Red Emitting Phosphors $K_2Ge_4O_9:Mn^{4+}$ and $Rb_2Ge_4O_9:Mn^{4+}$

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Background

- **Luminous efficacy and CRI of Mn^{4+} comprising warm white pcLEDs are strongly influenced by choice of host:**

450 nm LED + YAG:Ce + Mn^{4+} activated phosphor

$K_2SiF_6:Mn^{4+}$ → 337 lm/W, R_a = 93 Peak emission @ 620 nm
$Mg_{14}Ge_5O_{24}:Mn^{4+}$ → 241 lm/W, R_a = 78 Peak emission @ 660 nm

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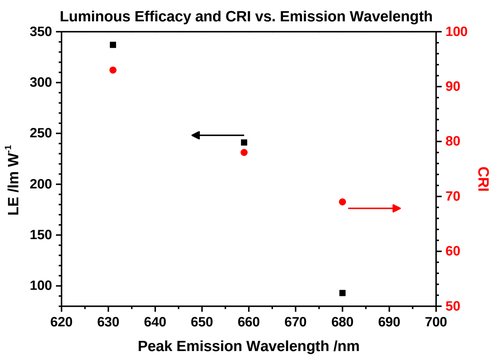

Fig. 1: LE and CRI of warm-white pcLEDs comprising various Mn^{4+} activated phosphors

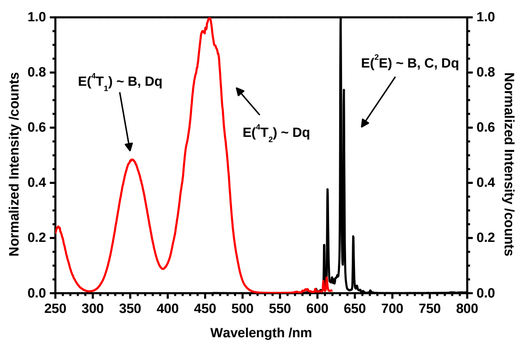

Fig. 2: Influence of Racah parameters B and C and crystal field parameter Dq on Mn^{4+} properties

Synthesis and Structure

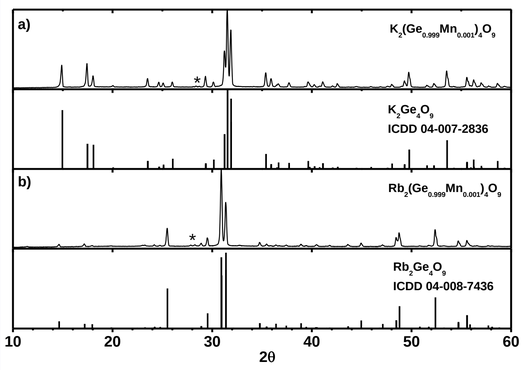

Fig. 3: XRD patterns of a) $K_2(Ge_{0.999}Mn_{0.001})_4O_9$ and b) $Rb_2(Ge_{0.999}Mn_{0.001})_4O_9$ for Cu Kα radiation

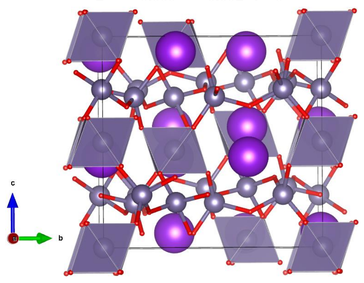

Table 1: Structural data after Redhammer, Tippelt, Acta Cryst C69 (2013) 995

	$K_2Ge_4O_9$	$Rb_2Ge_4O_9$
a/nm	1.18461	1.21008
b/nm	0.98009	0.98722
Ge1 octahedron		
< Ge–O > /pm	190.8	190.7
Angle axial–axial	180.00°	180.00°
Site symmetry	$\bar{3}$	$\bar{3}$
Ge4 octahedron		
< Ge–O3 >	188.6	189.1
< Ge–O4 >	186.5	187.0
Angle axial–axial	178.18°	178.58°
Site symmetry	3	3

- **$K_2Ge_4O_9$ and $Rb_2Ge_4O_9$ are isostructural**
- **Ge_3O_9 rings form layers connected by GeO_6 octahedra**
- **Two crystallographically distinct GeO_6 octahedra:**
  - **Ge(1) exhibits inversion symmetry**
  - **Ge(4) does not exhibit inversion symmetry**

