Photoluminescence and persistent luminescence properties of non-doped and Ti^{4+}-doped Mg_2SnO_4 phosphors*

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Mg_2SnO_4 exhibits green photoluminescence and persistent luminescence, which originate from oxygen vacancies. When Ti^{4+} ions were doped, an interesting Mg_2SnO_4:Ti^{4+} phosphor with bluish white photoluminescence under ultraviolet irradiation and with green persistent luminescence was first obtained. Our investigation reveals that two emission centres exist in Mg_2SnO_4:Ti^{4+}. The centres responsible for the green emission are considered to be the F centres (oxygen vacancies) and the blue centres are the TiO_6 complex. Trap clusters in the band gap with different depths, such as $[Sn^{\bullet\bullet}_{Mg}–O''_i]$, $[Sn^{\bullet\bullet}_{Mg}–V^{\bullet}_{O}]$, $[Sn^{\bullet\bullet}_{Mg}–V^{\times}_{O}]$ and Mg''_{Sn}, correspond to the components at 85 °C, 146 °C and 213 °C of the thermoluminescence curve.

Keywords: phosphor, Mg_2SnO_4, persistent luminescence, photoluminescence

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1. Introduction

Persistent luminescence (PSL) is an interesting phenomenon, in which the luminescence of a long persistent phosphor exists for a long time after the removal of the excitation source. In recent years, much attention has been focused on long persistent phosphors because of their exciting properties and their potential application in emergency lighting, displays and the detection of high-energy rays.[1,2] Theoretically, persistent luminescence originates from the thermal stimulated recombination of holes and electrons stored in traps, the long-lived excited states at room temperature.[3] It is expected that persistent luminescence can be observed in phosphors if there are adequate hole and electron traps of suitable depths. Several hundred papers have been published in the search for better long persistent phosphors and to better understand their mechanisms

At present, the most efficient persistent phosphors are still based on alkaline-earth aluminates.[4–6] Generally, the luminescent properties of phosphors are strongly dependent on the crystal structure of the host materials. Finding a suitable host is still a critical step in obtaining rare-earth ion-doped or transition metal ion-doped long persistent phosphors with excellent properties.

Metal oxide-based materials have superior electrical, chemical and mechanical characteristics. They have been demonstrated to be the preferable choice for host materials. Recently, $(SnO_4)^{4-}$ anions have been reported as being optically inert and could be good candidates for host materials.[7–9] Significantly, Mg_2SnO_4 is a chemically stable host with a cubic inverse spinel crystal structure that belongs to the space group Fd3m.[8,1,11] It is well known that a large number of traps will inevitably be generated in an inverse spinel structure.[12] In general, a persistent luminescence process needs the presence of abundant traps to intercept free carriers, ie., electrons, holes or pairs formed by them (the latter can not be excluded although they are rarely considered), and to immobilize them for an appropriately long time.[13,14] Therefore Mg_2SnO_4 is expected to be a good candidate for a long persistent phosphor.

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According to Macke, Mg_2SnO_4 and Mg_2TiO_4 compounds have an inverse spinel structure with $Mg[MgSn]O_4$ and $Mg[MgTi]O_4$ cation distribution, and a certain degree of order between the octahedral ions.[15] The SnO_6 and TiO_6 octahedra are not isolated but are coupled via edge-sharing. Thus, Mg_2SnO_4 and Mg_2TiO_4 are completely miscible. In order to obtain a new phosphor with a white persistent luminescence, the Ti^{4+} is doped into the Mg_2SnO_4 host in this work.

In this paper, we present non-doped and Ti^{4+}-doped Mg_2SnO_4 phosphors prepared by using the solid state method. A novel optical material with bluish photoluminescence and a green persistent luminescence is first obtained. This new kind of phosphor with two colours has potential applications in many fields, such as the symbol for true and false, printing and light, and may be used widely in the future. In addition, our luminescent studies provide useful information about the electronic excitations and the traps in the sample. Based on the research results, we also try to discuss the mechanisms of the photoluminescence and the long persistent luminescence.

2. Experiment

The Mg_2SnO_4 powder samples were synthesized by using the traditional solid state reaction method. The original materials were $(MgCO_3)_4Mg(OH)_25H_2O$ (99.5%), TiO_2 (99.9%) and SnO_2 (99.5%). The mixtures were fired in alumina crucibles at 1350 °C for 24 h in air.

