Supplementary information

Unveiling luminescence property of $Li_2MgGeO_4:Mn^{4+}$ featuring tetrahedral crystallographic-site occupancy of Mn^{4+}

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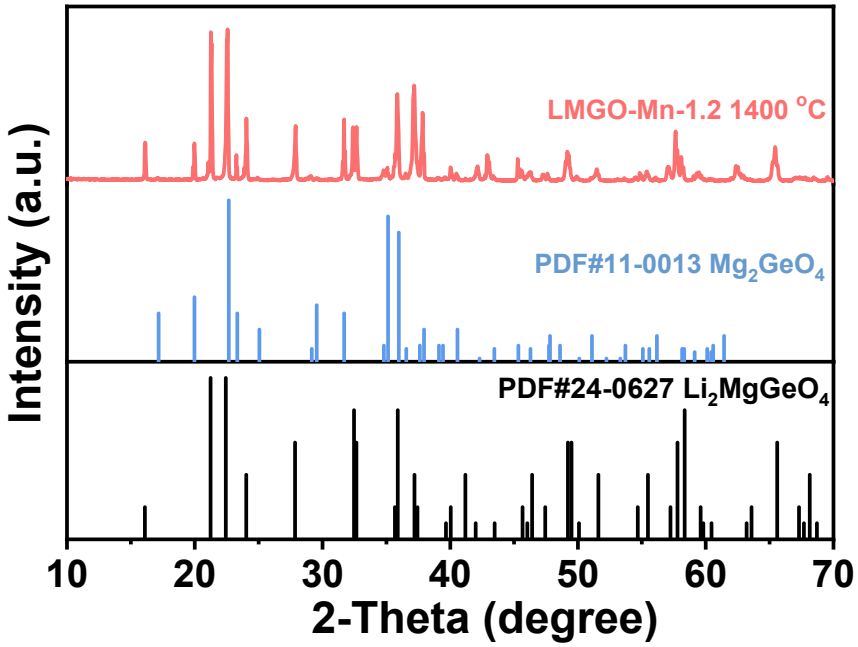

Fig. S1 XRD patterns of LMGO-Mn-1.2 sintered at 1400 °C.

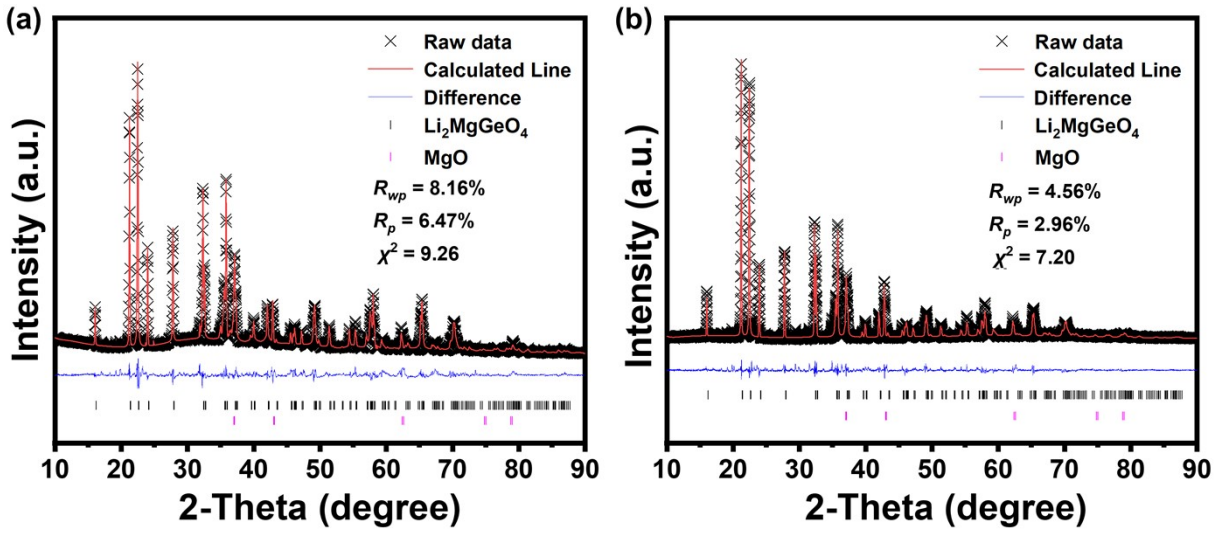

Fig. S2 Rietveld refinement of (a) LMGO-Mn-0.6 and (b) LMGO-Mn-1.0. The black cross, red line and blue line represent the experimental data, calculated result and their difference, respectively. The black and pink vertical lines below the different profiles represent the position of Li_2MgGeO_4 and MgO Bragg reflections, respectively.

