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Broadband emission from $Ce^{3+}/Mn^{2+}/Yb^{3+}$ tri-doped oxyfluoride glasses for glass greenhouse

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ABSTRACT

In this work, a kind of oxyfluoride glasses tri-doped with $Ce^{3+}/Mn^{2+}/Yb^{3+}$ ions was prepared by a simple and fast high temperature melting method. Under excitation with 300 nm light, two meaningful broad band emissions (ranged from 340 to 500 nm and 510–700 nm) were obtained, which matched well with the absorption of the chlorophylls. Under near-infrared (980 nm) excitation, an abnormal up-conversion luminescence was demonstrated in the oxyfluoride glasses by the energy transfer from Yb^{3+} to Mn^{2+}. In addition, the up-conversion emission has a red shift along with the increase of the doping concentration of Mn^{2+}, which would contribute to match the action spectrum of photosynthesis better. Our materials will be favored to extend the utilization of solar energy in glass greenhouse for plant cultivation.

1. Introduction

Currently, a fast-growing interest has been witnessed on the approaches to improve the photosynthesis of the green plants [1–5]. As one of significant parameters for plant growth, light is not only the energy source of greenery photosynthesis, but also the power source of sprout, blossom, and fruit as well as other morphogenesis for plants. Therefore, the light quality for plants plays a significant role on the harvest. The main light bands absorbed by chlorophyll of greenery are reddish orange (600–700 nm) and bluish violet (400–480 nm) lights, which is only a small percentage of the whole solar spectrum. Longer wavelengths can hardly been absorbed by chlorophylls and other photosynthetic antenna pigments, while the ultraviolet (UV) in the sunlight are even harmful to the plant. Therefore, it is meaningful to convert the useless sunlight to reddish-orange and bluish violet light for improving the utilization level of solar light in the process of photosynthesis.

In order to promote the growth and achieve higher yields of the crops, many kinds of methods have been studied and used in the past years. Notably, the use of plastic greenhouses in low-temperature seasons has attracted considerable attention. However, there are still many shortcomings of plastic greenhouse, such as short service lifetime, toxicity to the environment, and chemical instability [6–9]. To solve these problems, the glass greenhouses which show superior performance to the traditional plastic greenhouses in many respects have attracted widely attention [6–9]. The glass materials have better stability against ultraviolet irradiation, better thermal retardation, and excellent chemical durability which directly determines a long service life. Moreover, lanthanide-doped transparent materials have wonderful luminous traits in the UV, visible (Vis) and near-infrared (NIR) wavelength regions [5–18]. Hence, the predominant properties of rare earth doped transparent glass materials allow them to realize promising applications in greenhouses.

Recently, solar spectral conversion phosphor has been embedded within a specific reactor device [5,6]. It is experimentally demonstrated that the tune of useless green photons to red can greatly improve the energy harvesting of chlorophylls. However, the complex assembly process and high cost may hinder the development of the device for its large-scale production and application. The solar spectral conversion glass greenhouse can be a

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suitable substitution, for it can be easily assembled and constructed like traditional glass greenhouses. Beneficially, the glass material exhibits excellent resistance to water and corrosion. It is known that the down-conversion (DC) glass material shows an excellent optical performance which is favorable to convert more violet and green photons to red ones via rare-earth or transition-metal ions co-doped in transparent phosphate glasses [7–9]. Likewise, the light use efficiency of photosynthetic systems would also be greatly improved if photosynthesis could use NIR radiation. Therefore, an ability to simultaneously use UV and NIR radiation would a more potential approach to improve the efficiency of photosynthesis.

In the previous works, we have studied the $Ce^{3+}/Er^{3+}/Yb^{3+}$ tri-doped oxyfluoride glass ceramics for glass greenhouses [11]. The glasses are highly transparent in the visible light range and own intense absorption in the UV and NIR wavelength region. Especially, the glasses can transfer ultraviolet and part of NIR into reddish orange light. However, the emission region of the red light is not broad enough. In addition, the energy transfer between the Ce^{3+} to Er^{3+} ions is not very effective. This will result in a poor utilization rate of the materials to sunlight. Hence, the material which not only shows a wider region of excitation but also exhibits a broad emission of bluish violet and reddish orange light is still very promising.

