On the Luminescence and Energy Transfer of White Emitting $Ca_3Y_2(Si_3O_9)_2$:Ce^{3+},Mn^{2+} Phosphor

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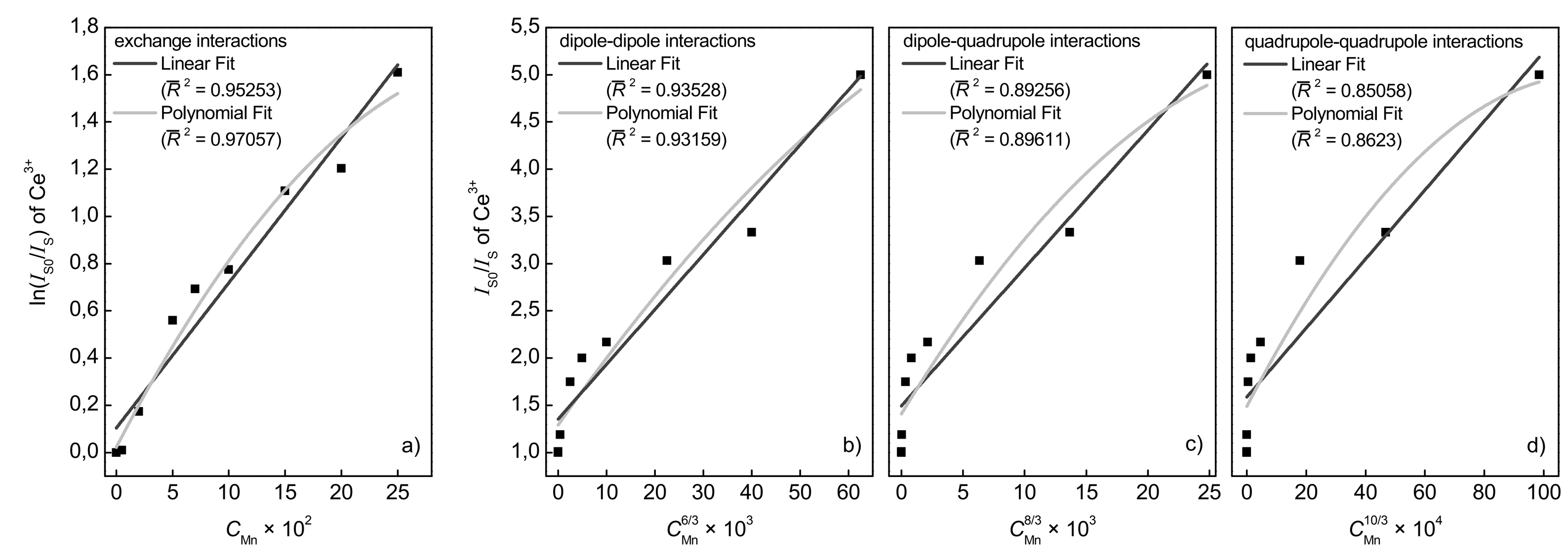
Conclusions

- Co-doped $(Ca_{1-x}Mn_x)_3(Y_{0.99}Ce_{0.01})_2(Si_3O_9)_2$ exhibits two emission bands under UV excitation, located at about 385 and 555 nm.
- Ce^{3+} ions occupy two different crystallographic sites in the host structure whereas the Mn^{2+} ions occupy three different crystallographic sites. This allegation is backed by luminescence lifetime measurements since Ce^{3+} exhibits a bi-exponential decay behavior while Mn^{2+} shows a tri-exponential decay behavior in $(Ca_{1-x}Mn_x)_3(Y_{0.99}Ce_{0.01})_2(Si_3O_9)_2$.
- The highest PL intensity was found for a Mn^{2+} concentration of $x = 0.20$.
- It was demonstrated that the ET from Ce^{3+} to Mn^{2+} is resonant type and occurs via dipole-quadrupole interaction. The critical distance between Ce^{3+} and Mn^{2+} was determined using Blasse's approach as well as the spectral overlap method and was calculated to be 8.1 and 8.8 Å, respectively.
- PL of $(Ca_{1-x}Mn_x)_3(Y_{0.99}Ce_{0.01})_2(Si_3O_9)_2$ exhibits good thermal stability. The $T_{1/2}$ value for $(Ca_{1-x}Mn_x)_3(Y_{0.99}Ce_{0.01})_2(Si_3O_9)_2$ was calculated to be 675 K. Temperature dependent PLD measurements revealed that thermal quenching in $(Ca_{1-x}Mnx)_3(Y_{0.99}Ce_{0.01})_2(Si_3O_9)_2$ is mainly caused by the Mn^{2+} ions.
- The color point of the emission of $(Ca_{1-x}Mn_x)_3(Y_{0.99}Ce_{0.01})_2(Si_3O_9)_2$ can be tuned from the blue to the yellow spectral range by increasing the Mn^{2+} concentration. Moreover, for $x = 0.05$ and 0.07, $(Ca_{1-x}Mn_x)_3(Y_{0.99}Ce_{0.01})_2(Si_3O_9)_2$ shows an emission spectrum yielding a white color point.

