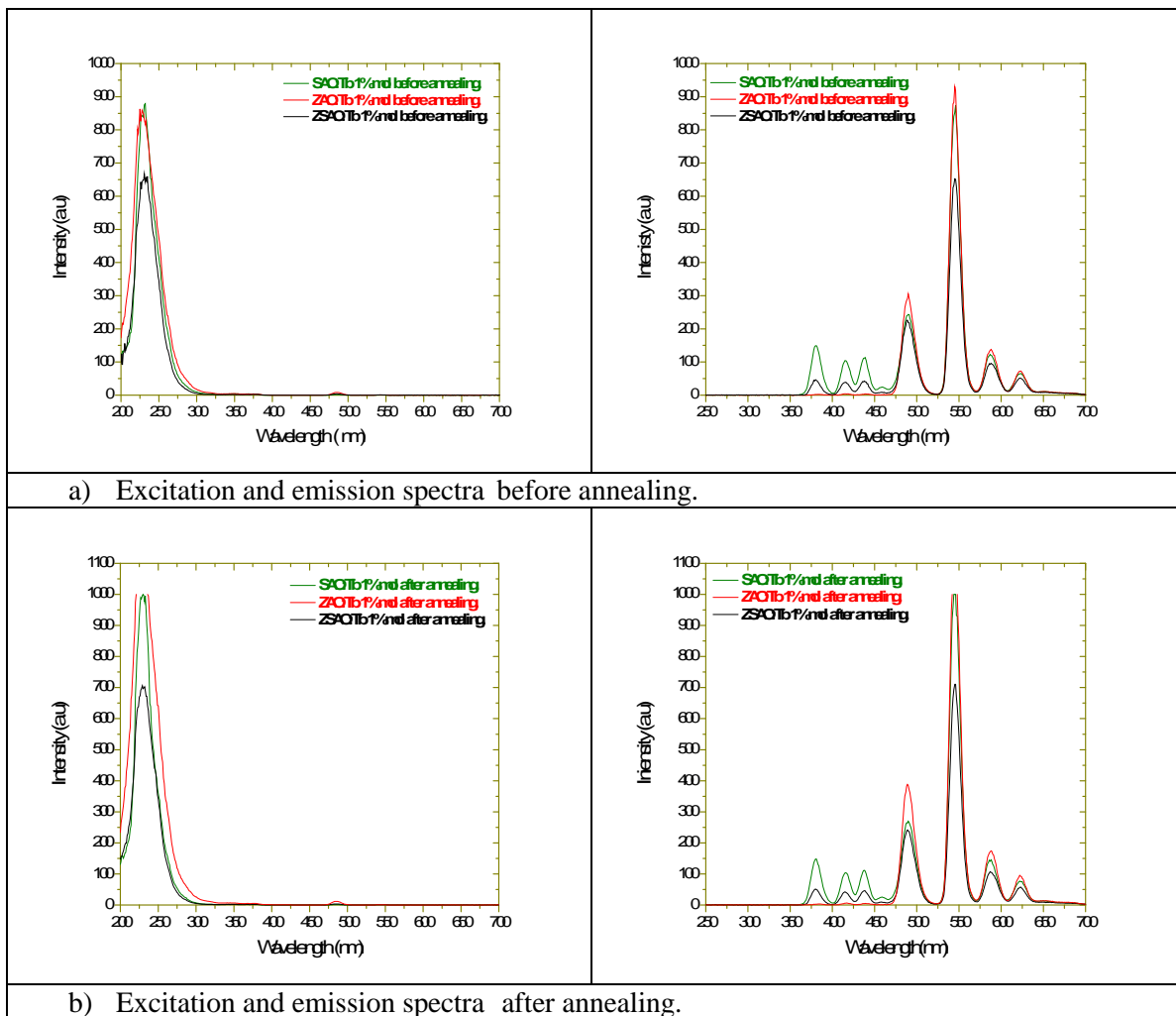


Figure 3: PL (excitation and emission) spectra of ZSAO:Tb³⁺ 1.0% mol before and after annealing.

