Sb/Mn co-doped oxyfluoride silicate glasses for potential applications in photosynthesis

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ABSTRACT

A series of Sb/Mn co-doped oxyfluoride silicate glasses were prepared via the melt-quenching method to explore red luminescent materials for potential applications in photosynthesis of green plants, and these glasses are investigated by means of luminescence decay curves, absorption, emission, and excitation spectra. We find that the as-prepared glasses are transparent in the visible region and can emit strong red light under ultraviolet, purple, and green light excitations. Furthermore, energy transfer from Sb^{3+} to Mn^{2+} ions occurs in Sb/Mn co-doped glasses. The results demonstrate that the as-prepared Sb/Mn co-doped oxyfluoride silicate glasses may serve as a potential candidate for developing glass greenhouse, which can enhance the utilization of solar energy for the photosynthesis of the green plants.

Keywords: **Luminescence; Glasses; Photosynthesis; Energy transfer**

1. Introduction

Photosynthesis is a process to convert light energy, normally from the sun, into chemical energy that can be later released to fuel the plants' activities. In the solar spectrum, the energy

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percentage of the ultraviolet (UV), visible, and infrared lights is about 7%, 50%, and 43%, respectively **[1]**. Generally, the green plants (chlorophylls) absorb more red light than other wavelengths for the photosynthesis. In addition, the green light can hardly be absorbed by the green plants for photosynthesis and the UV light is harmful to the growth of the plants. The lights absorbed by green plants for photosynthesis are only a very small portion in the whole solar spectrum **[2,3]**. Thus, to convert the UV and green lights into red light is a very promising and valuable work for the growth of the plants. At present, most greenhouses are made of the plastic materials, which have some drawbacks such as short lifetime, poor transparency, and instability. In recent years, the glass greenhouses are attracting more and more research attention due to the superior light transmittance, low production cost, and long service life compared to plastic greenhouses **[2,3]**. In particular, luminescent glasses can be used for the realization of solar spectrum modification, e.g., to convert the ultraviolet and green lights into the red light for photosynthesis. In other words, luminescent glasses are strongly expected to be an interesting and excellent alternative approach to fabricate greenhouses compared to traditional plastic materials.

The oxyfluoride silicate glasses possess excellent chemical stability, good mechanical strength, high transparency for visible light, as well as low phonon energy environment for luminescence ions **[4,5]**. Sb and Mn are regarded as promising low-cost and environmental-friendly elements compared to rare earth. Additionally, Sb_2O_3 can also be used as a fining agent in glass melting. Based on above considerations, herein we fabricated a series of Sb-, and Mn-doped oxyfluoride silicate glasses for greenhouse application and the optical properties of the glasses are investigated. Although some preliminary works on the

luminescent glasses or glass-ceramics for greenhouses have been reported **[2,3]**, the Sb/Mn co-doped oxyfluoride silicate glasses have not been considered for photosynthesis applications yet.

2. Experimental

All the investigated glasses have the glass matrix (GM) composition of $45SiO_2$-$15Al_2O_3$-10ZnO-$20CaF_2$-10CaO (in mol.%). Samples GMS2 (doped with 2 mol.% Sb), GMM4 (doped with 4 mol.% Mn), GMS2M2 (co-doped with 2 mol.% Sb and 2 mol.% Mn), GMS2M4 (co-doped with 2 mol.% Sb and 4 mol.% Mn), and GMS2M6 (co-doped with 2 mol.% Sb and 6 mol.% Mn) were prepared by melt-quenching method. The chemicals SiO_2, Al_2O_3, ZnO, CaF_2, $CaCO_3$, Sb_2O_3, and $MnCO_3$ were used as raw materials and they are analytical grade reagents. The starting materials calculated based on the compositions of the as-designed samples were taken in an agate mortar and grounded well to obtain homogenous mixtures. The homogenous batches were put into corundum crucibles and melted in an electrical furnace at 1460°C for 1 hour in air atmosphere. After melting, the glass melts were quickly casted into a preheated stainless steel mould for quenching. To relieve the internal stress of these glasses, which is induced during the quenching process, the obtained glasses were annealed at 450 °C for 2 hours in air atmosphere, followed by natural cooling.

