On the Optical Properties of $Sr_3SiAl_{10}O_{20}$ and $Sr_3SiAl_{10}O_{20}:Mn^{4+}$

Thomas Jansen and Thomas Jüstel

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

Corresponding authors: t.jansen@fh-muenster.de ; tj@fh-muenster.de

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Background

Mn^{4+} activated luminescent materials have attracted much attention recently. In particular, alkaline earth aluminates, such as $Sr_4Al_{14}O_{25}:Mn^{4+}$ or $CaAl_{12}O_{19}:Mn^{4+}$, emit light in the red region, which can be exploited in phosphor converted LEDs. We applied a sol-gel precursor with following ceramic method in order to synthesize highly crystalline Mn^{4+} doped $Sr_3SiAl_{10}O_{20}$. The compound $Sr_3SiAl_{10}O_{20}:Mn^{4+}$ exhibits deep red photoluminescence peaking at 663 nm, which can be assigned to the $^2E_g \rightarrow {}^4A_{2g}$ intraconfigurational transition of Mn^{4+} ([Ar]3*d*^{3} configuration) within the $[MnO_6]^{8-}$ octahedra on the aluminum site in the $Sr_3SiAl_{10}O_{20}$ (Space group *C*12/*m*1) host structure. Photoluminescence (PL) properties, such as temperature dependence of the PL intensity and luminescence lifetime are presented. Furthermore, the PL intensity as function of activator concentration has been evaluated. Additionally, the band structure of the undoped host material has been treated with Density Functional Theory (DFT). The theoretical results were evaluated experimentally with diffuse UV-reflectance spectroscopy.

Structure

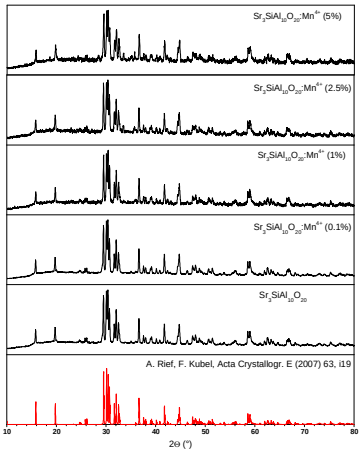

Fig. 1 X-ray (Cu Kα radiation) powder diffraction pattern of monoclinic $Sr_3SiAl_{10}O_{20}$ with various Mn^{4+} doping concentrations.

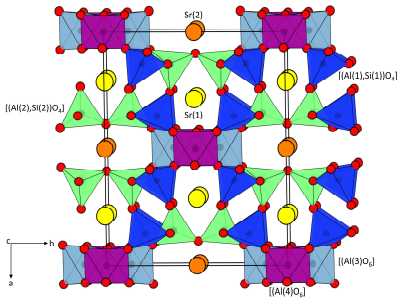

Fig. 2 Crystal structure of monoclinic $Sr_3SiAl_{10}O_{20}$.

	$Sr_3SiAl_{10}O_{20}$
Space group	*C*12/*m*1 (12)
a /nm	1.51438(18)
b /nm	1.11858(13)
c /nm	0.49018(6)
α, β, γ /°	90, 108.137(2), 90
Al(3) octahedron	
<Al-O1> /pm	194.2
<Al-O4> /pm	188.6
<Al-O5> /pm	192.5
Site symmetry	C_2
Al(4) octahedron	
<Al-O4> /pm	192.6
<Al-O5> /pm	184.9
Site symmetry	C_{2h}
Angle <Al(4)-O(5)-Al(3)> /°	96.43

Table 1: Structual data of $Sr_3SiAl_{10}O_{20}$ (According to A. Rief and F. Kubel)

Results and Discussion

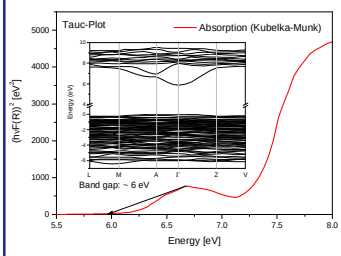

Fig. 3 Tauc plot of undoped $Sr_3SiAl_{10}O_{20}$ (derived from diffuse UV reflectance measurement). Inset shows LDA calculated band structure.

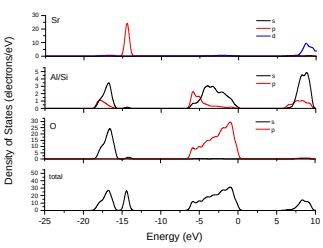

Fig. 4 The calculated DOS diagrams for $Sr_3SiAl_{10}O_{20}$. From the top: Sr, Si/Al, O partial DOS and total DOS.

