Divalent Lanthanides

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

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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 ←		
crystal system	unknown	orthorhombic	cubic

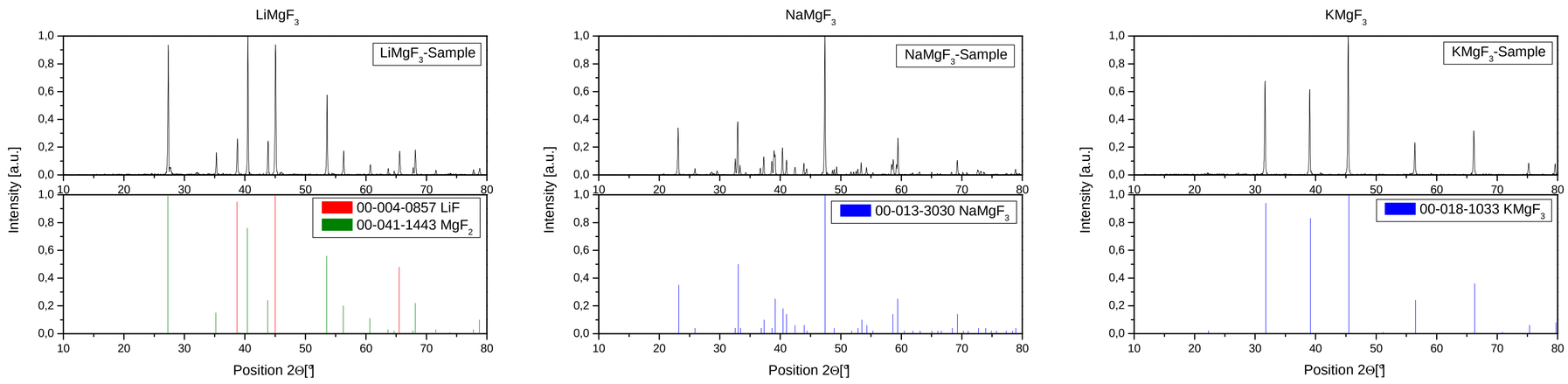
In this study, the divalent lanthanide ions, viz. Sm^{2+} (141 pm), Eu^{2+} (139 pm), and Yb^{2+} (128 pm) were doped into fluoride host lattices. Host lattices based on fluorides exert low covalency because of the high electronegativity of the fluoride anion. For this reason, the position of the lowest energy level of the 4f5d band depends mostly on the crystal field splitting. The crystal field splitting is related to the size, coordination geometry and number of the crystallographic site whereat the dopant is located.

To evaluate these characteristics, host lattices according to the general formula $M(I)MgF_3$ (M(I) = Li, Na, K were chosen. The dopant is incorporated onto the M(I) positions, while the size tuning was achieved by the cations Li^+ (106 pm), Na^+ (132 pm) and K^+ (165 pm). For charge compensation Li^+ is doped onto the M(II) sites.

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.

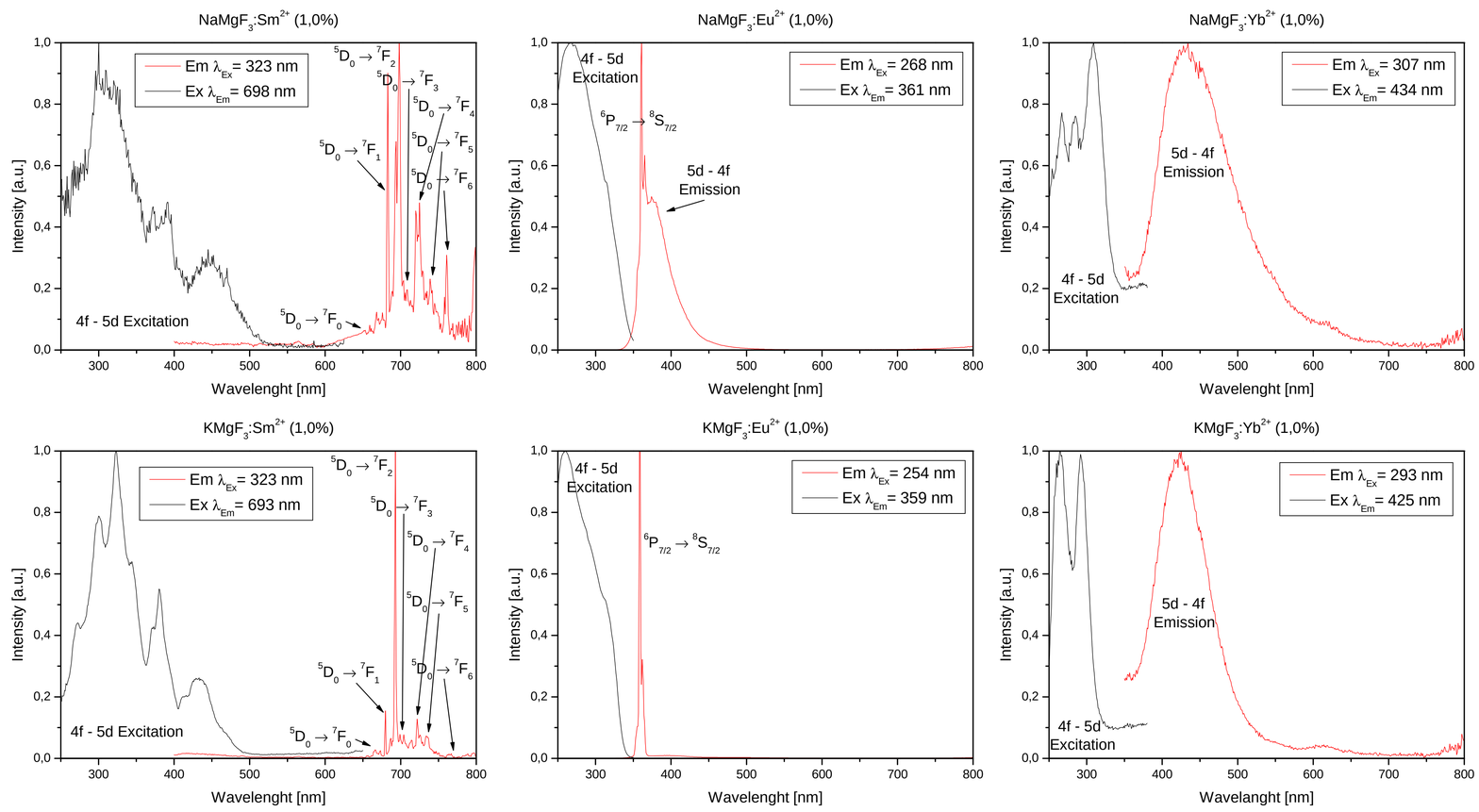
While the synthesis of $NaMgF_3$ and $KMgF_3$ lead to samples of single phase, the formation of a $LiMgF_3$ phase was not observed. So far the crystal system of $LiMgF_3$ is unknown.



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 $4f^65d^1$- $4f^7$-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.

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