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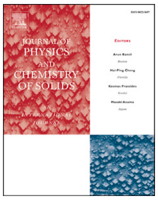

The effect of Ce^{3+} concentration and heat treatment on the luminescence efficiency of YAG phosphor

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ABSTRACT

$Y_3Al_5O_{12}$ (YAG) phosphor powders doped with Ce^{3+} at different concentrations (YAG:xCe, $x = 0.02$, 0.04, 0.06, 0.08, 0.1 wt%) were synthesized by the solid-state reaction method with the addition of BaF_2 flux. The effects of cerium concentration and heat treatment on the luminescence efficiency of the YAG:Ce^{3+} phosphor were investigated. The introduction of Ce^{3+} ions leads to an increase in luminescent intensity of the YAG phosphor at 560 nm. The band at 530 nm is attributed to Ce^{3+} ions (optical transitions from the 4f–5d excited state). We assumed that such an increase in the luminescent intensity is due to the ability of Ce^{3+} to act as a luminescence sensitizer of intrinsic defects in YAG phosphor. The analysis of luminescence decay kinetics in the investigated samples has shown that the decay time in all samples does not differ significantly and equals $\tau \approx 60 \pm 3$ ns. We showed experimentally that increasing the luminescence intensity has an effect observed with relatively low temperature treatment ($T = 400$ K). The nature of possible luminescence centers and the effect of low heat treatment on the luminescence properties of the powders are discussed.

1. Introduction

The production of white-light-emitting diodes (w-LEDs) is one of the promising directions in modern lighting engineering [1–3]. At present, the most effective and economical method is obtaining white light by means of a blue LED chip and yttrium aluminum garnets doped with Ce^{3+} ions (YAG:Ce) [4,5]. Phosphors provide a high transformation yield of the blue chip radiation in the 450 nm spectral region into visible radiation, thus opening the possibility for obtaining the necessary luminescence spectrum. They are also recyclable and toxin-free [6–8]. In general, the optical properties of phosphors are dependent not only on the doping agent but also on the synthetic conditions such as temperature, time, and atmosphere [9]. For the spray-drying method, for example, the annealing temperature plays a critical role in the crystal structure, morphology, and photoluminescence (PL) properties of phosphors [10].

For the successful long-term use of w-LEDs, the stability of the color and output power are important. The degradation of phosphor materials has been studied [1], as well as the thermal management of the device [10] and the effects of temperature-induced changes in the final output spectrum [11]. It is known that the increase in the w-LED operation temperature along with the increase in current is the determining factor for LED chip and phosphor degradation [12,13]. It is necessary to know how the radiative characteristics of phosphors vary with the thermal conditions of their operation [14]. Much theoretical and experimental research has been devoted to the study of phosphor degradation. Typically, such studies use temperature regimes in the range of 4–2000 K [14–17]. The variation of the light output has been shown to be complex and to involve changes in the absorption strength of the different f–d absorption bands and the temperature-dependent energy transfer to defects [18]. By increasing chip temperatures, investigators observed an intensity decrease of the blue emission from the LED (InGaN) combined with the shift of the emission maximum to a longer wavelength [19]. They also observed a decrease in the YAG:Ce emission band intensity. In a previous study [14], the temperature dependence of the Ce^{3+} emission intensity and its steady decrease above 700 K have been reported. The authors have shown that temperature-dependent luminescence lifetime measurements for low Ce concentrations (0.033%) are possible if the intrinsic temperature for quenching of the Ce^{3+} is high (well above 700 K). The lower quenching temperatures reported for the commercial YAG:Ce phosphor are explained by thermally activated concentration quenching [20]. When the energy of a LED is converted by a phosphor, the latter has been shown to heat up to about 470 K. The authors limited the heating of the phosphor to 400 K to study the processes occurring at real operating temperatures of the w-LED. Most of the previous studies on

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the effect of Ce^{3+} concentration were concerned with range of 0.1 and higher. We were not able to obtain information devoted to investigations of luminescence efficiency in relation to the particle size of YAG phosphors. Therefore, the effect of low temperature on YAG phosphor with slight change in cerium concentration (from 0.02 to 0.1 wt%) on the luminescence efficiency has not been studied yet.

In this work, undoped and YAG:xCe^{3+} powders ($x = 0$; 0.02, 0.04, 0.06, 0.08, 0.1 wt%) with added BaF_2 flux were synthesized by solid-state reaction in order to determine the effect of doping on the luminescent and thermal properties. The study examined the preparation technique, the luminescent properties, decay characteristics, and the effect of thermal treatment in the temperature range of 325–400 K on the luminescent properties of phosphors.

2. Experimental details

2.1. Sample preparation

The raw materials used, Y_2O_3 (99.99%), CeO_2 (99.99%), and Al_2O_3 (99.99%), were of high purity. The flux BaF_2 was added to the starting materials to attain a weight percentage of 10%. The addition of BaF_2 for decreasing the synthesis temperature is reported in a previous work [21]. A single-phase YAG:Ce^{3+} phosphor was obtained at 1500 °C. The introduction of BaF_2 flux to the synthetic process to form eutectic compositions with a low melting point and the subsequent solid–liquid reaction proceeded, forming YAG:Ce^{3+} phosphor [22]. The addition of flux produces wetted microdomains, which improve mass diffusion and accelerate solid-state reactions. The reactants were weighed stoichiometrically and thoroughly ground. The obtained mixture was combined with ethanol for 6 h using a rotational device. Next, the mixture slurry was dried at 800°C for 2 h. The powders were then fired under a reducing atmosphere (90% N_2, 10% H_2) at 1600°C for 12 h in a high-temperature furnace (KSL-1700X). In the final stage, the obtained mixture was ground using an agate mortar and pestle for about 30 min to 1 h to ensure the homogeneity of the mixture.