6. Conclusion

Nanocrystalline ZSAO:Tb³⁺ 1.0% mol was prepared using combustion method and the initiating temperature of 500 °C. The formation of the spinel phase was confirmed by X-ray diffraction data. The well known characteristic platelet-like particles of the combustion method was confirmed from the SEM data. Characteristic blue and green luminescence from Tb³⁺ ions was observed in ZSAO:Tb³⁺ nanophosphors. The green line emission at 543 nm was more intense in annealed versus as prepared samples.

Acknowledgement

The authors are grateful to the financial support from the South African National Research Foundation (NRF).

References

- [1] Geng B.Y., Ma J.Z. and Zhan F.M., 2009, *J. of Alloys and Compounds*, 473, 530.
- [2] Palilla F.C., Levine A.K. and Tomkus M.R., 1968, *J. Electrochem. Soc.* 115, 642.
- [3] Zhang Y., Lan L.I., Zhang X., Wang D. and Zhang S., 2008, *J. of Rare Earths*, 26, 656.
- [4] Lou Z. and Hao J., 2005, *Appl. Phys. A*, 80, 151.
- [5] Xiulan D., Duorong Y., Xinqiang W. and Hongyan X.U., 2005, *J. of Sol-Gel Science and Technology*, 35, 221.
- [6] Zuoling F.u., Shihong Z. and Siyuan Z., 2005, *J. Phys. Chem. B*, 109, 14396.
- [7] Su Q., Liang H., Tao Y. and Wang S., 2001, *J. of the Chinese Rare Earth Society (in Chin.)*, 19(6), 482.
- [8] Mu-Tsun T., Yu-Xiang C., Pei-Jane T. and Yen-Kai W., 2010, *Thin Solid Films*, 518 e9–e11.
- [9] Adak A.K., Pathak A. and Pramanik P., 1998, *J. Mater. Sci. Lett.*, 17, 559.
- [10] Valenzuela M.A., Bosch P., Aguilar-rios G., Montoya A. and Schifter I., 1997, *J. Sol-Gel Sci. Technol.* 8, 107.
- [11] Minami T. et al. In *Extend. Abstr. 4th Int. Conf.*, 1998, *Science and Technology of Display Phosphors*, Bend, OR, 370.
- [12] Matsui H., Xu C.N. and Tateyama H., 2001, *Appl. Phys. Lett.* 78, 1068.
- [13] Wu S., Zhang S. and Yang J., 2007, *Mater. Chem. Phys.*, 102(1), 80.
- [14] Chang C.K., Yuan Z.X. and Mao D.L., 2006, *J. Alloys Compd.*, 415(1-2), 220.
- [15] Barros B.S., Melo P.S., Kiminami R.H.G.A., Costa A.C.F.M., Sa' G. F.D. and Alves S.J., 2006, *J. Mater Sci* , 41, 4744.
- [16] Esparza A., Garcia M. and Falcony C., 1998, *Thin Solid Films*, 325, 14.
- [17] Golego N. and Cocivera M., 1998, *Thin Solid Films*, 322, 14.
- [18] Hanyan D., Gengshen L. and Jiayue S., 2007, *J. of Rare Earths*, 25(1), 19.
- [19] Huajie S. and Donghua C., 2007, *Luminescence*, 22, 554.
- [20] Pitale S.S., Vinay K., Nagpure I.M., Ntwaeaborwa O.M. and Swart H.C., 2011, *Applied Surface Science*, 257, 3298.
- [21] Shu F.W., Feng G., Meng K. L., Xiu F.C., Wen G.Z., Guang J.Z., Shu M.W. and Yuan Y.Z., 2005, *J. of Alloys and Compounds*, 394, 255.
- [22] Kingsley J.J. and Patil K.C., 1988, *Mater. Lett.*, 6(11-12), 427.
- [23] Kingsley J.J., Suresh K. and Patial K.C., 1990, *J. Mater. Sci.*, 25(2), 1305.