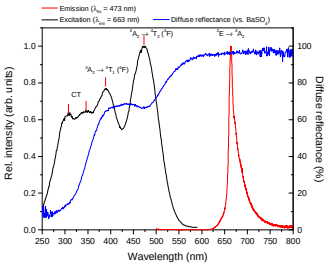

Fig. 5 Excitation, emission, and reflectance spectra of $Sr_3SiAl_{10}O_{20}:Mn^{4+}$ (0.1%) at room temperature.

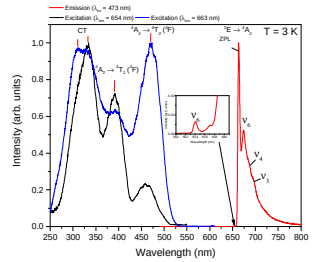

Fig. 6 Very low temperature (3 K) excitation and emission spectra of $Sr_3SiAl_{10}O_{20}:Mn^{4+}$ (0.1%). The inset shows the v_6 anti-Stokes phonon side band.

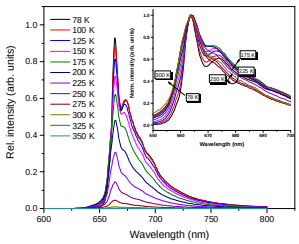

Fig. 7 Temperature-dependent emission spectra of $Sr_3SiAl_{10}O_{20}:Mn^{4+}$ (0.1%). The inset shows normalized emission spectra in the temperature range of 78 - 300 K.

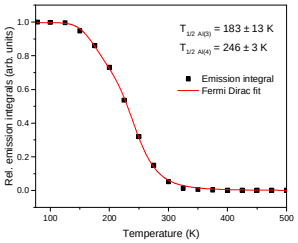

Fig. 8 Emission integrals versus temperature with a double Fermi Dirac fit in the temperature range of 300 - 500 K.

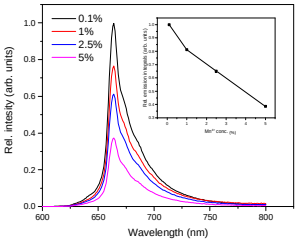

Fig. 9 Emission spectra as function of the Mn^{4+} concentration. Inset shows the drop of the emission integrals.

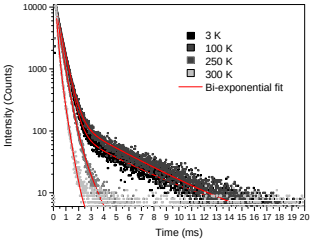

Fig. 10 Lifetime measurements with increasing temperature (Ex = 473 nm; Em = 663 nm) for exemplary chosen temperatures.

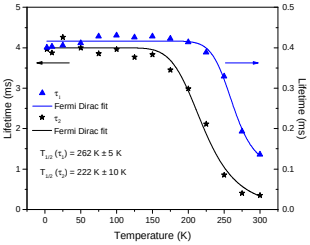

Fig. 11 Lifetime measurements with increasing temperature (Ex = 473 nm; Em = 663 nm) for exemplary chosen temperatures.

Table 2: Calculated Racah parameter

$^4A_2 \rightarrow {}^4T_2$	21276 cm^{-1}
$^4A_2 \rightarrow {}^4T_1$	25575 cm^{-1}
$^2E \rightarrow {}^4A_2$	15083 cm^{-1}
Dq	2128
B	528
C	3655
β*	0.964

- $Sr_3SiAl_{10}O_{20}:Mn^{4+}$ was successfully synthesized *via* sol-gel precursors followed by a ceramic method.
- The band structure was investigated by DFT calculations and experimentally evaluated with UV-reflectance spectroscopy.
- $Sr_3SiAl_{10}O_{20}$ shows a direct band gap at ~6 eV.
- At very low temperature (3 K) distinct PL from two different crystallographic sites can be identified.
- Unusual Racah parameter have been found, which is explained by the strong deviation of the Mn^{4+}-O^{2-}-Mn^+ bond angle from 180°.
- Weak concentration quenching up to 5% Mn^{4+} of the PL has been found with the highest PL intensity at 0.1%.
- Strong bi-sigmoidal shaped PL drop with increasing temperature.
- $Sr_3SiAl_{10}O_{20}:Mn^{4+}$ has two $T_{1/2}$ values: 183 K and 246 K.
- Lifetime measurements proof the statement, that luminescent takes place from two distinct sites with major contribution from the Al(4) site.

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