Table S1 Refined parameters of LMGO-Mn-0.6 derived from the Rietveld refinement of the X-ray diffraction data.

Atom	*X*	*Y*	*Z*	Occupancy
Ge	0.0000	0.6732	0.0057	1.0000
Mg	0.0000	0.3389	0.4774	1.0000
Li	0.2557	0.1784	0.0023	1.0000
O3	0.2301	0.8384	0.8867	1.0000
O4	0.0000	0.3486	0.9118	1.0000
O5	0.0000	0.7108	0.3791	1.0000

Cell parameters: a = 6.3914 Å, b = 5.4725 Å, c = 4.9998 Å, $\alpha = \beta = \gamma = 90°$, V = 174.878 Å^3; space group: Pmn21(31).

Table S2 Refined parameters of LMGO-Mn-1.0 derived from the Rietveld refinement of the X-ray diffraction data.

Atom	*X*	*Y*	*Z*	Occupancy
Ge	0.0000	0.6731	0.00413	1.0000
Mg	0.0000	0.3219	0.4853	1.0000
Li	0.2534	0.1705	0.0019	1.0000
O3	0.2218	0.8399	0.8680	1.0000
O4	0.0000	0.3585	0.9099	1.0000
O5	0.0000	0.7087	0.3675	1.0000

Cell parameters: a = 6.3918 Å, b = 5.4742 Å, c = 4.9996 Å, $\alpha = \beta = \gamma = 90°$, V = 174.935 Å^3; space group: Pmn21(31).

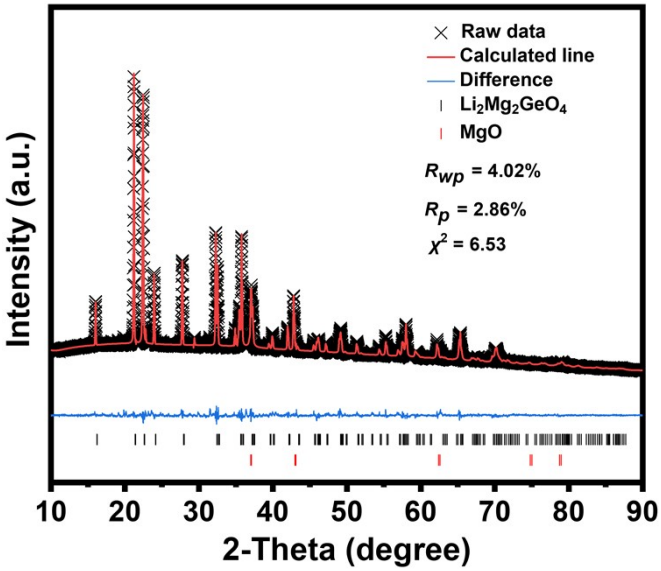

Fig. S3 Rietveld refinement of the LMGO:1.0%Mn:1.0MgO.

Table S3 Lattice parameters and agreement factors for LMGO:1.0%Mn:1.0MgO refined by Rietveld method, when Mn^{4+} ions occupy the cationic sites of Ge^{4+}.

Doped concentration	***x* = 0.01**
Crystal system	orthorhombic
Space group	*Pmn21*
a (Å)	6.39174
b (Å)	5.47387
c (Å)	4.99974
Volume (Å^3)	174.928
Z	2
R_{wp} (%)	4.02
R_p (%)	2.86
χ^2	6.53

Table S4 Resulted occupancy of atoms assuming Mn^{4+} ions occupy the Ge^{4+} sites for LMGO:1.0%Mn:1.0MgO.

