Electronic Supplementary Information

Achieving excellent thermostable red emission in singly Mn^{2+}-doped near zero thermal expansion (NZTE) material $Li_2Zn_3(P_2O_7)_2$

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Table S1. Main parameters of processing and refinement for $Li_2Zn_{3-x}(P_2O_7)_2$:xMn^{2+} (LZPO:xMn^{2+}) samples.

x	Space Group	Cell parameters (Å), Cell Volume (Å^3)	R_{wp}, R_p, R_B, χ^2
0	*Pbcm*	a = 5.18166(14), b = 13.1903(3), c = 16.1267(4), V = 1102.22(5)	5.34, 4.08, 1.61, 2.5
0.01	*Pbcm*	a = 5.180246(75), b = 13.19576(14), c = 16.13265(21), V = 1102.784(24)	5.63, 4.14, 2.03, 2.68
0.1	*Pbcm*	a = 5.18097(18), b = 13.1996(4), c = 16.1532(5), V = 1104.66(6)	5.99, 4.43, 1.53, 2.51
0.2	*Pbcm*	a = 5.191046(93), b = 13.20336(21), c = 16.16339(28), V = 1107.827(33)	5.49, 4.23, 0.0, 2.07
0.3	*Pbcm*	a = 5.195002(94), b = 13.20857(21), c = 16.18377(28), V = 1110.507(33)	6.32, 4.89, 0.0, 2.35

Table S2. Fractional atomic coordinates and isotropic displacement parameters (Å^2) of

LZPO:xMn^{2+} samples.

Atom	x	y	z	B_{iso}	*Occ.*
$x = 0$					
Zn1	0.3993(3)	0.55199(15)	0.58356(16)	1.0(2)	1
Zn2	1.1524(10)	0.7570(4)	0.8381(4)	0.4(2)	0.5
Li1	1.232(12)	0.779(6)	0.846(4)	0(2)	0.5
Li2	0.125(10)	0.395(3)	0.703(3)	1.0(13)	0.5
P1	0.0895(9)	0.3587(3)	0.5054(2)	0.8(2)	1
P2	0.5644(13)	0.4521(4)	0.75	0.8(2)	1
P3	0.6578(12)	0.6588(5)	0.75	0.8(3)	1
O1	0.3026(14)	0.4357(6)	0.4982(5)	0.2(2)	1
O2	-0.0942(18)	0.3560(5)	0.4318(5)	0.2(2)	1
O3	0.229(2)	0.25	0.5	0.2(2)	1
O4	-0.0526(15)	0.3651(4)	0.5825(6)	0.2(2)	1
O5	0.4032(18)	0.4533(7)	0.6756(5)	0.2(2)	1
O6	0.7542(19)	0.5511(9)	0.75	0.2(2)	1
O7	0.4898(15)	0.6747(6)	0.6746(4)	0.2(2)	1
O8	0.888(2)	0.7261(7)	0.75	0.2(2)	1
O9	0.2582(19)	0.8591(8)	0.75	0.2(2)	1
$x = 0.01$					
Zn1	0.39916(28)	0.55236(12)	0.58363(12)	1.00(13)	1
Zn2	0.15391(68)	0.75683(29)	0.83927(25)	0.20(15)	0.5
Li1	0.2520(82)	0.7764(35)	0.8413(31)	0.2(13)	0.5
Li2	0.0501(80)	0.3854(23)	0.7073(21)	0.20(85)	0.5
P1	0.08720(68)	0.35830(22)	0.50482(18)	0.63(14)	1
P2	0.56426(97)	0.45056(33)	0.75	0.47(16)	1
P3	0.65483(95)	0.66205(35)	0.75	0.91(18)	1
O1	0.3022(12)	0.43640(44)	0.49778(40)	0.24(13)	1
O2	0.9015(13)	0.35675(39)	0.43166(40)	0.24(13)	1
O3	0.2348(16)	0.25	0.5	0.24(13)	1
O4	0.9558(12)	0.36462(35)	0.58454(48)	0.24(13)	1
O5	0.4036(14)	0.44957(50)	0.67382(39)	0.24(13)	1
O6	0.7486(15)	0.55276(71)	0.75	0.24(13)	1
O7	0.4908(12)	0.67625(44)	0.67239(34)	0.24(13)	1
O8	0.8824(19)	0.72816(56)	0.75	0.24(13)	1
O9	0.2560(18)	0.86302(64)	0.75	0.24(13)	1
$x = 0.1$					
Zn1	0.3993(4)	0.55181(18)	0.5833(2)	1.0(3)	1
Zn2	1.1565(9)	0.7556(4)	0.8375(3)	0.2(3)	0.5
Li1	1.236(11)	0.806(5)	0.856(4)	0.2(18)	0.5
Li2	0.085(13)	0.390(4)	0.703(3)	0.2(14)	0.5
P1	0.0888(11)	0.3591(3)	0.5054(3)	0.7(3)	1
P2	0.5655(16)	0.4521(5)	0.75	1.0(3)	1
P3	0.6626(15)	0.6595(6)	0.75	0.7(3)	1
O1	0.3075(18)	0.4371(7)	0.4995(6)	0.2(3)	1

