# On the Luminescence of $\mathbf{M n}^{4+}$ and $\mathbf{M n}^{2+}$ 

Andre Bleise, Holger Winkler and Thomas Jüstel Fachhochschule



Fig. 1: Tanabe-Sugano-diagramm of the $\mathrm{d}^{3}$ configuration ${ }^{[1]}$


Fig. 2: Tanabe-Sugano-diagramm of the $d^{5}$ configuration ${ }^{[1]}$

## Intention

Tetravalent Manganese is a known red emitter which could have the possibility to replace the well established $\mathrm{Eu}^{3+}$ activator. One of the problems here is the deep red emission which leads only to moderate luminous efficiency. So it is one of the intensions to shift this emission towards the blue spectral range by increasing the crystal field splitting.

## Experimental

We investigated the influence of the increasing of the crystal field by replacing the cations at their crystallographic sites. With full details we compared $\mathrm{Y}_{3} \mathrm{Al}_{5} \mathrm{O}_{12}: \mathrm{Mn}^{4+}, \mathrm{Ca}^{2+}$ with $\mathrm{Lu}_{3} \mathrm{Al}_{5} \mathrm{O}_{12}: \mathrm{Mn}^{4+}, \mathrm{Ca}^{2+}$ and $\mathrm{Sr}_{3} \mathrm{Lu}_{2} \mathrm{Ge}_{3} \mathrm{O}_{12}: \mathrm{Mn}^{2+}$ with $\mathrm{Sr}_{3} \mathrm{In}_{2} \mathrm{Ge}_{3} \mathrm{O}_{12}: \mathrm{Mn}^{2+}$. The ratio of the replaced Ions $\mathrm{Y}^{3+}$ and $\mathrm{Lu}^{3+}\left(\mathrm{r}_{\mathrm{Y}} / \mathrm{r}_{\mathrm{Lu}}: 1,04\right)$ and accordingly $\mathrm{Lu}^{3+}$ and $\mathrm{In}^{3+}\left(\mathrm{r}_{\mathrm{Lu}} / \mathrm{r}_{\mathrm{In}}: 1,06\right)$ are comparable. In the same manner are we able to compare the increase of the crystal field by this exchange of ions.

## Results:

It is clearly visible that an similar increase of the crystal field strength in case of tetravalent Manganese leads to different spectroscopic shifts towards shorter wavelengths compared with $\mathrm{Mn}^{2+}$. The $\mathrm{Mn}^{4+}$ emission is shifted 7 nm and the $\mathrm{Mn}^{2+}$ one 70 nm . This can be traced back to the steepness of the energy levels visible in the Tanabe-Sugano-diagrams. The irradiative transitions are in the case of $\mathrm{Mn}^{4+}:{ }^{2} \mathrm{E}_{\mathrm{g}} \rightarrow{ }^{4} \mathrm{~A}_{2 \mathrm{~g}}$ and in case of $\mathrm{Mn}^{2+}:{ }^{6} \mathrm{~A}_{2} \rightarrow{ }^{2} \mathrm{~T}_{2}$.

## Conclusions:

In general it is possible to shift the $\mathrm{Mn}^{4+}$ emission towards the blue by increasing the crystal field of the host lattice. Due to this small shift that could be realized with the garnet structure other host lattices should be investigated to enforce this effect to reach a more significant shift. Especially Aluminates are interesting in this manner.

## Background

The luminescent properties of activator ions are very much dependent on the chemical surrounding. Especially the crystal field and the covalence of the host lattice are responsible for this effect. Tanabe-Sugano-diagrams demonstrate the energetic states of the different transitions in correlation to the crystal field and the electron-electron interaction graphically. So the position of the different energetic states is dependent on the one hand on the electronically configuration of the activator ion and on the other hand on the crystallographic positions within the host lattice. For comparable results the luminescence was investigated in the garnet structure.


Fig. 3: The garnet structure ${ }^{[2]}$

> | Crystallographic positon | Ion |
| :--- | :--- |

Pseudo-dodecahedral site C Octahedral site A Tetrahedral site D
$\mathrm{Mg}^{2+}, \mathrm{Ca}^{2+}, \mathrm{Sr}^{2+}, \mathrm{Fe}^{2+}, \mathrm{Mn}^{2+}, \mathrm{Y}^{3+}$ and $\mathrm{Lu}^{3+}$ $\mathrm{Al}^{3+}, \mathrm{Ge}^{4+}, \mathrm{Cr}^{3+}, \mathrm{Fe}^{3+}, \mathrm{In}^{3+}, \mathrm{Ga}^{3+}, \mathrm{Y}^{3+}$ and $\mathrm{Lu}^{3+}$ $\mathrm{Al}^{3+}, \mathrm{Ga}^{3+}, \mathrm{Fe}^{3+}, \mathrm{Si}^{4+}$ and $\mathrm{Ge}^{4+}$

Fig. 4: Crystalographic positions within the garnet structure

Fig. 5: Emission spectra of $\mathrm{Y}_{3} \mathrm{Al}_{5} \mathrm{O}_{12}: \mathrm{Mn}^{4+}$ and $\mathrm{Lu}_{3} \mathrm{Al}_{5} \mathrm{O}_{12}: \mathrm{Mn}^{4+}$


Fig. 6: Emission spectra of $\mathrm{Sr}_{3} \mathrm{Lu}_{2} \mathrm{Ge}_{3} \mathrm{O}_{12}: \mathrm{Mn}^{2+}$ and $\mathrm{Sr}_{3} \mathrm{In}_{2} \mathrm{Ge}_{3} \mathrm{O}_{12}: \mathrm{Mn}^{2+}$

References
[1] Phosphor Handbook 2nd Edition, M. J. Weber, 2007 Taylor \& Francis Group, LCC