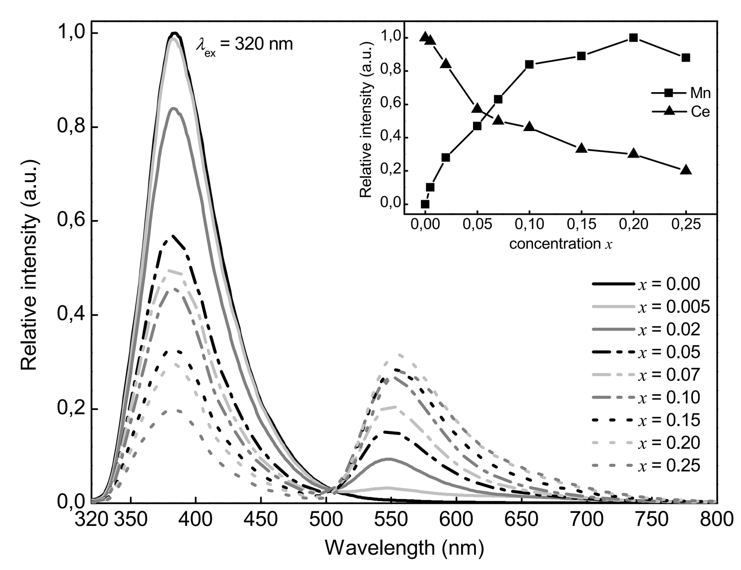
Experimental Section

- $(Ca_{1-x}Mn_x)_3(Y_{0.99}Ce_{0.01})_2(Si_3O_9)_2$ samples were synthesized by a high temperature solid state reaction.
- The samples were annealed first at 1000 °C for 2 h in air and finally sintered in BN-crucibles at 1300 °C for 8 h in reductive forming gas atmosphere.
- Phase purity was investigated using x-ray powder diffraction.
- Optical properties were investigated by recording PL spectra and PLE spectra as well as performing PLD and DR measurements.

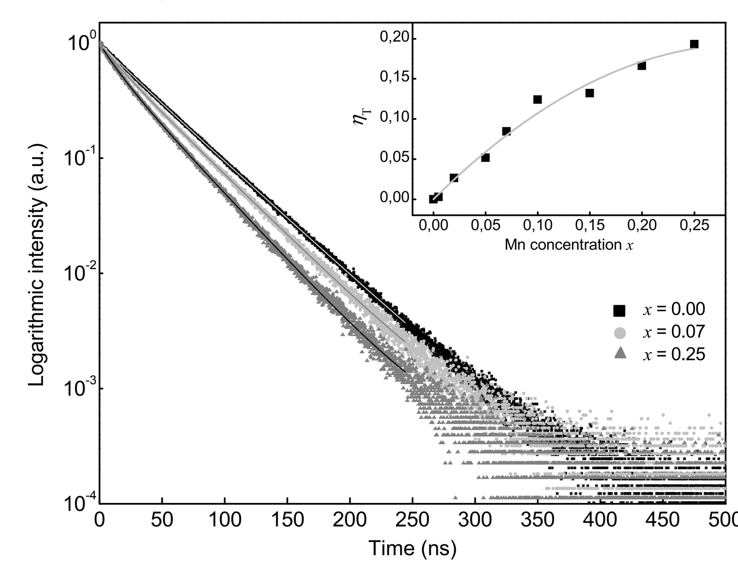
Dependence of ln(I_{s0}/I) of Ce^{3+} on C a) and dependence of I_{s0}/I of Ce^{3+} on $C^{6/3}$ b), $C^{8/3}$ c) and $C^{10/3}$ d).



