Preparation, structural and optical characteristics of a deep red-emitting $Mg_2Al_4Si_5O_{18}$: Mn^{4+} phosphor for warm w-LEDs

Anjie Fu [a], Liya Zhou [a, *], Song Wang [b], Yinghao Li [a]

[a] School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China
[b] Hubei Key Laboratory of Low Dimensional Optoelectronic Materials and Devices, Hubei University of Arts and Science, Xiangyang 441053, China

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ABSTRACT

A novel red-emitting phosphor $Mg_2Al_4Si_5O_{18}$:Mn^{4+} is successfully synthesized using a solid-state reaction method. Aluminosilicate $Mg_2Al_4Si_5O_{18}$ of low-symmetry orthorhombic phase contains abundant octahedrons and is suitable for Mn^{4+} doping. A broad absorption band ranging from 240 nm to 550 nm in the ultraviolet−visible spectra corresponds to the photoluminescence excitation spectrum. The emission spectrum from 650 nm to 750 nm exhibits a strong emission peak at 680 nm because of the $^2E_g \rightarrow {^4}A_{2g}$ transition of Mn^{4+} ion. The critical distance Rc for concentration quenching is ~33.3 Å, and the energy transfer mechanism is determined to be dipole−dipole interaction. Luminescence mechanism is analyzed using the energy level diagram of Mn^{4+} ion. Racha parameters B and C are evaluated and used to discuss the nephelauxetic effect for the Mn^{4+} ions in the $Mg_2Al_4Si_5O_{18}$. Temperature-dependent fluorescence test demonstrates the good thermal optical properties of the phosphor. An assembled light-emitting diode (LED) device with efficient luminescence demonstrates its practical use. Results indicate the potential application of the phosphor for white LEDs.

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1. Introduction

The growing population and the excessive exploitation have made the energy crisis threatening to human existence, and energy saving and environmental protection have become the major concerned topics in the 21st century. In the face of the crisis, all countries are exploring new alternative energy sources for human beings. White light-emitting diodes (WLEDs) have been recognized as next-generation lighting sources because of their high performance, environmental friendliness, and long-term stability [1−3]. However, the traditional WLED consisted of a InGaN blue light-emitting diode (LED) and a yellow phosphor YAG:Ce^{3+} exhibits very poor color rendering index (CRI) and high color temperature (CT) because of the deficiency of the red light in the spectral region of 650−750 nm [4−6]. This red light is optimum for plant cultivation and close to the maximum absorbance for chlorophyll. Combining the green, blue, and red phosphors with a near-ultraviolet (UV) LED is a common strategy to improve the color quality of WLEDs. Therefore, searching for a novel red phosphor that can be effectively excited by near-UV LED is urgently

demanded. In recent years, various kinds of red phosphors have been explored and investigated. Rare-earth ions, such as Eu^{3+} and Sm^{3+}, are the most commonly used activators in red phosphors. However, costly raw materials and sharp absorption in the UV region also limit the applications of red phosphors with these activators [7,8]. Non-rare-earth ion, such as Mn^{4+}, has been widely used as the activator for red phosphor because of its low cost and availability. The $^2E_g - {^4}A_{2g}$ transition of Mn^{4+} in the octahedral environment of the emitting host leads to the sharp peaks of the phosphor in the deep red region, which can meet the application for WLEDs [9].

Aluminates, germanates, and titanate are considered excellent host materials for Mn^{4+} because of their high luminescence efficiency (LE) and chemical stability. Previous studies have achieved and investigated various Mn^{4+}-doped phosphors, such as $CaAl_2O_4$:Mn^{4+}, $SrMgAl_{10}O_{17}$:Mn^{4+}, K_2LiAlF_6:Mn^{4+}, La_2MgTiO_6:Mn^{4+}, $Y_2Ti_2O_7$:Mn^{4+}, $LiAlGe_2O_6$:Mn^{4+}, and $SrGe_4O_9$:Mn^{4+} [10−16]. Silicates are known host of many phosphors. However, Mn^{4+}-doped silicate phosphor is rarely reported; the reason is that the polyhedral networks of silicate phases are only composed of SiO_4 tetrahedrals, thereby lacking the octahedral environment for Mn^{4+} ions to emit photoluminescence (PL) [17].

