

## Time resolved fluorescence measurements on Tb<sup>3+</sup> and Mn<sup>2+</sup> doped glasses

Andreas Herrmann and Doris Eht

Otto-Schott-Institut für Glaschemie, Friedrich-Schiller-Universität Jena, Jena, (Germany)

---

Tb<sup>3+</sup> (4f<sup>8</sup>) and Mn<sup>2+</sup> (3d<sup>5</sup>) ions, known as active luminescent centres for blue, green and red fluorescence, were doped in various fluoride, phosphate and silicate glasses with well known structure. Narrow bands of f-f transitions with strong emission of Tb<sup>3+</sup> in the blue, green and red and broad bands of d-d transitions of Mn<sup>2+</sup> were measured with green emission in high optical basicity glasses with tetrahedrally coordinated Mn<sup>2+</sup>. Orange to red Mn<sup>2+</sup> emission was found in glasses with low optical basicity where Mn<sup>2+</sup> is octahedrally coordinated. Lifetimes,  $\tau_{\text{e}}$ , in the range of milliseconds were recorded in dependence of glass composition and dopant concentration for both Tb<sup>3+</sup> and Mn<sup>2+</sup> doped glasses. Fluorescence lifetimes are as well shortened by higher basicity of the glasses as by increasing dopant concentration.

---

### 1. Introduction

Luminescent glasses are of increasing interest for fundamental research and technical applications. They are already used widely as active material for laser and amplifier equipment, especially in the infrared region of the electromagnetic spectrum. Recent research tries to extend their use into applications in the visible spectral range. Luminescence in the blue, green and red is particularly interesting. On the other hand dopants that lead to these fluorescent glasses can act as indicator to study glass structure variations since their fluorescence properties change due to modifications in their local surroundings.

Up to now predominantly static fluorescence emission has been studied for most structural investigations, but time-resolved fluorescence measurements provide direct access to the formerly rather neglected parameter of glass structure, the fluorescence lifetime behaviour of the doped ions. Fluorescence lifetime investigations can lead to a better understanding of fluorescence itself and also glass structure. They can for instance offer new insight into energy migration processes or topology of the glass forming molecules.

Two well-known luminescent ions with different electronic configuration have been chosen to study these effects: the rare earth ion Tb<sup>3+</sup> (4f<sup>8</sup>) and the transition metal ion Mn<sup>2+</sup> (3d<sup>5</sup>). The optical properties of these two ions are considerably different. Mn<sup>2+</sup> fluorescence is very sensitive

to glass matrix changes while the Tb<sup>3+</sup> fluorescence offers better insight into energy migration processes and their dependency on host material variations [1].

To study the influence of the glass structure various fluoride, phosphate and borosilicate glasses with known properties and global structure [2 to 6] have been used as host materials. In most cases these have been fluoroaluminate glasses with varying phosphate content of  $x$  mol% (FP $x$  series). Additionally dopant concentration of Tb<sup>3+</sup> and Mn<sup>2+</sup> has been varied to study fluorescence quenching.

### 2. Experimental procedures

The glasses used were prepared with ultra high purity raw materials to ensure a high optical quality. The composition of the different glasses is given in tables 1 and 2, respectively. Dopant concentration of Tb<sup>3+</sup> and Mn<sup>2+</sup> was varied between 10<sup>19</sup> and 10<sup>22</sup> cm<sup>-3</sup>. For detailed information on preparation techniques of these glasses see previous papers [2 to 6].

To be able to record the luminescence emission spectra, polished plates ((15 × 20) mm<sup>2</sup>, thickness 0.2 to 10 mm) were made from the glass samples. A double beam spectrometer (RF-5301PC, Shimadzu (Japan)) was used for these studies.

Figure 1 shows the experimental setup for the fluorescence lifetime measurements. The glass samples were excited at 337 nm by a focussed, short (<500 ps) N<sub>2</sub>-laser pulse (MSG 800, LTB Lasertechnik, Berlin (Germany)). Fluorescence light then was collected and focussed on a spectrometer (H.25, Jobin, Yvon (France)) by a lens array. The

---

Received 23 August, revised manuscript 6 December 2004.

Presented in German at: 78<sup>th</sup> Annual Meeting of the German Society of Glass Technology (DGG) in Nürnberg on 9 June 2004.

Table 1. Basic compositions and physical properties of fluoride and phosphate glasses

glass	composition in mol%					physical properties			
	Sr(PO <sub>3</sub> ) <sub>2</sub>	MgF <sub>2</sub>	CaF <sub>2</sub>	SrF <sub>2</sub>	AlF <sub>3</sub>	T <sub>g</sub> in °C	n <sub>e</sub>	v <sub>e</sub>	ρ in g/cm <sup>3</sup>
FP0	=	10	28	23	39	400	1.405	105	3.42
FP3	3	10	28	23	38	420	1.427	97	3.50
FP10	10	10	30	15	35	440	1.460	90	3.46
FP20	20	10	22	18	30	480	1.504	80	3.52
P100	100	–	–	–	–	490	1.561	66	3.20

Table 2. Basic compositions and physical properties of silicate glasses

glass	composition in mol%						physical properties			
	Na <sub>2</sub> O	CaO	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	BaO	T <sub>g</sub> in °C	n <sub>e</sub>	v <sub>e</sub>	ρ in g/cm <sup>3</sup>
NCS	16	10	74	=	=	=	530	1.520	60	2.49
NBS1	16	–	74	10	–	–	550	1.510	63	2.45
NBS2	4	–	74	22	1	–	440	1.470	65	2.19
Duran®	4	–	83	12	1	–	530	1.473	66	2.22
BC	–	10	65	–	15	10	830	1.556	60	2.85

