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An efficient, broad-band red-emitting $Li_2MgTi_3O_8:Mn^{4+}$ phosphor for blue-converted white LEDs

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ABSTRACT

We describe the preparation of a novel red-emitting $Li_2MgTi_3O_8:Mn^{4+}$ nanocrystalline phosphor by a soft chemical method. $Li_2MgTi_3O_8:Mn^{4+}$ phosphor gained our attention and interest due to its low-cost and unique luminescent properties. The deep red emission from $Li_2MgTi_3O_8:Mn^{4+}$ shows an abnormal broad band at 680 nm, with a quantum efficiency (QE) of 34%, and good thermal resistance of $\Delta E = 0.214$ eV $Li_2MgTi_3O_8:Mn^{4+}$ phosphor exhibits the most intense excitation absorption in the blue region which matches the emission wavelength of the blue LEDs, indicating its potential to enhance the color rendering performance of white LEDs. The deep red emission originates from the $^2E_g \rightarrow {}^4A_{2g}$ transition of Mn^{4+}. The spectral features are well explained by the Tanabe-Sugano diagram, with crystal-field and Racah parameters of $Dq = 2.06 \times 10^3$ cm^{-1}, $B = 0.76 \times 10^3$ cm^{-1} and $C = 3.00 \times 10^3$ cm^{-1}. A device was fabricated in which this red phosphor $Li_2MgTi_3O_8:Mn^{4+}$ was used to coat the blue LEDs. The fabricated device demonstrated that the prepared material can act as a novel potential red phosphor for warm white LEDs.

1. Introduction

From the point of view of sustained social development, energy saving has been one of the most critical topics in the 21st century. Owing to their high efficiency, energy saving ability, long lifetime and environmental friendliness, white light-emitting diodes (LEDs) are widely seen as a superior replacement for conventional inefficient incandescent and fluorescent lightings [1–5]. LEDs are in the spotlight for several applications, e.g., backlighting, general illumination, and in liquid crystal displays of digital cameras, cellular phones, and monitors of notebook computers. Therefore, the white LEDs industry has gradually found an important position in global economic growth, which provides the motivation for further studies of white LEDs.

To date, a variety of strategies have been developed to produce white LEDs. Tri-phosphor LED chips, which combine red, green, and blue LEDs to produce white light, exhibit drifts of the color rendering index (CRI) and color temperature (CT), because the devices are susceptible to temperature [6]. The most well-known approach for commercial, white LEDs is based on the combination of an InGaN blue LED and a yellow phosphor, $Y_3Al_5O_{16}$:Ce (YAG:Ce) [7,8]. When driven by a certain current, white light is obtained by combining the emitted yellow light from YAG:Ce with the transmitted blue light. However, the lack of a red spectral component usually results in a highly correlated CT (7756 K) and a poor CRI (Ra = 75), which largely restricts the broader applications of white LEDs [1,2,9]. To overcome the above drawbacks, one of the best strategies is the addition of a red-emitting phosphor, which can efficiently absorb blue light. Thus, there is an urgent demand for a novel red phosphor with ideal luminescent performance. This high demand has motivated studies of novel red-emitting luminescent materials activated by rare earth elements, such as Eu^{2+}-doped nitrides, oxynitrides, silicates, phosphates and aluminosilicates [10–13]. Among these systems, Eu^{2+}-doped (oxy)nitrides have been the subjects of many studies due to their excellent performance parameters, such as high quantum efficiency and good thermal stability. However, in addition to economic considerations, extreme operating conditions restrict a wide range of application of Eu^{2+}-doped (oxy)nitrides. For example, β-SiAlON:Eu^{2+} red phosphor was synthesized at 1900 °C under nitrogen at 10 MPa [14]. However, the photon reabsorption is unavoidable in nitrides, resulting in color change and luminous reduction. Recently, CdSe quantum dots (QDs) have attracted much

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attention because they can provide tunable emission ranging from 500 nm to 650 nm. Thus, CdS QDs might be good candidates as promising red-emitting components for blue-LEDs converted white LEDs [15,16]. However, the synthetic process for CdS QDs is still under study.