Aluminosilicates have been recognized as candidates for Mn^{4+}-

doped phosphors, such as Sr3Al10SiO20 [17]. Si(Al)O$_4$ tetrahedrals and AlO$_6$ octahedrons are abundant in the crystal structure, in which the Al^{3+} ions are octahedrally coordinated using six oxygen ions and can be replaced by Mn^{4+} ions. Thus, in this study, cordierite (Mg$_2$Al$_4$Si$_5$O$_{18}$) was selected as the host for doping Mn^{4+} ions. The polymorph of cordierite is a low-symmetry orthorhombic phase with hexagonal structure with many hexagonal rings. The [(Si$_4$Al$_2$)O$_{18}$] layer is based on the arranging order of [SiO$_4$] and [AlO$_4$] tetrahedrons, and the alternative layer is connected through [Mg(Al)O$_6$] octahedrons and [Si(Al)O$_4$] tetrahedrons [18]. The Al^{3+} ions are in an octahedral coordination environment and very suitable for Mn^{4+} doping. In this study, Mg$_2$Al$_4$Si$_5$O$_{18}$:Mn^{4+} phosphor was successfully synthesized through standard solid-state reaction. The crystal structure of the product was investigated. X-ray diffraction (XRD), UV−visible (UV−vis) absorption, fluorescent lifetime, and high-temperature PL were performed to characterize the material. Racah parameters B and C were calculated and considered when the nephelauxetic effect was analyzed. The temperature-dependent fluorescence analysis was used to confirm the good fluorescence thermal stability of the proposed material.

2. Experimental procedure

2.1. Materials and synthesis

Mn^{4+}-doped Mg$_2$Al$_4$Si$_5$O$_{18}$ (MAS:Mn^{4+} hereinafter) was prepared by high-temperature solid-state reaction using analytical reagent grade chemicals, namely, MgO, Al$_2$O$_3$, SiO$_2$, and MnCO$_3$. The powders were weighed in a certain stoichiometric ratio of Mg$_2$Al$_{4-x}$Si$_5$O$_{18}$:xMn^{4+} ($x = 0-0.03$) and thoroughly mixed in a mortar to improve the homogeneity. After grinding, the samples were placed in crucibles and heated at 1673 K for 5 h under air atmosphere. Thereafter, the samples were cooled down to room temperature and ground again for subsequent characterization.

2.2. Sample characterization

The sample phase was recorded through XRD using Cu Kα radiation on a RIGAKU D/max 2200 vpc X-ray diffractometer. Step scan was conducted over the angle range of 10°−90° with a step size of 0.02°. The UV−vis absorption spectra of the powders were recorded on a Cary 5000 UV−vis spectrophotometer. The excitation and emission spectra of the samples were recorded using a fluorescence spectrometer (Hitachi F-4600, Japan) equipped with a 150 W xenon lamp as excitation source. The luminescence decay curve was obtained using an FLS920, and a 350 W xenon lamp was used as excitation source. The temperature-dependent PL spectra and decay curves were recorded in an FLS-980 Edinburgh fluorescence spectrometer and measured between 300 and 500 K. LED lamps were fabricated by depositing the Mg$_2$Al$_4$Si$_5$O$_{18}$:Mn^{4+} phosphor on a UV chip with an emission of ~370 nm. The current for exciting the UV chip was fixed at 60 mA. The CRI, CT, and LE of the constructed LED were evaluated using a photo-electricity test system (V2.00 LED spec system). All measurements were performed at room temperature.

