Supporting Information

Highly-distorted Octahedron with $C_{2v}$ Group Symmetry

Inducing Ultra-intense Zero Phonon Line in Mn$^{4+}$ Activated

$\text{Na}_2\text{WO}_2\text{F}_4$ Oxyfluoride

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Crystal field strength and Racah parameters:

The crystal-field strength ($D_q$) of Mn$^{4+}$ can be roughly estimated by the peak energy of $^4A_{2g} \rightarrow ^4T_{2g}$ transition: [1]

$$D_q = E(^4T_{2g} - ^4A_{2g}) / 10$$

(1)

Based on the peak energy difference between $^4A_{2g} \rightarrow ^4T_{1g}$ and $^4A_{2g} \rightarrow ^4T_{2g}$, the Racah parameter $B$ can be calculated by the following equation: [1]

$$\frac{D_q}{B} = \frac{15(x-8)}{(x^2-10x)}$$

(2)

where the parameter $x$ is defined as

$$x = \frac{E(^4A_{2g} \rightarrow ^4T_{1g}) - E(^4A_{2g} \rightarrow ^4T_{2g})}{D_q}$$

(3)

According to the peak energy at 10 K for Mn$^{4+}$: $^2E_g \rightarrow ^4A_{2g}$ transition, the Racah parameter $C$ is evaluated by the following equation: [1]

$$\frac{E(^2E_g \rightarrow ^4A_{2g})}{B} = \frac{3.05C}{B} - \frac{1.8B}{D_q} + 7.9$$

(4)
Temperature dependent integrated emission intensity (please find the more detailed theoretical deduction in Ref. [2]):

$S_0(T)$, representing the sum of the intensities of all possible vibronic transitions corresponding to a given electronic transition $I \rightarrow II$, can be expressed as

$$S_0(T) = \sum_i n_i \sum_f W(I_i \rightarrow II_f)$$

(5)

where $n_i$ is the number of systems in the $i$-th vibrational level of the initial electronic state and the summation over $f$. The summation over $I$ with weights $n_i$ signifies an averaging over vibrational sublevels in both zero phonon and phonon transitions.

A parameter $R$, representing an abbreviated notation for the set of all coordinates describing the vibrations, is introduced in the calculation:

$$S_0(T) = \sum_i n_i \sum_f \left| \int \psi_{II}^*(R) M(R) \psi_u(R) dR \right|^2$$

$$= \sum_i n_i \int dR \left| M(R) \right|^2 \left| \psi_u(R) \right|^2$$

(6)

where $M(R)$ is the electronic matrix element in the dipole approximation.

When the Condon approximation is considered, $M(R)=M=\text{const}$, we have

$$S_0(T) = \sum_i n_i |M|^2 \int |\psi_u(R)|^2 dR = N |M|^2 = \text{const}$$

(7)

where $N$ is the total number of systems (impurity centers in the crystal).

The obtained final result indicates that the integrated intensity of the whole spectra is independent of the distribution function $n_i$ in the Condon approximation, i.e., it does not depend on the temperature. There is a peculiar conservation of the area under the spectra curve. The drop in the ZPL intensity with increasing the temperature should be accompanied by the growth of the intensity in the vibronic band.
Table S1. Color gamut of phosphor-converted wLEDs for LCD backlights

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Green</th>
<th>Red</th>
<th>CCT (K)</th>
<th>Color gamut in CIE 1931 (% NTSC)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCFL</td>
<td>-</td>
<td>-</td>
<td>75.0</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>RGB LED</td>
<td>-</td>
<td>-</td>
<td>105.0</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>β-Sialon:Eu²⁺</td>
<td>CASN:Eu²⁺</td>
<td>8620</td>
<td>82.1</td>
<td>[4]</td>
<td></td>
</tr>
<tr>
<td>Sr₃Si₁₃Al₃O₇N₂₁:Eu²⁺</td>
<td>CASN:Eu²⁺</td>
<td>12723</td>
<td>83.8</td>
<td>[5]</td>
<td></td>
</tr>
<tr>
<td>Sr₂SiO₄:Eu²⁺</td>
<td>CASN:Eu²⁺</td>
<td>8000</td>
<td>74.7</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>Sr₂Ga₅:Eu²⁺</td>
<td>K₂SiF₄:Mn⁴⁺</td>
<td>8330</td>
<td>86.4</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>YAG:Ce³⁺</td>
<td></td>
<td>8000</td>
<td>67.9</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>CsPbBr₃</td>
<td>K₂SiF₄:Mn⁴⁺</td>
<td>-</td>
<td>102.0</td>
<td>[7]</td>
<td></td>
</tr>
<tr>
<td>CsPbBr₃</td>
<td>Na₂WO₂F₄:Mn⁴⁺</td>
<td>12123</td>
<td>107.1</td>
<td>this work</td>
<td></td>
</tr>
</tbody>
</table>
Figure S1. Luminescent decays of NWOF: $x\text{Mn}^{4+}$ with various $\text{Mn}^{4+}$ doping content

Figure S2. Schematic illustration of energy splitting of $\text{Mn}^{4+}$ under the combined effects of site symmetry lowering and spin-orbit interaction
Figure S3. Temperature dependent (a) ZPL FWHM, and (b) Huang-Rhys factor (S)

References:


