Luminescent Properties of a Novel Mn$^{2+}$ doped 3CaO-CaF$_2$-2SiO$_2$ Glasses

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Abstract—The transition metal Mn$^{2+}$ ions doped materials have been widely reported for the luminescent properties for its broad emission band from green to red due to the spin-forbidden $^4T_1\to^6A_1$ transitions. To investigate the luminescent properties of Mn$^{2+}$ ions in cuspidine glass, the 3CaO-CaF$_2$-2SiO$_2$ glasses doped with different Mn$^{2+}$ concentration were prepared with traditional melt-quenching method. The luminescence emission spectra, excitation spectra and luminescence decay curves were recorded and analyzed. The tunable broadband emission from orange to red was obtained. The luminescence intensity and lifetime of Mn$^{2+}$ $^4T_1$ level showed different quenching points with the increasing of Mn$^{2+}$ concentration. All these results indicate that Mn$^{2+}$ doped 3CaO-CaF$_2$-2SiO$_2$ glass could be applied as light conversion material for solid-state lighting applications.

1. Introduction
The transition metal Mn$^{2+}$ ions doped materials have been widely reported for the luminescent$^{[1-4]}$, electrical$^{[5]}$, magnetic$^{[6]}$, and mechanical$^{[7]}$ properties. Due to the spin-forbidden $^4T_1\to^6A_1$ transitions of Mn$^{2+}$ ions, the Mn$^{2+}$ doped luminescent materials can give broad emission band from green to red$^{[8-11]}$. According to the Tanabe-Sugano diagram, the emission transition of $^4T_{1g}(G)\to^6A_{1g}(G)$ in Mn$^{2+}$ ions depends on the crystal field strength of the substituted sites$^{[12]}$. For example, Mn$^{2+}$ with octahedral coordination usually gives red emission, whereas the Mn$^{2+}$ with tetrahedral coordination gives green emission. Generally, because of the spin-forbidden d-d transition of Mn$^{2+}$ ion, the emission intensity of Mn$^{2+}$ doped phosphors is usually weak.

Cuspidine is a contact metamorphic mineral with formula: 3CaO-CaF$_2$-2SiO$_2$ (Ca$_4$Si$_2$O$_7$F$_2$). Natural cuspidine is basically granular aggregates, which is colorless, light pink or light brown. It has glass luster from translucent to transparent. The crystal structure of cuspidine has been determined as monoclinic with P2$_1$/c space group. The rare-earth ion activated Ca$_4$Si$_2$O$_7$F$_2$ phosphors have been reported by many researchers. The electronic structure and photoluminescence properties of Eu$^{2+}$ doped Ca$_4$Si$_2$O$_7$F$_2$ phosphor were reported by Jia et al$^{[13]}$. The photoluminescence properties of Ca$_4$Si$_2$O$_7$F$_2$: Ce$^{3+}$ phosphors with tunable emission were reported by Xie et al$^{[14]}$. However, there is no report on the luminescent properties of transition metal activated 3CaO-CaF$_2$-2SiO$_2$ glasses.

In this paper, transparent Mn$^{2+}$ doped 3CaO-CaF$_2$-2SiO$_2$ glasses for red emission with different doping-concentration were successfully fabricated. The luminescent properties of prepared glasses...
were studied in detail and the results proved Mn\textsuperscript{2+} ion have continuously tunable broadband emission from orange to red in 3CaO-CaF\textsubscript{2}-2SiO\textsubscript{2} glasses.

2. Experimental

The 3CaO-CaF\textsubscript{2}-2SiO\textsubscript{2} glass with basic composition in mol\% of 50CaO-16.7CaF\textsubscript{2}-33.3SiO\textsubscript{2} and xMnO (x=0.1, 0.3, 0.5, 0.75, 1.0, 1.5) as activator were prepared using conventional melt-quenching method. The powder of CaCO\textsubscript{3}, CaF\textsubscript{2}, SiO\textsubscript{2} and MnSO\textsubscript{4}ꞏH\textsubscript{2}O with 99.5% purity were used as raw materials. Carbon was also additionally incorporated with 5 wt\% to form the reducing atmosphere during melting. All raw materials were mixed in a agate mortar by grinding, then the mixture was transferred into a corundum crucible, melted at 1450 °C for 30min by a lifting electrical furnace under ambient atmosphere. The glass melts were quenched on a stainless steel plate, annealed in a muffle furnace at 650 °C for 8 h, and then cooled down to room temperature. The obtained glasses were cut and polished into the size of 20 mm×15 mm×2 mm for measurements.

X-ray diffraction (XRD) patterns of the glass samples were recorded by a Rigaku MiniFlex/600 X-ray diffraction apparatus (Tokyo, Japan) with CuKa radiation (λ = 1.5418 Å). Data were collected over the 2θ range of 10°–85° with a step width of 0.02° and scanning speed of 8°/min. Excitation spectra and emission spectra were recorded by an Edinburgh FS5 spectrofluorometer (Livingston, UK), the excitation source is a continuous wave Xe lamp (150 W). Fluorescence decay curves were recorded by an Edinburgh FLS920 fluorescence spectrometer (Livingston, UK), the excitation source is a microsecond flashlamp (μF900).

3. Results and Discussions

XRD patterns of undoped and 0.5 mol\% Mn\textsuperscript{2+} doped glass samples were measured to check the non-crystallinity of the glass samples, the results are shown in Fig.1. The XRD diffraction patterns of the glass samples show only the broad amorphous halo which characteristic to the presence of short range order in glass matrix. The similar phenomenons were also observed in other Mn\textsuperscript{2+} doped glass samples with different concentration. The results indicate the prepared samples are amorphous glass structure and there is no crystals in glass samples.

