Luminescence properties of Y5Si3O12N:Ce3+/Tb3+ co-doped oxynitride phosphors

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Abstract. As possible alternative applying to trichromatic white LEDs, oxynitride phosphors which are consist of a range of Y-Si-ON: single doped Ce3+ and Y-Si-ON: Ce3+/Tb3+ co-doping were smoothly prepared with the use of typical solid state reaction route. Not only the purity of the resulting phosphors was raised, but also the intensity of emission was enhanced due to the introduction of Li2CO3 flux (5wt %). A strong wide excitation band is suitable for UV LED chips that is ranging from 200 nm to 400 nm having maximum peak around 358 nm has been noticed. In the Ce3+ mono-doped phosphor, we noted a strong blue emission whose peak is at 439 nm at this excitation wavelength and in the Y5Si3O12N:Ce3+/Tb3+ co-doped phosphors two different light bands were also noted: the blue band was at 439 nm when reached its peak due to the Ce3+ ion and because of the and a highly efficient green emission of having maximum peak around 549 nm as a result of Tb3+ ions transitions (5D4→7F5).

1. Introduction

Solid-state lighting (SSL) considering a highly regarded area with novel solid-state lighting technologies. In addition to those conversion-based white-LEDs (light emitting diodes) with phosphors, there is an efficient and attractive way to produce high quality white light that is effectively excited under blue (460 nm) and ultraviolet (310 nm – 390 nm) light chips involving an assembly of the three primary colors namely red, green and blue (RGB) phosphors. [1-4].

The trivalent Tb3+ ion considering an effective luminescent activator for which it can emit green light efficient under UV-light (ultraviolet light) and n-UV-light(near-ultraviolet light) irradiation. Tb3+ ions which produce green emission can be remarkably enhance as a Ce3+ substitution as a co-dopant. Furthermore the substitutions of Ce3+ as a co-dopant broad the excitation to higher wavelength regions (from UV to near UV and blue) because Ce3+ shows a broad band spin allowed 4f – 5d transition [5].
The trivalent Ce$^{3+}$ is consider a best sensitizers which effectively transfer its energy to its nearest co-dopant ions which intern emit light with higher wavelength.

There are many reports on the effective energy that transfers from the trivalent Ce$^{3+}$ (sensitizer) to the trivalent Tb$^{3+}$ (activator) for many different phosphor hosts, such as nitrides, oxides and oxinitrides [6-8]. The process of energy transfer make the emission spectrum broaden to longer wavelengths (green, yellow, and red), which rests with the activator’s concentration and the crystalline field that the host compounds are split of [9-10]. Therefore, it is very important for producing white light to choose the right phosphor host and activator.

Oxinitride phosphors, which like the other quaternary system of Y-Si-O-N, can be efficiently stimulated by ultraviolet light and near-ultraviolet light irradiation. Hence, they are used as the down conversion phosphor host for the production of WLEDs. The following crystal phases were intensively researched: Y$_2$Si$_3$O$_7$N, Y$_3$Si$_3$N$_4$, Y$_5$Si$_3$N$_6$O, Y$_4$Si$_2$O$_7$N$_2$ and Y$_5$Si$_3$O$_{12}$N [11-12], however, the crystal structure investigation and luminescence characteristics of the phosphor in the Y-Si-O-N system were insufficiently recorded. To be more specific, merely a few research are obtainable on the luminescent properties of the trivalent rare earth (RE$^{3+}$) doped Y-Si-O-N Phosphors [13-15].

Within this paper, we described the synthesis of Y$_5$Si$_3$O$_{12}$N:Ce$^{3+}$ phosphors which involves fluxes such as H$_3$BO$_3$, Li$_2$CO$_3$ and MgCl$_2$. Their presence is intended to increase the purity of the materials produced, thereby improving luminescence characteristics. The primary portion of the presented research intends to find the optimized the host composition and concentration of doped sensitizer (as illustrated in the experimental section, it is Y$_5$Si$_3$O$_{12}$N: 0.18Ce$^{3+}$ composition) [16]. The prepared optimized phosphors compounds is co-doped with another trivalent Tb$^{3+}$ ion. As well as the luminescent ability of color tuning and decay time, the luminescence properties of these optimized phosphors single doping and co-doping were discussed in this article at different temperatures (namely high temperature as well as normal temperature). Its efficiency and mechanism of energy transfer are also discussed in detail. In this article, we often mention optimized compositions, which contain specific contents of the trivalent Tb$^{3+}$ and Ce$^{3+}$ ions causing the highest emission peak intensity.