The energy dispersive spectroscopy (EDS) was measured using an EDS detector attached on the Scanning Electron Microscope (SEM, Hitachi S-4800, Japan) to analyze the compositions of the glasses. The absorption spectra were recorded using a Lambda 1050 UV/VIS/NIR spectrometer (PerkinElmer, USA). The excitation and emission spectra were measured using an FLS920 fluorescence spectrometer (Edinburgh Instruments Ltd., UK) using a 450 W Xe lamp (Xe900) as light source. The fluorescence decay curves were

measured by using a standard storage digital oscilloscope and by exciting the samples at 266 nm with a frequency-quadrupled Nd:YAG laser providing 6 ns laser pulses. All the measurements were performed at room temperature with the same experimental parameters.

3. Results and Discussion

Since some raw materials, e.g., CaF_2 and ZnO, can be volatile during the melting process, the final compositions of as-prepared glasses may deviate the nominal ones as designed. All the mentioned glasses in this paper have the identical glass matrix compositions. As an example, we carried out the composition analysis of sample GMS2 using EDS technique, as shown in Fig. 1. It can be seen that the content of F, Zn, and Sb decreased compared to the nominal compositions, indicating that these three elements were partially lost during preparing these glasses by melt quenching method.

Fig. 2 shows the absorption spectra of samples GMS2, GMS2M2, GMS2M4, and GMS2M6 in the wavelength region of 200–800 nm. The samples present distinct absorption from 200 to 300 nm, which can be attributed to the partially forbidden electronic transition $^1S_0 \rightarrow {}^3P_1$ of Sb^{3+} ions **[6]**. The absorption peaks at 415 nm shown in the inset are due to the electronic transition of $^6A_{1g} \rightarrow [^4A_{1g}; {}^4E_g]$ of Mn^{2+} ions **[7]**. We can see that the glasses are highly transparent in the visible range and demonstrate intense absorption in the ultraviolet region, which indicates that the as-prepared glasses can efficiently absorb the ultraviolet light, and transmit the visible light. These optical features of the glasses are very helpful and effective for the protection, the growth and photosynthesis enhancement of the greenhouse plants.

In order to investigate the possibility of the Sb/Mn co-doped glass to convert the

UV-purple-green lights into red light, we measured the excitation and emission spectra of sample GMS2M4, as shown in Fig. 3. The excitation spectrum monitored at 652 nm mainly contains four excitation bands. A broad excitation band at ~ 255 nm is due to the electronic transition of $^1S_0 \rightarrow {}^3P_1$ of Sb^{3+}. The additional three excitation bands peaking at ~ 353, 415, and 507 nm correspond to the electronic transitions from ground state $^6A_1$g to excited states $^4T_{2d}$, [$^4A_{1g}$; ^4E_g], and $^4T_{2g}$ of Mn^{2+}, respectively **[8]**. To further examine the potential application of the glass in greenhouse, we measured the emission spectra under the excitation of 255, 353, 415, and 507 nm, respectively, which correspond to the respective excitation peaks of sample GMS2M4. It can be seen that the shapes of the emission spectra under aforementioned excitation wavelengths are nearly the same except for the emission intensities. The emissions are attributed to the electronic transitions of $^4T_{1g} \rightarrow {}^6A_{1g}$ of Mn^{2+} ions **[9]**. The energy ratios of the UV and green lights are ~ 7% and ~ 10% in the solar spectrum, which are waste for the photosynthesis of the green plants. Thus, it is very interesting to transfer the UV and green lights into the red light, which is helpful for photosynthesis. We can see in Fig. 3 that the as-prepared glasses can effectively convert the UV and blue-green lights into red emission, implying that these materials can improve the utilization of the solar energy for photosynthesis of green plants.