O2	-0.091(2)	0.3528(6)	0.4338(6)	0.2(3)	1
O3	0.226(2)	0.25	0.5	0.2(3)	1
O4	-0.0549(19)	0.3647(5)	0.5821(8)	0.2(3)	1
O5	0.406(2)	0.4524(8)	0.6773(6)	0.2(3)	1
O6	0.756(2)	0.5507(11)	0.75	0.2(3)	1
O7	0.4921(18)	0.6732(7)	0.6739(5)	0.2(3)	1
O8	0.889(3)	0.7230(9)	0.75	0.2(3)	1
O9	0.259(2)	0.8586(9)	0.75	0.2(3)	1
$x = 0.2$					
Zn1	0.39926(31)	0.55137(13)	0.58381(14)	1.00(21)	1
Zn2	0.14769(89)	0.75708(42)	0.83921(32)	0.20(23)	0.5
Li1	0.235(11)	0.7650(55)	0.8424(39)	0.2(19)	0.5
Li2	0.2363(82)	0.4308(29)	0.7014(23)	1.0(14)	0.5
P1	0.08838(75)	0.35849(25)	0.50465(19)	0.43(22)	1
P2	0.5688(12)	0.45206(37)	0.75	0.52(23)	1
P3	0.6518(10)	0.66121(40)	0.75	0.36(24)	1
O1	0.3027(13)	0.43465(52)	0.49828(43)	0.20(21)	1
O2	0.9102(15)	0.35866(44)	0.43107(44)	0.20(21)	1
O3	0.2338(18)	0.25	0.5	0.20(21)	1
O4	0.9575(13)	0.36479(39)	0.58374(51)	0.20(21)	1
O5	0.4144(16)	0.45596(58)	0.67285(46)	0.20(21)	1
O6	0.7514(17)	0.55119(81)	0.75	0.20(21)	1
O7	0.4872(13)	0.67560(53)	0.67292(38)	0.20(21)	1
O8	0.8855(20)	0.72985(64)	0.75	0.20(21)	1
O9	0.2493(16)	0.85422(71)	0.75	0.20(21)	1
$x = 0.30$					
Zn1	0.39951(34)	0.55071(14)	0.58368(15)	1.00(21)	1
Zn2	0.1478(11)	0.75751(47)	0.83948(37)	0.20(24)	0.5
Li1	0.227(12)	0.7693(60)	0.8443(45)	0.2(22)	0.5
Li2	0.2196(86)	0.4256(32)	0.7012(26)	1.0(15)	0.5
P1	0.08907(81)	0.35803(27)	0.50466(21)	0.20(23)	1
P2	0.5663(13)	0.45126(41)	0.75	0.76(25)	1
P3	0.6537(11)	0.66010(43)	0.75	0.61(25)	1
O1	0.2958(14)	0.43320(56)	0.49858(48)	0.20(21)	1
O2	0.9135(16)	0.35626(50)	0.43281(48)	0.20(21)	1
O3	0.2324(20)	0.25	0.5	0.20(21)	1
O4	0.9545(15)	0.36233(44)	0.58227(57)	0.20(21)	1
O5	0.4132(18)	0.45273(64)	0.67374(50)	0.20(21)	1
O6	0.7460(18)	0.54991(89)	0.75	0.20(21)	1
O7	0.4845(15)	0.67532(57)	0.67228(41)	0.20(21)	1
O8	0.8811(22)	0.73398(71)	0.75	0.20(21)	1
O9	0.2455(18)	0.85927(80)	0.75	0.20(21)	1

Table S3. Main bond lengths (Å) of LZPO:xMn^{2+} samples.