2. Materials used and Method

When the reaction is in the atmosphere of ammonia, a range of the trivalent Ce$^{3+}$ and Tb$^{3+}$ single doping as well as co-doped Y$_5$Si$_3$O$_{12}$N phosphors having apatite structure were purely produced by using a typical high temperature solid state reaction route. In the results of this experimental report, the exact compositions of prepared phosphors samples are reported. Highly fine powders of Y$_2$O$_3$, CeO$_2$ and SiO$_2$ (99.99% pure obtained from sinopharm chemical reagent (Co. Ltd., Shanghai, PR China), Si$_3$N$_4$ (Ube Industries, Ltd., Japan), and Tb$_4$O$_7$, (99.99% pure obtained from Yuelong Co. Ltd. Shanghai, PR China) were directly employed without further purification. In accordance with stoichiometric compositions, the obtained fine powders were efficiently weighed. Fine powders of H$_3$BO$_3$, Li$_2$CO$_3$ and MgCl$_2$ (99% pure obtained from sinopharm chemical reagent Co., Ltd. Shanghai, China) were weighed at 5% respective to all samples and added as a flux agents in the batches. The stoichiometric amount of powders were thoroughly mixed in a mortar, and ground completely with hand lasting 30 minutes. The prepared homogeneous mixtures were transferred to BN (boron nitride) crucibles. The crucibles having the prepare batches were gently transfer to high temperature zone of the horizontal tube furnace. Rise the temperature of tubular furnace to 1600 °C at rate of 10$^\circ$/minuets which is then keep at the same highest temperature for 4 hours under the continues flow of ammonia (NH$_3$) gas. After calcination the prepare samples were cool to room temperature at the same rate of heat and gas same atmosphere. The prepared phosphors were reground for further characterization.

The crystalline phase which belongs to the produced phosphors were determined by X-ray diffraction (XRD) analysis by using Cu Kα1 radiation at the constant scanning rate of 0.5$^\circ$/per minutes (Philips PW-1700, with a graphite mono-chromator, 100 mA and 40kV).

The luminescence characteristics like PL excitation and emission were measured by using 150 W xenon lamp spectrometer (Hitachi F-7000 spectrophotometer).
3. Results and discussion

The effect of the trivalent Tb\(^{3+}\) concentrations on the crystal structure of prepared Y\(_5\)Si\(_3\)O\(_{12}\)N:0.18Ce\(^{3+}\):yTb\(^{3+}\) co-doped phosphors host lattice is illustrated in the diffraction pattern of Fig. 1. Which clearly shown that all the phosphors samples were prepared with high purity. The diffractograms of high concentration Tb\(^{3+}\) shows some small impurity peaks which belongs to Y\(_4\)Si\(_2\)O\(_7\)N\(_2\) phase. The obtained results clearly shows that the trivalent sensitizer (Ce\(^{3+}\)) as well as activators (Tb\(^{3+}\)) in the mention concentration were both completely dissolved in Y\(_5\)Si\(_3\)O\(_{12}\)N phosphors host. It has been postulated that the Y\(_5\)Si\(_3\)O\(_{12}\)N phosphor belongs to apatite structure which offer two various crystallographic sites i.e. Y(1) and Y(2) for the occupation of the activators. The trivalent Ce\(^{3+}\) and Tb\(^{3+}\) randomly occupied these two crystallographic sites [16].

