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Synthesis and luminescence properties of nitrided lanthanum magnesium hexaluminate $LaMgAl_{11}O_{19}$ phosphors

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Abstract

Nitrided $LaMgAl_{11}O_{19}$ phosphors were prepared by a two-step method involving synthesis at 1550 °C for 4 h, trituration, and firing at 1650 °C for 5 h under a nitrogen atmosphere. Nitrogen was doped into $LaMgAl_{11}O_{19}$ and bonded with aluminium atoms. The nitrided $LaMgAl_{11}O_{19}$ phosphors showed plate-like morphology with a rough surface and exhibited strong blue emission at 442 nm and 450 nm, which may be attributed to the energy transition between defect levels. A weak emission band at 590 nm was ascribed to the transition between the V_{Al} acceptor and the valence band, which was excited at 254 nm.

Keywords: $LaMgAl_{11}O_{19}$; Oxynitrides; Phosphors; Luminescence

1. Introduction

Lanthanum magnesium hexaluminate, $LaMgAl_{11}O_{19}$ (LMA), has garnered the attention of researchers because of its high-temperature performance and properties [1,2]. Thus, LMA has been widely investigated for many applications, such as a thermal barrier coating, combustion catalyst support, and active element of solid-state lasers [1–5]. Among this body of research, studies of the material's optical properties (*i.e.*, for laser and phosphor hosts) are of particular interest in this work. Because it is similar to other hexaluminates, the crystalline structure of $LaMgAl_{11}O_{19}$ is of the magnetoplumbite type with a $P6_3/mmc$ space group [6–9]. Materials with this structure can be easily doped or replaced with other transition-metal and rare-earth ions and their performance thereby rendered tuneable [7,8,10–17]. Thus, current work on $LaMgAl_{11}O_{19}$ phosphors shows that the material exhibits various efficient luminescent properties when doped with transition-metal and rare-earth ions. For example, $LaMgAl_{11}O_{19}$ doped with Tb^{3+} ions emits weakly in both the blue and orange regions of the visible spectrum and strongly in the green region when excited by ultraviolet light with a wavelength of 261 nm [16]; $LaMgAl_{11}O_{19}$ doped with Mn^{2+} and Tb^{3+} is known to emit in the green region when excited by ultraviolet radiation [18].

Although extensive work on the luminescence properties of doped $LaMgAl_{11}O_{19}$ has been reported in detail, little published work concerning $LaMgAl_{11}O_{19}$ oxynitride phosphors exists. Compared with oxide phosphors, the nitrogen–metal bonds in oxynitride-based materials are more strongly covalent than their oxygen–metal counterparts [19]. Oxynitrides doped with rare-earth metal ions can also shift their excitation and emission spectra across a broad range (*e.g.*, $Sr_2SiO_4{:}Eu \rightarrow SrSi_2O_2N_2{:}Eu \rightarrow Sr_2Si_5N_8{:}Eu$ phosphors and $BaAl_{2-x}Si_xO_{4-x}N_x{:}Eu^{2+}$ phosphors emitting green light) [20–22]. Thus, research on $LaMgAl_{11}O_{19}$ oxynitrides has been deemed highly significant.

The authors synthesised nitrided $LaMgAl_{11}O_{19}$, a blue-emitting phosphor, by initially preparing $LaMgAl_{11}O_{19}$ as a precursor and then introducing nitrogen by high-temperature solid-state reaction under a nitrogen atmosphere. The structural and luminescent characteristics of the phosphors are herein discussed.

2. Experimental

$LaMgAl_{11}O_{19}$ powders were synthesised by solid-state reaction in air using $Al(OH)_3$ (purity: 99.9%), La_2O_3 (purity: 99.95%),

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and $Mg(OH)_2$ (purity: 99.9%) as raw materials. La_2O_3 powder could rapidly absorb atmospheric water, so it was heated to 1100 °C for 1 h and weighed at a temperature above 100 °C. The stoichiometric powders were mixed and ball-milled in ethanol for 6 h to homogenise them before being dried at 75 °C. The mixtures were calcined at 1550 °C for 4 h, triturated, and fired at 1650 °C for 5 h under a nitrogen atmosphere to form nitrided $LaMgAl_{11}O_{19}$, using coke particles to surround and protect the material.

The phase and crystal structure of the phosphors were identified by X-ray diffraction (XRD, D8 Advance diffractometer, Bruker Corporation, Germany) using Cu-Kα radiation (λ=1.5406 Å). A PHI 5300 X-ray photoelectron spectroscopy system (XPS, Perkin Elmer, USA) was used to determine the chemical states of La 3d5, Mg 1s, Al 2p, and O 1s with a chamber base pressure of approximately 10^{-7} Torr. XPS data were acquired using Mg Kα X-rays at a take-off angle of 45° and a total power of 400 W. Micrographs of the phosphors were obtained using a scanning electron microscope (SEM, JSM-6460LV, JEOL, Japan) equipped with an energy dispersive analysis (EDS) attachment. Photoluminescent emission (PL) and excitation (PLE) spectra were recorded using a PMT and xenon lamp (PSI, South Korea). All measurements were carried out at room temperature.