$x = 0$			
Zn1—O1	2.1210(82)	Zn1—O1^{i}	2.0373(78)
Zn1—O2^{ii}	2.0083(85)	Zn1—O5	1.9743(89)
Zn1—O7	2.2350(76)	Zn2—O2^{iii}	2.1438(94)
Zn2—O4^{iv}	1.9849(95)	Zn2—O7^{v}	2.0680(93)
Zn2—O8	2.0153(93)	Zn2—O9^{vi}	2.0329(95)
Li1—P1^{iv}	3.102(65)	Li1—P2^{vii}	2.953(73)
Li1—P3^{vi}	3.127(67)	Li1—O2^{iii}	2.365(73)
Li1—O3^{iii}	3.467(64)	Li1—O4^{iv}	1.866(70)
Li1—O5^{vii}	2.996(73)	Li1—O7^{vi}	3.364(67)
Li1—O7^{v}	1.946(71)	Li1—O8	2.461(65)
Li1—O9^{vi}	1.879(69)	Li2—P1	3.227(48)
Li2—P2^{viii}	3.095(51)	Li2—P2	2.515(50)
Li2—P3^{ix}	3.398(42)	Li2—O1	3.470(49)
Li2—O4	2.186(49)	Li2—O5	1.692(50)
Li2—O5^{x}	2.549(49)	Li2—O6^{viii}	2.916(47)
Li2—O8^{ix}	2.354(41)	Li2—O9^{xi}	2.177(51)
Li2—O9^{ix}	3.318(52)	P1—O1	1.5047(87)
P1—O2	1.5218(94)	P1—O3	1.6080(62)
P1—O4	1.4475(99)	P2—O5	1.4620(93)
P2—O6	1.634(12)	P2—O9^{ix}	1.532(11)
P3—O6	1.505(13)	P3—O7	1.5100(78)
P3—O8	1.486(11)		
$x = 0.01$			
Zn1—O1^{xii}	2.0347(65)	Zn1—O1^{xiii}	2.1241(63)
Zn1—O2^{xii}	1.9811(63)	Zn1—O5^{xiii}	1.9893(66)
Zn1—O7^{xiii}	2.2245(59)	Zn2—O2^{iii}	2.1331(70)
Zn2—O4^{iv}	1.9639(72)	Zn2—O7^{x}	2.0522(70)
Zn2—O8^{xiv}	2.0482(78)	Zn2—O9^{x}	2.0778(73)
Li1—P1^{xv}	3.227(47)	Li1—P2^{iv}	2.890(46)
Li1—P3^{x}	2.966(45)	Li1—O2^{iii}	2.417(47)
Li1—O4^{iv}	1.986(47)	Li1—O5^{iv}	2.909(45)
Li1—O7^{x}	1.823(44)	Li1—O7^{xiii}	3.271(48)
Li1—O8^{xiv}	2.498(46)	Li1—O9^{x}	1.864(48)
Li2—P1^{xiii}	3.291(33)	Li2—P2^{xiv}	2.747(40)
Li2—P2^{x}	2.882(40)	Li2—P3^{ix}	3.390(33)
Li2—O4^{xiv}	3.404(34)	Li2—O4^{xvi}	2.058(35)
Li2—O5^{x}	2.783(37)	Li2—O5^{xvi}	3.496(41)
Li2—O5^{xiii}	2.088(39)	Li2—O6^{xiv}	2.791(35)
Li2—O8^{ix}	2.214(31)	Li2—O9^{xi}	1.753(40)
P1—O1^{xiii}	1.5216(68)	P1—O2^{xvi}	1.5227(72)
P1—O3^{xvii}	1.6226(49)	P1—O4^{xvi}	1.4575(80)
P2—O5^{x}	1.4843(71)	P2—O6^{x}	1.6524(99)
P2—O9^{ix}	1.4836(99)	P3—O6^{x}	1.521(10)
P3—O7^{x}	1.5247(63)	P3—O8^{x}	1.466(10)

