

Synthesis and characterization of green SrAl₂O₄:Tb³⁺ phosphor using solution combustion method

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Abstract. SrAl₂O₄:Tb³⁺ phosphors doped with different concentration of Tb³⁺ varied from 0.25 - 2% were synthesized by the solution combustion method. The crystalline structure, morphology and luminescent properties of the phosphors were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) spectroscopy respectively. The XRD analysis reveals a polycrystalline monoclinic structure and the calculated average particle sizes ranged between 80 and 90 nm. SEM images show non uniform and irregular shape particles. The Tb³⁺ doped SrAl₂O₄ phosphor showed green emission when illuminated with an excitation wavelength of 229 nm. The emission spectra show a weak blue emission in the region of 415—459 nm and strong green emission in the 489—622 nm range. The 4f—4f emission from ⁵D₄ to ⁷F_J (J= 6, 5, 4, 3) states of Tb³⁺ were found at 489, 543, 585 and 622 nm, respectively. Other emission peaks from the ⁵D₃ to ⁷F_J (J=5, 4, and 3) transitions (blue) were found at 415, 436 and 459 nm. The decay curves of SrAl₂O₄:Tb³⁺ phosphor showed rapid decay followed by a long afterglow. The intensity of the phosphorescent decreased with an increase in the concentration of the Tb ions of 1% in the host lattice.

1. Introduction

Long lasting phosphor materials are energy storing materials and can potentially light up for long times in darkness. The materials can absorb visible light, store the energy and gradually release the energy as visible light [1]. SrAl₂O₄ is one of the typical matrices for long duration luminescent materials, which are doped with Eu, Ce, Tb, etc. and is an efficient host lattice with a wide band gap which can generate a broad band emission [2]. As compared with other synthesis methods, the combustion method is very simple, saving energy and it takes only a few minutes without requiring subsequent intermediary calcination stages [3, 4]. Tb³⁺ is one of the most widely used rare-earth ions activator for green luminescent materials and has been used widely in tri-color energy saving fluorescent lamps and its emission mainly originate from the ⁵D₄ to ⁷F_J (J=0-6) transitions [5, 6]. The SrAl₂O₄ host belongs to the tridymite-like structure. The structure is formed by a three dimensional corner-sharing AlO₄ tetrahedron frame-work. The divalent Sr²⁺ cation balance the charge and occupies an interstitial site within the tetrahedral frame-work [7, 8].

In the present work we have prepared and investigated SrAl₂O₄ phosphor material doped Tb³⁺ ion as an activator. The different concentrations of Tb³⁺ were used and its effect on structure, photoluminescence and luminescence lifetimes was investigated.

2. Experimental

2.1. Sample Preparation

The nitrates of Sr, Al, Tb and urea were taken as starting materials, and were dissolved in enough deionized water and kept stirring for 30 minutes until the solution becomes clear. The mixed solution was placed into a muffle furnace maintained at 500 °C. In about five minutes the solution boiled and underwent dehydration followed by decomposition with escaping large amounts of gases (oxides of nitrogen and ammonia) then spontaneous combustion with enormous swelling produced foamy and voluminous powder. As soon as the reaction was over, the product was cooled at room temperature. The foamy powder was crushed into powder using a pestle mortar and the obtained white powder was characterized. This was repeated for different concentrations of Tb 0.25, 0.4, 0.5, 1, 1.5 and 2%.

2.2. Characterization

The crystalline structure and particle size of the phosphor were investigated using the D8 advanced AXS GmbH X-ray diffractometer (XRD), the morphology and chemical composition analyses have been carried out using a Shimadzu's S5X-550 scanning electron microscope (SEM) equipped with an electron dispersive X-ray spectrometer (EDS). PL measurements were made on a Carry Eclipse photoluminescence spectrophotometer system, equipped with a 150 W xenon lamp as the excitation source.

3. Results and Discussion

3.1. X-ray diffraction

Figure 1 shows the XRD patterns of the $\text{SrAl}_2\text{O}_4:\text{Tb}^{3+}$ phosphor doped with different concentration of Tb^{3+} . It was found that the main peaks formed correspond to the SrAl_2O_4 monoclinic phase according to the JCPDS, card number (74-0794). Although the main peaks of the crystal structures were observed there were some unknown peaks (marked with stars and dots) and maybe attributed to impurity phases such as $\text{SrAl}_{11}\text{O}_{19}$ and $\text{Sr}_7\text{Al}_2\text{O}_{25}$, or some of the unreacted precursors during the combustion method. The particle sizes of each peak of the phosphor were calculated using the Scherrer's equation and are shown in table 1.