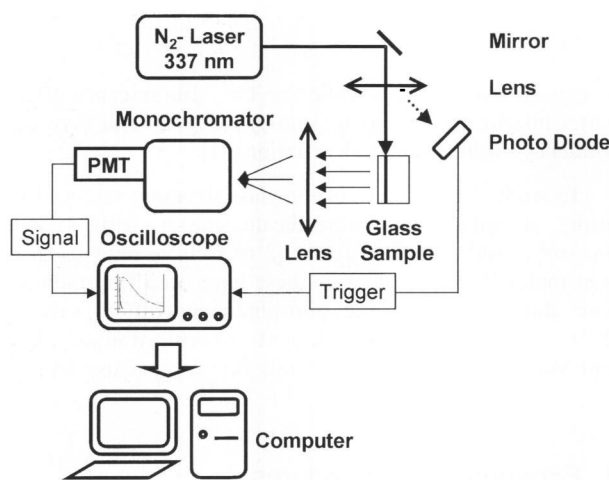


Figure 1. Experimental setup for fluorescence lifetime measurements (schematically).

resulting filtered fluorescence light was then detected by a photomultiplier tube PMT (R5929, Hamamatsu (Japan)) and its fluorescence decay curves recorded with a digital storage oscilloscope (TDS2012, Tektronix (USA)). The data obtained was transferred to a PC and analysed with commercial scientific graphing software. This setup allows wavelength specific lifetime measurements. That means the lifetime of every single fluorescence peak of Tb<sup>3+</sup> for instance can be measured separately or wide fluorescence bands can be investigated at different positions.

The lifetime τ<sub>c</sub> is the time that is (after short excitation) needed until normalized fluorescence intensity has dropped to 1/e (36.8 %) of its initial value. So it can be evaluated by looking at the intersection point of the fluorescence decay

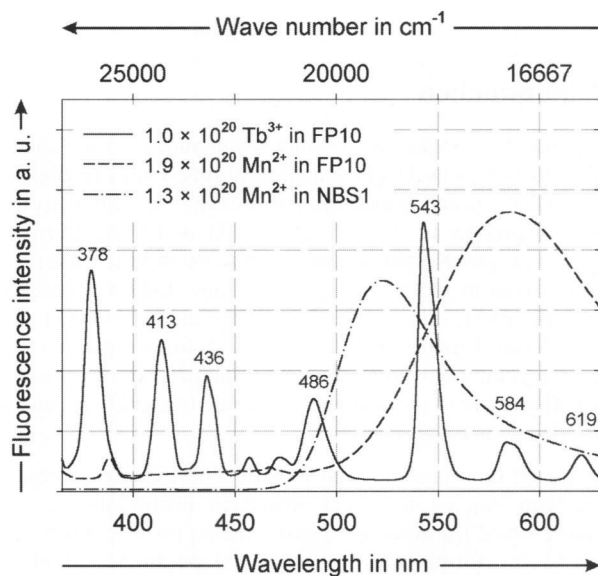


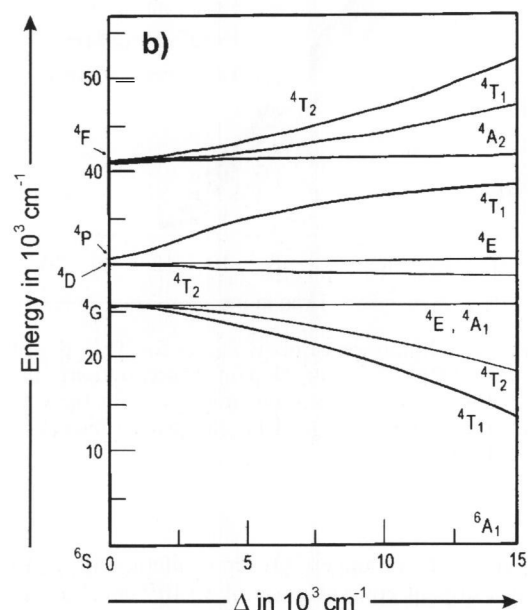
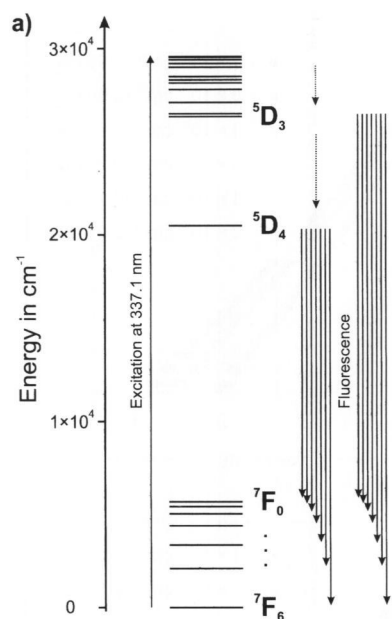
Figure 2. Typical fluorescence emission spectra of Tb<sup>3+</sup> and Mn<sup>2+</sup> doped glasses.

curves with the line drawn at 36.8 % of fluorescence intensity.

All measurements were conducted at room temperature.