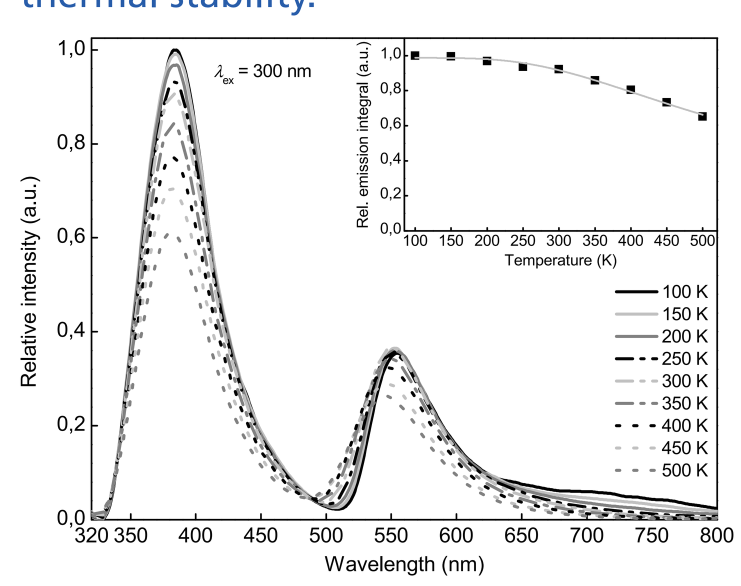
PL intensity of Ce^{3+} decreases with increasing Mn^{2+} concentration.



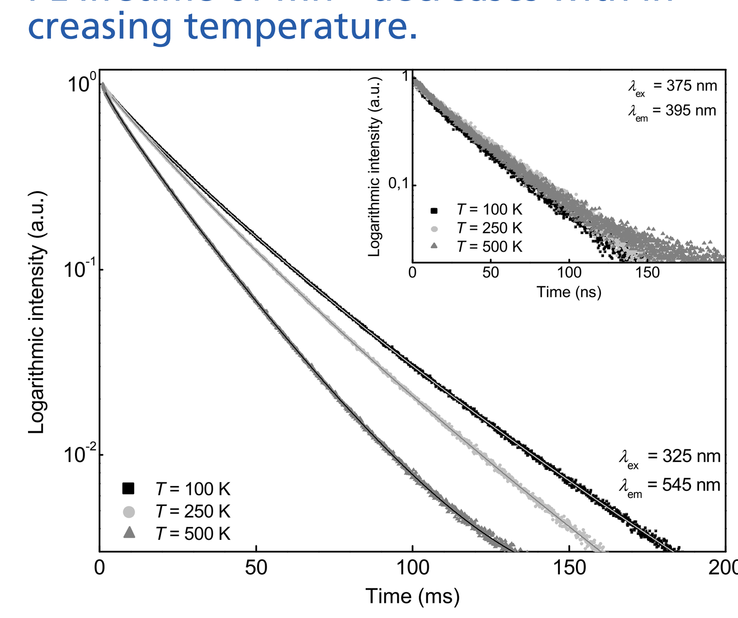
PL lifetime of Ce^{3+} decreases with increasing Mn^{2+} concentration.



PL of $Ca_3Y_2(Si_3O_9)_2$:Ce^{3+},Mn^{2+} shows good thermal stability.

