Supporting Information

On the role of Zr substitution in structure modification and photoluminescence of $Li_{5+2x}La_3(Ta_{1-x}Zr_x)_2O_{12}$:Eu garnet phosphor

Panpan Du,[a,b] Siyuan Li,[a] Xuejiao Wang,[c] Qi Zhu,[a] Ji-Guang Li[b,*]

[a] *Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), School of Materials Science and Engineering, Northeastern University, Shenyang, Liaoning 110819, China*

[b] *Research Center for Functional Materials, National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan*

[c] *College of Chemistry and Materials Engineering, Bohai University, Jinzhou, Liaoning 121007, China*

[*]Corresponding author

Dr. Ji-Guang Li

National Institute for Materials Science

Tel: +81-29-860-4394

E-mail: LI.Jiguang@nims.go.jp

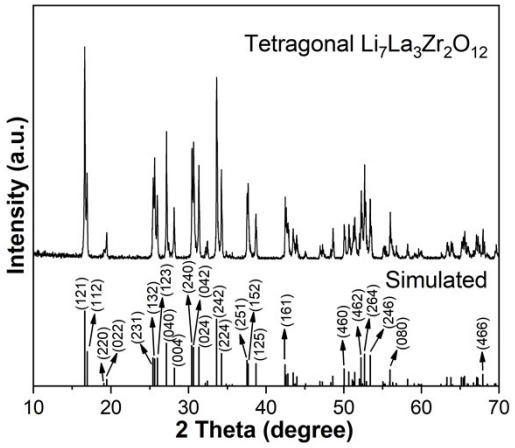

Fig. S1 Measured and simulated XRD patterns of tetragonal $Li_7La_3Zr_2O_{12}$.

Table S1 The 2-theta, miller indices (*hkl*) and *d*-spacing derived via Rietveld refinement of the XRD pattern for $Li_6(La_{0.6}Eu_{0.4})_3(Ta_{0.5}Zr_{0.5})_2O_{12}$.

No.	2θ (°)	*h*	*k*	*l*	*d*-spacing (Å)
1	16.945	2	1	1	5.2282
2	19.590	2	2	0	4.5278
3	26.012	3	2	1	3.4227
4	27.843	4	0	0	3.2016
5	31.209	4	2	0	2.8636
6	32.774	3	3	2	2.7304
7	34.275	4	2	2	2.6141
8	35.721	4	3	1	2.5116
9	38.471	5	2	1	2.3381
10	39.785	4	4	0	2.2639
11	43.528	5	3	2	2.0775
12	43.528	6	1	1	2.0775
13	44.719	6	2	0	2.0249
14	45.885	5	4	1	1.9761
15	48.152	6	3	1	1.8882
16	49.256	4	4	4	1.8485
17	50.341	5	4	3	1.8111
18	51.410	6	4	0	1.7759
19	52.463	5	5	2	1.7428
20	52.463	7	2	1	1.7428
21	52.463	6	3	3	1.7428
22	53.502	6	4	2	1.7113
23	56.538	7	3	2	1.6264
24	56.538	6	5	1	1.6264
25	57.526	8	8	0	1.6008
26	58.504	7	4	1	1.5764
27	59.472	8	2	0	1.5530
28	60.429	6	5	3	1.5307
29	61.378	8	2	2	1.5093

