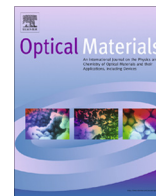




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Short Communication

A high efficiency rare earth-free orange emitting phosphor

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ABSTRACT

This communication provides a brief summary on rare earth (RE)-based and RE free-based nitrides and oxynitride phosphors reporting for the first time the photoluminescence quantum yield (PLQY) of a highly emissive AlN:Mn²⁺ obtained at relatively low temperatures. The PLQY of the AlN:Mn emitter was measured to be 82%, a value among the highest measured for non-RE phosphors. Though the AlN matrix shows an emission peak at a similar position to the emission peak observed for AlN:Mn product, the Mn-containing species generates orange emission by a different mechanism, which was supported by the emission life time studies and in accordance with previous reports on this material.

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1. Introduction

Commercially available energy efficient lighting products (LED and Fluorescent) are based on down conversion of ultraviolet luminescence to visible by rare earth (RE)-based phosphors. RE concentration can be as high as 15% in current phosphors used in compact fluorescent lighting (CFL) and represents more than 50% of total product cost [1]. High-efficiency fluorescent lighting represents approximately 85% of global demand for RE phosphors (a linear fluorescent lamp uses ~5 g of rare-earth oxides per bulb) [2]. Although LEDs can theoretically use smaller amounts of phosphors, the current products based on external phosphor layers have heavy dependence on the RE-based materials. Phosphors that do not include RE ions, such as ZnO, CdS, CdSe, and ZnS:Mn, always contain toxic elements (Cd, S, and Se) which have long-term adverse effects on the environment. Semiconductor Today predicts that packaged LEDs in general lighting to grow from \$500 mn (2010) to \$13.4 bn in 2020 [3]. The market for compact fluorescent lamps (CFL) was estimated \$1.6 billion for 2010 and is expected to be worth nearly \$20 billion by 2015 [3]. As lighting energy efficiency standards are implemented globally, heavy rare earths used in lighting phosphors may be in short supply. In the United States, two sets of lighting energy efficiency standards took effect in 2012 leading to an increase in demand for fluorescent lamps

containing phosphors made with europium, terbium and yttrium. Therefore, the replacement of down conversion RE-based phosphors will reduce the market demand and US dependence on foreign sources, decrease environmental impact, and promote new industry development in the US.

Nitrides and oxynitrides have attracted significant attention in recent years because of their remarkable (thermal and chemical) stability, good fracture toughness while exhibiting unusual PL under near-ultraviolet or blue-light irradiation when activated with RE ions [4–6]. Examples of these materials are M₂Si₅N₈:Eu²⁺, Ce³⁺ [7–12]; MSi₂O_{2–δ}N_{2+2/3δ}:Eu²⁺, Ce³⁺ (M = Ca, Sr, Ba) [8,11]; MSiN₂:Eu²⁺, Ce³⁺ (M = Ca, Sr, Ba) [12,13]; MgSiN₂:Eu²⁺ [14,15]; MYSi₄N₇:Eu²⁺, Ce³⁺ (M = Sr, Ba) [16,17]; MSi_xAl_{2–x}O_{4–x}N_x:Eu²⁺ (M = Ca, Sr, Ba) [18]; α-SiAlON:RE (RE = Eu²⁺, Ce³⁺, Yb²⁺, Tb³⁺, Pr³⁺, Sm³⁺) [19–25]; β-SiAlON:Eu²⁺ [26]; and CaAlSiN₃:Eu²⁺ [27–29]. As for the application of Mn²⁺-doped phosphors in the field of wLED, many studies have been performed. A good number of these studies have been focused on Eu²⁺- and Mn²⁺-co-activated materials, such as Ba₃MgSi₂O₈:Eu²⁺, Mn²⁺; CaAl₂Si₂O₈:Eu²⁺, Mn²⁺; SrZn₂(PO₄)₂:Eu²⁺, Mn²⁺; La_{0.827}Al_{11.9}O_{19.09}:Eu²⁺ and Mn²⁺ [30–32]. In these Eu²⁺- and Mn²⁺-co-activated materials strong green, yellow and/or red emission of Mn²⁺ was obtained besides the blue emission of Eu²⁺ due to the strong absorption of Eu²⁺ in the wavelength range of 250–400 nm and efficient energy transfer from Eu²⁺ to Mn²⁺ [30–32]. Nevertheless, a handful of nitride-based phosphor materials where Mn is the only dopant have been reported by Hintzen et al. [33–35]. For example, Mn²⁺-activated M₂Si₅N₈

