Crystal structure and luminescence properties of a novel green-yellow-emitting $Ca_{1.5}Mg_{0.5}Si_{1-x}Li_xO_{4-\delta}:Ce^{3+}$ phosphor with high quantum efficiency and thermal stability

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Supporting Information

Table S1. Anisotropic atomic displacement parameters ($Å^2$) of $Ca_{1.51(1)}Mg_{0.49(1)}Si_{0.925(5)}Li_{0.075(5)}O_{4-\delta}$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ca1	0.0032(4)	0.0039(5)	0.0055(5)	0.0011(3)	-0.0008(3)	0.0006(3)
Mg1	0.0032(4)	0.0039(5)	0.0055(5)	0.0011(3)	-0.0008(3)	0.0006(3)
Ca2	0.0032(4)	0.0169(4)	0.0075(4)	0.0064(3)	0.0004(2)	-0.0003(3)
Mg2	0.0032(4)	0.0169(4)	0.0075(4)	0.0064(3)	0.0004(2)	-0.0003(3)
Ca3	0.0039(4)	0.0076(4)	0.0038(4)	0	-0.0003(2)	0
Mg3	0.0039(4)	0.0076(4)	0.0038(4)	0	-0.0003(2)	0
Ca4	0.0039(4)	0.0184(5)	0.0044(4)	0	0.0004(2)	0
Mg4	0.0039(4)	0.0184(5)	0.0044(4)	0	0.0004(2)	0
Si1	0.0017(5)	0.0117(6)	0.0031(5)	0	0.0007(3)	0
Li1	0.0017(5)	0.0117(6)	0.0031(5)	0	0.0007(3)	0
Si2	0.0018(5)	0.0245(7)	0.0033(5)	0	0.0003(3)	0
Li2	0.0018(5)	0.0245(7)	0.0033(5)	0	0.0003(3)	0
O1	0.0078(11)	0.0155(13)	0.0093(12)	0	0.0003(9)	0
O2	0.0074(12)	0.0366(16)	0.0102(12)	0	0.0013(9)	0
O3	0.0111(12)	0.0247(14)	0.0078(12)	0	0.0002(9)	0
O4	0.0094(12)	0.0251(15)	0.0072(11)	0	-0.0009(9)	0
O5	0.0081(8)	0.0157(9)	0.0094(8)	0.0012(7)	0.0000(6)	-0.0008(6)
O6	0.0145(9)	0.0237(10)	0.0100(8)	0.0045(7)	0.0022(7)	0.0089(7)

Table S2. Main bond lengths of $Ca_{1.51(1)}Mg_{0.49(1)}Si_{0.925(5)}Li_{0.075(5)}O_{4-\delta}$

(Ca1/Mg1)—O3^{i}	2.203 (2)	(Ca3/Mg3)—O3	2.288 (2)
(Ca1/Mg1)—O3^{ii}	2.203 (2)	(Ca3/Mg3)—O6^{iv}	2.348 (2)
(Ca1/Mg1)—O6^{iii}	2.277 (2)	(Ca3/Mg3)—O6^{xii}	2.348 (2)
(Ca1/Mg1)—O6^{iv}	2.277 (2)	(Ca3/Mg3)—O1	2.417 (2)
(Ca1/Mg1)—O2^{v}	2.293 (2)	(Ca3/Mg3)—O5^{xiii}	2.419 (2)
(Ca1/Mg1)—O2^{vi}	2.293 (2)	(Ca3/Mg3)—O5	2.419 (2)
(Ca2/Mg2)—O4^{vii}	2.287 (2)	(Ca4/Mg4)—O4^{ii}	2.308 (2)
(Ca2/Mg2)—O4	2.287 (2)	(Ca4/Mg4)—O5^{xi}	2.345 (2)
(Ca2/Mg2)—O1	2.335 (2)	(Ca4/Mg4)—O5^{vii}	2.345 (2)
(Ca2/Mg2)—O1^{vii}	2.335 (2)	(Ca4/Mg4)—O6^{xiv}	2.428 (2)
(Ca2/Mg2)—O5	2.374 (2)	(Ca4/Mg4)—O6^{ii}	2.428 (2)
(Ca2/Mg2)—O5^{vii}	2.374 (2)	(Ca4/Mg4)—O2	2.473 (2)
(Si1/Li1)—O1^{xvi}	1.620 (2)	(Si2/Li2)—O2	1.627 (2)
(Si1/Li1)—O5	1.638 (2)	(Si2/Li2)—O6^{xiii}	1.641 (2)
(Si1/Li1)—O5^{xiii}	1.638 (2)	(Si2/Li2)—O6	1.641 (2)
(Si1/Li1)—O4	1.655 (2)	(Si2/Li2)—O3^{xviii}	1.651 (2)

