Fluoride Host Lattices Doped by Divalent Lanthanides like Sm$^{2+}$, Eu$^{2+}$ and Yb$^{2+}$

Benjamin Herden and Thomas Jüstel

University of Applied Sciences Münster, Stegerwaldstraße 39, D-48565 Steinfurt, Germany

Background

The photoluminescence of divalent lanthanide ions is strongly dependent on the host lattice since the excited state is strongly interacting with the surrounding anions. Thus the emission colour of these ions is easily tuneable by the chemical environment. Moreover, their absorption bands are broad and intense, due to the involved allowed 4f-5d transitions. Consequently, Eu$^{2+}$, Sm$^{2+}$, and Yb$^{2+}$ are very interesting ions either as activators in luminescent materials or as converters in solid state LASER gain media.

### activator ion | ground state configuration | redox potential $E_0$ [V vs. NHE]
--- | --- | ---
Sm$^{3+} + e^- \rightarrow$ Sm$^{2+}$ | [Xe]4f$^6$ | -1.150
Eu$^{3+} + e^- \rightarrow$ Eu$^{2+}$ | [Xe]4f$^7$ | -0.429
Yb$^{3+} + e^- \rightarrow$ Yb$^{2+}$ | [Xe]4f$^{14}$ | -0.578

host lattice | Li$^+$ | Na$^+$ | K$^+$
--- | --- | --- | ---
MgF$_3$ | covalent character | crystal field splitting

### Synthesis

The preparation of the doped host lattices was made by the “Mix and Fire” method. As starting materials fluorides of metals were used. Since lanthanide trifluorides were applied, it was necessary to work under a reductive atmosphere to obtain the lanthanide activator in the divalent state.

While the synthesis of NaMgF$_3$ and KMF$_3$ lead to samples of single phase, the formation of a LiMgF$_3$ phase was not observed. So far the crystal system of LiMgF$_3$ is unknown.

The use of forming gas ensures that the trivalent lanthanides were reduced to divalent lanthanides during the synthesis, which is illustrated by the fluorescence spectra.

- Sm$^{2+}$ just shows narrow emission lines stemming from 4f$^6$-$4f^6$-transitions
- Eu$^{2+}$ shows a combination of narrow 4f$^7$-$4f^7$ emission lines and a broad emission band, which is assigned to a 4f$^7$5d$^1$-$4f^7$-transition
- Yb$^{2+}$ just shows a broad emission band belonging to the 4f$^{13}$5d$^1$-$4f^{14}$-transition

The position of the lowest energy level of the 4f5d band shifts to the red by tuning the host lattice from KMgF$_3$ to NaMgF$_3$.

### Conclusions

The results of this study fulfilled our expectations. The divalent lanthanides could be incorporated onto the M(I) position of the host lattice. Moreover, a shift to the red of the lowest energy level of the 4f5d band by tuning the host lattice could be observed.