Optical Materials 34 (2012) 1195–1201

Contents lists available at SciVerse ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Synthesis and optical properties of green emitting garnet phosphors for phosphor-converted light emitting diodes

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ARTICLE INFO

Article history:
Received 24 November 2011
Received in revised form 22 January 2012
Accepted 23 January 2012
Available online 22 February 2012

Keywords:
Sol–gel combustion
Photoluminescence spectroscopy
Quantum efficiency
Luminous efficacy
Color point
Phosphors

ABSTRACT

A series of Ce^{3+} doped $CaLu_2Al_4SiO_{12}$ garnet phosphors was prepared by a sol–gel combustion technique. All samples were characterized by powder X-ray diffraction (XRD), thermal quenching (TQ), fluorescence lifetime and photoluminescence (PL) measurements. Moreover, luminous efficacies (LE), CIE 1931 color points and quantum efficiencies (QE) were determined and discussed. XRD patterns confirmed the presence of single phase garnet for all samples independent of Ce^{3+} concentration at least up to 3 mol%. Phosphors showed a broad band emission in the range 460–720 nm. The emission band maximum is blue-shifted in comparison to $Lu_3Al_5O_{12}:Ce^{3+}$ and shifts from 520 to 542 nm by increasing the Ce^{3+} concentration. High quantum efficiencies of 80 to 86% were obtained for those samples doped with 0.25% and 0.5% of Ce^{3+}, however, a higher Ce^{3+} doping levels resulted in concentration quenching, i.e. in a substantial decrease of the photoluminescence quantum efficiency.

1. Introduction

Since the venue of blue inorganic light emitting diodes (LEDs) in 1993 [1] and the first organic LEDs in 1987 [2] the generation of all colors and especially white light has become possible by using solid state light sources. Continuous improvement in materials and deposition technologies has enabled high efficiencies which already surpass those of incandescent sources and steadily continue to improve.

Phosphor-converted LEDs (pcLEDs) employs a short wavelength LED (usually blue or ultraviolet) and a phosphor layer which absorbs a portion of blue light and emits a longer wavelength light. The additive mixing of blue light from the chip and yellow light from the phosphor, which is most commonly a Ce^{3+} doped garnet, yields white light, whereby the effective color temperature of the emitted light depends on the optical thickness of the phosphor layer. By increasing the layer thickness the color shifts from bluish white (cool white) to yellowish white (warm white).

To enlarge the range of accessible color temperatures and to enhance the color rendering of solid state light sources, a large range of novel phosphors based on Eu^{2+}, Yb^{2+} and Ce^{3+} doped sulphides [3–5], nitrides [6–9], oxynitrides [10–13] and SiAlONes [14–16] have been invented. Since these materials require dedicated synthesis schemes, the search for modified garnet type phosphors [17–21] is an ongoing research area.

This paper deals thus with the modification of lutetium aluminum garnet $Lu_3Al_5O_{12}$:Ce to yield adapted garnet type phosphors for solid state lighting applications. The modification of LuAG:Ce with Ca^{2+}–Si^{4+} pair was inspired by naturally occurring mineral grossular $Ca_3Al_2(SiO_4)_3$. It was expected that the substitution of Lu by Ca will lower the crystal field strength and blue shifted phosphors will be obtained if compared to LuAG:Ce.

2. Experimental

Herewith described $CaLu_2Al_4SiO_{12}:Ce^{3+}$ samples with a Ce^{3+} concentration between 0.0 and 3.0 mol% were synthesized by sol–gel combustion method employing tris(hydroxymethyl)-aminomethane as both complexing agent and fuel. The gels were prepared using high purity Lu_2O_3 (99.99% Treibacher), $AL(NO_3)_3 \cdot 9H_2O$ (≥98% Sigma–Aldrich), $Ca(NO_3)_2 \cdot 4H_2O$ (99.0% Merck), $Ce(NO_3)_3 \cdot 6H_2O$ (99.9% ChemPur), nano scale SiO_2 (99.0% Merck) and $H_2NC(CH_2OH)_3$ (99.9% Merck). In the sol–gel combustion process lutetium oxide was dissolved in hot diluted nitric acid. Then the solution was evaporated till dryness to remove the excess of nitric acid. The dry residue was again dissolved in distilled water and appropriate amounts of aluminum, calcium and cerium