The emission of Mn^{2+} is based on the $^4T_{1g}(4G) \rightarrow {}^6A_{1g}(6S)$ transition. By introducing an efficient sensitizer, the emission of Mn^{2+} can be considerably improved. At present, many Mn^{2+}/Ce^{3+} co-doped red luminescence materials have been studied, such as ZnS: Ce^{3+}, Mn^{2+} [19], $Ca_3Sc_2Si_3O_{12}$: Ce^{3+}, Mn^{2+} [20], $MgY_4Si_3O_{13}$: Ce^{3+}, Mn^{2+} [21], and $Ca_4Si_2O_7F_2$: Ce^{3+}, Mn^{2+} [22] phosphors or Ce^{3+}/Mn^{2+} co-doped glass-ceramics containing β-Zn_2SiO_4 nanocrystals [23]. Furthermore, in order to obtain the broadband up-conversion (UC) luminescence, Mn^{2+}/Yb^{3+} co-doped phosphors has also been reported and led to some new and unexpected results in the search for novel UC materials and process [24–27].

In this paper, we report the $Ce^{3+}/Mn^{2+}/Yb^{3+}$ tri-doped oxyfluoride glasses. The $50SiO_2$-$20Al_2O_3$-$20CaF_2$-10NaF glasses were selected as the host materials because of its high transparency, low-melting temperature, simple manufacturing procedure, and good solubility for $Ce^{3+}/Mn^{2+}/Yb^{3+}$ ions. Among the glasses systems, the oxyfluoride glasses are expected to combine the advantages of high mechanical strength of oxide glasses and low phonon energy of fluoride glasses. This will be favored to the energy transfer between neighbor ions. With the broad band excitation of UV–Vis and NIR 980 nm lights, a strong and broadband of reddish orange light has been obtained. Furthermore, the energy transfer mechanisms among $Ce^{3+}/Mn^{2+}/Yb^{3+}$ of up and down conversion have also been revealed by detail analysis of the excitation, up and down conversion emission spectra, and the luminescent decay curves of the samples.

2. Experiment section

The oxyfluoride glass samples with the compositions in mol% of $50SiO_2$-$20Al_2O_3$-$20CaF_2$-10NaF (G): xCe^{3+}, yMn^{2+}, zYb^{3+} were prepared by high temperature melting method. The doped CeF_3 and YbF_3 content were fixed to x = 0.1 mol% and z = 5 mol%, while the $MnCO_3$ content was y = 0.1 mol%, 0.5 mol%, 1 mol%, and 1.5 mol % respectively. According to the doping concentration of Ce^{3+}, Mn^{2+} and Yb^{3+} ions, the samples would be denoted further in the text as G:0.1Ce^{3+}, G:1Mn^{2+}, G:0.1Ce1Mn, G:0.1Ce0.1Mn5Yb, G:0.1Ce0.5Mn5Yb, G: 0.1Ce1Mn5Yb and G:0.1Ce1.5Mn5Yb, respectively. For each batch, about 10 g raw materials including SiO_2 (AR), Al_2O_3 (AR), CaF_2 (AR), NaF (AR), CeF_3 (99.9%), $MnCO_3$ (99.9%), YbF_3 (99.9%) were mixed thoroughly and then heated in a covered corundum crucible at 1350 °C for 2 h to achieve a homogeneous melt, then the melt was cast into a copper mold to process quenching. The resulted glasses were kept at 300 °C for 120 min in an annealing furnace to relinquish inner stress. The obtained samples were polished to optical quality.

The photoluminescence (PL) and the photoluminescence excitation (PLE) spectra were measured by a Tau-3 fluorescence spectrophotometer (Jobin Yvon-Inc, France). Luminescence decay curves and the UC luminescence spectrums were measured with a FLS980E spectrometer (Edinburgh Instruments Ltd., UK).