$x = 0.1$			
Zn1—O1	2.0859(98)	Zn1—O1^{i}	2.0292(98)
Zn1—O2^{ii}	2.0525(97)	Zn1—O5	2.007(10)
Zn1—O7	2.2226(91)	Zn2—O2^{iii}	2.140(10)
Zn2—O4^{iv}	2.009(11)	Zn2—O7^{v}	2.059(10)
Zn2—O8	2.025(11)	Zn2—O9^{vi}	2.0317(97)
Li1—P1^{iv}	2.887(62)	Li1—P2^{vii}	2.776(64)
Li1—P3^{vi}	3.399(62)	Li1—O2^{iii}	2.556(65)
Li1—O3^{iii}	3.418(61)	Li1—O4^{iv}	1.574(63)
Li1—O5^{vii}	2.732(62)	Li1—O7^{v}	2.250(63)
Li1—O8	2.713(62)	Li1—O9^{vi}	1.851(64)
Li2—P1	3.217(48)	Li2—P2^{viii}	2.914(65)
Li2—P2	2.728(65)	Li2—P3^{ix}	3.397(55)
Li2—O4	2.109(52)	Li2—O5	1.901(64)
Li2—O5^{x}	2.680(57)	Li2—O6^{viii}	2.825(59)
Li2—O8^{ix}	2.335(53)	Li2—O9^{xi}	1.981(65)
P1—O1	1.533(10)	P1—O2	1.487(11)
P1—O3	1.6083(63)	P1—O4	1.447(13)
P2—O5	1.435(11)	P2—O6	1.633(15)
P2—O9^{ix}	1.532(13)	P3—O6	1.515(16)
P3—O7	1.5245(96)	P3—O8	1.441(16)
$x = 0.2$			
Zn1—O1^{xii}	2.0465(70)	Zn1—O1^{xiii}	2.1301(71)
Zn1—O2^{xii}	2.0123(73)	Zn1—O5^{xiii}	1.9142(78)
Zn1—O7^{xiii}	2.2301(69)	Zn2—O2^{iii}	2.1517(84)
Zn2—O4^{iv}	1.9676(85)	Zn2—O7^{x}	2.0741(83)
Zn2—O8^{xiv}	2.0151(87)	Zn2—O9^{x}	2.0005(83)
Li1—P1^{xv}	3.233(63)	Li1—P2^{iv}	3.060(68)
Li1—P3^{x}	2.964(62)	Li1—O2^{iii}	2.299(67)
Li1—O4^{iv}	2.039(66)	Li1—O5^{iv}	3.119(68)
Li1—O7^{x}	1.780(64)	Li1—O7^{xiii}	3.257(63)
Li1—O8^{xiv}	2.395(60)	Li1—O9^{x}	1.903(67)
Li2—P1^{xiii}	3.408(37)	Li2—P2^{x}	1.917(42)
Li2—O1^{xiii}	3.301(37)	Li2—O4^{xvi}	2.543(39)
Li2—O5^{x}	2.257(38)	Li2—O5^{xiii}	1.085(42)
Li2—O6^{xiv}	3.078(42)	Li2—O6^{x}	3.208(42)
Li2—O8^{ix}	2.838(39)	Li2—O9^{xi}	2.827(42)
Li2—O9^{ix}	2.961(42)	P1—O1^{xiii}	1.5031(77)
P1—O2^{xvi}	1.5066(81)	P1—O3^{xvii}	1.6209(55)
P1—O4^{xvi}	1.4500(85)	P2—O5^{x}	1.4832(84)
P2—O6^{x}	1.616(11)	P2—O9^{ix}	1.600(10)
P3—O6^{x}	1.541(11)	P3—O7^{x}	1.5226(70)
P3—O8^{x}	1.514(11)		
$x = 0.3$			
Zn1—O1^{xii}	2.0791(77)	Zn1—O1^{xiii}	2.1438(78)
Zn1—O2^{xii}	2.0555(79)	Zn1—O5^{xiii}	1.9504(85)

