Supporting Information

Synthesis, luminescence and energy transfer properties of Ce^{3+}/Mn^{2+} co-doped $CaCN_2$ phosphors

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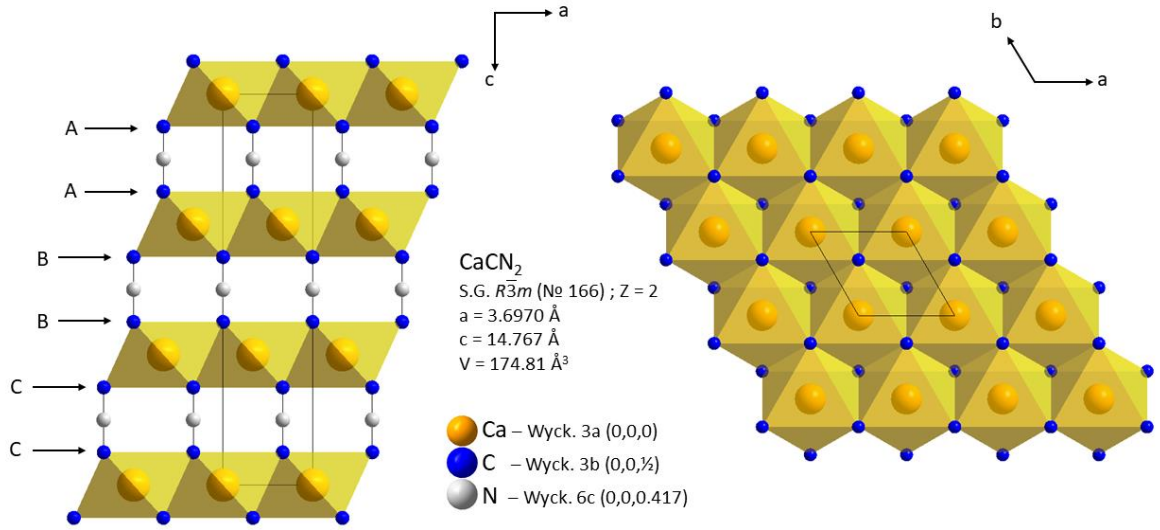

Figure S1. Crystal structure of $CaCN_2$.

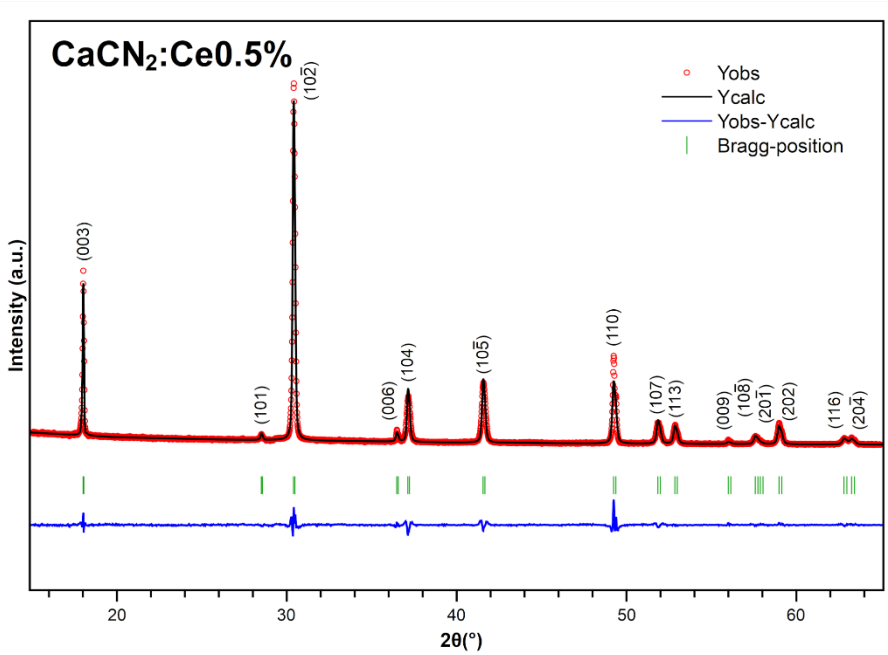

Figure S2. Final Rietveld refinement pattern for $Ca_{0.995}Ce_{0.005}CN_2$: observed (red dotted line), calculated (black full line) and difference (blue line) X-ray powder diffraction profiles from the pattern matching plot obtained with Fullprof.