Results and Discussion

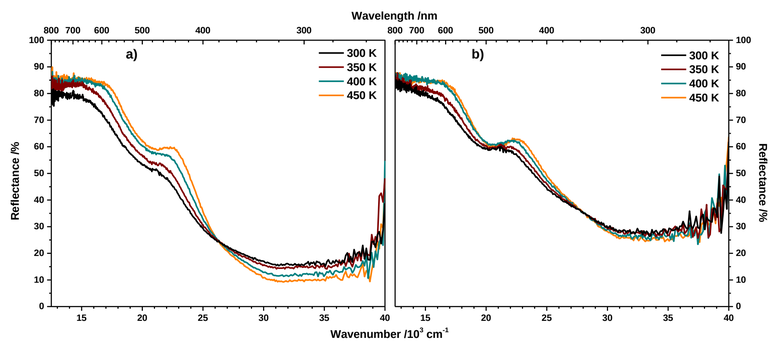

Fig. 4: Reflection spectra of a) $K_2(Ge_{0.999}Mn_{0.001})_4O_9$ and b) $Rb_2(Ge_{0.999}Mn_{0.001})_4O_9$ recorded at various temperatures.

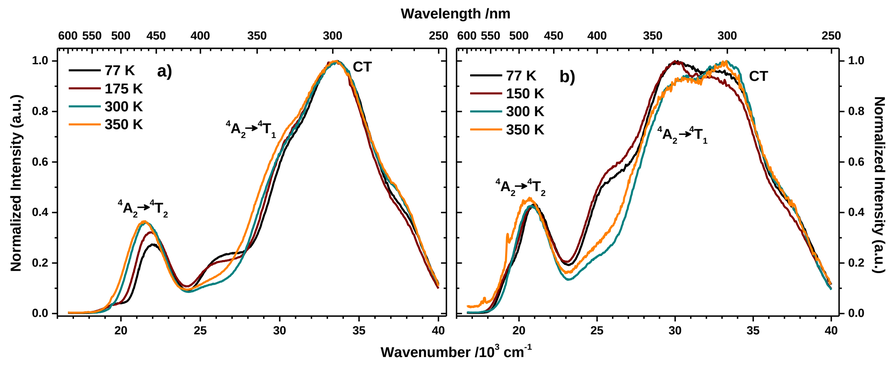

Fig. 5: Excitation spectra of a) $K_2(Ge_{0.999}Mn_{0.001})_4O_9$ and b) $Rb_2(Ge_{0.999}Mn_{0.001})_4O_9$ recorded at various temperatures.

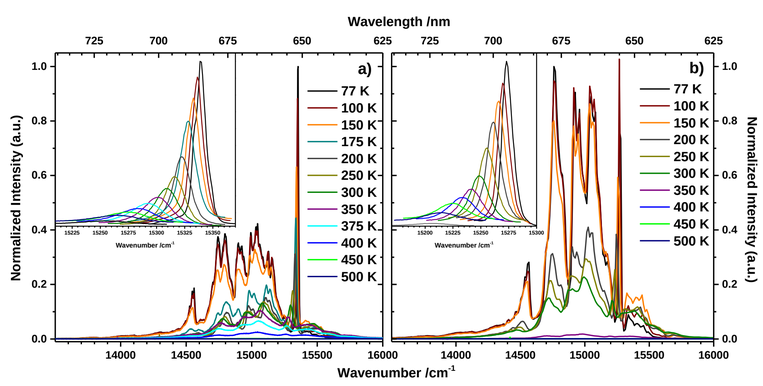

Fig. 6: Emission spectra of a) $K_2(Ge_{0.999}Mn_{0.001})_4O_9$ and b) $Rb_2(Ge_{0.999}Mn_{0.001})_4O_9$ recorded at various temperatures.

- **Significant changes of the optical properties can be observed with increasing temperature:**

- **$^4A_2 \rightarrow {}^4T_2$ transition red-shifts from 453 nm (22072 cm^{-1}) to 467 nm (21395 cm^{-1})**
- **Distance between $^4T_2$ and $^4T_1$ peak increases**
- **$^2E \rightarrow {}^4A_2$ transition ZPL blue-shifts from 652.0 nm (15339 cm^{-1}) to 655.5 nm (15256 cm^{-1})**

- **Crystal field splitting increases with increasing temperature**
- **Racah parameter B increases with increasing temperature**
- **Racah parameter C decreases with increasing temperature**

- **Increase of Dq and B can be explained by thermal expansion of the host material**
- **Decrease of C is unexpected!**