Zn1—O7^{xiii}	2.2271(74)	Zn2—O2^{iii}	2.1543(94)
Zn2—O4^{iv}	1.9501(97)	Zn2—O7^{x}	2.0674(96)
Zn2—O8^{xiv}	2.0281(98)	Zn2—O9^{x}	2.0399(95)
Li1—P1^{xv}	3.169(71)	Li1—P2^{iv}	3.042(75)
Li1—P3^{x}	3.053(69)	Li1—O2^{iii}	2.309(75)
Li1—O3^{xviii}	3.479(68)	Li1—O4^{iv}	1.952(73)
Li1—O5^{iv}	3.073(73)	Li1—O7^{x}	1.844(71)
Li1—O7^{xiii}	3.328(72)	Li1—O8^{xiv}	2.403(68)
Li1—O9^{x}	1.936(75)	Li2—P1^{xiii}	3.372(42)
Li2—P2^{x}	1.995(44)	Li2—O1^{xiii}	3.304(42)
Li2—O4^{xvi}	2.509(43)	Li2—O5^{x}	2.288(43)
Li2—O5^{xiii}	1.156(45)	Li2—O6^{xiv}	3.061(44)
Li2—O6^{x}	3.286(45)	Li2—O8^{ix}	2.702(43)
Li2—O9^{xi}	2.688(45)	Li2—O9^{ix}	3.018(45)
P1—O1^{xiii}	1.4659(83)	P1—O2^{xvi}	1.4780(88)
P1—O3^{xvii}	1.6112(60)	P1—O4^{xvi}	1.4385(96)
P2—O5^{x}	1.4683(92)	P2—O6^{x}	1.602(12)
P2—O9^{ix}	1.559(11)	P3—O6^{x}	1.532(12)
P3—O7^{x}	1.5476(77)	P3—O8^{x}	1.532(12)

Symmetry codes: (i) -x+1, -y+1, -z+1; (ii) -x, -y+1, -z+1; (iii) -x+1, -y+1, z+1/2; (iv) -x+1, y+1/2, -z+3/2; (v) x+1, y, -z+3/2; (vi) x+1, y, z; (vii) -x+2, y+1/2, -z+3/2; (viii) x-1, y, z; (ix) -x+1, y+1/2, -z+3/2; (x) x, y, -z+3/2; (xi) -x, y+1/2, -z+3/2; (xii) x+1, y+1, z+1; (xiii) -x, -y, -z; (xiv) x-1, y, -z+3/2; (xv) -x, y+1/2, -z+3/2; (xvi) -x-1, -y, -z; (xvii) x, -y+1/2, -z+1; (xviii) -x, -y+1, z+1/2.

Table S4. The emission peak position and corresponding lifetime of LZPO:xMn^{2+} (x = 0.01-0.5) samples fitted by a second-order exponential function.

x	Emission peak position (nm)	Fitting constants		Lifetime (ms)		
	P	A1	A2	τ_1	τ_2	τ
0.01	636	518.8144	2922.971	20.29	41.72	40.02
0.05	642	589.1242	4111.909	11.80	39.60	38.46
0.1	651	913.6996	3859.072	11.11	37.80	36.07
0.2	666	1685.376	3397.359	9.77	32.13	29.19
0.3	672	1787.116	3334.888	8.20	26.60	23.99
0.5	672	2215.139	2926.589	4.76	18.35	16.12

Table S5. The emission peak position fitted by Gaussian method and corresponding lifetime of LZPO:xMn^{2+} samples.

x	Emission peak position (nm)			Lifetime (ms)		
	P	P1	P2	τ_P	τ_{P1}	τ_{P2}
0.01	636	628	680	40.02	40.13	38.73
0.05	642	633	684	38.46	38.39	37.96
0.1	651	642	688	36.07	36.57	36.58
0.2	666	654	698	29.19	28.90	29.61
0.3	672	654	700	23.99	23.86	24.59
0.5	672	654	700	16.12	16.01	16.63