### 3. Results

Sections of typical Tb<sup>3+</sup> and Mn<sup>2+</sup> fluorescence emission spectra are shown in figure 2. Most lines of Tb<sup>3+</sup> can easily be resolved because of the only slight line broadening. Fig-



Figures 3a and b. Electronic energy levels of the fluorescent ions Tb<sup>3+</sup> and Mn<sup>2+</sup>; a) energy levels in Tb<sup>3+</sup> and some radiative (solid arrows) and nonradiative (dotted arrows) transitions, b) simplified Tanabe-Sugano diagram for Mn<sup>2+</sup> (d<sup>5</sup> electronic configuration in octahedral coordination) [7]. The diagram shows the energy levels as a function of the crystal field  $\Delta$ .

Figure 3a presents a substantial part of the energy levels originating from the 4f<sup>8</sup> configuration of Tb<sup>3+</sup>. In general two sets of Tb<sup>3+</sup> fluorescence lines can be distinguished. The lines at 378, 413, 436, 457, 471, 484 and 492 nm form the 'blue emission band', and the lines at 486, 543, 584, 619, 647, 666 and 676 nm form the fluorescence band that is later referred to as the 'green to red band'.

In contrast to the spectrum of terbium the emission of Mn<sup>2+</sup> consists only of one broad band. Its position varies from green to deep red, strongly depending on the host lattice because its 3d valence electrons are not shielded from their surroundings. So the crystal field has a strong influ-

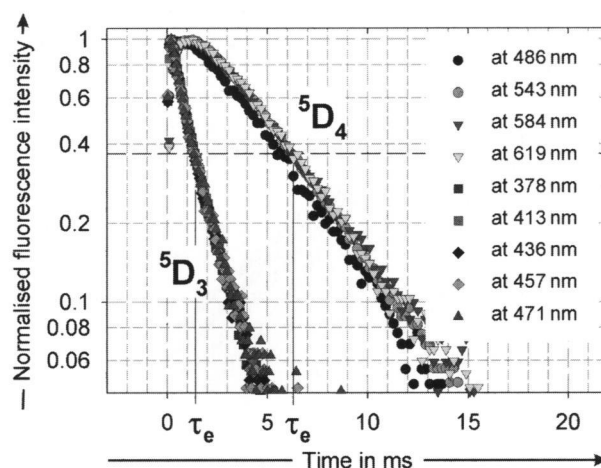


Figure 4. Fluorescence decay curves for  $1 \times 10^{20} \text{ cm}^{-3}$  Tb<sup>3+</sup> doped fluoride phosphate glass FP10. Although measurements have been conducted at various wavelengths, only two discrete lifetimes  $\tau_e$  can be separated.

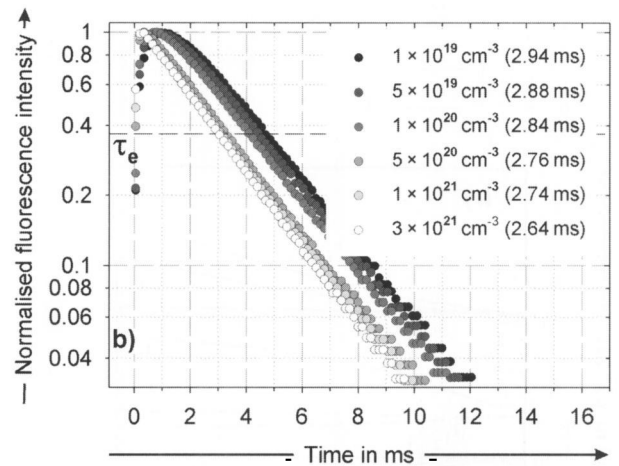
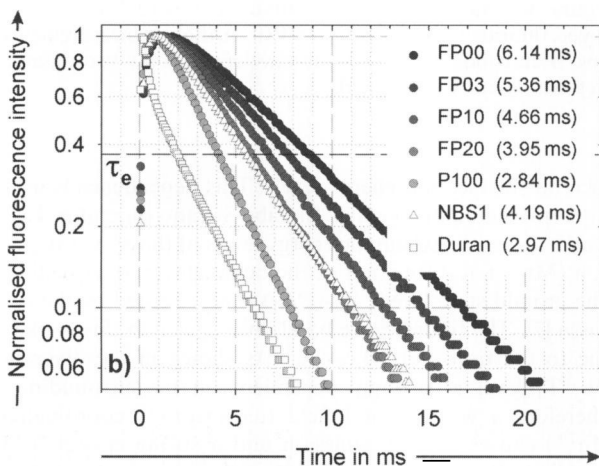
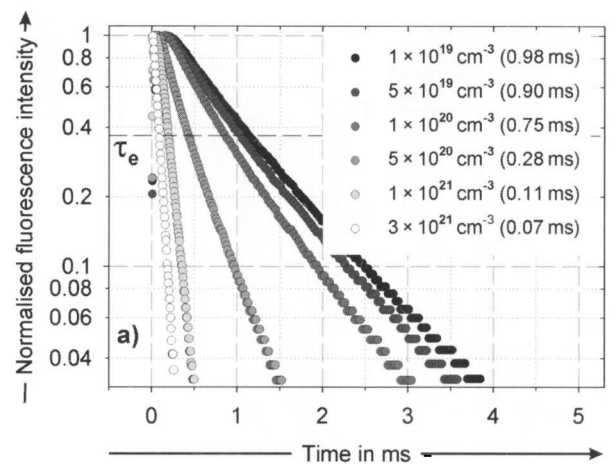
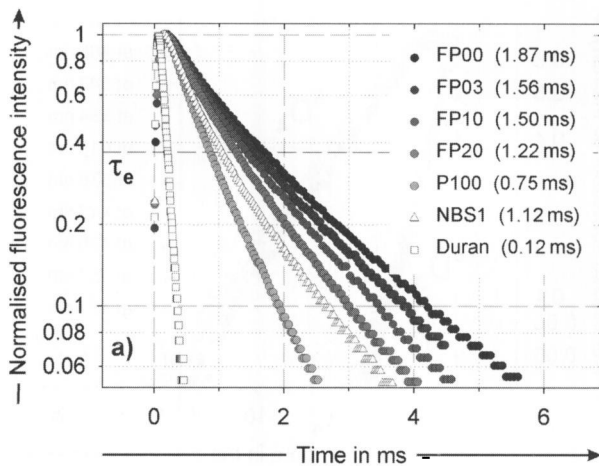
ence on the electron energy levels. This dependence is usually represented in so called Tanabe-Sugano diagrams. Figure 3b shows the schematic energy levels of the d<sup>5</sup> configuration (Mn<sup>2+</sup>) as a function of the octahedral crystal field  $\Delta$ . The ground state level ( ${}^6S \rightarrow {}^6A_1$ ) is represented by the abscissa [7]. The fluorescence band investigated in this work is due to the transition  ${}^4T_1 \rightarrow {}^6A_1$ . As shown in the diagram the  ${}^4T_1$  level is strongly dependent on its surroundings. Therefore a weak crystal field (tetrahedrally coordinated Mn<sup>2+</sup>) causes a green emission and a strong crystal field (octahedrally coordinated Mn<sup>2+</sup>) gives an orange to red fluorescence [7].