30	61.378	6	6	0	1.5093
31	62.319	7	4	3	1.4887
32	62.319	8	3	1	1.4887
33	64.176	7	5	2	1.4501
34	65.094	8	4	0	1.4318
35	66.909	8	4	2	1.3973
36	67.807	7	6	1	1.3810
37	67.807	6	5	5	1.3810
38	67.807	9	2	1	1.3810
39	68.700	6	6	4	1.3652
40	69.587	8	5	1	1.3499
41	69.587	7	5	4	1.3499
42	71.347	7	6	3	1.3209
43	71.347	9	3	2	1.3209
44	72.220	8	4	4	1.3071
45	73.089	8	5	3	1.2937
46	73.089	9	4	1	1.2937
47	73.953	8	6	0	1.2807
48	74.814	7	7	2	1.2680
49	74.814	10	1	1	1.2680
50	75.672	8	6	2	1.2558
51	75.672	10	2	0	1.2558
52	76.526	9	4	3	1.2439
53	78.225	7	6	5	1.2211
54	78.225	10	3	1	1.2211
55	78.225	9	5	2	1.2211
56	79.914	8	7	1	1.1994
57	80.755	10	4	0	1.1891
58	80.755	8	6	4	1.1891
59	81.595	10	3	3	1.1789
60	81.595	9	6	1	1.1789
61	82.432	10	4	2	1.1691
62	83.267	8	7	3	1.1595
63	83.267	9	5	4	1.1595
64	84.935	11	2	1	1.1409
65	84.935	10	5	1	1.1409
66	84.935	9	6	3	1.1409
67	85.767	8	8	0	1.1320
68	88.258	7	7	6	1.1063
69	88.258	10	5	3	1.1063
70	88.258	9	7	2	1.1063
71	88.258	11	3	2	1.1063
72	89.087	8	6	6	1.0982
73	89.087	10	6	0	1.0982
74	89.916	8	7	5	1.0902
75	89.916	11	4	1	1.0902
76	90.745	10	6	2	1.0824
77	91.575	9	6	5	1.0747

78	92.404	8	8	4	1.0672
79	92.404	12	0	0	1.0672
80	93.235	11	4	3	1.0599
81	93.235	9	8	1	1.0599
82	93.235	9	7	4	1.0599
83	94.065	12	2	0	1.0527
84	94.897	10	5	5	1.0457
85	94.897	10	7	1	1.0457
86	94.897	11	5	2	1.0457
87	95.730	12	2	2	1.0388
88	95.730	10	6	4	1.0388
89	96.564	9	8	3	1.0320
90	96.564	12	3	1	1.0320
91	98.236	11	6	1	1.0188
92	98.236	10	7	3	1.0188
93	99.075	12	4	0	1.0124
94	99.916	11	5	4	1.0062
95	100.758	10	8	0	1.0000
96	100.758	12	4	2	1.0000
97	101.604	9	7	6	0.9940
98	101.604	11	6	3	0.9940
99	101.604	9	9	2	0.9940
100	102.451	10	8	2	0.9880
101	103.302	12	5	1	0.9822
102	103.302	9	8	5	0.9822
103	105.012	11	7	2	0.9709
104	105.012	10	7	5	0.9709
105	105.012	13	2	1	0.9709
106	105.873	12	4	4	0.9653
107	106.736	12	5	3	0.9599
108	107.604	12	6	0	0.9545
109	107.604	10	8	4	0.9545
110	108.476	11	6	5	0.9493
111	108.476	10	9	1	0.9493
112	108.476	13	3	2	0.9493
113	109.353	12	6	2	0.9441
114	110.234	13	4	1	0.9390
115	110.234	11	8	1	0.9390
116	110.234	11	7	4	0.9390

Table S2 Results of ICP analysis and derived molar ratios for $Li_{5+2x}(La_{0.6}Eu_{0.4})_3(Ta_{1-x}Zr_x)_2O_{12}$ (x = 0, 0.5, 1.0).

Sample	Experimental contents (wt%)					Li:La:Eu:Ta:Zr molar ratio
	Li	La	Eu	Ta	Zr	
x = 0	4.3	30.0	22.0	43.7	<0.1	5.162:1.800:1.206:2.013:0
x = 0.5	5.5	33.5	24.5	24.4	12.1	5.913:1.800:1.203:1.007:0.990
x = 1.0	7.5	37.6	27.4	<0.1	27.5	7.185:1.800:1.199:0:2.005

Table S3 Wyckoff lattice position (Wyck), atomic coordinates (x, y, z), isotropic displacement parameter (B_{iso}) and atom occupancy (Occ.) for $Li_{5+2x}(La_{0.6}Eu_{0.4})_3(Ta_{1-x}Zr_x)_2O_{12}$ (x = 0, 0.5, 1.0).