![Fig.1 XRD patterns of undoped and 0.5 mol\% Mn\textsuperscript{2+} doped glass samples](image)

The concentration dependence of the emission and excitation spectra on the Mn\textsuperscript{2+} doping was investigated. The emission spectra of glass samples with different doping concentration are shown in Fig.2. All the spectra of 3CaO-CaF\textsubscript{2}-2SiO\textsubscript{2} glasses show a broad emission due to the \(^4\text{T}_1 \rightarrow ^6\text{A}_1\) transitions of Mn\textsuperscript{2+} ions. The luminescence intensity is enhanced with the doping concentration of Mn\textsuperscript{2+} increasing until the maximum intensity reaches at 1 mol\% (peaked at 650 nm), and then it decreases at the higher concentration.

Meanwhile, with the Mn\textsuperscript{2+} concentration increasing, the emission band of Mn\textsuperscript{2+} ions have significant red-shift, gradually shifting from ~622 nm to ~653 nm. Fig.3 showed the relation between the wavelength of emission center and the Mn\textsuperscript{2+} doping concentration, the tendency is approximately
linear. The explanation of this tendency is that the interaction between Mn$^{2+}$ ions and the ligand field strength are enhanced surrounding Mn$^{2+}$ ions because of the decreasing distance of Mn$^{2+}$ ions with MnO content increasing, which making the Mn$^{2+}$ ion in excited state closer to its ground d state, and it gives a longer wavelength emission$^{[15,16]}$.

Fig.2 Emission spectra of 3CaO-CaF$_2$-2SiO$_2$ glass with different Mn$^{2+}$ doping concentrations

Fig.3 Variation of emission band center wavelength as Mn$^{2+}$ concentration in 3CaO-CaF$_2$-2SiO$_2$ glass

Fig.4 shows the excitation spectra of glass samples with different doping concentration. It can be seen that there are two broadband excitations which can be assigned to the electronic transitions from the ground state $^6A_1$ to excited state $^4T_1$ and $^4A_1$ of Mn$^{2+}$ ion. The intensity of $^6A_1 \rightarrow ^4A_1$ transition is about two times than that of $^6A_1 \rightarrow ^4T_1$ transition. It should be noted that excitation bands show a similar red-shift tendency with the emission bands because of the concentration quenching.

Fig.4 Excitation spectra of 3CaO-CaF$_2$-2SiO$_2$ glass with different Mn$^{2+}$ doping concentrations

Furthermore, the photoluminescence decay curves of the $^4T_1$ level of Mn$^{2+}$ ions in the 3CaO-CaF$_2$-2SiO$_2$ glass were also recorded and demonstrated in Fig.5. The corresponding luminescent decay curves can be fitted into single-exponential decay model with following equation

$$I_t = I_0 \exp \left( -\frac{t}{\tau} \right)$$

(1)

where $I_t$ is the intensity at time $t$, $I_0$ is the intensity at $t = 0$, and $\tau$ is the decay lifetime. The results obtained are listed in Table.1. Different with the luminescence intensity, the lifetimes are increased with Mn$^{2+}$ concentration reaches at $x = 0.75$, and then it decreases at the concentration higher than 0.75 mol%. The variation of the decay time value and the emission intensity as dopant ion concentration are shown in Fig.6.
Fig. 7 displays the CIE chromaticity coordinates of the 3CaO-CaF$_2$-2SiO$_2$ glass doped with different Mn$^{2+}$ concentration calculated from the emission spectra in Fig. 2. The calculated coordinate results are shown in Table 2. These results indicate that the emission color can be tuned from orange to red in visible region by systematically adjusting the Mn$^{2+}$ doping concentrations.

Table 1. Lifetimes of $^4T_1$ level of Mn$^{2+}$ ions in 3CaO-CaF$_2$-2SiO$_2$ glass with different doping concentrations

| Doping concentration (mol%) | Lifetime (μs) |
|----------------------------|---------------|
| 0.1                        | 0.2075        |
| 0.3                        | 0.3514        |
| 0.5                        | 0.6199        |
| 0.75                       | 0.7382        |
| 1.0                        | 0.4612        |
| 1.5                        | 0.3216        |

Table 2. CIE coordinates of 3CaO-CaF$_2$-2SiO$_2$ glass with different Mn$^{2+}$ doping concentrations

| Doping concentration (mol%) | CIE x       | CIE y       |
|----------------------------|-------------|-------------|
| 0.1                        | 0.50828     | 0.47944     |
| 0.3                        | 0.53532     | 0.45705     |
| 0.5                        | 0.53909     | 0.45374     |
| 0.75                       | 0.5551      | 0.43919     |
| 1.0                        | 0.56085     | 0.43355     |
| 1.5                        | 0.58546     | 0.41076     |

4. Conclusion

In summary, the 3CaO-CaF$_2$-2SiO$_2$ glasses with different Mn$^{2+}$ doping concentration were prepared by traditional melt-quenching method. To study the luminescent properties of Mn$^{2+}$ doped 3CaO-CaF$_2$-2SiO$_2$ glasses, the luminescence emission spectra, excitation spectra and luminescence decay curves were recorded and analyzed. The obtained experimental results indicate that Mn$^{2+}$ doped 3CaO-CaF$_2$-2SiO$_2$ glass shows continuously tunable broadband emission from orange to red due to the $^4T_1 \rightarrow ^6A_1$ transitions of Mn$^{2+}$ ions. Thus, the luminescence intensity and lifetime of Mn$^{2+}$: $^4T_1$ level have different Mn$^{2+}$ quenching point with the increasing of Mn$^{2+}$ concentration. All these properties indicate that Mn$^{2+}$ doped 3CaO-CaF$_2$-2SiO$_2$ glass can be applied as light conversion material for solid-state lighting applications.

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