Figure 4 shows typical fluorescence decay curves recorded at the nine different fluorescence bands of the emission spectrum of Tb<sup>3+</sup> doped FP20 glass depicted in figure 2. Dopant concentration had been set to  $1 \times 10^{20} \text{ cm}^{-3}$ . Two sets of bands can clearly be separated by their fluorescence lifetime (figure 4). The higher lying  ${}^5D_3$  level (blue fluorescence) has a shorter lifetime than the  ${}^5D_4$  level with its transitions at longer wavelengths. Since all transitions of one band have the same lifetime, further measurements have only been done for one transition per band, at 413 nm for the  ${}^5D_3$  level and at 543 nm for the  ${}^5D_4$  level.

Figures 5a and b show fluorescence decay curves for various  $1 \times 10^{20} \text{ cm}^{-3}$  Tb<sup>3+</sup> doped glasses for the two energy levels  ${}^5D_3$  and  ${}^5D_4$ , respectively. Both diagrams show the same dependencies: fluorescence lifetime drops with increasing phosphate content. The shape of the decay curves for the borosilicate glasses Duran and NBS2 (not shown) with low alkali content and mostly bridging oxygens differs significantly from the other curves.

Figure 6 compares the dependencies of the fluorescence lifetime on the phosphate content for both energy levels. Although the lifetimes of the two energy levels are different, the influence of the phosphate content on both is about the same: fluorescence lifetime drops to about 50 % of its initial value in FP0 for P100 glass.

The dopant concentration dependency investigations which have been done for P100 glass show a completely different result. Figures 7a and b display the measurements



Figures 5a and b. Fluorescence decay curves for various  $1 \times 10^{20} \text{ cm}^{-3}$   $\text{Tb}^{3+}$  doped glasses, the measured lifetimes  $\tau_e$  are given in parentheses; a) for the blue emission at 413 nm ( $^5\text{D}_3$  level), b) for the green emission at 543 nm ( $^5\text{D}_4$  level).

Figures 7a and b. Fluorescence decay curves for  $\text{Tb}^{3+}$  doped phosphate glass P100 (varying dopant concentration), the measured lifetimes  $\tau_e$  are given in parentheses; a) for the blue emission at 413 nm ( $^5\text{D}_3$  level), b) for the green emission at 543 nm ( $^5\text{D}_4$  level).

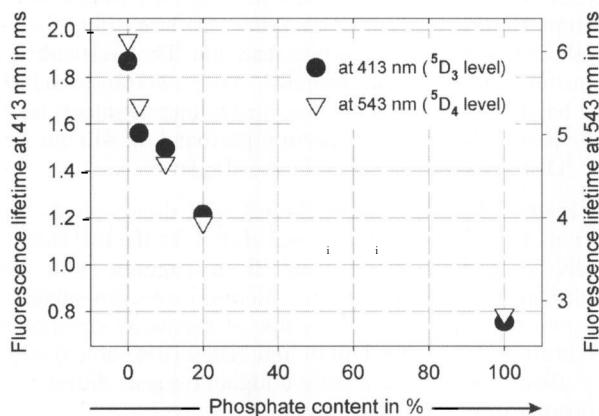


Figure 6. Fluorescence lifetime  $\tau_e$  dependency on phosphate content of  $1 \times 10^{20} \text{ cm}^{-3}$   $\text{Tb}^{3+}$  doped fluoride phosphate glasses for the blue and green emission (different scale).

for the two energy levels  $^5\text{D}_3$  and  $^5\text{D}_4$ , respectively. It is clearly to be seen that the dopant concentration has little effect on the fluorescence lifetime of the lower lying  $^5\text{D}_4$  level. Its lifetime decreases only by about 10 % as figure 7b

shows. In contrast, the upper  $^5\text{D}_3$  level's lifetime drops to nearly 0 at a dopant concentration of  $3 \times 10^{21} \text{ cm}^{-3}$  as depicted in figure 7a.