Fig. 4 shows the emission spectra of the Mn^{2+} single doped and Sb^{3+}/Mn^{2+} co-doped glasses excited at 415 nm. The broad emission bands come from the electronic transitions of $^4T_{1g} \rightarrow {}^6A_{1g}$ of Mn^{2+} ions **[10]**. With the increasing of the Mn^{2+} ion concentration, the emission intensity increases firstly and then decreases, which could be due to the luminescence concentration quenching of Mn^{2+} caused by the cross-relaxation between Mn^{2+} ions. The red-shift of the emission peak of Mn^{2+} is also observed with increasing Mn^{2+} content. This

phenomenon could be induced by the following aspect: increasing Mn^{2+} content results in the reduction of Mn^{2+} − Mn^{2+} distance, which leads to the enhancement of the interaction of Mn^{2+} − Mn^{2+}. That is to say, the ligand field strength surrounding Mn^{2+} is enhanced, making the excited state of Mn^{2+} energetically closer to its ground state and finally gives a longer wavelength emission **[11]**. Comparing the emission spectra of samples GMM4 and GMS2M4, it is found that emission blue-shift occurs with the introduction of Sb^{3+} ions. The emission of transition metal Mn^{2+} ion corresponds to d-d transition, and its emission is sensitive to the surrounding environment **[12]**. The introduction of Sb^{3+} may lead to the variation of the local environment around Mn^{2+} ions, which might be the reason for emission blue-shift of sample GMS2M4.

To further investigate the conversion of UV to red light via the as-prepared glasses, the emission spectra for samples GMS2, GMS2M2, GMS2M4, and GMS2M6 excited at 266 nm are illustrated in Fig. 5. It can be seen that these glasses present a broad emission band ranging from 350 to 505 nm, which can be assigned to the electronic transition of $^3P_1 \rightarrow {}^1S_0$ of Sb^{3+}. With the increase of the Mn^{2+} concentration, the intensity of the 350-505 nm emission from Sb^{3+} decrease, whereas the intensity of the 550-800 nm emission from Mn^{2+} increases firstly and then decreases (luminescence concentration quenching of Mn^{2+}). This phenomenon indicates the energy transfer (ET) from Sb^{3+} to Mn^{2+} occurs. The ET from Sb^{3+} to Mn^{2+} can enhance the red emission intensity and cause the variety of emission color of the glasses.

Excitation spectra (λem = 661 nm) of samples GMM4 and GMS2M4 and emission spectra of samples GMS2 (λex = 266 nm) and GMM4 (λex = 415 nm) are presented in Fig. 6. The emission spectrum of sample GMS2 (λex = 266 nm) gives a broader emission band related to the $^3P_1 \rightarrow {}^1S_0$ transition of Sb^{3+}. It should be noted that there is a significant overlap between the emission spectrum of Sb^{3+} doped glass GMS2 and the excitation spectrum of Mn^{2+} doped glass GMM4 in the range of 350 to 640 nm. Therefore, it is expected that the ET process can

efficiently occur from Sb^{3+} to Mn^{2+}. In order to further clarify this, the excitation spectrum of sample GMS2M4 monitored at 661 nm is also included in Fig. 6. A broad excitation band at ~ 261 nm exists for sample GMS2M4 compared to GMM4, which further confirms the ET process of Sb^{3+} to Mn^{2+}. It is known that the transition metal Mn^{2+} can provide a broad emission band corresponding to d-d transition. Since the absorption and emission of Mn^{2+} are weak due to the spin- and parity-forbidden d-d transition of Mn^{2+} **[13]**, herein, we employ Sb^{3+} as efficient sensitizing ions to enhance the luminescence of Mn^{2+} by means of ET.