	Wyck	x	y	z	B_{iso} (Å^2)	Occ.
$Li_5(La_{0.6}Eu_{0.4})_3Ta_2O_{12}$						
La	24c	0.12500	0.00000	0.25000	1.14(3)	0.6
Eu	24c	0.12500	0.00000	0.25000	1.14(3)	0.4
Ta	16a	0.00000	0.00000	0.00000	2.06(4)	1
Li1	24d	0.25000	0.87500	0.00000	1.8(33)	0.80(29)
Li2	96h	0.054(12)	0.695(12)	0.583(11)	3.0(39)	0.22(7)[a]
O	96h	0.2816(4)	0.1047(4)	0.1955(5)	1.17(18)	1
$Li_6(La_{0.6}Eu_{0.4})_3(Ta_{0.5}Zr_{0.5})_2O_{12}$						
La	24c	0.12500	0.00000	0.25000	1.21(2)	0.6
Eu	24c	0.12500	0.00000	0.25000	1.21(2)	0.4
Ta	16a	0.00000	0.00000	0.00000	1.05(3)	0.5
Zr	16a	0.00000	0.00000	0.00000	1.05(3)	0.5
Li1	24d	0.25000	0.87500	0.00000	2.0(18)	0.53(8)
Li2	96h	0.082(4)	0.687(4)	0.569(4)	4.0(16)	0.37(2)[a]
O	96h	0.2819(3)	0.1047(3)	0.1941(3)	1.28(12)	1
$Li_7(La_{0.6}Eu_{0.4})_3Zr_2O_{12}$						
La	24c	0.12500	0.00000	0.25000	0.85(3)	0.6
Eu	24c	0.12500	0.00000	0.25000	0.85(3)	0.4
Zr	16a	0.00000	0.00000	0.00000	1.82(6)	1
Li1	24d	0.25000	0.87500	0.00000	2.7(46)	0.33(11)
Li2	96h	0.076(3)	0.684(3)	0.568(3)	0.1(11)	0.50(3)[a]
O	96h	0.2817(4)	0.1022(5)	0.1926(5)	0.99(17)	1

[a] The occupancy of Li2 site is constrained to be Occ(Li2) = [5+2x-3×Occ(Li1)]/12.[1,2]

Table S4 The bond lengths (Å) derived via Rietveld refinement of the XRD patterns for $Li_{5+2x}(La_{0.6}Eu_{0.4})_3(Ta_{1-x}Zr_x)_2O_{12}$ (x = 0, 0.5, 1.0).

$Li_{5+2x}(La_{0.6}Eu_{0.4})_3(Ta_{1-}$	x = 0	x = 0.5	x = 1.0
(La/Eu)-O1 (×4)	2.495(5)	2.519(4)	2.530(5)
(La/Eu)-O2 (×4)	2.532(6)	2.533(4)	2.541(6)
Li1-O (×4)	1.915(5)	1.932(4)	1.937(6)
Li2-O1	1.65(6)	1.90(5)	1.85(4)
Li2-O2	1.84(13)	1.93(5)	1.97(4)
Li2-O3	2.13(5)	2.15(5)	2.19(4)
Li2-O4	2.42(2)	2.23(5)	2.23(4)
Li2-O5	2.99(8)	2.69(5)	2.71(4)
Li2-O6	3.01(11)	2.94(5)	3.06(4)
(Ta/Zr)-O (×6)	2.014(5)	2.035(4)	2.090(6)

