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Full Length Article

A novel solid-state synthesis of long afterglow, Si–N co-doped, $Y_3Al_5O_{12}:Ce^{3+}$ phosphor

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ABSTRACT

Si–N co-doped $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) phosphor was synthesized via a novel solid-state reaction method using $CeSiO_2N$ to simultaneously incorporate Si–N and Ce^{3+}. The achieved phosphor exhibits increased red light component and better thermal quenching property. Additionally, an evident long afterglow luminescence was detected for the first time. The analysis of the experimental results (X-ray diffraction, photoluminescence, X-ray absorption near edge spectroscopy, infrared spectroscopy, and thermoluminescence) suggests that the Si–N was homogeneously incorporated into YAG host lattice and most of the Ce^{3+} ions were directly coordinated with nitrogen. The deeper trap depth and greater number of oxygen vacancies around Ce^{3+} are responsible for the significantly enhanced long afterglow in Si–N co-doped YAG:Ce phosphor.

1. Introduction

Trivalent cerium-doped yttrium aluminum garnet (YAG:Ce) is an excellent yellow-emitting phosphor which can be effectively excited by the blue light. The YAG:Ce phosphor is regarded as a robust color converter that can be applied in GaN/InGaN-based white light-emitting diodes (w-LEDs) due to its high brightness and excellent thermal and chemical stability [1–3].

In the case of aluminate phosphors, Al–O pairs can be substituted by Si–N pairs due to the similar bond lengths and bond characters [4,5]. Therefore, the incorporation of Si–N into YAG:Ce phosphor has been considered as a promising topic for researchers. Liu [6] and Song [7] modified the host structure of YAG:Ce phosphor by the addition of Si_3N_4. However, in that case, Si^{4+} ions were the major substituent in host lattice, resulting in a blue shift in emission spectrum. Setlur [8] and Sopicka-Lizer [9] successfully incorporated Si–N into YAG:Ce host lattice, and achieved an increased red light component in emission spectrum, well-suited for single phosphor w-LEDs with low color temperatures and good color rendering. However, this modification caused a significant decrease in photoluminescence intensity, and the low-energy emission band of nitrogen coordinated Ce^{3+} showed stronger thermal quenching.

Long afterglow phosphors are a kind of material that can continue to emit light after removing the excitation source [10,11]. The energy absorbed from the excitation source can be stored in defect levels and gradually released in the form of afterglow [12–14]. Our previous study on $CaAl_2O_4:Eu^{2+},Sm^{3+}$ phosphor indicated that its long afterglow properties can be slightly improved by Si–N doping [15], which means the incorporation of Si–N in host lattice would be an available approach to enhance the long afterglow properties of phosphors.

The YAG:Ce phosphor is able to exhibit a very short afterglow when synthesized at reducing atmosphere [16–18]. However, there is no report on the enhancement of the afterglow in YAG:Ce phosphor with Si–N incorporation. In the products from conventional synthesis methods, most of the Si–N pairs are not directly coordinated to the activator. Thus, the energy absorbed from the excitation source is not stored in the defect levels related to Si–N incorporation. Therefore, there is no improvement in the afterglow energy. Moreover, the non-uniformly distributed Si–N pairs in the host lattice cause a reduction in the photoluminescence intensity and result in a stronger thermal quenching effect [8,9].

In this study, we propose a novel solid-state method to achieve the Si–N co-doped YAG:Ce phosphor using $CeSiO_2N$ powder instead of Si_3N_4 as a reactive starting material. The work-hypothesis is that

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the strong covalent bonds of Ce–N and Si–N in $CeSiO_2N$ will favor the direct coordination of Ce with nitrogen and facilitate the homogeneous dispersion of Si–N in host lattice, which will finally enhance the long afterglow of YAG:Ce phosphor, as well as the photoluminescence intensity and thermal quenching property. The achieved Si–N co-doped YAG:Ce phosphor exhibits increased red light component, better thermal quenching property, and, most importantly, enhanced long afterglow, as expected. The recorded Fourier transform infrared spectroscopy (FTIR), X-ray absorption near edge spectroscopy (XANES), and thermoluminescence(TL) spectra of the Si–N co-doped YAG:Ce phosphor are discussed to shed light on the mechanism of the enhanced long afterglow luminescence.

2. Experimental section

2.1. Preparation of Si–N co-doped YAG:Ce phosphors

$CeSiO_2N$ preparation: $CeSiO_2N$ was prepared by heating powders of CeO_2 (99.99%, Yuelong Co. Ltd, P. R. China), SiO_2 (99.99%, Sinopharm Chemical Reagent Co. Ltd, China) and Si_3N_4 (SN-E10, Ube Industries, Japan) at 1600 °C for 4 h under NH_3 atmosphere. The achieved pure phase $CeSiO_2N$ will be used to incorporate Si–N and Ce into YAG host in following experiment.

Si–N co-doping: The Si–N co-doped YAG:Ce phosphor was produced using a solid-state reaction method. The starting materials, Y_2O_3, Al_2O_3 (99.99%, Sinopharm Chemical Reagent Co. Ltd, China) and achieved $CeSiO_2N$, were thoroughly mixed by ball-milling in ethanol medium for 4 h with the formula of $Y_{3-x}Al_{5-x}Si_xO_{12-x}N_x{:}Ce_x(x=0.02-0.08)$. With respect to the weight of the total powder mixture, 5 wt% BaF_2 powder was also added as a flux agent. The well-mixed powder mixture was calcined at 1500 °C for 3 h under the N_2/10% H_2 atmosphere. The obtained phosphor was designated as YAG-CSON.

