Photoluminescence properties of green emitting phosphor Y₄Al₂O₉: Tb³⁺ derived by modified combustion route

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Abstract: The Tb³⁺-doped Y₄Al₂O₉ powders were synthesized by combustion technique employing dual (Glycine + Urea) fuel. Formation of the compound was confirmed by XRD technique. Photoluminescence (PL) properties of Tb³⁺ ions doped Y₄Al₂O₉ (with Tb³⁺ concentration = 0.5, 1, 1.5, 2, 2.5 mol%) were investigated. It was found that Y₄₋ₓTbₓAl₂O₉ phosphor exhibits green emission under 251 nm excitation. The emission intensity is found to be maximum at 2 mol % of Tb³⁺ activation further increase in Tb³⁺ incorporation decreases the emission intensity exhibiting concentration quenching.

1. Introduction

The compounds with different Y: Al stoichiometry were derived namely– yttrium orthoaluminate YAlO₃ (YAP). Yttrium aluminum garnet Y₃Al₅O₁₂(YAG) and monoclinic Y₄Al₂O₉ (abbreviated YAM) from pseudo-binary Y₂O₃-Al₂O₃ system. To a great extent, rare earth activated former two compounds were studied widely with respect to its crystal growth, physiochemical and optical properties including laser action. Investigation on optical characteristics of Y₄Al₂O₉ is considerably below par because of the associated complications experienced during preparation of compound and firmness of a sole-phase compound. Initial study begins with gauging crystal structure of YAM on the basis of quantifying the sample prepared by method of flame fusion [1]. Structural clarification of YAM has been described lately [2]. It was thus discovered that Y₄Al₂O₉ crystal acquires monoclinic pattern with space group P21/c. While growing single crystal by soft chemical route, YAM may undergo phase transition at about 1300 °C producing YAG phase and unknown X phase [3]. In further studies decay of YAM to YAG and YAP has been noticed [4, 5]. In recourse of problems associated with synthesis process, great attention has been paid latterly to prepare YAM at lesser temperatures to bypass incidence of phase transitions.

In recent years [6], the evolution of rare-earth doped luminescent compounds has been material of substantial research. One of such highly efficient Trivalent terbium ion (Tb³⁺) is well known for its green emission. Terbium (Tb³⁺) activated phosphors are worthy for various technological industrial applications [7], just to mention a few: Cathode ray tubes, fluorescence lamps, field emission displays and light emitting diodes. Being ability to responds precisely to high energy excitation, terbium doped phosphors are used in X-ray screens [8] and as scintillators. Not so recently, terbium activated phosphors offers applications as a luminescence probes in biochemistry [9] as well as high-temperature luminescence thermometry [10], including barrier coatings [11] and nanoscale measurements [12].

Number of soft chemical synthesis processes have been investigated for preparation of rare-earth activated YAM, most of these methods put up with relatively complicated and expensive for the industrialization. Though hydrothermal synthesis and Sol–gel techniques are widely explored for the synthesis of YAM, these routes require expensive chemicals equipment along with procedural complications. Moreover, prolonged annealing at temperatures around 1000°C is necessary to obtain Phase pure compound.
In the present study, we have prepared YAM in one step using combustion synthesis executing at 550°C furnace temperature utilizing mixed (Urea+Glycine) fuel. Incorporation with Tb³⁺ in YAM host can also be attained in the course of preparation without any post combustion annealing.

2. Experimental
The powder samples of Tb³⁺doped Y₃₋ₓTexAl₂O₉ (x = 0.005, 0.01, 0.015, 0.02, 0.025) were prepared using solution combustion synthesis. The rare earth nitrates were prepared by dissolving corresponding reagent grade (Indian Rare-earth Ltd) oxides/carbonates in nitric acid. The nitrates so prepared were dried by lengthy, gentle warming. In mortar and pestle Stoichiometric amounts of hydrated nitrates of yttrium, aluminum, and Terbium were rigorously crushed with fuel urea and glycine. The oxidizer/ fuel ratios were estimated by the technique described previously [13, 14]. Due to existence excess crystallization water present in aluminum nitrate, thick paste in mortar and pestle was formed while crushing the mixture. The paste was poured in china dish. A china dish containing thick paste was kept in a furnace preheated at 550°C. Within some time, the paste violently boiled and foamed producing a flame which lasted for few seconds. The china dish was soon withdrawn from the furnace and allowed to cool at room temperature. No further annealing was needed. Phase identification were studied on Rigaku- Miniflex- II diffractometer. Morphology of crystalline sample was studied using JEOL (JSM-6380) scanning electron microscope. PL characteristics were studied on RF-5301 Spectrofluorophotometer using 1.5 nm spectral width within the wavelength range 220 nm – 700 nm. The composition/green mixture for preparation of various dopant concentration of Tb³⁺ ion is illustrated below in table no.1.

Table 1 Green mixtures for various YAM doped with Tb³⁺ phosphors

| Sr. No. | Composition       | Ingredient, mole fraction * | Remark          |
|---------|------------------|-----------------------------|-----------------|
| 1       | Y₃.₉₈Tb₀.₀₂Al₂O₉ | YN 3.98, TbN 0.02, AlN 2.0, Glycine 6.67, Urea 5.0 | Phase Pure compound Moderate PL |
| 2       | Y₃.₉₆Tb₀.₀₄Al₂O₉ | YN 3.96, TbN 0.04, AlN 2.0, Glycine 6.67, Urea 5.0 | Phase Pure compound Moderate PL |
| 3       | Y₃.₉₄Tb₀.₀₆Al₂O₉ | YN 3.94, TbN 0.06, AlN 2.0, Glycine 6.67, Urea 5.0 | Phase Pure compound Moderate PL |
| 4       | Y₃.₉₂Tb₀.₀₈Al₂O₉ | YN 3.92, TbN 0.08, AlN 2.0, Glycine 6.67, Urea 5.0 | Phase Pure compound Strong PL |
| 5       | Y₃.₉₀Tb₀.₀₁Al₂O₉ | YN 3.90, TbN 0.1, AlN 2.0, Glycine 6.67, Urea 5.0 | Phase Pure compound Moderate PL |

Note: * Here YN = Y (NO₃)₃, 6H₂O, TbN = Tb (NO₃)₃, 6H₂O, AlN = Al(NO₃)₃, 9H₂O

3. Results and discussion
YAM being yttrium rich phase, high degree of temperatures may be expected during the combustion process due to exothermic reaction between glycine and yttrium nitrate. This may lead to decay of YAM and formation of detrimental phases YAP and YAG. In view of complications met during endeavor to have single phase Y₄Al₂O₉ compound, careful approach towards material preparation is of preeminent importance.
In present study, crystallinity was not attained using urea as a fuel. Corresponding XRD study shows noisy pattern due to the fact that, urea only forms exothermic reaction with aluminum nitrate and not with Yttriumnitrate. To circumvent this problem, we have tried a dual (glycine + urea) fuel. Phase purity of the compound YAM was thus attained by the combustion synthesis with mixed (glycine + urea) fuel due to respective exothermic reaction initiated between (Glycine with yttrium nitrate) and (urea with aluminum nitrate). The phase identification of the sample was checked on Rigaku- Miniflex- II X-ray diffractometer. It can be seen from Figure.1 that the XRD pattern of as prepared compound matches notably with the stick pattern of ICDD file 83-0935. Any lines analogous to YAH, YAP or YAG could not be seen implying the phase purity of the compound.

Figure 1. X-ray diffraction pattern of Y₄Al₂O₉ doped with Tb³⁺

SEM analysis was performed to study the morphology of crystallized Y₄Al₂O₉ powder. SEM micrograph of prepared powder sample Y₄Al₂O₉ appear to have strong agglomeration with porous network as shown in Figure. 2. Typical combustion synthesized powders [15, 16] shows such kind of porous network due to rapid release of by-products gases during the process.

Figure 2. SEM Image of Y₄Al₂O₉:Tb³⁺ prepared by Combustion method

Tb³⁺ activated with Y₄Al₂O₉ phosphors were prepared by combustion synthesis. Tb³⁺ ions doped Y₄Al₂O₉ (With molar concentration Tb³⁺ = 0.5, 1.1, 1.5, 2, 2.5 mol%) were prepared by method discussed
above. Photoluminescence spectra of YAM:Tb$^{3+}$ samples with varying Tb$^{3+}$ dopant concentration from 0.5 to 2.5 at.% under 251 nm excitation wavelength at room temperature are shown in Figure 3.

![Figure 3: Photoluminescence Spectrum of Y$_{3.92}$Tb$_{0.08}$Al$_2$O$_9$ Phosphor](image)

Few strong overlapped absorption bands (230-330 nm) and number of weak lines (330-500 nm) appear in the excitation spectrum of Tb$^{3+}$ in Y$_4$Al$_2$O$_9$ attributed to parity allowed 4f$^8$–4f$^7$5d transitions and parity forbidden intra-4f$^8$ transitions [17]. Considering their high intensity and wide range, efficient excitation in the 4f$^8$–4f$^7$5d transitions is desirable.

Under UV light excitation, Tb$^{3+}$ activated with Y$_4$Al$_2$O$_9$ phosphors shows fairly strong green emission. Emission spectrum of YAM: Tb$^{3+}$ phosphor with dopant concentration 2 mol% under excitation wavelength 251 nm is shown in Figure 3. The emission spectrum consists of familiar 5D$_{4}$–7F$_J$ ($J = 4, 5$) transition lines [18] with most prominent green emission peak attributed to 5D$_{4}$–7F$_5$ transition. It is obvious that Tb$^{3+}$ ion in Y$_4$Al$_2$O$_9$ occupy crystallographically different sites as Eu$^{3+}$ ion do. Every group of emission line of Tb$^{3+}$ contains contribution from different centers.

Figure 4 illustrate the deviation of PL intensities (5D$_{4}$–7F$_5$ transition of Tb$^{3+}$) with varying Tb$^{3+}$ concentration (mole %)

![Figure 4: PL Intensity of Y$_{4-x}$Tb$_{4x}$Al$_2$O$_9$ Phosphor for (x = 0.005, 0.01, , 0.015, 0.02, 0.025)](image)
The PL intensity is found to increases from 0.5 % and attained maximum value for 2 mol % of Tb\(^{3+}\) concentration. Further increase in dopant concentration more than 2 mol % causes drop in PL intensity due to the phenomenon of concentration quenching.

4. Conclusion

Single phase monoclinic Y\(_{4-x}\)Tb\(_x\)Al\(_2\)O\(_9\) Phosphor for (x = 0.005, 0.01, 0.015, 0.02, 0.025) were well prepared by combustion method utilizing dual (Urea + Glycine) fuel. The process discussed here is simple and safe for rapidly rendering fine and homogeneous powders. The process is self-propagating ignition route requires low temperature with added advantage of low procedural complexity. YAM:Tb shows adequately strong green emission under UV light excitation. The emission spectrum consists of familiar \(^{5}D_4\rightarrow^{7}F_j\) (J = 4, 5) transition lines with prominent \(^{5}D_4\rightarrow^{7}F_5\) green emission located at 544 nm. To commit color rendering and lumen output these transitions are crucial. So, these green phosphors may be exploited for fluorescent lamp to acquire higher lumen output and better color rendering index.

5. References

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