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

Table S3. Crystallographic data and main parameters for processing and refinement of $Ca_3MgSi_{1.961(6)}Li_{0.039(6)}O_8$.

Crystal data	
Chemical formula	$Ca_3MgSi_{1.961(6)}Li_{0.039(6)}O_8$
M_r	327.91
Space group, Z	$P2_1/c$, 4
a, (Å)	9.3416 (4)
b, (Å)	5.3045 (3)
c, (Å)	13.2848 (7)
β, (º)	92.088 (2)
V, (Å^3)	657.86 (6)
D_x, Mg/m^3	3.337
μ, mm^{-1}	2.981
Size	30×30×20 μm
Data collection	
Wavelength	Mo K_α, λ=0.7106Å
Measured reflections	24619
Independent reflections	1509
Reflections with I>2σ(I)	1366
Absorption correction	Multiscan
R_{int}	0.0564
$2\theta_{max}$ (°)	50.48
h	-12 → 12
k	-6 → 6
l	-17 → 17
Refinement	
$R[F^2>2\sigma(F^2)]$	0.0295
$wR(F^2)$	0.0780
S	1.064
Weight	$w=1/[\sigma^2(F_o^2)+(0.0532P)^2+0.4782P]$ where
$(\Delta/\sigma)_{max}$	<0.001
$\Delta\rho_{max}$, e/Å^3	0.833
$\Delta\rho_{min}$, e/Å^3	-0.459

Table S4. Coordinates of atoms, occupancy, and equivalent isotropic displacement parameters of $Ca_3MgSi_{1.961(6)}Li_{0.039(6)}O_8$.

	x	*y*	*z*	U_{eq}	Occ.
Ca1	0.07532 (5)	0.22717 (9)	0.91873 (4)	0.0107 (2)	1
Ca2	0.77479 (5)	0.17888 (9)	0.74409 (3)	0.0105 (2)	1
Ca3	0.57485 (5)	0.73283 (9)	0.90277 (4)	0.0117 (2)	1
Mg	0.25314 (7)	0.7565 (1)	0.50395 (5)	0.0066 (2)	1
Si1	0.09329 (6)	0.2278 (1)	0.64126 (5)	0.0045 (2)	0.982 (4)
Li1	0.09329 (6)	0.2278 (1)	0.64126 (5)	0.0045 (2)	0.018 (4)
Si2	0.60032 (6)	0.7292 (1)	0.63311 (5)	0.0048 (2)	0.979 (4)
Li2	0.60032 (6)	0.7292 (1)	0.63311 (5)	0.0048 (2)	0.021 (4)
O1	0.1752 (2)	0.4571 (3)	0.5831 (1)	0.0119 (4)	1
O2	0.6772 (2)	0.4539 (3)	0.6252 (1)	0.0102 (4)	1
O3	0.6936 (2)	0.9205 (3)	0.5644 (1)	0.0133 (4)	1
O4	0.1847 (2)	-0.0276 (3)	0.6268 (1)	0.0099 (4)	1
O5	-0.0590 (2)	0.2057 (3)	0.5770 (1)	0.0129 (4)	1
O6	0.0691 (2)	0.3135 (3)	0.7546 (1)	0.0111 (4)	1
O7	0.4453 (2)	0.7124 (3)	0.5740 (1)	0.0147 (4)	1
O8	0.5936 (2)	0.8594 (3)	0.7415 (1)	0.0129 (4)	1

