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 demanded wavelength for photosynthesis. The crystal field strength (D_q) and the Racah parameters (B and C) were estimated by Tanabe-Sugano diagram. The thermal conductivity of the $\text{Mg}_2\text{Ti}_{(0.999)}\text{O}_4\text{:0.001Mn}^{4+}$ ceramic was 7.535 W/(m·K) at room temperature, which was one order of magnitude higher than that of the traditional packaging method using the 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 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 the incandescent lamps, the metal-halide lamps, the fluorescent lamps and the high-pressure sodium lamps, suffer from low energy efficiency because the green and yellow spectral part of these light sources are unsuitable for plant growth^[2]. Due to that the blue light (400-500 nm) and the red light (640-680 nm) affect photosynthesis and phototropism, the artificial light source should contain blue and red light^[3-5]. 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^[6]. The combination of red and blue LEDs has been widely used in the greenhouse lighting for plant cultivation and horticulture^[7]. 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^[8]. To this end, another path to obtaining the stable light source for plant growth is using the red phosphor excited by the 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 ($\text{Ca, Sr)AlSiN}_3\text{:Eu}^{2+}$, which has red luminescence of high efficiency under the 460 nm or the 405 nm excitation^[9]. However, the harsh synthesis conditions of nitrides and the environmentally harmful mining process of rare earth materials makes it costly^[10]. Tetravalent manganese (Mn^{4+}) doped materials have been considered as an ideal candidate for rare-earth free red phosphors excited by the 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 $^4A_{2g} \rightarrow ^4T_{1g}$ and $^4A_{2g} \rightarrow ^4T_{2g}$

transitions while the red emission is associated with the ${}^2E_g \rightarrow {}^4A_{2g}$ transition. The emission peak of Mn^{4+} doped materials is closely related to the host matrix, such as fluorides and oxides^[11-12]. Hence, selecting a suitable host material is the key point to obtain the luminescence properties needed by plant lighting.

Mn^{4+} doped fluorides have a strong excitation band corresponding well with blue LED chips, but the sharp red emission is usually peaked at $< 640\text{ nm}$ ^[13], and the use of toxic HF solution is harmful to the environment.. By contrast, Mn^{4+} doped oxides usually present a deep red emission, which is more suitable for plant lighting. Among the oxide matrices, Mg_2TiO_4 has been considered as a particularly noteworthy host matrix for Mn^{4+} due to its excellent stability. Fig. 1. shows the inverse spinel structure of Mg_2TiO_4 . The distribution of the atoms in the Mg_2TiO_4 unit cell can be described as the structural formula $Mg[MgTi]O_4$ ^[14] (where [] denote the octahedral site). All of the Ti^{4+} cations and half of the Mg^{2+} cations randomly occupy octahedral sites and the rest of Mg^{2+} occupy tetrahedral sites.

Compared with the Mg^{2+} cations (0.720 Å , CN=6) in the octahedral sites, the ionic radius of Ti^{4+} (0.605 Å) is closer to Mn^{4+} (0.530 Å)^[15], and there is no charge difference between the Ti^{4+} and the Mn^{4+} , so the Mn^{4+} tends to replace the Ti^{4+} site in Mg_2TiO_4 , resulting in an efficient red emission peaked at about 658 nm ^[16,17]. Therefore, $Mg_2TiO_4:Mn^{4+}$ is a promising red phosphor that can be excited by the blue LED for plant lighting.

However, the emission intensity of $Mg_2TiO_4:Mn^{4+}$ is sensitive to the temperature, which greatly limits its application in illumination^[18]. Compared with powders, phosphor ceramics have a higher thermal conductivity that can efficiently dissipate the heat^[19]. Here, translucent $Mg_2TiO_4:Mn^{4+}$ ceramics were fabricated and the optical as well as the thermal properties were analyzed and discussed.

2 Experimental

2.1 Materials Synthesis

$Mg_2Ti_{(1-x)}O_4:xMn^{4+}$ ($x=0.01\%$, 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 (99.99%, Aladdin, China), TiO_2 (99.9%, Macklin, China) and MnO_2 (99.99%, Aladdin, China). First, stoichiometric amounts of the raw materials were weighted, 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 ($\Phi 15\text{ mm}$) 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 the 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 ($\lambda=1.5418$ Å) with the x-ray tube operated at 40 kV, 15 mA. The morphology of the fracture surface of the phosphor ceramic was observed by scanning electron microscope (SEM) (Tescan, MIRA3, Czech). 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 a fluorescence spectrophotometer (Edinburgh Instruments, FLS-1000, 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). The CIE coordinates of the blue LED chips packaged with the prepared ceramic of different thicknesses were measured in an integrating sphere, which was connected to a CCD detector with an optical fiber.

3 Results And Discussion

Fig. 2 shows the X-ray diffraction (XRD) patterns of the as prepared Mg₂Ti_(1-x)O₄: xMn⁴⁺ (x=0.01%, 0.05%, 0.07%, 0.1%, 0.3% and 0.5%) powders. The position of all samples was well corresponded to the ICSD 82912 card of Mg[MgTi]O₄, indicating that the doping of Mn⁴⁺ did not transform the crystal structure. A weak peak appeared at 22° was corresponded to SiO₂, which may be introduced during the milling process since agate balls were used. Since the radius of Mn⁴⁺ (0.530 Å) is smaller than that of Ti⁴⁺ (0.605 Å), with the concentrations of Mn⁴⁺ increased, the diffraction peaks of the Mg₂Ti_(1-x)O₄: xMn⁴⁺ phosphor showed a slight shift to higher 2 θ angles.

Fig. 3 shows the SEM images of Mg₂TiO₄: 0.1%Mn⁴⁺ ceramics under different magnifications. Relatively dense microstructure can be observed from the images while a certain number of pores existed in the grain. Such intragranular pores were mainly caused by the rapid grain growth velocity during the sintering process, and the doping of MnO₂ can hardly restrain the grain growth. These pores can increase the light scattering in the ceramic and as a result, more blue light can be absorbed instead of leaking from the ceramics and more red light can be extracted from the ceramics [20-22]. Hence, the proper ratio of the transmitted blue light and converted deep-red light can be achieved by a piece of thinner ceramic. Although the existence of pores had adverse effects on the thermal conductivity [23], in this work, the thermal conductivity was maintained a relatively high value, which will be discussed below.

Fig. 4. The optical reflectance spectra of the Mg₂TiO₄ host and the Mg₂Ti_(1-x)O₄: xMn⁴⁺ (x=0.01%, 0.05%, 0.07%, 0.1%, 0.3% 0.5%) ceramics, the inset graph showed the digital photograph of these ceramics.

The reflectance spectra of all the ceramic samples are shown in Fig. 4. It can be detected that the doping of Mn⁴⁺ brought a strong absorption band in the near ultraviolet (nUV) region, which was caused by the combined action of spin-allowed ⁴A_{2g}→⁴T_{1g} and spin-forbidden ⁴A_{2g}→²T_{2g} transitions. Another strong

absorption band located around 487 nm was from the spin-allowed ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition. The absorption band in the deep ultraviolet region (240 nm-310 nm) might be caused by a O^{2-} - Mn^{4+} ligand-to-metal charge transfer (LMCT) [24]. 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 became shorter [25].

Fig. 5 shows the PLE spectra of $Mg_2Ti_{(1-x)}O_4: xMn^{4+}$ ($x=0.01\%$, 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. Due to the smaller ionic radius of Mn^{4+} (0.530 Å) compared with that of Ti^{4+} (0.605 Å), the $[TiO_6]$ octahedron will shrink when the Ti^{4+} was substituted by the Mn^{4+} , strengthening the crystal field splitting energy (Dq) [26]. From the Tanabe-Sugano diagram, the excitation band of $Mg_2TiO_4: Mn^{4+}$ will be blue-shifted with the increasing Dq . On the other hand, the excitation intensity ratio of nUV band to blue band decreases with increasing Mn^{4+} concentration, implying the modification of the crystal field may lead to the enhancement of the excitation intensity of the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition.

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 ${}^4A_{2g} \rightarrow {}^4T_{1g}$ and ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transitions, respectively. Between these two peaks, a weaker peak at 24343 cm^{-1} was corresponded to the spin-forbidden ${}^4A_{2g} \rightarrow {}^2T_{2g}$ transition. Another peak at 32265 cm^{-1} was attributed to the LMCT transition [24].

Fig. 6 shows the PL spectra of the $Mg_2Ti_{(1-x)}O_4: xMn^{4+}$ ($x=0.01\%$, 0.05% , 0.07% , 0.1% , 0.3% and 0.5%) ceramics under the 465 nm excitation. All the samples had a red emission with a sharp peak at 658 nm due to the ${}^2E_g \rightarrow {}^4A_{2g}$ 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 of the 0.10% Mn^{4+} doped Mg_2TiO_4 ceramic under the 465 nm excitation was also measured and shown in Fig. 7. The calculated external (η_e), internal (η_i) quantum efficiencies and absorption efficiency (α) in Fig. 7 were 15.2%, 26.5%, and 57.3% respectively. In addition, over 53% of the emission energy was located in the range between 640 nm to 680 nm. As the maxima of photosynthesis efficiency were around 640-680 nm for quantum yield and around 660-680 nm for action spectrum [27], 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 Dq of Mg_2TiO_4 can be explained by the Tanabe-Sugano diagram [28-31], as seen in Fig. 8, and the crystal field splitting energy

D_q and Racah parameters B and C can be obtained by following Equations.

$$D_q = E(^4A_{2g} \rightarrow ^4T_{2g})/10 \quad (1)$$

$$D_q/B = 15(x-8)/(x^2-10x) \quad (2)$$

$$x = [E(^4A_{2g} \rightarrow ^4T_{1g}) - E(^4A_{2g} \rightarrow ^4T_{2g})]/D_q \quad (3)$$

$$E(^2E_g \rightarrow ^4A_{2g})/B = 3.05C/B + 7.9 - 1.8B/D_q \quad (4)$$

where the transition energy $E(^4A_{2g} \rightarrow ^4T_{2g})$, $E(^4A_{2g} \rightarrow ^4T_{1g})$ and $E(^2E_g \rightarrow ^4A_{2g})$ 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 the Mn^{4+} cations were located in a strong crystal field environment in the Mg_2TiO_4 host.

However, from the Tanabe-Sugano diagram, the energy level of 2E_g is almost independent of crystal field splitting energy. The different positions of emission peak between Mn^{4+} doped Mg_2TiO_4 and other hosts were caused by the nephelauxetic effect. Brik et al. established a non-dimensional linear correlation to explain the relationship between the emission energy level (2E_g) and the nephelauxetic ratio (β_1).^[32] The nephelauxetic ratio β_1 can be calculated by Equation 5.

$$\beta_1 = \sqrt{(B/B_0)^2 + (C/C_0)^2} \quad (5)$$

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

Fig. 9. The dependence of $\text{Mn}^{4+} \ ^2E_g$ energy level on the β_1 value in different hosts^[33-50].

Fig. 9 shows the dependence of the $\text{Mn}^{4+} \ ^2E_g$ 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 was 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 2E_g energy level of the Mn^{4+} in the Mg_2TiO_4 host than other oxides was owing to a weaker nephelauxetic effect.

Fig. 10 shows the luminescence decay curves of the $\text{Mg}_2\text{Ti}_{(1-x)}\text{O}_4: x\text{Mn}^{4+}$ ($x = 0.01\%, 0.05\%, 0.07\%, 0.1\%, 0.3\%$ and 0.5%) ceramics under the 465 nm excitation, with the 658 nm monitored. The decay curves almost remained unchanged at low doping concentrations. However, when the doping concentrations were increased 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 and Equation 7 [51].

$$I = A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) \quad (6)$$

$$\tau_s = (B_1\tau_1^2 + B_2\tau_2^2) / (B_1\tau_1 + B_2\tau_2) \quad (7)$$

where A , B_1 and B_2 are constants, I represents the emission intensity at time t , τ_1 and τ_2 represent the two luminescence lifetime values of the ceramics. The fitting results were shown in Table 1. The average luminescence lifetime values first decreased slightly, with the Mn^{4+} concentration further increasing, the average distant between Mn^{4+} and Mn^{4+} was shorten, and the ion-ion interaction of transition metal ions occurs more frequently, resulting in the fast decay of luminescence intensity [52].

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

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% Mn^{4+} doped Mg_2TiO_4 ceramic under the 465 nm excitation from 304 K to 424 K was shown in Fig. 11. The emission band had no obvious change while the emission intensity decreased gradually with increasing temperature. At 364 K, the emission intensity dropped to 51% of that at room temperature, owing to the thermal quenching effect [53]. In the traditional packaging process, the phosphor powder was wrapped in silicone gel, when excited by the high-power LED chips, a lot of heat would generate in the phosphor, and the temperature of phosphor will easily reach up to 364 K or even above due to the weak heat dissipation capacity of silicone gel. Such a high temperature would cause serious thermal quenching and the emission intensity of $\text{Mg}_2\text{TiO}_4: \text{Mn}^{4+}$ phosphor would plunge. To reduce the accumulation of heat and help heat spreading, phosphor ceramics with high thermal conductivity is required.

The thermal conductivity values of 0.01% Mn⁴⁺ doped Mg₂TiO₄ ceramics at 303 K, 373 K, 423 K, 473 K and 573 K are shown in Table 2. Benefiting from the dense micro-structure, the ceramic has a much higher thermal conductivity (7.545 W/(m·K) at room temperature) compared with the traditional packaging method using silicone gel (0.1-0.4 W/(m·K)) [54]. The high thermal conductivity was conducive to keep the ceramics working at a relatively low temperature, which can keep the phosphor away from thermal quenching.

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

Temperature (K)	303	373	423	473	573
Thermal conductivity (W·m ⁻¹ ·K ⁻¹)	7.545	6.527	5.549	5.277	4.432

A simple light source prototype for plant lighting was fabricated by mounting the 0.01% Mn⁴⁺ doped Mg₂TiO₄ ceramic samples of four different thickness (0.6 mm, 1.2 mm, 1.8 mm, and 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 (see Fig. 12), the color of the light source can be changed from blue to purple by adjusting the thickness of the ceramics. The CIE coordinates, luminous flux and luminous efficacy of the LED chip packed with 1.8 mm thick ceramic driven by increasing current were listed in Table 3. By increasing the driven current, the luminous efficacy did not drop much until the power achieved 9 W, indicating the ceramic with high thermal conductivity had a positive effect on relieving the thermal quenching of luminescence.

Table. 3. The CIE coordinates, luminous flux and luminous efficacy of 1.8 mm thick ceramic driven by increasing current.

Current (mA)	x	y	luminous flux (lm)	luminous efficacy (lm/W)	Voltage (v)	Power (W)
200	0.3497	0.1591	2.2301	1.327	8.397	1.618
300	0.3517	0.1527	2.9719	1.139	8.69	2.609
500	0.3395	0.1462	4.1484	0.912	9.099	4.551
900	0.3181	0.1366	5.6476	0.643	9.764	8.788

4 Conclusions

In summary, the Mg_2TiO_4 ceramics with different amounts of Mn^{4+} 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 external, internal quantum efficiencies of the 0.10% Mn^{4+} doped Mg_2TiO_4 ceramic were 15.2%, 26%, respectively. And over 53% of the emission energy was useful to plant growth. The thermal conductivity of ceramics was $7.545 \text{ W}/(\text{m}\cdot\text{K})$, about 20 times higher than that of the 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 Mn^{4+} doped Mg_2TiO_4 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 patterns 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%) powders.

Figure 3

The SEM images of the fracture surface of the Mg_2TiO_4 host and the $\text{Mg}_2\text{Ti}(1-x)\text{O}_4: x\text{Mn}^{4+}$ ($x=0.01\%$, 0.05% , 0.07% , 0.1% , 0.3% and 0.5%) ceramics.

Figure 4

The optical reflectance spectra of the Mg_2TiO_4 host and the $\text{Mg}_2\text{Ti}_{1-x}\text{O}_4: x\text{Mn}^{4+}$ ($x=0.01\%$, 0.05% , 0.07% , 0.1% , 0.3% 0.5%) ceramics, the inset graph showed the digital photograph of these ceramics.

Figure 5

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

Measurements of quantum efficiencies for the 0.10% Mn⁴⁺ doped Mg₂TiO₄ ceramic.

Figure 8

The Tanabe-Sugano diagram of Mn⁴⁺.

Figure 9

The dependence of Mn^{4+} $2E_g$ energy level on the β_1 value in different hosts[33-50].

Figure 10

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

Figure 11

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 12

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

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