Supporting Information

Highly-distorted Octahedron with C_{2v} Group Symmetry Inducing Ultra-intense Zero Phonon Line in Mn^{4+} Activated $Na_2WO_2F_4$ Oxyfluoride

Tao Hu,[ab] Hang Lin,[*a] Yao Cheng,[a] Qingming Huang,[c] Ju Xu,[a] Yan Gao, [a]
Jiaomei Wang,[a] Yuansheng Wang[*a]

[a] CAS Key Laboratory of Design and Assembly of Functional Nanostructures, and Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences，Fuzhou, Fujian, 350002 (P. R. China);

[b] College of Materials Science and Engineering, Fujian Normal University, Fuzhou, Fujian, 350007 (P. R. China);

[c] Instrumentation Analysis and Research Center, Fuzhou University, Fuzhou, Fujian 350002 (P. R. China)

*E-mail: lingh@fjirsm.ac.cn; Tel/Fax: +86-591-63179423
*E-mail: yswang@fjirsm.ac.cn; Tel/Fax: +86-591-63179438

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]

$$D_q = E(^4T_{2g} - {}^4A_{2g})/10 \quad (1)$$

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]

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

where the parameter x is defined as

$$x = \frac{E(^4A_{2g} \rightarrow {}^4T_{1g}) - E(^4A_{2g} \rightarrow {}^4T_{2g})}{D_q} \quad (3)$$

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]

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

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→II, can be expressed as

$$S_0(\mathrm{T}) = \sum_i n_i \sum_f W(\mathrm{I}_i \rightarrow \mathrm{II}_f) \tag{5}$$

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 sublevles 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:

$$\begin{aligned} \mathrm{S}_0(\mathrm{T}) &= \sum_i n_i \sum_f \left| \int \psi^*_{\mathrm{II}f}(\mathrm{R}) \mathrm{M}(\mathrm{R}) \psi_{\mathrm{I}i}(\mathrm{R}) d\mathrm{R} \right|^2 \\ &= \sum_i n_i \int d\mathrm{R} \left| \mathrm{M}(\mathrm{R}) \right|^2 \left| \psi_{\mathrm{I}i}(\mathrm{R}) \right|^2 \end{aligned} \tag{6}$$

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

When the Condon approximation is considered, M(R)=M=const, we have

$$\mathrm{S}_0(\mathrm{T}) = \sum_i n_i \left| \mathrm{M} \right|^2 \int \left| \psi_{\mathrm{I}i}(\mathrm{R}) \right|^2 d\mathrm{R} = \mathrm{N} \left| \mathrm{M} \right|^2 = const \tag{7}$$

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

Phosphor		CCT (K)	Color gamut in CIE 1931 (% NTSC)	Ref.
Green	Red			
CCFL		-	75.0	[3]
RGB LED		-	105.0	[3]
β-Sialon:Eu^{2+}	CASN:Eu^{2+}	8620	82.1	[4]
$Sr_3Si_{13}Al_3O_2N_{21}$:Eu^{2+}	CASN:Eu^{2+}	12723	83.8	[5]
Sr_2SiO_4:Eu^{2+}	CASN:Eu^{2+}	8000	74.7	[3]
Sr_2GaS_4:Eu^{2+}	K_2SiF_4:Mn^{4+}	8330	86.4	[3]
β-Sialon:Eu^{2+}	K_2SiF_4:Mn^{4+}	8000	85.9	[6]
YAG:Ce^{3+}		8000	67.9	[3]
$CsPbBr_3$	K_2SiF_4:Mn^{4+}	-	102.0	[7]
$CsPbBr_3$	$Na_2WO_2F_4$:Mn^{4+}	12123	107.1	this work