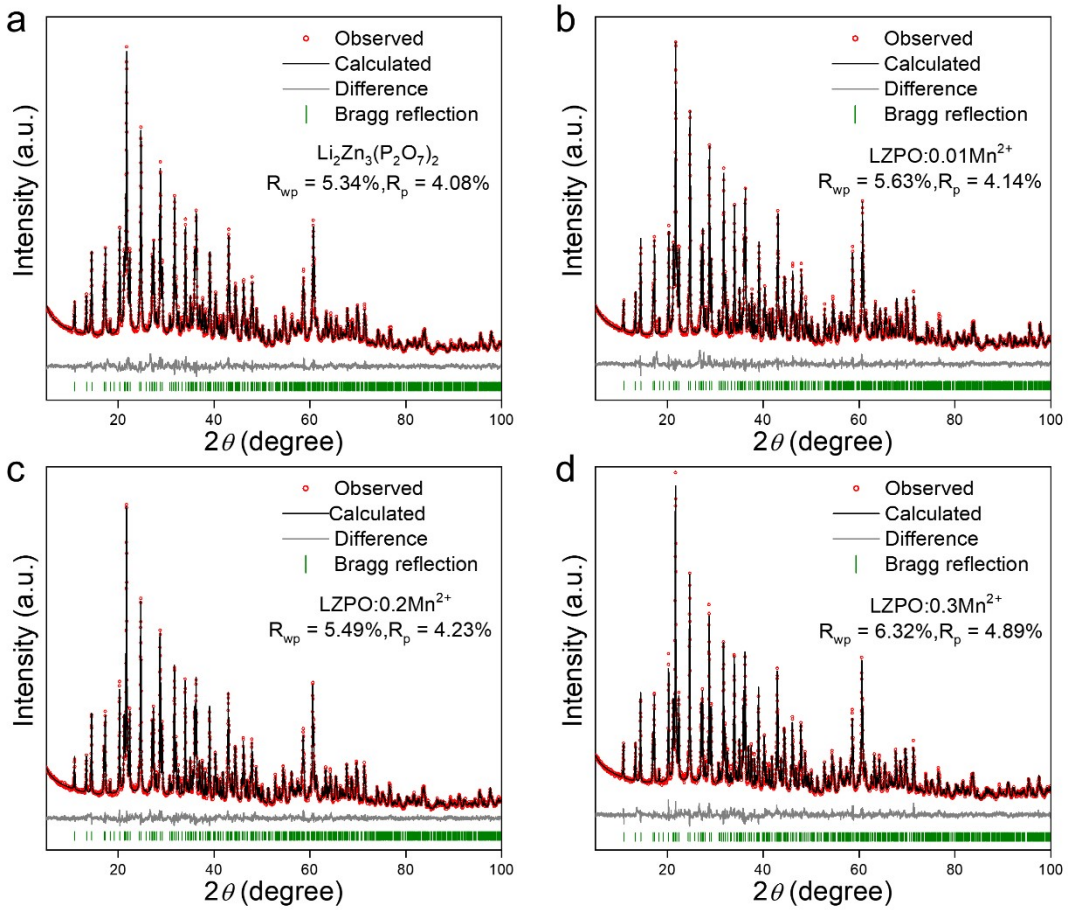

Fig. S1. The Rietveld refinement XRD pattern for (a) LZPO host sample, (b) LZPO:0.01Mn^{2+}, (c) LZPO:0.2Mn^{2+}, (d) LZPO:0.3Mn^{2+}.

