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Red-emitting $Sr_2MgGe_2O_7:Mn^{4+}$ phosphors: Structure, luminescence properties, and application in warm white light emitting diodes

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ABSTRACT

To achieve efficient phosphors that address the shortage of red emission for use in white light emitting diodes (WLED), a series of red-emitting phosphors of $Sr_2MgGe_2O_7$ doped with different concentrations of Mn^{4+} have been successfully fabricated by a high-temperature solid-state method. The crystal structure properties including the phase purity were analysed by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Absolute quantum yield, temperature stability, and lifetime were utilized to characterize the samples. Furthermore, the excitation spectra of the samples exhibit two broad absorption bands with peaks located at approximately 308 nm and 419 nm, which could be excited by near-UV/blue LED light. The emission spectra range from 600 nm to 700 nm and exhibited a sharp peak at 659 nm due to the $^4E \rightarrow {}^4A_2$ spin- and parity-forbidden transition of Mn^{4+}. The optimal Mn^{4+} doping concentration in the $Sr_2MgGe_2O_7$ host is determined to be 0.7%. The critical energy transfer distance of these phosphors is calculated to be about 26.61 Å, and the concentration quenching mechanism is proved to correspond to a dipole-dipole interaction. The luminescence of the $Sr_2MgGe_2O_7:Mn^{4+}$ phosphors decrease gradually with increasing temperature, and the $Sr_2MgGe_2O_7:Mn^{4+}$ sample exhibits better thermal stability than the commercial $Sr_2Si_5N_8:Eu^{2+}$ red phosphors. The warm WLED is fabricated by combining the $Sr_2MgGe_2O_7$:0.7%Mn^{4+} and YAG:Ce^{3+} phosphor with a 420-nm blue LED chip to explore its possible applications in warm WLED.

1. Introduction

In recent years, white light emitting diodes (WLED) have been evolved to achieve several desirable properties, such as small volume, high luminance, high efficiency, long lifetime, and environmental friendliness [1–3]. Most prominently, WLED have been widely used in response to the energy crisis due to their excellent energy-saving characteristics. Their excellent performance has initiated a revolution in the lamp industry to address the increasing requirements to improve quality of life [4,5]. Until now, the standard method to fabricate WLED involved combining a blue InGaN chip with a yellow YAG:Ce^{3+} ($Y_3Al_5O_{12}:Ce^{3+}$) phosphor [6]; this approach is economical and easy to perform. However, there are drawbacks in the light emission of the WLED such as a highly correlated colour temperature, poor colour rendition index, and cold white light because of insufficient red emission in system [7]. Obviously, these problems need to be solved urgently. Improving the performance of WLED requires not only advances in LED chips but also new types of down-conversion phosphors. Moreover, the changing solid-state lighting technology leads to growing demands for new phosphors with specific performances [8]. Therefore, red phosphor research and development are very important, and it has become a hot topic in the field of WLED.

Former studies on red phosphors have mainly focused on Eu^{2+}-doped nitrides in rare earth-doped systems [9]. Recently, Mn^{4+}-doped host materials for environment-friendly non-rare earth phosphors, which can be synthesized under relatively mild conditions, have attracted great attention. The Mn^{4+} ion exhibits a quite complicated optical spectrum. It shows absorption throughout the UV region and deep red (620–720 nm) fluorescence emission due to the $^2E \rightarrow {}^4A_2$ transition [10–13]. There are many reports on Mn^{4+}-doped red phosphors, such as $Li_2Ge_4O_9:Mn^{4+}$, $K_2SiF_6:Mn^{4+}$, $Mg_2TiO_4:Mn^{4+}$, $SrMgAl_{10}O_{17}:Mn^{4+}$, etc. [14–17]. However, further research on the luminescent properties of Mn^{4+}-doped materials is necessary to meet the practical application requirements of WLED.

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The red-emitting Mn^{4+} ion is associated with several electronic vibrational sidebands that are affected by the covalent environment and the coordination symmetry [18]. Therefore, it is closely related to the optical properties of the host matrix. It is obvious from the expression for the effective compensating factor, $j = Z/r$ (Z is the electric charge number and r is the ionic radius), that the size of the dopant ions and the replaced ions should be as similar as possible [19]. Based on this requirement and after comparing several hosts, germinate hosts have been determined to be a sensible choice for Mn^{4+}-doped red phosphors as Mn^{4+} has the same ionic radius as Ge^{4+}. Therefore, we chose $Sr_2MgGe_2O_7$ as the host for designing a new phosphor.

In this study, $Sr_2MgGe_2O_7$ doped with different Mn^{4+} concentrations were successfully synthesized by a high-temperature solid-state method in air. The structure and photoluminescence properties of $Sr_2MgGe_2O_7$:Mn^{4+} are discussed in detail. The results show that $Sr_2MgGe_2O_7$:Mn^{4+} is a promising red phosphor in the field of warm WLED applications.

2. Experimental section

2.1. Synthesis

Conventional solid-state reactions at high temperature were adopted to prepare these phosphors. Samples with nominal compositions of $Sr_2MgGe_{2(1-x)}O_7$:xMn^{4+} were synthesized with Mn^{4+} concentrations of 0, 0.1%, 0.3%, 0.5%, 0.7%, 0.9%, 1.1%, and 2%. The reagents in these experiments, including $SrCO_3$(A.R.), $MgCO_3$(A.R.), GeO_2(A.R.), and $MnCO_3$(A.R.), were used directly without any further purification. All starting raw materials were purchased from Aladdin Chemistry Co., Ltd, Shanghai, China.