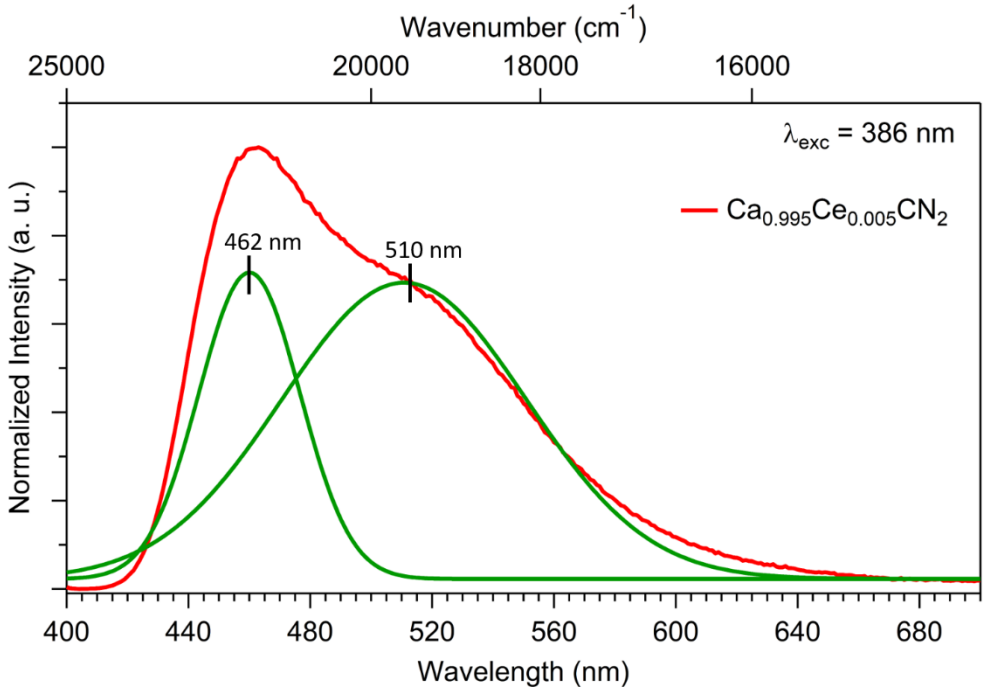

Figure S3. Deconvolution of the double emission band of $Ca_{0.995}Ce_{0.005}CN_2$.

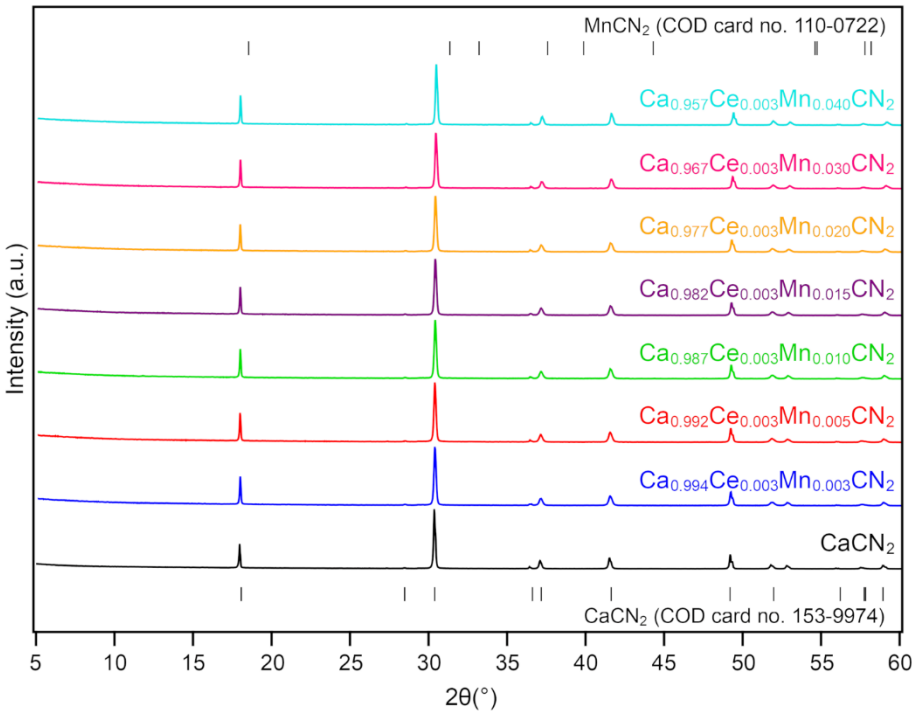

Figure S4. Powder X-ray diffraction diagrams of $Ca_{0.997-y}Ce_{0.003}Mn_yCN_2$ ($0.003 \leq y \leq 0.04$) samples.

