

## Einladung zum Kolloquium

Am Mittwoch, den 13. Juni 2012, 17:00 Uhr, spricht

**Herr Professor Dr. Thomas Schleid**

**Institut für Anorganische Chemie, Universität Stuttgart**

zum Thema:

### **Geo-Inspired Phosphors Based on Rare-Earth Metal(III) Fluorides with Complex Oxoanions**

Bulk and  $M^{3+}$ -doped *bastnaesite*-type  $\text{LaF}[\text{CO}_3]$  (hexagonal,  $P\bar{6}2c$ ) can be prepared from aqueous solutions, containing  $\text{La}^{3+}$ ,  $\text{F}^-$  and  $[\text{HCO}_3]^-$  ions along with up to 3%  $M^{3+}$  dopant ( $M = \text{Eu}$  or  $\text{Tb}$ ) if desired. Its thermal decomposition at  $450^\circ\text{C}$  yields volatile  $\text{CO}_2$  and single-phase  $\text{LaOF}$  (trigonal,  $R\bar{3}m$ ) as solid residue, which shows brilliant red ( $\text{Eu}^{3+}$ ) or green ( $\text{Tb}^{3+}$ ) luminescence. Fluoride-derivatized rare-earth metal oxosilicates are available from appropriate  $\text{M}_2\text{O}_3:\text{MF}_3:\text{SiO}_2$  mixtures at high temperatures. For *bastnaesite*-related  $\text{LaF}(\text{SiO}_3)$  ( $\equiv \text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]$ ; hexagonal,  $P\bar{6}2c$ ) UV-luminescence has already been proven with  $\text{Ce}^{3+}$ -doped samples. *Thalenite*-type  $\text{Y}_3\text{F}[\text{Si}_3\text{O}_{10}]$  (monoclinic,  $P2_1/n$ ) can be doped with medium-size lanthanoids ( $M = \text{Sm} - \text{Er}$ ) and exhibits not only the expected visible, but also IR-luminescence. In contrast,  $\text{Er}_4\text{F}_2(\text{Si}_3\text{O}_{11})$  ( $\equiv \text{Er}_4\text{F}_2[\text{Si}_2\text{O}_7][\text{SiO}_4]$ ; triclinic,  $P\bar{1}$ ) has no analogous yttrium counterpart as host for lanthanoid dopants so far. A very promising *apatite*-type candidate contains di- and trivalent europium simultaneously:  $\text{Eu}_5\text{F}(\text{Si}_3\text{O}_{12})$  ( $\equiv (\text{Eu}^{\text{II}})_2(\text{Eu}^{\text{III}})_3\text{F}[\text{SiO}_4]_3$ ; hexagonal,  $P6_3/m$ ). Therefore it should be possible to dope isotypic samples of *i.e.*  $\text{Ba}_2\text{La}_3\text{F}[\text{SiO}_4]_3$  with both suitable di- and trivalent lanthanoid cations. From the structural point of view more or less planar  $[\text{FM}_3]^{8+}$  triangles and regular  $[\text{SiO}_4]^{4-}$  tetrahedra are present in all four examples, which occur either isolated or condensed. The cations  $[\text{FM}_3]^{8+}$  share vertices to form layers ( $\infty \{[\text{FLa}_3/3]^{2+}\}$ ) like in *tysonite*-type  $\text{LaF}_3$  or edges to build up dimers ( $\infty \{([\text{FEr}_{2/1}\text{Er}_{2/2}]^{5+})_2\}$ ) if necessary, while the anions  $[\text{SiO}_4]^{4-}$  use common corners, whenever they need to condense at all. Fluoride oxoselenates(IV) with the composition  $\text{MF}[\text{SeO}_3]$  ( $M = \text{La}, \text{Ce}, \text{Ho} - \text{Yb}$ ,  $Y$ : monoclinic,  $P2_1/c$ ;  $M = \text{Lu}$ : triclinic,  $P\bar{1}$ ) no longer exhibit a planar oxoanion such as  $[\text{CO}_3]^{2-}$ , but a  $\psi^1$ -tetrahedral  $[\text{SeO}_3]^{2-}$  unit. This pyramidal  $[\text{SeO}_3]^{2-}$  anion with a stereochemically active lone pair of electrons can serve as an extra energy reservoir due to possible s-p transitions, which may synergetically influence the f-f or f-d transitions of the lanthanoid  $M^{3+}$  cations doped into the different  $\text{LaF}[\text{SeO}_3]$ ,  $\text{YF}[\text{SeO}_3]$  and  $\text{LuF}[\text{SeO}_3]$  host lattices. Even  $\text{Gd}_3\text{F}[\text{SeO}_3]_4$  (hexagonal,  $P6_3mc$ ) might serve as a suitable host for  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$  dopants. A similar effect could be achieved in the case of rare-earth metal(III) fluoride oxomolybdates(VI) with the composition  $\text{MF}[\text{MoO}_4]$  ( $M = \text{Sm} - \text{Tm}$ ; monoclinic,  $P2_1/c$ ), since charge-transfer excitation within their isolated  $[\text{MoO}_4]^{2-}$  should also work as synergetic assist for the f-f or f-d transitions of the doping lanthanoid  $M^{3+}$  cations in their optically innocent  $\text{YF}[\text{MoO}_4]$  host. The potential of new compounds such as  $\text{La}_3\text{F}[\text{MoO}_4]_4$  (triclinic,  $P\bar{1}$ ) and  $\text{YF}[\text{Mo}_2\text{O}_7]$  (monoclinic,  $P2/c$ ) still needs to be explored.

**Ort:** Fakultät für Chemie und Mineralogie, Johannisallee 29, kl. HS 015, 04103 Leipzig

**Alle Interessenten sind zu diesem Vortrag herzlich eingeladen.**

Prof. Dr. C. Schneider  
Dekan

Die Professoren des Institutes  
für Anorganische Chemie

Nähere Informationen bei Frau Professor Dr. E. Hey-Hawkins, Tel.: 36151