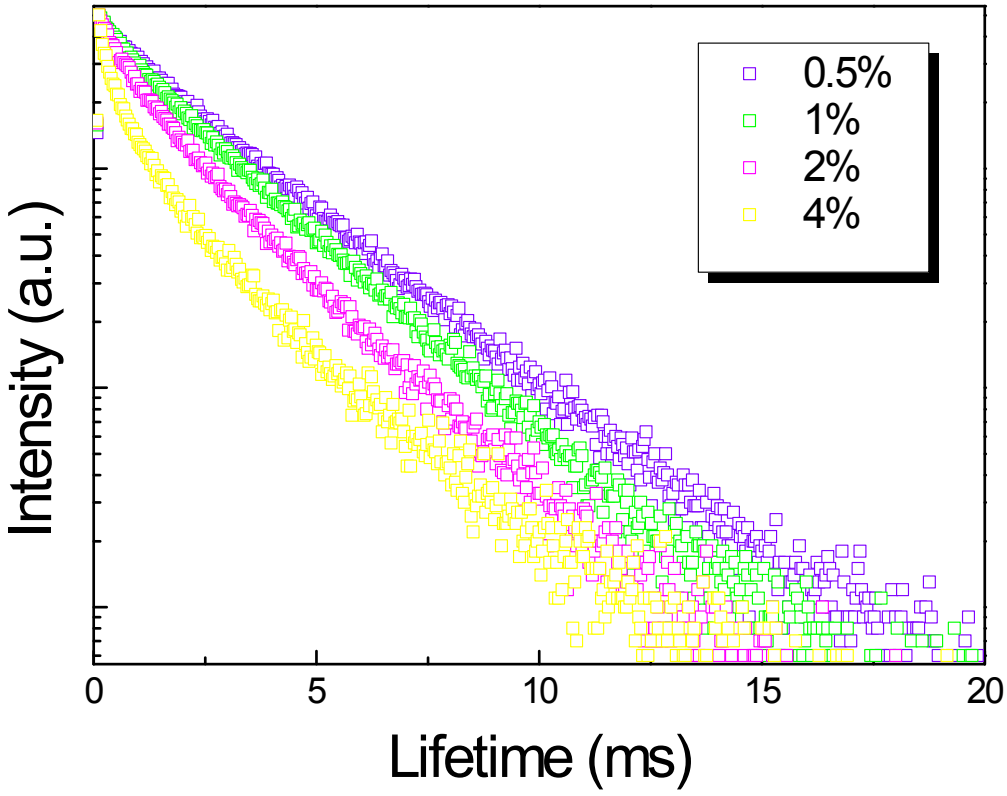

Figure S1. Luminescent decays of NWOF: xMn^{4+} with various Mn^{4+} doping content

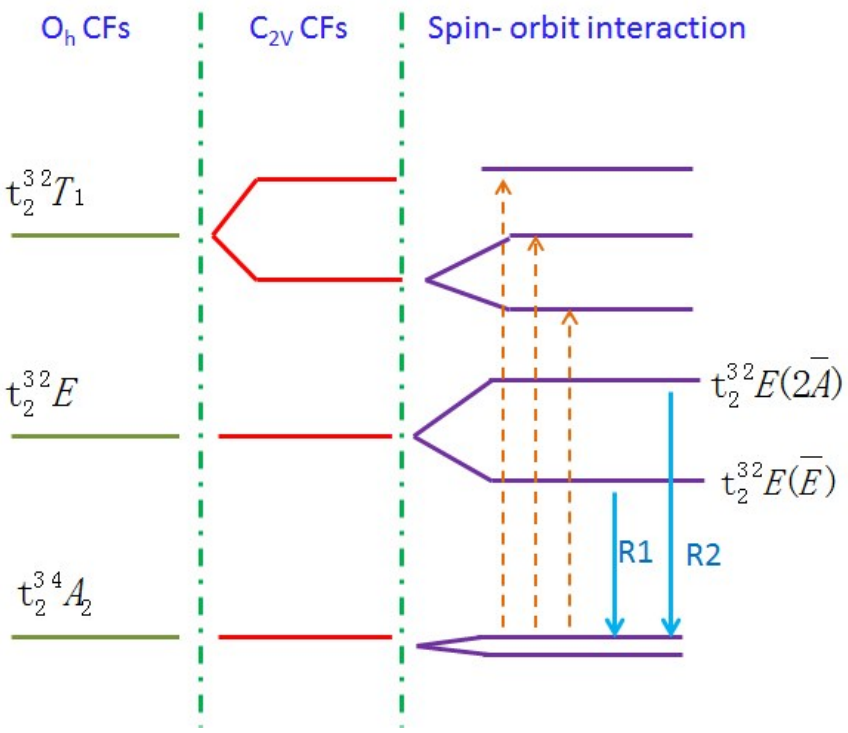

Figure S2. Schematic illustration of energy splitting of Mn^{4+} under the combined effects of site symmetry lowering and spin-orbit interaction

