Photoluminescence properties of glassy yttrium aluminum borate powders: Dopant-free phosphors for solid-state lighting

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ABSTRACT

Glassy yttrium aluminum borate powders (g-YAB) obtained by the polymeric precursor method show intense photoluminescence (PL) in the visible range under near-ultraviolet (NUV) excitations. The PL properties strongly depend on the thermal treatment of powders as well as the excitation wavelengths. The broad PL of g-YAB powders cover whole visible spectral range between 380 nm and 780 nm under NUV excitations. The PL internal quantum yield (i-QY) was determined using the integrating sphere method and is found to reach up to 91 ± 5% under 365 nm light emitting diode (LED) excitation. Moreover, the associated color coordinates in transmission mode revealed preferably warm-white light with correlated color temperature (CCT) tunable between 2800 K and 5300 K, ideal for general household and workplace lighting. The use of NUV-LED excitation accompanied with broadband visible emission profile helps in achieving high color-rendering ability with color-rendering index (CRI) higher than 90. Furthermore, these g-YAB phosphors exhibit excellent PL thermal stability (> 200 °C) and stability with time under device operating conditions. The overall favorable PL properties and low cost synthesis suggest huge potential of g-YAB phosphors as new lanthanide (Ln)-free white light phosphors with very high CRI under NUV-violet LED excitations.

1. Introduction

Solid-State Lighting (SSL) technology, such as white Light Emitting Diodes (wLEDs) and Organic Light-Emitting Diodes (OLEDs) exhibits great potential of energy saving over other commonly used white-light devices such as Hg discharge based fluorescent and high temperature incandescence lamps [1]. The main goals for the development of SSL sources are the cost reduction associated with the enhancement of the energy efficiency and color quality of the resulting lighting devices. Another important advantage of SSL sources is their high stability to produce long lifetime devices [1]. At present, majority of wLED devices are phosphor-coated LEDs, where the white lighting is generated by mixing the light coming from a blue or near-UV LED (NUV-LED) with that arising from a phosphor layer placed just above the chip [1]. The typical commercial wLED device, developed by Nichia Chemical Co. in 1997 [2], is constituted of a blue InGaN LED chip coated with a yellow phosphor (YAG: Ce^{3+}) [3]. The blue light generated by the chip, at around 455 nm, is partly absorbed and converted to yellow by the phosphor. Even if these wLED devices are now extensively commercialized due to their competitive cost and high emission efficiency, the red spectral deficiency of the phosphors leads to cold-white lighting with a major blue component. These bluish emissions give uncomfortable and blinding lightings associated to poor color rendering indexes (CRI), around 70–80 [4], and "blue light hazards", so-called in the literature for potential retinal damages, disturbances of the biological circadian clock, alertness and metabolic disturbance [5]. In this context, to generate comfortable and safe warm white lightings, intense researches are dedicated to design new phosphors exhibiting efficient photoluminescence (PL) component in the orange-red range. Indeed, the phosphor is a key point in pc-wLEDs as it represents significant production cost (around 19% of pc-wLED devices) owing to the use, in general, of expensive rare earths (Ce^{3+}, Eu^{3+}, Eu^{2+}, etc.) and sometimes high purity transition metals (Mn^{4+}, Mn^{2+}) activated oxides, nitrides, oxy-nitrides, fluorides and oxy-fluorides [1,4]. The need of high purity metal active ions, their huge demand, the export monopoly as well as synthesis intellectual rights make phosphors a valuable and expensive

component in wLED technology [4].

An alternate route in this regard, is to involve the so-called *defect-related phosphors* generating broad PL bands extended in the whole visible range. The wide PL emissions in such materials arise from defects or impurities present in the materials that act as emitting centers. Indeed, previous works have shown on silicate matrices that this type of phosphors can generate PL extended in the visible range with promising internal quantum yields, between 20% and 45% under NUV excitations [6,7]. Since these pioneering works, several types of metal oxides, phosphates and boronitrides or borooxynitrides (BN or BNO compounds) matrices were studied [7–10]. Even if this new type of phosphors is very promising for the development of pc-wLEDs involving a full-color single phosphor, the nature of the defects at the origin of the broad PL emissions is not well established. Several hypotheses were suggested, such as non-bridging oxygen atoms, oxygen vacancies, interstitial carbon atoms and more recently carbons dots and other carbogenic species (aromatic groups, peroxyl, CO_2^-, etc.) [6–12]. These defects or impurities give rise to additional energy levels within the bandgap of the matrix and are involved in the PL process. All these previous results revealed promising PL efficiencies suggesting these defect-related phosphors are very interesting for the development of pc-wLED lighting devices. However, a detailed thermo-optical investigation is not carried out on such phosphors for evaluating their possible applications as commercial wLED phosphor.

In this very challenging context of global energy saving through inexpensive SSL devices, we have recently proposed to use a low cost lanthanide (Ln)-free phosphor based on glassy yttrium aluminum borate powders (g-YAB) [13]. These g-YAB phosphors were synthetized at low temperature from non-toxic and low cost precursors using the generic polymeric precursor method. The g-YAB compositions of these white emissive phosphors are close to the stoichiometry of the crystalline yttrium aluminum borate $YAl_3(BO_3)_4$ (c-YAB). Indeed, c-YAB is a well-known optical material (laser and quadratic nonlinear optical crystal), which presents good chemical and thermal stabilities, a wide bandgap of around 5.7 eV, high hardness and extended transparency window, down to 200 nm [14]. The optimized g-YAB powders exhibit excellent thermal and chemical stabilities and tunable PL properties, from bluish to warm-white emissions, by simply adjusting the temperature of thermal treatments (calcination). Moreover, we showed in a previous work that these defects and the associated PL efficiency are directly related to paramagnetic centers (radicals) [13].