A Rigaku D/Max-2400 X-ray diffractometer (XRD) was employed to check the phase of the phosphors. All samples could be indexed and matched well with JCPDS card No. 24-0723. Absorption spectra were obtained by using a UV-visible spectrophotometer (PE Lambda 950). The excitation and the emission spectra were measured by using an FLS-920T fluorescence spectrophotometer with Xe900 (450 W). The thermoluminescence (TL) curves were measured with a FJ-427A TL meter (Beijing Nuclear Instrument Factory). The decay curves were measured with a PR305 long afterglow instrument.

3. Results and discussion

Figure 1 shows the emission spectrum of the Mg_2SnO_4:0.002Ti^{4+} sample under 254 nm excitation and the persistent emission spectrum after ceasing the UV excitation. It is found that the sample excited by the 254 nm light shows a broad emission band covering the spectrum range of 370–670 nm, which is comprised of blue light (458 nm) and green light (498 nm) emissions. After removing the ultraviolet light, a narrow persistent luminescence band peaking at 498 nm is observed in the spectrum range of 470–550 nm. The features of the persistent emission spectrum are found to be different from that of the photoluminescence. Accordingly, it is implied that there may be two emission centres existing in the Ti^{4+}-doped Mg_2SnO_4 sample. As a matter of course, we name the emission centres responsible for the blue emission (458 nm) the blue centres, while those leading to the green emission (498 nm) are called the green centres. In order to identify these emission centres, the emission spectrum (Fig. 1(c)) excited under the 254 nm excitation and the persistent emission spectrum (Fig. 1(d)) of the non-doped Mg_2SnO_4 materials are also presented for comparison. It is observed that both the emission spectrum under 254 nm excitation and the persistent emission spectrum of Mg_2SnO_4 exhibit a wide emission band peaking at 498 nm, which is the same as the persistent emission spectrum of the Ti^{4+}-doped Mg_2SnO_4 sample. The results suggest that the non-doped Mg_2SnO_4 possesses only one kind of emission centre (a green centre), which generates both the green photoluminescence and the persistent luminescence. In addition, we conclude that the persistent luminescence of the Ti^{4+}-doped Mg_2SnO_4 sample essentially originates from the Mg_2SnO_4 host.

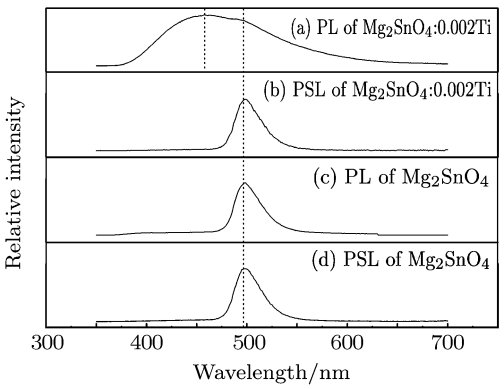


Fig. 1. Emission spectra of Mg_2SnO_4:0.002Ti^{4+} (a) and non-doped Mg_2SnO_4 (c) samples under 254 nm excitation and persistent emission spectra of Mg_2SnO_4:0.002Ti^{4+} (b) and non-doped Mg_2SnO_4 (d) samples after ceasing the ultraviolet excitation.

The photoluminescence mechanism of Mg_2SnO_4 is essentially different from that of the rare earth-

doped phosphors. Not only the photoluminescence but also the persistent luminescence of Mg_2SnO_4 originates from the recombination of F centres (negative oxygen vacancies) with holes. It is well known that oxygen vacancies will inevitably be generated in an inverse spinel structure such as Zn_2SnO_4 and these oxygen vacancies will lead to the characteristic green emission band peaking at 490–495 nm.[16−18] In our case, Mg_2SnO_4 is a chemically stable host with a cubic inverse spinel crystal structure similar to that of Zn_2SnO_4, $A(AB)O_4$ (A=Mg, B=Sn). A large number of defects will inevitably be generated for the considerable degree of cation disorder.[19−21] Some of these defects serve as electron or hole trap centres. The oxygen vacancies may play an important role as F-centre-like electron traps and luminescence centres.[21]

As shown in the following reaction,

$$e^- + F^+ + h\nu_1\ (4.26\ \text{eV}) \rightarrow F + h^+, \quad (1)$$

$$F + h^+ \rightarrow (F^+)^* \rightarrow F^+ + h\nu_2\ (2.49\ \text{eV}), \quad (2)$$

the photoluminescence process in the non-doped Mg_2SnO_4 host can be described as follows. (1) Under UV irradiation (4.26 eV), the electrons (e^-) excited from the valence band are trapped by the F^+ centres, creating F centres and holes (h^+). (2) Then the recombination of the F centres (negative oxygen vacancies) with the holes creates the excited states of the emitter, $(F^+)^*$. Lastly, the excited emitters decay to the ground state and give out the green light emission (2.49 eV).