Furthermore another effect is evident: the shape of the decay curves changes with increasing dopant concentration. The peak gets more pointed at higher dopant concentrations. This results in a shift of the decay curves that is especially well to be seen in figure 7b because there is hardly any influence on the fluorescence lifetime (constant slope of the curve). It is the same effect that could also be observed for the Duran measurements in figures 5a and b.

The influence of the dopant concentration on the fluorescence lifetime of the two energy levels  $^5\text{D}_3$  and  $^5\text{D}_4$  is compared directly in figure 8.

A very good correlation to these findings can be found in the static fluorescence spectra (figure 9): while the blue transitions originating from the  $^5\text{D}_3$  level are much stronger than the green and red fluorescence ( $^5\text{D}_4$  level) at lower dopant concentrations, the effect is exactly opposite at high dopant concentrations. Here all peaks of the blue fluorescence band ( $^5\text{D}_3$ ) have nearly disappeared, while the  $^5\text{D}_4$  band is very strong.

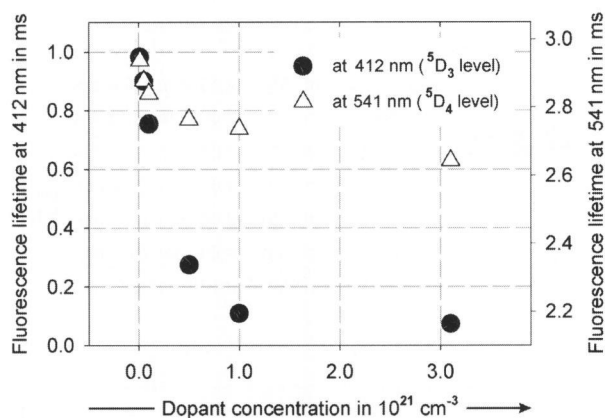


Figure 8. Fluorescence lifetime  $\tau_c$  dependency on Tb<sup>3+</sup> dopant concentration for phosphate glass P100.

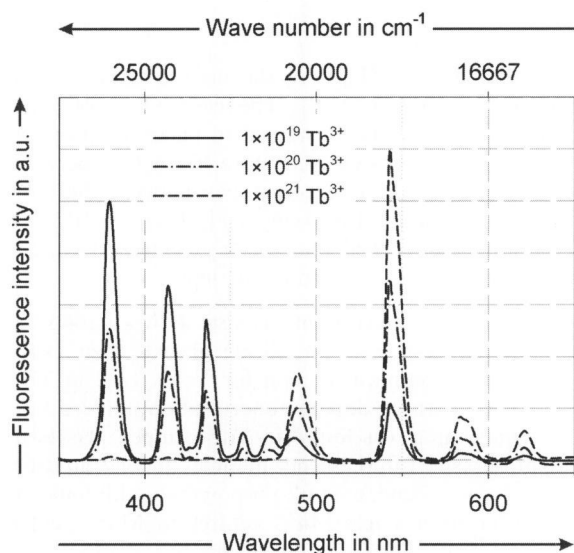


Figure 9. Influence of dopant concentration changes on static fluorescence emission spectra of Tb<sup>3+</sup> doped fluoride phosphate glass FP20. The glass samples have been excited at a wavelength of 340 nm.

The measurements with manganese doped glasses show about the same correlations as the measurements on terbium doped glasses: the fluorescence decay curves for various different types of glass are to be seen in figure 10. As in Tb<sup>3+</sup> doped glasses also the Mn<sup>2+</sup> fluorescence investigated has a long lifetime in fluoride and phosphate glasses slightly shortened with increasing phosphate content (not shown). The lifetime of Mn<sup>2+</sup> doped silicate glasses is much shorter than in fluoride and phosphate glasses and the rate of concentration quenching is much higher. It was not possible to detect any luminescence emission and lifetime at Mn<sup>2+</sup> dopant concentration  $\geq 8 \times 10^{20} \text{ cm}^{-3}$ . Surprisingly, these quenching effects were nearly independent of the coordination number of the Mn<sup>2+</sup> ions, that means they were independent of the spectral shift of their fluorescence spectrum (green to orange-red emission).

The variation of the dopant concentration tends to show nearly the same influence as for the blue fluorescence of Tb<sup>3+</sup> doped glasses: as figures 11 and 12 show fluorescence

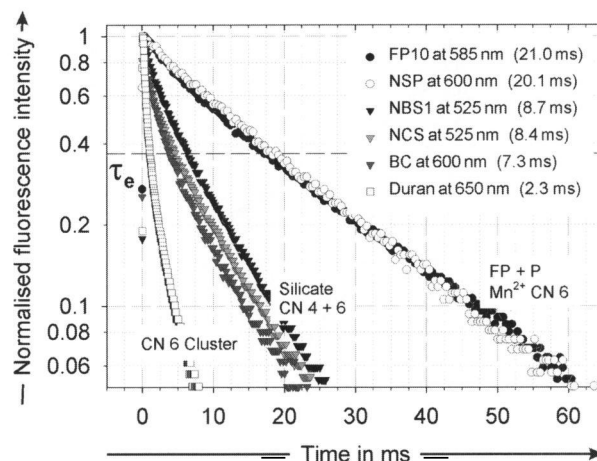


Figure 10. Fluorescence decay curves for various Mn<sup>2+</sup> doped glasses at their fluorescence maximum (dopant concentration about  $1 \times 10^{20} \text{ cm}^{-3}$ ), the measured lifetimes  $\tau_c$  are given in parentheses.

lifetime almost drops to 0 at dopant concentrations of about  $10^{22} \text{ cm}^{-3}$ . Remarkable is the longer lifetime of Mn<sup>2+</sup> doped NSP glass ( $\text{Na,Sr}_{1-x}\text{Mn}_x(\text{PO}_3)_2$ ) that has been added to figure 12 for comparison with pure  $\text{Sr}_{1-x}\text{Mn}_x(\text{PO}_3)_2$ .

#### 4. Discussion

In most cases fluorescence emission spectra of rare earth elements show various relatively sharp lines (figure 2). The 4f electrons that are responsible for the fluorescence emission are well shielded from their surroundings by the 5s<sup>2</sup> and 5p<sup>6</sup> electrons lying outside the 4f orbitals. That means, the influence of the ion's surroundings on the 4f electron energy levels is rather weak. Thus only a relatively slight line broadening and line shift in the fluorescence emission spectrum of rare earth ions can be found in glasses compared to their spectra in crystals or aqueous solution. To understand the fluorescence spectra and lifetime measurements the electronic energy levels of Tb<sup>3+</sup> have to be studied at first (figure 3). Tb<sup>3+</sup> fluorescence is split into two band systems, one originating from the <sup>5</sup>D<sub>3</sub> level with lines in the blue at 378, 413, 436, 457, 471, 484 and 492 nm and the other originating from the lower <sup>5</sup>D<sub>4</sub> level with lines in the green to red at 486, 543, 584, 619, 647, 666 and 676 nm.

The static Mn<sup>2+</sup> fluorescence measurements revealed a strong influence of the coordination of the doped Mn<sup>2+</sup> ions on the position of their fluorescence peak and therefore on the colour at which the fluorescence light appears. As figure 2 shows a strong shift of the fluorescence spectra into red region of the visible spectrum has been found for octahedrally coordinated Mn<sup>2+</sup> while the fluorescence of tetrahedrally coordinated Mn<sup>2+</sup> appears green. Only a very slight shift (less than 1 nm) of the fluorescence peaks could be found for Tb<sup>3+</sup> doped glasses. The different behaviour of these two ions can be explained by their electronic properties. The f-f transitions in rare earth ions as Tb<sup>3+</sup> are well shielded by their surrounding 5s and 5p electrons. Such shielding is completely missing in transition metals as Mn<sup>2+</sup>. So, their d-d transitions are strongly influenced by the ion's surroundings and bonding.



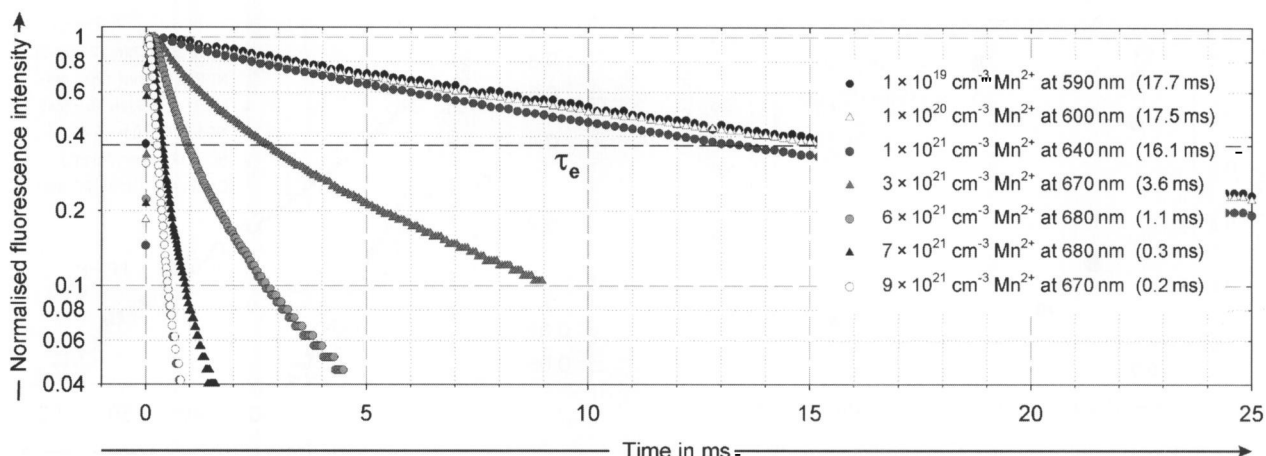


Figure 11. Fluorescence decay curves for metaphosphate glasses  $Sr_{1-x}Mn_x(PO_3)_2$  with increasing  $Mn^{2+}$  content at their fluorescence maximum; the measured lifetimes  $\tau_e$  are given in parentheses.