Table 1. Particle sizes for $\text{SrAl}_2\text{O}_4:\text{xTb}^{3+}$ (x=0.4, 0.5, 1 and 2%) phosphor

hkl	020	211	220	211	031	400	
$\text{SrAl}_2\text{O}_4:\text{xTb}^{3+}$	Particle sizes						Average
X=2%	88nm	84nm	98nm	94nm	60nm	72nm	82nm
X=1%	94nm	90nm	104nm	108nm	56nm	62nm	86nm
X=0.5%	88nm	88nm	98nm	102nm	56nm	52nm	80nm
X=0.4%	92nm	90nm	98nm	100nm	56nm	52nm	82nm

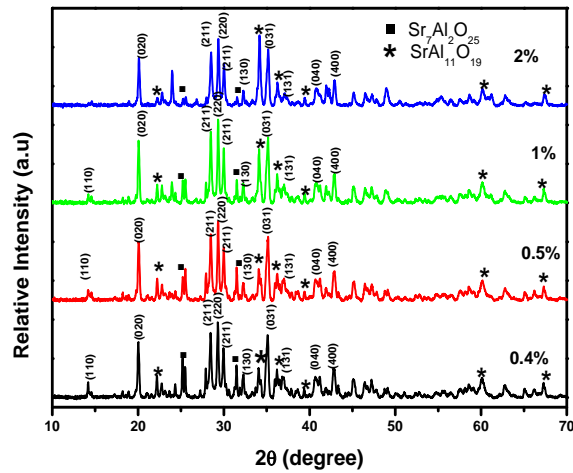


Figure 1. XRD patterns of $\text{SrAl}_2\text{O}_4:\text{Tb}^{3+}$ with different concentration of terbium

3.2. Scanning Electron Microscopy and Energy Dispersive Spectroscopy

Figure 2 shows SEM images of (a) $\text{SrAl}_2\text{O}_4:0.5\text{Tb}^{3+}$ and (b) 1% phosphor prepared by the combustion method. The samples show the pores and voids on the surface that formed by the escaping gases during the combustion method. The morphology of the powders reflects the inherent nature of the combustion process. The images show non uniform and irregular shapes of the particles and there was no big difference as the concentration of Tb increased from 0.5% up to 2%. Among the images the 0.5 % was presented. All the elements were included in $\text{SrAl}_2\text{O}_4:\text{Tb}^{3+}$ phosphor were detected in EDS spectra, except for dopant Tb^{3+} , this is because its concentration was too far small to be detected. The presence of $\text{SrAl}_2\text{O}_4:\text{Tb}^{3+}$ is confirmed with the Ca, Al, and O peaks. Carbon peak in EDS spectra is for carbon tape. The EDS spectra are similar for all samples and therefore the representative spectrum is provided.

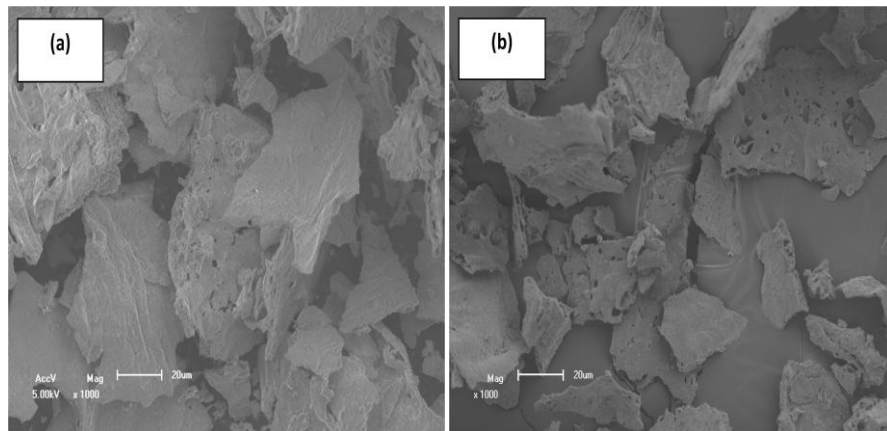


Figure 2. SEM image of $\text{SrAl}_2\text{O}_4:0.5\text{Tb}^{3+}$ (a) and $\text{SrAl}_2\text{O}_4:0.5\text{Tb}^{3+}$ (b) at 1000x magnification

