On the Luminescence and Energy Transfer of White Emitting Ca₃Y₂(Si₃O₉)₂:Ce³⁺,Mn²⁺ Phosphor

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Conclusions

• Co-doped (Ca₃Mnₓ)(YₓCeₓ)₂(Si₃O₉)₂ exhibits two emission bands under UV excitation, located at about 385 and 555 nm.

• Ce³⁺ ions occupy two different crystallographic sites in the host structure whereas the Mn²⁺ ions occupy three different crystallographic sites. This allegation is backed by luminescence lifetime measurements since Ce³⁺ exhibits a bi-exponential decay behavior while Mn²⁺ shows a tri-exponential decay behavior in (Ca₃Mnₓ)(YₓCeₓ)₂(Si₃O₉)₂.

• The highest PL intensity was found for a Mn²⁺ concentration of x = 0.20.

• It was demonstrated that the ET from Ce³⁺ to Mn²⁺ is resonant type and occurs via dipole-quadrupole interaction. The critical distance between Ce³⁺ and Mn²⁺ 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 (Ca₃Mnₓ)(YₓCeₓ)₂(Si₃O₉)₂ exhibits good thermal stability. The T₂ value for (Ca₃Mnₓ)(YₓCeₓ)₂(Si₃O₉)₂ was calculated to be 675 K. Temperature dependent PLD measurements revealed that thermal quenching in (Ca₃Mnₓ)(YₓCeₓ)₂(Si₃O₉)₂ is mainly caused by the Mn²⁺ ions.

• The color point of the emission of (Ca₃Mnₓ)(YₓCeₓ)₂(Si₃O₉)₂ can be tuned from the blue to the yellow spectral range by increasing the Mn²⁺ concentration. Moreover, for x = 0.05 and 0.07, (Ca₃Mnₓ)(YₓCeₓ)₂(Si₃O₉)₂ shows an emission spectrum yielding a white color point.

Experimental Section

• (Ca₃Mnₓ)(YₓCeₓ)₂(Si₃O₉)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 reducing 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.

Background

Presently most of the commercial white emitting pc-LEDs consist of a blue emitting (In,Ga)N chip and for instance Y₃Al₅O₁₂:Ce. These LEDs provide a high luminous efficacy due to the additive color mixing of blue primary radiation with yellow luminescence of Ce³⁺. 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 Ce³⁺ and Mn²⁺ in suitable host materials. The broad emission bands in the blue and red spectral region of Ce³⁺ and Mn²⁺, respectively, can be complementary to white light due to additive color mixing. Additionally, in many host structures Ce³⁺ exhibits a broad excitation band in the UV region due to the spin and parity allowed [Xe]4d⁴'[Xe]5s² interconfigurational electric-dipole transition. Hence, Ce³⁺ is well appropriated for pumping by UV LEDs. Since the absorbing and emitting transitions of Mn²⁺ are spin and parity forbidden, it has to be sensitized by ET from Ce³⁺ to Mn²⁺.

Results

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

DR spectra proof the white body color of the samples.

PL and PLE spectra of the phosphors.

PL intensity of Ce³⁺ decreases with increasing Mn²⁺ concentration.

PL lifetime of Ce³⁺ decreases with increasing Mn²⁺ concentration.

PL lifetime of Mn²⁺ decreases with increasing temperature.

Color point can be tuned from blue to yellow.

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