Name	**Site**	***x***	***y***	***z***	**Occupancy**
Li0	4b	0.25366	0.17089	0.00196	1.00000
Mg1	2a	0.00000	0.32036	0.48690	1.00000
Ge2	2a	0.00000	0.67277	0.00413	0.99057
O3	4b	0.22242	0.84096	0.86858	1.00000
O4	2a	0.00000	0.35849	0.90992	1.00000
O5	2a	0.00000	0.70913	0.36687	1.00000
Mn6	2a	0.00000	0.67277	0.00413	0.00943

In the following Table S5 to S14, there is a special treatment to Mn ion: As stated in the work of "*Dalton Trans.* 2021, **50**, 8803", when the Mn ion was doped in the site of Li^{+}/Mg^{2+} in tetrahedral [LiO_4] and [MgO_4], the Mn ion should be Mn^{2+}. Therefore, in our assumption cases of Mn ion located at Li^{+}/Mg^{2+}, Mn^{2+} instead of Mn^{4+} was adopted for Rietveld refinement.

Table S5 Lattice parameters and agreement factors for LMGO:1.0%Mn:1.0MgO refined by Rietveld method, assuming that the cationic sites of Li^{+} is occupied by Mn^{2+}.

Doped concentration	***x* = 0.01**
Crystal system	orthorhombic
Space group	*Pmn21*
a (Å)	6.39131
b (Å)	5.47845
c (Å)	4.99874
Volume (Å^3)	175.028
Z	2
R_{wp} (%)	5.898
R_p (%)	3.88
χ^2	12.9

Table S6 The resulted occupancy of atoms assuming that the Li^{+} sites in LMGO:1.0%Mn:1.0MgO is occupied by Mn^{2+}.

Name	**Site**	***x***	***y***	***z***	**Occupancy**
Li0	4b	0.25639	0.18232	0.00201	0.99704
Mg1	2a	0.00000	0.30742	0.45615	1.00000
Ge2	2a	0.00000	0.66240	0.00398	1.00000
O3	4b	0.20555	0.83343	0.86434	1.00000
O4	2a	0.00000	0.35587	0.88967	1.00000
O5	2a	0.00000	0.70666	0.38923	1.00000
Mn6	4b	0.25639	0.18232	0.00201	0.00296

Table S7 Lattice parameters and agreement factors for LMGO:1.0%Mn:1.0MgO refined by Rietveld method, assuming that the cationic sites of Mg^{2+} is occupied by Mn^{2+}.

Doped concentration	***x* = 0.01**
Crystal system	orthorhombic
Space group	*Pmn21*
a (Å)	6.39092
b (Å)	5.47866
c (Å)	4.99722
Volume (Å^3)	174.971
Z	2
R_{wp} (%)	6.305
R_p (%)	4.12
χ^2	14.7

Table S8 The resulted occupancy of atoms assuming that the Mg^{2+} sites in LMGO:1.0%Mn:1.0MgO is occupied by Mn^{2+}.

Name	Site	*x*	*y*	*z*	Occupancy
Li0	4b	0.26098	0.17580	0.001867	1.00000
Mg1	2a	0.00000	0.31757	0.46675	1.00051
Ge2	2a	0.00000	0.66046	0.00452	1.00000
O3	4b	0.20998	0.85298	0.86268	1.00000
O4	2a	0.00000	0.36168	0.89009	1.00000
O5	2a	0.00000	0.71328	0.40975	1.00000
Mn6	2a	0.00000	0.31757	0.46675	-0.00051

Table S9 Lattice parameters and agreement factors for LMGO:1.0%Mn:1.0MgO refined by Rietveld method, assuming that the Mn^{4+} ions occupy the cationic sites of Ge^{4+} and the Mn^{2+} ions occupy Li^{+} ion sites.

Doped concentration	*x* = 0.01
Crystal system	orthorhombic
Space group	*Pmn21*
a (Å)	6.39178
b (Å)	5.47948
c (Å)	4.99978
Volume (Å^3)	175.111
Z	2
R_{wp} (%)	5.122
R_p (%)	3.36
χ^2	9.70

Table S10 Resulted occupancy of atoms when Mn^{4+} ions occupy the Ge^{4+} sites and Mn^{2+} ions occupy the Li^{+} sites for LMGO:1.0%Mn:1.0MgO.