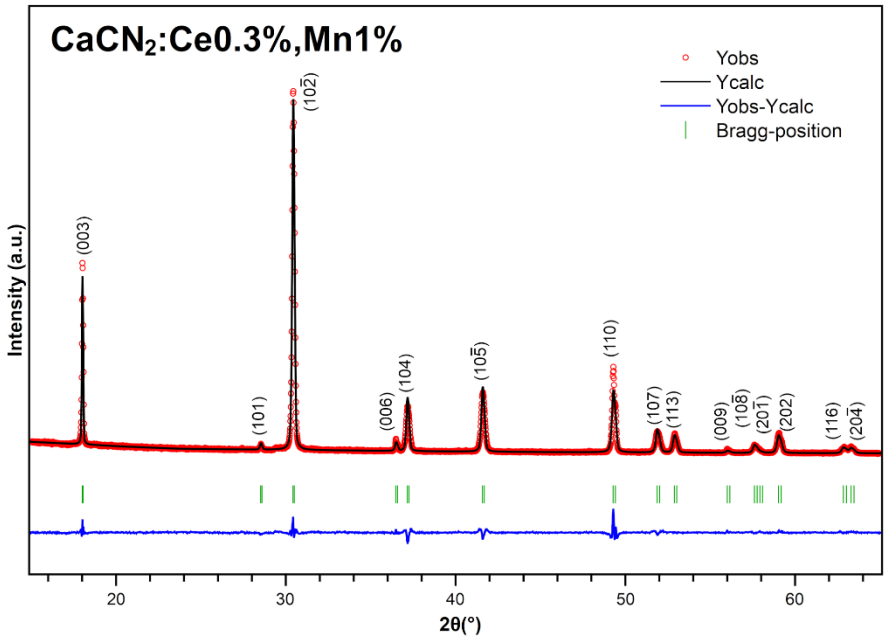

Figure S5. Final Rietveld refinement pattern for $Ca_{0.995}Ce_{0.003}Mn_{0.010}CN_2$: observed (red dotted line), calculated (black full line) and difference (blue line) X-ray powder diffraction profiles from the pattern matching plot obtained with Fullprof.

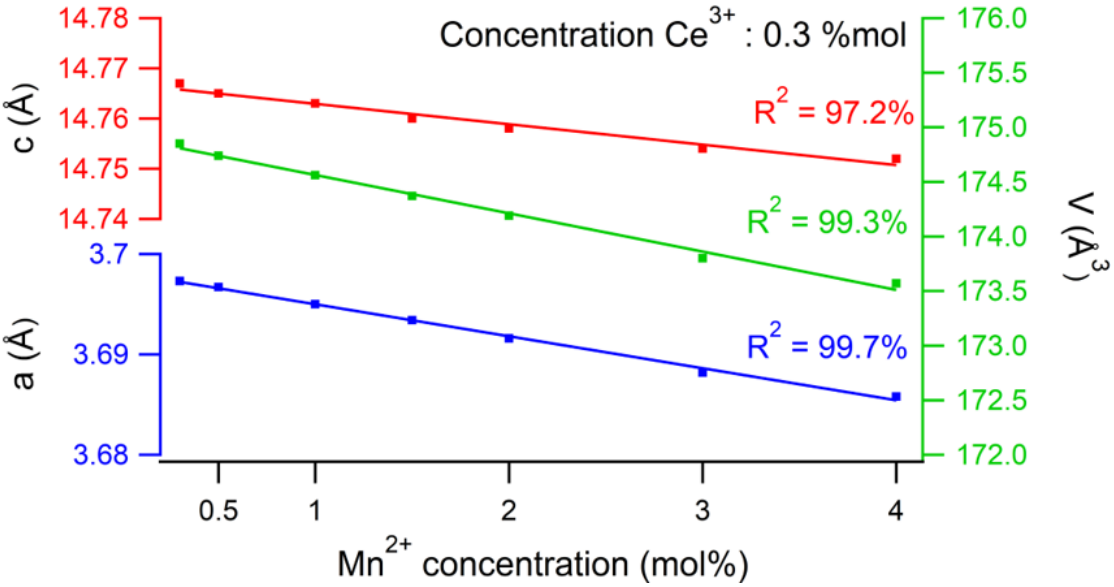

Figure S6. Evolution of the unit cell parameters (*a, c)* and cell volume (*V)* in $Ca_{0.997-y}Ce_{0.003}Mn_yCN_2$ ($0.003 \leq y \leq 0.04$) samples versus Ce^{3+} doping concentration. The linear decrease of the cell parameters (*a*, *c* and *V*) of the $Ca_{0.997-y}Ce_{0.003}Mn_yCN_2$ ($0.003 \leq y \leq 0.04$) samples follows Vegard's law and confirms the insertion of Mn^{2+} within the structure of the host material $CaCN_2$ as Mn^{2+} activator has a lower radius ($r_{Mn^{2+}}$ = 0.66 Å) than Ca^{2+} ($r_{Ca^{2+}}$ = 1.0 Å) in octahedral coordination.