With regard to the wide band emission of the Ti^{4+}-doped Mg_2SnO_4 sample under 254 nm excitation in Fig. 1(a), the emission centres (blue centres) are still unknown and the photoluminescence is not clearly understood. However, we believe that the TiO_6 complexes are possible emission centres (blue centres) and the isolation of the complexes in the crystal structure is important for irradiative transition. Here we provide three points of evidence.

(i) Figure 2 shows the emission spectra of the Mg_2SnO_4 doped with different Ti^{4+} concentrations (Ti^{4+}mol%= 0, 0.002, 0.005, 0.01, 0.03 and 0.05). As the Ti^{4+} doping content increases from 0.002 to 0.01, the intensity of the emission peak increases remarkably, while the peak location remains unchanged at 458 nm. A higher Ti^{4+} ion doping amount decreases the emission intensity, which is due to the concentration quenching effect.[22] The fact that the intensity of the emission is related to the doped-Ti^{4+} content implies that the doped-Ti^{4+} ion is the origin of the broad emission peaking at 458 nm. (ii) Figure 3 shows the excitation spectrum of the Mg_2SnO_4:0.002Ti^{4+} sample along with the absorption spectrum of the non-doped Mg_2SnO_4 host material. The excitation spectrum was measured by fixing the emission wavelength at 458 nm. In the absorption spectra, an intense absorption peaking at 232 nm appears and is attributed to the fundamental absorption of the Mg_2SnO_4 host material. Meanwhile, the excitation spectrum of the Ti^{4+}-doped Mg_2SnO_4 sample shows common broad bands just below the absorption edge of the host crystal. This observation suggests that the electrons in the valence band or the oxygen ions are not excited directly to the conduction band but are excited to the Ti-related trap levels, and then the Ti-related centres emit bluish white light along with a Stokes shift. The Stokes shift of the Mg_2SnO_4:0.002Ti^{4+} sample is estimated to be approximately 2.01 eV. The large Stokes shift and the broad emission band covering 300 nm are typical luminescence features of the d^0 complex ions. (iii) As reported by Yamashita, blue luminescence was not observed in the Ti^{4+}-doped ASnO$_3$ (A=Ca, Sr, Ba).[23] In general, the Ti–O bonds in the TiO_6 complexes should include some covalent character and need to compete with the neighboring Sn–O bonds in these stannates to draw the O ions to the Ti^{4+} sides for the formation of the complexes. All six O ions around a Ti^{4+} ion are next to the Sn ions in the Ti^{4+}-doped ASnO$_3$, while only four O ions in the Ti-doped A_2SnO_4. This local structural difference seems to make it difficult to form TiO_6 complexes in the three-dimensional ASnO$_3$ perovskite. Therefore, it is suggested that the bluish white luminescence is not observed in the Ti-doped ASnO$_3$ but in the Ti-doped A_2SnO_4 (A=Ca, Sr, Ba),

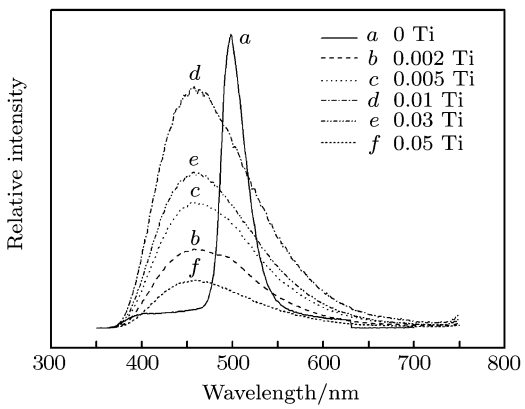


Fig. 2. Emission spectra of Mg_2SnO_4 doped with different Ti^{4+} concentrations (Ti^{4+} mol%= 0, 0.002, 0.005, 0.01, 0.03 and 0.05).

in which the SnO_6 octahedra are connected in the low dimensional form and the TiO_6 complexes are isolated at the low Ti^{4+} concentration.