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(M = Ca, Sr, Ba) phosphors were reported exhibiting emission bands with maxima at 567, 599 and 606 nm for M = Ba, Ca, Sr showing narrow emission as compared to red Eu^{2+} emission in these host-lattices [33]. $\text{CaAlSiN}_3:\text{Mn}^{2+}$ was reported by the same group exhibiting a broad band emission in the wavelength range of 475–750 nm originated from the overlapping emission bands of two different Mn sources, one located in the Ca site and another one in the Al site [35]. The quantum efficiencies of these materials were not reported but predicted to be lower than commercial phosphors [33–35].

There have been a number of reports on RE-free phosphors with high photoluminescence quantum yields (PLQY) proving that RE-free phosphors are prospective candidates for replacing RE-based phosphors in lighting or display applications. $\text{Ca}_5(\text{PO}_4)_3(\text{Cl}, \text{bF}):\text{Sb}, \text{Mn}$ phosphors have been known since 1960s to have high quantum yields, and were the basis of for the fluorescent lighting industry up until the 1990s [36]. Furthermore, Mn-containing non-RE high-efficiency phosphors $\text{Zn}_2\text{SiO}_4:\text{Mn}$ and $\text{K}_2\text{SiF}_6:\text{Mn}$ have been synthesized [37–39]. Other examples of non-RE phosphors include $\text{Zn}_3\text{V}_2\text{O}_8$, which was synthesized by Luitel et al. and showed a broadband yellowish white emission with a PLQY of 60% when excited with 260 nm light [40]. Another example is the yellow-green emitting $\text{NaZnPO}_4:\text{Mn}$ phosphor doped with 12 mol% Mn which exhibited a 63% PLQY when excited at 418 nm [41]. A titanium-included silicate, $\text{BaZr}_{0.99}\text{Ti}_{0.01}\text{Si}_3\text{O}_9$, exhibited the highest quantum yield in the titanosilicate mineral family with 72% PLQY blue emission when excited at 230 nm [42]. RE-free boron carbon oxynitride (BCNO) phosphors have also shown to be promising down-converter materials with reported color tunability and PLQY from 10% for emission in the yellow (@571 nm) to 79% for emission in the blue (@469 nm) [42]. Nevertheless, there is still some way to go to achieve PL efficiencies comparable to RE-based emitting materials, in particular the yellow emission of YAG:Ce standard phosphor (PLQY = 90%) [43].

AlN-based emitters are very promising materials for light emitting diodes and electroluminescence devices, because their high thermal, chemical and mechanical stability, high thermal conductivity and because AlN has a wide bandgap (6.2 eV) [44–48]. Recently, AlN:Eu²⁺ phosphor was reported for utilization in FEDs [47]. The AlN-based phosphors have good physical and chemical, wide bandgap, and meet the requirements of afterglow phosphors due to their high luminescence intensity. Therefore, it might be possible to develop Mn²⁺ doped AlN phosphor for lighting and displays applications, particularly if the emitting wavelength is in the orange-red part of the visible spectrum. Indeed, an AlN:Mn phosphor was reported exhibiting cathodoluminescence and photoluminescence as well as long lasting phosphorescence in the red [49,50]. The materials, which were synthesized at 1900 and 1750 °C contained 1 mol% and 2.5 mol% of Mn, respectively and showed a strong red emission upon irradiation with 254 nm UV light. Nevertheless, no report on the PLQY is available in this very promising phosphor material. We report the synthesis of AlN:Mn RE-free phosphor at a lower temperature and measure for the first time the phosphor PLQY which turn out to be one of the highest photoluminescence quantum yield (PLQY) reported on a RE-free phosphor material.