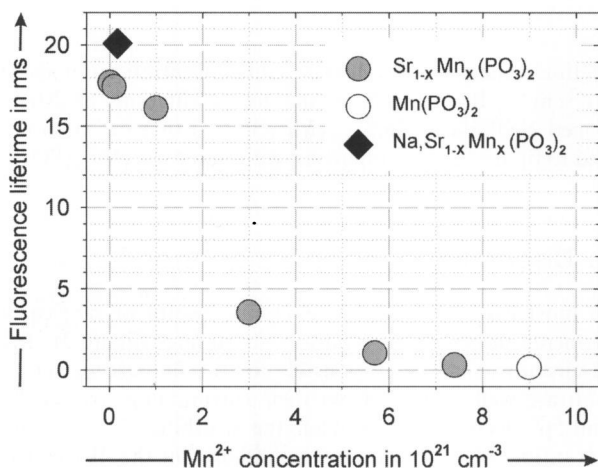


Figure 12. Fluorescence lifetime  $\tau_e$  dependency on  $Mn^{2+}$  content for  $Sr_{1-x}Mn_x(PO_3)_2$  glasses.

The lifetime measurements for both dopants have been separated into two parts: the influence of the basic glass structure and the influence of the dopant concentration including local site distribution.

In  $Tb^{3+}$  doped fluoride phosphate glasses  $FP_x$  a lifetime decrease was found with increasing phosphate content. That means lifetime decreases with increasing optical basicity and covalence. While this dependence in general was also found for  $Mn^{2+}$  doped glasses the lifetimes of silicate glasses were found much shorter than the lifetimes of phosphate glasses. This effect was not to be seen for  $Tb^{3+}$ .

The dependency of the fluorescence lifetime on the dopant concentration variation can be well understood. The blue fluorescence band of  $Tb^{3+}$  originating from the upper  $^5D_3$  level is getting weaker with increasing dopant concentration while the green to red fluorescence ( $^5D_4$  level) is preferred. The cause of this phenomenon should be  $Tb^{3+}$  cross relaxation processes ( $^5D_3 \rightarrow ^5D_4 \Rightarrow ^7F_6 \rightarrow ^7F_0$ ) strongly favoured by high dopant concentrations [6]. According to Carnall et al. the energy gap between  $^5D_3$  and  $^5D_4$  levels is about less than  $5800\text{ cm}^{-1}$  in aqueous solution while the

gap between  $^7F_0$  and  $^7F_6$  is of the same magnitude lying slightly above  $5600\text{ cm}^{-1}$  [8]. The electron energy level broadening in glasses is considered to make the proposed cross relaxation processes even more likely. On the other hand there is quite a large energy gap between the levels  $^5D_4$  and  $^7F_0$  of about  $14800\text{ cm}^{-1}$  [8]. Therefore the  $^5D_4$  level cannot be quenched that easily and dopant concentration has only little effect on its lifetime.

Although  $Mn^{2+}$  measurements also show a strong lifetime shortening especially in silicate glasses, their explanation is more complicated than for  $Tb^{3+}$ . Like in  $Tb^{3+}$  doped glasses a strong dopant concentration induced fluorescence quenching was found in  $Mn^{2+}$  doped glasses resulting in very short fluorescence lifetimes at concentrations above  $10^{21}\text{ cm}^{-3}$ . Benecke et al. proposed an additional energy transfer from single  $Mn^{2+}$  centres to  $Mn^{2+}$  centres with higher  $Mn^{2+}$  doping levels [9 and 10]. More detailed investigations will be needed to better understand these energy migration processes.

Interestingly the fluorescence lifetime of  $Na,Sr_{1-x}Mn_x(PO_3)_2$  ( $Mn^{2+}$  doped NSP glass) was determined remarkably longer than the lifetime of  $Sr_{1-x}Mn_x(PO_3)_2$  glasses at similar dopant concentrations. Hoppe et al. stated that the distance between  $Sr^{2+}$  ions in  $Sr(PO_3)_2$  is with  $2.2\text{ nm}$  much smaller than the distance between  $Na^+$  in  $NaPO_3$  with  $4.8\text{ nm}$  [11]. Since  $Sr^{2+}$  and  $Na^+$  could be substituted by  $Mn^{2+}$  ions, it can be assumed that also the distance between  $Mn^{2+}$  ions is shortened in  $Sr_{1-x}Mn_x(PO_3)_2$  glass in comparison to NSP glass. This would well explain the longer fluorescence lifetime of  $Mn^{2+}$  doped NSP glass.

Another effect that has been observed is the shift of the fluorescence decay curves because of the change of the curve's shape. The peak of the curves is getting more pointed with increasing dopant concentration. That means energy migration processes that precede the emission of the fluorescence light (dotted arrows in figures 3a and b) were favoured by the higher dopant concentration. These mechanisms can as well be understood as the quenching of the  $^5D_3$  level:  $Tb^{3+}$  has nine electron levels between  $26000$  and  $30000\text{ cm}^{-1}$  lying close together [8]. The lowest of them is the  $^5D_3$  level. The small energy differences between these

levels can easily be transferred to the various <sup>7</sup>F<sub>J</sub> levels or excite vibronic levels of the surrounding glass molecules similar to the quenching process described above (<sup>5</sup>D<sub>3</sub> → <sup>5</sup>D<sub>4</sub> ⇒ <sup>7</sup>F<sub>6</sub> → <sup>7</sup>F<sub>0</sub>). These relaxation mechanisms proceed until the <sup>5</sup>D<sub>3</sub> level is reached.

