Borate and silicate glasses doped with Ce^{3+} and Mn^{2+} ions for UV-VIS spectral shifting

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1 Introduction

This study is aimed to investigate the possibilities of spectral shifting of light radiation by using the combination of Ce^{3+} and Mn^{2+} ions in glasses. We focused on the possibility of shifting the radiation from UV (280-370 nm) and green (470-550 nm) region of spectra to blue (370-450 nm) or red (650-730 nm) regions. The combination of Ce^{3+} and Mn^{2+} ions has been shown to manifest this kind of shifting in special types of crystalline matrices [1-3], however it is yet to be investigated in glass. The type of used matrix and method of preparation can influence the oxidation state of doped ions and their photoluminescence properties (shape and position of emission spectra, photoluminescence lifetime). The use of glass also has several benefits over crystals in practical applications such as low cost and easy preparation.

To study the influence of glass matrix on photoluminescence, we prepared several types of glasses doped by mixture of Ce^{3+} and Mn^{2+} ions. First, two glasses with completely different matrices – silicate and borate – were prepared to study their suitability as host matrix for both ions. In addition, a set of borosilicate glasses with varying contents of SiO_2 and B_2O_3 were prepared and reducing agents were added to the batch to preserve cerium and manganese in +III and +II oxidation state, respectively. The glasses were prepared by a standard melt-quenching technique.

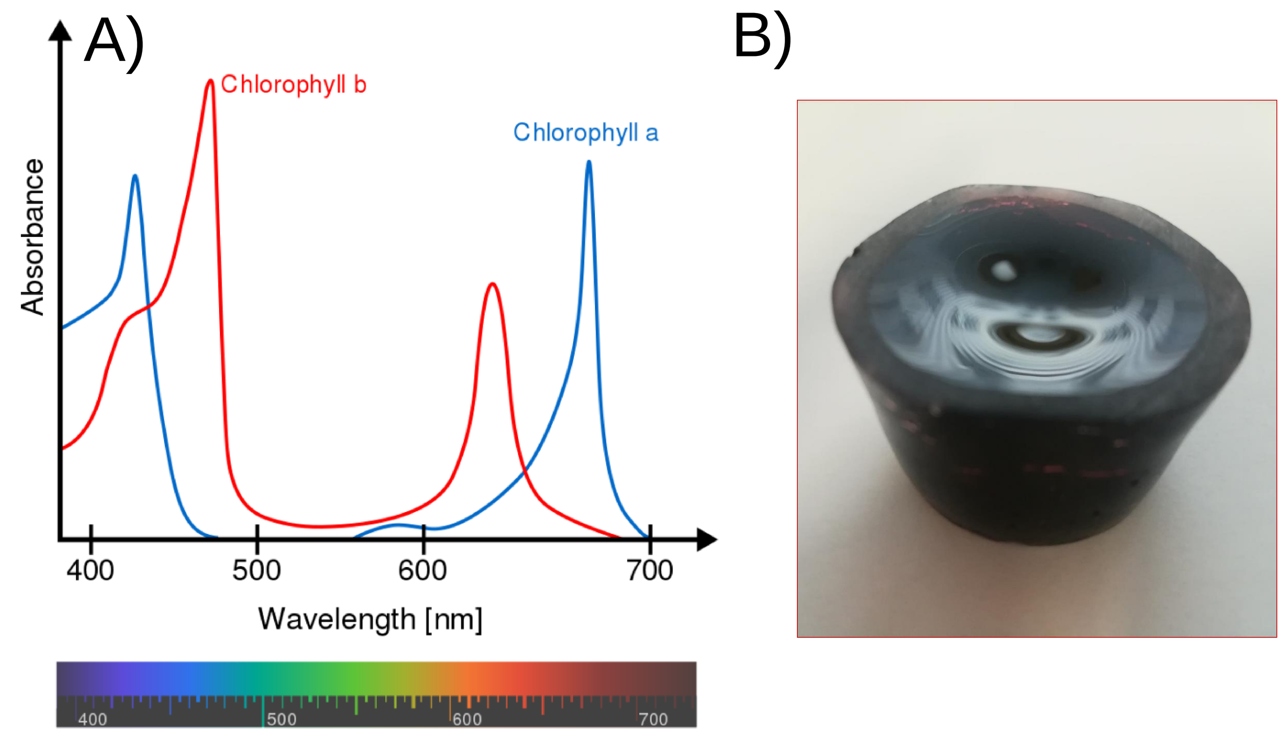


Figure 2. A) Absorption spectra of Chlorophyll *a* and *b*, B) as-prepared $4SiO_2{:}1B_2O_3$ glass with Na_2SO_3

2 Glass composition

Table 1. Composition of prepared glasses in wt. %

	SiO_2	B_2O_3	Na_2O	BaO	Al_2O_3	MnO	CeO_2	SnO	Na_2SO_3
SiO_2	60.82	-	13.09	17.27	4.40	2	2.42	-	-
B_2O_3	-	64.31	11.92	15.74	4	1.82	2.21	-	-
$1SiO_2.1B_2O_3$	32.21	29.40	12.83	16.92	4.31	1.96	2.37	-	-
$4SiO_2.1B_2O_3$	45.82	15.00	13.09	17.27	4.40	2	2.42	-	-
$4SiO_2.1B_2O_3$ + Na_2SO_3	45.82	15.00	13.09	17.27	4.40	2	2.42		SO_3^{2-}:MnO 5:2
$4SiO_2.1B_2O_3$ + SnO:MnO_2 1:2	44.97	14.72	12.85	16.95	4.32	1.96	2.37	1.86	-
$4SiO_2.1B_2O_3$ + SnO:MnO_2 5:2	41.85	13.70	11.95	15.77	4.02	1.83	2.21	8.67	-

3 Experimental procedure

The chemicals used for the glass preparation were SiO_2, H_3BO_3, $Al(OH)_3$, Na_2CO_3, $BaCO_3$, MnO, CeO_2, SnO and Na_2SO_3. The components were weighed, mixed in a platinum crucible and melted in the range from 1100 °C to 1500 °C for 10 hours.

The absorption spectra of the glasses were measured on a AVANTES Avaspec Starline spectrometer equipped with deuterium-halogen lamps in the range from 350 to 1100 nm. The photoluminescence spectra and emission-excitation matrices were measured on AGILENT fluorescence spectrometer with xenon lamp and photomultiplier detector. The emission wavelengths were in the 300-800 nm range with 1 nm step, the excitation wavelengths were in the 240-600 nm range with 20 nm range.

4 Absorption

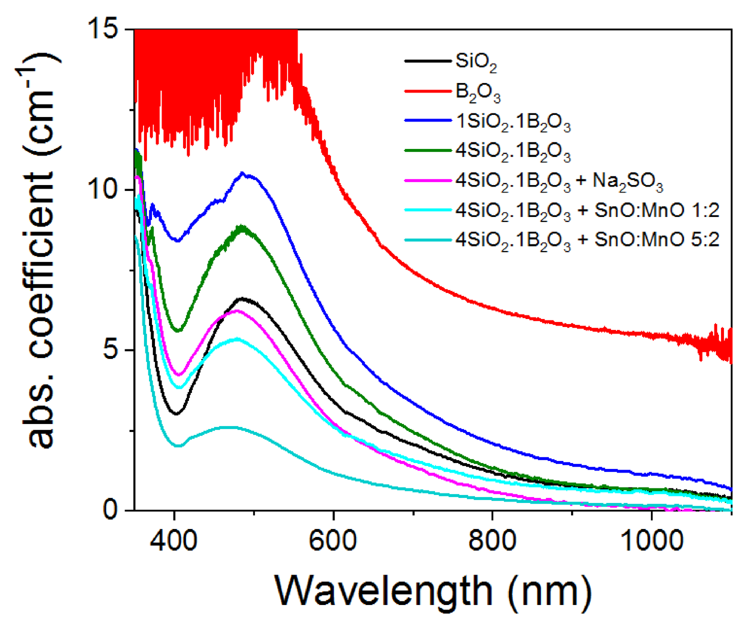
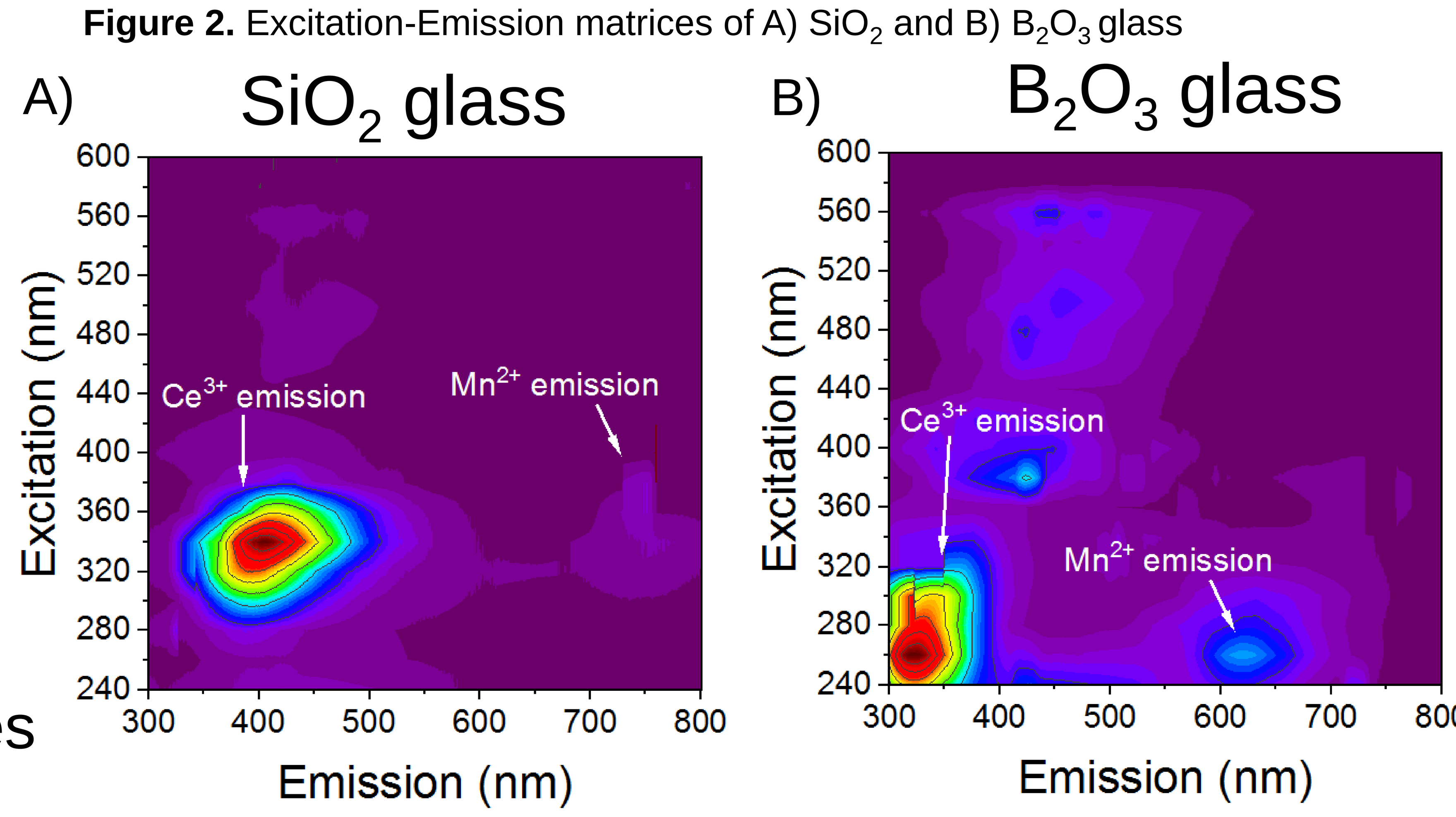


Figure 1. Absorption spectra of the prepared glasses

Glasses with high content of B_2O_3 („B_2O_3" and „$1SiO_2.1B_2O_3$" glass) exhibited high Absorption due to the hygroscopic properties causing corrosion. Absorption in the 400 – 600 nm range indicates presence of Mn(VII). The Absorption corresponding to Mn(VII) decreased with the addition of reducing agents. SnO appeared to be a more effective reducing agent compared to Na_2SO_3.

5 Excitation-Emission matrix

Figure 2. Excitation-Emission matrices of A) SiO_2 and B) B_2O_3 glass



6 Emission spectra

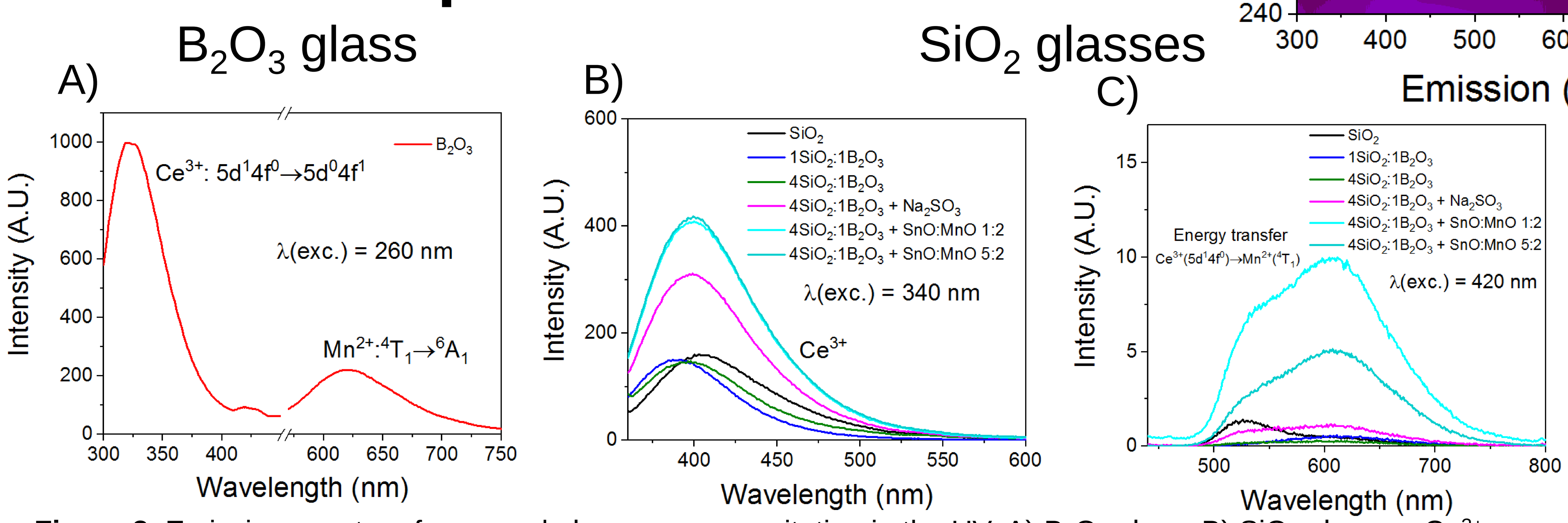


Figure 3. Emission spectra of prepared glasses upon excitation in the UV: A) B_2O_3 glass, B) SiO_2 glasses, Ce^{3+} related emission, C) SiO_2 glasses, Mn^{2+} related emission

Glasses exhibited emission in the 300-500 nm range due to Ce^{3+} ions and 500-800 nm range due to Mn^{2+} ions upon UV excitation. B_2O_3 caused blue-shift of the emission, as illustrated by **Figure 2**. Reduction agents increased the emission intensity thanks to preserving Ce and Mn in the +III and +II oxidation states, respectively. The optimal excitation range for UV-VIS spectral shifting in bioreactors would be 300-600 nm with emission in the range of 600-700 nm, which has been previously achieved in Ce^{3+}/Mn^{2+}-doped CaO phosphor [4]. The $4SiO_2{:}1B_2O_3$ glass with the addition of SnO exhibited strong emission around 600 nm upon 420 nm excitation, as shown in **Figure 3C**. However, further research is needed to optimise the glass composition.

7 Conclusion

We have prepared several glasses based on B_2O_3 and SiO_2 oxides doped with Ce^{3+} and Mn^{2+} ions. Glasses with high content of B_2O_3 exhibited hygroscopic properties causing corrosion and high absorption. All glasses exhibited photoluminescence in the UV-blue and red-NIR regions thanks to Ce^{3+} and Mn^{2+} ions, high content of B_2O_3 caused a blue-shift of the excitation and emission bands. The addition of reducing agents increased the emission intensity thanks to preserving Ce and Mn in the lower oxidation states. Glasses with ratio $4SiO_2{:}1B_2O_3$ exhibited optimal red emission upon 420 nm excitation. However, further research is needed to optimize the glass composition to achieve the desired excitation-emission range.

8 References

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