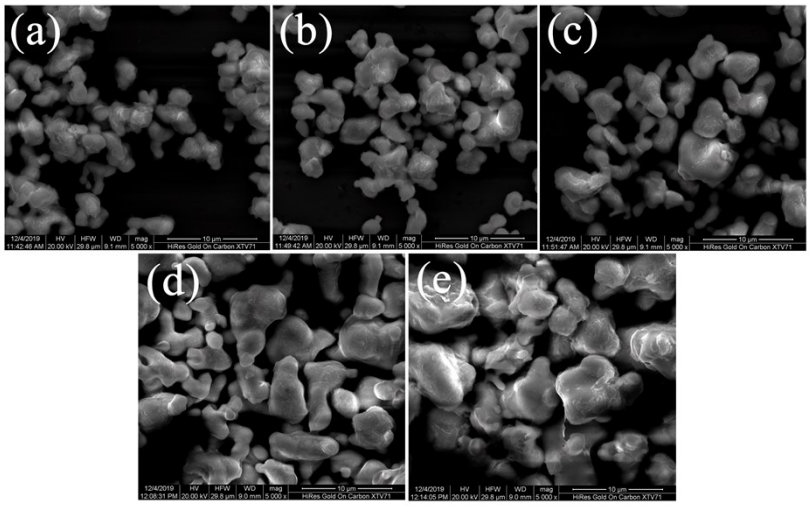

Fig. S2 FE-SEM morphologies of the $Li_{5+2x}(La_{0.6}Eu_{0.4})_3(Ta_{1-x}Zr_x)_2O_{12}$ powders, where x = 0 (a), 0.25 (b), 0.5 (c), 0.75 (d), and 1.0 (e).

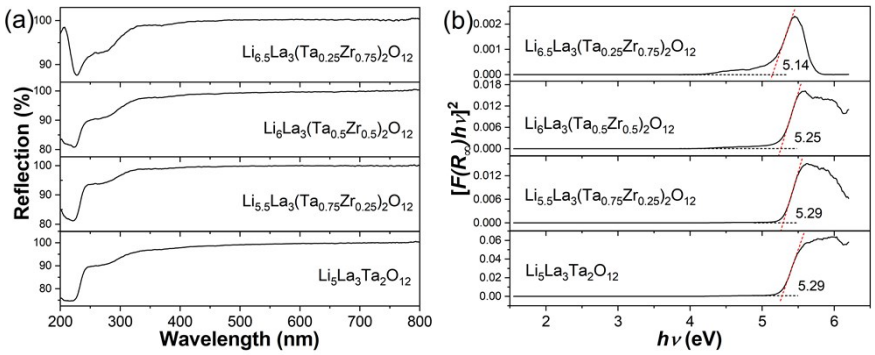

Fig. S3 Diffuse reflectance spectra (DRS, a) and determination of bandgap energy (b) for the $Li_5La_3Ta_2O_{12}$, $Li_{5.5}La_3(Ta_{0.75}Zr_{0.25})_2O_{12}$, $Li_6La_3(Ta_{0.5}Zr_{0.5})_2O_{12}$ and $Li_{6.5}La_3(Ta_{0.25}Zr_{0.75})_2O_{12}$ garnet hosts.