Table S5. Main parameters of processing and refinement of the $Ca_3MgSi_2O_8$:Li sample

Compound	$Ca_3Mg(Si_{1.92(3)}Li_{0.08(3)})O_8$
Space Group	$P2_1/c$
a, Å	9.3401 (8)
b, Å	5.3096 (5)
c, Å	13.303 (1)
β, º	92.061 (1)
V, Å^3	659.3 (1)
Z	4
d-interval, Å	0.580-3.627
No. of reflections	3527
No. of refined parameters	100
R_{wp}, %	3.40
R_p, %	5.53
R_{exp}, %	2.44
χ^2	1.40
R_B, %	3.02

Table S6. Main bond lengths of $Ca_3MgSi_2O_8$:Li

Ca1—O2^{i}	2.852 (9)	Ca3—O2^{ix}	2.43 (1)
Ca1—O3^{ii}	2.325 (8)	Ca3—O3^{viii}	2.72 (1)
Ca1—O4^{i}	2.375 (7)	Ca3—O4^{ii}	2.32 (1)
Ca1—O5^{iii}	2.817 (9)	Ca3—O7	2.55 (1)
Ca1—O6^{iv}	2.436 (7)	Ca3—O8^{viii}	2.47 (1)
Ca1—O6^{iii}	2.809 (7)	Mg—O1	2.025 (9)
Ca1—O7	2.356 (9)	Mg—O2^{ix}	2.01 (1)
Ca1—O8	2.622 (9)	Mg—O3^{x}	2.149 (9)
Ca2—O2^{v}	2.527 (8)	Mg—O5^{vi}	2.098 (9)
Ca2—O3^{v}	2.919 (8)	Mg—O7	2.14 (1)
Ca2—O5	2.512 (9)	Mg—O8	2.08 (1)
Ca2—O5^{iv}	2.808 (9)	(Si1/Li1)—O1	1.584 (9)
Ca2—O5^{vi}	2.473 (9)	(Si1/Li1)—O2	1.651 (9)
Ca2—O6^{iii}	2.168 (8)	(Si1/Li1)—O3	1.649 (8)
Ca2—O7	2.733 (8)	(Si1/Li1)—O4	1.584 (8)
Ca2—O8	2.703 (8)	(Si2/Li2)—O5	1.624 (9)
Ca2—O8^{vii}	2.620 (8)	(Si2/Li2)—O6	1.63 (1)
Ca3—O1	2.78 (1)	(Si2/Li2)2—O7	1.59 (1)
Ca3—O1^{viii}	2.58 (1)	(Si2/Li2)—	1.61 (1)
Ca3—O1^{ix}	2.69 (1)		

Symmetry codes: (i) -*x*+1, *y*-1/2, -*z*+1/2; (ii) -*x*+1, *y*+1/2, -*z*+1/2; (iii) -*x*, *y*-1/2, -*z*+1/2; (iv) *x*, *y*-1, *z*; (v) *x*-1, *y*, *z*; (vi) -*x*, -*y*+1, -*z*; (vii) -*x*, -*y*, -*z*; (viii) *x*, *y*+1, *z*; (ix) -*x*+1, -*y*+1, -*z*; (x) -*x*+1, -*y*, -*z*.

Table S7. Full set of 15 CRIs and R_a of WLED based on 365 nm near-UV chip and 410 nm violet chip.