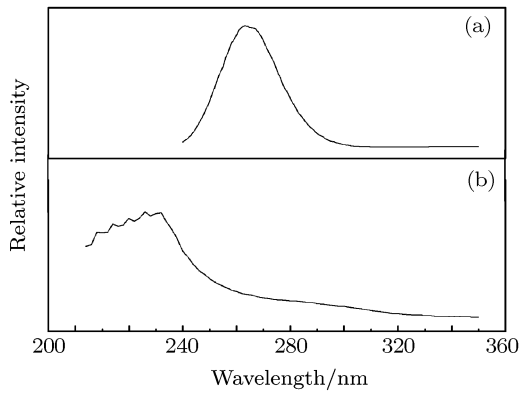


Fig. 3. (a) Excitation spectrum of a Mg_2SnO_4:0.002Ti^{4+} sample, and (b) the absorption spectrum of the non-doped Mg_2SnO_4 host material.

The green persistent luminescence of the non-doped Mg_2SnO_4 sample can be seen by the naked eye in dark for 6 h and the green afterglow of a typical Mg_2SnO_4:0.002Ti^{4+} sample can last for about 2.5 h. It is clear that the time of the persistent luminescence decreases as the doping of Ti^{4+} increases. Figure 4 shows the decay curves of the persistent luminescence intensities of the non-doped Mg_2SnO_4 and the Mg_2SnO_4:0.002Ti^{4+} phosphors recorded after ceasing the UV excitation (254 nm). Both decay curves cannot be fitted, even using a function with three exponential terms.

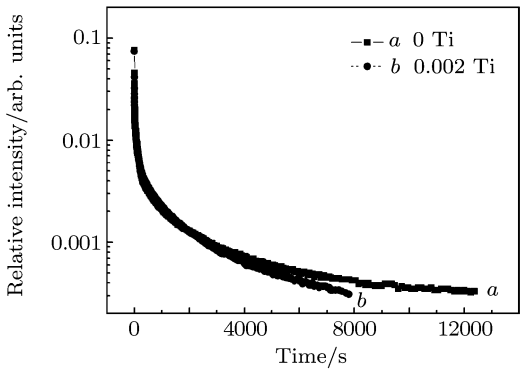


Fig. 4. Decay curves of persistent luminescence intensities of non-doped Mg_2SnO_4 and Mg_2SnO_4:0.002Ti^{4+} phosphors recorded after ceasing the ultraviolet excitation (254 nm).

The thermoluminescence glow curve was measured to probe the trap levels in the samples. It is found that the TL glow curves of the non-doped and the Ti^{4+} doped samples are the same as each other. This result indicates that both samples have the same traps. The TL glow curve of the Mg_2SnO_4:0.002Ti^{4+} sample is shown in Fig. 5. It is obvious that the Mg_2SnO_4:0.002Ti^{4+} material possesses a significantly more complex TL glow curve. In order to clarify the structure of the TL curve, the curve was fitted using multi-Gaussians peaks. The result exhibits three components locating at about 85 °C, 146 °C and 213 °C, respectively. The most intensive peak has a maximum at 146 °C. The TL glow curve also reveals that there may be three trap levels with rather different depths in the Ti^{4+}-doped Mg_2SnO_4 that intercept the electrons and/or holes freed upon UV excitation. Some of the traps are relatively shallow (85 °C and 146 °C), while the others are somewhat deeper (213 °C). These shallower traps allow the trapped carriers to be freed slowly by thermal energy at room temperature, leading to long persistent luminescence.

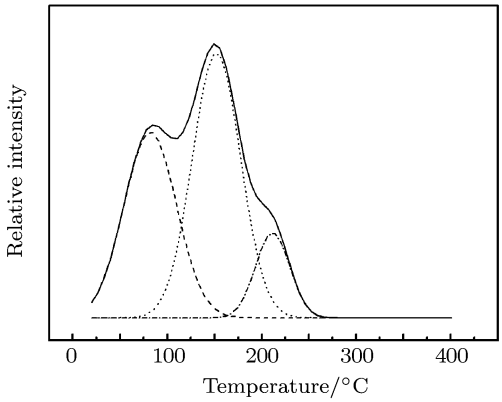


Fig. 5. Deconvolution of the thermoluminescence glow curve of the Mg_2SnO_4:0.002Ti^{4+} sample.

As mentioned in the previous part, photoluminescence can result from the recombination of a photo-excited hole with an electron occupied oxygen vacancy (F^+ centre). However, the final realization of persistent and photostimulated luminescence still needs some deep traps for energy storage (electrons trapping), which are created by Dy^{3+} in $SrAl_2O_4$:Eu^{2+} and Sm^{3+} in ZnS:Eu^{3+}. In the case of the Ti^{4+}-doped Mg_2SnO_4 phosphor with the cubic inverse spinel structure, the unit cell has 96 cation sites with 24 being occupied by the cations, 8 of the 64 tetrahedral sites occupied by Mg^{2+} and 16 of the 32 octahedral sites occupied by other Mg^{2+} and Sn^{4+}. In addition to the large number of unoccupied sites, the degree of cation disorder is also considerable (as large as 30%), so a large number of defects can be created.[19−21] Some of these defects serve as electron or hole traps. For example, a Mg^{2+} at Sn^{4+} site can trap a hole and is named Mg''_{Sn}, a Sn^{4+} at a Mg^{2+} site will form an electron trap and is labeled as $Sn^{\bullet\bullet}_{Mg}$. Furthermore, the charge compensation due to one Sn^{4+}

ion replacing one Mg^{2+} ($Sn^{\bullet\bullet}_{Mg}$) by one extra interstitial O^{2-} ion (O''_i) may lead to the formation of a [$Sn^{\bullet\bullet}_{Mg}$–O''_i] trap cluster owing to the electrostatic interaction between these point traps.[16−18] In addition, the vacant oxygen sites may be occupied by an electron or electrons forming negatively charged e′ and/or e″centres, i.e., the vacant oxygen sites with one or two trapped electrons ($V^{\bullet}_O$ or $V^{\times}_O$), respectively. The electrons can be bounded to $Sn^{\bullet\bullet}_{Mg}$ with electrostatic forces and several slightly different [$Sn^{\bullet\bullet}_{Mg}$–$V^{\bullet}_O$] (or [$Sn^{\bullet\bullet}_{Mg}$–$V^{\times}_O$]) trap clusters can be anticipated. As shown in Fig. 5, these different trap clusters result in trap levels with different depths in the band-gap of the Ti^{4+}-doped Mg_2SnO_4. These trap levels correspond to the TL glow bands (85 °C, 146 °C and 213 °C), and play a crucial role in the energy storage for persistent luminescence.

In the light of the considerations presented above, the persistent luminescence mechanism could be proposed as shown in Fig. 6. (i) Excited by the ultraviolet irradiation (4.26 eV), electrons (e^-) are excited from the valence band leaving holes (h^+) there. (ii) Then the electrons (e^-) are trapped by the trap clusters, such as [$Sn^{\bullet\bullet}_{Mg}$–O''_i], [$Sn^{\bullet\bullet}_{Mg}$–$V^{\bullet}_O$] and [$Sn^{\bullet\bullet}_{Mg}$–$V^{\times}_O$], and the holes (h^+) are trapped by Mg''_{Sn}. (iii) Because the depth of most trap clusters is somewhat shallow in the band-gap, the trapped electrons and the trapped holes can be thermally released at room temperature at a slow rate and then are transferred to the F^+ centres. As a result of the recombination of electrons with holes, the characteristic green long persistent luminescence is seen.

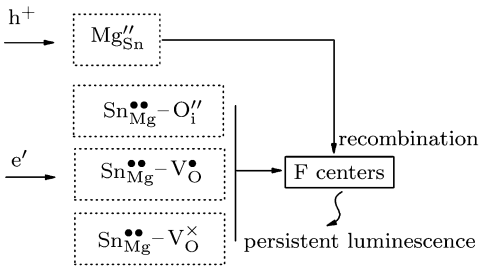


Fig. 6. Scheme diagram of the persistent luminescence procedures of the Ti^{4+}-doped Mg_2SnO_4 under ultraviolet excitation.

4. Conclusion

Green photoluminescence and persistent luminescence were observed in Mg_2SnO_4. Meanwhile, Mg_2SnO_4:Ti^{4+} exhibited a bluish white light under 254 nm excitation and green persistent luminescence. The bluish photoluminescence originates from the combination of blue (458 nm) and green (498 nm) emissions. The centres responsible for the blue emission are considered to be the F centre (oxygen vacancies) and the green centres are the TiO_6 complex. The green persistent luminescence can last for about 2.5 h after ceasing the irradiation. Some different trap clusters, such as [$Sn^{\bullet\bullet}_{Mg}$–O''_i], [$Sn^{\bullet\bullet}_{Mg}$–$V^{\bullet}_O$], [$Sn^{\bullet\bullet}_{Mg}$–$V^{\times}_O$] and Mg''_{Sn}, exist in the Ti^{4+}-doped Mg_2SnO_4. The thermoluminescence glow curve contains three components (85 °C, 146 °C and 213 °C), and its maximum is at 146 °C. According to the results, the photoluminescence and the persistent luminescence mechanisms of the Ti^{4+}-doped Mg_2SnO_4 materials are first proposed.

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