3. Result and discussion

The XRD patterns of Mg$_2$Al$_4$Si$_5$O$_{18}$:xMn^{4+} ($x = 0, 0.01, 0.02, 0.03$) are depicted in Fig. 1(a). The powder diffraction standard of Mg$_2$Al$_4$Si$_5$O$_{18}$ (PDF#13-0294) as a reference is also shown for comparison. All diffraction peaks of as-prepared samples match well with the standard card. This condition indicates that the sample contains a single phase of Mg$_2$Al$_4$Si$_5$O$_{18}$ without any impurity phases, and the additive Mn^{4+} is successfully incorporated
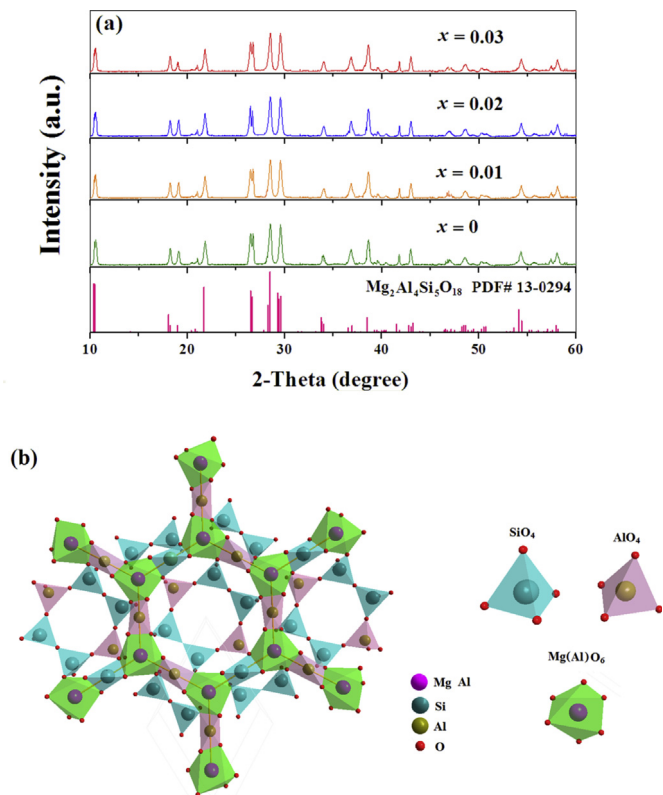
Fig. 1. (a) X-ray powder diffraction patterns of Mg$_2$Al$_4$Si$_5$O$_{18}$:xMn^{4+} ($x = 0, 0.01, 0.02, 0.03$) phosphors and the Mg$_2$Al$_4$Si$_5$O$_{18}$ standard PDF card. (b) Projection view of crystal structure of Mg$_2$Al$_4$Si$_5$O$_{18}$ six-membered ring.

into the host with no significant influence on the MAS host crystal structure.

The coordination environment of the octahedral sites that accommodated the activator Mn^{4+} can be investigated by analyzing the crystal structure. The structure diagram of Mg$_2$Al$_4$Si$_5$O$_{18}$ is shown in Fig. 1(b), in which [(Si,Al)O$_4$] tetrahedrons are arranged orderly on the six-membered rings of [(Si$_4$Al$_2$)O$_{18}$] and construct a low-symmetry orthorhombic phase called the polymorph of cordierite (Cccm). Alternate layers of [(Si$_4$Al$_2$)O$_{18}$] hexagonal rings are connected by [Mg(Al)O$_6$] octahedrons, one [SiO$_4$] tetrahedron, and two [AlO$_4$] tetrahedrons. In this structure, Mg^{2+} and Al^{3+} ions are coordinated by 6 O^{2-}. Si^{4+} and another Al^{3+} ion are surrounded by 4 O^{2-} ions and form tetrahedrons [18]. Although two tetrahedral sites and two octahedral sites are found in Mg$_2$Al$_4$Si$_5$O$_{18}$, the Mn^{4+} ions are found to be introduced into the MAS host and mainly substitute the octahedral Al^{3+} sites, considering the octahedral sites are the only luminescence center for Mn^{4+} cation and the similar ionic radii of Al^{3+}(r = ~0.535 Å, N = 6) and Mn^{4+}(r = ~0.530 Å, N = 6). On the basis of this explanation, the influence of Mn^{4+} ions in other phases upon the emission spectrum is not prominent and is ignored.

The UV−vis absorption spectra of Mg$_2$Al$_4$Si$_5$O$_{18}$:xMn^{4+} ($x = 0, 0.01, 0.02, 0.03$) are shown in Fig. 2(a). Compared with the host band, Mn^{4+}-doped phosphor exhibits a broad absorption band ranging from 240 nm to 550 nm. The intensities of the bands increase with the Mn^{4+} concentration. Several absorption edges are observed. A noticeable shift at approximately 251 nm in the absorption edges is due to the Mn$^{4+} \rightarrow$O^{2-} charge transfer transitions. Two shifts centered at 316 and 475 nm are ascribed to strong spin-allowed $^4A_{2g} \rightarrow {^4T_{1g}}$ and $^4A_{1g} \rightarrow {^4T_{2g}}$ transitions of Mn^{4+}, respectively. The weak absorption edge located at 400 nm results from the