In recent years, non-rare-earth Mn^{4+}-activated red phosphor has emerged as a potential competitor to commercial Eu^{2+}-doped nitrides, driven by the soaring price of rare earths and the strong desire to minimize the cost of white LED devices. Compared with Eu^{2+}-doped (oxy)nitrides and CdS QDs, red phosphors $AMF_6:Mn^{4+}$ (A = Na, K, Cs, Ba, Rb; M = Si, Ti, Ge, Zr), such as $KNaSiF_6:Mn^{4+}$ [17], $K_2SiF_6:Mn^{4+}$ [18], $BaSiF_6:Mn^{4+}$ [19], $Cs_2ZrF_6:Mn^{4+}$ [20], $K_2GeF_6:Mn^{4+}$ [21], $Cs_2TiF_6:Mn^{4+}$ [22], $K_2TiF_6:Mn^{4+}$ [23], have become a hot research topic for their potential applications in white LEDs. This is due to their milder preparative conditions and admirable luminescent characteristics, which make them suitable for use in warm white LEDs. These Mn^{4+}-doped fluorides give narrow emissions in the visible red spectral region, which are highly perceived by the human eye and lead to excellent chromatic saturation of red spectra. Furthermore, red-emitting Mn^{4+}-activated oxide phosphors have received burgeoning interest due to their low cost and excellent physical/chemical stability. For example, Peng et al. found that the non-rare-earth phosphor $Sr_4Al_{14}O_{25}:Mn^{4+}$ exhibited red luminescence more intensely than the commercial phosphor $3.5MgO{\cdot}0.5MgF_2.GeO_2:Mn^{4+}$ ($Li_2MgTi_3O_8$: Mn^{4+}) upon blue excitation [24]; Wang et al. proved that the non-rare-earth $BaMgAl_{10-2x}O_{17}$:$x$$Mn^{4+}$, $x$$Mg^{2+}$ phosphor exhibited bright, narrow-band luminescence and could serve as red component for warm white LEDs [25]; Hu et al. reported that Mn^{4+} activated Li_2MgTiO_4 phosphor exhibited a deep red emission as a color converter for warm white LEDs [26].

Herein, $Li_2MgTi_3O_8:Mn^{4+}$ phosphor was prepared successfully by a mild soft chemical technology. As displayed in Fig. 1, the spinel structure of $Li_2MgTi_3O_8$ consists of a cubic close-packed array of anions, with one eighth of the tetrahedral and one half of the octahedral interstics occupied by cations; in the $Li_2MgTi_3O_8$ host, Li^+/Mg^{2+} occupies a tetrahedral site, whereas Ti^{4+} shows a strong preference for an octahedral site [27]. It is generally known that Mn^{4+} ion is accommodated and stabilized only in octahedral sites [23–25]. When Mn^{4+} occupies an octachedral site, it generally gives a deep red emission between 600 and 760 nm and shows a strong and broad absorption band from 250 to 480 nm. Such a close-packed structure with abundant TiO_6 octahedral sites is highly favorable for accommodating and stabilizing Mn^{4+} ions, and is thus expected to enable a high efficiency of luminescence when Mn^{4+} is doped into the $Li_2MgTi_3O_8$ host. Indeed, $Li_2MgTi_3O_8:Mn^{4+}$ shows a brilliant deep red emission with a QE of 34% under excitation at 470 nm and exhibits a broad excitation band ranging from 250 to 500 nm. Unexpectedly, its emission intensity is much brighter than that of the commercial MMG:Mn phosphor. A variety of techniques, such as diffuse reflection spectra, photoluminescence (PL) spectra, and temperature-dependent PL/decay measurements, were utilized to characterize the photoluminescence properties of the $Li_2MgTi_3O_8:Mn^{4+}$ phosphor. To demonstrate its potential as a novel red phosphor for blue-converted white LEDs, white LEDs were fabricated using blue LED chips coated with the commercial yellow phosphor (YAG:Ce) and the as-prepared phosphor $Li_2MgTi_3O_8:Mn^{4+}$.