To further evaluate the energy transfer from Sb^{3+} to Mn^{2+} in the as-prepared glasses, the decay curves of emission of Sb^{3+} were measured with excitation at 266 nm and monitoring at 408 nm for samples GMS2, GMS2M2, GMS2M4 and GMS2M6, as shown in Fig. 7. The decay processes of these four samples are characterized by average lifetime $\bar{\tau}$, which can be derived from: $\bar{\tau} = \int_0^\infty tI(t)dt / \int_0^\infty I(t)dt$, where *I(t)* stands for the intensity at time *t* **[14,15]**. The calculated lifetimes $\bar{\tau}$ are 4.53, 3.55, 2.71, and 2.45 μs for samples GMS2, GMS2M2, GMS2M4 and GMS2M6, respectively. ET efficiency (η_{ET}) can be calculated by the following equation, $\eta_{ET} = 1- \bar{\tau}/\tau_0$, where $\bar{\tau}$ and τ_0 are the lifetimes of Sb^{3+} in the presence and absence of Mn^{2+}, respectively **[16]**.The calculated ET efficiencies are 21.6, 40.2, and 45.9% for samples GMS2M2, GMS2M4, and GMS2M6, respectively. The decay times and ET efficiency indicate the ET process from Sb^{3+} to neighboring Mn^{2+} in the Sb/Mn co-doped glasses, which is very efficient.

4. Conclusions

In summary, Sb-and Mn- doped oxyfluoride silicate glasses were synthesized by melt quenching method. We find that the as-prepared glasses demonstrate high transparency in the visible light range and intense absorption in the ultraviolet region. We use the Sb/Mn

co-doped glasses as light converter to successfully transfer the ultraviolet and green lights into the red light, which could be efficiently absorbed by green plants for their photosynthesis. Additionally, energy transfer from Sb^{3+} to Mn^{2+} occurs in the glasses. Our investigation shows that Sb/Mn co-doped glasses may be used for the fabrication of greenhouses in the future for enhancing the photosynthesis of the green plants.

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Figure Captions

Fig. 1. EDS spectrum of sample GMS2. The inset shows the comparison of the nominal and EDS measured element content.

Fig. 2. Absorption spectra of the glasses. The inset shows the enlarged absorption spectra in the range of 360-500 nm.

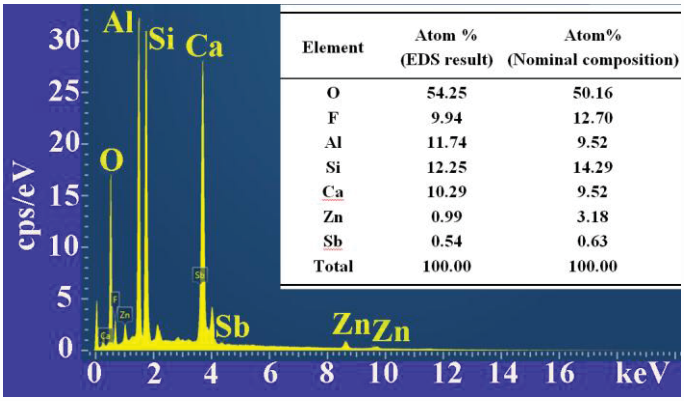
Fig. 3. Excitation and emission spectra of sample GMS2M4. The electronic transitions, excitation (λex) and the monitored (λem) wavelengths are explicitly indicated in the figure.

Fig. 4. Emission spectra of glasses excited at 415 nm.

Fig. 5. Emission spectra of glasses under 266 nm excitation.

Fig. 6. Excitation spectra of samples GMM4 and GMS2M4 monitored at 661 nm; Emission spectra of samples GMS2 and GMM4 excited at 266 and 415 nm, respectively.

Fig. 7. Luminescence decay curves of samples GMS2, GMS2M2, GMS2M4 and GMS2M6, which were obtained using the excitation wavelength of 266 nm and monitoring the emission at 408 nm.



Element	Atom % (EDS result)	Atom% (Nominal composition)
O	54.25	50.16
F	9.94	12.70
Al	11.74	9.52
Si	12.25	14.29
Ca	10.29	9.52
Zn	0.99	3.18
Sb	0.54	0.63
Total	100.00	100.00