	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15	Ra
365 nm UV chip	98	96	90	90	97	94	90	88	79	90	93	90	98	94	93	92.8
410 nm violet	93	96	93	80	88	95	88	89	91	94	82	45	93	95	87	90.4

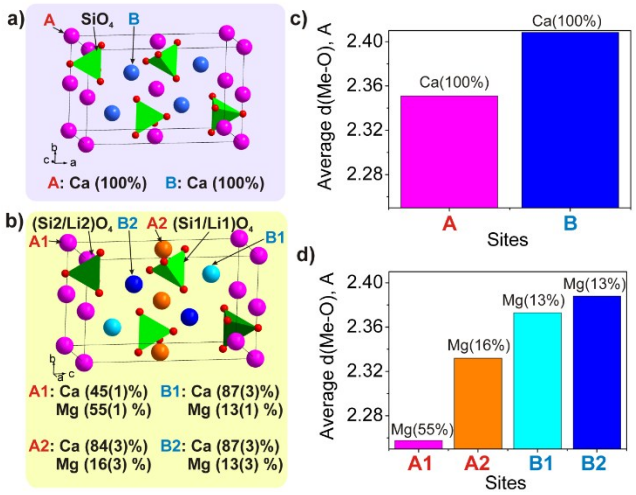

Figure S1. Comparison of crystal structures of γ-Ca_2SiO_4 (a), with $Ca_{1.51(1)}Mg_{0.49(1)}Si_{0.925(5)}Li_{0.075(5)}O_4$ (b). Each of the sites A and B of γ-Ca_2SiO_4 is split into two sites A1, A2 and B1, B2 separately in $Ca_{1.51(1)}Mg_{0.49(1)}Si_{0.925(5)}Li_{0.075(5)}O_4$. The sites A1 and A2 are preferably occupied by Mg^{2+} ions and, therefore, the average bond lengths d(Me-O) of A1 and A2 sites differ noticeably from the bond length of B1 and B2 sites (d), contrary to the situation in the γ-Ca_2SiO_4 structure (c).

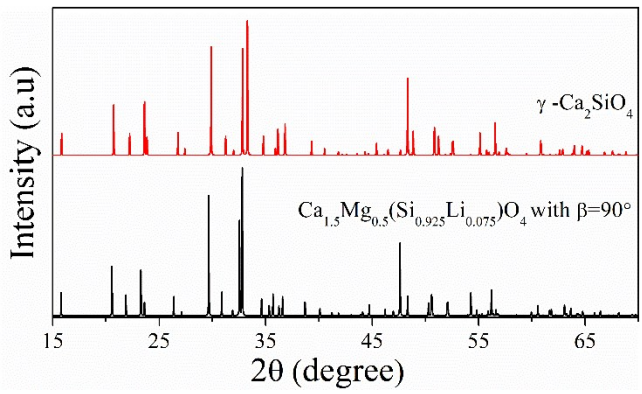

Figure S2. X-ray diffractograms of γ-Ca_2SiO_4 and $Ca_{1.51(1)}Mg_{0.49(1)}Si_{0.925(5)}Li_{0.075(5)}O_4$ with β = 90°.

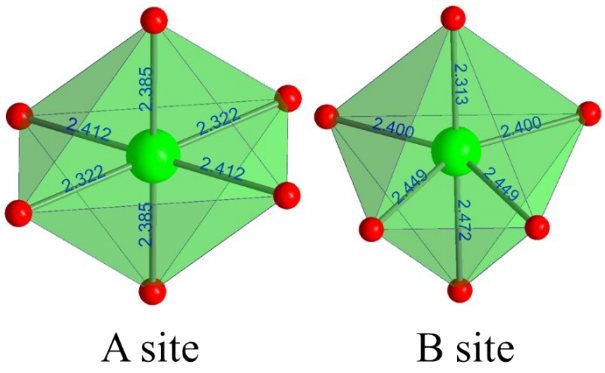

Figure S3. Coordination polyhedra of two kinds of Ca sites in γ-Ca_2SiO_4. The green spheres correspond to Ca, and the red spheres to O. The average coordination distances of A and B sites are 2.352 Å and 2.359 Å, respectively.