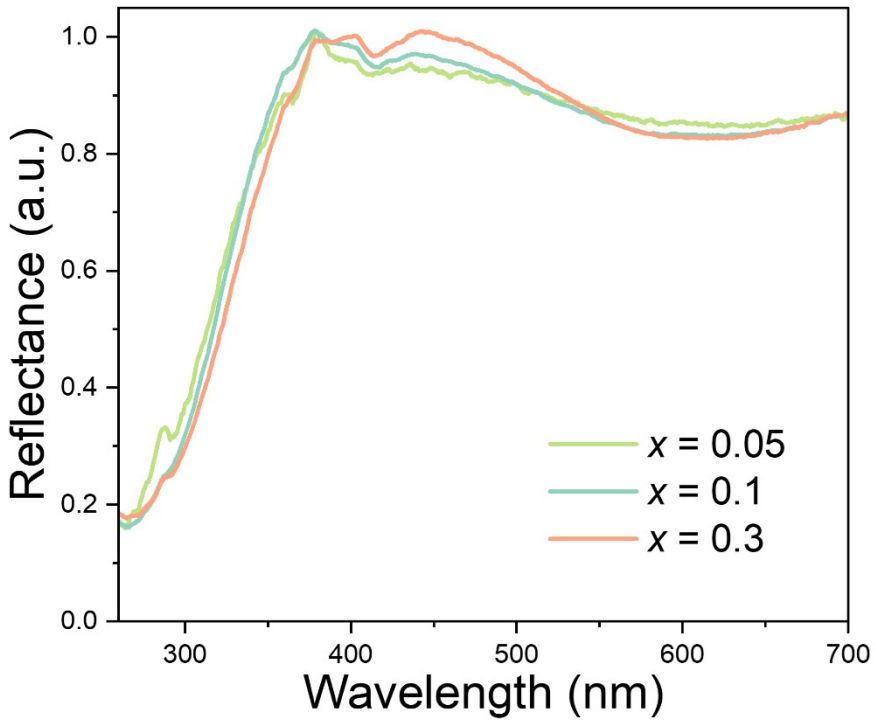

Fig. S2. The diffuse reflectance spectra of LZPO:xMn^{2+} (x = 0.05, 0.1, 0.3) phosphors.

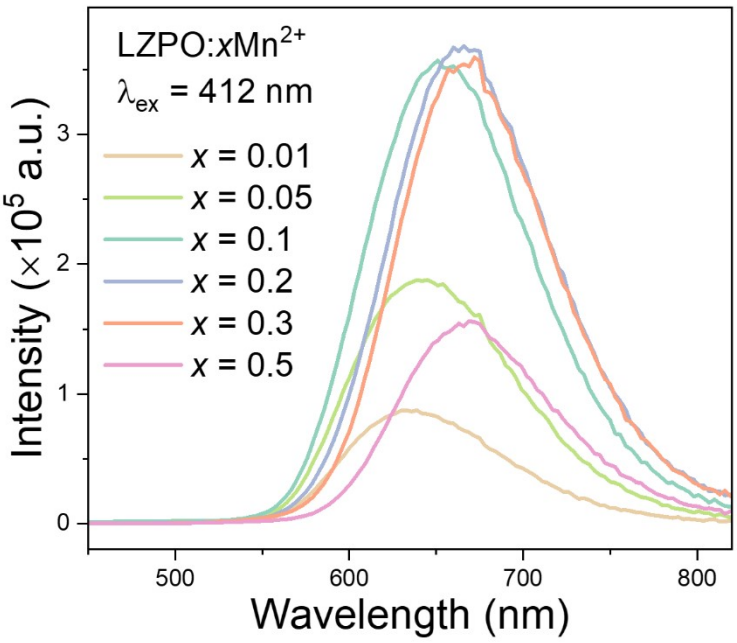

Fig. S3. PL spectra of LZPO:xMn^{2+} (x = 0.01-0.5) under 412 nm wavelength excitation.

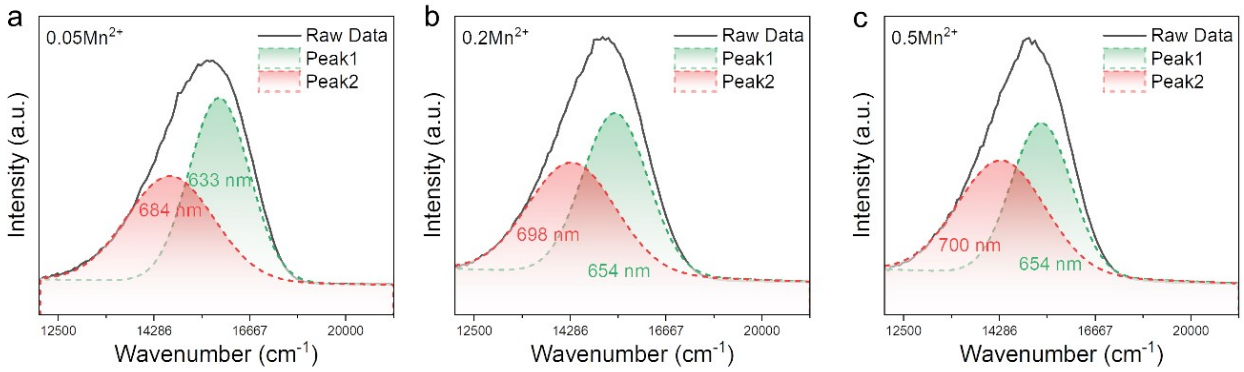

Fig. S4. The Gaussian fitting of (a) LZPO:0.05Mn^{2+}, (b) LZPO:0.2Mn^{2+} and (c) LZPO:0.5Mn^{2+}.