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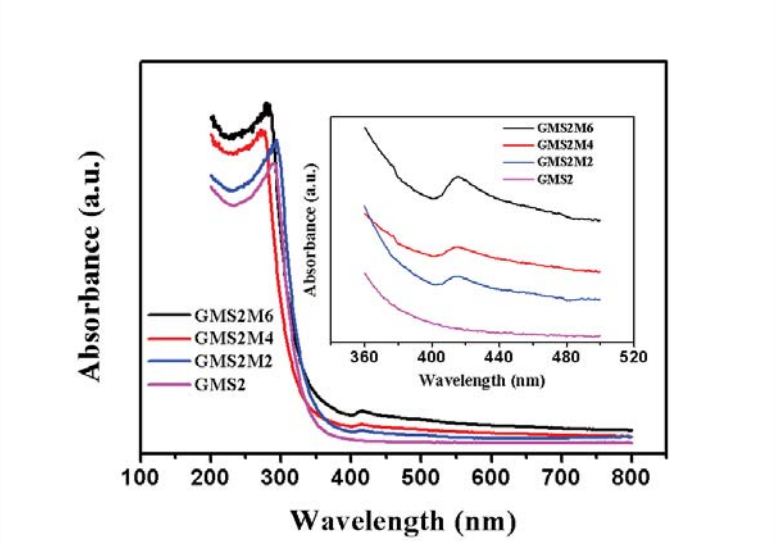

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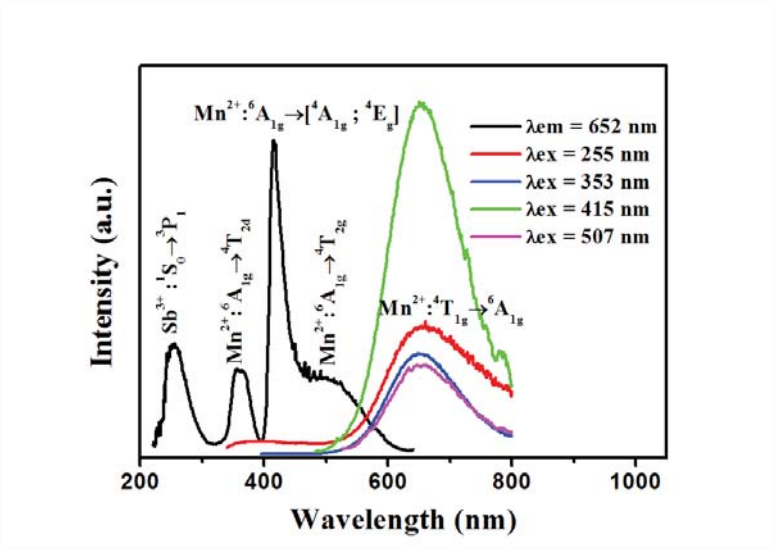


Fig. 3. Excitation and emission spectra of sample GMS2M4. The electronic transitions, excitation (λex) and the monitored (λem) wavelengths are explicitly indicated in the figure.

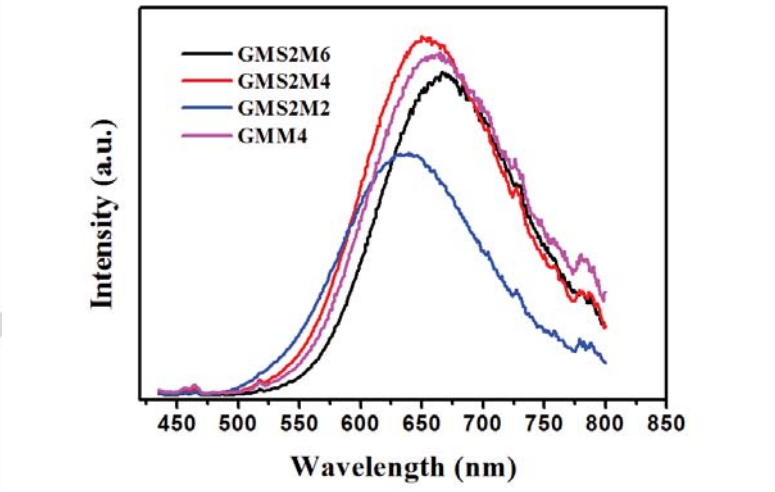


Fig. 4. Emission spectra of glasses excited at 415 nm.