2.2. Characterization

The purity and crystal structure were characterized by X-ray diffraction (XRD, D8 Advance, Bruker, Germany) with Cu Kα radiation of 40 kV and 40 mA at room temperature. Inspection was performed using a microstructure equipped with a scanning electron microscope (SEM, JSM-6700F). The photoluminescence (PL) and PL excitation (PLE) spectra of these samples were obtained using a spectrofluorometer (Edinburgh, FS5) equipped with a Xe lamp. The temperature-dependent luminescence properties were recorded on the same spectrophotometer connected to a computer-controlled electric furnace and a self-made heating attachment. X-ray photoelectron spectroscopy (XPS, AXI ULTRA DLD) with monochromatic Al Kα radiation was used for characterization. The decay curves of the samples were measured using a HORIBA Jobin Yvon FluoroMax-4 fluorescence spectrometer fitted with a 150-W Xe lamp as the excitation source. The luminescent efficiency (LE), colour rendition index (CRI), correlated colour temperature (CCT), and commission internationale de l'eclairage (CIE) of the fabricated WLED devices were evaluated at 20 operating currents using an integrating sphere (PMS-50; Everfine Photo-E-Info Ltd, Hangzhou, China). All measurements were made at room temperature.

3. Results and discussion

3.1. Phase formation and structural characteristics

The Mn^{4+}-doped $Sr_2MgGe_2O_7$ (SMGO) samples were prepared at 1200 °C. The samples were examined by XRD to identify the composition and assess the phase purity of the as-prepared products. Fig. 1(a) shows the XRD patterns of the pure SMGO:Mn^{4+} host sample and the representative SMGO:0.7%Mn^{4+} sample. All diffraction peaks coincide well with those of the standard card. To further determine the structure of the synthesized samples, ICSD NO.420522 ($Sr_2MgGe_2O_7$) was used as standard, and the structural analysis of the XRD data was performed using the Materials Studio program. Fig. 1(b) shows the experimental and refined XRD patterns of the SMGO sample. The "×" represents the measured diffraction data. The red solid curve shows the calculated diffraction data, and the green vertical line shows the position of the simulated diffraction peak. The solid blue line indicates the deviation between the measured value and the calculated value. The peaks of the calculated and experimental patterns are consistent. No impurity phase was found, which indicates that the sample consists of a single phase. The calculated residual factor is Rp = 5.57%, and Rwp = 7.32%.

The SEM image of the SMGO:0.7%Mn^{4+} sample is shown in Fig. 2(a). The phosphor particles are clearly aggregated into a coral shape (owing to the high synthesis temperature), and the sample surface is smooth. XPS was employed to further confirm the valence of the Mn ions in the host. Fig. 2(b) shows the XPS survey spectrum of the representative SMGO:0.7%Mn^{4+} sample. The elements Sr, Mg, Ge, O, and C can be observed. Moreover, relatively weak Mn signals also appear in the spectrum. The absorption of CO_2 results in the presence of carbon. The core level binding energy of $Mn2p_{3/2}$ is evaluated to be about 642.42 eV. Furthermore, the peaks at 641.5 eV, 641.6 eV, and 642.2 eV are assigned to $Mn^{2+}2p_{3/2}$ (MnO), $Mn^{3+}2p_{3/2}$ (Mn_2O_3), and $Mn^{4+}2p_{3/2}$ (MnO_2), respectively [20]. Therefore, the Mn element in the SMGO matrix is mainly in the Mn^{4+} state [21,22].

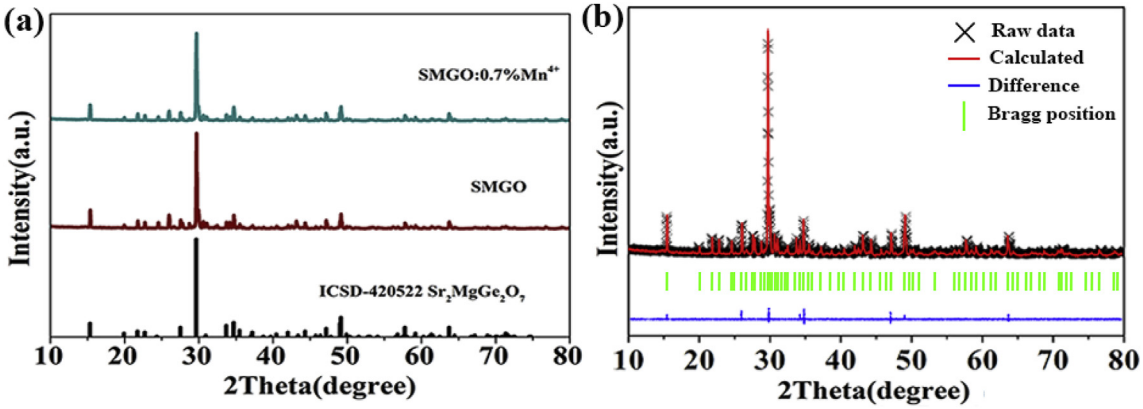

Fig. 1. (a) XRD patterns of the SMGO host, SMGO:0.7%Mn^{4+}, and the standard card (ICSD-420522); (b) Rietveld refinement of the powder XRD profile of SMGO:0.7%Mn^{4+}.