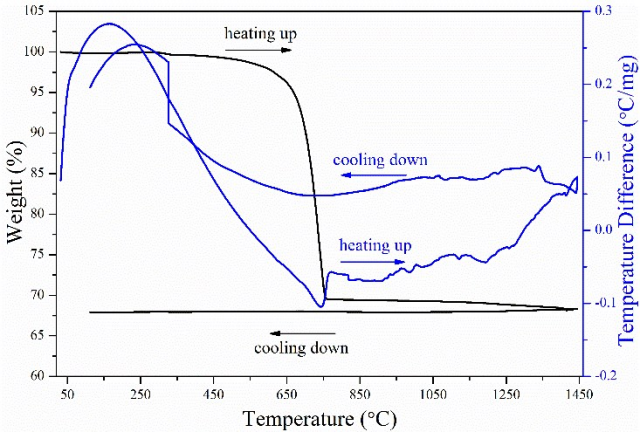

Figure S4. DSC-TGA curves of CMSL:0.005Ce^{3+} precursor recorded from room temperature to 1450 °C at a heating rate of 10 K/min in flowing N_2 gas atmosphere. The decrease of mass from 750 to 1450 °C is attributed to the evaporation of Li, and the exothermic effect in the cooling curve at ~325 °C is ascribed to the phase transformation of $Ca_3MgSi_2O_8$ to $Ca_{1.51(1)}Mg_{0.49(1)}Si_{0.925(5)}Li_{0.075(5)}O_{4-\delta}$.

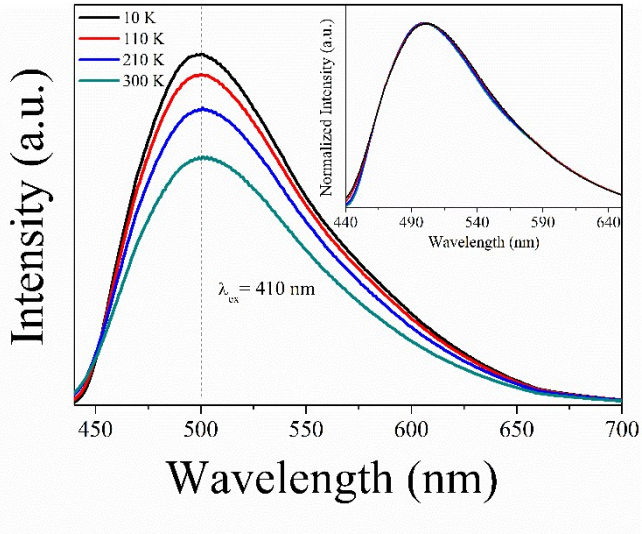

Figure S5. The low-temperature emission spectra (λ_{ex} = 410 nm) of the CMSL:0.005Ce phosphor.

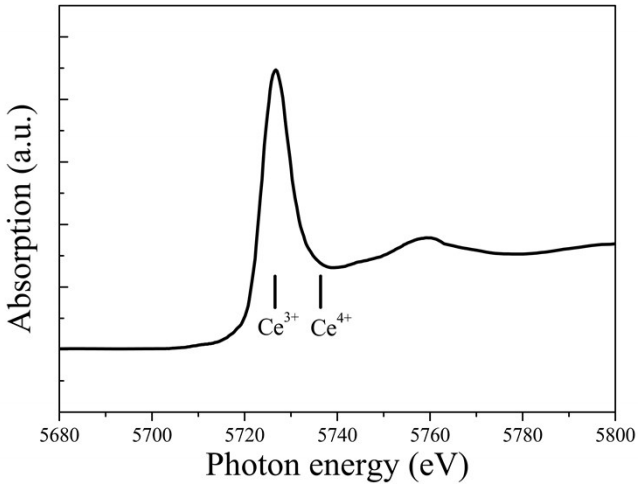

Figure S6. Ce LIII-edge XANES spectrum of CMSL:0.01Ce fine powder. The positions of Ce^{3+} and Ce^{4+} are marked. There is no evidence for Ce^{4+} in this sample.