3. Results and discussion

3.1. Phase composition analysis

Fig. 1 shows the XRD patterns of the as-prepared $LaMgAl_{11}O_{19}$ and nitrided $LaMgAl_{11}O_{19}$ powders: the pattern of the nitrided $LaMgAl_{11}O_{19}$ phosphor matched that of the as-prepared $LaMgAl_{11}O_{19}$ (JCPDS card number 26-0873). The observed XRD pattern shows that the nitrided $LaMgAl_{11}O_{19}$ also possessed a magnetoplumbite structure and was included in the $P6_3/mmc$ space group, showing a structure similar to that of other hexagonal, rare-earth aluminates. This result demonstrated that doping with nitrogen did not change the crystal structure of LMA. The XRD spectrum of the material in the range from 33.5° to 35° is shown in Fig. 1(b), which indicates that the peaks broadened and split into two different peaks as nitrogen was incorporated into the $LaMgAl_{11}O_{19}$ lattice, thus changing the symmetry of the corresponding crystal planes.

3.2. Chemical states of La, Mg, O, Al, and N in nitrided $LaMgAl_{11}O_{19}$ phosphors

Fig. 2(a)–(f) shows the high-resolution XPS spectra of the La 3d, Mg 2p, Al 2p, O 1s, and N 1s states of nitrided $LaMgAl_{11}O_{19}$ phosphors prepared by the aforementioned two-step process. The La $3d_{5/2}$ and La $3d_{3/2}$ peaks at 835.1 eV and 851.8 eV are shown in Fig. 2, which match the spectrum for an La_2O_3 standard with peak values of 834 eV and 851 eV reported in the literature [23,24]. These values indicated the presence of a La^{3+} species. Moreover, characteristic satellites were observed at approximately 4 eV to each of the $3d_{5/2}$ and $3d_{3/2}$ peaks, which are attributed to a ligand-to-metal charge-transfer process [25]. In Fig. 2(b), the Mg 2p peak of 50.2 eV is consistent with the value of 50.2 eV for crystalline $MgAl_2O_4$ [26]. The O 1s spectrum shown in Fig. 2c is composed of three peaks at 529 eV, 530.7 eV, and 531.84 eV, which are due to the lattice oxygen of the La–O octahedral structure [27], the lattice oxygen of the spinel structure [28], and surface-adsorbed oxygen [29], respectively. The Al 2p spectra shown in Fig. 2(d) exhibit an asymmetrical peak composed of two sub-peaks at 73.6 eV and 74.3 eV; these peaks were fitted with the Bes of AlN and Al_2O_3 at 73.5 eV and 74.5 eV within experimental error bounds [30]. Fig. 2(f) shows two peaks in the spectrum of N 1s at 398 eV and 400 eV. Thus, it can be concluded that some nitrogen was doped into the $LaMgAl_{11}O_{19}$ lattice and that it replaced the position held by oxygen in the lattice of LMA to form nitrided $LaMgAl_{11}O_{19}$.

According to the results of XRD analysis discussed above, this luminescent nitrided $LaMgAl_{11}O_{19}$ phosphor exhibited the same structure as $LaMgAl_{11}O_{19}$. Fig. 3 shows the crystal structure of nitrided $LaMgAl_{11}O_{19}$, also composed of two spinel layers and an $LaAlO_3$ layer, which exhibited reflective symmetry in its lattice. The aluminium and lanthanum atoms were both surrounded by six oxygen atoms; however, the La–O bonds were more stable than the Al–O bonds. Thus, the nitrogen atoms were doped into the structure, replacing the oxygen atoms to form more stable bonds with aluminium atoms, as shown in Fig. 3(b).

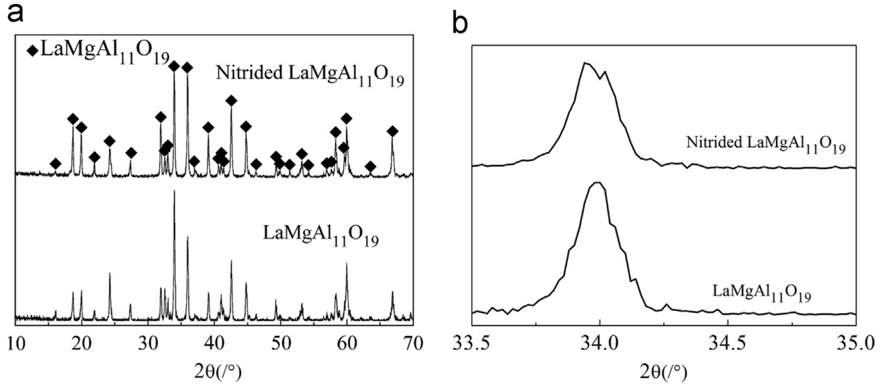

Fig. 1. XRD patterns of as-prepared $LaMgAl_{11}O_{19}$ and nitrided $LaMgAl_{11}O_{19}$ phosphors. (a) $10° \leq 2\theta \leq 70°$ and (b) $33.5° \leq 2\theta \leq 35°$.