Table S1. Details of the Rietveld refinement of the XRD diagrams of the $Ca_{1-x}Ce_xCN_2$ samples.

Ce^{3+} (%)	**0**	**0.3**	**0.5**	**1**	**1.5**	**2**	**3**	**4**
Space group, *Z*	Rhombohedral, $R\bar{3}m$ (No. 166), 3							
Lattice parameters								
***a* (Å)**	3.6970(1)	3.6978(2)	3.6978(2)	3.6983(1)	3.6986(2)	3.6993(1)	3.7000(2)	3.6996(3)
***c* (Å)**	14.767(1)	14.7688(9)	14.7690(9)	14.7725(8)	14.7728(8)	14.7740(9)	14.774(1)	14.775(1)
***V* (Å^3)**	174.81(2)	174.89(1)	174.90(2)	174.99(1)	175.02(2)	175.10(1)	175.17(2)	175.14(2)
Figure of merits								
R_p (%)	16.3	16.7	16.3	16.0	17.0	18.2	22.5	25.7
R_{wp} (%)	16.6	16.8	16.4	15.6	16.2	16.3	18.5	21.2
R_{exp} (%)	9.05	9.24	9.16	9.24	9.48	9.86	10.6	11.0
R_{bragg}	3.20	3.27	3.35	3.52	3.78	3.80	4.27	4.66
χ^2	3.37	3.29	3.19	2.86	2.90	2.74	3.02	3.69

Table S2. Occupied Wyckoff sites, refined atomic coordinates (in Å), isotropic atomic displacement parameters B_{iso} (in Å^2) and site occupancies of $Ca_{1-x}Ce_xCN_2$ samples (standard deviation in parentheses).

Atom	*Position*	*x*	*y*	*z*	B_{iso} (Å^2)	*Occupation*
			$Ca_{0.997}Ce_{0.003}CN_2$			
Ca	*3b*	*0*	*0*	*0*	*0.88(9)*	*0.997*
Ce	*3b*	*0*	*0*	*0*	*0.88(9)*	*0.003*
C	*3a*	*0*	*0*	*0.5*	*0.8(2)*	*1*
N	*6c*	*0*	*0*	*0.4162(3)*	*0.8(1)*	*1*
			$Ca_{0.995}Ce_{0.005}CN_2$			
Ca	*3b*	*0*	*0*	*0*	*0.87(8)*	*0.995*
Ce	*3b*	*0*	*0*	*0*	*0.83(8)*	*0.005*
C	*3a*	*0*	*0*	*0.5*	*0.9(2)*	*1*
N	*6c*	*0*	*0*	*0.4164(3)*	*0.7(1)*	*1*
			$Ca_{0.99}Ce_{0.01}CN_2$			
Ca	*3b*	*0*	*0*	*0*	*0.93(8)*	*0.99*
Ce	*3b*	*0*	*0*	*0*	*0.93(8)*	*0.01*
C	*3a*	*0*	*0*	*0.5*	*1.0(2)*	*1*
N	*6c*	*0*	*0*	*0.4162(3)*	*1.0(1)*	*1*
			$Ca_{0.985}Ce_{0.015}CN_2$			
Ca	*3b*	*0*	*0*	*0*	*0.87(9)*	*0.985*
Ce	*3b*	*0*	*0*	*0*	*0.87(9)*	*0.015*
C	*3a*	*0*	*0*	*0.5*	*0.9(2)*	*1*
N	*6c*	*0*	*0*	*0.4163(3)*	*0.9(2)*	*1*
			$Ca_{0.98}Ce_{0.02}CN_2$			
Ca	*3b*	*0*	*0*	*0*	*0.86(9)*	*0.98*
Ce	*3b*	*0*	*0*	*0*	*0.86(9)*	*0.02*
C	*3a*	*0*	*0*	*0.5*	*0.9(2)*	*1*
N	*6c*	*0*	*0*	*0.4165(3)*	*0.8(1)*	*1*
			$Ca_{0.97}Ce_{0.03}CN_2$			
Ca	*3b*	*0*	*0*	*0*	*0.8(1)*	*0.97*
Ce	*3b*	*0*	*0*	*0*	*0.8(1)*	*0.03*
C	*3a*	*0*	*0*	*0.5*	*0.6(3)*	*1*
N	*6c*	*0*	*0*	*0.4168(3)*	*0.6(2)*	*1*
			$Ca_{0.96}Ce_{0.04}CN_2$			
Ca	*3b*	*0*	*0*	*0*	*0.9(1)*	*0.96*
Ce	*3b*	*0*	*0*	*0*	*1.0(1)*	*0.04*
C	*3a*	*0*	*0*	*0.5*	*0.7(2)*	*1*
N	*6c*	*0*	*0*	*0.4165(5)*	*0.5(2)*	*1*