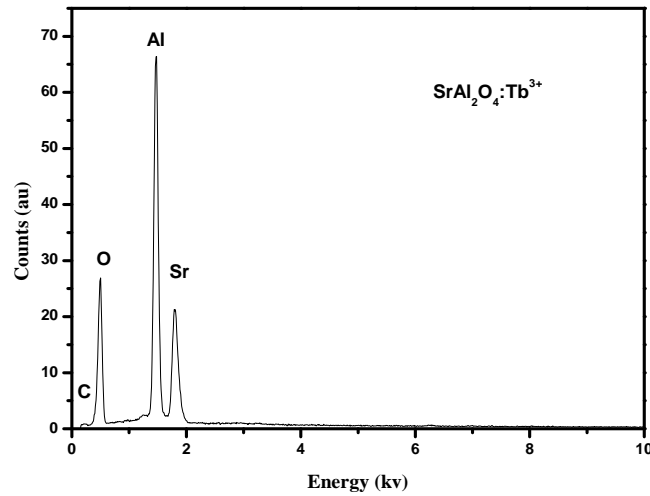


Figure 3. EDS spectrum of SrAl₂O₄:0.5%Tb³⁺

3.3 Photoluminescence

Figure 4 shows the excitation spectra for the SrAl₂O₄ doped with different moles concentration of Tb³⁺. A broad band centred at 229 nm was observed when the 543 nm emission of Tb³⁺ was monitored. The strong 229 nm peak is related to the f–d excitation of the Tb³⁺. Figure 5 shows the emission spectra of the SrAl₂O₄:Tb³⁺ phosphor. The Tb³⁺ doped SrAl₂O₄ phosphor shows a green emission when illuminated by 229 nm. The emission spectra show the weak blue emission in the region of 415–459 nm and strong green emission in the 489–622 nm range. The 4f–4f emission from ⁵D₄ to ⁷F_J (J= 6, 5, 4, 3) states of Tb³⁺ are found at 489, 543, 585 and 622 nm, respectively. Other emission peaks from the ⁵D₃ to ⁷F_J (J=5, 4, and 3) transitions were also found at 415, 436, and 459 nm [8,9].

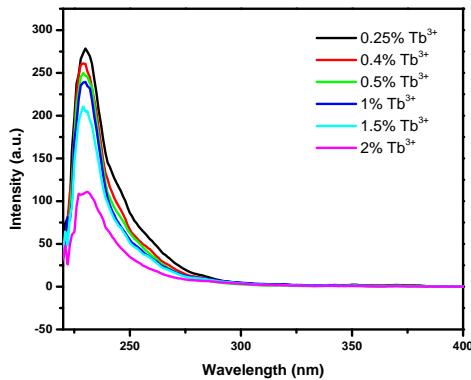


Figure 4. Excitation spectra of SrAl₂O₄:Tb³⁺ with different concentration of Tb³⁺ $\lambda_{em}=543$ nm

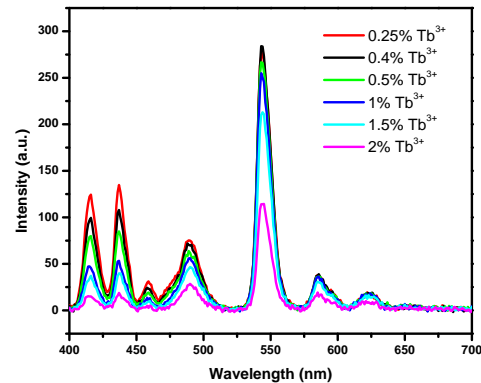


Figure 5. Emission spectra of SrAl₂O₄:Tb³⁺ with different concentration of Tb³⁺ $\lambda_{ex}=229$ nm

It was found that when the mole concentration of the terbium was increased up to 1% in the host lattice, there was a significant decrease in intensity of all the Tb transition due to the concentration quenching as shown in figure 6. The average distance between luminescent centers is related to the luminescent intensity. The distance between active ions decreases with the increase of doping concentration. When this distance is short enough, the interaction between active ions cause concentration quenching [10].

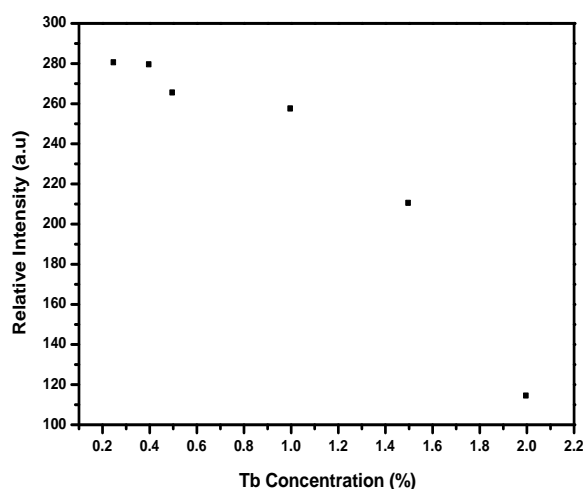


Figure 6. Graph of concentration dependence of the emission maximum intensity of Tb^{3+} doped SrAl_2O_4

3.3. Decay curves and afterglow characteristics

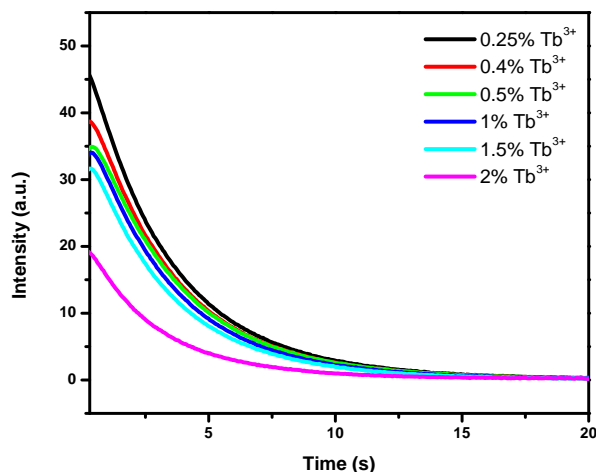


Figure 7. Decay curves of $\text{SrAl}_2\text{O}_4:\text{Tb}^{3+}$ with different concentration of Tb

Figure 7 shows decay curves of $\text{SrAl}_2\text{O}_4:\text{Tb}^{3+}$ phosphor with different moles concentration of Tb^{3+} . The phosphor showed the rapid decay and long afterglow. The initial intensity of the phosphorescent decreases as the concentration of terbium ions increased in the host lattice. The exponential decay times as shown in table 2 are described as (1) initial rapid decay, and (2) slow decay components. The decay constants have higher values for sample with concentration of 0.25 mol% and lower value for the sample with 2 mol%.

Table 2. Decay parameters of the SrAl₂O₄:Tb³⁺ phosphor with different Tb³⁺ concentrations

Tb ³⁺ %	0.25%	0.4%	0.5%	1%	1.5%	2%
Components	Decay constants					
τ ₁ (ms)	0.25	0.21	0.20	0.17	0.11	0.01
τ ₂ (ms)	3.52	3.42	3.40	3.32	3.39	3.18

4. Conclusion

SrAl₂O₄:Tb³⁺ phosphor has been successfully prepared by the combustion method. The XRD results showed that the phosphor has a monoclinic crystal structure. Characteristic green luminescence from Tb³⁺ was observed. The SrAl₂O₄:Tb³⁺ exhibited a predominant green emission at 543 nm, which was assigned to the ⁵D₄ to ⁷F₅ transition of Tb³⁺. The SrAl₂O₄:Tb³⁺ (0.25 mol%) phosphor showed the maximum emission intensity. The non uniform and irregular shapes of the particles was shown by scanning electron microscopy. All the elements of SrAl₂O₄:Tb³⁺ were confirmed by EDS. The decay curves of the phosphors were observed and its intensity was decreased as concentration of Tb³⁺ increased to 1%.

References

- [1] Song H, Chen D, Tang W and Peng Y 2008 *Displays*. **29** 41-44
- [2] Zuoling F, Shihong Z and Siyuan Z 2005 *J. Phys. Chem. B* **109** 14396-14400
- [3] Huajie S and Donghua C 2007 *Luminescence*. **22** 554-558
- [4] Barros B S, Melo P S, Kiminami R H G A, Costa A C F M, de Sá G F and Alves Jr S 2006 *J. Mater Sci.* **41** 4744-4748
- [5] Verma R K, Kumar K and Rai S B 2010 *Solid State Sciences*, **12** 1146-1151
- [6] Zhang Y, Li L, Zhang X, Wang D and Zhang S 2008 *J. Rare Earths*. **26** 656
- [7] Ryu H and Bartwal K S 2009 *Physica. B* **404** 1714-1718
- [8] Shin-Hei C, Nam-Hoon K, Young-Hoon Y and Sung-Churl C 2006 *J. Ceramic Processing Research*. **7** 62-65
- [9] Lu C H, Godbole S V and Natarajan V 2005 *Materials Chemistry and Physics*. **94** 73-77
- [10] Zhu H, Yang D, Yang H, Zhu L, Li D, Jin D and Yao K 2008 *J. Nanopart Res.* **10** 307-312