Furthermore a distinct behaviour of the Duran (and NBS2) glass samples was as well observed for Tb<sup>3+</sup> as for Mn<sup>2+</sup>. The fluorescence decay curves of Duran differ strongly from all other measurements. While the fluorescence lifetime of the <sup>5</sup>D<sub>3</sub> level for Tb<sup>3+</sup> doped Duran glass is extremely short only a curve shape change is to be seen for the <sup>5</sup>D<sub>4</sub> measurement. Both phenomena have just been explained as being effects of higher dopant concentration. So we assume that the luminescent ions accumulate in sodium borate clusters as well in Duran as in NBS2 glass leading to a locally increased dopant concentration with smaller distances between the luminescent species. It is well known that sodium borosilicate melts with Duran or NBS2 composition show a tendency to subliquidus immiscibility which should be suppressed by Al<sub>2</sub>O<sub>3</sub> doping.

## 5. Conclusions

It has been shown that the fluorescence lifetime of rare earth and transition metal ions in glasses is a very sensitive parameter of glass structure. Strong dependencies on dopant concentration and glass composition have been pointed out for dopants as Tb<sup>3+</sup> and Mn<sup>2+</sup>. While dopant concentration has strong influence on fluorescence lifetime in most cases a not as big but clearly detectable lifetime change was also observed for ion changes in the vicinity of the dopant ions: fluorescence lifetime is in general very long in fluoride glasses with extremely low optical basicity and strong ionic bonds. The lifetime is shortened by adding phosphate groups that increase optical basicity and covalence of the glass network. This effect is especially well to be seen in Tb<sup>3+</sup> doped FP<sub>x</sub> glasses with *x* being the phosphate fraction in mol%. The lifetime decrease there was observed to be about 50 % from fluoride glass FP0 to phosphate glass P100. Even stronger is the influence of the dopant concentration on the fluorescence lifetime. The blue fluorescence of Tb<sup>3+</sup> as well as the fluorescence of Mn<sup>2+</sup> is strongly quenched at dopant concentrations above 10<sup>21</sup> cm<sup>-3</sup>, especially for Mn<sup>2+</sup> in silicate glasses. This effect is independent of the coordination number of Mn<sup>2+</sup> and was as well found with fourfold coordination and green emission as with six fold coordination and orange-red emission. An exception to these findings is the green to red fluorescence of

Tb<sup>3+</sup>. Its lifetime is only slightly shortened (approximately 10 %) due to the state of its electron energy levels.

Thus it was shown that the fluorescence lifetime can well be used as an indicator for segregation and other glass structure changing processes.

\*

The authors thank Mrs. R. Atzrodt for preparing the glass samples and the Carl Zeiss-University Jena-Cooperation for the financial support.

## 6. References

- [1] Van Dongen, A. M. A.: Tb<sup>3+</sup> luminescence in fluorozirconate glasses: indicator for homogeneous Tb<sup>3+</sup> distribution. *J. Non-Cryst. Solids* **139** (1992) pp. 271–273.
- [2] Ehrt, D.; Leister, M.; Matthai, A.: Polyvalent elements iron, tin and titanium in silicate, phosphate and fluoride glasses and melts. *Phys. Chem. Glasses* **42** (2001) pp. 231–239.
- [3] Möncke, D.; Ehrt, D.: Influence of melting and annealing conditions on the optical spectra of a borosilicate glass doped with CoO and NiO. *Glass Sci. Technol.* **75** (2002) pp. 163–173.
- [4] Ebendorff-Heidepriem, H.; Ehrt, D.: Spectroscopic properties of Eu<sup>3+</sup> and Tb<sup>3+</sup> ions for local structure investigations of fluoride phosphate and phosphate glasses. *J. Non-Cryst. Solids* **208** (1996) pp. 205–216.
- [5] Ehrt, D.: Photoluminescence in the UV-VIS region of polyvalent ions in glasses. *J. Non-Cryst. Solids* **348** (2004) pp. 22–29.
- [6] Ebendorff-Heidepriem, H.; Ehrt, D.: Relationships between glass structure and spectroscopic properties of Eu<sup>3+</sup> and Tb<sup>3+</sup> doped glasses. *Ber. Bunsenges. Phys. Chem.* **100** (1996) pp. 1621–1624.
- [7] Blasse, G.; Grabmaier, B. C.: *Luminescent materials*. Berlin et al.: Springer, 1994.
- [8] Carnall, W. T.; Fields, P. R.; Rajnak, K.: Electronic energy levels of the trivalent lanthanide aquo ions. III. Tb<sup>3+</sup>. *J. Phys. Chem.* **49** (1968) pp. 4447–4449.
- [9] Benecke, C.; Gumlich H.-E.: in: Jain, M. (ed.): *The Luminescence of Wide Band Gap II-Mn-VI Semimagnetic Semiconductors in Diluted Magnetic Systems*. London: World Scientific, 1992.
- [10] Benecke C.; Busse, W.; Gumlich, H.-E. et al.: Time-resolved spectroscopy of the low-energy emission bands of highly doped Zn<sub>1-x</sub>Mn<sub>x</sub>S. *Phys. Status Solidi B* **142** (1987) pp. 301–309.
- [11] Hoppe, U.; Walter, G.; Kranold, R. et al.: Structural specifics of phosphate glasses probed by diffraction methods: a review. *J. Non-Cryst. Solids* **263&264** (2000) pp. 29–47.

■ E305N001

Contact:

A. Herrmann  
 Otto-Schott-Institut für Glaschemie  
 Friedrich-Schiller-Universität Jena  
 Fraunhoferstraße 6  
 D-07743 Jena  
 E-mail: andreas.herrmann@uni-jena.de