Discovery of New Phosphor via Aliovalent Cation Substitution: DFT Predictions, Phase Transition and Luminescence Properties for Lighting and Anti-Counterfeiting Applications

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ABSTRACT:
Peoples are seeking suitable compositions to make new phosphors in the last two decades because phosphors are key materials for solid-state lighting and security applications. Aliovalent cations have different radii, electronegativity and certainly valence states, remarkably modifying the crystal structures. Here, we report a new $Sr_{33}Lu_6(PO_4)_{28}$ phase from $Sr_3(PO_4)_2$ by the method of aliovalent cation substitution. The DFT calculation predicted the possibility of new phase formation when substituting three Sr^{2+} by two Lu^{3+} ions. The new phase $Sr_{33}Lu_6(PO_4)_{28}$ was confirmed by X-ray diffraction, electron diffraction and photoluminescence spectra. Different from the purple phosphor $Sr_3(PO_4)_2:Eu^{2+}$, the $Sr_{33}Lu_6(PO_4)_{28}:Eu^{2+}$ exhibited broad green emission under near-UV excitation due to the multi-site occupancy of Eu2+. Combining the near-UV chip, blue, red and Sr33Lu6(PO4)28:Eu2+ green phosphor, a white light-emitting diode of high color rendering index (~92) was made, implying the potential lighting application. Additionally, the transparent security ink fabricated by the $Sr_{33}Lu_6(PO_4)_{28}:Eu^{2+}$ phosphor showed high concealment and recognition. This work is not confined to the report of new phosphor $Sr_{33}Lu_6(PO_4)_{28}:Eu^{2+}$. The aliovalent cation substitution is expected to be a general method for new materials discovery.

Table S1. Crystallographic parameters from Rietveld refinement for $Sr_{33}Lu_6(PO_4)_{28}$ ($Sr_{2.97-1.5x}Lu_xEu_{0.03}(PO_4)_2$ (x = 0.35)).

Site	Atom	Fraction	*x*	*y*	*z*	U_{iso} (Å)
M1	Sr	1	0.2827(4)	0.0007(8)	0.0865(4)	0.0105(18)
M2	Sr	1	0.0570(4)	0.2196(6)	0.3611(4)	0.0119(19)
M3	Sr	0.8726	0.4383(5)	0.2816(7)	0.1363(5)	0.013(2)
M4	Sr/Lu	0.2437/0.2563	0.0146(11)	0.510(2)	0.0259(8)	0.068(5)
M5	Sr	1	0.2671(4)	0.2345(6)	0.2520(5)	0.0098(17)
M6	Lu	1	0	0	0	0.0055(9)
P1	P	1	0	0.5302(16)	0.25	0.0109
P2	P	1	0.1123(11)	-0.0139(18)	0.2090(11)	0.0109
P3	P	1	0.1501(12)	0.2632(14)	0.0445(12)	0.0109
P4	P	1	0.3404(11)	0.2498(14)	0.4362(11)	0.0109
O1	O	1	0.40394	0.09632	0.20796	0.0109
O2	O	1	0.01283	0.46096	0.34847	0.0109
O3	O	1	0.18069	-0.0349	0.17796	0.0109
O4	O	1	0.1159	0.12199	0.25843	0.0109
O5	O	1	0.39835	0.38654	0.24969	0.0109
O6	O	1	0.03012	0.01508	0.12771	0.0109
O7	O	1	0.2552	0.25725	0.11988	0.0109
O8	O	1	0.34214	0.13557	-0.000240	0.0109
O9	O	1	0.10902	0.12524	0.02338	0.0109
O10	O	1	0.08987	0.29344	0.10552	0.0109
O11	O	1	0.38429	0.19462	0.39012	0.0109
O12	O	1	0.13673	0.34821	0.47599	0.0109
O13	O	1	0.22904	0.27392	0.3831	0.0109
O14	O	1	0.12928	0.13661	0.5097	0.0109

Space Group: $C2/c$ (NO.15). a = 14.5637 Å, b = 10.7049 Å, c = 18.0870 Å, β = 112.139°. R_{wp} = 13.53%, R_p = 9.88%, GOF = 3.02. The atomic fraction of Eu is not refined due to the low concentration. The atomic positions of oxygen were refined at the beginning then fixed in the stage of double phase refinement, due to the overlapping of diffraction.