3. Results and discussion

The excitation and emission spectra of the Ce^{3+} or Mn^{2+} singly doped glass are shown in Fig. 1(a) and (b). As shown in Fig. 1(a), the PL spectrum of G:0.1Ce^{3+} displays a broad band extending from 340 to 500 nm, which can be attributed to the typical transition from 5d level to the ground state of Ce^{3+}. The excitation spectrum monitored at 362 nm shows a broad absorption band within the 250–350 nm UV range, which is due to 4f-5d transition of the Ce^{3+}. G:1Mn^{2+} presents a broad band emission centered at 585 nm under 410 nm excitation in Fig. 1(b), which corresponds to the $^4T_1(G) \rightarrow {}^6A_1(S)$ transition of Mn^{2+}. The excitation spectrum of G:1Mn^{2+} sample consists of two bands centered at 355 and 410 nm, which are assigned to the transitions from $^6A_1(S)$ to $^4T_2(D)$ and $^4T_1(G)$ levels of Mn^{2+}, respectively. Obviously, there is a significant spectral overlap between the Ce^{3+} PL and Mn^{2+} PLE spectra as shown in Fig. 1(c), indicating the possibility of energy transfer from Ce^{3+} to Mn^{2+} in our oxyfluoride glasses. Fortunately, the assumption is confirmed by the PLE spectra of G:0.1Ce1Mn monitoring the board emission peaks at 585 nm. As shown in Fig. 1(d), three broad excitation bands of 350–500 nm and 250–350 nm can be observed, which respectively corresponding to the transitions from $^6A_1(S)$ to $^4T_2(D)$ and $^4T_1(G)$ levels of Mn^{2+} and the 4f-5d transition of the Ce^{3+}. And it shows the existence of energy transfer from Ce^{3+} to Mn^{2+}.

The down-conversion emission spectra (ranged from 360 to 680 nm) of the $Ce^{3+}/Mn^{2+}/Yb^{3+}$ tri-doped oxyfluoride glasses has been measured under excitation of 300 nm with a xenon lamp, and illustrated in Fig. 2. It is clearly noticed that all samples exhibit two broad emission band centered at 360 and 620 nm, corresponding to the emission of Ce^{3+} and Mn^{2+}, respectively. As the content of Mn^{2+} increases from 0.1% to 1.5 mol%, the shape and peak positions of the DC emission spectra show no obvious variation. However, the total DC emission intensity and the luminescence intensity distribution are changed largely. By comparing the intensity of Ce^{3+} ranged from 360 to 500 nm, a gradually decrease trend is showed along with the increase of the concentration of Mn^{2+}. In addition, the luminescence intensity of Mn^{2+} also shows a monotone increase along with the doping concentration of Mn^{2+} increasing from 0.1 to 1 mol%. Further increasing the Mn^{2+} ions doping concentration would result in emission intensity decrease due to the concentration quenching effect.

Fig. 3 show that the decay curves of Ce^{3+} emission at 362 nm along with various Mn^{2+} concentrations doping, which corresponds to Ce^{3+}:5d-4f transition, upon excitation of Ce^{3+} at 300 nm. With the increase doping concentration of Mn^{2+}, the deviation from the exponential rule becomes more obvious. By calculation, the average lifetime of Ce^{3+} ions are found to be about 30.8, 28.2, 24.8, and 22.6 ns corresponding to the G:0.1Ce0.1Mn5Yb, G:0.1Ce0.5Mn5Yb, G:0.1Ce1Mn5Yb and G:0.1Ce1.5Mn5Yb, respectively. Apparently, the fluorescence lifetime of Ce^{3+} ions in the glass sample become shorter as the concentration of Mn^{2+} increasing, which is the clear evidence of energy transfer from Ce^{3+} to Mn^{2+} in this tri-doped glass systems.

According to this DC energy transfer mechanism, the DC emission intensity of Mn^{2+} should mainly depend on the conversion