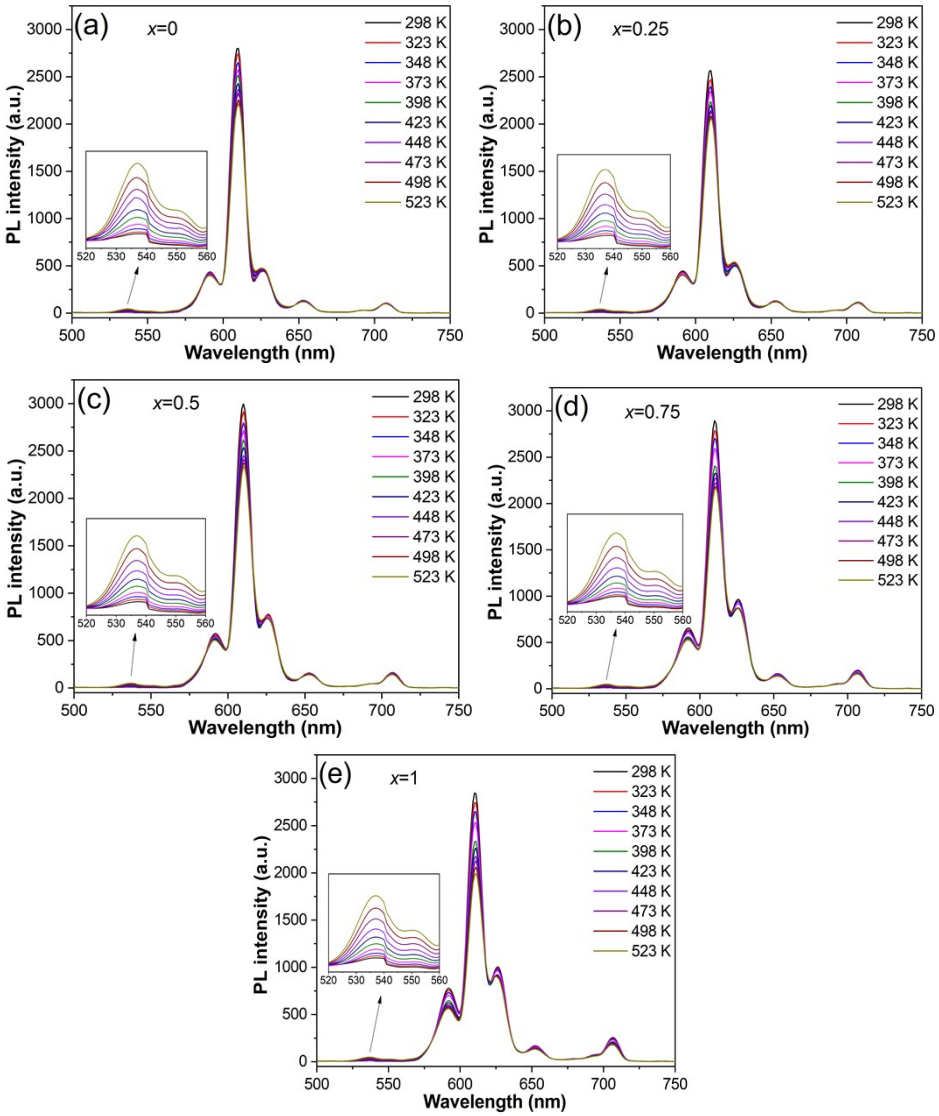

Fig. S4 Temperature-dependent PL spectra for the $Li_{5+2x}(La_{0.6}Eu_{0.4})_3(Ta_{1-x}Zr_x)_2O_{12}$ phosphors under 393 nm excitation, where x = 0 (a), 0.25 (b), 0.5 (c), 0.75 (d) and 1.0 (e). The insert in each part magnifies the 520-560 nm spectral region.