Name	Site	*x*	*y*	*z*	Occupancy
Li0	4b	0.24711	0.18355	0.00197	0.99854
Mg1	2a	0.00000	0.31348	0.47098	1.00000
Ge2	2a	0.00000	0.66286	0.00432	0.99146
O3	4b	0.22182	0.85114	0.86260	1.00000
O4	2a	0.00000	0.32528	0.91200	1.00000
O5	2a	0.00000	0.68906	0.68907	1.00000
Mn6	2a	0.00000	0.66286	0.00432	0.00854
Mn7	4b	0.24711	0.18355	0.00197	0.00146

Table S11 Lattice parameters and agreement factors for LMGO:1.0%Mn:1.0MgO refined by Rietveld method, when Mn^{4+} ions occupy the cationic sites of Ge^{4+} and Mn^{2+} ions occupy Mg^{2+} ion sites.

Doped concentration	***x* = 0.01**
Crystal system	orthorhombic
Space group	*Pmn21*
a (Å)	6.39155
b (Å)	5.47882
c (Å)	4.99861
Volume (Å^3)	175.042
Z	2
R_{wp} (%)	6.395
R_p (%)	4.17
χ^2	15.16

Table S12 Resulted occupancy of atoms when Mn^{4+} ions occupy the Ge^{4+} sites and Mn^{2+} ions occupy the Mg^{2+} sites for LMGO:1.0%Mn:1.0MgO.

Name	**Site**	***x***	***y***	***z***	**Occupancy**
Li0	4b	0.26231	0.17589	0.00224	1.00000
Mg1	2a	0.00000	0.31289	0.49641	0.99936
Ge2	2a	0.00000	0.66278	0.00411	0.99064
O3	4b	0.20954	0.83981	0.85298	1.00000
O4	2a	0.00000	0.36349	0.89458	1.00000
O5	2a	0.00000	0.70737	0.39061	1.00000
Mn6	2a	0.00000	0.31289	0.49641	0.00064
Mn7	2a	0.00000	0.66278	0.00411	0.00936

Table S13 Lattice parameters and agreement factors for LMGO:1.0%Mn:1.0MgO refined by Rietveld method, when Mn^{4+} ions occupy the cationic sites of Ge^{4+} and Mn^{2+} ions occupy Mg^{2+}/ Li^+ ion sites.

Doped concentration	***x* = 0.01**
Crystal system	orthorhombic
Space group	*Pmn21*
a (Å)	6.39129
b (Å)	5.47864
c (Å)	4.99747
Volume (Å^3)	174.989
Z	2
R_{wp} (%)	6.502
R_p (%)	4.23
χ^2	15.68

Table S14 Resulted occupancy of atoms when Mn^{4+} ions occupy the Ge^{4+} sites and Mn^{2+} ions occupy the Mg^{2+}/Li^{+} sites for LMGO:1.0%Mn:1.0MgO.

Name	Site	*x*	*y*	*z*	Occupancy
Li0	4b	0.24165	0.17913	0.00204	0.99864
Mg1	2a	0.00000	0.33117	0.46905	1.00047
Ge2	2a	0.00000	0.65853	0.00510	0.99089
O3	4b	0.17075	0.86279	0.86167	1.00000
O4	2a	0.00000	0.33681	0.89365	1.00000
O5	2a	0.00000	0.68398	0.40508	1.00000
Mn6	4b	0.24165	0.17913	0.00204	0.00136
Mn7	2a	0.00000	0.33117	0.46905	-0.00047
Mn8	2a	0.00000	0.65853	0.00510	0.00911