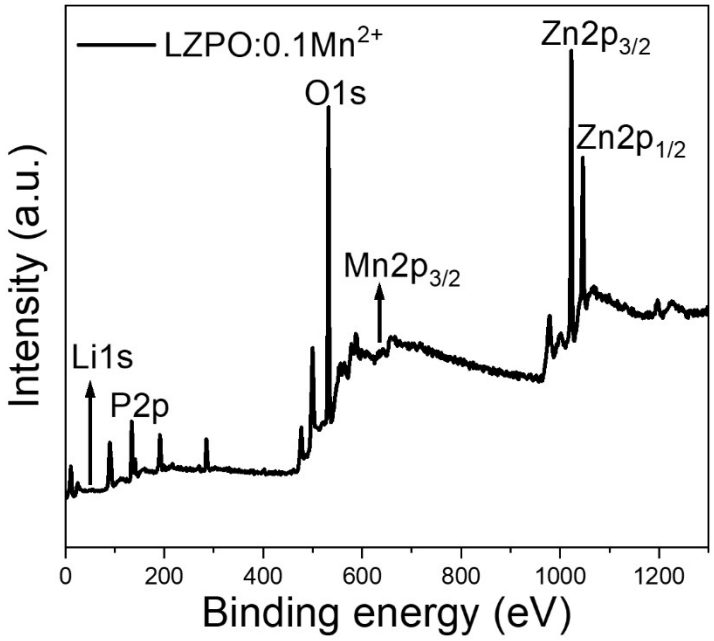

Fig. S5. XPS spectrum of representative LZPO:0.1Mn^{2+}.

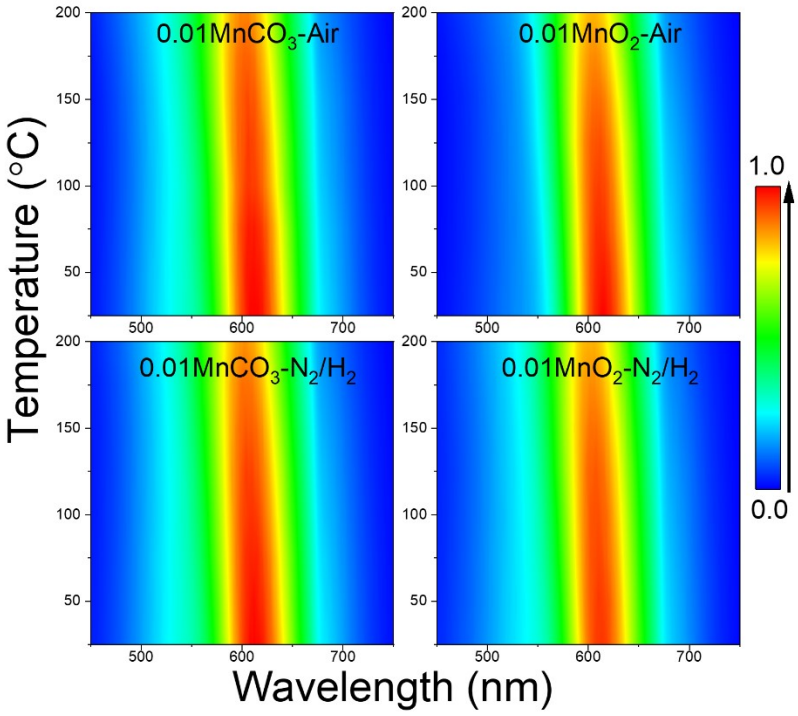

Fig. S6. Temperature-dependent PL spectra of LZPO:0.01Mn^{2+} with different Mn-source sintered in air and N_2(90%)-H_2(10%) atmosphere.