Phosphor	B /cm^{-1}	C /cm^{-1}	M-O-Mn angle
$CaZrO_3:Mn^{4+}$	650	3173	146.50 °
$SrTiO_3:Mn^{4+}$	719	2812	180.00 °
$GdAlO_3:Mn^{4+}$	600	~ 3200	156.65 °
$LaAlO_3:Mn^{4+}$	700	~ 2900	171.90 °

- **Racah parameter C can apparently be linked to M-O-Mn bond angle**
  - **Bond angles close to 180 ° result in low value of C**
  - **Racah parameter B and C do not necessarily follow the same trend**
  - **Small Mn-O distance results in a lower thermal quenching temperature**

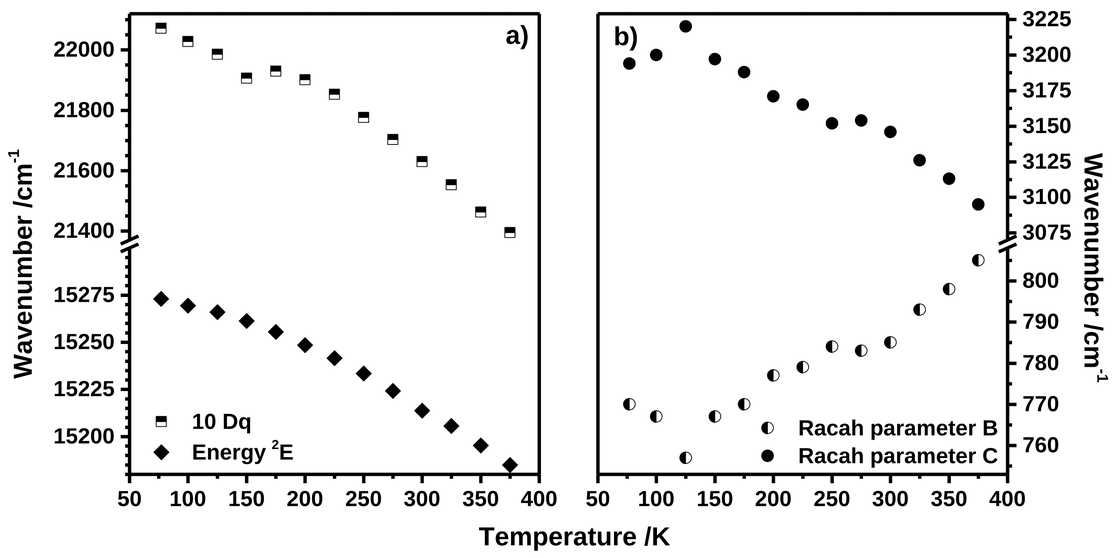

Fig. 7: a) Crystal field parameter Dq and energy of ^2E and b) Racah parameters B and C of $K_2(Ge_{0.999}Mn_{0.001})_4O_9$ depending on temperature.

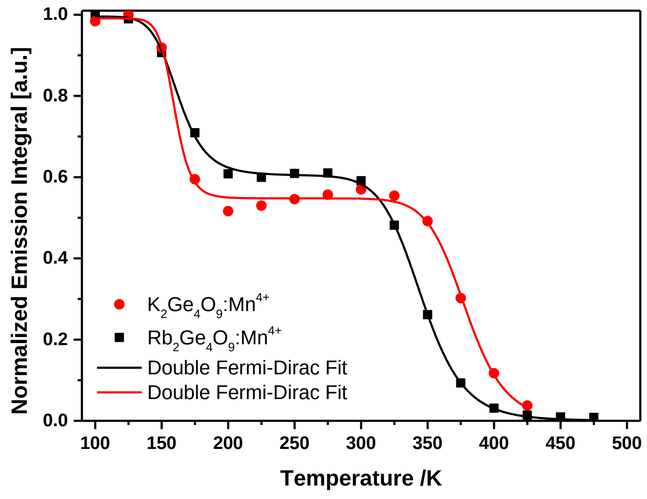

Fig. 8: Thermal quenching curves of (red) $K_2Ge_4O_9:Mn^{4+}$ (black) $Rb_2Ge_4O_9:Mn^{4+}$.

- **Bi-sigmoidal TQ-curves were observed**
- **Thermal quenching curves show strong correlation of $T_{1/2}$ to the Mn-O distance**

$K_2Ge_4O_9:Mn^{4+}$	$Rb_2Ge_4O_9:Mn^{4+}$
$T_{1/2,a}$ = 160 K	$T_{1/2,a}$ = 162 K
$T_{1/2,b}$ = 379 K	$T_{1/2,b}$ = 346 K

- **Compare to Table 1!**

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RG Tailored Optical Materials – http://www.fh-muenster.de/juestel