2.2. Measurements

The surface morphology of phosphors was investigated by scanning electron microscopy (SEM) using a Quanta 250 (FEI, USA) operated at an accelerating voltage of 10 kV, and by optical microscopy using a μVisio Lomo with blue-LED chip illumination ($\lambda = 447$ nm, 20 nm FWHM). For the analysis of the crystalline phase of all samples, we used an X-ray diffractometer (TD-3500; Dandong, China) utilizing Cu $K_\alpha 1$ radiation at 30 kV and 20 mA. The particle size distribution of the phosphor powders was determined by laser diffraction technique using an SALD-7101 analyzer (Shimadzu, Japan).

Steady-state photoexcitation (PE) and PL spectra at room temperature were recorded with a fluorescence spectrophotometer (F-7000, Hitachi, Japan) using a 150 W xenon lamp. Integrated emission spectra were acquired on an AvaSpec-3648 optical fiber spectrometer (200–1100 nm spectral range, 2.1 nm spectral resolution). An LED chip in pulse mode was used as excitation source for PL measurements: (70 ns pulse duration, $\lambda = 447$ nm 20 ns FWHM, 16 mW cm^{-2} irradiance, 10 ms integration time). The luminescence decay kinetics was measured with an MDR-204 grating monochromator, detected by a Hamamatsu 10720-20 PMT, and recorded by a Tektronix DPO3033 (300 MHz) digital oscilloscope. The time resolution of the setup was 2 ns.

The spectral power distribution of the total radiant flux of the PL spectra was measured by using an integrating sphere that was connected to a CCD detector (AvaSpec-3648). Samples were prepared in such a way that the surface area was ~1 cm^2. The phosphors were placed between two glass plates (glass type KU-10, ~88% transmittance in the 300–900 nm spectral range). The energy efficiency of the phosphors was evaluated as the ratio of the radiation flux of the blue chip and the radiation flux of the phosphors. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Sample characterization

The X-ray diffraction (XRD) patterns show no phase transitions in the samples obtained in the experiment (Fig. 1a). The intensity and FWHM of the peaks for the investigated powders do not change when the concentration of Ce^{3+} varies. This result suggests that the introduction of Ce^{3+} does not affect the crystallization processes in the samples. It should be noted that the maxima of the peaks for the different samples could shift within the measurement errors of the diffractometer. The diffraction peaks of the sample are in good agreement with the cubic phase of YAG [23].

We can see that the particle size varies from 1 μm to 100 μm, with the average particle size being ~10 μm for all phosphors (Fig. 1b–d). However, particle sizes greater than 100 μm were observed only for YAG:0.02Ce phosphor (Fig. 1c). Upon co-doping with Ce^{3+} at 0.02 wt% concentration, round irregularly shaped particles with sizes of ~100–300 μm formed. They intensely luminesced under the LED chip irradiation flux (Fig. 1d). There were smaller particles that do not luminesce; these were likely due to the presence of undoped YAG phosphor (the blue color is due to the scattering of the blue LED chip from the YAG white phosphor powder). A further increase in Ce^{3+} concentration led to the redistribution and size reduction of the luminescent particles that decreased the luminescence signal, as discussed below.

Phosphors with large particle size have many advantages over small ones [24] because the larger particles result in less scattering processes, which leads to an increase in the luminescence intensity. Moreover, small particles tend to agglomerate, forming large clusters due to their higher specific surface area, while large particles can effectively reduce agglomeration.

3.2. Excitation and pulse photoluminescent characteristics

The excitation spectra obtained at 530 nm show two bands with maxima at 342 and 452 nm (Fig. 2a). These bands were recorded both for the undoped and Ce^{3+}-doped YAG powders. The results show that the intensities of these bands significantly increase upon introduction of Ce^{3+} ions into the YAG structure. The spectra show two excitation bands, which are assigned to transitions between the two lowest energy levels of the five crystal field levels expected in D_2 symmetry. The two bands are centered at 342 and 460 nm, which is in agreement with previous experimental data [25,26].

The PL spectra of undoped and doped YAG phosphor powders under blue LED chip excitation ($\lambda_{ex} = 447$ nm) are not significantly different. In the luminescence spectrum of the YAG phosphors, three peaks at 2.8 and 2.6 eV, as well as a weakly intense emission with a maximum at 2.3 eV were recorded (Fig. 2b). When Ce^{3+} ions were introduced into the YAG phosphor, however, the following changes were observed in the PL spectra of the samples:

- The band at 2.6 eV was not recorded
- The intensity of luminescence band at 2.83 eV increased, and an insignificant shift to 2.81 nm was apparent.
- The luminescence of YAG:Ce^{3+} phosphor in the 2.4–1.7 eV spectral range became much more intense as compared with undoped YAG phosphor. The luminescence band could be decomposed into two Gaussians with maxima at 2.3 and 2.2 eV (Fig. 2b, blue dashed line).

One possible reason for the disappearance of the band at 2.6 eV is the change in the absorption spectrum with the introduction of Ce^{3+} ions [15]. The absorption in this spectral region increased significantly possibly because of the change in the energy structure.

A previous study [27] demonstrated that the "yellow" luminescence band of YAG:Ce^{3+} phosphor measured at 8 K splits into two peaks with maxima at 523 and 567 nm. One group [28] observed two peaks at 510 and 579 nm in the luminescence spectrum at 80 K. The authors attributed