In this paper, we extended our spectroscopic investigation on this new family of Ln-free phosphors. We investigated the PL properties in reflection as well as in transmission modes using NUV to violet LEDs, the possible candidates for excitation in the wLED devices, using such broad white emitting high CRI phosphors. The color chromaticity of various combinations of LEDs and phosphors along with the correlated color temperature (CCT) and CRI were also determined and discussed.

2. Experimental section

The g-YAB powders were synthetized by the polymeric precursor method. Aqueous solutions of Al and Y citrate complexes were mixed with boric acid and d-sorbitol, which on reflux (24 h) followed by water evaporation (the half of solution volume), lead to the polymerization (poly-esterification) of organic networks, where the constituent metal ions (Y, Al and B) are homogeneously dispersed. The resulting yellowish and viscous resins were then dried at 250 °C and annealed at around 700 °C involving a two-step process under controlled atmospheres: a pyrolysis under N_2 at 700 °C for 24 h followed by a calcination under O_2 at varied temperatures from 650 °C to 750 °C for 24 h [13]. This allowed a gradually removal the organic moieties of the starting materials without creating combustion hot spots and avoided the formation of pyrolytic carbon or carbonate impurities, which are detrimental to the PL emission. Homogeneous beige-white powders with grain diameters ranging around 5–20 μm were obtained giving

broad visible PL. In the previous work, we demonstrated that the calcination near glass transition temperature ($T_g = 740$ °C) of g-YAB powders led to the highest PL intensity with broadband white emission, and it showed good correlation with the presence of high amount of paramagnetic centers, believed to be the emitting centers in the Ln-free g-YAB phosphors [13]. Therefore, we selected 740 °C, 720 °C and 650 °C annealed samples in this study to get more insights on their optical properties.

The steady-state PL measurements were carried out in reflection and transmission modes using a broadband laser driven Xe plasma lamp (Energetiq, LDLS EQ. 99X) and NUV LEDs (365 nm, 385 nm and 405 nm from ThorLabs, models M365L2, M385L2 and M405L2, respectively). In order to measure the PL in transmission mode, the g-YAB powders were deposited onto a silica plate (1 mm thick), and were then compacted by adding some ethanol drops. Thus, after drying, sample layers of approximately 1 mm thickness were obtained. These samples were set at the entrance of the integrating sphere and were excited by different NUV-LEDs (LED optical power was set to 3 mW). The PL signals were collected by an optical fiber coupled with a CCD detector (Avantes – AVASpec-2048 TEC). The signals were corrected for intensity irradiance using a standard halogen lamp (Avantes-Avalight-HAL). The PL excitation spectrum was recorded using the Xe lamp linked to a UV–Visible grating Jobin-Yvon monochromator. Intensity calibration was carried out using a standard UV-enhanced Si power meter. The signals were collected using an optical fiber attached to a Scientific Pixis 100 CCD camera cooled at −65 °C and coupled with an Acton SpectraPro 2150i spectrophotometer. The same detector configuration and a closed cycle He cryostat (Sumitomo Cryogenics HC-4E) connected to a Lakeshore 340 temperature controller with integrated heating was used for the PL thermal stability and the thermoluminescence (TL) glow curve measurements. For PL stability, the PL emission was recorded as a function of the sample temperature under continuous excitation of 365 nm LED, and that for time stability, the sample was heated at 150 °C while the PL was recorded under continuous excitation as a function of time. For TL, the sample was cooled down to 15 K and irradiated with 254 nm Hg lamp for 10 min, and then introduced to a controlled heating up to 600 K at 10 K/min heating rate. The PL decay measurements were carried out using a pulsed N_2 laser (337 nm, temporal resolution 0.8 ns) and a fast response deep cooled CCD detector (Horiba Instruments). For slow afterglow decay measurements, the samples were irradiated using a 254 nm low pressure Hg lamp for 1 min and the luminescence decay was recorded using optical fiber attached to Scientific Pixis 100 CCD camera coupled with an Acton SpectraPro 2150i spectrophotometer. The PL quantum yields were determined using a 50 mm integrating sphere (Avantes – AvaSphere-50 covered by Spectralon polymer) using NUV-LEDs as excitation with optical power of 1 mW.

3. Results and discussion

3.1. PL and PLE spectra collected in reflection mode

Fig. 1 shows the PL spectra of 740 °C calcined g-YAB phosphor recorded in reflection mode under different excitations in the UV to violet region. For longer wavelength excitations, high pass optical filters were used to avoid the excitation beam contribution, since there is excitation-emission overlap in this range. All the spectra are normalized at 550 nm. It is clear from Fig. 1 that the g-YAB phosphors exhibit broad emission under all excitations. It covers violet to deep red colors of visible spectrum that makes it potential single lighting phosphor to have complete visible spectrum. Moreover, such continuous distribution of colors favors high color rendering lighting owing to its ability to reproduce natural color of the objects under illumination, as we will see in Section 3.5.

The PL spectrum under 254 nm excitation includes at least three Gaussian profiles on fitting and may be due to the contributions from