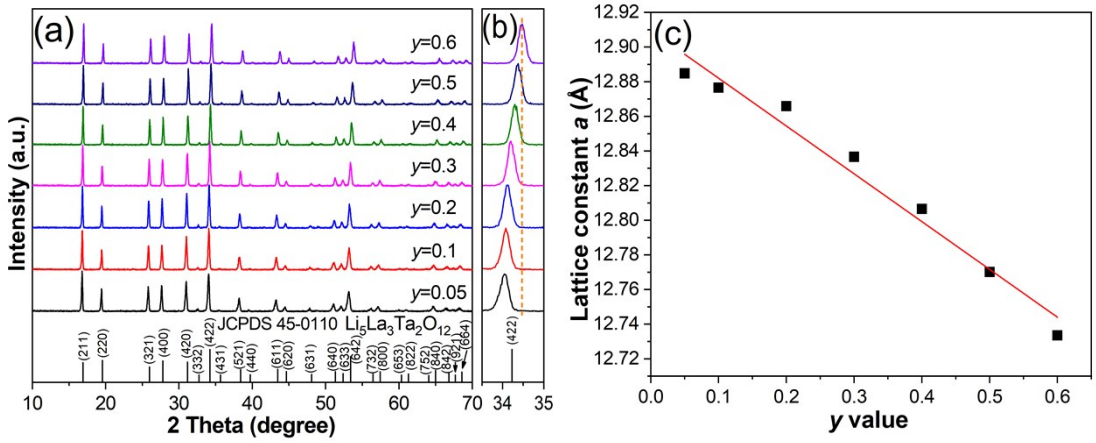

Fig. S5 XRD patterns (a), magnified view of the (422) main diffractions (b) and lattice parameter *a* as a function of the Eu^{3+} content (c) for $Li_6(La_{1-y}Eu_y)_3(Ta_{0.5}Zr_{0.5})_2O_{12}$ ($0.05 \le y \le 0.6$).

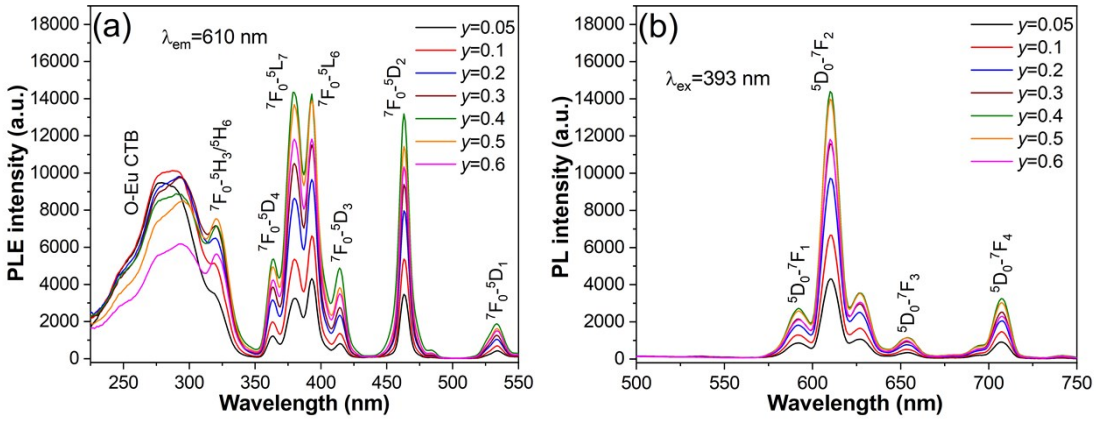

Fig. S6 PLE (a) and PL (b) spectra of the $Li_6(La_{1-y}Eu_y)_3(Ta_{0.5}Zr_{0.5})_2O_{12}$ phosphors.

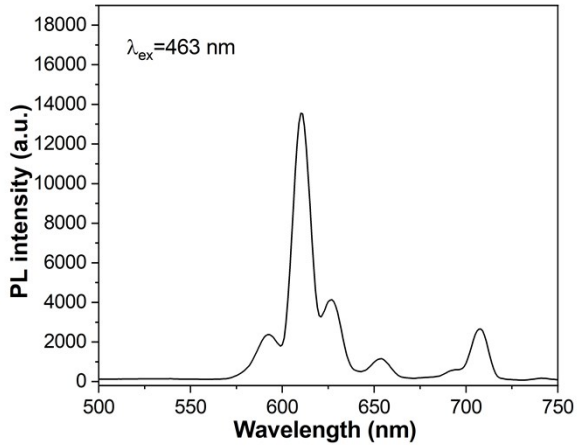

Fig. S7 PL spectrum taken for the $Li_6(La_{0.6}Eu_{0.4})_3(Ta_{0.5}Zr_{0.5})_2O_{12}$ phosphor under 463 nm blue-light excitation.

References

1 J. Awaka, N. Kijima, Y. Takahashi, H. Hayakawa, J. Akimoto, *Solid State Ionics*, 2009, **180**, 602-606.

2 R. P. Rao, W. Y. Gu, N. Sharma, V. K. Peterson, M. Avdeev, S. Adams, *Chem. Mater.*, 2015, **27**, 2903-2910.