Table S3. Details of the Rietveld refinement of the XRD diagrams of the $Ca_{0.997-y}Ce_{0.003}Mn_yCN_2$ ($0.003 \leq y \leq 0.04$) samples.

Ce^{3+} (%)	0.3						
Mn^{2+} (%)	0.3	0.5	1	1.5	2	3	4
Space group, *Z*	Rhombohedral, $R\bar{3}m$ (No. 166), 3						
Lattice parameters							
***a* (Å)**	3.6973(2)	3.6967(2)	3.6950(2)	3.6934(2)	3.6916(2)	3.6882(1)	3.6858(1)
***c* (Å)**	14.767(1)	14.765(1)	14.762(1)	14.759(1)	14.758(1)	14.753(1)	14.753(8)
***V* (Å^3)**	174.8(2)	174.7(2)	174.5(2)	174.3(2)	174.2(2)	173.8(1)	173.6(1)
Figure of merits							
R_p (%)	17.8	17.9	17.9	17.9	18.4	18.3	16.7
R_{wp} (%)	17.5	17.7	17.8	17.6	17.7	17.2	15.4
R_{exp} (%)	11.4	11.4	11.4	11.6	11.8	11.9	11.7
R_{bragg}	3.68	3.63	3.76	3.71	3.67	4.01	3.06
χ^2	2.35	2.43	2.45	2.30	2.26	2.08	1.74

Table S4. Chemical composition and Ce^{3+}, Mn^{2+} contents of $Ca_{0.997-y}Ce_{0.003}Mn_yCN_2$ ($0.003 \leq y \leq 0.04$) samples obtained using EDS and the inert gas fusion technique. The amounts of Ce^{3+} and Mn^{2+} in all samples are in good agreement with the targeted values. The nitrogen contents are in good agreement with the calculated values while the oxygen levels do not exceed 1 wt%.

y	**Ca at%**	**Ce at%***	**Mn at%***	**Na at%**	**N_{exp} wt%**	**N_{calc} wt%**	**ΔN %****	**O wt%**
0.003	97.51	0.38 (0.38)	0.21 (0.21)	1.90	34.26	34.81	1.58	0.17
0.005	97.14	0.30 (0.31)	0.48 (0.49)	2.08	34.75	34.80	0.14	0.89
0.01	95.97	0.34 (0.35)	1.01 (1.04)	2.68	34.72	34.77	0.14	0.98
0.015	95.14	0.35 (0.36)	1.57 (1.62)	2.94	34.60	34.74	0.40	0.47
0.02	95.91	0.39 (0.40)	2.05 (2.08)	1.65	34.62	34.70	0.23	0.52
0.03	93.90	0.31 (0.32)	2.98 (3.07)	2.81	34.07	34.64	1.64	0.50
0.04	92.88	0.32 (0.33)	3.95 (4.06)	2.86	34.68	34.58	0.29	0.65

*Values without brackets represent Mn and Ce rates taking into account Na; the values in brackets are the Mn and Ce rates recalculated without considering Na.

**Deviation of the experimental nitrogen rate from the theoretical value.

Table S5. Chromaticity coordinates (x, y) of the $Ca_{0.997-y}Ce_{0.003}Mn_yCN_2$ ($0.003 \leq y \leq 0.04$) samples.

Ce^{3+} (%)	0.3							
Mn^{2+} (%)	0	0.3	0.5	1	1.5	2	3	4
Chromaticity coordinates								
x	0.19	0.23	0.25	0.30	0.35	0.39	0.44	0.46
y	0.27	0.28	0.28	0.28	0.29	0.29	0.29	0.30