The photoluminescence excitation (PLE) and emission (PL) spectra of the single doped Ce\(^{3+}\) (0.18), Tb\(^{3+}\) (0.2) and Ce\(^{3+}\)/Tb\(^{3+}\) co-doped Y\(_5\)Si\(_3\)O\(_{12}\)N oxynitride phosphors are shown in Figure. 2 (2a, 2b, as well as 2c, severally). The Y\(_5\)Si\(_3\)O\(_{12}\)N: Tb\(^{3+}\) single doped phosphor exhibits a broad excitation spectrum having a strong peak around 250 nm, as a result of spin allowed transition (f–d transition), some weak peaks in higher wavelength region ranging from 300 – 450 nm were also observed in the excitation spectrum which is originated to the assimilation of f–f spin forbidden transitions. The emission spectrum of Tb\(^{3+}\) single doped Y\(_5\)Si\(_3\)O\(_{12}\)N phosphor illustrate a high intensive green emission band between 400 and 700 nm having maximum peak at 548 nm with various small peaks around 417, 438, 488, 548, 586, and 626 nm, assigned to the \(^{5}\)D\(_J\)\(\rightarrow\)^{7}F\(_J\) \((J=5, 4)\) and \(^{3}\)D\(_4\)\(\rightarrow\)^{7}F\(_J\) \((J=6, 5, 4, 3)\) transitions under UV (250 nm) light irradiations. Fig. 2c illustrate that broad excitation spectrum was observed in case of Ce\(^{3+}\) and Tb\(^{3+}\) co-doped which ranging from 200 nm to 400 nm having maximum peak around 358 nm which is ascribe to 4f – 5d allowed transition of the trivalent Ce\(^{3+}\) ions. Under the excitation of 358 nm UV light this Y\(_5\)Si\(_3\)O\(_{12}\)N:Ce\(^{3+}\)/Tb\(^{3+}\) co-doped phosphors emit a double emission band having maximum peak at 439 nm (blue emission) as a consequence of 5d\(^1\)\(\rightarrow\)4f\(^1\) transitions in Ce\(^{3+}\) and an efficient emission of green having maximum emission peak at 549 nm assigned to \(^{3}\)D\(_4\)\(\rightarrow\)^{7}F\(_J\) transitions in Tb\(^{3+}\). The obtained results shows that, when adding the trivalent Ce\(^{3+}\) ions as a sensitizer remarkably, it strengthens the luminescence intensity (approximately triple), as making comparison to Tb\(^{3+}\) single doped Y\(_5\)Si\(_3\)O\(_{12}\)N phosphor. This indicates that an energy transduction efficiently occurred from the Ce\(^{3+}\) sensitizer to the activator Tb\(^{3+}\).

Figure 1. X-ray diffractograms of co-doped Y\(_5\)Si\(_3\)O\(_{12}\)N:0.18Ce\(^{3+}\):yTb\(^{3+}\) oxynitride phosphors for \(y = 0, 0.1 – 0.5\). The standard PDF card number of the host lattice Y\(_5\)Si\(_3\)O\(_{12}\)N (JCPDS 48 – 1625) are also shown at the bottom.
Figure 2. PL excitation and emission spectra of (a) Y5Si3O12N:0.18Ce³⁺, (b) Y5Si3O12N:0.2Tb³⁺ and (c) Y5Si3O12N:0.18Ce³⁺/0.2Tb³⁺ oxynitride phosphors. (a) and (c) $\lambda_{\text{ex}} = 358$ nm and $\lambda_{\text{em}} = 439$ nm, and in (b) $\lambda_{\text{ex}} = 250$ nm and $\lambda_{\text{em}} = 549$ nm.

Figure 3. PL emission spectra of Y₅Si₃O₁₂N: zCe³⁺/0.4Tb³⁺ oxynitride phosphors at different concentrations of Ce³⁺ ($\lambda_{\text{ex}}=358$ nm).

It shows that green light emission increases (y axes-intensity) accompanied by the increase of Ce³⁺ contents. (Figure 3). The result ulteriorly suggests that occur successfully from the sensitization state of Ce³⁺ to activated state of Tb³⁺ in the co-doped phosphors. Specifically, the emission intensity increases which belongs to the green emission of Tb³⁺, as a result of increasing concentration of Ce³⁺ even though the concentration of Tb³⁺ were keep constant at y=0.4 which further proved that its energy transduction from Ce³⁺ to Tb³⁺ within Y₅Si₃O₁₂N phosphors. The appearance enhancements of green emission were observed at z=0.4. It is reflected in the figure that further rise of Ce³⁺ concentration (z > 0.4) create a lessen in emission intensity of green emission as a concentration quenching phenomenon.

4. Conclusion

Using high-temperature solid state reaction route surrounded by ammonia (NH₃) along with Li₂CO₃ flux, High-efficiency green color emitting Y₅Si₃O₁₂N:Ce³⁺/Tb³⁺ co-doped oxynitride phosphors were efficiently produced. The resulting phosphor has a wide excitation range from 200 nm to 400 nm UV region, a broad emission band from the blue spectral region (0.174, 0.169) to the effective green spectral region (0.293, 0.469), along with high level of photoluminescence quantum
yields (PLQY) up to 85%. Gently adjusting the concentrations of Ce$^{3+}$ and Tb$^{3+}$ ions, the wide emission spectrum can be effectively adjusted.

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