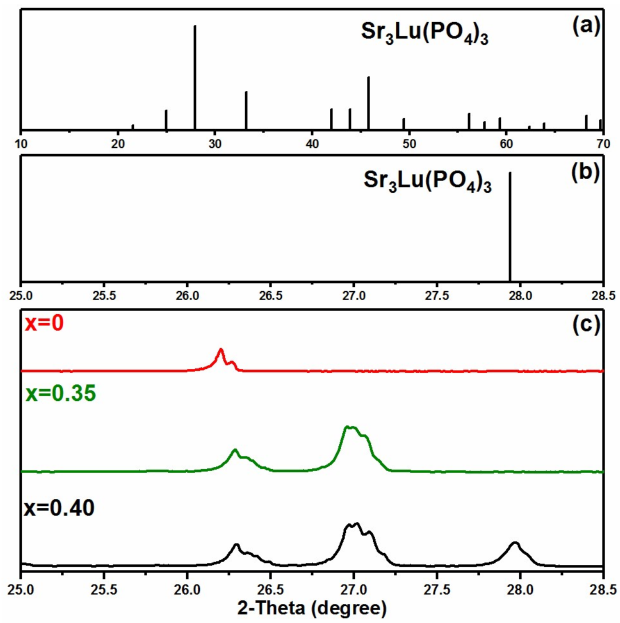

Figure S1. (a),(b) Simulated diffraction pattern of $Sr_3Lu(PO_4)_3$ and (c) XRD patterns of samples in the range of 25.0°~28.5°.

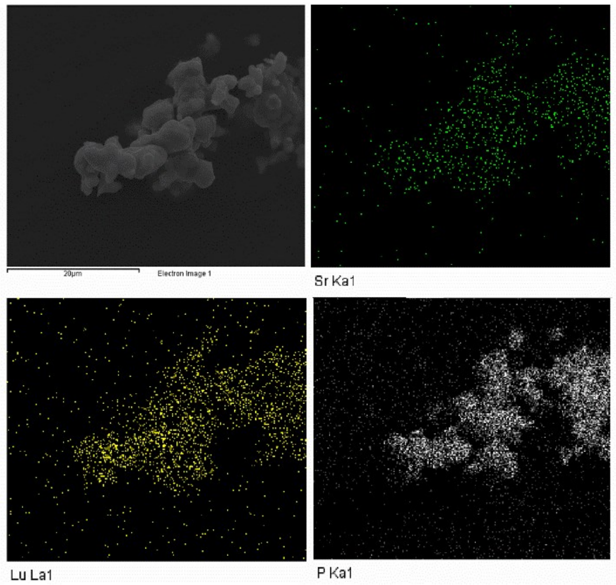

Figure S2. EDS mapping result of the $x = 0.35$ sample.

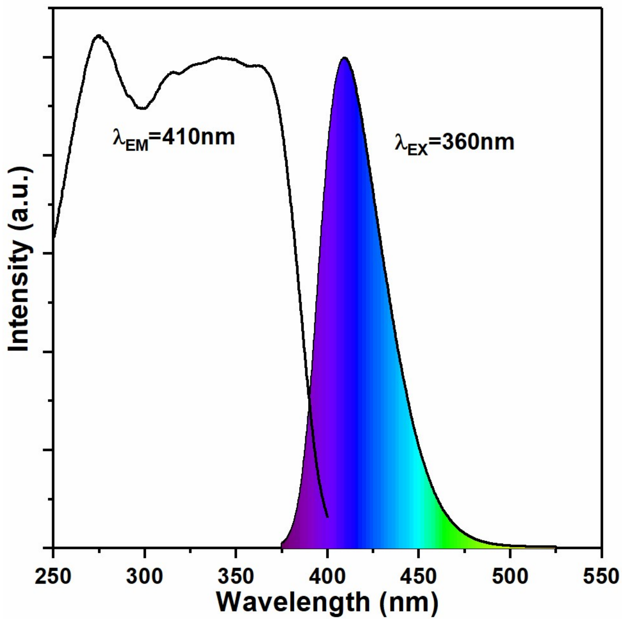

Figure S3. PL and PLE spectra of $Sr_{2.97}Eu_{0.03}(PO_4)_2$.

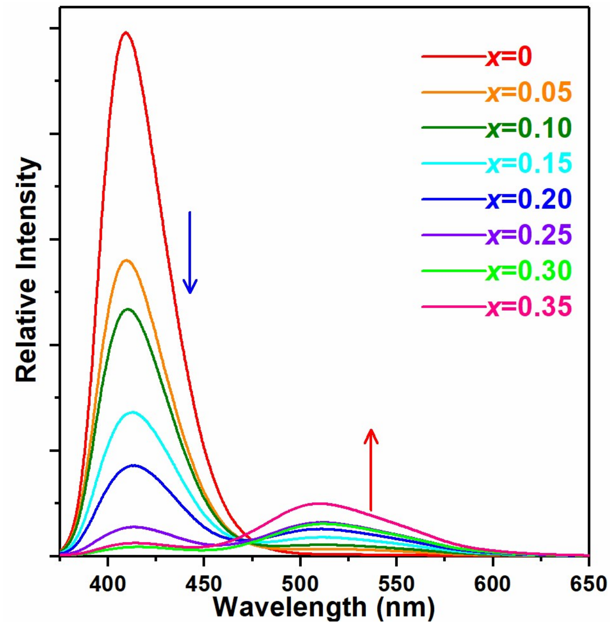

Figure S4. PL spectra of $Sr_{2.97-1.5x}Lu_xEu_{0.03}(PO_4)_2$ under 360 nm excitation.