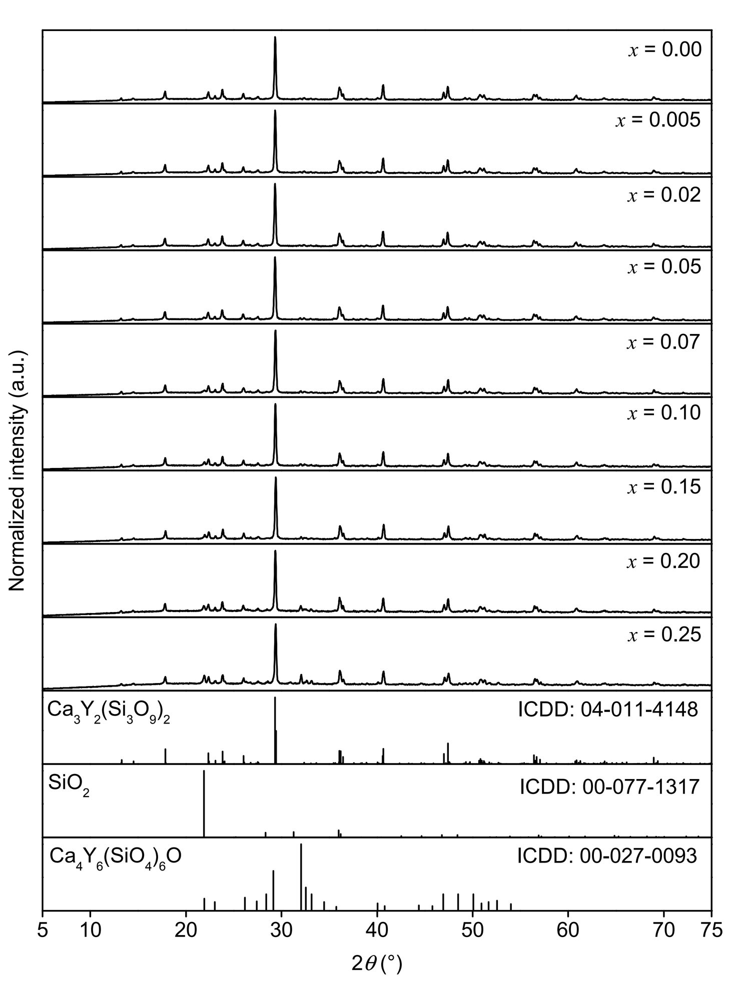


PL lifetime of Mn^{2+} decreases with increasing temperature.

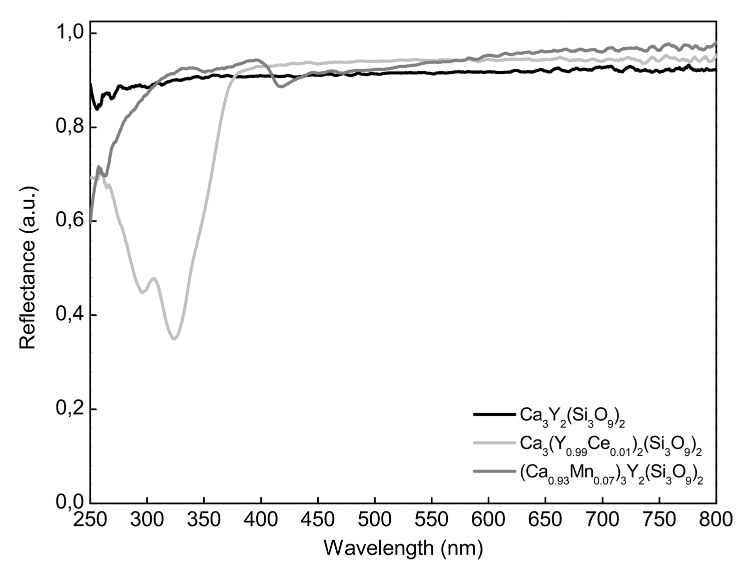


Results

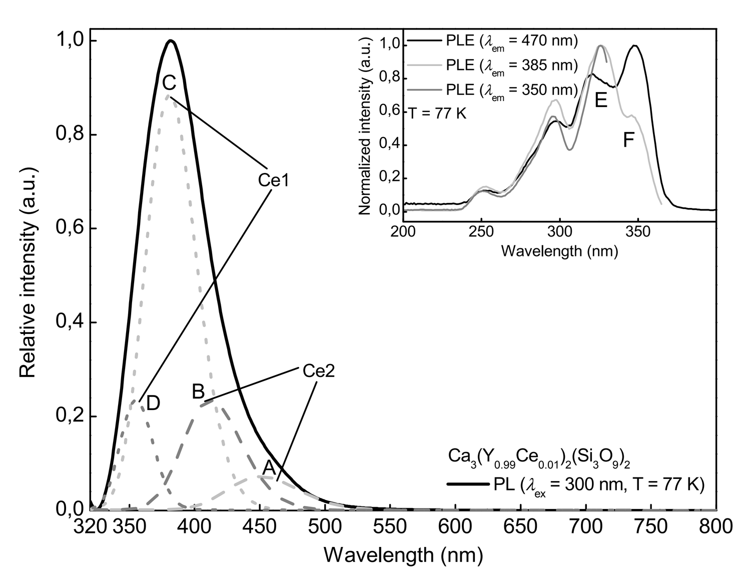
Phosphors can be obtained without impurities up to $x = 0.20$.