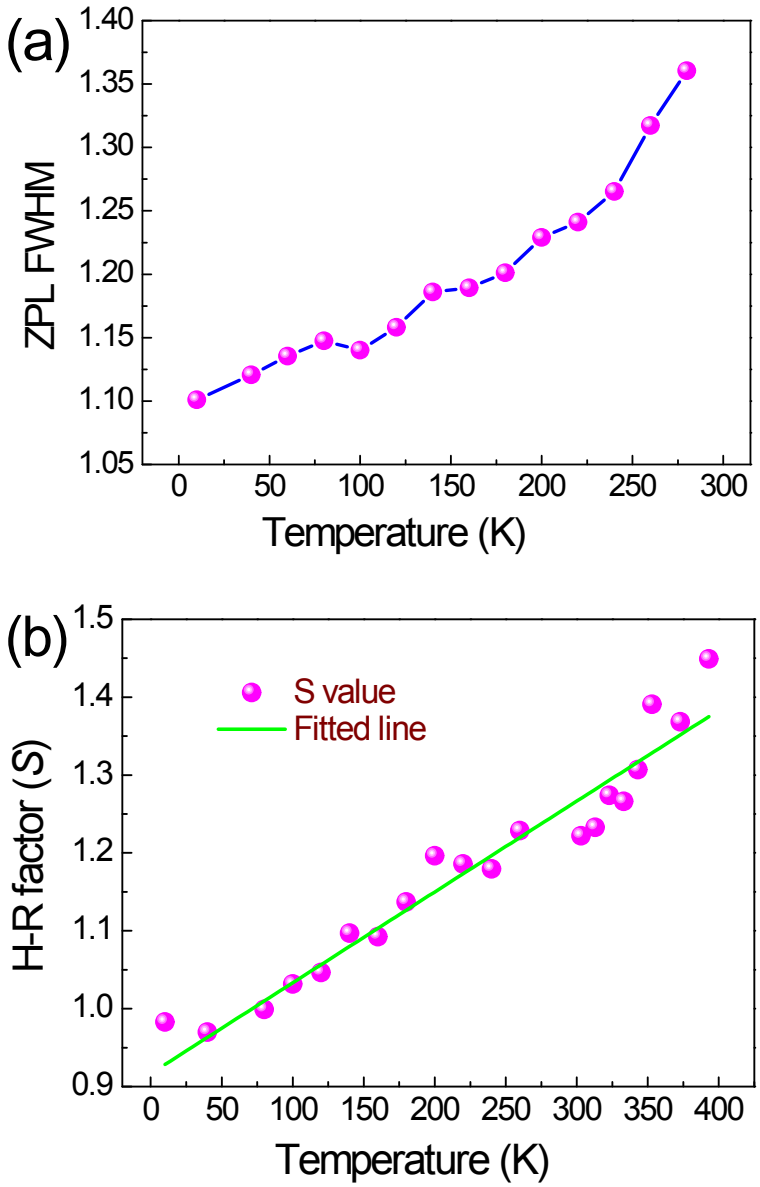

Figure S3. Temperature dependent (a) ZPL FWHM, and (b) Huang-Rhys factor (S)

References:

[1] B. Henderson, G. F. Imbusch, Optical Spectroscopy of Inorganic Solids; Clarendon Press: Oxford, U. K., 1989.

[2] K. K. Rebane, Impurity Spectra of Solids: Elementary Theory of Vibrational Structure. *Plenum Press: New York,* 1970.

[3] J. H. Oh, H. Kang, M. Ko, Y. R. Do, *Opt. Express,* 2015, **23,** A791-A804.

[4] R. J. Xie, N. Hirosaki, T. Takeda, *Appl. Phys. Express*, 2009, ***2*****,** 022401.

[5] Y. Fukuda, N. Matsuda, A. Okada, I. Mitsuishi, *Jpn. J. Appl. Phys.* 2012, ***51*****,** 122101.

[6] L. Wang, X. J. Wang, T. Kohsei, K. I. Yoshimura, M. Izumi, N. Hirosaki, R. J. Xie, *Opt. Express* 2015, **23,** 28707-28717.

[7] X. J. Zhang, H. C. Wang, A. C. Tang, S. Y. Lin, H. C. Tong, C. Y. Chen, Y. C. Lee, T. L. Tsai, R. S. Liu, *Chem. Mater.* 2016, **23,** 8493-8497.