

Red-emitting manganese-doped aluminum nitride phosphor



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ABSTRACT

We report high efficiency luminescence with a manganese-doped aluminum nitride red-emitting phosphor under 254 nm excitation, as well as its excellent lumen maintenance in fluorescent lamp conditions, making it a candidate replacement for the widely deployed europium-doped yttria red phosphor. Solid-state reaction of aluminum nitride powders with manganese metal at 1900 °C, 10 atm N₂ in a reducing environment results in nitrogen deficiency, as revealed diffuse reflectance spectra. When these powders are subsequently annealed in flowing nitrogen at 1650 °C, higher nitrogen content is recovered, resulting in white powders. Silicon was added to samples as an oxygen getter to improve emission efficiency. NEXAFS spectra and DFT calculations indicate that the Mn dopant is divalent. From DFT calculations, the UV absorption band is proposed to be due to an aluminum vacancy coupled with oxygen impurity dopants, and Mn²⁺ is assumed to be closely associated with this site. In contrast with some previous reports, we find that the highest quantum efficiency with 254 nm excitation (Q.E. = 0.86 ± 0.14) is obtained in aluminum nitride with a low manganese doping level of 0.06 mol.%. The principal Mn²⁺ decay of 1.25 ms is assigned to non-interacting Mn sites, while additional components in the microsecond range appear with higher Mn doping, consistent with Mn clustering and resultant exchange coupling. Slower components are present in samples with low Mn doping, as well as strong afterglow, assigned to trapping on shallow traps followed by detrapping and subsequent trapping on Mn.

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1. Introduction

Nitride phosphors have taken on significance in recent years, particularly for solid-state lighting [1]. Among the red-emitting nitride phosphors reported, most are activated with Eu²⁺, providing absorption of blue LED excitation and broad emission bands extending beyond 750 nm. Most nitrides offer luminescence without activation, some emitting in the red [2] and some red-emitting Mn²⁺ doped nitrides have been studied [3,4]. Red luminescence in aluminum nitride (AlN) has been reported in numerous publications since the 1960s [5,6], and while the emission was originally interpreted as deriving from Mn⁴⁺ [7,8], more recently it has been interpreted as Mn²⁺ [9]. Mn²⁺-activated phosphors have been used

extensively in fluorescent lighting. In early years, the natural Willemite mineral, (Zn,Be)₂SiO₄:Mn²⁺, was employed, and later the Sb³⁺,Mn²⁺-doped halophosphates [10].

Aluminum nitride is widely used as a substrate for circuitry and semiconductor devices, owing to its excellent thermal conductivity and compatibility with other nitrides. Synthesis of AlN powder used for sintered AlN ceramics is performed industrially through a variety of synthetic pathways, including carbothermal reduction nitridation [11], gas-reduction nitridation of powders or aerosols [11,12], and metal-organic routes [13]. We demonstrate here a simple, scalable approach for low-cost manufacture of aluminum nitride phosphors, employing solid-state reaction of pure hexagonal wurtzite AlN powders with Mn dopant.

To obtain the highest light yields in Mn²⁺-doped phosphors, Mn clustering must be avoided, as it results in quenching of emission, described as early as 1963 by McClure in ZnS, and in other hosts, such as MgAl₂O₄ and ZnGa₂O₄ [14–16]. The optimal Mn concentration in AlN studied in thin films was found to be 3–8 × 10¹⁹ cm³ (0.03–0.08 at.%) by Sato [7,8], though several recent papers have

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surprisingly reported optimal doping concentrations of 1–3% [9,17].

The origin of the near-UV absorption band at 4.5–5 eV, observed for undoped AlN (band gap 6.2 eV), has been assigned by Trinkler and others to radiative recombination of two proximal oxygen-related defects forming a donor-acceptor pair: O_N-V_{Al} (an oxygen ion substituting for nitrogen O_N and aluminum vacancy V_{Al} nearby), the excited state of which may ionize to populate the conduction band [18–20]. Subsequently, AlN intrinsic luminescence is thought to derive from trapping of this excitation on another O_N . A simplified energy level diagram, shown in Fig. 1, describes the luminescence mechanism for AlN:Mn. For Mn-doped AlN, the intrinsic luminescence of AlN is a minor pathway, and therefore is not shown, instead, the excited state of Mn^{2+} is populated directly from the conduction band, or indirectly after trapping on shallow defects. The strong afterglow reported previously for both undoped [18] and doped AlN phosphors [17] is consistent with the UV absorption populating the conduction band of AlN, and the subsequent delayed luminescence resulting from the presence of shallow traps (likely nitrogen vacancies). Other recent studies have found that AlN:Mn is an excellent cathodoluminescent phosphor [9], and reported emission efficiency of ~80% with 320 nm excitation [21]. There are no prior published studies of the use of AlN phosphors in a mercury discharge lamp, which is the focus of this paper.

Requirements for fluorescent lamp phosphors include high efficiency luminescence under 254 nm Hg line excitation and minimal reaction with mercury or degradation by UV [22]. These requirements eliminate many candidate phosphors. Furthermore, a useful red phosphor must emit only in the narrow spectral range of 590–650 nm (C.I.E. coordinates of $x = 0.62$ – 0.66 and $y = 0.33$ – 0.38), most preferably near 615 nm, where the balance between lumen efficiency (human eye sensitivity) and color rendition is optimal. Fig. 2 shows that the emission spectra of AlN:Mn and $Y_2O_3:Eu$ are remarkably well-matched, with CIE coordinates ($x = 0.620$, $y = 0.379$) and ($x = 0.644$, $y = 0.354$) respectively; slightly more yellow emission is present in the AlN:Mn spectrum, resulting in higher lumen efficiency, while the emission band in $Y_2O_3:Eu$ beyond 700 nm is off the eye sensitivity curve. The product of the absorbance at 254 nm (A_{254}) and the quantum efficiency (Q.E.) measured for the best AlN:Mn phosphors, described here, is comparable to the $A_{254} \times Q.E.$ product for $Y_2O_3:Eu$, which has a

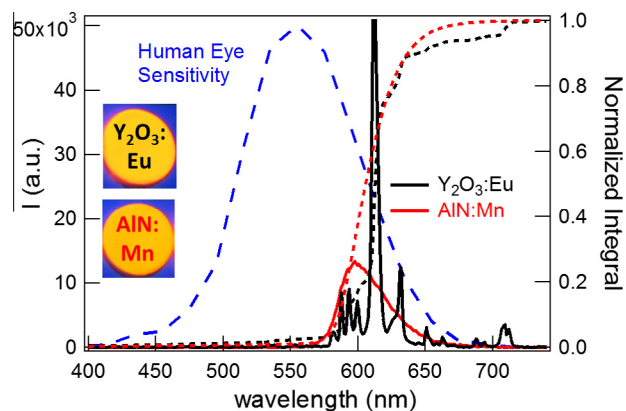


Fig. 2. Emission spectra excited at 254 nm of AlN:Mn and $Y_2O_3:Eu$ (solid lines), data acquired with identical geometry and slit widths and thus the spectra may be compared quantitatively. The integrated intensities of the spectra, normalized to the value at 700 nm for $Y_2O_3:Eu$ (short dashed lines) show that under these conditions the $(A_{254} \times Q.E.)$ product for AlN:Mn is comparable to that of $Y_2O_3:Eu$. Also shown is the human eye sensitivity curve (long dashed line curve).

moderate absorbance of $A_{254} = 0.77$, but a Q.E. = 1.00 [10]. We report here for the first time that the red AlN:Mn phosphor meets the requirements for implementation in fluorescent lamps, including emission color, high efficiency, and survival in mercury discharge.

2. Experimental

2.1. Synthesis

Commercial aluminum nitride powders (Materion or H.C. Starck; materials used here are nominally 33.3% N, 0.1% C, <1% O, <0.005% Fe, with surface area of $2 \text{ m}^2/\text{g}$) were ground with Mn and Si dopants (Sigma Aldrich) in an agate mortar, placed in boron nitride crucibles, and heated under 10–100 atm nitrogen pressure at 1900 °C for 2–4 h. Specimens prepared in this way had grayish-white body color. Powders were then ground again, and annealed in flowing nitrogen at 1650 °C, after which the body color became white. Mn concentration was determined by GDMS

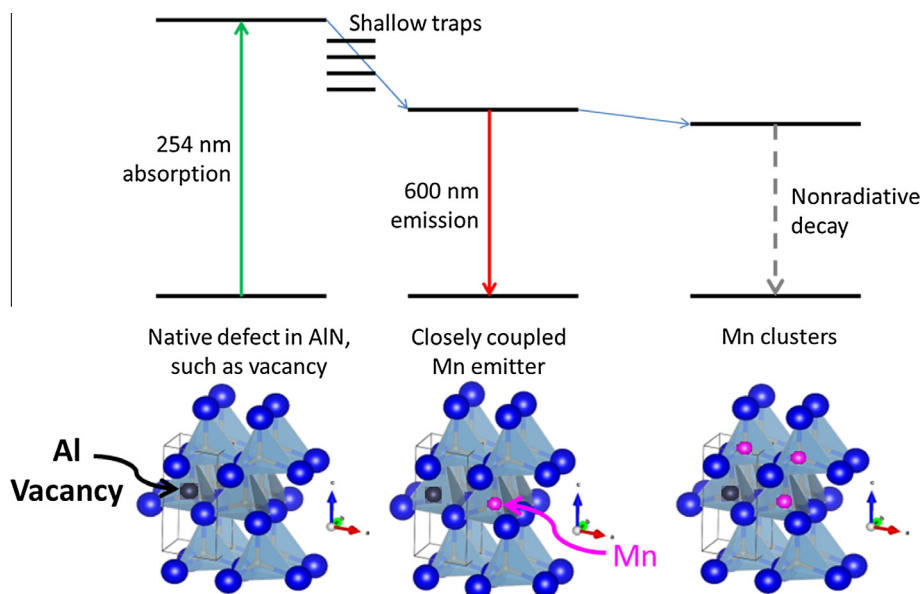


Fig. 1. Energy level diagram for functionality of the AlN:Mn phosphor in a fluorescent lamp. Crystal structure diagrams were generated with Vesta (jp-minerals.org/vesta).

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