Deep-red emitting $\text{Mg}_2\text{TiO}_4\text{:Mn}^{4+}$ phosphor ceramics for plant lighting

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Abstract

In this study, deep red emitting $\text{Mg}_2\text{TiO}_4\text{:Mn}^{4+}$ phosphor ceramics were synthesized by the high temperature solid-state reaction method. The ceramics can be excited by the 465 nm blue light and had a narrow emission with a full width at half maximum (FWHM) value of 31 nm. The peak wavelength was located at 658 nm, which matched the most efficient wavelength for photosynthesis. The crystal field strength (D_q) and the Racah parameters (B and C) are estimated by Tanabe-Sugano diagram. The thermal conductivity of the ceramics was 7.535 W/(m·K) at room temperature, which was one order of magnitude higher than that of the traditional packaging method using silicone gel. A set of phosphor converted LEDs were fabricated by mounting the phosphor ceramics onto the 460 nm blue LED chips and the CIE coordinates can move from the blue light region to the purple light region with the thickness of the ceramic increasing. These results indicated that the $\text{Mg}_2\text{TiO}_4\text{:Mn}^{4+}$ phosphor ceramic was suitable for plant lighting when combined with a blue LED chip.

1 Introduction

In the past few decades, it has been proved that artificial light sources can improve the growth of plants [1]. But the conventional light sources such as incandescent lamps, metal-halide, fluorescent and high-pressure sodium, suffer from low energy efficiency because the green and yellow spectral part of these light sources is unsuitable for plant growth [2]. As a new generation lighting technology, light emitting diode (LED) has the advantages of long lifetime, narrow emission bandwidth and adjustable output, which makes it possible to achieve a specific spectral composition [3]. The combination of red and blue LED has been widely used in the greenhouse lighting for plant cultivation and horticulture [4]. However, due to the difference in the spectral drifting and the degradation rates between the red and the blue LED chips, the ratio of red light to blue light is unstable [5]. To this end, another path to obtain stable light source for plant growth is using the red phosphor excited by blue LED instead. Hence, a reliable red phosphor for plant growth is brought into focus.

At present, most of the red phosphors in the market is the Eu^{2+} doped nitrides $(\text{Ca, Sr})\text{AlSiN}_3\text{:Eu}^{2+}$, which has red luminescence of high efficiency under the 460 nm or the 405 nm excitation [6]. However, the harsh synthesis conditions of nitrides and the environmentally harmful mining process of rare earth makes it costly [7]. Tetravalent manganese (Mn^{4+}) doped materials have been considered as an ideal candidate for rare-earth free red phosphors excited by blue LED owing to their low cost and nice photoluminescence properties. In most instances, Mn^{4+} ions occupy the octahedral sites in the host lattices, and its 3d states will be split into the t_{2g} and the e_g states. The electron interaction further leads the energy level of Mn^{4+} to a more complicated situation. The broad excitation bands in the near ultraviolet (nUV) and the blue region of Mn^{4+} are associated with the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transitions while the deep red emission is associated with the ${}^2E_g \rightarrow {}^4A_{2g}$ transition. The emission peak of Mn^{4+} doped materials is closely related to

host matrix, such as fluorides and oxides^[8-9]. Hence, selecting a suitable host material is the key point to obtain the optical properties needed by plant lighting.

Mg₂TiO₄ has been considered as a particularly noteworthy host matrix for Mn⁴⁺ due to its excellent stability and fluoride-free synthetic progress. Fig. 1. shows the inverse spinel structure of Mg₂TiO₄. The distribution of the atoms in the Mg₂TiO₄ unit cell can be described as the structural formula Mg[MgTi]O₄^[10] (where [] denote the octahedral site). All of Ti⁴⁺ and half of Mg²⁺ randomly occupy octahedral site and the rest of Mg²⁺ occupy tetrahedral sites.

Due to the similar ionic radius of Ti⁴⁺ (0.605 Å) and Mn⁴⁺ (0.530 Å)^[11], Mn⁴⁺ can be stable in the octahedral site without breaking the charge balance through replacing Ti⁴⁺, resulting in an efficient red emission peaked at about 658 nm^[12]. Therefore, Mg₂TiO₄: Mn⁴⁺ is a promising red phosphor which can be excited by blue LED for plant lighting.

However, the emission intensity of Mg₂TiO₄:Mn⁴⁺ is sensitive to the temperature, which greatly limits its application in illumination^[13]. Compared to powders, phosphor ceramics have higher thermal conductivity that can efficiently dissipate the heat^[14]. Here, the translucent Mg₂TiO₄: Mn⁴⁺ ceramics were fabricated and the optical as well as the thermal properties were analyzed and discussed.

2 Experimental

2.1 Synthesis

The Mg₂Ti_(1-x)O₄: xMn⁴⁺ (x=0.01%, 0.05%, 0.07%, 0.1%, 0.3% and 0.5%) ceramics were prepared by a traditional high temperature solid-state reaction method with high purity MgO, TiO₂ and MnO₂. Stoichiometric amounts of raw materials were weighed, and then mixed by ball milling for 12 h in ethanol. The mixtures were dried at 80 °C for 12 h, and the dried mixtures were screened with a 100-mesh sieve. The fine powders were pressed to pellets (Φ15 mm) followed by cold isotactic pressing at 200 MPa and finally sintered at 1650 °C for 5 h in an oxygen atmosphere. Then the ceramics were cooled down to room temperature naturally, cut and polished for subsequent measurements.

2.2 Characterizations

The phases purity of the as-obtained samples was analyzed by X-ray diffraction (Rigaku, Model Mini Flex 600, Japan) using Cu K_α irradiation (λ=1.5418 Å) operated at 40 kV. The morphology of the fracture surface of the phosphor ceramic was observed by scanning electron microscope (SEM). The reflectance spectra were recorded by an ultraviolet-visible-NIR spectrophotometer (Perkin Elmer, Model Lambda 1050, U. S. A.). The steady photoluminescence (PL), photoluminescence excitation (PLE) spectra, dynamic emission decay curves and temperature-dependent PL spectra were recorded by an FLS-1000 fluorescence spectrophotometer (Edinburgh Instruments, U. K.). The quantum efficiency (QE) was

measured by an integrating sphere coated with Teflon lining attached to the spectrophotometer at room temperature. The thermal conductivity of the phosphor ceramic was studied by the laser flash method (Netzsch, LFA-457, Germany).

3 Results And Discussion

Fig. 2 shows the X-ray diffraction (XRD) pattern of the as prepared $\text{Mg}_2\text{Ti}_{(1-x)}\text{O}_4: x\text{Mn}^{4+}$ ($x=0.01\%$, 0.05% , 0.07% , 0.1% , 0.3% and 0.5%) ceramics. The position of all samples were well corresponded to the JCPDS 87-1174 card of $\text{Mg}[\text{MgTi}]\text{O}_4$, indicating that the doping of Mn^{4+} did not transform the crystal structure.

Fig. 3 shows the SEM images of $\text{Mg}_2\text{TiO}_4: 0.1\%\text{Mn}^{4+}$ ceramics with different magnification times. A relative dense microstructure with pure phase and clear grain boundaries can be observed from the images. The grain size was dozens of micrometers and a certain number of pores one of several micrometers in diameter existed in the grain. These pores can increase the light scattering in the ceramic phosphor, in result will enhance the light extraction to some extent. Although the existence of pores had adverse effects on the thermal conductivity^[15], in this work, the thermal conductivity was maintained a relative high value, which will be discussed below.

The reflectance spectra of all the ceramic samples were shown in Fig. 4. It can be detected that the doping of Mn^{4+} brought a strong absorption band in the near ultraviolet (nUV) region, which was caused by the combined action of spin-allowed $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}$ and spin-forbidden $^4\text{A}_{2g} \rightarrow ^2\text{T}_{2g}$ transitions. Another strong absorption band located around 487 nm was from the spin-allowed $^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}$ transition. The absorption band in the deep ultraviolet region (240 nm-310 nm) might be caused by a ligand-to-metal charge transfer (LMCT) from O^{2-} - Mn^{4+} ^[16]. With the doping concentration increasing, an absorption band began to appear around 520 nm, which may be due to the metal-to-metal charge transfer (MMCT) when the distance between the Mn^{4+} cations becomes shorter^[17].

Fig. 5 shows the PLE spectra of $\text{Mg}_2\text{Ti}_{(1-x)}\text{O}_4: x\text{Mn}^{4+}$ ($x=0.01\%$, 0.05% , 0.07% , 0.1% , 0.3% and 0.5%) ceramics, with the 658 nm emission monitored. In good agreement with reflectance spectra, two broad excitation bands were shown in the nUV and the blue light region, respectively, so the ceramics can be excited by the ultraviolet as well as the blue LED chips. The excitation intensity in the blue light region achieved the maximum when the concentration was 0.1%, then decreased with the concentration further increasing due to the occurrence of concentration quenching.

The PLE spectrum of 0.1% Mn^{4+} doped Mg_2TiO_4 can be well fitted by 4 Gaussian peaks. Two strong peaks located at 28902 cm^{-1} and 20534 cm^{-1} were corresponded to spin-allowed $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}$ and $^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}$ transitions, respectively. Between these two peaks, a weaker peak at 24343 cm^{-1} was corresponded to spin-forbidden $^4\text{A}_{2g} \rightarrow ^2\text{T}_{2g}$ transition. Another peak at 32265 cm^{-1} was attributed to the LMCT transition^[18].

Fig. 6 shows the PL spectrum of $\text{Mg}_2\text{Ti}_{(1-x)}\text{O}_4: x\text{Mn}^{4+}$ ($x=0.01\%$, 0.05% , 0.07% , 0.1% , 0.3% and 0.5%) ceramics under 465 nm excitation. All the samples had a red emission with a sharp peak at 658 nm due to the ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$ transition. The strongest emission appeared when the concentration was 0.10%, and the full width at half maximum (FWHM) was 31 nm, as shown in the inset graph of Fig. 6. The quantum efficiency (QE) of the 0.10% Mn^{4+} doped Mg_2TiO_4 ceramic under the 465 nm excitation was 26.47% in full emission range and over 53% of the emission ($\text{QE}=14.25\%$) energy were located in the range between 640 nm to 680 nm. As the maxima of photosynthesis efficiency were around 640-680 nm for quantum yield (per absorbed light unit) and around 660-680 nm for action spectrum (per incident light unit) [19], Mn^{4+} doped Mg_2TiO_4 had the potential to be a promising candidate for plant lighting.

The relationship between the energy level of Mn^{4+} and the crystal field splitting energy D_q of Mg_2TiO_4 can be explained by Tanabe-Sugano diagram [19-23], as seen in Fig. 7, and the crystal field splitting energy D_q and Racah parameters B and C can be obtained by following Equations. (see Equations 1-4 in the Supplementary Files)

where the transition energy $E({}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g})$, $E({}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g})$ and $E({}^2\text{E}_g \rightarrow {}^4\text{A}_{2g})$ can be roughly estimated from fitting peak energy (20534 cm^{-1} , 28902 cm^{-1} and 15198 cm^{-1}), as shown in Fig. 5. (b). The crystal field splitting energy D_q , Racah parameters B and C for Mn^{4+} doped Mg_2TiO_4 were finally calculated to be 2053 cm^{-1} , 842 and 3006, indicating that Mn^{4+} ions were located in a strong crystal field environment in the Mg_2TiO_4 host.

However, from Tanabe-Sugano diagram, the energy level of ${}^2\text{E}_g$ is almost independent of crystal field splitting energy. The different position of emission peak between Mn^{4+} doped Mg_2TiO_4 and other hosts were caused by nephelauxetic effect. Brik et al. established a non-dimensional linear correlation to explain the relationship between the emission energy level (${}^2\text{E}_g$) and the nephelauxetic ratio (β_1). [24] The nephelauxetic ratio β_1 can be calculated by Equation 5. (see Equation 5 in the Supplementary Files)

where B_0 and C_0 was the Racah parameters of the Mn^{4+} free ion, equal to 1160 and 4303, respectively.

Fig. 8 shows the dependence of $\text{Mn}^{4+} {}^2\text{E}_g$ energy level on the β_1 value in different hosts. The solid straight line represented the linear function of the β_1 parameter. The region between the two dash lines represented the acceptable deviation of the data from the linear function. The nephelauxetic ratio β_1 in this work was finally calculated to be 1.0074 and drawn on the diagram as the blue square. The data point of this work showed a little deviation from the fitted straight line but was included in the area restricted by the two dash lines, as shown in Fig. 8, indicating that the higher ${}^2\text{E}_g$ energy of Mn^{4+} in Mg_2TiO_4 host than other oxides was owing to weaker nephelauxetic effect.

Fig. 9 shows the luminescence decay curves of $\text{Mg}_2\text{Ti}_{(1-x)}\text{O}_4: x\text{Mn}^{4+}$ ($x=0.01\%$, 0.05% , 0.07% , 0.1% , 0.3% and 0.5%) ceramics under the 465 nm excitation, with the 658 nm monitored. The decay curves were

almost unchanging at low doping concentration. However, when the doping concentrations were increasing to 0.3% and 0.5%, an initial faster decay appears. The luminescence lifetime values can be obtained by fitting the curves with a double exponential decay function, as shown in Equation 6^[38] and Equation 7^[44]. (see Equations 6 and 7 in the Supplementary Files)

where A, B₁ and B₂ are constants, I represents the emission intensity at time t, τ₁ and τ₂ represent the two luminescence lifetime values of the ceramics. The fitting results were shown in the Table. 1. The average luminescence lifetimes first decrease slightly, with the Mn⁴⁺ concentration further increasing, more Mn⁴⁺ entered the site beside quenching site such as a vacancy or impurity, and the possibility of the single-step energy transfer between Mn⁴⁺ ions and quenching site was increased, result in the fast decay of luminescence intensity^[45].

Table. 1. The luminescence lifetime values of Mg₂Ti_(1-x)O₄: xMn⁴⁺ (x=0.01%, 0.05%, 0.07%, 0.1%, 0.3% and 0.5%) ceramics.

Concentration (%)	0.01	0.05	0.07	0.10	0.30	0.50
τ _s (ms)	0.528	0.528	0.527	0.525	0.494	0.383

Temperature-dependent emission spectra of 0.01% Mn⁴⁺ doped Mg₂TiO₄ ceramics excited at 465 nm from 304 K to 424 K was showed in Fig. 10. The emission band had no obvious change while the emission intensity decreased gradually with increasing temperature. At 364 K, the emission intensity has dropped to 51% of it at room temperature owing to the thermal quenching effect^[45]. Due to the energy difference between the ⁴T_{2g} and ²E_g energy level, the excited electron must undergo a non-radiation transition to reach ²E_g energy level with the generation of heat. If the heat can not be released efficiently, the temperature of phosphor will keep rising, result in the thermal quenching. Hence, high thermal conductivity was also an important requirement for Mn⁴⁺ doped Mg₂TiO₄ phosphor.

The thermal conductivity of 0.01% Mn⁴⁺ doped Mg₂TiO₄ ceramics at 303 K, 373 K, 423 K, 473 K and 573 K was showed in Table. 2. Benefit from dense crystal structure ,the ceramic has a much higher thermal conductivity (7.545 W/(m·K) at room temperature) compared with traditional packaging method using silicone gel (0.1-0.4 W/(m·K))^[46]. The high thermal conductivity was conducive to keep the ceramics working at a relative low temperature, which can keep the phosphor from thermal quenching.

Table. 2. Thermal conductivity of Mg₂TiO₄: 0.01% Mn⁴⁺ ceramics at 303 K, 373 K, 423 K, 473 K and 573 K.

Temperature (K)	303	373	423	473	573
Thermal conductivity (W/(m·K))	7.545	6.527	5.549	5.277	4.432

A simple light source for plant lighting was fabricated by mounting the 0.01% Mn⁴⁺ doped Mg₂TiO₄ ceramics of four different thickness (0.6 mm, 1.2 mm 1.8 mm 2.4 mm) onto the surface of a 460 nm blue

LED chip. Driven by a 300 mA current at 8.9 V, the CIE coordinates of these four light sources were (0.1604, 0.0562), (0.2316, 0.0872), (0.39990, 0.1627) and (0.4857, 0.1956), respectively. As presented in the CIE chromaticity diagram (Fig. 11), the color of the light source can be changed from blue to purple by adjusting the thickness of the ceramics, which demonstrate the Mn⁴⁺ doped Mg₂TiO₄ ceramics has the potential for plant lighting application.

4 Conclusions

In summary, the Mg₂TiO₄ ceramics with different amounts of Mn⁴⁺ doping concentrations have been synthesized via the high temperature solid-state reaction method. All the samples had deep-red emission under the 465 nm blue light excitation. The QE was 26.47% and over 53% of the emission energy was useful to plant growth. The thermal conductivity of ceramics was 7.545 W/(m·K), about 20 times higher than silicone gel, which can be helpful to avoid the thermal quenching effect by keeping the phosphor material at a relatively cool working temperature. The ceramics plates were mounted to the 460 nm blue LED chips and the color of these simple light sources can be adjusted by changing the thickness of the ceramics. All these results indicated that the Mn⁴⁺ doped Mg₂TiO₄ ceramics are promising for plant lighting.

Declarations

Acknowledgement

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Conflicts of Interest Statement

The authors declare that they have no conflict of interest.

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Figures

Figure 1

(a) The unit cell of Mg_2TiO_4 . (b) $[\text{Mg}/\text{TiO}_6]$ octahedron in the Mg_2TiO_4 . (c) $[\text{MgO}_4]$ tetrahedron in the Mg_2TiO_4 .

Figure 2

The XRD pattern of $\text{Mg}_2\text{Ti}(1-x)\text{O}_4: x\text{Mn}^{4+}$ ($x=0.01\%$, 0.05% , 0.07% , 0.1% , 0.3% and 0.5%) ceramics.

Figure 3

(a)-(d) The SEM images of Mg₂TiO₄: 0.1%Mn⁴⁺ ceramics with different magnification times.

Figure 4

The optical reflectance spectra of $\text{Mg}_2\text{Ti}(1-x)\text{O}_4:x\text{Mn}^{4+}$ ($x=0.01\%$, 0.05% , 0.07% , 0.1% , 0.3% and 0.5%) ceramics.

Figure 5

(a) The PLE spectra of $\text{Mg}_2\text{Ti}(1-x)\text{O}_4: x\text{Mn}^{4+}$ ($x=0.01\%$, 0.05% , 0.07% , 0.1% , 0.3% , 0.5%) ceramics. (b) Peak fitting of the PLE spectrum of the $\text{Mg}_2\text{Ti}(0.999)\text{O}_4: 0.001\text{Mn}^{4+}$ sample.

Figure 6

The PL spectra of $\text{Mg}_2\text{Ti}(1-x)\text{O}_4: x\text{Mn}^{4+}$ ($x=0.01\%$, 0.05% , 0.07% , 0.1% , 0.3% and 0.5%) ceramics. The inset graph shows the full width at half maximum of PL spectra.

Figure 7

The Tanabe-Sugano diagram of Mn⁴⁺.

Figure 8

The dependence of Mn⁴⁺ ²E_g energy level on the β_1 value in different hosts[25-42].

Figure 9

The luminescence decay curves of $\text{Mg}_2\text{Ti}(1-x)\text{O}_4: x\text{Mn}^{4+}$ ($x=0.01\%$, 0.05% , 0.07% , 0.1% , 0.3% and 0.5%) ceramics under the 465 nm excitation..

Figure 10

Temperature-dependent emission spectra of the $\text{Mg}_2\text{Ti}(\text{O.999})\text{O}_4: 0.001\text{Mn}^{4+}$ sample excited at 465 nm from 304 K to 424 K.

Figure 11

CIE chromaticity diagram of the blue LED chip packaged with $\text{Mg}_2\text{TiO}_4: 0.1\% \text{Mn}^{4+}$ ceramics of different thickness, the inset graph gives a photo of the purple light emission.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Equations.pdf](#)