2. Experimental procedures

2.1. Synthesis

$Li_2MgTi_3O_8:Mn^{4+}$ samples were prepared by the Pechini-type sol–gel method, as follows. All the chemicals, namely, Li_2CO_3 (AR), $Mn(CH_3COO)_2{\cdot}4H_2O$ (AR), $Mg(CH_3COO)_2{\cdot}4H_2O$ (AR), TiO_2 nanoparticles (99.999%, 28 nm) and citric acid were used as starting materials. A typical synthesis procedure for $Li_2MgTi_3O_8$:0.5%Mn^{4+} phosphor is as follows: 0.953 g Li_2CO_3, 1.072 g $Mn(CH_3COO)_2{\cdot}4H_2O$, 0.018 g $Mg(CH_3COO)_2{\cdot}4H_2O$ and 1.192 g TiO_2 were weighed based on the chemical proportion, $Li_2MgTi_{3\times(1-0.005)}O_8:0.005Mn^{4+}$, with the addition of 5 mol% excess of Li_2CO_3. Excess lithium was added to compensate for loss, which occurs at a high temperature. The molar ratio of citric acid to total metal ions was 1:1. Li_2CO_3, $Mn(CH_3COO)_2{\cdot}4H_2O$, $Mg(CH_3COO)_2{\cdot}4H_2O$, and TiO_2 were dissolved in deionized water under vigorous stirring. Simultaneously, a stoichiometric amounts of citric acid was added to the solution. At the end, the pH value of the mixed solution was adjusted to 7-8 by dropwise addition of $NH_3{\cdot}H_2O$, and the transparent solution was heated to 100 °C in a water bath to produce a brown transparent resin. The resin was further dried at 160 °C in an oven for 10 h. Finally, the dried gel was annealed at

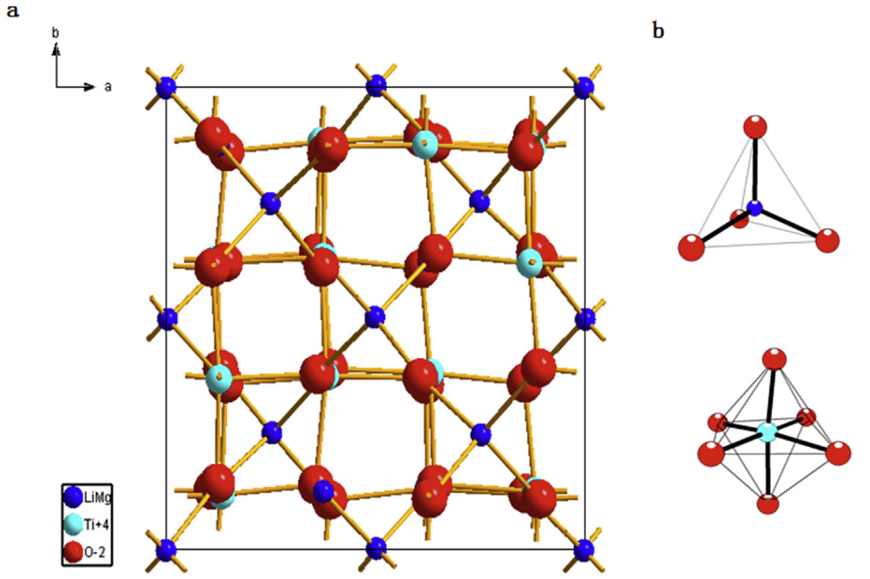

Fig. 1. (a). Schematic illustration of the crystal structure of $Li_2MgTi_3O_8$; (b) shows the of LiO_4 or MgO_4 tetrahedron and the TiO_6 octahedron.