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doi:10.1016/j.optmat.2012.01.034

nitrates as well as silicon dioxide were added. The resulting mixtures were stirred for 1 h at a temperature between 65 °C and 75 °C. Then tris(hydroxymethyl)-aminomethane at the molar ratio of 1:1 to all metal ions was added and the obtained mixtures were stirred for an additional hour at the same temperature. Subsequently, after concentrating the final mixtures by slow evaporation, the sols turned into transparent gels. Then the temperature was raised to 250 °C and the self maintaining gel combustion process has started accompanied with an evolution of a huge amount of gas. The resulting products were dried in the oven overnight at 150 °C and ground to fine powders, which were preheated for 2 h at 1000 °C in air to remove the residual carbon after the combustion process. The obtained white–greenish powders were further sintered for 4 h at 1400–1500 °C under CO atmosphere.

TG/DTA measurements of the precursor gels were recorded on Thermoanalyser Netzsch STA 409. The heating rate was 10 K/min, while ~50 mg of the sample were placed into an Al_2O_3 crucible. The atmosphere was synthetic air.

XRD data were collected from $10 \leqslant 2\theta \leqslant 60°$ (step width 0.02° and integration time 1 s) using Ni-filtered Cu $K\alpha$ radiation on Rigaku MiniFlex II diffractometer working in Bragg–Brentano ($\theta/2\theta$) geometry.

Reflection spectra were recorded on Edinburgh Instruments FS900 spectrometer equipped with a 450 W Xe arc lamp, a cooled single-photon counting photomultiplier (Hamamatsu R928) and an integration sphere coated with barium sulphate. A $BaSO_4$ sample (99% Sigma–Aldrich) was used as reflectance standard.

Excitation and emission spectra were recorded on an Edinburgh Instruments FSL900 fluorescence spectrometer equipped with 450 W Xe arc lamp, mirror optics for powder samples and a cooled (−20 °C) single-photon counting photomultiplier (Hamamatsu R2658P). The photoluminescence emission spectra were corrected by a correction file obtained from a tungsten incandescent lamp certified by the NPL (National Physics Laboratory, UK). For PL decay kinetics studies a 445.6 nm picosecond pulsed diode laser from Edinburgh Instruments (model – EPL445) was used as excitation source. For thermal quenching measurements a cryostat "MicrostatN" from Oxford Instruments has been applied to the present spectrometer. Measurements were carried out from 77 to 500 K in 50 K steps.

Quantum efficiencies were calculated according to equation:

$$QE = QE_{Ref} \times \frac{\int(I_{Sample})\,d\lambda - \int(I_{Black})\,d\lambda}{\int(I_{Ref})\,d\lambda - \int(I_{Black})\,d\lambda} \times \frac{1 - R_{Ref}}{1 - R_{Sample}} \quad (1)$$

where QE_{Ref} is the quantum efficiency (95%) of the reference material (YAG:Ce, U728, Philips), $\int(I_{Sample})d\lambda$ – emission integral of the sample, $\int(I_{Black})d\lambda$ – emission integral of the black standard, $\int(I_{Ref})d\lambda$ – emission integral of the reference material, R_{Ref} and R_{Sample} – reflection value at 450 nm of reference material and sample, respectively. The black standard (Flock Paper #55, Edmund Optics) was used to eliminate the dark count rate of the detector. For QE determination of all phosphor samples were excited at 450 nm. The error of the quantum efficiency calculations has been found to be ±5%.

All measurements were performed at room temperature and ambient pressure in air unless mentioned otherwise.