For comparison purposes, the traditional doping method with the using of Si_3N_4 was also proceed to incorporate Si–N into YAG: Ce phosphor (using powders of Y_2O_3, Al_2O_3, BaF_2, SiO_2, Si_3N_4, and CeO_2 at a molar ratio of Y:Al:Si:Ce=2.94:4.94:0.06:0.06), according to an earlier study [9], designated as YAG-SiN. Moreover, YAG: Ce phosphor without Si–N doping was similarly produced (using powders of Y_2O_3, Al_2O_3, BaF_2, and CeO_2 at a molar ratio of Y:Al: Ce=2.94:5.00:0.06), designated as YAG. The Ce^{3+} concentration was optimized for the two phosphors.

2.2. Measurement and characterization

The crystalline phases were analyzed by the X-ray diffractometer (XRD, Philips PW 1700) using Cu $K_{\alpha 1}$ radiation and KCl was added as an internal standard. The lattice parameter was calculated from the XRD pattern by using Jade 6.5 software through the standard procedure. The photoluminescence (PL) spectra were measured using a fluorescent spectrophotometer (F-4600, Hitachi Ltd., Japan). The temperature-dependent photoluminescence measurements were carried out using a Hamamatsu MPCD-7000 multichannel photodetector with a 200 W Xe lamp as the excitation source.

The decay curves were measured by a steady state/transient fluorescence spectrometer (JY Fluorolog-3-Tou, Jobin-Yvon, France). Before measuring the decay curves, all the samples were excited by a 450 nm Xe-lamp for 5 min. The measurements of the decay curves began as soon as possible after irradiation.

The FTIR of the produced phosphors was recorded to provide the information of Si–N units in host lattice using a Nicolet 8700 spectrophotometer in the range of 500–1300 cm^{-1}, and all samples were processed with the same conditions. The XANES of Ce L_3-edge was measured at the BL14W1 beam-line of the Shanghai Synchrotron Radiation Facility (SSRF) with an electron beam energy of 3.5 GeV.

The TL spectra of the samples were determined by the thermoluminescence spectrometer (FJ-427A1, Beijing Nuclear Instrument Factory, China) at a heating rate of 1 K/s from room temperature to 400 °C. Before TL measurements, the samples were excited by a 254 nm UV-lamp for 10 min.

3. Results and discussion

3.1. Phase analysis

The XRD patterns of YAG, YAG-SiN, and YAG-CSON (with $x=0.02-0.08$) are shown in Fig. 1. All samples match well with the phase of $Y_3Al_5O_{12}$ (JCPDS card 01-079-1891) and there is no evidence of impure phases related to Si–N doping. A small peak shift can be noticed for Si–N doped samples, and the magnified diffractograms provide a clear view of the peak shift in the range of 33.0–33.6°, indicating a shrinkage in unit cell. Similar results can also be tracked in previous studies on Si–N co-doped YAG:Ce and $BaMgAl_{10}O_{17}{:}Eu^{2+}$ (BAM:Eu) phosphors [4,5,9]. For YAG, YAG-SiN, and YAG-CSON ($x=0.06$) samples, which possess the same Ce concentration, Si–N incorporation have decreased the lattice parameters, as shown in Table 1. Furthermore, YAG-CSON ($x=0.06$) have a much lower lattice parameter than YAG-SiN (with the same Si–N concentration), which potentially qualifies $CeSiO_2N$ as an effective compound with regard to the incorporation of Si–N.

3.2. Photoluminescence analysis

The PL spectra of YAG, YAG-SiN, and YAG-CSON ($x=0.06$) samples are plotted in Fig. 2a. The excitation spectra exhibit three absorption bands and Si–N incorporation has improved the symmetry of the peak at 225 nm. The $4f^1$ configuration of Ce^{3+} in YAG host lattice has two ground states ($^2F_{7/2}$ and $^2F_{5/2}$) with only one electron, and the next higher $5d^1$ configuration is split by the strong crystal field of O^{2-}. Therefore, three Ce^{3+} absorption bands were recorded in excitation spectrum (at about 225, 345, and 460 nm). The weakest absorption band at 225 nm is caused by the overlap of upper $5d^1$ configuration with the conduction band [19]. Thus, the aforementioned features in the band of 225 nm suggest that the Si–N is coordinated close to Ce^{3+}ions, thereby affecting the centroid of upper $5d^1$ configuration.

According to earlier studies, when nitrogen is coordinated to rare earth ions in phosphors, the high negative charge of nitrogen (-3) leads to creation of a stronger crystal field, which moves the

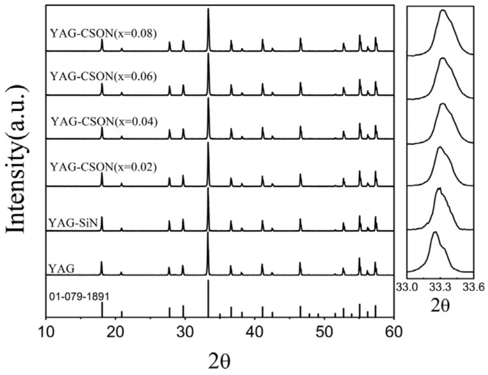

Fig. 1. The XRD patterns of YAG, YAG-SiN and YAG-CSON with different x values (0.02, 0.04, 0.06, and 0.08).