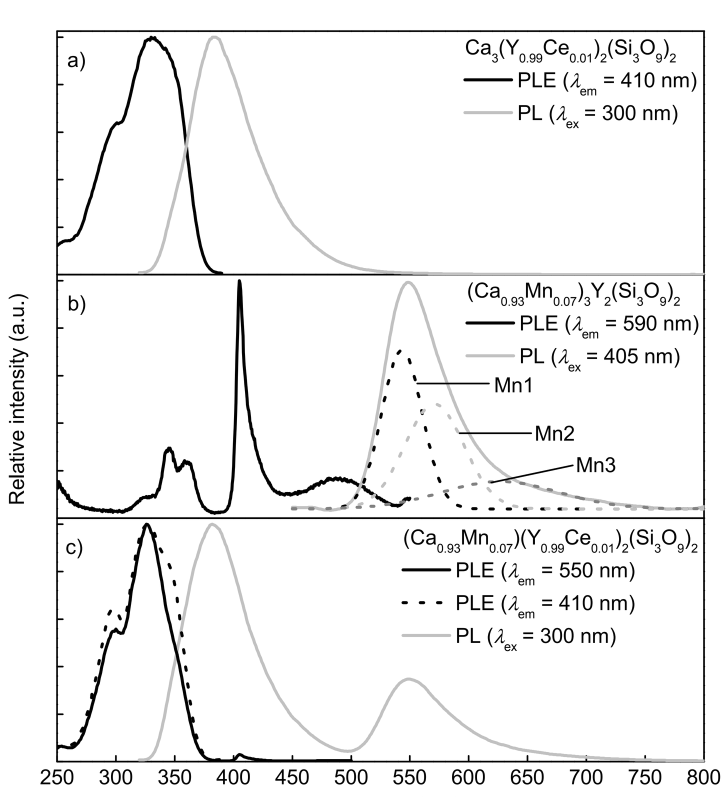
DR spectra proof the white body color of the samples.



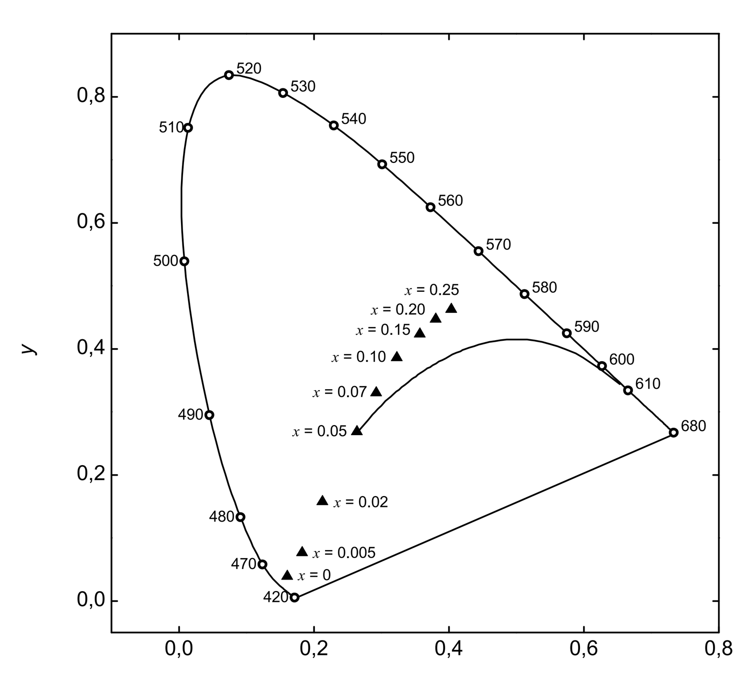
Ce^{3+} emission from two distinct sites.



PL and PLE spectra of the phosphors.



Color point can be tunend from blue to yellow.



Background

Presently most of the commercial white emitting pc-LEDs consist of a blue emitting (In,Ga)N chip and for instance $Y_3Al_5O_{12}$:Ce. These LEDs provide a high luminous efficacy due to the additive color mixing of blue primary radiation with yellow luminescence of Ce^{3+}. However, this approach suffers from a high color temperature and a low *CRI* because of the lack of radiation in the red spectral region. An obvious approach to overcome these drawbacks is the application of an UV emitting LED chip pumping a RGB phosphor blend.This radiation conversion concept provides warm and cold white emitting light sources with excellent *CRI*. Unfortunately, these systems suffer from a lack of blue emission due to the strong re-absorption of the blue light by the green and red phosphors.

Therefore, many research groups are developing single component white emitting phosphors for UV emitting LEDs on the basis of the incorporation of the ion couple Ce^{3+} and Mn^{2+} in suitable host materials. The broad emission bands in the blue and red spectral region of Ce^{3+} and Mn^{2+}, respectively, can be complementary to white light due to additive color mixing. Additionally, in many host structures Ce^{3+} exhibits a broad excitation band in the UV region due to the spin and parity allowed $[Xe]4f^1$-$[Xe]5d^1$ interconfigurational electric-dipole transition. Hence, Ce^{3+} is well appropriated for pumping by UV LEDs. Since the absorbing and emitting transitions of Mn^{2+} are spin and parity forbidden, it has to be sensitized by ET from Ce^{3+} to Mn^{2+}.

Acknowledgement

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