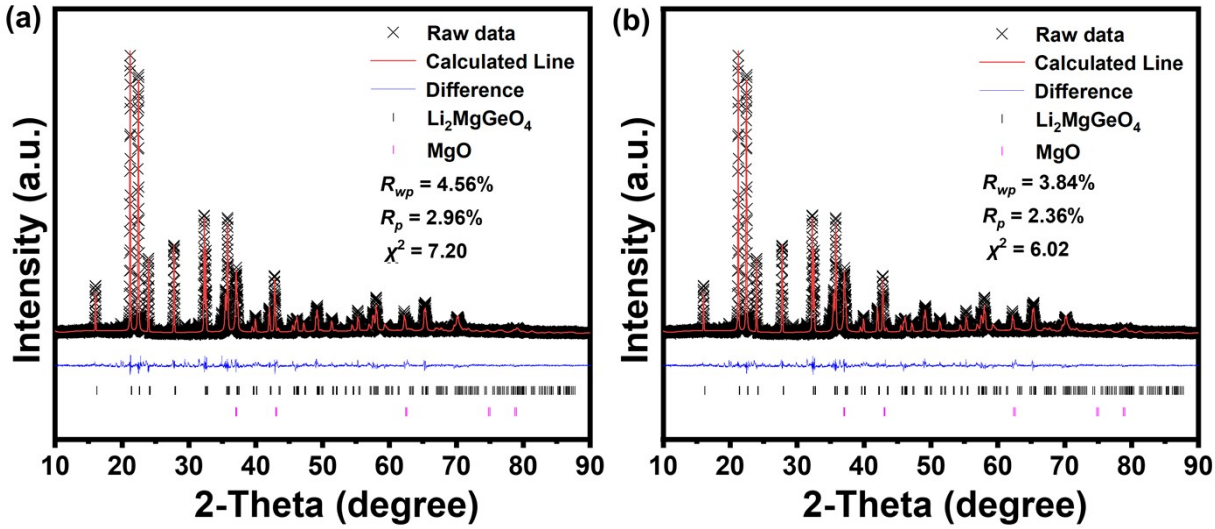

Fig. S4 Rietveld refinements of LMGO-Mn-1.0 without (a) and with (b) compensation of Li^{+} defects with Mg^{2+}.

Table S15 Refined results of LMGO-Mn-1.0 (Mg^{2+} ions occupy Li^{+} positions).

Atom	*X*	*Y*	*Z*	Occupancy
Ge	0.0000	0.6722	0.0042	1.0000
Mg	0.0000	0.3202	0.4867	1.0000
Li	0.2537	0.1709	0.0019	0.8353
O3	0.2224	0.8410	0.8686	1.0000
O4	0.0000	0.3587	0.9102	1.0000
O5	0.0000	0.7095	0.3669	1.0000
Mg6	0.2537	0.1709	0.0019	0.1647

Cell parameters: a = 6.3915 Å, b = 5.4799 Å, c = 4.9994 Å, $\alpha = \beta = \gamma = 90°$, V = 175.103 $Å^3$; space group: Pmn21(31).

Table S16 The phase molar fraction of LMGO and MgO in LMGO-Mn-1.0 obtained by Rietveld refinement of X-ray diffraction data.

	Expectation value	Calculated value 1	Calculated value 2
LMGO molar fraction	50%	50.86%	54.26%
MgO molar fraction	50%	49.14%	45.74%
Ratio	1.0	1.03	1.19

The expectation value is the stoichiometric ratio of the sample weighing, the calculated value 1 is the result of Mg^{2+} not compensating for the Li^{+} defects, and the calculated value 2 is the result when Mg^{2+} compensates for the Li^{+} defects.

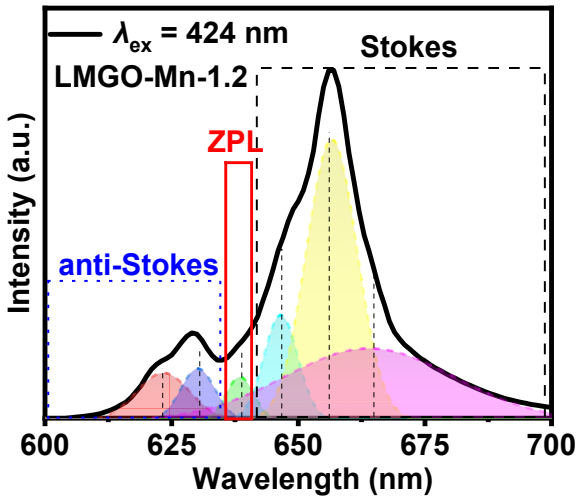

Fig. S5 The fitted results from PL spectrum of LMGO-Mn-1.2.

Table S17 The decay dynamics parameters of LMGO-Mn-0.0 to LMGO-Mn-1.5 red phosphors.

Samples	A_1	τ_1 (ms)	A_2	τ_2 (ms)	τ_{avg} (ms)	R^2
LMGO-Mn-0.0	621.261	0.573	215.591	2.631	1.837	0.986
LMGO-Mn-0.4	113.252	0.628	138.770	2.684	2.354	0.986
LMGO-Mn-0.6	145.137	0.616	205.196	2.760	2.467	0.989
LMGO-Mn-1.0	687.535	0.762	920.248	2.762	2.420	0.998
LMGO-Mn -1.2	652.086	0.596	988.597	2.699	2.432	0.998
LMGO-Mn -1.5	538.823	0.670	837.863	2.739	2.458	0.997