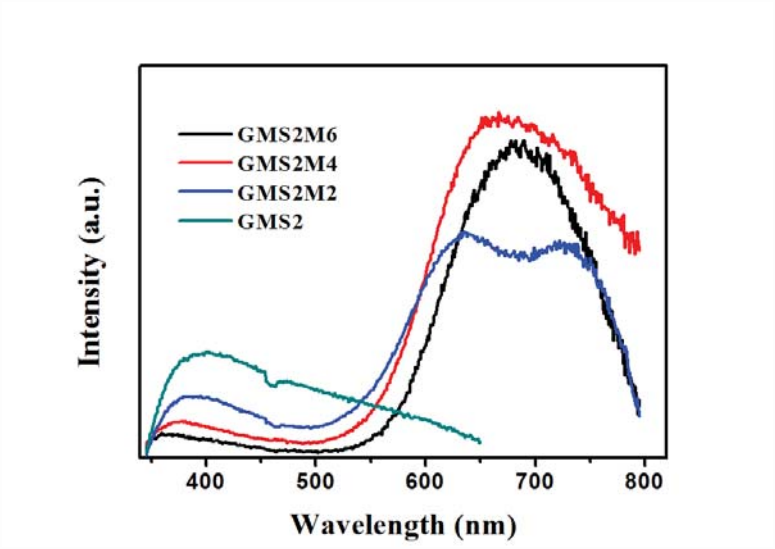
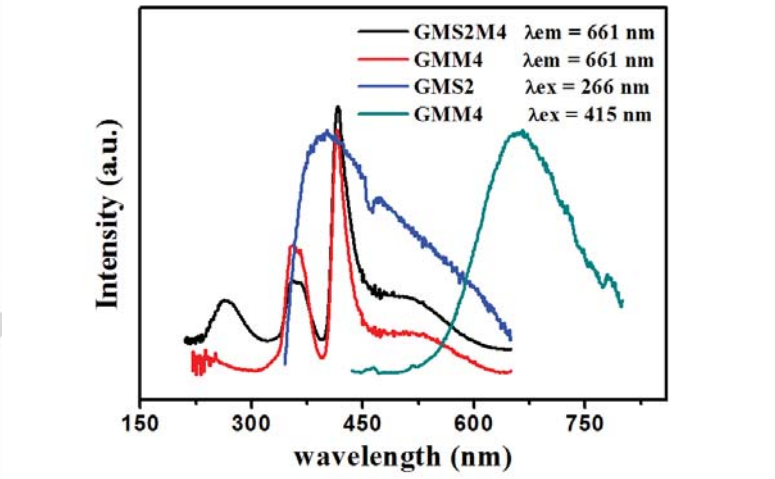


Fig. 5. Emission spectra of glasses under 266 nm excitation.



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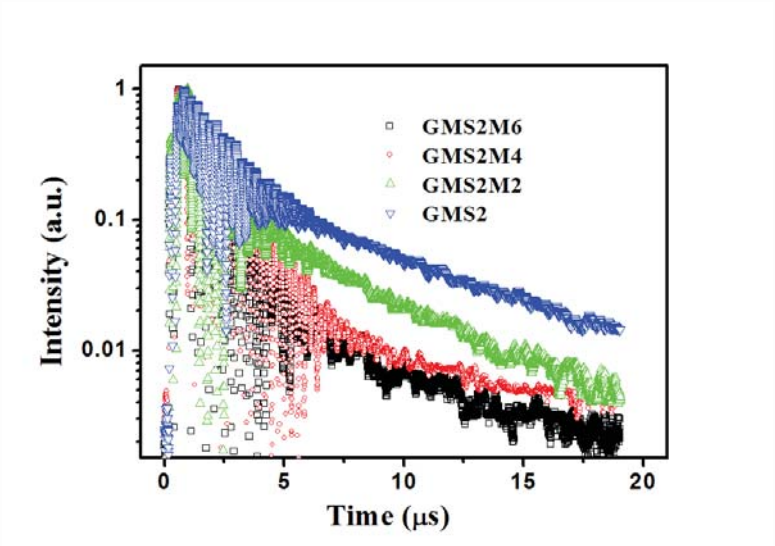

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