3. Results and discussion

The TG/DTA curves of Ca–Lu–Al–Si–O precursor gel, obtained after the combustion process are shown in Fig. 1. The TG curve reveals that the mass loss happens in two steps. The first step (peak at 550 °C) yielded in a mass loss of about 12% and can be attributed to burning of organic residues that remained after the combustion process. This is in line with the DTA curve (peak at 520 °C), which shows exothermic processes occurring in that temperature range. The second mass loss step of 5% takes place in the temperature range 800–1000 °C and can be attributed to the decomposition of metal carbonates or oxycarbonates. This is in good agreement with the DTA curve showing endothermic processes in this temperature range. According to the DTA curve, the garnet phase starts to form around 996 °C, which was confirmed by powder XRD measurements depicted in Fig. 2.

XRD patterns of undoped $CaLu_2Al_4SiO_{12}$ powders as a function of sintering temperature are shown in Fig. 2 along with a reference pattern of $Lu_3Al_5O_{12}$. It is obvious that during the combustion process no crystallization takes place. However, the garnet phase with some minor secondary phases was already obtained after annealing powders at 1000 °C for 2 h in air. The peaks that do not belong to the garnet phase are marked with an asterisk. Unfortunately, we were not able to identify the secondary phases formed after the calcination at 1000 °C. Subsequent sintering at 1400–1500 °C for 4 h resulted in single phase garnet type materials. Besides, no differences in the XRD patterns were observed if the synthesized garnets were doped with Ce^{3+} (at least up to 3 mol%). The samples sintered at temperatures higher than 1500 °C were molten, suggesting that the melting point of the materials is close to this temperature.

The body color of undoped sample was bright white indicating that there is no absorption in the visible spectral region. However, Ce^{3+} doped samples possessed a slightly greenish to pale yellow body color depending on dopant concentration caused by the strong absorption of the activator in the blue spectral region. This is in line with the reflection spectra depicted in Fig. 3. As expected, absorption increased with increasing doping level of Ce^{3+}. It is also evident that the absorption band of phosphors under investigation is slightly shifted towards shorter wavelengths if compared to conventional LuAG:Ce phosphor, 440 vs. 450 nm, respectively. This indicates that the lowest 5d crystal-field component of Ce^{3+} in $CaLu_2Al_4SiO_{12}$ host lattice lies at a higher energy than in LuAG:Ce. Samples also possess high brilliance since the reflectance at longer wavelengths is rather close to unity. However, reflectance at longer wavelengths decreases with increasing Ce^{3+} concentration, probably due to defect formation in the lattice.

Fig. 4a and b display excitation and emission spectra of $CaLu_2Al_4SiO_{12}:Ce^{3+}$ phosphors as a function of Ce^{3+} concentration, respectively. LuAG:Ce is also included in the spectra for comparison. The excitation spectra contain two broad bands attributed to the $[Xe]4f^1 \rightarrow [Xe]5d^1$ transitions of Ce^{3+} ions. The higher energy band is much weaker than its counterpart at lower energy. This is quite different from the excitation spectrum of LuAG:Ce whose low and high energy bands are of comparable intensities. This phenomenon might be attributed to photoionization, i.e. the higher crystal-field component of the excited $[Xe]5d^1$ configuration of Ce^{3+} in the $CaLu_2Al_4SiO_{12}$ host lattice is likely close to or in the conduction band. This is in line with VUV reflection measurement of the undoped sample. It shows that the optical band gap of $CaLu_2Al_4SiO_{12}$ host lattice is at 215 nm (5.77 eV), whereas the optical band gap of LuAG is about 177 nm (7.01 eV) [22]. The emission spectra comprise one broad band, which is a result of the strong overlap of the two bands originating in the transitions from the lowest crystal-field component of the $[Xe]5d^1$ configuration to the spin–orbit split sublevels $^2F_{5/2}$ and $^2F_{7/2}$ of the $[Xe]4f^1$ configuration of Ce^{3+} ions [21,23]. It turns out that the emission properties are very sensitive to variations of the Ce^{3+} concentration. With increasing Ce^{3+} concentration from 0.1 to 3.0 mol% the emission maximum shifts from 520 to 542 nm. This is probably caused by re-absorption process (an emitted photon is again absorbed by activator due to overlapping absorption and emission bands). However, at higher activator concentrations the emission intensity drops down indicating concentration quenching. The