2. Results

Aluminum nitride with different molar percentages of Manganese AlN:*x*Mn (*x* = 0.5, 1, 2, 5 and 10 mol%) powder phosphors were prepared by weighing, mixing, and grinding appropriate amounts of the precursor materials in an agate mortar by hand under an air/moisture free atmosphere. Subsequently, the homogeneous powder mixtures were transferred to a

Molybdenum crucible and calcined at different temperatures for 5 h in a 90/10 N₂/H₂ gas mixture. After firing, the samples were cooled to room temperature (RT) in the furnace and characterized by powder X-ray diffraction (pXRD), scanning electron microscopy coupled to energy dispersive scattering analysis (SEM/EDS), inductive coupling plasma mass spectrometry (ICP-MS) and absorption as well as photoluminescence spectroscopy.

Powder XRD studies on AlN and AlN:Mn samples show that the main component of the AlN:Mn phosphors is AlN hexagonal Wurzite phase (Fig. S1 in Supporting Information). SEM/EDS analysis on AlN samples with and without manganese were performed to learn about the main elements present in the material that can not be identified by ICP-MS, i.e., nitrogen and potentially oxygen. Fig. S2 shows a scanning electron micrograph of AlN and AlN:Mn 1 mol% while Fig. S3 shows the EDS spectra of both Mn-doped and undoped AlN samples where the presence of aluminum, nitrogen, and oxygen is observed. It has been reported that the presence of oxygen in the samples is critical to the optical properties of these materials and it will be discussed later. One surprising finding was the absence of manganese in the EDS spectrum of the AlN:Mn doped samples. This may be due to the relatively low concentrations of the dopant as compared to the host matrix. Although the presence of manganese was not observed by either EDS or XRD analysis, ICP-MS performed on samples prepared with different Mn content showed in all cases a concentration of Mn that ranged between 1.06 and 1.27 mol% independently of the manganese starting concentration. This could be an indication that at these temperatures there is loss of excess manganese by sublimation even though the crucibles were tightly sealed. For example, increasing the reaction temperature from 1500 °C to 1800 °C obtained emissive samples with the same manganese content range while decreasing the reaction temperature to minimize manganese sublimation resulted in non-emissive samples as described later. The photoluminescence emission and excitation spectra of the AlN: Mn 1.06 mol% Mn (from now on 1 mol%) at 1500 °C under N₂ atmosphere are depicted in Fig. 1. The reaction product of AlN with Mn at 1500 °C emits bright orange light with a peak maximum at around 595 nm when excited by UV radiation (Fig. 2). The part of excitation spectrum monitored at 595 nm shown in Fig. 1 contains features characteristic of presence of Mn²⁺ species in the samples [13], though these features are very weak since the transitions are spin and parity forbidden.

The reaction temperature was optimized by monitoring the PL emission of the fired mixtures. It was found that below 1500 °C

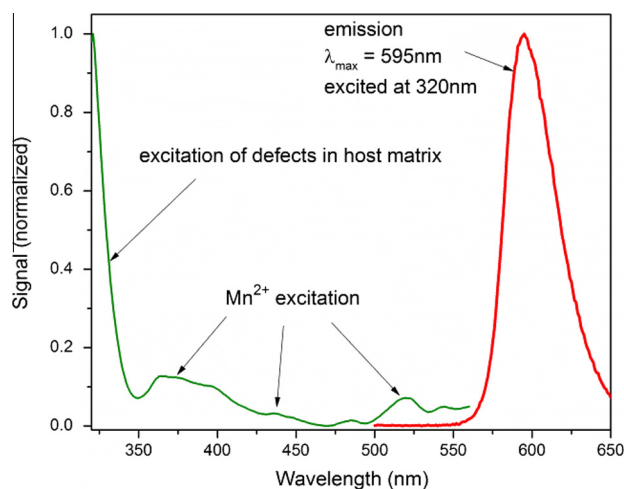


Fig. 1. Normalized emission and excitation spectra of AlN:Mn. Excitation was monitored at 595 nm.

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