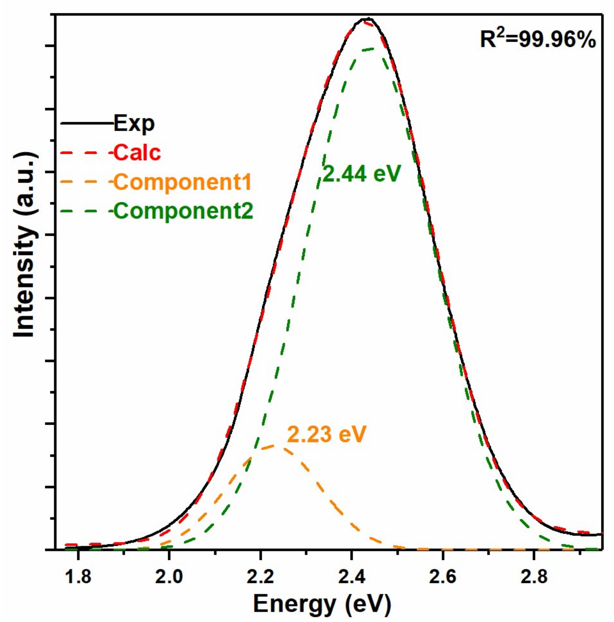

Figure S5. PL spectrum of $Sr_{2.97-1.5x}Lu_xEu_{0.03}(PO_4)_2$ (x = 0.35) under the λ_{EX} = 380 nm excitation and the Gaussian profile fitting results.

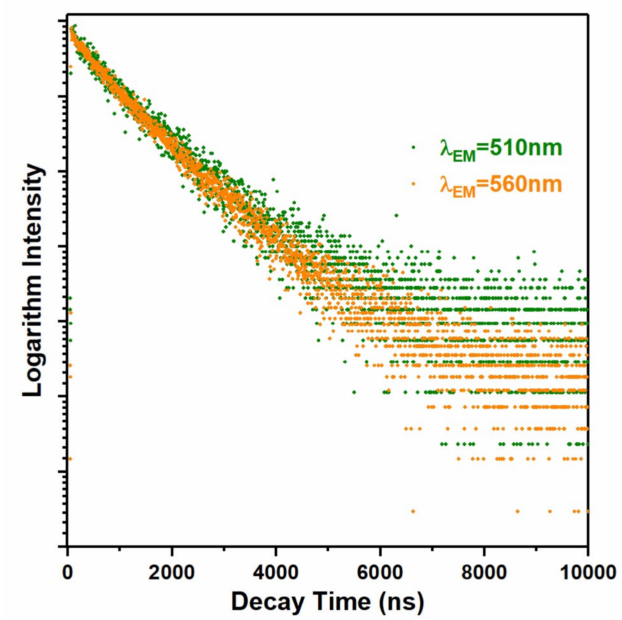

Figure S6. Luminescence decay curves of $Sr_{2.97-1.5x}Lu_xEu_{0.03}(PO_4)_2$ (x = 0.35) monitoring the 510 and 560 nm emission under the λ_{EX} = 375 nm laser excitation.

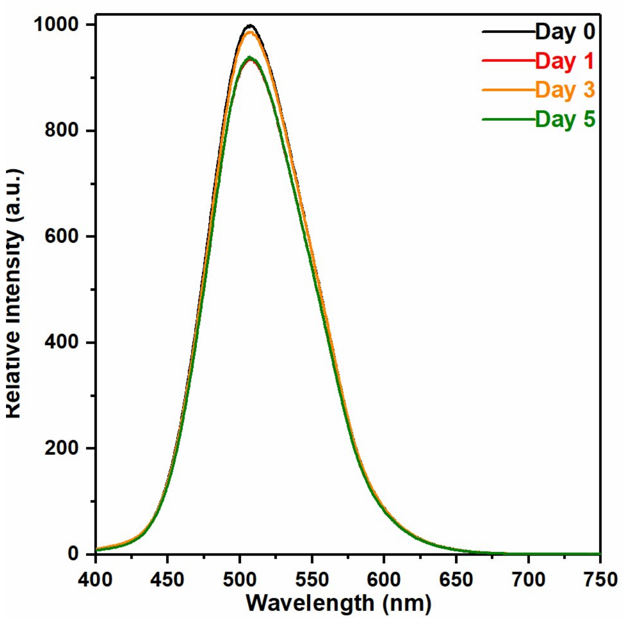

Figure S7. The PL spectra of $Sr_{2.97-1.5x}Lu_xEu_{0.03}(PO_4)_2$ (x = 0.35) after immersed in water (λ_{EX} = 380 nm).